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# BACHELOR THESIS

(EXPLANATORY NOTE)

SPECIALTY 101 “ECOLOGY”,  
EDUCATIONAL AND PROFESSIONAL PROGRAM:  
“ECOLOGY AND ENVIRONMENT PROTECTION”

**Theme: «Assessment of the warfare impact on the content and distribution of heavy metals in soils of the Sumy oblast»**

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МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ  
НАЦІОНАЛЬНИЙ АВІАЦІЙНИЙ УНІВЕРСИТЕТ  
ФАКУЛЬТЕТ ЕКОЛОГІЧНОЇ БЕЗПЕКИ,  
ІНЖЕНЕРІЇ ТА ТЕХНОЛОГІЙ  
КАФЕДРА ЕКОЛОГІЇ

ДОПУСТИТИ ДО ЗАХИСТУ  
Завідувач випускової кафедри  
\_\_\_\_\_ Тамара ДУДАР  
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**КВАЛІФІКАЦІЙНА РОБОТА**  
**(ПОЯСНЮВАЛЬНА ЗАПИСКА)**

ВИПУСКНИКА ОСВІТНЬОГО СТУПЕНЯ БАКАЛАВРА

ЗА СПЕЦІАЛЬНІСТЮ 101 «ЕКОЛОГІЯ»  
ОПП «ЕКОЛОГІЯ ТА ОХОРОНА НАВКОЛИШНЬОГО СЕРЕДОВИЩА»

**Тема: «Оцінка впливу воєнних дій на вміст та поширення важких металів у ґрунтах Сумської області»**

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« \_\_\_\_\_ » \_\_\_\_\_ 2023

**BACHELOR THESIS ASSIGNMENT**

Bohdan Yu. Tuzhyk

1. Theme: «Assessment of the warfare impact on the content and distribution of heavy metals in soils of the Sumy oblast» approved by the Rector on April 19, 2023, № 529/сr.
2. Duration of work: from 29.05.2023 to 20.06.2023.
3. Output work (project): Statistical data on contamination of soils with heavy metals; standards of Ukraine, Europe, USA, World Health Organization on permissible limits of heavy metals in soil, scientific sources.
4. Content of explanatory note: (list of issues): 1. Environmental pollution with heavy metals and its consequences. 2. The impact of military operations on the spread of heavy metals in soilsю 3. The influence of military operations on the distribution of heavy metals in the soils of the Sumy region.
5. The list of mandatory graphic (illustrated materials): tables, figures, charts, graphs.

## 6. Schedule of thesis fulfillment

№ з/П	Task	Term	Advisor's signature
1	Justification of the goal, object and subject of research	29.05.2023 – 03.06.2023	
2	Review of literary sources	01.06.2023 – 09.06.2023	
3	Collection and analysis of materials	01.06.2023 – 10.06.2023	
4	Writing chapters I of the thesis	02.06.2023 – 05.06.2023	
5	Writing chapters II of the thesis	05.06.2023 – 12.06.2023	
6	Writing chapters III of the thesis	09.06.2023 – 12.06.2023	
7	Issuance of an explanatory note	13.04.2023 – 19.06.2023	
8	Defense of the thesis	20.06.2023	

7. Date of task issue: «19» April 2023

Diploma (project) advisor:

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Task is taken to perform:

\_\_\_\_\_ Bohdan TUZHYK  
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# НАЦІОНАЛЬНИЙ АВІАЦІЙНИЙ УНІВЕРСИТЕТ

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«\_\_\_\_\_» \_\_\_\_\_ 2023 р.

## ЗАВДАННЯ

на виконання кваліфікаційної роботи

Тужика Богдана Юрійовича

1. Тема роботи «Оцінка стійкості геосистем до антропогенно-техногенного впливу» затверджена наказом ректора від «19» квітня 2023 р. № 529/ст.
2. Термін виконання роботи: з 29.05.2023 р. по 20.06.2023р.
3. Вихідні дані роботи: Статистичні дані про забруднення ґрунтів важкими металами; стандарти України, Європи, США, Всесвітньої організації охорони здоров'я щодо допустимих норм вмісту важких металів у ґрунті, наукові джерела.
4. Зміст пояснювальної записки: 1. Забруднення навколишнього середовища важкими металами та його наслідки. 2. Вплив військових дій на поширення важких металів у ґрунтах. 3. Вплив військових дій на розподіл важких металів у ґрунтах Сумської області.
5. Перелік обов'язкового графічного (ілюстративного) матеріалу: таблиці, рисунки, діаграми, графіки.

## 6. Календарний план-графік

№ з/п	Завдання	Термін виконання	Підпис керівника
1	Обґрунтування мети, об'єкта та предмета дослідження	29.05.2023 – 03.06.2023	
2	Огляд літературних джерел	01.06.2023 – 09.06.2023	
3	Збір та аналіз матеріалів	01.06.2023 – 10.06.2023	
4	Написання I розділу кваліфікаційної роботи	02.06.2023 – 05.06.2023	
5	Написання II розділу кваліфікаційної роботи	05.06.2023 – 12.06.2023	
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Завдання прийняв до виконання: \_\_\_\_\_ Богдан ТУЖИК  
(підпис випускника) (П.І.Б.)

## **ABSTRACT**

Explanatory note to the thesis «Assessment of the warfare impact on the content and distribution of heavy metals in soils of the Sumy oblast» : 57 pages, 9 figures, 2 tables, 25 literary sources.

Object of research: soil contamination with heavy metals as a result of hostilities.

Aim of work: study of the impact of military operations on the content of heavy metals in soils in the areas of active hostilities in the Sumy\_ oblast and the development of measures to restore contaminated soil.

Methods of research: statistical analysis, comparison, generalization.

Environmental pollution with heavy metals and its consequences on human health and agriculture are generalized. The impact of hostilities on the soil structure is considered. Sources of heavy metals associated with hostilities are identified. The consequences of military operations in the Sumy region are summarized. Data on contents of heavy metals in soils of the Sumy oblast are analyzed. Recommendations on method of soil detoxication on investigated territories are worked out.

HEAVY METALS, PERMISSIBLE LIMITS, THE SUMY  
OBLAST, WARFARE IMPACT, ACCUMULATION FACTOR, BACKGROUND  
CONTENT OF HEAVY METALS IN SOIL.

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## INTRODUCTION

***Relevance of the work.*** The enemy's invasion of the territory of Ukraine in 2014 significantly disturbed the soil environment and caused comprehensive and long-term environmental degradation. Russia's military actions since February 24, 2022 exacerbated the problem of soil degradation, and the high level of intensity of hostilities in certain areas called into question the safety of using lands directly affected by the war. The war is still ongoing, but already today we can observe the tangible negative impact of military operations on the health and productivity of soil covers: eruptions from air bombs and artillery attacks, mined areas, destroyed heavy military equipment, oil spills, burnt areas from fires, landslides the main markers signaling a strong influence on soil resistance to pollution.

That is why soil disturbance causes severe socio-economic consequences, both at the regional and national level. The drastic change of landscapes requires an immediate and comprehensive study, followed by the development of policies for the management of war-contaminated lands. Failure to act on the outlined problem risks causing accelerated soil erosion, negatively impacting production, spreading toxic/contaminated agricultural or other types of products, as well as negatively impacting people's health. However, monitoring of soil condition assessment is still fragmentary.

Therefore, we consider it necessary to investigate the impact of hostilities on the content and distribution of heavy metals in soils on the territory of Ukraine, which in the future will serve as a theoretical basis for the implementation of effective measures to improve the ecological condition of the soils of Ukraine.

***Aim of the work:*** study of the impact of military operations on soils by assessing their ecological and geochemical state in the areas of active hostilities on the territory of Ukraine and development of measures to restore contaminated soil.

***Tasks of the work:***

1. To assess the level of environmental pollution by heavy metals and its consequences on the territory of Ukraine.
2. To determine the influence of military operations on the distribution of heavy metals in the soil.
3. To analyze the content of heavy metals in the soils of the regions of the Sumy region that were most affected by the war.
4. Develop a program of measures to overcome the negative consequences of hostilities on the content and distribution of heavy metals in soils on the territory of Ukraine

***Object of research*** – the ecological state of the upper crust of a separate area on the territory of Ukraine that has undergone negative changes due to hostilities.

***The subject of research*** – damage to the territory affected by hostilities (Sumy region).

***Methods of research*** – analysis, comparison, synthesis and systematization; generalization of scientific theoretical and experimental data; systematic approach, methods of observation and comparison, method of territory research using the ArcMap program and the Sentinel-2 satellite.

***Scientific novelty of the obtained results.*** To restore the top layer of the soil, it was proposed to carry out rough reclamation in the selected area in the Sumy region using heavy equipment. In order to improve the condition and fertility of the land, it was proposed to carry out reclamation measures using a perennial plant - miscanthus, which performs the role of a soil veterinarian.

***Practical significance of the obtained results.*** The use of the methodology for determining the amount of damage caused to the land resources of Ukraine as a result of Russia's military actions will contribute to the fixation of ecocide, which in the future can ensure compensation and restoration of the natural environment.

***Personal contribution of the graduate.*** An assessment of the environmental damage caused by the war on the territory of Sumy Oblast was carried out using the method of determining the damage caused as a result of military operations, and measures were proposed to reduce the effects of environmental damage to the land fund of Ukraine from Russia's military operations.

# CHAPTER I

## ENVIRONMENTAL POLLUTION WITH HEAVY METALS AND ITS CONSEQUENCES

### 1.1 Sources of heavy metals in the environment

Heavy metals are a vaguely defined group of elements with metallic properties, which usually includes transition metals, some metalloids, lanthanides, and actinoids. Historically, many definitions of this term have been proposed, some based on density, others on atomic number or atomic mass, and still others on chemical properties or toxicity [1]. An IUPAC technical report called the term "heavy metals" "meaningless and confusing" due to conflicting definitions and the lack of a "coherent scientific basis" behind it [1]. Depending on the context, even elements lighter than carbon can be called "heavy metals", but not some much heavier metals.

When developing legal acts that regulate issues related to the content of heavy metals in food products, in household appliances, devices, accumulators and batteries and similar objects, when classifying certain wastes as hazardous due to the presence of heavy metals in their composition, problems such as:

Heavy metals are not only in soils, but also in air and water. They enter the water from the soil. Into the air, mainly during the combustion of various complex substances, which are part of them, for example, during gas emissions from cars, thermal power plants, factories. [4].

Also, these substances enter the environment during emissions of ore residues, etc., by mining enterprises. heavy metals can also be found in garbage that is in landfills, for example in plastics. After all, in order to achieve better qualities in the production of plastics, various chemical additives are added to their composition. These are so-called stabilizers that protect plastics against high temperatures and solar radiation. They are

poisonous. These are coloring substances, flame retardants (fire retardant), etc. These include heavy metals (lead, mercury, cadmium, bromine, tin).

Conventionally, the group of heavy metals includes metals with a specific gravity of more than 4.5 g/cm<sup>3</sup>. These are lead, cadmium, mercury, chromium, copper. Metals, and among them heavy metals, are widespread in nature, where they are usually in the form of ores, less often - elements. Metals in the form of pure elements most likely do not cause toxic effects, since they are practically insoluble. An exception is volatile metals, for example, mercury vapor, which can enter the body through the respiratory system or skin. Toxic properties are revealed by metal compounds that are easily soluble and strongly dissociate. Dissolution and dissociation facilitate the penetration of toxins through tissue membranes into the body.

Similar to dioxins, which will be discussed below, almost 70% of toxic metals enter the body together with food, and since today it is food products that are the subject of intensive international trade, the joint commission of the FAO (food organization) and the World Health Organization (WHO) from the Food Codex (Codex Alimentarius) included the eight most dangerous toxic elements: mercury, cadmium, lead, arsenic, copper, tin, zinc, iron in the composition of food components that are subject to control during international trade.

Heavy metals and their compounds are dispersed naturally in the environment. We are then talking about the presence of the so-called background (Table 1) [5, c. 85-86].

Values of concentrations that are higher than the background ones indicate environmental pollution. The main source of environmental pollution with heavy metals is various industries. Thus, the chemical industry (production of dyes, plant protection products, plastics, dyeing business) is a source of As, Ba, Cd, Cr, Cu, Fe, Hg, Pb, Se, Sr, Sn, Ti, Zn pollution. The pulp and paper industry supplies the environment with such metals as Cr, Cu, Hg, Ni, Zn, Pb; electrochemical industry — Cd, Co, Cr, Cu, Hg, Mo, Ni, Se, Ti, V, W, Zn; metallurgical industry — Fe, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Zr; ceramic industry — Cr, Ni, Cu, Co, Pb, Sr. Electric and thermal power plants are a significant source of heavy metals. In the latter case, the complex of heavy metals entering the

environment with effluents, with the release of gases and dust, with solid waste, depends to a large extent on the type of fuel processed, i.e. coal, oil, gas, etc. [7, c. 71-72]

## **2.2 Heavy metals as a risk factor for human health**

In recent years, anthropogenic pollution of the environment with heavy metals has become one of the priority threats to living organisms, including humans, and economic and technical progress is increasingly becoming the cause of disruption of natural ecosystems.

Heavy metals include more than forty chemical elements of Mendeleev's table. Among them are chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, molybdenum, cadmium, tin, stibium, tellurium, tungsten, mercury, thallium, lead, bismuth, etc. They are often used in industry and are part of inorganic and organic compounds, herbicides, insecticides and medical preparations.

Developed industry, extensive transport networks, many residential complexes and an increase in road traffic (as well as an increase in gas stations) are all factors that significantly increase the risk of increasing the concentration of heavy metals in environmental components.

As you know, heavy metals can accumulate at all levels of the ecological pyramid, which significantly exacerbates the problem. Their influence can lead to distant effects. Among them: carcinogenic, mutagenic effects, as well as long-term toxic effects on the gastrointestinal tract, cardiovascular, endocrine, nervous, and reproductive systems, increasing the risk of infertility. Due to their accumulation in the body, they eventually lead to a weakening of the immune system, exacerbation of chronic diseases. Each heavy metal has its own specific effects on the body. So, for example, with mercury poisoning, the nervous system and kidneys are mainly affected, and with cadmium poisoning, the lungs, nasal mucosa, and gastrointestinal tract are affected.

But it is almost impossible to abandon heavy metals now, so they continue to be comprehensively used in many areas of industry, being global pollutants of the planet.

Ín this regard, the content of heavy metals in environmental components is strictly regulated. Maximum permissible emissions (MPEs) were developed, compliance with which is mandatory and the hazard ratio of the enterprise and the size of its sanitary protection zone depend on comparison with them.

It is important to know that atmospheric air pollution is a very important problem, because heavy metals can enter the human body directly from the air, but one should not forget that this is also dangerous because they can be transported from the atmosphere to a considerable distance, settle on the surface of the soil, getting into the cycle of substances in nature and causing global pollution.

As humanity evolves, the concentration of heavy metals in soils steadily increases over the years, they accumulate in the soil layer, especially in the upper humus horizons, which negatively affects their fertility, microbiological activity and the quality of plants grown on them.

In terrestrial ecosystems, soil performs the most important functions. Its ecological and geochemical state determines the stability of the biosphere. Man-made load on the soil leads to its degradation and a decrease in quality and productivity indicators, namely thermal and water regimes, the presence of humus and plant nutrients, granulometric composition; degree of salinity, acidity, pollution, erosion [11].

Soil is the main medium for heavy metals to enter, including surface runoff, from groundwater and bedrock, as well as from the atmosphere. VM, together with other elements, are assimilated by plants, which are food for animals and humans. Along the trophic chain, the above-mentioned elements enter the body of humans and animals. Also, heavy metals serve as a secondary source of pollution of the water environment and surface air. On the surface of the soil, DM enters in the form of various salts (both soluble and practically insoluble in water) and oxides [11]. Soil not only accumulates pollutants, but also serves as a natural buffer and controls the transfer of chemical elements and their compounds to other environments (hydrosphere, atmosphere, and living matter) [11].

The consequences of contamination of the soil environment with heavy metals depend on such indicators as the geochemical composition of the soil, parameters of contamination and soil stability. Pollution parameters include:

- the nature of the metal (chemical and toxicological properties of the element);
- the form of a chemical compound;
- metal content in the soil;
- the term from the moment of pollution.

Soil resistance to pollution depends on the following parameters:

- content of organic matter;
- granulometric composition;
- activity of biogeochemical and microbiological processes;
- redox conditions;

-acid-base conditions. The ability of living organisms to accumulate heavy metals in significant quantities and the resistance of these organisms to an increase in the concentration of the above-mentioned elements can pose a threat to human health due to the fact that, thanks to them, VM penetrates into food chains [11].

### **1.3. Negative impact of heavy metals on agricultural activity**

In the form of pure elements, heavy metals mostly do not have a toxic effect, since in this case they are practically insoluble (the exception is mercury vapor). Compounds of these elements are toxic. These compounds are easily soluble and their dissociation is quite strong. Dissociation and dissolution create better conditions for the penetration of the above-mentioned compounds into the body through tissue membranes [1-2].

A significant number of metallic elements can form quite strong complexes with organic matter. Such complexes are considered one of the most important forms of migration of heavy metals in natural waters. Complexes that form soil acids with salts of copper, iron, aluminum and other heavy metals dissolve relatively well in weakly alkaline, weakly acidic and neutral environments. This is the reason for the ability of organometallic complexes to migrate in natural waters over considerable distances. This is especially important for surface and slightly mineralized waters, since the formation of other complexes is impossible in them [2].



The central place in the soil system is occupied by the soil solution, the composition of which is formed under the influence of a number of factors. The mobility and strength of the connection with various components of the soil is important when studying the migration processes of BM in the soil environment, as they determine the degree of toxicity of the elements and the degree of their migration [12].

Heavy metals entering the soil environment also have a negative impact on vegetation. Therefore, studying the transition of these elements into plant organisms is important. The consequence of man-made entry of BM into the soil environment is also a negative effect on biological complexes. The consequence of such influence is changes in the groups of living organisms, including microscopic fungi [12].

The content of heavy metals in soils depends on the composition of the source rocks. Their significant diversity is associated with the complex geological history of the development of the territories. The chemical composition of soil-forming rocks determines the chemical composition of source rocks and depends on the conditions of hypergenic transformation [12].

Human activity is intensively involved in the migration of metallic elements in the natural environment. The amount of chemical elements that enters it as a result of human activity in most cases is significantly greater than the level of the above-mentioned elements as a result of natural processes. During this process, metallic elements are quickly distributed in natural components by anthropogenic flows, where the interaction of these elements with humans is inevitable. Volumes of metallic elements entering the natural environment grow every year and cause significant damage to ecosystems, their elements, and human health [3].

Agricultural objects suffer significant damage, because heavy metals, when entering the soil environment, accumulate in the soil layer (especially in the upper layers of the humus horizon), where they are slowly removed by erosion, leaching and consumption by plants. VMs also enter groundwater. These elements are considered the most dangerous pollutants [13].

Mechanisms of entry of VM into the organisms of animals and humans: inhalation (is quite rare), oral (with food and water. It is the most common) and through the skin.

Inhalation of metal dust has the most serious toxic effect on the human body, and particles with a diameter of 0.1-1  $\mu\text{m}$  are considered particularly dangerous, since they are effectively adsorbed by the lungs and then enter the liquid environments of the body much faster than with oral penetration of these elements into the body. However, as mentioned above, such cases are rare and the most widespread is the oral way of toxic elements entering the body [13].

In general terms, the mechanism of the toxic effect of VM on the body is as follows. Metal ions are necessary for the stabilization and activation of many proteins (in particular, they are necessary for the functioning of almost all enzymes). When toxic elements enter, there is a competition between necessary and toxic ions for possession of binding sites in proteins. Multiprotein macromolecules contain free sulfhydryl groups in their composition, which are able to interact with BM (Hg, Cd, Pb, etc.).

The negative effect of interaction of VM with biologically active macromolecules includes the following processes:

- displacement of necessary metals from their active binding sites by a heavy metal;
- binding of a part of a macromolecule necessary for the normal functioning of an organism;
- crosslinking of macromolecules with the formation of biological aggregates harmful to the body;
- depolymerization of biologically important macromolecules;
- incorrect combination of nucleotide bases and errors in protein synthesis processes.

The result of such influence of VM on the body is a violation of the functioning of its vital systems and the initiation of negative processes.

Analysis of literary sources shows that heavy metal pollution of the environment has such negative consequences as:

- man-made soil degradation;
- decrease in productivity;
- violation of the process of photosynthesis in plants;
- death of microorganisms;

- functional disorders in the cells of the brain, kidneys, liver, and human bones;
- the occurrence of cancerous tumors, genetic modifications, changes in sexual development and reproduction of organisms and their growth rate, as well as diseases of the circulatory and nervous systems;
- increasing the probability of a number of diseases (anemia, allopathy, Alzheimer's disease, etc.).

When soil is polluted, heavy metals become a secondary source of pollution of natural waters and surface air:

- decrease in humus content and decrease in yield of agricultural plants;
- anatomical and morphological changes or destruction of perennial plants;
- the formation of degraded soil areas with increased acidity;
- change in the chemical and biological composition of soils as a result of an increase in mobile forms of heavy metals and the content of sulfate ions;
- increased acid impact in soils and, as a consequence, the formation of man-made deserts and chemical weathering of primary minerals [9].

Heavy metals are also the cause of a decrease in the yield of agricultural crops, a decrease in the productivity of their growth, a deterioration in the activity of the vegetative organs of plants and an impoverishment of the flora of the adjacent territories. There are several ways to reduce soil pollution with heavy metals: reducing the amount of toxicants entering the agro-environment, minimizing existing pollution by removing heavy metals beyond the soil cover, and their accumulation in the upper soil horizon by transferring them to an inaccessible immobile state. Such a radical method as removing the contaminated soil layer is also proposed [13].

It is known that up to 50 million tons of WEEE (waste of electrical and electronic equipment) is generated every year in the world, and their accumulation is three times faster than the growth of the amount of other types of waste. Lead, cadmium and zinc are considered the main soil pollutants.

Lead is a heavy metal of the first class of danger [21], is one of the most toxic chemical elements even in small quantities. Soil lead contamination threatens the

population living in the affected areas with this element, and primarily children, who are more sensitive to the effects of heavy metals [22]. The element has low phytotoxicity. Most of the lead that reaches the plant is retained in its root system. Gross lead content at soil sampling points in the combat zone varied from 14.17 to 347.43 mg/kg of soil, outside the combat zone (background value) — from 7.45 to 48.96 mg/kg of soil. Exceeding the background level for this element was noted in all soil samples, and the average lead content in the contaminated areas exceeded the background value by 5.4 times

Cadmium and its compounds are the most important when studying pollution problems. They are characterized by extreme toxicity even in small concentrations and belong to the I class of danger [21], easily migrate in soils, are quickly absorbed and accumulate in plants [1; 16]. Due to contaminated food products of plant and animal origin, cadmium can enter the body, where it disrupts bone tissue formation processes and provokes respiratory diseases. Cadmium reduces the body's ability to resist diseases. It has mutagenic and carcinogenic properties, negatively affects heredity, destroys erythrocytes, leads to kidney and testicular disease, causes gastritis and anemia. For humans, the permissible dose of cadmium is 70 mg/kg per day for adults and completely excludes its presence in drinking water and food for children.

Zinc belongs to metals of the I hazard group [21], is characterized by moderate toxicity and weak phytotoxicity [1]. With high soil moisture, it has a high migration capacity. In case of excessive entry into the body of humans and animals, it has a toxic effect on the heart, blood and other organs, and has a carcinogenic effect.

Copper belongs to heavy metals of the II hazard class [21], has weak phytotoxicity, but is very toxic to the human body [1; 16]. In case of excessive entry into the body of people and animals, it has a carcinogenic effect and has a toxic effect on the heart, blood and other organs.

Nickel belongs to elements of the II hazard class [21], getting on the skin and in the respiratory organs can cause acute and chronic poisoning.

Iron is one of the most common elements in nature, belongs to the III class of danger. It exists in nature in three states, of which the most harmful for the environment is the state of rust [21; 22].

Manganese belongs to heavy metals of the IIIrd class of danger, has weak phytotoxicity, however, its excess content in the soil has a harmful effect on the human body and leads to the destruction of the nervous system [21; 22].

There is a trend of a sharp increase in the use of electronic devices and a decrease in the period of their use. According to estimates of the US Environmental Protection Agency, only 15-20% of WEEE is reused, and the rest is buried together with household waste, despite the fact that it is a source of useful elements suitable for further use [14].

Heavy metals in the cycle of substances in the natural environment return to the human body and cause various diseases.

## CHAPTER 2.

### INFLUENCE OF MILITARY ACTIONS ON THE DISTRIBUTION OF HEAVY METALS IN SOILS

#### 2.1. The impact of hostilities on the soil structure

In Ukraine since February 24, 2022 (and in the East of Ukraine - for years already) shelling with permitted and prohibited projectiles is intensively conducted every day, eruptions are formed from air bombs and artillery fire, new mined areas are created, heavy military equipment is destroyed, which leads to the leakage of oil products, land burning, etc. All these consequences of military operations pollute the soil, and with it, negatively affect the country's economy and people's health.

The devastating consequences of military-technogenic pollution for the health of the population have been proven. The concentrated content of heavy metals can disrupt the activity of the nervous system, hematopoietic and internal secretion systems. Chemical pollution induces the appearance of malignant formations, atherosclerosis and disorders of the heredity apparatus.

Damage to the soil as a result of military operations can be mechanical, physical and chemical. Each of these influences is critical in its own way and causes destruction of the earth's structure and functions. Let's consider each in more detail.

**Mechanical influence.** It deforms the soil cover, which leads to the disturbance of the soil structure during the movement of military equipment, the movement of troops, the construction of protective structures, bombing sites (ed. — disturbance of the ground due to the formation of craters from bombing), demining of territories. The consequence of this impact is compaction, waterlogging, and soiling of the territory with products of combat activity.

Separately, we note that the demining of territories also has a negative impact - the humus horizon is usually destroyed, the physical and chemical properties of the soil are

lost, and changes in the granulometric and aggregate state occur. For its part, this affects the fertility and water-holding capacity of the soil.

Chemical influence. Changes the natural physical and chemical parameters of the soil cover. First of all, pH, cation exchange and humus content. The concentration of toxic and chemical substances also increases, and various local landscape and geochemical anomalies may form. Therefore, these lands cannot be used in the long term.

Agents of chemical pollution include vehicle fuel, lubricants, solvents, electroplating waste, residues of explosives, decontamination substances, heavy metals and their compounds, radioactive substances.

Physical impact. Presupposes a change in the physical parameters of the soil as a result of the use of weapons and military equipment. This refers to vibrational, radioactive and thermal effects.

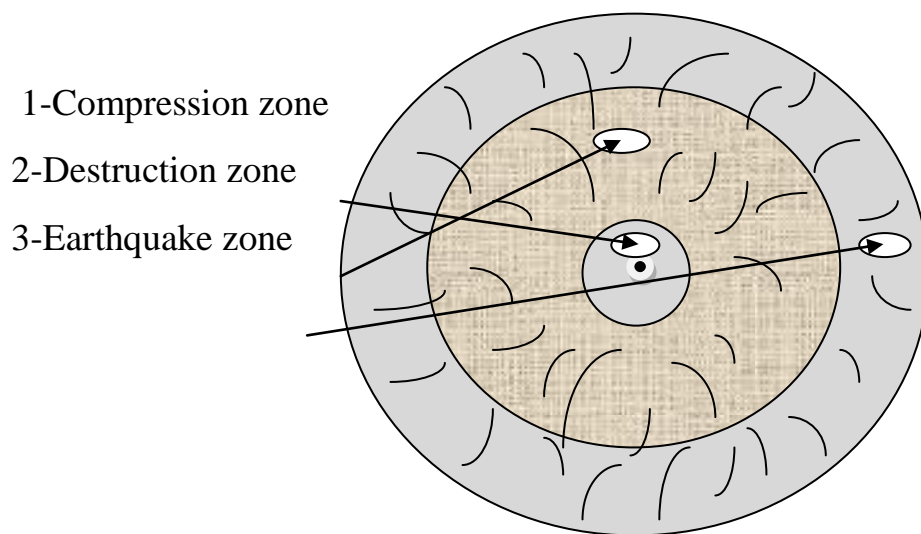


Fig. 2.1. Zones that arise as a result of a projectile explosion

Already at a depth of 2 meters in the territory where the shooting took place, the homogeneity of the soil is disturbed. The entire space from the surface to the depth of groundwater is completely transformed into a cracked-porous one (Fig. 2.2).

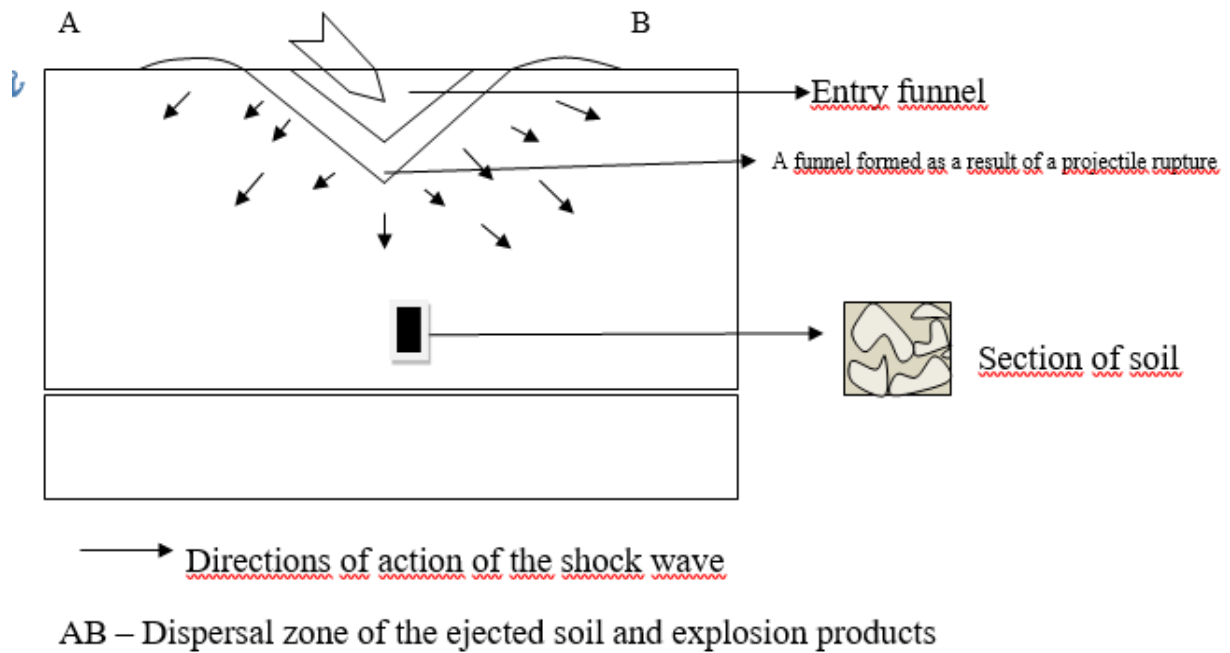


Fig. 2.2. Projectile action on the environment

As a result of the change in the soil structure, heavy metal ions that settle on the soil infiltrate into the deeper layers of the soil, and then enter the groundwater (Fig. 3.3 and 3.4).

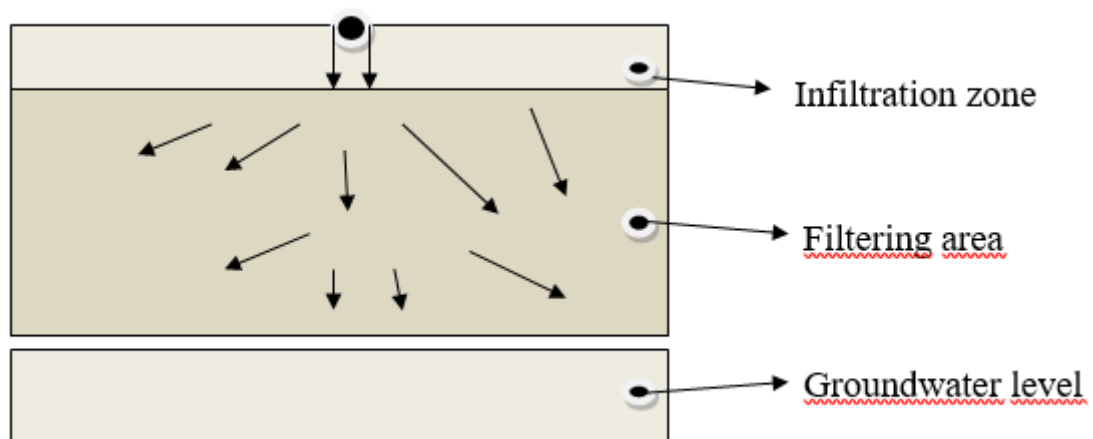


Fig. 2.3. Spread of pollution from a point source



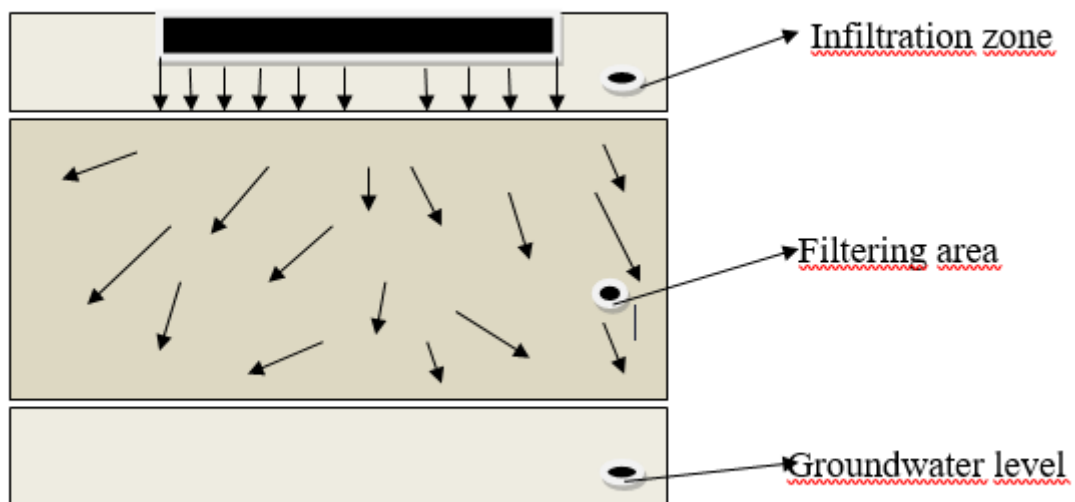


Fig. 2.4. Spread of pollution from a plain source

It should be added that each of the above-mentioned impacts leads to the destruction of vegetation, disturbance of soil cover, lack of natural moisture and desertification. As a result, the level of biota is also sharply reduced.

A very negative point is that pollutants can move. This happens in two ways:

- 1) horizontal — occurs immediately after the bombing, primarily due to air transport;
- 2) vertical - it is connected with such factors as diffusion of ions, transfer with the flow of moisture or plant root systems, activity of soil mesofauna, economic activity of man.

Most often, the migration of pollutants occurs through groundwater, which has the ability to retain heavy metals through selective absorption (adsorption). Many factors influence the proportion of heavy metals that migrate. In particular, the composition of the soil, organic substances in it, humidity, microbiological activity, etc., are important. The presence of plants also affects the mobility of explosives and heavy metals.

Pollution begins with the absorption of particles through the liquid solution present in the porous soil matrix. The soil solution containing compounds of explosive substances

penetrates into the roots of the plant. Compounds of explosive substances inside the roots move freely between the membranes, and eventually completely settle in the plant.

## **2.2.Sources of heavy metals associated with military actions**

Studying the consequences of wars in a historical aspect makes it possible to better understand the environmental problems of today. Soil cover has always been a hostage of military activity. The two main sources of degradation are the use of weapon systems and military maneuvers, depriving the enemy of resources. The first two are a recurring pattern throughout history. The most obvious is the direct destruction of soil and plant cover: the purposeful infliction of damage to achieve a specific military objective, such as burning fields and gardens, or defoliating jungles to reveal enemy shelters.

Incidental direct destruction is caused by targeted actions that have some other tactical purpose, such as digging trenches and bombing supply routes. The type of consequences that are often less obvious during hostilities can have long-term effects on the terrestrial environment. Indirect effects are usually the most difficult to predict. An example of an indirect effect on soils is the loss of soil buffering capacity, salinization, etc.

During the execution of each fire mission, the soil is contaminated by explosion products and ammunition fragments, the nature of which distribution and impact on the environment largely depends on the speed of the explosive transformation of the explosive substance, the mass of the explosive substance of the projectile.

Since most of the pure high-explosive substances are very sensitive to mechanical influences, alloys of the above explosive substances are used to equip modern ammunition used in combat shooting exercises. This significantly increases the power of explosive processes, and therefore their negative impact on the environment.

Thus, alloys of TNT with hexane (TG) and aluminum (TGA) are characterized by an increased ability to destructive actions (explosiveness). Therefore, they are used as charges for aerial bombs, warheads of guided and unguided missiles, and for large-caliber artillery shells. Hexogen A-IX-1, which contains 5-6% of phlegmatizers, is used to equip

combat units of missiles, artillery shells, and mines. To increase the destructive and incendiary effect of small-caliber air missiles, ammunition of artillery weapons, a mechanical mixture of A-IX-2 phlegmatized hexane with aluminum powder is used.

Vaseline, paraffin are used as phlegmatizers, and carbon dioxide salts of sodium, calcium, and ethyl alcohol are used as stabilizers. These explosives are characterized by a high detonation speed (4500-8000 m/s). This determines the high speed (800-900 m/s) of spreading and penetration into the environment, including the soil, of explosion products, debris from ammunition and explosives, as well as the short duration of the effect of this factor at the initial stage of the process. Gunpowder is used as a propellant in artillery shells to create reactive power in rockets, that is, a multicomponent solid system capable of burning without access to oxygen with the release of a significant amount of gaseous products. Modern rocket powders use nitrates and perchlorates, plastics, and resins. Yes, smokeless gunpowder contains more hydrogen and hydrocarbons, than is necessary to create the final products (water and carbon dioxide), so in powder gases about 1/3 of the combustion products are carbon monoxide, which is a strong poison. The explosion and burning of powders and explosives is accompanied by the formation of a significant amount of gases (Table 6), which contain such substances as nitrogen, soot, hydrocarbons, lead, manganese dioxide, iditol, etc. Up to 30% of gases will disperse in the air, and most of them (heavy fractions, heavy metals) will settle on the soil. As the explosion products contain up to 15% water vapor, heavy metal ions and fine particles can penetrate the soil in the form of aqueous solutions. The explosion and burning of powders and explosives is accompanied by the formation of a significant amount of gases (Table 6), which contain such substances as nitrogen, soot, hydrocarbons, lead, manganese dioxide, iditol, etc. Up to 30% of gases will disperse in the air, and most of them (heavy fractions, heavy metals) will settle on the soil. As the explosion products contain up to 15% water vapor, heavy metal ions and fine particles can penetrate the soil in the form of aqueous solutions. The explosion and burning of powders and explosives is accompanied by the formation of a significant amount of gases (Table 6), which contain such substances as nitrogen, soot, hydrocarbons, lead, manganese dioxide, iditol, etc. Up to 30% of gases will disperse in the air, and most of them (heavy fractions, heavy metals) will settle on the soil. As the

explosion products contain up to 15% water vapor, heavy metal ions and fine particles can penetrate the soil in the form of aqueous solutions.

Aluminum, magnesium, kerosene, salts of nitric and perchloric acids, iron oxides, barium peroxide, magnesium dioxide, strontium compounds, iditol are used in pyrotechnic devices (incendiary, lighting, signaling). With concentrated application, they affect not only natural complexes, but also equipment and weapons, causing metal corrosion. So, for example, white phosphorus is used in smoke projectiles, the smoke of which consists of drops of a solution of phosphoric acid, a very dangerous poisonous liquid.

During smoke release, which is performed with the help of equipment installed on special combat vehicles, the smoke is small droplets of petroleum products. Analysis of the chemical composition of explosives used to equip modern munitions during combat firing shows that as a result of combustion, explosion and detonation, various derivative products are formed, most of which are either toxic or dangerous pollutants.

Therefore, as a result of combat firing, soil deformation occurs in all directions of shock wave propagation. Therefore, already at a depth of up to 2 m in the territory of the shooting, the homogeneity of the soil is disturbed and cracks are formed, which separate the porous blocks.

Thus, taking into account the above factors, it can be assumed that the harmful effects on the soil caused by the fire preparation are pulse-point in nature.

Firstly, they are quite short-lived in their effect compared to the time of the filtration process (which can take several months or even years).

Secondly, they are limited to the place of influence, the size of which is much smaller than the territory where the process of spreading pollution takes place.

Scientists point out that the question of restoring the fertility of the land after Russia's aggression is already relevant. Areas of agricultural land studded with mines and ammunition, contaminated with petroleum products and chemical compounds, and destroyed by ravines are increasing every day. And above all, in the regions with the most fertile soils in Ukraine.

The most polluted places are those where the equipment burned. But the soils suffer not only from currently not defused mines and ammunition. As a result of the war, another huge problem is the contamination of arable land with compounds of heavy metals.

Fertile soils are one of the greatest natural resources of Ukraine and the world, because a third of the world's chernozems are our land. As a result of military actions, the upper, most fertile, layers of the soil suffer the most. They also recover the slowest: the natural rate of recovery of the fertile soil layer is one centimeter per hundred years. Already now we have to plan how to help our country recover faster after this war.

By according to the calculations of the Ukrainian environmental protection group, since the beginning of the full-scale offensive of Russia, approximately 34% of the territory of Ukraine is the zone that has undergone direct military aggression, where there is already or there is a risk of systemic disturbance of the surface layer of the soil or pollution (mines, oil products, unexploded ammunition, etc.). This is a disaster. But it did not start on February 24. Even before the full-scale war, Ukraine had a huge amount of land suffering from degradation due to intensive farming. Yes, the myth of fertility blinded farmers so much that they did not think about the future, depleting the land. Military operations exacerbate this problem and can accelerate degradation processes.

## **CHAPTER 3.**

### **THE INFLUENCE OF MILITARY ACTIONS ON THE CONTENT OF HEAVY METALS IN THE SOILS OF THE SUMY OBLAST**

#### **3.1. Consequences of military actions in the Sumy oblast**

Military and man-made impacts cause specific contamination of the soil environment. Along with emissions of organic pollutants, including polyaromatic hydrocarbons and polychlorinated biphenyls, military activities are closely linked to soil contamination with heavy metals. In particular, a significant accumulation of metals was observed in the territories of hostilities as a result of the use of various weapon systems. Thus, emissions of pollutants associated with military activities can indicate a direct impact on the living environment and play a significant role in the health of the civilian population.

It has been proven that exposure to pollutants of military and man-made origin causes negative health consequences related to cardiovascular, metabolic, neurological and oncological diseases. Getting these substances into the human body is a risk factor for the development of various pathologies, the growth and complication of the course of a number of diseases. Many trace elements, including those necessary for living organisms, are toxic to humans in abnormally high concentrations.

It turns out that even small concentrations of pollutants change the activity of enzymes in the human body, participate in the circulation of nuclei and protein synthesis, cause changes at the genetic level. Forecasting the behavior of pollutants in the soil cover is not an easy task, since the soil is a complex colloid-disperse system. In it, the accumulation of pollutants and their redistribution under the influence of military and man-made factors with further translocation to trophic chains (soil-plant-human) takes place.

The mechanism of pollutant mobilization in the soil largely depends on the formation of organic complexes, since complexation changes the bioavailability and

solubility of the substances themselves. Complex formation also changes the existing forms of soil pollutants, and therefore changes their bioavailability and solubility. After entering the soil, the "behavior" of explosive compounds and heavy metals is influenced by both abiotic and biotic processes. The speed of their migration and transformation is regulated by physico-chemical and biological factors of the soil environment (dissolution, evaporation, adsorption, photolysis, hydrolysis, biodegradation). The mobility of pollutants in the soil environment depends on the granulometric and mineralogical composition of the soil, humus content, redox and acid-alkaline conditions, and the presence of geochemical barriers.

The behavior of pollutants is greatly influenced by the time aspect. Soluble organic substances and acidification of the soil environment increase the rate of pollutant migration. The redistribution of pollutants occurs both horizontally and vertically. Horizontal migration is most noticeable immediately after bombing and occurs primarily through air transport. Vertical migration is associated with the following factors: diffusion of ions, transfer with moisture flow, transfer by root systems of plants, activity of soil mesofauna, economic activity of man.

The water regime exerts the greatest influence on the intensity of pollutant migration in the soil profile. In the soil solution, pollutants are in both ionic and bound forms, which are in a certain equilibrium. The existence of metals in natural waters in the form of complex compounds with inorganic ligands and anions of organic acids significantly increases their mobility. According to the degree of mobility, pollutants, in particular heavy metals, in the liquid phase of the soil are divided into three main forms: insoluble, colloidal and true solution. Heavy metals in the substance can be in the form of hydroxide, in the composition of organo-mineral HA and FC-complexes (humic acids and fulvic acids). Possible compounds of the colloidal group of heavy metals can be mineral, organic and organomineral forms.

Within organo-mineral forms, heavy metals are part of complex chelate compounds or complex metal-organic complexes formed as a result of sorption of heavy metals by colloidal organic matter, as well as formed hydroxides of iron, manganese, aluminum. Getting into the soil, the mineral forms of heavy metals turn into more complex formations

under the influence of the biotic component of the soil. Not only lithophilic, rock-forming minerals, but also chalcophilic metals are removed from solutions and fixed in the solid phase of the soil. The processes of fixation of heavy metals, covering the entire thickness of the soil, collectively form a sorption landscape-geochemical barrier.

The Ukrainian Helsinki Union documented the crimes committed by the occupiers in the Sumy region during the year of the full-scale war. The most terrible consequences are human casualties. Very large damage was caused to civil infrastructure objects, in particular, 1,749 such objects were documented (table 3.1).

Table 3.1

Damage caused to objects of civil infrastructure

<b>Type of objects</b>	<b>Number</b>
Residential buildings	975
Buildings of educational institutions	69
Buildings of health care institutions	28
Buildings of state institutions	26
Buildings of cultural and entertainment institutions	27
Buildings of religious purpose	33
Objects of entrepreneurial activity and commercial and industrial purpose	176
Objects of transport infrastructure	13
Life support infrastructure facilities	188
Historical monuments	9
Agricultural lands, forests	34
Bridges	6
Cars, vehicles	165

Regarding environmental damage, at the end of May and during June, the State Environmental Inspection in Sumy Oblast continues to calculate and publicize the damage caused to the surrounding natural environment of Sumy Oblast by Russian troops as a result of shelling, among which is the damage caused by clogging, fires, shelling of oil depots etc. In February-March, the State Environmental Inspection in the Sumy region processed the information received from the Specialized Environmental Prosecutor's Office and the



Sumy OVA regarding the pollution of the Vorskla River. It is about the destruction of the road bridge near the village Klimentov of the Okhtyr territorial community. As a result, about 3,000 tons of construction structures collapsed in the Vorskla River, which led to the clogging of surface waters and the general deterioration of the ecosystem.

During August, active "arrivals" were recorded on the infrastructure of the region: water towers, gas pipelines, power lines.

They are damaged during shelling agricultural enterprises, in particular, fields and forests. Mining of territories is especially threatening.

According to the Ukrainian Helsinki Union, at least the following events took place during the year of the war in Sumy Oblast:

Table 3.2.

Numerous shelling of the border of the northern region continues.

<b>Event</b>	<b>Episodes</b>
Artillery shelling (bombardment)	539
Small arms fire	56
Explosive device	43
Environmental disaster due to shelling	23



During the chronological analysis of events by the type of damaged objects, the following pattern is observed: at the beginning of the full-scale invasion, large objects of entrepreneurial activity and commercial production were under the enemy's sights, most likely due to the freezing of the region's economy, in the future, transport routes (bridges and roads) to slow down the military logistics of the Armed Forces, after the enemy destroyed "places of possible deployment" and other objects of the environmental fund. That is, the priority for the enemy was to damage the objects of strategic importance, which is the basis for putting forward the issue of strengthening the protection of untouched objects of this category to the fore.

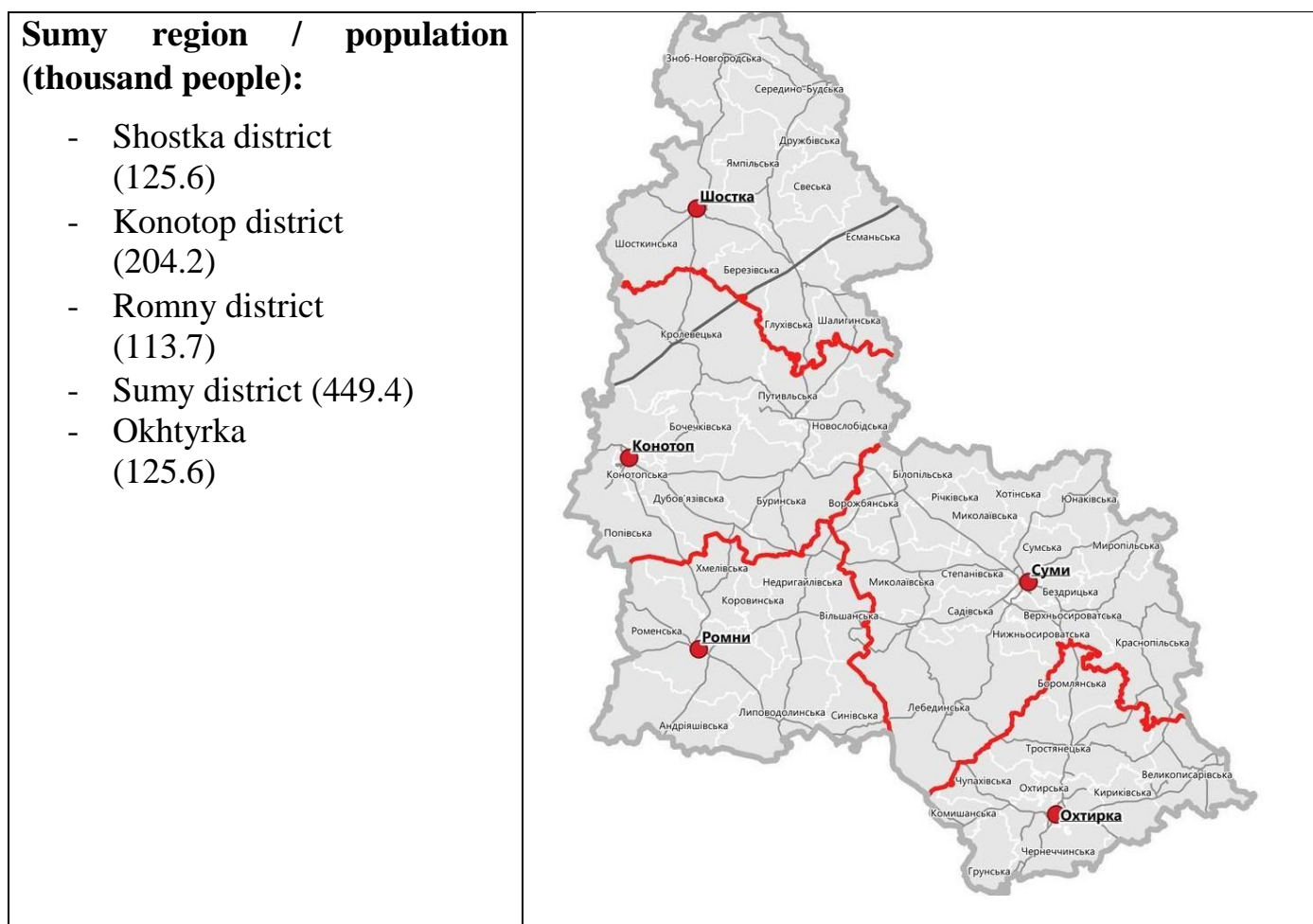
The nature of the object of concessions, namely the environmental fund of Ukraine, is quite complex: the environmental sector in different parts of the country is very different. The recovery of the environmental sector after the war is likely to be more difficult than that of other industries. It is safe to say that much more money will need to be spent than we are currently calculating in the numerous damage reports. Moreover, it will be even more difficult to determine the priority areas where exactly to accumulate funds in the first place.

### **3.2. The content of heavy metals in the soils of the districts of Sumy region, which were most affected by the war**

In 2022, after the liberation of Sumy region from the Russian invaders, specialists of the Institute of Soil Protection of Ukraine (Kyiv) and Dnipro National University named after Oles Honchar (Dnipro) conducted a laboratory study of soil samples for the content of heavy metals [ ].

The object of research was soil samples taken on agricultural lands of Sumy and Okhtyr districts of Sumy oblast (Fig. 3.3).

## Administrative system of Sumy oblast



Seven soil samples were taken from the places where air bombs fell (samples 1-7) and three samples were taken from the places of broken military equipment (samples 8-10). Control (background) samples — from territories that were nearby (100 m from the point of damage) were characterized by the same type of soil, except for the influence of hostilities. Laboratory analysis of samples was carried out in the laboratory. The content of gross forms of heavy metals was determined in accordance with DSTU ISO 11047:2005 [ ] (Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc in the extract obtained after treating the soil with aqua regia. Methods of flame and electrothermal atomic absorption spectrometry).

Assessment of the ecological state of soils by the content of heavy metals was carried out by comparing their content in the soil disturbed as a result of hostilities with

the content in the soil sampled outside the hostilities zone and the maximum permissible concentration (MPC) (table 3.3).

Table 3.3

Maximum permissible limits of heavy metals in soil (mg/kg)

	UA STD	EU STD	UK STD	US STD	WHO STD
Pb	32	300	70	300	0.3 - 190
Zn	300	300	200	200 - 300	12 - 16
CD	3	3.0	1.4	400	0.002 - 0.5
Cu	100	140	6.3	80 - 200	1 – 12
No	50	-	-	-	0.1 - 5
Fe	-	-	-	-	-

UA STD = Standard of Ukraine [ ]

EU STD = Standard of Europe

UK STD = Standard of the United Kingdom

US STD = Standard of The United States of America

WHO STD = Standard of the World Health Organization

[6] VF Ediene, SBA Umoetok. Concentration of Heavy Metals in Soils at the Municipal Dumpsite in Calabar Metropolis / Asian Journal of Environment & Ecology (2017). 3(2): 1-11. URL:<https://www.researchgate.net/publication/317945118>

Results of laboratory analysis are presented in tables 1 and 2.

Table 3.4

Content of gross forms of heavy metals of I hazard class on agricultural lands of Sumy and Okhtyr districts of Sumy oblast, mg/soil kg

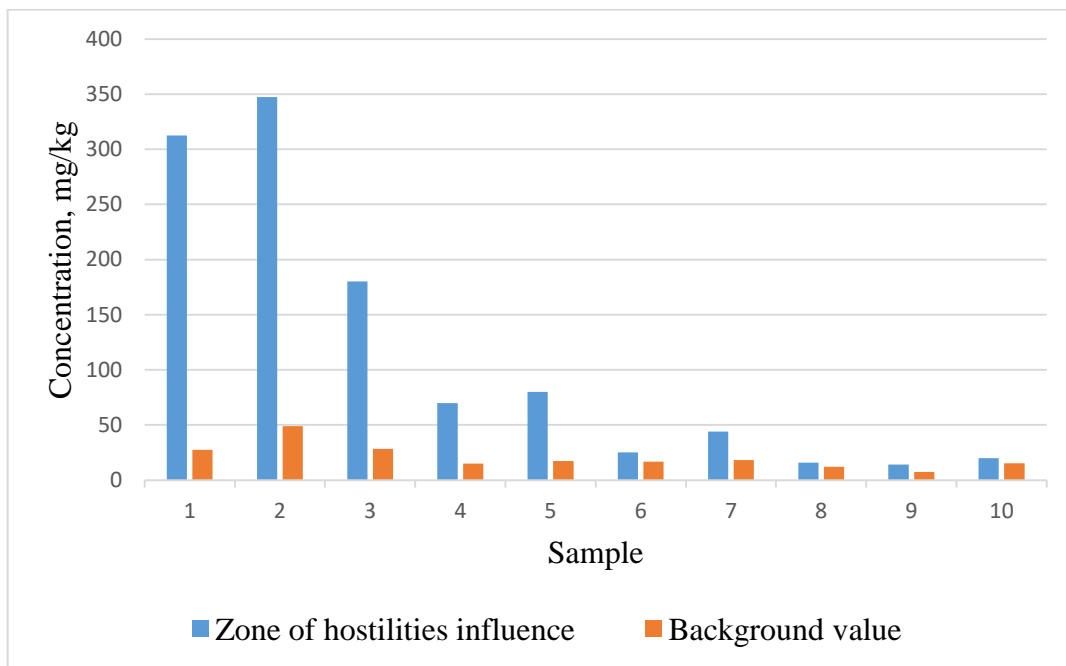
Soil sample	Lead			Zinc			Cadmium		
	Zone of hostilities influence	Background value	% to the background	Zone of hostilities influence	Background value	% to the background	Zone of hostilities influence	Background value	% to the background
1	312.38*	27,39	1140.5	209.85	84.6	248	1.71	0.51	333.3
2	347.43*	48.96*	709.6	1012.31*	214.86	471.1	1.76	0.69	255.1
3	180.19*	28,44	633.6	397.47*	51.97	764.8	0.72	0.67	107.5
4	69.74*	15.06	463.1	201.83	37.53	537.8	0.6	0.87	69
5	80.12*	17,14	467.4	193.77	43.92	441.2	0.56	0.51	109.8
6	25.1	16.58	151.4	126.68	57,64	219.8	0.44	0.43	102.3
7	44.08*	18,18	242.5	201.25	39.56	508.7	0.61	0.45	135.6
8	15.74	11.94	131.8	35.52	35.98	98.7	0.54	0.54	100
9	14,17	7.45	190.2	132.78	38.56	344.3	0.22	0.15	146.7
10	19.88	15,19	130.9	104.68	66.1	158.4	0.42	0.41	102.4
Mean	110.88	20.63	537.4	261.61	67.07	390	0.76	0.52	144.7
Standard error	39.79	3.73		88.63	17,13		0.17	0.06	
Mean square deviation	125.83	11.8		280.29	54.17		0.53	0.19	
Variation coefficient	113.5	57.2		107.1	80.8		70.1	37	
Min	14,17	7.45		35.52	35.98		0.22	0.15	

<b>Max</b>	<b>347.4</b>	<b>48.96</b>		<b>1012.31</b>	<b>214.86</b>		<b>1.76</b>	<b>0.87</b>	
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Analysis shows that the highest concentrations of lead are characteristic of the in the places of broken military equipment (especially samples 1-4)(Fig. 3.2). At the same time, a significant excess of the maximum permissible concentrations is observed (till 1000%). Exceeding the maximum permissible concentrations is also observed in the places where air bombs fell, but within smaller limits (30 - 90%).

Fig. 3.4.

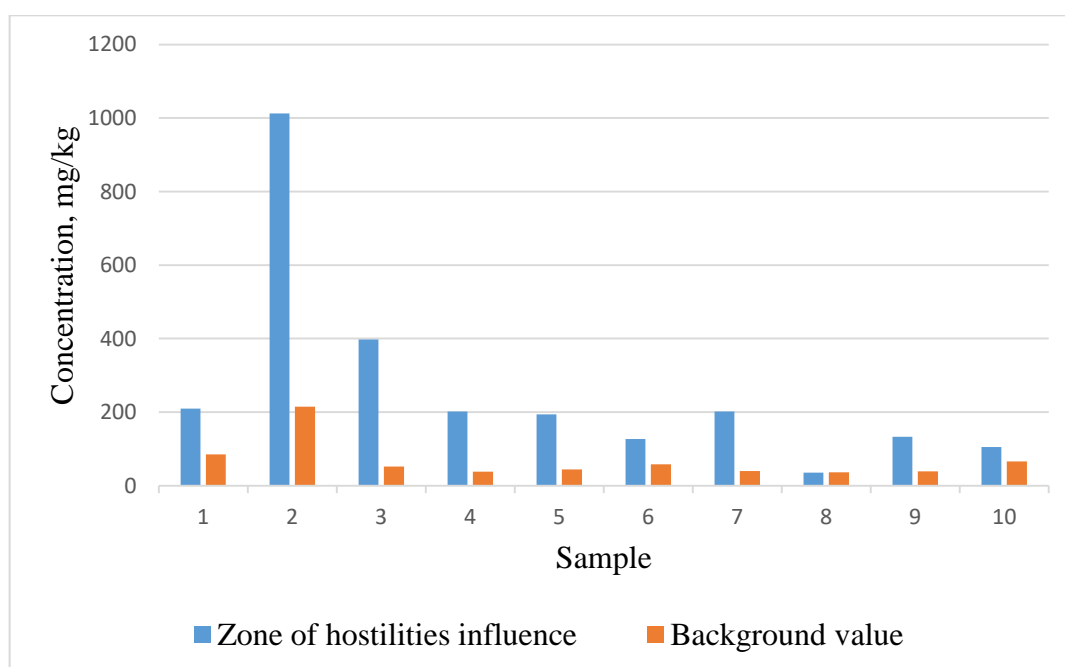
Comparison of lead concentration in soil of hostilities influence zone and background concentration



Analysis of zinc content demonstrates similar results – the largest concentrations were observed at places of broken military equipment (especially samples 2, 3) in comparison with background concentrations (Fig. 3.4).

Fig. 3.5.

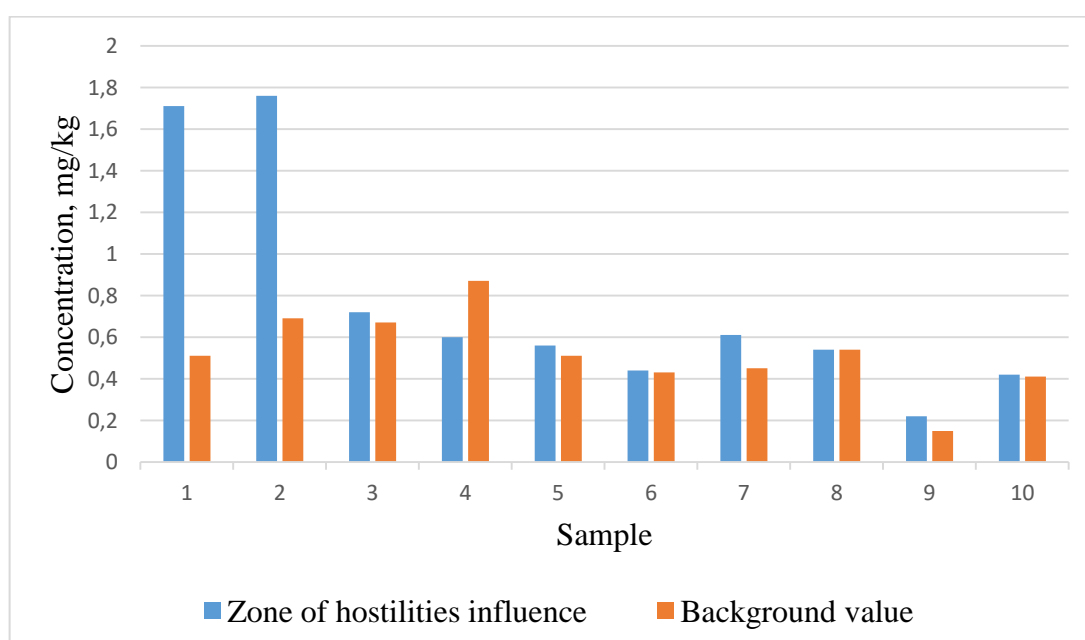
Comparison of zinc concentration in soil of hostilities influence zone and background concentration



Comparison of cadmium concentration in soil of hostilities influence zone and background concentration is represented in figure 3.5. A significant excess is typical for samples 1 and 2.

Fig. 3.5.

Comparison of cadmium concentration in soil of hostilities influence zone and background concentration





In all three cases (lead, zinc and cadmium) soil sample 2 (taken in village Stare Selo of Sumy region) demonstrates the highest concentrations of highly toxic heavy metals. Unfortunately, authors [8] do not provide information about the type of military equipment that led to such a high level of pollution.

Analysis of content of II and III hazard class heavy metals are represented by copper and nickel (table 3.4 and 3.5).

Table 3.5

Content of gross forms of heavy metals of II hazard class on agricultural lands of Sumy and Okhtyr districts of Sumy oblast, mg/soil kg

Soil sample	Cuprum			Niskel		
	Zone of hostilities influence	Background value	% to the background value	Zone of hostilities influence	Background value	% to the background value
<b>1</b>	<b>554.76*</b>	25.85	2146.1	7.04	6.49	108.5
<b>2</b>	<b>610.38*</b>	83.52	730.8	23,22	6.38	363.9
<b>3</b>	<b>122.33*</b>	14.77	828.2	6.28	7.09	88.6
<b>4</b>	<b>141.88*</b>	11.97	1185.3	6.50	6.80	95.6
<b>5</b>	<b>111.71*</b>	<b>177.07*</b>	63.1	6.40	7.69	83.2
<b>6</b>	27.71	15.33	180.8	7.05	7.43	94.9
<b>7</b>	53.69	12.33	435.4	7.72	8.32	92.8
<b>8</b>	21,21	14.66	144.7	5.06	7.24	69.9
<b>9</b>	4.50	0.79	569.6	2.50	1.74	143.7
<b>10</b>	6,10	6.13	99.5	2.68	3.63	73.8
<b>Mean</b>	<b>165.43</b>	<b>36,24</b>	<b>638.35</b>	<b>7.45</b>	<b>6.28</b>	<b>121.49</b>
<b>Standard error</b>	<b>71.37</b>	<b>17,28</b>		<b>5.82</b>	<b>0.64</b>	
<b>Mean square deviation</b>	<b>225.68</b>	<b>54.63</b>		<b>5.82</b>	<b>2.02</b>	
<b>Variation coefficient</b>	<b>136.40</b>	<b>150.70</b>		<b>78.24</b>	<b>32,28</b>	
<b>Min</b>	<b>4.50</b>	<b>0.79</b>		<b>2.50</b>	<b>1.74</b>	
<b>Max</b>	<b>610.38</b>	<b>177.07</b>		<b>23,22</b>	<b>8.32</b>	

From histograms (Fig. 3.5 and 3.6) we see that significant excess is typical for sample 1 and 2 for copper and sample 2 for nickel.

Fig. 3.6.

Comparison of cuprum concentration in soil of hostilities influence zone and background concentration

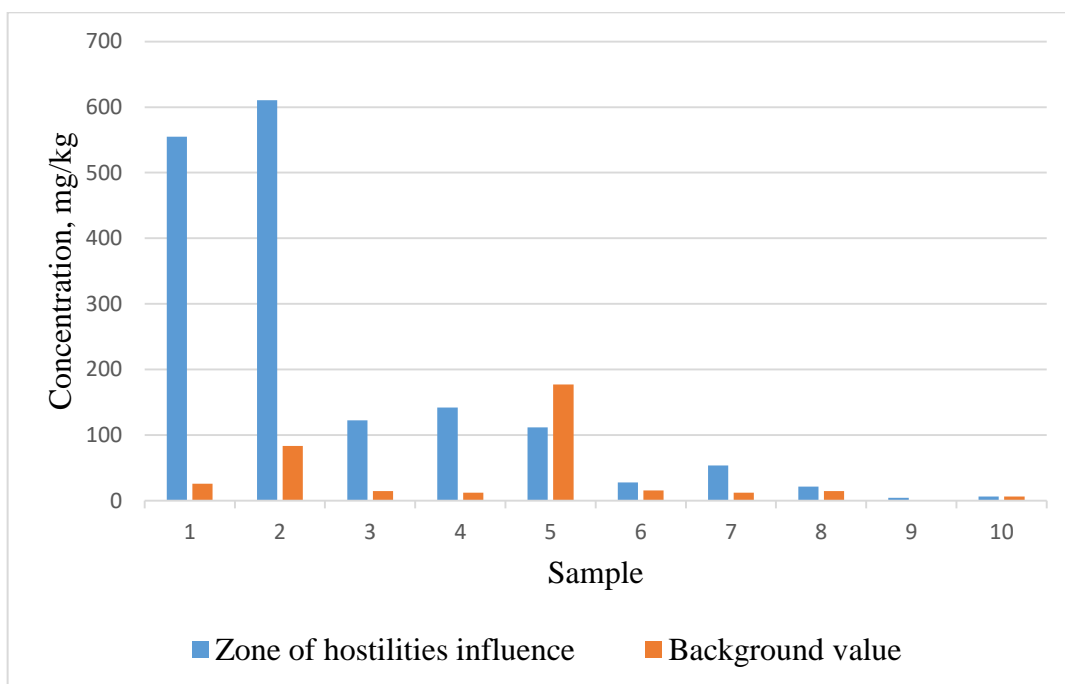


Fig. 3.7.

Comparison of nickel concentration in soil of hostilities influence zone and background concentration

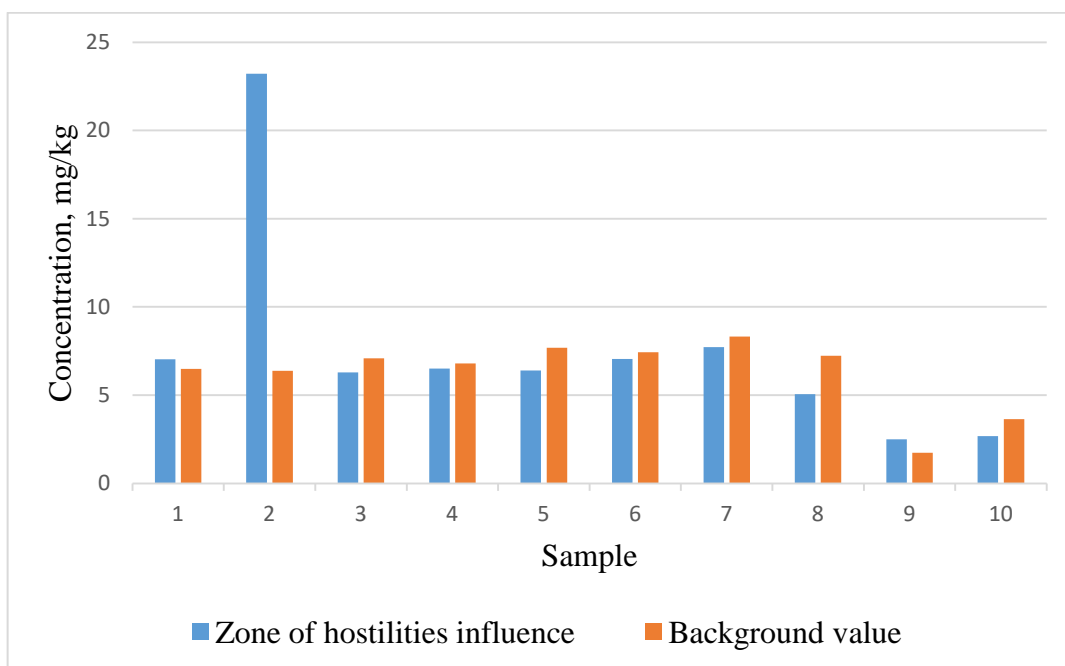


Table 3.6

Content of gross forms of heavy metals of III hazard class on agricultural lands of Sumy and Okhtyr districts of Sumy oblast, mg/soil kg

Soil sample	Iron			Manganese		
	Zone of hostilities influence	Background value	% to the background value	Zone of hostilities influence	Background value	% to the background value
<b>1</b>	26353	11219	234.9	<b>3545.19*</b>	312.91	1133
<b>2</b>	11599	15195	76.6	872.3	172.32	506.2
<b>3</b>	10887	10189	106.9	332.16	201.44	164.9
<b>4</b>	9784	11888	82.3	322.01	182.85	176.1
<b>5</b>	9234	11428	80.8	216.36	333.81	64.8
<b>6</b>	12392	12604	98.3	197.06	199.74	98.7
<b>7</b>	8728	12158	81.8	99.56	188.42	52.8
<b>8</b>	9536	10031	95.1	<b>3524.15*</b>	242.46	1453.5
<b>9</b>	3430	470	729.8	62.29	21.86	284.9
<b>10</b>	3656	4687	78.0	83.09	87.71	94.7
<b>Mean</b>	<b>10559.90</b>	<b>9986.90</b>	<b>105.7</b>	<b>923.49</b>	<b>194.08</b>	<b>476.2</b>
<b>Standard error</b>	<b>1997.90</b>	<b>1352.40</b>		<b>441.37</b>	<b>29,37</b>	
<b>Mean square deviation</b>	<b>6317.77</b>	<b>4276.54</b>		<b>1395.70</b>	<b>92.89</b>	
<b>Variation coefficient</b>	<b>59.80</b>	<b>42.80</b>		<b>150.70</b>	<b>47.80</b>	
<b>Min</b>	<b>3430</b>	<b>470</b>		<b>62.29</b>	<b>21.86</b>	
<b>Max</b>	<b>26356</b>	<b>15195</b>		<b>3545.19</b>	<b>333.81</b>	

Table 3.7

## Degree of soil pollution

Degree of soil pollution	AF
uncontaminated soils	1 – 2
lightly polluted soils	Less than 10
medium polluted soils	10 – 30
highly polluted soils	30 – 60
very highly polluted soils	More than 60

Accumulation factor (AF) = C/B

C = content of gross forms of heavy metal, B = background content

Table 3.8.

## Gradation of soils according to the degree of pollution

Sample	Lead	Zinc	Cadmium	Cuprum	Nikel	Iron	Manganese
1	11,40	2,48	3,35	21,46	1,08	2,35	11,33
2	7,10	4,71	2,55	7,31	3,64	0,76	5,06
3	6,34	7,65	1,07	8,28	0,89	1,07	1,65
4	4,63	5,38	0,69	11,85	0,96	0,82	1,76
5	4,67	4,41	1,10	0,63	0,83	0,81	0,65
6	1,51	2,20	1,02	1,81	0,95	0,98	0,99
7	2,42	5,09	1,36	4,35	0,93	0,72	0,53
8	1,32	0,99	1,00	1,45	0,70	0,95	14,53
9	1,90	3,44	1,47	5,70	1,44	7,30	2,85
10	1,31	1,58	1,02	1,00	0,74	0,78	0,95

Among the measures of soil detoxification, the following methods can be distinguished:

- Soil liming (вапнування ґрунту)
- Application of manure, peat, organo-mineral components (застосування гною, торфу, органімінеральних компонентів)

- Use of phosphorus fertilizers (фосфорні добрива)
- Use of zeolites of both natural and artificial origin (цеоліти)
- Use of oppositely directed interactions
- Use of biological measures. These include the cultivation of tolerant agricultural crops, or the use of contaminated land resources for the cultivation of technical and forest crops and the breeding of flowers

Creation of a new arable horizon both through plantation plowing, which ensures the burial of a layer at a depth of 40-50 cm and the upturning of uncontaminated subsoil to the surface, and through the creation of a bulk layer due to soil brought from an uncontaminated territory. It is also possible to remove the toxic layer and place normal soil in its place.

Table 3.9

Selection of the soil detoxification method for investigated territories

<b>Method of soil detoxication</b>	<b>heavy metals (highest effect)</b>	<b>Recommendation for samples</b>
Soil liming	Cadmium	1 and 2
Application of manure, peat, organo-mineral components	All heavy metals	1 – 9
Phosphorus fertilizers	Lead, zinc	1 – 5, 7
Zeolites	Lead, cationic form of metals	1
Use of oppositely directed interactions	[Usually used for pollution by Hg]	-
Biological measures	For very highly polluted soils	-
Creation of a new arable horizon	For very highly polluted soils	-

After the war, such an analysis of soil contamination should be made for all regions and districts of Ukraine that are in the zone of active military operations.

## **Recommendations**

Speaking of recommendations, in the short term, Ukraine should focus first of all on methods of recording and assessing the environmental damage inflicted on it every day. In the future, it is necessary to focus on the elimination and reduction of immediate risks to human health and the environment associated with the consequences of war. Comprehensive environmental cleanup measures, especially the collection, safe disposal and disposal of military and other waste, can help reduce health risks. However, this will require rebuilding and rebuilding a more efficient environmental infrastructure to ensure safe drinking water, adequate sanitation and proper waste management. Prioritization needs to be guided by the human health consequences that already exist, as well as those that may arise in the future.

In the long term, the process of post-war economic development should be used for the fundamental transformation of Ukraine into a green economy with a net zero level of harmful emissions. Reconstruction should be based exclusively on European "green" standards: new types of materials, modern complexes for waste processing, innovative housing construction technologies, renewable energy systems, etc.

The process of transforming contaminated land into usable land is called reclamation. The choice of remediation technology depends on the nature and degree of pollution, the intended purpose or use of the area being restored, as well as on the availability of efficient and cost-effective technologies.

But before choosing a technology, you need to analyze the consequences of hostilities according to the following algorithm:

- identification of land damaged by hostilities;
- identification of influencing factors (e.g., these were troop maneuvers or movement of equipment);
- determination of the type of impact (chemical, mechanical or physical) and consequences for land;

- assessment of the level of soil contamination as a result of a certain type of impact (e.g. assessment of areas littered with fragments);
- assessment of the level of soil pollution.

Based on the conclusions of the analysis, it is possible to choose the optimal reclamation option. In turn, methods of treatment of contaminated soil include physical, chemical and biological remediation (cleaning).

Among the measures for detoxification of excess heavy metals in the soil, the following can be distinguished:

1. Soil liming. It was established that the lowest solubility of heavy metals is observed at pH 6.5. In the experiments conducted by Karpova and Potatuyeva, it was established that lime significantly reduces the intake of cadmium in plants. Also, the antagonism between Ca and heavy metals is often noted in the literature.

2. The use of manure, peat, and organo-mineral components makes it possible to use the property of many organic compounds to complex with heavy metals. The formed organometallic complexes are either immobile or unable to overcome cell membranes in the "soil-root" system.

3. Phosphorous fertilizers have a significant ability to detoxify heavy metals. Phosphates of Pb, Zn and other metals are poorly soluble compounds that are not readily available to plants. Applying 3 t/ha of monosubstituted calcium phosphate to the soil due to the effect of Pb detoxification (the content of Pb in plants was taken into account) corresponded to the application of 1 to 4 t of CaCO<sub>3</sub>/ha (Lagerwerff, 1972). To reduce expenses on superphosphate, it is advisable to use phosphorite flour. Therefore, the phosphorization of acidic soils with the aim of inactivating excess BM is considered as one of the important measures of human and animal health protection (Mineev, 1988).

4. To detoxify an excess of heavy metals in the soil, you can use zeolites of both natural and artificial origin. It should be noted that this refers to metals found in the soil solution in the form of cations. The presence of zeolites does not reduce the migration of anionic forms of metals into plants (Yelishchevta et al., 1987). When using different types of zeolite in acidic soils contaminated with lead, it was possible to reduce the content of



this metal by 30%. However, in some soils the effect of the presence of zeolite was insignificant (Orowiak et al., 1985).

5. Use of oppositely directed interactions. As is known from agrochemistry, when plants absorb chemical elements from the soil, oppositely directed interactions occur: synergistic, when the presence of one element promotes the entry of another into the roots, and antagonistic, when it opposes its entry. In particular, the antagonism between Hg and Zn was pointed out and the possibility of using zinc, in this case as much less toxic, to limit the entry of mercury into food chains was allowed (Agerwerff, 1972).

6. Use of biological measures. These include the cultivation of tolerant agricultural crops, or the use of contaminated land resources for the cultivation of technical and forest crops and the breeding of flowers.

7. Creation of a new arable horizon both through plantation plowing, which ensures the burial of a layer at a depth of 40-50 cm and the upturning of uncontaminated subsoil to the surface, and through the creation of a bulk layer at the expense of soil brought from an uncontaminated territory. It is also possible to remove the toxic layer and place normal soil in its place.

## CONCLUSIONS

As a result of the conducted research, an excess of the background level in terms of the gross content of lead was found in all ten soil samples, zinc – nine, cadmium and copper – eight, manganese – six, nickel and iron – three, and the average content of lead in the contaminated territories was 5.4 times exceeded the background value, manganese — 4.8 times, copper — 4.6, zinc — 3.9, cadmium — 1.4, nickel and iron — 1.2 and 1.1 times.

Exceeding the MPC of gross lead content was found in six soil samples, copper in five soil samples, zinc and manganese in two soil samples from the sites of hostilities. The content of gross forms of cadmium and nickel did not exceed the MPC.

The highest degree of disturbance of the soil cover as a result of hostilities was noted in the places of burned equipment (the village of Kosivshchyna, the village of Stare Selo, the village of Nyzy, Sumy District, Sumy oblast).

A significantly higher coefficient of variation of the content of gross forms of heavy metals in the combat zone, compared to the content outside the combat zone (background value), may indicate the intensity of the influence of a negative factor on the soil cover.

According to the results of the correlation analysis, an extremely strong dependence was established between the content of the studied forms of heavy metals.

In order to prevent negative consequences for the human body, it is necessary to carry out careful monitoring of soil areas damaged and contaminated as a result of hostilities, which will make it possible to take timely measures for their reproduction and rehabilitation, as well as to establish the boundaries of contaminated areas for the purpose of their restoration.

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