ENVIRONMENTAL ASSESSMENT OF CHEMICAL POLLUTION OF SOILS AS A RESULT OF THE WAR

Екологічні збитки України від повномасштабної агресії РФ становлять майже 2 трлн. грн., частину природних ресурсів втрачено назавжди, повідомив міністр захисту довкілля та природних ресурсів України. За 2021 рік в атмосферу викинули близько 2 тонн токсичних речовин. За півроку війни в Україні у 2022 році викиди в атмосферу становлять 46 млн тонн. Війна отруїла значну частину української землі. Шкода, завдана забруднен- ням ґрунтів, оцінюється у 18 млрд.доларів. За даними ООН, Україна є однією з найбільш замінованих країн у світі (майже 15% загальної площі). Розмінування цієї території або детонація мін теж буде призводити до забруднення ґрунтів і ґрунтових вод. Під час вибуху у довкілля потрапляють уламки снарядів, які містять домішки чавуну, заліза, вуглецю, сірки та міді, і можуть призводить до забруднення ґрунтових і підземних вод. Окрему небезпеку становить замінування сільськогосподарських угідь – забруднення землі може призвести до того, що деякий час на цих територіях не можна буде нічого вирощувати. А оскільки в нас аграрна країна і ми досить залежні від вирощування на наших землях, то це також буде впливати на продовольчу безпеку України та світу. Значні території Укра- їни забруднені органічними речовинами у складі нафтопродуктів, сольвентів, антифризів тощо. До них належать парафіни, нафтени, ароматичні сполуки (бензол, толуол, етил- бензол, ксилол), поліциклічні вуглеводні (нафталін, перилен), галогенопохідні вуглеводнів дихлоретан, хлороформ, хлорбензол, органічні розчинники, поверхнево-активні речовини, синтетичні феноли, діоксини та інші. Це відбувається під час ремонту, заправляння вій- ськової техніки в польових умовах, в місцях збереження паливно-мастильних матеріалів, під час поривів нафтопроводів, влучання в нафтобази. Потрапляючи в ґрунт, ці речовини порушують його структуру і процеси газообміну, перешкоджають поглинанню вологи, створюючи умови, що непридатні для життя рослин, тварин, мікроорганізмів. **Ключові слова**: хімічне забруднення, екологія, ґрунти, війна.

Relevance of the topic of research. As the war continues to rage across the country, soil and waterway contamination is a major concern for environmental activists. Ukraine is one of the most industrialized countries in Europe, with an estimated 6 billion tons of liquid waste generated by coal mines, chemical plants, and other heavy industries. Over the past six months, such extremely sensitive objects have been constantly subjected to Russian shelling. During the detonation of military missiles, artillery shells, mines, a number of chemical compounds are formed: carbon monoxide, carbon dioxide, water vapor, brown gas, nitrogen, etc. In addition, a large amount of toxic organic matter is formed, the surrounding soils, wood, and structures are oxidized. There are also a number of toxic elements, such as oxides of sulfur and nitrogen, which during oxidation can lead to acid rain. They can change the pH of the soil, cause burns of plants, mucous tissues of the respiratory organs of humans, birds, and mammals [1]. As a result, shelling can pollute not only air and soil, but also groundwater. Since agricultural products can be grown on the soil, and groundwater can be used as a source of drinking water, all these elements can enter food chains.

And if they get into the human body, it can lead to significant health problems in the future. According to the UN, Ukraine is one of the most mined countries in the world. Almost 15% of the total area is mined. This will directly affect soil pollution. Demining of this territory or detonation of mines will also lead to heavy metal contamination of soil and groundwater. In addition to oxidation during the explosion, projectile fragments that enter the environment are dangerous. They have impurities of cast iron, iron, carbon, sulfur and copper, which can lead to soil and underground water pollution [2]. A separate danger is the mining of fields – soil contamination can lead to the fact that it will not be possible to grow anything in these territories for some time. Since we are an agrarian country, and we are quite dependent on cultivation on our lands, this will also affect the food security of Ukraine and the world. The final scale of the impact of military operations and mining on agricultural land cannot yet be established.

The purpose of research is to analyze the scale of chemical pollution and ecological damage caused to the environment of Ukraine during the year of the full-scale war. Such data are made public by the State Environmental Inspection, the Ministry of Environmental Protection and Natural Resources of Ukraine, and the Ecodia Center for Environmental Initiatives. They contain information about the sources of toxic substances entering the soil.

Literature Review. The chemical impact of military measures leads to a change in the natural parameters of the ground cover under the influence of pollutants produced as a result of the use of weapon systems and military equipment. Long-term military activity leads to the formation of local military-technogenic geochemical anomalies with a different spectrum of explosive and other toxic substances, which can impose an indefinite ban on the use of land. Chemical pollution of military and technogenic origin includes: vehicle fuel, lubricants, solvents, galvanic production waste, explosives residues, decontamination substances, heavy metals and their compounds, radioactive substances [3]. Dangerous substances of the physico-chemical type are explosive materials. When shooting, ammunition with a different composition of gunpowder and explosives is used, the combustion of which produces such substances as nitrogen, soot, hydrocarbons, lead, manganese dioxide and other derivatives, which negatively affect human health and the natural environment. Thus, during the explosion of one 115 mm high-explosive munition equipped with hexane, about 4,000 liters of gas is formed, which contains the combustion products of this explosive substance. Up to 30% of gases are dispersed in the air, and most of them (heavy fractions and heavy metals) settle on the soil [5]. Explosives also play a significant role in the release of metals into the soil environment. Particles ejected from artillery strikes have been found to contain high levels of lead (Pb) and copper (Cu), which may belong to artillery shells and gun barrels. Explosive grenades were also considered a significant source of high concentrations of lead (Pb). Modern explosives or energetic materials are nitrogen-containing organic compounds with a high potential for self-oxidation to small gaseous molecules (N_2 , H_2O and CO_2). Explosives are classified as primary or secondary depending on their susceptibility to initiation. Primary explosives are often used to ignite secondary explosives such as TNT, Hexogen, Octogen and Tetryl [6]. A significant place in soil pollution is

occupied by heavy metals. According to research [7] in the area of the anti-terrorist operation (Donetsk and Luhansk regions) during 2016–2020, a high content of lead, copper, arsenic, zinc, chromium, cadmium, molybdenum, barium, potassium, magnesium and tungsten was found in the soil. The above-mentioned elements characterize the dominant spectrum of military-technogenic pollution and are leading indicators for forecasting changes in the ecological state of territories with contaminated soils and territories adjacent to them. During maintenance and repair of samples of weapons and military equipment in field camps, the soil is contaminated with fuel and lubricants, used oils, antifreezes and organic solvents. The highest concentration of petroleum products is noted in places where fuel and lubricants are stored, and where military equipment is maintained. Most often, in the places of significant spills of oil products in field filling stations, due to changes in the chemical composition of the soil, an important property of the soil – the ability to self-recovery – is violated, and the biological activity of the soil decreases [8]. Contamination can be caused by the detonation of explosives in the soil or the leakage of hydraulic fluids and fuel that may occur during the refueling of demining machines. Pollution of hydrocarbon origin can be represented by both oil products and components of oil and oil products – paraffins, naphthenes, aromatic hydrocarbons, their derivatives – benzene, toluene, as well as polycyclic hydrocarbons (naphthalene, perylene). A separate group consists of chlorohydrocarbon compounds – dichloroethane, trichloroethane, chlorobenzene, etc. They, like toluene and other homologues of benzene, represent the majority of solvents. Trichloroethane pollution is also associated with rocket fuel residues. Soils contaminated with hydrocarbons are a source of airborne toxic gases and dusts that have acute toxic effects on soil biodiversity [9]. Benzene, toluene, ethylbenzene, and xylene released from freshly contaminated soils can cause chronic effects on public health. After entering the soil, hydrocarbons can completely or partially occupy the pore space of the soil, blocking the flow of air and water. This affects the respiration of plant roots, soil microorganisms, and the provision of moisture to these biota. The use of white phosphorus in the use of incendiary bombs poses a threat to the productive use of soils over a long period of time. Over time, phosphorus acts as a fertilizer, although it tends to precipitate as apatite in neutral and alkaline soils or as Fe and Al phosphates in acidic soils. A wide set of such xenobiotics also includes heavy metals, organic solvents, surfactants, synthetic phenols, cyanides, dioxins, radionuclides [10]. The harmful effects of some of them on plants and organisms living in the soil can last relatively long.

Materials and Methods. In the article, we use the following research methods: deduction, induction, analysis, synthesis, explanation.

Results and Discussion. 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. The mechanical impact deforms the soil cover, which leads to a violation of the soil structure during the movement of military equipment, the movement of troops, the construction of protective structures, bombing sites, and demining of territories. The consequence of this impact is compaction, waterlogging, and soiling of the territory

with products of combat activity. The main mechanical impact on the soil is compaction with damage to the humus layer, which has direct negative consequences, such as disturbing the water balance of the soil, and causes the development of wind and water erosion. The destruction of the soil structure occurs as a result of the displacement of the particles of one layer relative to another under the influence of military-technogenic load [11]. According to the Ukrainian nature protection group, there are areas where experts have estimated approximately 2,052 funnels from various projectiles on just one square kilometer of the field, which means 50 tons of iron, a ton of sulfur compounds, and almost 2.5 tons of copper in terms of pollution for the soil. Demining of territories also has a negative impact – the humus horizon is usually destroyed, the physico-chemical properties of the soil are lost, and the granulometric and aggregate state changes. For its part, this affects the fertility and water-holding capacity of the soil. The installation of mines in itself predicts soil turbulence in the future. Detonation contaminates the ground with metal fragments and explosive remnants. Landmine clearance operations are often complex and expensive, so in developing countries these consequences can be interpreted as an absolute loss of soil resources [13]. 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. Chemical micro-components of pollution are mainly represented by heavy metals, such as cadmium, lead, zinc, copper. These elements are indicators for changes in the ecological state of territories with contaminated soils and territories adjacent to them [14].

Fig. 1. Satellite image of the agricultural territory of the Izyum district. Photo from the website of the Ukrainian Nature Protection Group [12]

Physical impact involves changing 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. The combination of various influencing factors leads to the emergence of a cumulative negative effect. The consequences are the loss of the soil's buffering capacity for recovery, the loss of humus and a decrease in natural fertility. 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: • horizontal – occurs immediately after the bombing, primarily due to air transport; • vertical – it is associated with such factors as diffusion of ions, transfer with the flow of moisture or plant root systems, activity of soil mesofauna, human economic activity. 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. If there are plants on the affected field, heavy metals will remain there. The intake of heavy metals in plants is influenced by several factors: species characteristics, soil type, concentration, form of presence of polluting elements, soil pH, granulometric composition. They are mostly found in roots and reproductive organs (seeds and fruits) [16].

Fig. 2. Behavior of compounds of explosive substances in soils* [15, 7]

*Note. The center icon represents unexploded ordnance, and the color behind it represents contamination diffusion. Water is marked with light arrows, and the presence of pollutants outside the central diffusion zone is marked with cultivated ones hexagons Plot (A) represents microbial interaction and metabolism, (B) sorption by soil particles, and (C) uptake andsequestration by above-ground and underground plant tissues 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. Regarding the accumulation of heavy metals, general patterns are observed among agricultural crops. In particular, heavy metals are most actively consumed by silage crops, the least by legumes, cereals, and technical crops. Pollutants can also affect the state of the biota. For example, high concentrations of hydrocarbons can cause symptoms of poisoning in earthworms.

Conclusions. The war in Ukraine caused enormous not only economic, but also environmental damage. The State Environmental Inspection has already documented more than 250 cases of ecocide for further lawsuits against the aggressor country. And, although the war is still ongoing, Ukraine has already begun to restore the environment, in particular thanks to the program of the President of Ukraine "Green Country", the creation of a new forest seed center and other projects. Due to the bursting of shells, mines and bombs, the spillage of fuel and lubricants, the destruction of energy and industrial infrastructure, many dangerous substances enter the soil. Land contaminated with heavy metals such as lead, nickel, cadmium. strontium, titanium, iron, become unsuitable for growing agricultural plants. As a result, there is a decrease in the production of crops and livestock, economic losses borne by farmers and the state, and an increase in prices for food and other goods. Damages already caused by soil pollution amount to more than 18 billion dollars.

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