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INFLUENCE OF HEAVY METALS OXIDES ON THE POLLUTION OF THE SOIL ENVIRONMENT AS A CONSEQUENCE OF MILITARY ACTIONS

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Abstract. Heavy metals enter the soil in the form of oxides and salts (both soluble and practically insoluble in water). There is an assumption that heavy metal oxides are fixed mainly in the solid phase of the soil, especially in a neutral or alkaline pH environment. It should be noted that their toxic effect depends entirely on such factors as the type of soil and the pH of the pore solution. The behavior of heavy metals in soils is significantly different from the behavior of most cations of macroelements. The purpose of this work is to assess the anthropogenic impact of heavy metal oxides, as well as accompanying oxides that are formed as a result of an explosion on the ground. To assess the degree of soil contamination, distribution and immobilization of heavy metals in the soils of industrial agglomerations.

Keywords: potentially toxic elements, soil pollution, military actions.

1. Introduction

War crimes against the environment are not only about harming nature. War can cause many early deaths in the future through polluted water, land, air, etc.

As a result of explosions, harmful substances are released into the air, which, due to the fact that they do not stay in the air for a long time, fall in the form of precipitation and accumulate in the soil.

In addition, areas contaminated by explosives and mined areas will be a threat for decades. Contamination of fertile soil and rock is the result of many destructive processes, including shell rupture, leakage of pollutants and hazardous substances from damaged reservoirs and wastes due to the failure of filter field dams, destruction of treatment or hydraulic structures. As a result of the mass death of people and animals, the soil and underground water were contaminated with corpse poison. All these environmental disasters lead to chemicals entering the soil (Pichtel, 2016).

One of the most dangerous ways of influencing soil properties is military activity. Ground disturbances caused by hostilities are mainly of three types – physical, chemical and biological. Physical disturbance of the soil includes compaction due to the construction of defense infrastructure, digging of trenches or tunnels, compaction due to the movement of equipment and troops, or cratering by bombs. It is important to note that the content of heavy metals in the soil significantly affects plants (Lima et al., 2011)

Chemical pollution as a result of military operations should be considered from 3 positions: pollution by potentially toxic elements, explosive substances and other elements.

The chemicals used in munitions and explosives are a long list of organic and inorganic substances that can be divided into: potentially toxic elements (PTE), energetic compounds (EC) and chemical warfare agents (CWA). PTE from war-affected areas are mainly Pb and its associated contaminants, including antimony (Sb), chromium (Cr), arsenic (As), mercury (Hg), nickel (Ni), zinc (Zn) and cadmium (Cd). Explosives contain huge amounts of Pb and Hg, including mercury (II) fulminate. Zn, Cu, Ni, Pb and Cr are used to coat bullets, missiles, gun barrels and

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military vehicles. Ba, Sb, and B are the charging compounds for weapons, and tungsten (W) is used for kinetic bombardment due to its high density (19.3 g/cm^3). After being released into the environment, most of the TE in ammunition is oxidised by air, while the rest enters the soil, where it undergoes various chemical processes (Fayiga et al., 2019). Missile and artillery explosions produce a variety of chemical compounds: carbon monoxide and dioxide (CO and CO_2), nitrogen oxides (NO and NO_2), formaldehyde, hydrogen cyanide (HCN) vapour, nitrogen (N_2) and loads of toxic organics. They also cause acidification of soil, wood, and corrosion of metal structures such as bridges. After the explosion, these compounds are completely oxidised and the reaction products are released into the atmosphere (Pereira et al., 2022).

Metal fragments from shells are also not completely safe for the environment. Cast iron mixed with steel is the most common material for ammunition casings and contains not only the usual iron and carbon, but also sulphur and copper. These substances leach into the soil and can drift into groundwater, eventually entering food chains and affecting humans and animals (Spuller et al., 2007).

On a smaller scale, pollution can also be caused by the burning of military equipment, vehicles, aircraft and other military equipment.

Given the numerous studies of scientists around the world on the impact of heavy metals on soil cover and its restoration, the main task for Ukraine, which has the largest reserves of black soil and supplies grain to countries suffering from hunger even during the war, is to restore soil fertility due to russia large-scale military invasion (Ecoaction, 2022). Therefore, the study of the impact of heavy metal oxides on the soil cover as a result of military operations is an urgent task.

2. Experimental part

The selection of soil samples was carried out on the territory of Ukraine affected by the war. In accordance with sampling standards, samples were taken with a plastic spatula for analysis to detect heavy metal ions. The samples were placed in a plastic (opaque) airtight container.

Sampling at each of the levels was carried out in concentric circles, the number of samples taken from each level in concentric circles – 3 samples, for the possibility of averaging experimental data. This method of soil sampling allows you to obtain the following information: the concentration of substances not only in the center of the explosion, but also along the height of the eruption; distribution of soil contamination depending on the depth of the funnel (Fig. 1).

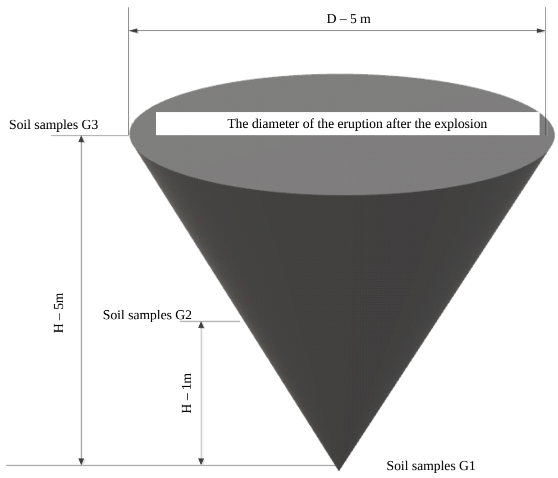


Fig. 1. Scheme of sampling from the crater after the explosion

Before studying the multi-element composition of the sample, the soil is spread evenly on filter paper and air-dried for 1 day at room temperature. Then the soil samples are crushed in a porcelain mortar and sieved through a sieve with a hole diameter of 250 µm. Powdered soil samples were placed in a sealed plastic container for further analysis.

The chemical composition of soil samples was determined by X-ray dispersive fluorescence (XRF) using an analyzer (Thermo Scientific ARL QUANT'X, Switzerland, WinTrace software).

XRF (X-ray fluorescence) is an analytical technique used to determine the elemental composition of materials. XRF analysers determine the chemical composition of a sample by measuring the fluorescent (or secondary) X-rays emitted by the sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays unique to that particular element, making XRF spectroscopy an excellent technology for qualitative and quantitative analysis of soil composition.A solid or liquid sample is irradiated with high energy X-rays from a controlled X-ray tube. The energy of this X-ray radiation is equal to the specific energy difference between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis (Fig. 2). (ThermoFisher,2020).

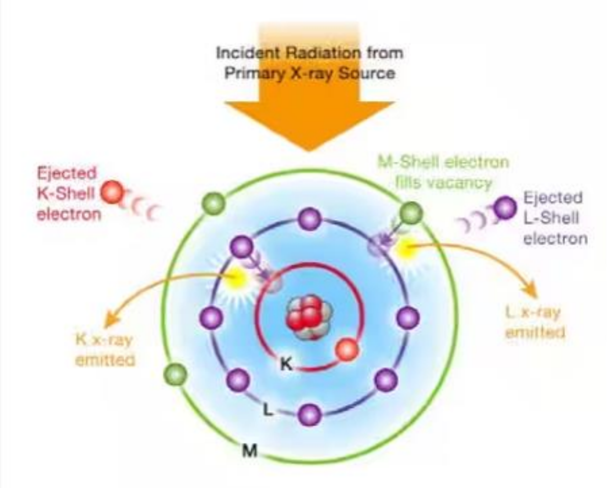


Fig. 2. The principle of X-ray fluorescence (XRF)

The instrument is pre-calibrated with reference metal samples (supplied with the instrument), the calibration process takes 15 minutes. The pre-prepared powdered soil samples are placed in the analysis vessel and analysed, with an analysis time of 1.5 hours.

The prepared soil samples are mixed into a special 25 ml analysis container with a 2 g powdered soil sample. The XRF analysis vessel consists of 3 parts: the bottom, the inner part and the lid. Before loading the powdered soil sample, the XRF analysis container must be prepared for analysis. To do this, a 3*3 (76 mm* 76 mm) sheet of Mylar TF-160-345 X-ray film should be placed between the bottom and the inside of the container, with the X-ray film sheet stretched tightly. After that, the soil samples are closed with a lid and each sample is signed.

The samples are gradually analysed through 8 spectra of the device and the device records the data on the screen. The maximum number of samples to be loaded is 9.

3. Results and Discussion

The explosion of a projectile of any type is the entry of a number of toxic compounds into the soil. Fragments of ammunition and artillery shells pose a danger. In war zones, heavy metals sometimes exceed background values by 30 times. These substances enter the soil, migrate to groundwater and eventually enter the food chain, affecting both animals and humans. That is, the soil poisoned by explosions will slowly kill us in the long run.

Concentrations of potentially hazardous substances (Pb, Ni, Zn, Al, Sr, Cr, Ti, Mn, Zr, P) were compared with the background given by the US EPA in the Official Guidelines for Explosives in Soils (US EPA, 2020). This approach is similar to that used to control industrial pollution, based on established maximum permissible concentrations of substances in the environment.

From the obtained experimental data regarding the elemental composition of the soil after rocket attacks, it is possible to assert a dangerous amount of such elements as titanium (Ti), zinc (Zn), lead (Pb), strontium (Sr) and chromium (Cr) (Table 1).

Accordingly, if these elements are present in the soil, they are capable of forming oxides. The results are shown in Fig. 3.

Table 1

Elemental composition of the studied soil in the areas of shelling

Elements	Sample, %											
	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12
Zn	0.0043	0.003	0.007	0.008	0.0123	0.0128	0.0137	0.0202	0.0135	0.0144	0.0149	0.0098
Pb	0.0024	0.001	0.001	0.004	0.0032	0.0041	0.0038	0.0054	0.0014	0.0019	0.0067	0.0098
Ni	0.0024	0.0014	0.0026	0.0020	0.0035	0.0042	0.0049	0.0048	0.0020	0.0023	0.0024	0.0064
Cr	0.0055	0.005	0.007	0.011	0.0073	0.0070	0.0074	0.0054	0.0059	0.0071	0.00720	0.01140
Sr	0.0082	0.007	0.0079	0.0088	0.0111	0.0217	0.0213	0.0206	0.0091	0.0096	0.01010	0.02560
Mn	0.0436	0.0156	0.019	0.0314	0.1720	0.1310	0.3610	0.1700	0.0336	0.0327	0.03380	0.06770
Px	0.0436	0.869	0.958	0.9460	0.9760	0.8650	0.8680	0.8350	0.8710	1.060	1.04000	0.53600
Zr	0.0522	0.053	0.050	0.0472	0.0315	0.0278	0.0254	0.0269	0.0587	0.0513	0.04920	0.07390
Ti	0.372	0.338	0.288	0.3290	0.2620	0.2610	0.2220	0.2450	0.3630	0.3710	0.39400	0.45400
Al	0.0436	2.900	0.0195	3.1200	3.330	2.870	2.790	3.020	3.710	3.6700	3.80000	1.46000

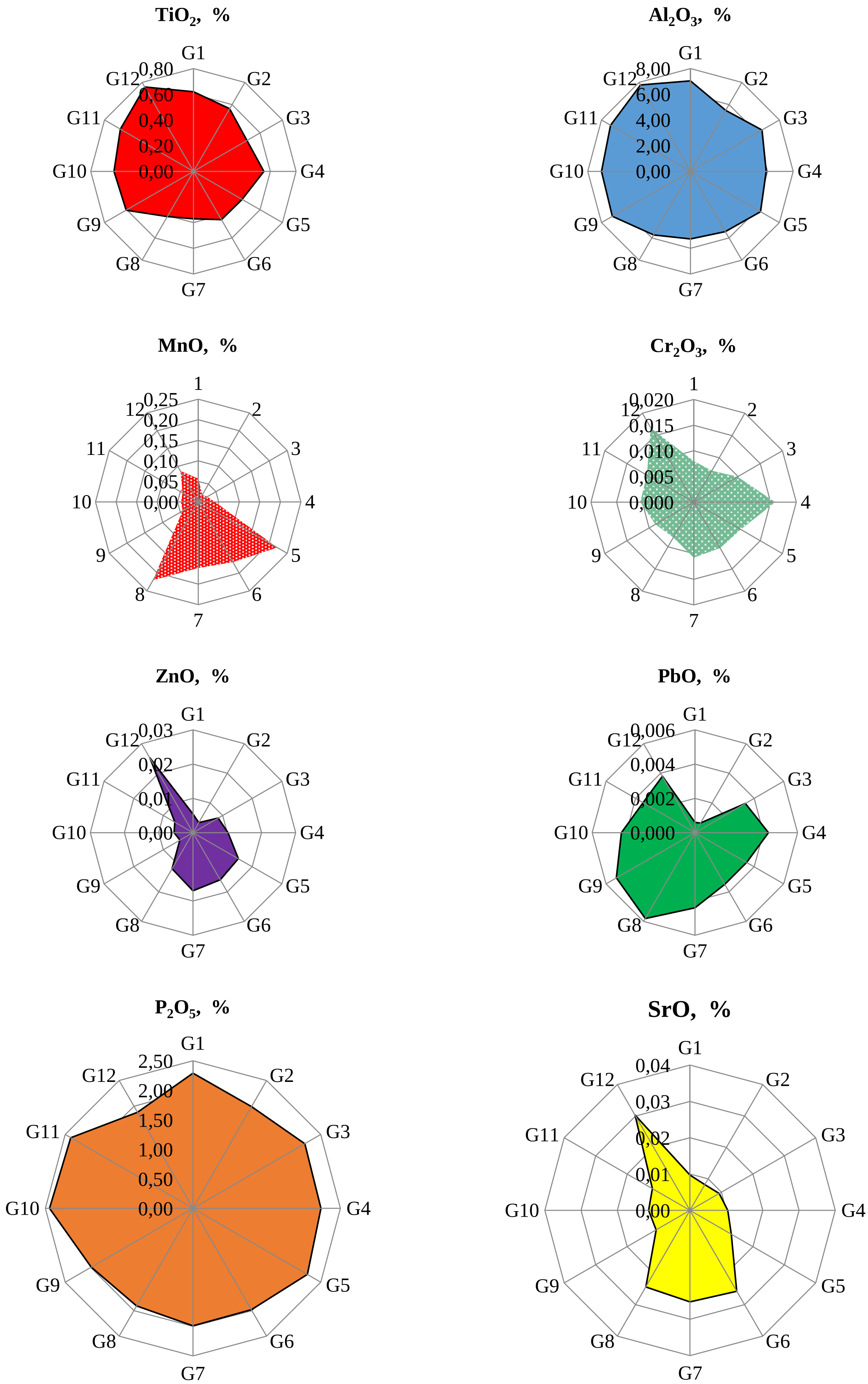
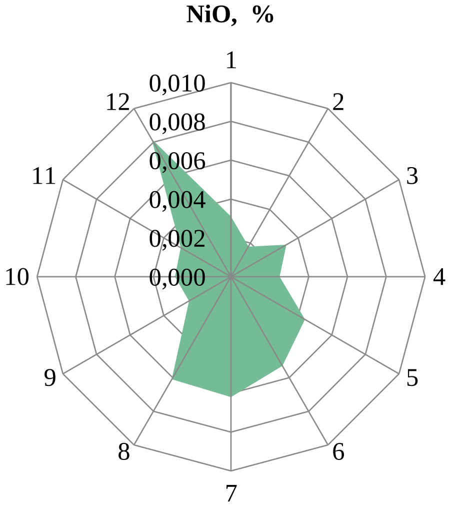


Fig. 3. Oxide content in soil samples after the explosion



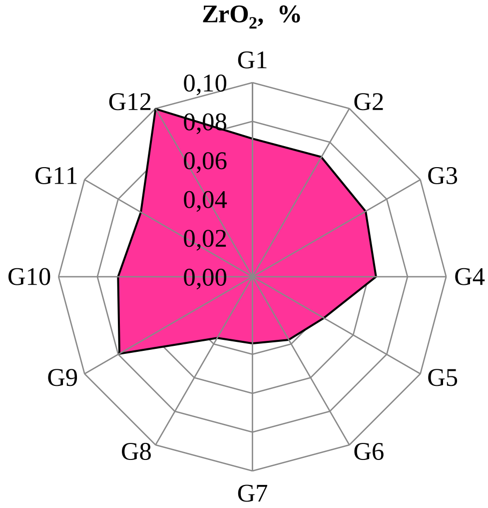


Fig. 3. Oxide content in soil samples after the explosion

Titanium dioxide TiO_2 is a chemical compound in the form of a finely dispersed, white, odorless crystalline powder. When heated, titanium dioxide changes color to yellow. Dissolves in water, acids, alkalis. In nature, it is found in the composition of minerals – rutile, anatase, and brook. Physical properties of titanium dioxide: high whitening ability of materials of various origins; moisture resistance, resistance to environmental factors (ultraviolet); chemical stability of the compound; optimal interaction with film formers; light scattering properties; fire and explosion-proof - does not burn and does not support fire.

Currently, titanium is widely used in rocket and space technology, in shipbuilding and transport engineering, where a particularly important role is played by low density in combination with high strength and corrosion resistance. The fuselage and wings of high-speed aircraft, panels and frameworks of rockets, disks and blades of turbines are made of titanium alloys. from the very beginning of development, the rocket and space technology of all countries widely used titanium alloys. The TI-6A1-4U alloy is used for the manufacture of launch vehicle bodies (Germany, russia). At the moment, up to 75–80 % c of the total volume of titanium production is used in space and aviation technology (Allbest, 2016). The nature of nanoparticles is of particular concern to the scientific community. Scientists talk about a new mechanism of manifestation of toxicity in the form of a physicochemical reaction. This allows TiO_2 to accumulate in various tissues and cause oxidative stress (Ideas-center, 2022). Exceeding the maximum allowable concentrations of titanium oxide by 1.5–2 times is typical for all samples of the studied soil. However, the highest concentration of this oxide is characteristic of sample G12.

Aluminum is one of the chemical elements that is widely distributed in the earth's crust and in human life. The sources of aluminum entering the human body are atmospheric air, medicines, cosmetics, household chemicals, and water. In addition, aluminum and its oxides can enter food products from the soil, which contains aluminosilicates and which, due to anthropogenic influence, turn into mobile migratory forms. An excess of 2–4 times the background concentrations in the soil is observed in samples G9-G12.

Manganese is found in soils as a two-, three- and four-valent ion. Manganese compounds are highly soluble, especially in acidic environments. In soil, manganese can replace exchangeable bases such as Ca^{2+} and Mg^{2+}, and in soil solution it forms complexes with organic matter (mainly fulvic acids). Manganese forms ferromanganese nodules with iron hydroxides. The toxic effect of manganese on humans and warm-blooded mammals is associated with damage to the central nervous system, where it causes organic changes of an extrapyramidal nature, and in severe cases - parkinsonism. Extrapyramidal insufficiency in the case of chronic manganese poisoning is caused by damage to the dopaminergic system of the brain. However, manganese is also a polytropic poison that also affects the lungs, cardiovascular and hepatobiliary systems, affects erythropoiesis, embryogenesis, and causes allergic and mutagenic effects (Pedan, 2013). A 2.5-fold excess of background manganese oxide concentrations in the investigated soil was observed in samples G5 and G8.

The chromium content in soils is mainly determined by its content in the soil-forming rock. The global chromium standard for soils is 200 mg/kg. In acidic soils, chromium is practically immobile and precipitates at pH 5.5. Excessive chromium in the human body can cause cancer, asthma, and disorders of hydrocarbon metabolism. A slight exceedance of the maximum permissible concentrations of hexavalent chromium in terms of oxide was observed in soil samples G4 and G12.

Zinc oxide did not exceed the background concentrations in the soil samples.

Due to the large-scale contamination of the environment with lead (Pb), the upper horizons of most soils are enriched with this element. The concentration of lead in the soils of the world is 10 mg/kg. The MPC level of lead for soils is 0.032 mg/g. In soils, lead is less mobile than other heavy metals. In a neutral and alkaline environment, the mobility of lead is significantly reduced. Lead is well fixed by soil organic matter. In addition, this element is chemisorbed in soils in the form of phosphates, hydroxides and carbonates. The main part of lead that enters the body of animals and humans (up to 90 %) is deposited in bone tissue, where it can accumulate in significant concentrations due to a long half-life (5-20 years) (Bannon et al., 2009). According to the obtained experimental data regarding the presence of lead oxides in the soil, an excess of the MPC by 1.5–2 times is observed in samples G7, G8 and G10.

The presence of strontium oxide (SrO) in samples of the investigated soil after missile attack is due to the use of strontium nitrate ($Sr(NO_3)_2$), which is used in liquid-injected thrust vector control (LITVC) in missiles to provide rudder control with a simple fixed nozzle. Exceeding background concentrations by 1.7 times is observed in soil sample G12.

The concentration of nickel oxide in the investigated soil samples indicates its 1.7-fold excess in the G12 sample. The content of nickel in soils mainly depends on the saturation of soil-forming rocks with this element. However, in most cases, the level of nickel in soils is related to the scale of man-made pollution.

It is necessary to note the presence of such a rare oxide as ZrO in the soil samples under study. Zirconium metal has a wide range of applications in various fields of human activity: as a material for the manufacture of individual structural elements of nuclear reactors; Zirconium is a component of many alloys used in the production of rockets and other aircraft. Alloys of zirconium with other metals improve the technical characteristics, fire resistance and piezoceramic properties of materials. As an additive to other materials, the chemical element increases their ability to withstand a variety of aggressive environments (Broomandi et al., 2020; Sanderson et al., 2020).

4. Conclusions

Every war or even military training leaves a "chemical trail" on the soil. Soils lose their fertility due to changes in their physical, chemical and physicochemical properties when heavy metals enter them. According to experts, during the detonation of rockets and artillery shells, carbon monoxide, carbon dioxide, water vapor, nitrous oxide, nitrogen dioxide, formaldehyde, cyanic acid vapors, nitrogen, as well as a large amount of toxic organics are formed. Soil scientists note a systematic 6-8 times excess of mercury, zinc and cadmium indicators. High levels of copper, nickel, lead, phosphorus and barium are recorded at the sites of shelling. These trends have been noticed since the beginning of the war in the East of Ukraine in 2014, in the places of hostilities the maximum allowable concentrations of pig are exceeded by hundreds of times, strontium and titanium are also present, which are uncharacteristic for soils in significant quantities. It is clear that it will be impossible to grow anything on such soils for a long time.

Pollution with heavy metals can be felt for more than a dozen years. For example, bullets can release lead, which is then absorbed by plants. Lead distributed in different soil fractions may initially be inert but then become reactive due to changing soil conditions (e.g., pH, moisture). In addition to lead, such metals as chromium (Cr), arsenic (As), mercury (Hg), nickel (Ni), zinc (Zn) and cadmium (Cd) enter the soil with weapon residues (AgroPortal, 2022).

Considering the seriousness and danger of the current situation, scientists in Ukraine are already looking for ways to solve the problem of soil pollution as a result of the war. Specialists are busy developing tools and mechanisms, the implementation of which will minimize the consequences of hostilities in the years to come. Our studies of soil samples after the explosion of cruise missiles indicate a significant anthropogenic impact on the soil environment, which, accordingly, will have a negative impact on the environment.

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