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ECOLOGICAL RISKS OF CHROMIUM CONTAMINATION IN UKRAINIAN SOILS AFFECTED BY MILITARY ACTIVITY: SEM-EDS AND EPMA ANALYSIS

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Abstract. The contamination of soil with heavy metals as a result of military activity presents a significant and multifaceted environmental challenge. Chromium, in particular, is introduced into the environment through various military-related processes, such as the use of ammunition, explosives, fuels, and other military equipment. Once released, chromium can persist in the environment, especially in soil, where it exists primarily in two oxidation states: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). The latter is particularly toxic and poses a considerable risk to both environmental and human health. In this study, we focused on analyzing soil samples with the highest concentrations of chromium ions. The main objective was to identify chromium compounds present in the soil as a direct consequence of military actions, with the aim of assessing environmental risks and developing strategies to mitigate their impact. Prolonged contamination-over a span of several years-can result in ireversible ecological damage, affecting local biodiversity and potentially leading to the disruption of food webs. Furthermore, the accumulation of chromium in water sources and food chains increases the risk of adverse health effects for nearby populations. Therefore, chromium pollution arising from military operations has the potential to cause long-term degradation of ecosystems, highlighting the urgent need for remediation and preventive measures.

Keywords: chromium ions, migration, electron microscopy, soil.

1. Introduction

Hexavalent chromium (Cr(VI)) is widely acknowledged for its elevated toxicity and carcinogenicity compared to trivalent chromium (Cr(III)). Chromium contamination is a major environmental concern, as it contributes to soil degradation by altering its physical and chemical properties, ultimately leading to a decline in soil fertility. In aquatic systems, chromium ions exhibit slow rates of natural attenuation, creating long-term imbalances in background concentrations. This persistence facilitates the migration of Cr species into water bodies through surface runoff and infiltration, thereby contaminating both surface and groundwater resources and posing significant risks to drinking water safety and human health.

Cr(VI) is particularly hazardous due to its high solubility and bioavailability, which enable its rapid uptake by living organisms. Exposure to Cr(VI) has been associated with dermatological conditions, respiratory disorders, internal organ damage, and increased cancer incidence. In natural environments, chromium predominantly exists as Cr(III) in the form of stable, poorly soluble minerals. In contrast, Cr(VI) forms highly soluble chromate and dichromate salts, which are more mobile and reactive under environmental conditions.

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Elevated levels of Cr(VI) in soil and water typically originate from anthropogenic sources, particularly industrial activities. For example, solid wastes produced by the leather tanning industry are rich in Cr(III) oxides, which can become soluble under acidic conditions ($pH < 6$). Cr(VI) compounds also dissolve in both acidic and alkaline media and can be reduced to Cr(III) in the presence of reducing agents, particularly under acidic environments. Consequently, chromium in the environment may be present either in dissolved Cr(VI) form or as sedimented Cr(III) oxides. Given its greater solubility and ecological mobility, Cr(VI) poses a higher toxicological threat than Cr(III).

Regulatory bodies have established a maximum permissible concentration of total soluble chromium in drinking water at 0.05 mg/L (Peng et al., 2023; Chen et al., 2018; Mortazavian et al., 2022; Li et al., 2020). The primary natural source of chromium, chromite ($FeCr_2O_4$), can undergo oxidation to Cr(VI) in the presence of manganese oxides (Mn(III/IV)), which are common constituents in soils (Beukes et al., 2017; Hu et al., 2016; Luizon Filho et al., 2020). Conversely, various environmental components such as organic matter, iron-based compounds, and sulfides facilitate the reduction of Cr(VI) to Cr(III), leading to redox transformations that influence chromium speciation and mobility in contaminated soils, sediments, and water bodies (Wise et al., 2022; Karimi-Maleh et al., 2021).

Mineralogical analyses have identified calcium chromate ($CaCrO_4$) as a dominant crystalline phase in Cr(VI)-contaminated environments, while iron has been observed in complex forms such as $FeOHCrO_4$, as confirmed by X-ray diffraction data (Joint Committee on Powder Diffraction Standards, JCPDS card 8-0458) (Mishra & Bharagava, 2016).

However, chromium pollution sources have a significant impact on the environment during hostilities, as a result of the use of ammunition and explosives, fuel and lubricants, the accumulation of disrupted equipment and worn metal parts and debris, etc.

According to the environment, there are such recommendations for reducing the impact of chromium compounds on the environment: a) the use of remediation methods such as phytoremediation (the use of plants for soil cleaning), chemical treatment and bioremediation (the use of microorganisms for degradation of pollutants) can help reduce chromium level soil; b) constant monitoring of chromium levels in hostilities and regulation of the use of chromium materials may reduce the risks of contamination; c) the use of environmental recovery programs, including the reclamation of damaged land and protection of water resources, is important to reduce the impact of chromium on the environment.

2. Materials and Methods

The soil samples were analysed using SEM to determine their morphological characteristics. Some microphotographs illustrate the shape of the soil particles (Fig. 1). Soil is a heterogeneous material with a diverse particle size distribution. The soil particles were analysed using electron microscopy (EDS), which indicates the presence of chromium and its compounds in the soil (Fig. 2).

The EDS analysis is presented in the figures from different areas of the sample. It was found that the content of elements in the soil differs significantly due to the crystal lattice structure of such elements as: Si, Al, O, Fe, Ca, K, Mg, Na and Cr. It should be noted that the presence of Ba2+ in the soil is noteworthy (Fallahzadeh et al., 2018; Kim & Dixon, 2002). Barium is bound to clay components in soils, forming a chromate mineral phase, $BaCrO_4$, which can be a source of Cr (VI) (Matern et al., 2017; Matern and Mansfeldt, 2016). The presence of Ba^{2+} can be attributed to the erosion of intrusive rocks from the north of the study area (Kazakis et al., 2018). The iron content also varies and is based on EDS results; the untreated soil has the highest Fe content.

3. Results and Discussion

For the ESP and SEM, the analysis of soil samples in the places of explosion for the presence of heavy metals selected G7 samples, which contain a concentration that significantly exceeds the maximum permissible concentrations (Petrushka & Petrushka, 2023, Petrushka et al., 2023;), in which the XRF analysis, respectively, there are exceeding the background concentrations.

The G7 sample investigated region 1 (Fig. 1) with a multiplicity from 300 to 5740 times in Area 1-3.

The investigated area is characterised by a notably high silicon (Si) content. X-ray phase analysis revealed that the soil matrix contains a variety of metal oxides exhibiting hexagonal crystal structures. These oxides are formed from heavy metals such as chromium (Cr), manganese (Mn), nickel (Ni), zinc (Zn), titanium (Ti), copper (Cu), strontium (Sr), and zirconium (Zr), as evidenced by spectral peaks with Octane Elect Plus intensities in the range of 0.05 to 2.2.

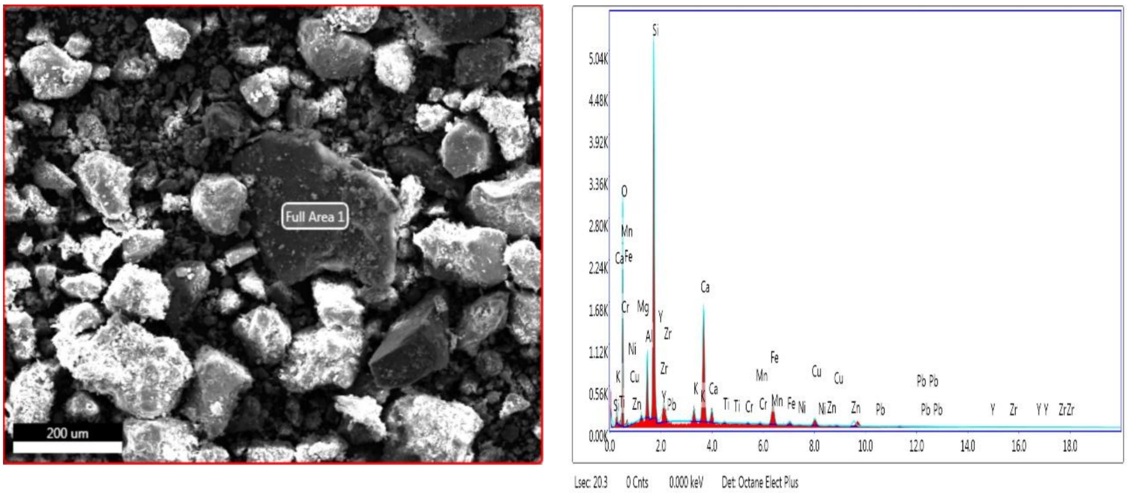
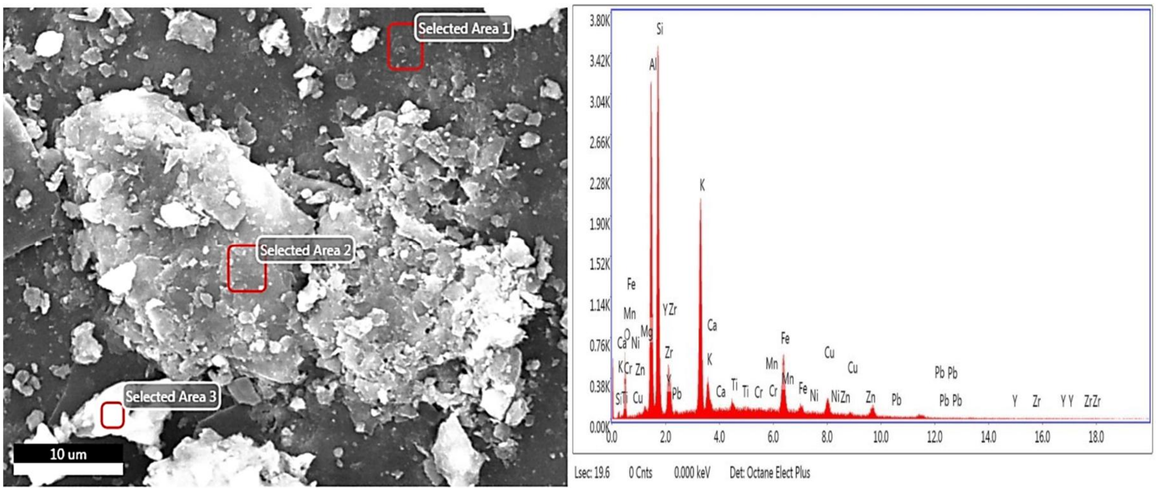
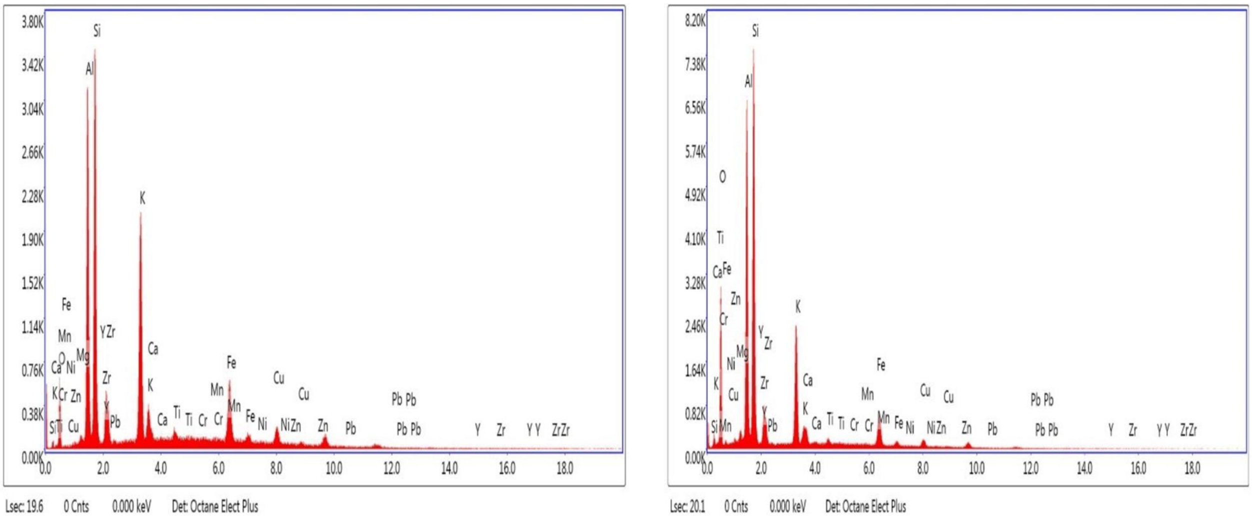


Fig. 1. Examination of zones at a magnification of 300x



Research Area 1 **Research Area 2**



Research Area 3

Fig. 2. Experimental data on selected zones (Area1-3) of G7 soil samples at a magnification of 5740 x

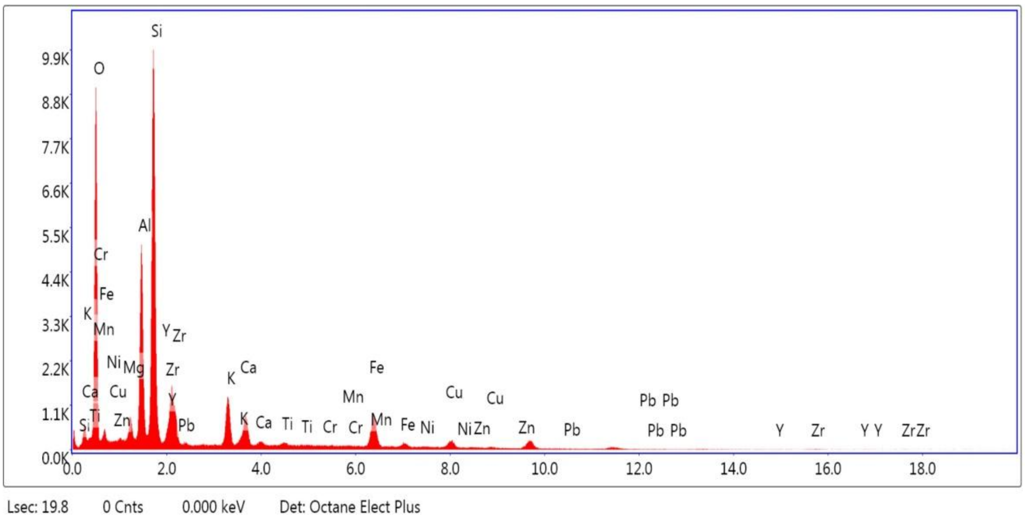


Fig. 2. (Continuation). Experimental data on selected zones (Area1-3) of G7 soil samples at a magnification of 5740 x

The presence of these elements suggests a complex geochemical environment with multiple sources of contamination. Of particular significance is the identification of calcium chromate ($CaCrO_4$) as the dominant crystalline phase. This compound was confirmed by reference to the Joint Committee on Powder Diffraction Standards (JCPDS card 8-0458) (Tumolo et al., 2022).

Furthermore, iron ions of varying oxidation states appear to participate in the formation of a secondary complex compound, ferric hydroxychromate ($FeOHCrO_4$). The occurrence of this mineral phase was initially reported by Rock et al. (2001), based on mineralogical observations in similar contaminated contexts. Leaching experiments indicated that the pH of the eluates during chromium extraction ranged between 6.5 and 8.5, suggesting that iron in the soil occurs predominantly in hydroxide rather than oxide form. This observation aligns with the solubility predictions provided by Puigdomenech (2004) and the ICDD database (ICDD Products, 2025), which indicate that $FeOHCrO_4$ is insoluble in solution and thus precipitates under environmental conditions. The presence and distribution of these compounds were further confirmed by X-ray fluorescence (XRF) analysis of the collected soil samples (Fig. 3), supporting the conclusion that heavy metals in the studied area are immobilised primarily as stable mineral phases with limited solubility, depending on pH and redox conditions.

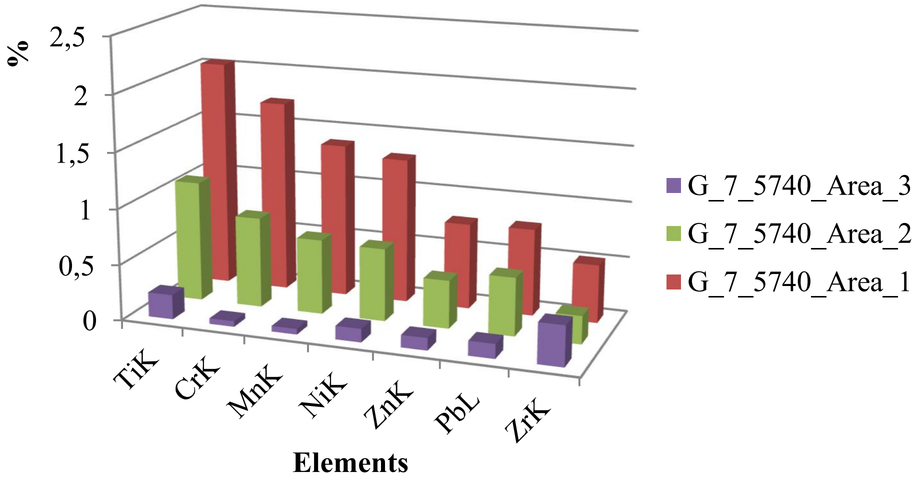
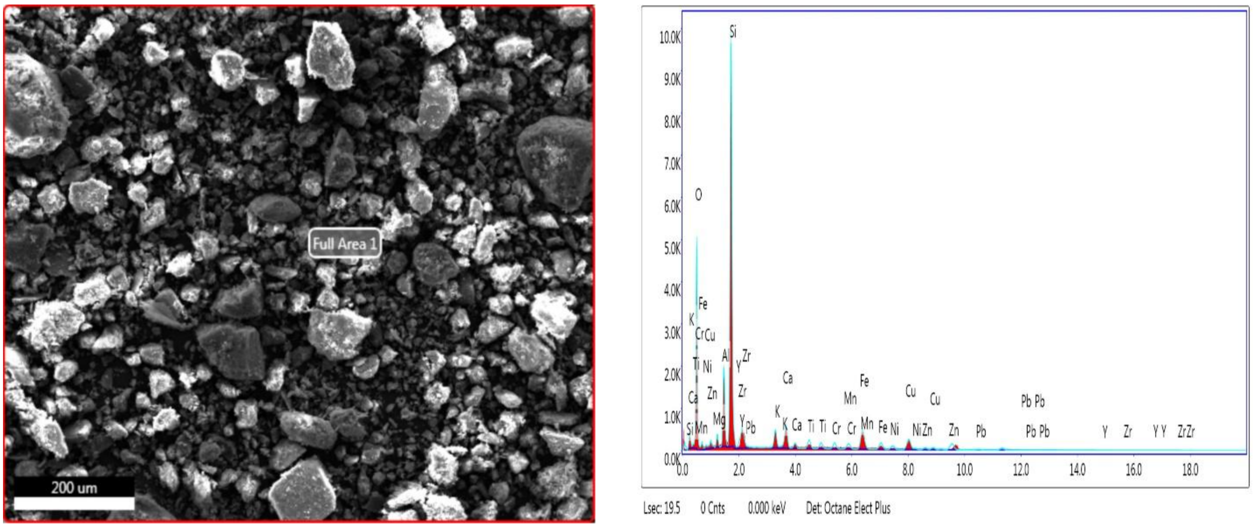
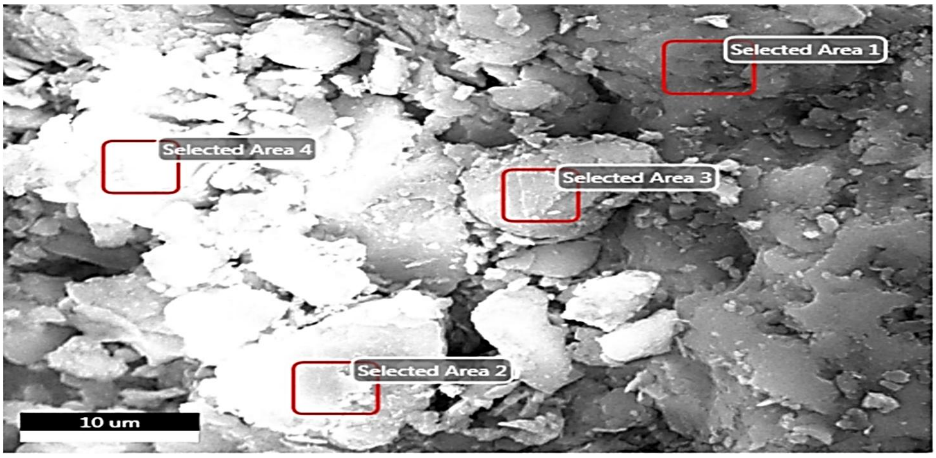


Fig. 3. XRF analysis of a sample for the content of heavy metals in the soil under study G7

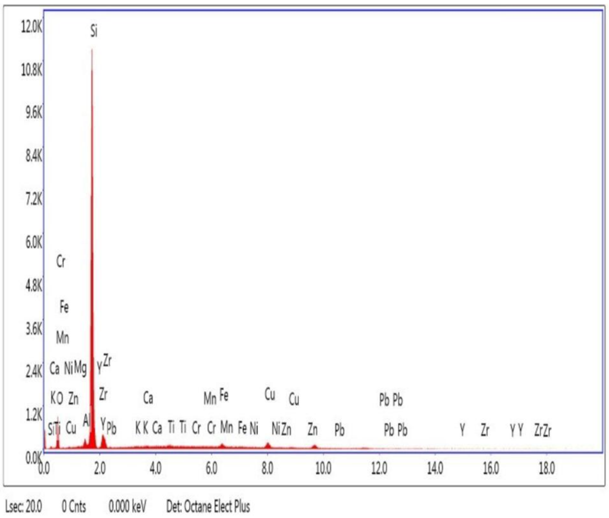
When analysing other samples, we obtained confirmatory results, which are shown in Figs. 4- 9.



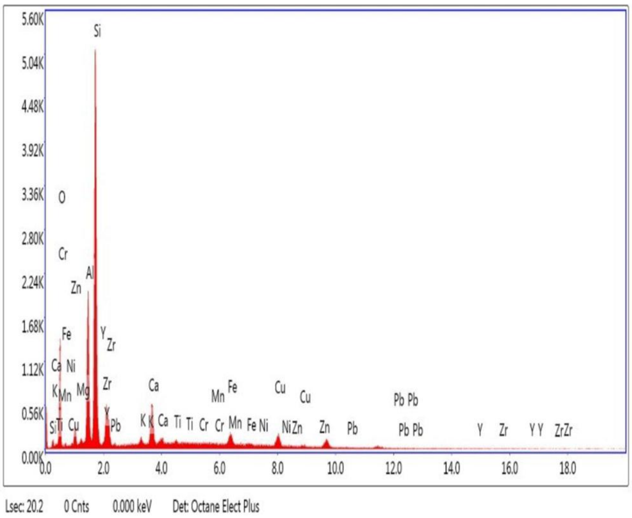
Examination of zones at a magnification of 300 x



Research Area 1



Research Area 2



Research Area 3

Fig. 4. Experimental data on selected zones (Area1-3) of G10 soil samples at a magnification of 5740 x

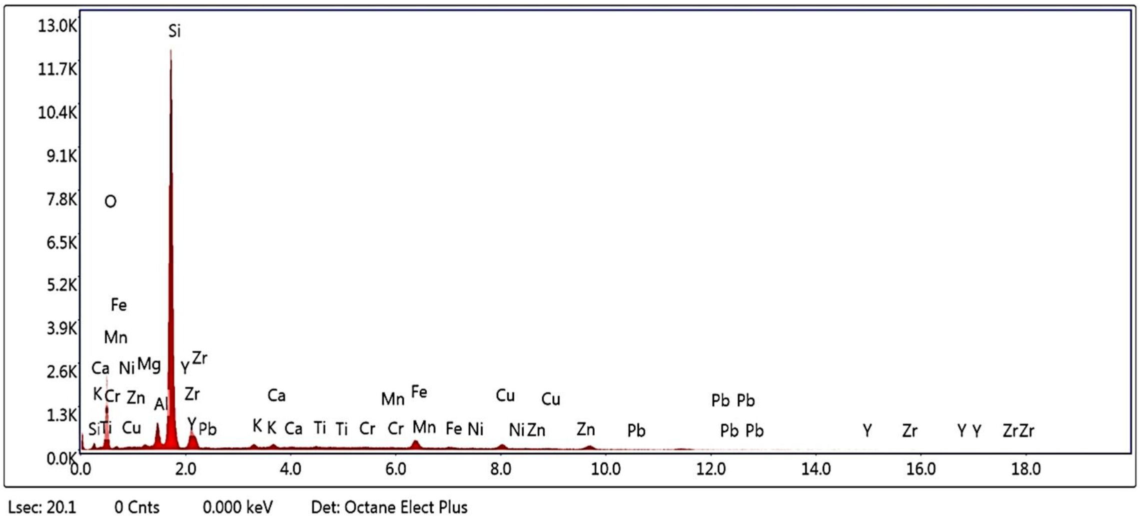


Fig. 4. (Continuation). Experimental data on selected zones (Area1-3) of G10 soil samples at a magnification of 5740 x

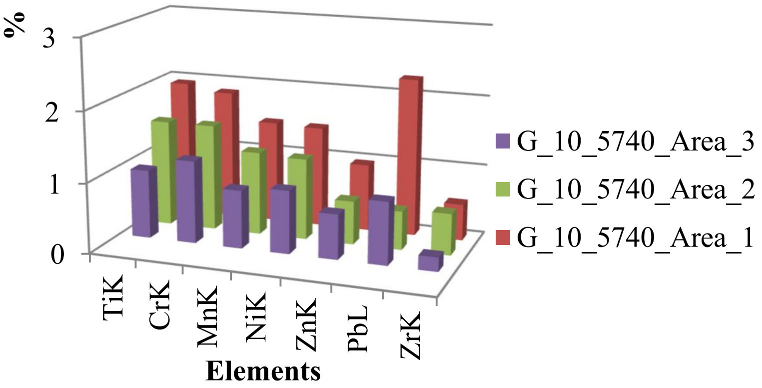
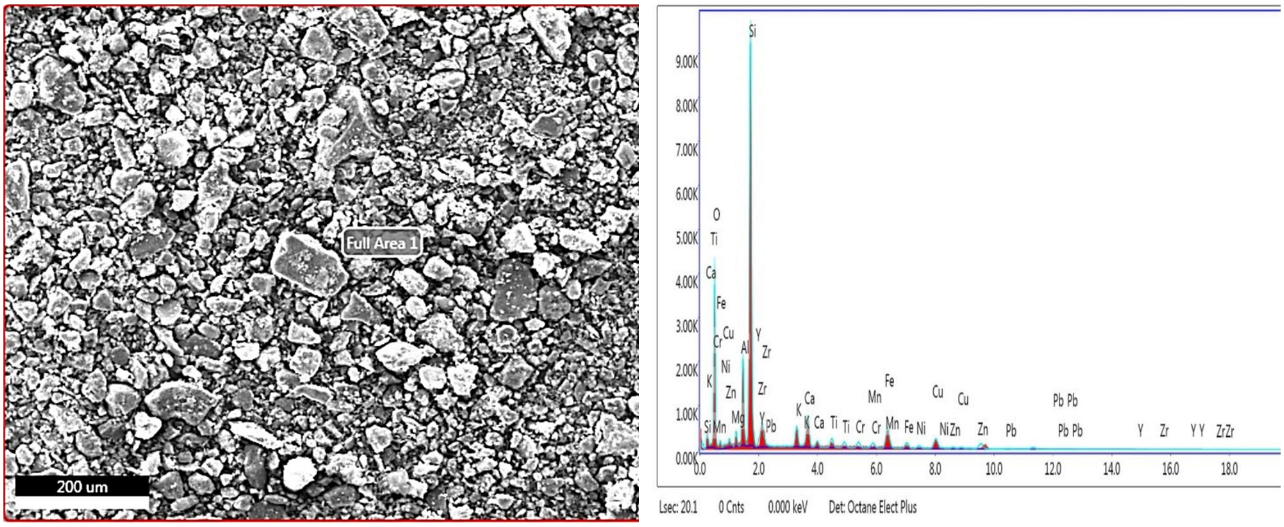
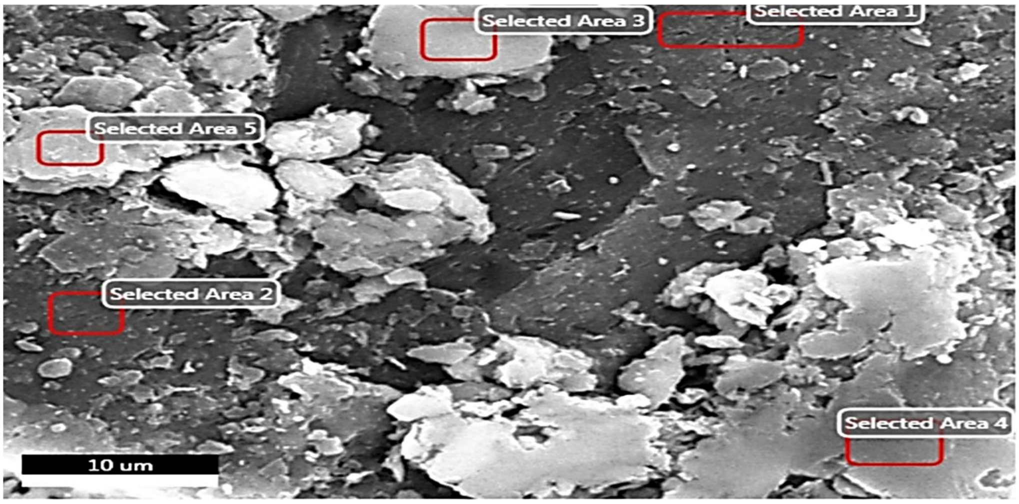


Fig. 5. XRF analysis of a sample for the content of heavy metals in the soil under study G10



Examination of zones at a magnification of 300 x

Fig. 6. Experimental data on selected zones (Area 1-5) of G11 soil samples at a magnification of 5740 x



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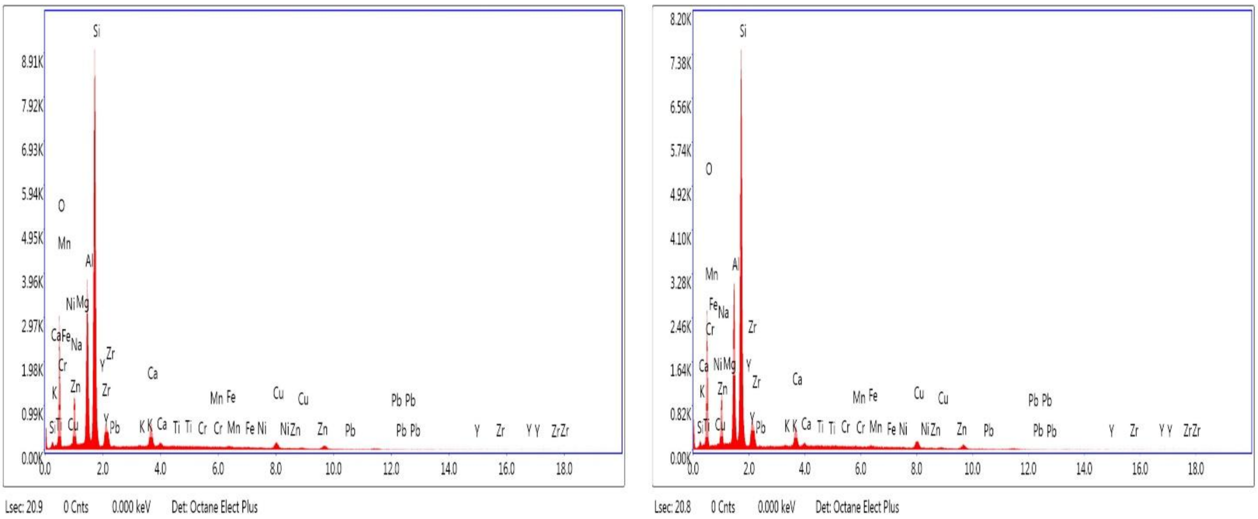

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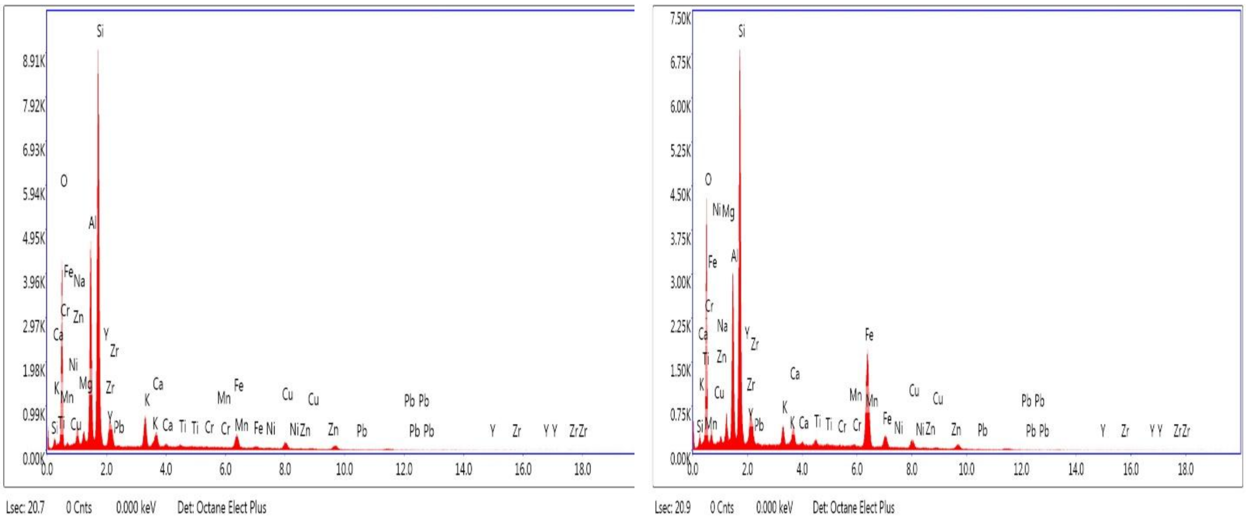


Research Area 5

Fig. 6. (Continuation). Experimental data on selected zones (Area 1-5) of G11 soil samples at a magnification of 5740 x

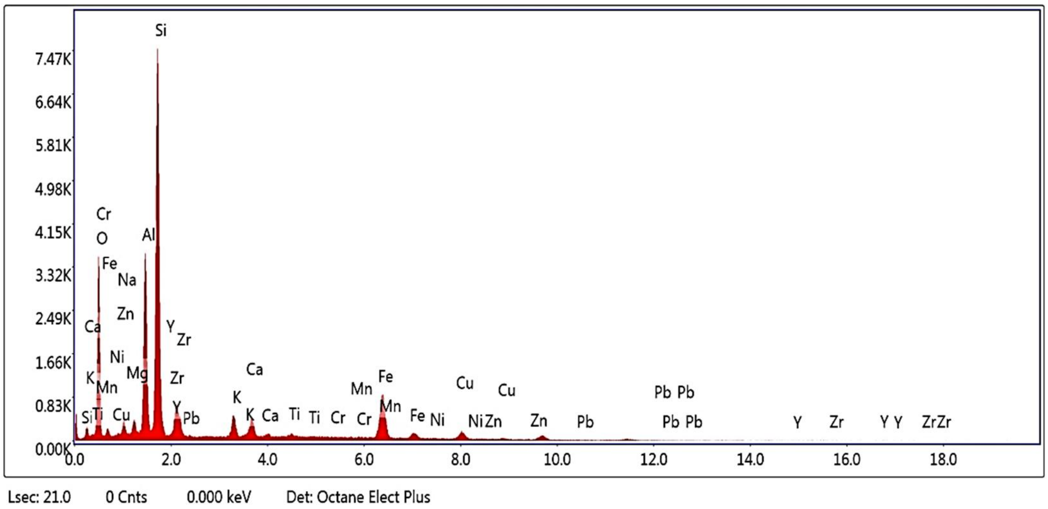


Fig. 6. (Continuation). Experimental data on selected zones (Area 1-5) of G11 soil samples at a magnification of 5740 x

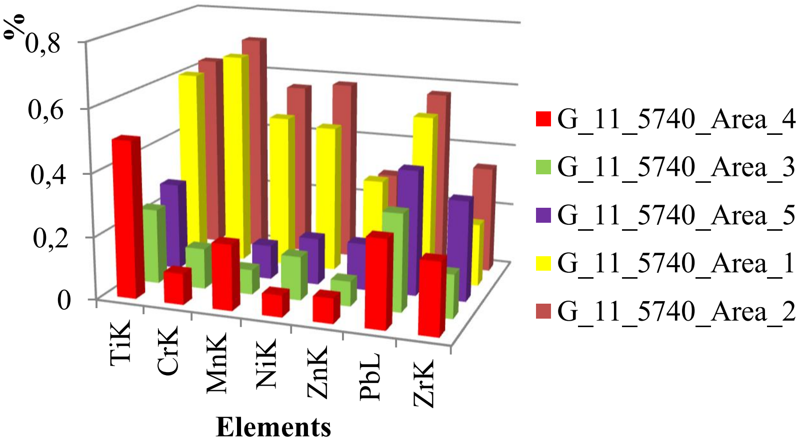
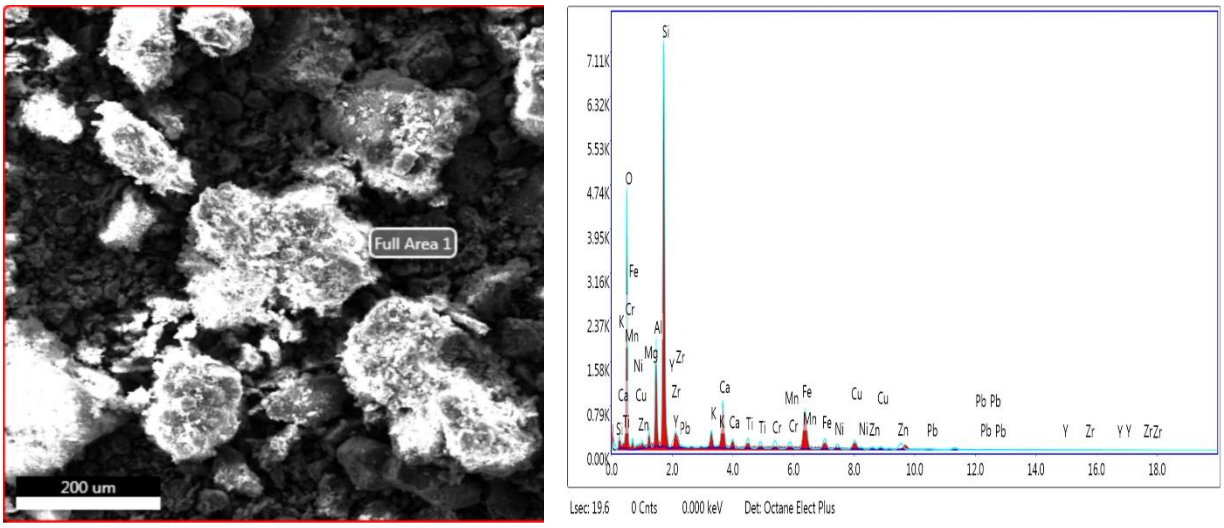
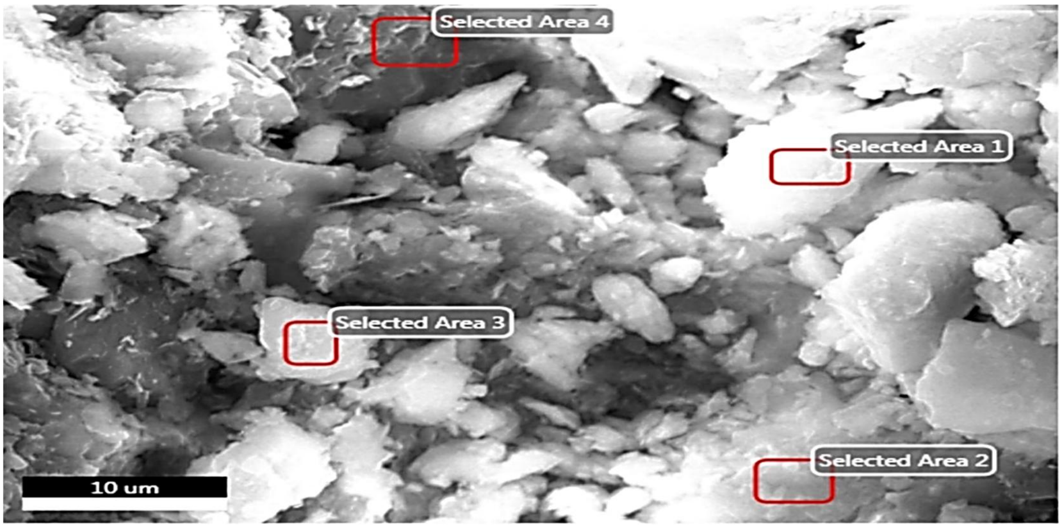


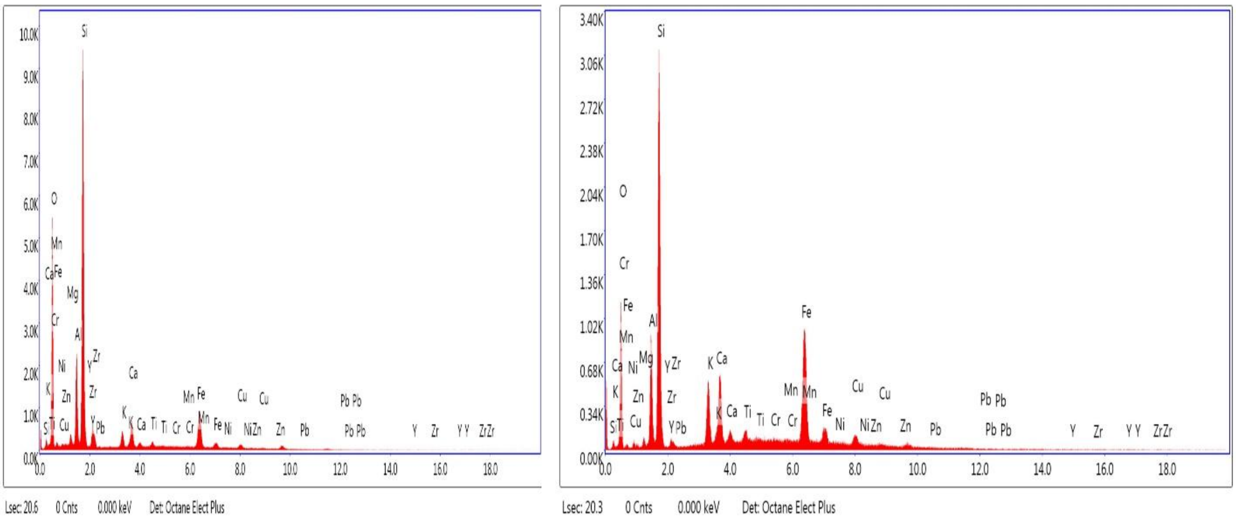
Fig. 7. XRF analysis of a sample for the content of heavy metals in the soil under study G11



Examination of zones at a magnification of 300 x

Fig. 8. Experimental data on selected zones (Area 1-4) of G12 soil samples at a magnification of 5740 x




Research Area 1 **Research Area 2**

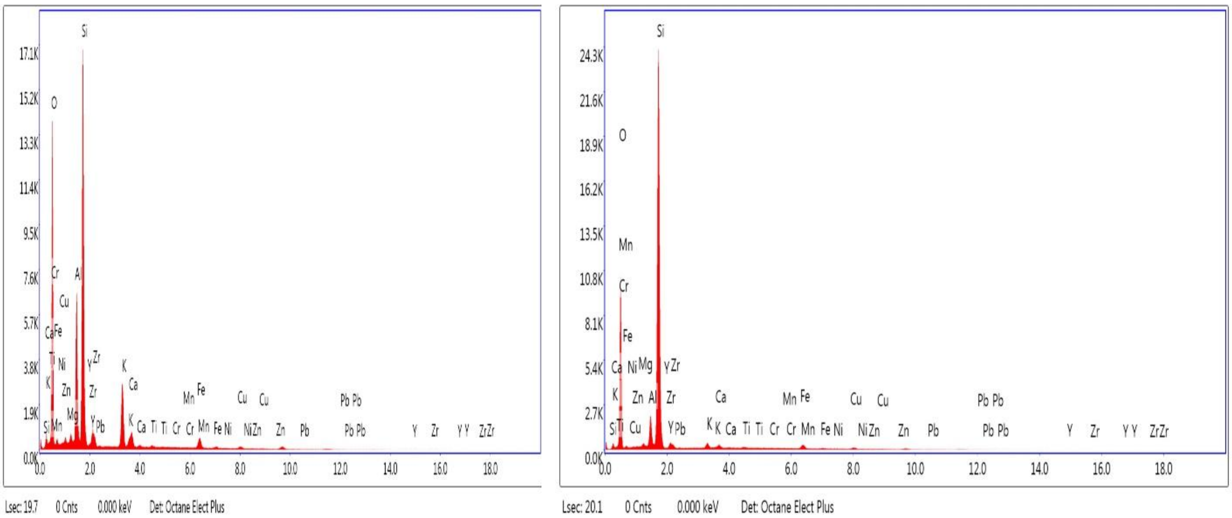

Research Area 3 **Research Area 4**

Fig. 8. (Continuation). Experimental data on selected zones (Area 1-4) of G12 soil samples at a magnification of 5740 x

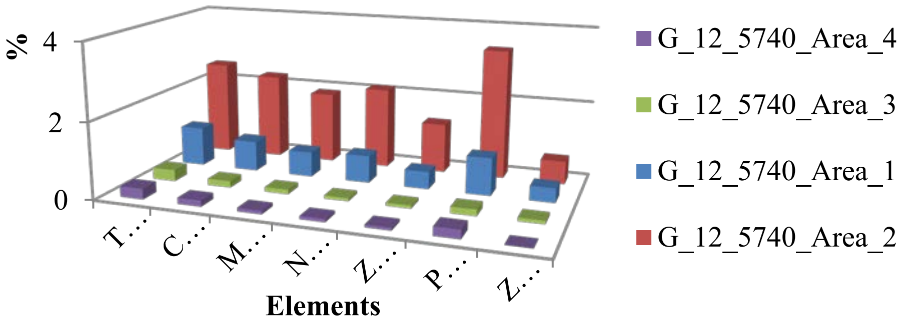


Fig. 9. XRF analysis of a sample for the content of heavy metals in the soil under study G12

In all the soil samples analyzed after the explosion, the concentrations of elements and their oxides were observed to exceed natural background levels. Lead, although chemically inert, rapidly forms a thin oxide layer when exposed to air. Its crystal structure is cubic and face-centered. Nickel compounds are of particular interest due to the unique properties of the metal. The addition of nickel to alloys enhances their strength, wear and corrosion resistance, as well as thermal and electrical conductivity. Moreover, it improves magnetic and catalytic performance. Because of its high chemical, thermal, and mechanical resistance, nickel is extensively used in metallurgy–accounting for approximately 80 % of its total application–for the production of stainless steel. It is also crucial in the aerospace, nuclear, electronics, energy, chemical, and food industries. The majority of nickel is used to produce alloy steels and various metal alloys, including those with iron (Fe), chromium (Cr), and copper (Cu). Zirconium dioxide (ZrO_2), another compound identified in the samples, can exhibit either a cubic or tetragonal crystal structure. However, these phases are unstable at room temperature. The tetragonal phase exists at high temperatures ranging from 1173 °C to 2370 °C, while the cubic phase is stable between 2370 °C and the melting point of 2680 °C.

Therefore, the experimental data obtained suggest that the anthropogenic impact of hostilities on the environment, which is difficult to predict for future generations.

4. Conclusions

The presence of chromium ions resulting from military hostilities constitutes a significant environmental hazard and poses serious risks to human health. These ions, released during various military activities, contaminate soil and surrounding ecosystems, leading to potential bioaccumulation and toxic effects. In backscattered electron (BSE) detector images, light-colored crystallites less than 0.5 μm in size are observed on soil grain surfaces. These crystallites correspond to elements with higher atomic numbers, typically associated with military materials and ordnance residues. Energy-dispersive X-ray spectroscopy (EDS) analysis confirms the presence of heavy metals such as copper (Cu), lead (Pb), titanium (Ti), zinc (Zn), and nickel (Ni), all of which contribute to the toxicity and persistence of contamination in the affected areas. Given the severity of these pollutants, it is essential to adopt comprehensive and proactive strategies aimed at reducing environmental pollution and restoring damaged ecosystems. These strategies should include soil remediation, continuous environmental monitoring, and public health assessments. Furthermore, compliance with international environmental protection standards and humanitarian laws, such as those outlined in the Geneva Convention, is critical. These frameworks emphasize the need to minimize ecological damage during armed conflicts and promote the sustainnable recovery of affected regions. Coordinated efforts between governments, environmenttal agencies, and the scientific community are necessary to mitigate the long-term consequences of chromium and other heavy metal contamination caused by military operations.

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