Phytoremediation of War-Induced Heavy Metal Pollution in Soils Using Humates from Ukrainian Lignite

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Abstract. *This study examines a combined remediation strategy that integrates humic acids derived from Ukrainian lignite with oat (Avena sativa L.) phytoremediation to restore soils contaminated with heavy metals as a result of military activities in Ukraine. Humic acids were extracted using an energy-efficient hydrocavitation method and applied to artificially contaminated peat at two dosages (1:5 and 1:10). The amendments markedly reduced the mobility and extractable concentrations of Pb, Cd, Ni, Cu, and Zn, with total decreases ranging from about 25% in the untreated control to nearly 47% under the highest humate application rate. Improved soil structure and stimulated root development contributed to enhanced plant tolerance and greater biomass production. Metal accumulation occurred predominantly in roots (68–90%), while only 10–32% was translocated into biomass, indicating effective stabilization within the soil–plant system and minimized risks for trophic transfer. These findings demonstrate that hydrocavitation-extracted lignite humates substantially reinforce phytoremediation efficiency and represent a scalable, low-cost, and environmentally sustainable solution for rehabilitating conflict-affected agricultural soils.*

KEYWORDS: *PHYTOREMEDIATION, HUMIC ACIDS, LIGNITE, SOIL CONTAMINATION, HEAVY METAL, AGRICULTURAL SOIL, OATS, CAVITATION TECHNOLOGY, ECOSYSTEM RECOVERY.*

Introduction

Large-scale military activities in Ukraine have resulted in the contamination of agricultural soils with toxic heavy metals, including lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), and zinc (Zn). These contaminants originate from explosive residues, metal fragments, and combustion products deposited during artillery shelling and missile strikes, leading to long-term risks for food safety, soil fertility, and ecosystem resilience [1]. War-disturbed soils exhibit altered physicochemical properties, reduced biological activity, and increased mobility of toxic elements, which complicates their natural recovery and requires targeted remediation strategies [2].

Phytoremediation has emerged as a sustainable, low-impact method for restoring contaminated soils. It involves the use of plants capable of accumulating and transforming pollutants, thereby reducing their bioavailability and ecological risk [3]. In temperate agroecosystems, oats (Avena sativa L.) present a promising phytoremediation candidate, due to their high adaptive capacity, tolerance to elevated metal concentrations, and ability to accumulate contaminants in both roots and aboveground biomass [4]. However, heavy metals in war-related contamination zones often occur in highly mobile forms, which may inhibit plant development and reduce remediation efficiency.

To overcome these limitations, the incorporation of humic substances has been proposed as an effective complementary strategy. Humic-acid-based sorbents derived from Ukrainian lignite demonstrate strong metal-chelating capacity due to their high content of aromatic and oxygen-containing functional groups [5]. Cavitation-assisted extraction further enhances humic reactivity, improving complexation with metal ions and promoting stabilization of contaminants in the soil matrix [6]. Besides immobilization effects, humic substances stimulate root growth, improve soil structure, and enhance microbial activity, thereby creating favorable conditions for phytoremediation [7]. Findings from our earlier agricultural experiments with lignite-derived humates highlighted their biological activity and soil-modifying potential, supporting the need to evaluate their performance under contamination stress [8].

This research integrates lignite-derived humic acid sorbents with oat-based phytoremediation to develop a scalable remediation protocol for war-contaminated soils. The study was carried out within a bilateral Latvian–Ukrainian collaboration and included controlled soil contamination modeling, variable sorbent-to-soil application ratios, and field plot monitoring using environmental sensors. The combined approach demonstrated reduced heavy-metal bioavailability, improved plant biomass production, and decreased phytotoxicity, confirming the practical potential of this strategy for the rehabilitation of conflict-affected agricultural landscapes.

The abundance of lignite resources in Ukraine and their high humic content make this material an economically attractive source for large-scale humate production and its integration into green remediation technologies.

Results and discussion

Ukraine has more than 2.5 billion tons of brown coal reserves located in 80 deposits. More than 50% of Ukrainian brown coal can be mined in the most cost-effective way – open pit – due to its shallow depth (usually 40-80 m) [9]. In this case, labor productivity is 2.5 times higher than in underground mining [10]. This determines the low cost of coal on the market, which is $70. A distinctive feature of local brown coal is its high humic acid content. This indicator ranges from 60 to 80% [11]. Humic acids have unique sorption properties that allow them to interact effectively with heavy metal ions. This activity is due to the presence of oxygen- and nitrogen-containing functional groups in humic acids, such as carboxyl, hydroxyl, methoxyl groups, and others. The interaction with metals occurs through several mechanisms: complexation, ion exchange, and physical sorption [12]. The extraction of humic acids from coals is performed by extraction in a weak alkaline solution, specifically a 1% NaOH solution in our case. To intensify the extraction, we applied hydrocavitation treatment of the coal slurry [13]. This method ensures deep extraction (up to 30-90%) of the available humic acids in the form of humates, with minimal energy consumption and processing time (Fig.1).

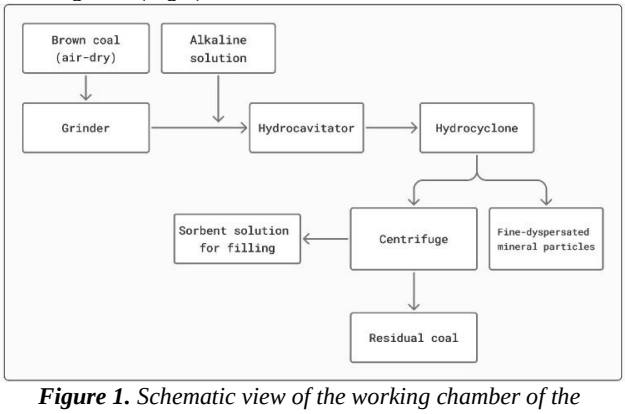

Figure 1. *Schematic view of the working chamber of the hydrocavitation reactor*

The advantages of the chosen treatment method also include the ability to isolate fine mineral particles (<0.05 mm) that are formed during the breakdown of coal-rock aggregates. In addition, spectral analysis using the Shimadzu IR Affinity-IS spectrometer has demonstrated the absence of structural changes in the extracted humates compared to the structure of humates obtained without hydrocavitation treatment.

An artificial contamination experiment was carried out to simulate heavy-metal-polluted agricultural soil and evaluate the efficiency of humic-acid-based sorbents in immobilizing toxic elements. A peat substrate was used as the soil medium. The experimental container had dimensions of 110 × 70 × 30 cm (length × width × height), corresponding to a total volume of 231 L and a total peat mass of 115.5 kg, based on a bulk density of 0.5 $kg \cdot L^{-1}$. For treatment uniformity, the container was divided into two identical sections, and each section contained 57.75 kg of peat.

The contamination level was set at twice the maximum allowable concentration (MAC) for agricultural soils. The required mass of each metal was calculated according to:

$$m_{met} = \frac{C_{MAC} \times m_{soil}}{1000} \quad (1)$$

Where m_{met} is the target mass of the element (g), C_{MAC} is the maximum allowable concentration ($mg \cdot kg^{-1}$), and m_{soil} is soil mass (kg).

The mass of the corresponding soluble salt required to achieve this concentration was calculated as:

$$m_{salt} = m_{met} \times \frac{M_{salt}}{M_{metal}} \quad (2)$$

where M_{salt} and M_{metal} are the molar masses of the salt and the target metal, respectively.

The following salts were used: $Pb(NO_3)_2$, $CdCl_2$, $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, and $ZnSO_4 \cdot 7H_2O$. All salts were dissolved in 10 L of distilled water, thoroughly mixed, and evenly applied to the peat surface, followed by manual homogenization. The contaminated soil was stabilized for 4 weeks under controlled moisture to allow metal fixation and equilibration. Humic-acid-based sorbents obtained from lignite were applied to the contaminated peat at mass ratios of 1:5 (Sample II) and 1:10 (Sample III) to assess their efficiency in immobilizing heavy metals. A contaminated but non-treated peat sample was used as the control to distinguish the effect of the sorbent application (Sample I). The contaminated soil was allowed to stabilize for two weeks under controlled moisture conditions before sowing oats and applying the humic sorbents. Oat sowing was carried out at a rate of 20 grams of seeds per section. The sowing depth was maintained at 1–1.5 cm, ensuring uniform distribution of seeds across the planting area. The experiment was conducted over a period of six weeks. Soil moisture, temperature, and salinity were continuously monitored using in-situ wireless sensors SOIL SCOUT (Lapinlahdenkatu, Helsinki, Finland) to maintain stable environmental conditions throughout the cultivation period. Oat biomass exhibited visually distinct growth responses among treatments, with denser and taller vegetation observed in the sorbent-amended sections compared to the contaminated control (Fig. 2). At the end of the experiment, the above-ground biomass was harvested and weighed, while root systems were carefully excavated, washed, and separated for further evaluation. Soil samples were collected from each treatment section to determine the residual concentrations of heavy metals and assess the effectiveness of humic sorbent application. Concentrated HNO_3 -extractable trace metal concentrations (CEM MARS 6 iWave) were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES; Thermo Fisher Scientific iCAP 7200 Duo) in accordance with ISO 11885:2009.

The application of lignite-derived humic acids in combination with oat cultivation resulted in a pronounced reduction of heavy-metal concentrations in contaminated soil. The concentration of Zn decreased by 42.8%, Cd by 43.9%, Ni by 47.3%, Cu by 33.1%, and Pb by 41.3% in the substrate treated with a 1:5 humate solution (Sample II) compared to the untreated soil (Sample I). A further decrease in metal concentrations was observed in the substrate treated with a higher humate dosage (1:10, Sample III), confirming that increasing the concentration of humic substances enhanced the immobilization of metals and reduced their uptake by plants. These findings demonstrate the synergistic interaction between humic amendments and phytoremediation, where humic substances stabilize metals in the soil matrix, while oat roots contribute to their accumulation.

Figure 2. *Oat (Avena sativa L.) biomass after six weeks of growth in artificially contaminated peat under different humic sorbent treatments, prior to harvest*

A clear differentiation in metal distribution between biomass and roots was observed. The majority of accumulated heavy metals were retained in the root system (68–90%), while only 10–32% were translocated to the aboveground biomass.

The highest root retention was observed for Ni indicating strong metal binding and limited translocation, which is advantageous for minimizing food-chain transfer risks.

In contrast, Zn and Cu demonstrated comparatively higher transport into the aerial parts of the crop, which reflects their higher physiological mobility in plant tissues and essential roles in enzymatic and redox processes. However, even for these elements, root retention remained predominant, suggesting that the added humic substances regulated ionic availability and reduced stress-induced translocation patterns.

Biomass production was higher in the humate-treated plots, indicating reduced phytotoxicity and improved physiological performance. This agrees with previous studies showing that humic substances enhance nutrient uptake, stimulate root development, and support microbial activity in soil, thereby improving plant tolerance to contamination stress [15].

In addition to their metal-immobilizing properties, humic substances exert a multifaceted influence on plant physiological processes, contributing to improved performance under stress conditions. Numerous studies indicate that humic acids enhance root system development by promoting cell elongation, increasing lateral root formation, and stimulating overall root biomass, which collectively strengthens the plant's ability to acquire water and nutrients from the soil. These effects are closely associated with improved soil physical structure, including increased porosity, aeration, and water-holding capacity, all of which create a more favorable environment for stable root functioning. Furthermore, humic amendments are known to activate soil microbial communities that participate in nutrient cycling and organic matter transformation, thereby enhancing the biological fertility of the substrate.

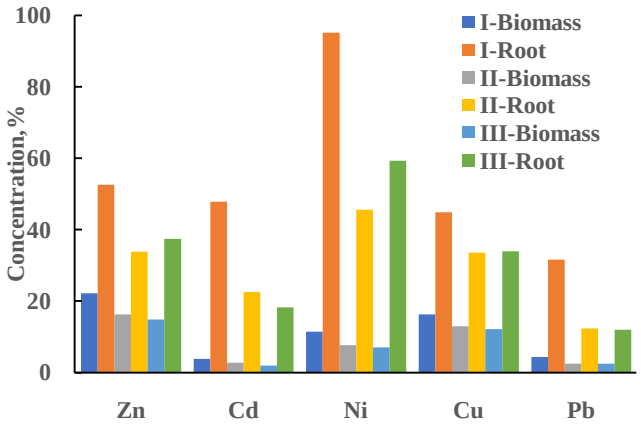

Figure 3. *Distribution of heavy-metal concentrations in oat (Avena sativa L.) biomass and roots after six weeks of phytoremediation*

Heavy-metal concentrations were consistently higher in roots than in biomass across all treatments (Fig.3), while the higher humate concentration (1:10) resulted in a marked decrease of metal accumulation in both roots and biomass, indicating enhanced stabilization in the soil.

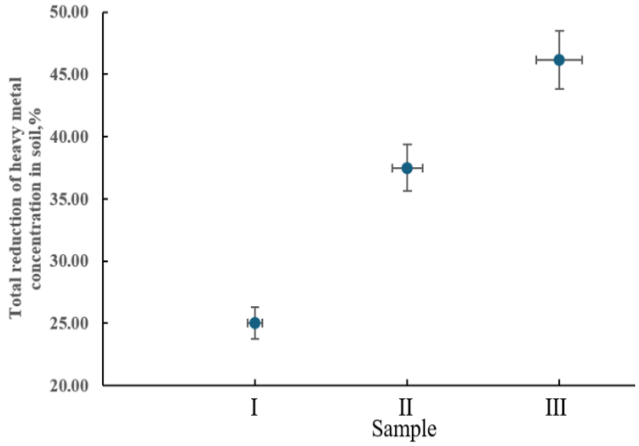

Figure 4. *Total reduction of heavy-metal concentration in peat after phytoremediation*

Heavy-metal reduction increased from approximately 25% in untreated soil (Sample I) to nearly 47% in the soil treated with the highest humate concentration (Sample III), confirming the strong positive impact of humate dosage on the remediation process. The soil amended with the moderate humate concentration (1:5, Sample II) also exhibited a notable decrease in total metal content (around 37%), demonstrating that even a relatively low dose of lignite-derived humates substantially enhances metal immobilization (Fig.4). The gradual improvement across the treatments suggests that humic substances play a critical role in binding and stabilizing heavy-metal ions within the soil matrix, thereby reducing their mobility and bioavailability. These results indicate that the application of humates in higher concentrations strengthens the sorption and complexation processes, improving overall soil quality and promoting a more efficient phytoremediation response.

Conclusions

Overall, the study demonstrates that lignite-derived humic acids obtained through energy-efficient cavitation extraction represent a cost-effective and sustainable material for soil remediation. The developed technology provides a rational approach to the valorization of brown coal, transforming a low-value fossil resource into a high-performance soil amendment. Owing to the abundance and low market price of Ukrainian lignite, humate production can be readily scaled up and integrated into agricultural restoration technologies without significant energy input or environmental burden. The application of these humates, in combination with phytoremediation using oat (Avena sativa L.), resulted in a substantial decrease in the mobility and bioavailability of heavy metals in contaminated peat-based soils. In particular, the concentrations of Zn, Cd, Ni, Cu, and Pb decreased by up to 47%, while metal uptake by biomass was effectively minimized, demonstrating the stabilizing capacity of humic substances in the soil matrix.

This integrated remediation approach not only limits the translocation of toxic elements from roots to edible biomass but also supports plant growth under stress conditions, improving the overall soil–plant health system. The synergy between humic substances and phytoremediation thus provides a practical, low-cost, and environmentally sound strategy for the rehabilitation of agricultural soils affected by military activities or industrial pollution. Considering the simplicity of the humate extraction process and the wide availability of brown coal deposits in Eastern Europe, this technology can be further scaled and adapted for various contaminated agroecosystems, contributing to long-term soil restoration and sustainable land management.

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