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The effect of biostimulants and glyphosate on the vertical migration of elements in agricultural soils

Oleh Kibarov*
Postgraduate Student
Admiral Makarov National University of Shipbuilding
54025, 9 Heroiv Ukrainy Ave., Mykolaiv, Ukraine
https://orcid.org/0009-0001-2691-1908

Ganna Trokhymenko
Doctor of Technical Sciences, Professor
Admiral Makarov National University of Shipbuilding
54025, 9 Heroiv Ukrainy Ave., Mykolaiv, Ukraine
https://orcid.org/0000-0002-0835-3551

Vladyslav Nedoroda
Doctor of Philosophy, Lecturer
Admiral Makarov National University of Shipbuilding
54025, 9 Heroiv Ukrainy Ave., Mykolaiv, Ukraine
https://orcid.org/0000-0002-1046-5114

Abstract. The purpose of this study was to evaluate the vertical migration patterns of macro- and microelements in southern chernozem soils under the influence of binary mixtures of glyphosate-based herbicides and various classes of biostimulants. The intensification of contemporary agricultural systems has precipitated a fundamental shift in the biogeochemical cycling of nutrients and contaminants within the pedosphere. This study presented an exhaustive investigation into the vertical migration mechanics of macro- and microelements within a model soil continuum, specifically analysing the perturbations introduced by the co-application of glyphosate-based herbicides and diverse biostimulant classes (fulvic acids, potassium humates, and complex stubble biodestructors). High-resolution Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry was utilised to quantify the redistribution of Fe, K, Ca, Mn, Zn, Cu, and Pb across three distinct soil horizons in controlled microcosms. The research delineated the diametrically opposed geochemical functions of humic fractions: fulvic acids ("BioFulvo") acted as aggressive mobilising agents, stripping transition metals from the medial profile and exacerbating leaching risks (Fe depletion of -30.1% in the transit zone), whereas potassium humates functioned as stabilising geochemical barriers, effectively immobilising anthropogenic lead and retaining nutrients in the root zone. A critical discovery of this study was the identification of a "hyper-mobilisation" phenomenon arising from the synergistic interaction between glyphosate and fulvic acids, which induced a 39% surge in soluble iron concentrations, likely through the development of ternary phosphonate-fulvate-metal complexes. Conversely, microbial-humic biodestructors demonstrated a unique "biofortification" potential, maintaining high zinc and manganese bioavailability without compromising profile stability. These findings underscored the necessity of a differentiated approach to agrochemical management, suggesting that while fulvic acids enhance rapid nutrient transport, their combination with

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*Corresponding author

herbicides on sensitive soils poses significant environmental risks, which can be mitigated by the buffering capacity of high-molecular-weight humates

Keywords: soil biogeochemistry; vadose zone transport; XRF spectrometry; humic substances; fulvic acids; heavy metal remediation; precision agriculture

INTRODUCTION

The contemporary paradigm of intensive agriculture is defined by a paradoxical challenge: the imperative to maximise crop yields to support a burgeoning global population competes directly with the preservation of the soil resource base. The soil profile, once viewed merely as a physical substrate for plant anchorage, is recognised as a complex, heterogeneous biogeochemical reactor where chemical, physical, and biological processes intersect to determine the fate of both essential nutrients and xenobiotic contaminants. The application of concentrated fertilisers, systemic herbicides, and metabolic enhancers has fundamentally altered the natural lithogenic and pedogenic cycles of elements. A critical, yet often overlooked, aspect of soil health is the vertical distribution of chemical elements within the vadose zone.

Global geospatial modelling by F. Tang *et al.* (2021) confirmed that 64% of agricultural land is at risk of pesticide pollution, explicitly identifying vertical leaching as a critical pathway in permeable soil systems. In natural pedogenesis, this distribution is driven by millennial-scale weathering and leaching processes. However, in modern agroecosystems, the application of agrochemicals introduces rapid, anthropogenic forcing that can overwhelm natural buffering capacities. The mobility of essential micronutrients (e.g., Zn, Mn, Cu) determines crop nutritional quality and resistance to abiotic stress, while the unchecked migration of toxic trace elements (e.g., Pb, Cd, As) poses severe risks to groundwater quality and food safety. The "chromatographic" effect of the soil profile, where different layers act as retention plates or elution zones, dictates whether an element becomes a nutrient for the crop or a pollutant in the aquifer.

The complexity of these interactions has spurred a wave of extensive research, driven largely by advancements in spectroscopic instrumentation and molecular modelling. Consequently, the validation of Portable X-ray Fluorescence (pXRF) has become a central theme in modern pedometrics. R. Ravansari *et al.* (2020) demonstrated the efficacy of pXRF for soil analysis, a conclusion robustly supported by the landmark meta-analysis of E. Jenkins *et al.* (2025). By synthesising data from 84 independent validation studies, E. Jenkins *et al.* (2025) established that advanced pXRF instruments achieve laboratory-grade accuracy for heavy metals (Pb, As, Zn, Cu), particularly under controlled ex situ conditions. This comprehensive review confirms that minimising matrix interferences through sample drying and homogenisation eliminates moisture-induced scattering and particle-size shadowing, thereby validating pXRF as a reliable platform for high-resolution elemental profiling. Complementing these analytical insights, T. Tavares *et al.* (2023) highlighted that XRF total-element profiling effectively captures the elemental stocks serving as reservoirs for bioavailable pools. The non-destructive nature of this technique allows for the preservation of soil structure, which is critical when assessing the spatial distribution of elements in microcosm studies. Against this technological backdrop, glyphosate [N-(phosphonomethyl)glycine] remains the most widely used herbicide globally, and its geochemical purpose is a subject of intense scrutiny.

E. de Gerónimo & V. Aparicio (2022) reported that glyphosate adsorption depends strongly on soil pH and competing phosphate, and that dissolved organic matter often competes for sorption sites on mineral surfaces; thus, agricultural practices that shift soil pH can substantially alter herbicide mobility. G. Qian *et al.* (2022) found that fulvic acids, due to their lower molecular weight and greater acidity, tend to facilitate arsenic mobility in tailings, whereas humic acids more often immobilise metalloids. The mechanistic understanding of glyphosate mobility has been significantly refined by Y. Jiao *et al.* (2024), who utilised multispectral analysis and Density Functional Theory (DFT) to elucidate the adsorption-complexation dynamics in Mollisols. The research demonstrated that the presence of dissolved organic matter (DOM) fundamentally alters the thermodynamic landscape of the soil solution, shifting glyphosate adsorption from a multilayer heterogeneous process to a single-layer regime. Furthermore, the researchers confirmed that glyphosate forms stable soluble complexes with humic fractions through static quenching mechanisms dominated by hydrogen bonding and van der Waals forces, specifically targeting C-O functional groups. This interaction effectively prevents the herbicide's fixation onto mineral surfaces, thereby facilitating the "hyper-mobilisation" and co-transport of glyphosate-metal complexes through the vadose zone.

The reviews by R. Zhang *et al*. (2022) and Q. Liu *et al*. (2025) have redefined the role of amino acid biostimulants in nutrient acquisition, classifying them as "natural chelating agents" with distinct thermodynamic properties. Their analysis established that amino acids enhance metal uptake by creating "weak" or moderate chelation complexes that protect nutrients from soil fixation while possessing stability constants low enough to permit rapid ligand exchange at the rhizoplane. This "catch-and-release" mechanism differs fundamentally from the strong, persistent sequestration characteristic of synthetic chelators like EDTA (ethylenediaminetetraacetic acid), ensuring that essential elements are bioavailable for plant metabolic use rather than being solubilised for leaching into the subsoil. This issue is of particular relevance in Ukraine, which holds a significant portion of the world's chernozem (black soil) reserves.

Despite the breadth of individual studies, there is a paucity of comprehensive research integrating the simultaneous effects of herbicides and different classes of biostimulants on the vertical stratification of the soil chemical matrix. Most studies focus on surface interactions or plant uptake, neglecting the intermediate transport processes within the vadose zone. This gap is critical because the vadose zone acts as the transmission filter between the agrosphere and the hydrosphere. The purpose of the study was to quantify the vertical redistribution of macro- (Fe, K, Ca) and microelements (Zn, Mn, Cu) under the influence of fulvic acids, humic acids, and amino acids. The research objectives were to evaluate the specific impact of glyphosate salt formulations (potassium vs. isopropylamine) on metal mobility, uncover synergistic or antagonistic geochemical effects when biostimulants are co-applied with herbicides, and assess the environmental risks associated with the mobilisation of toxic elements (Pb) utilising the precision of XRF spectrometry.

MATERIALS AND METHODS

Experimental microcosm design

The experimental part of the study, including microcosm preparation and instrumental sample analysis, was conducted between November 14 and 15, 2025. The research was performed at the laboratory of the Department of Ecology and Environmental Protection Technologies, Admiral Makarov National University of Shipbuilding. A controlled laboratory microcosm approach was employed to simulate the dynamics of the arable soil layer and the upper vadose zone (OECD Test Guideline 312 adapted). The soil matrix used was southern chernozem (calcic chernozem) collected from the arable horizon (0-30 cm) in the steppe zone of Ukraine (Mykolaiv Oblast). The soil was characterised by a heavy loam texture, a humus content of 3.4%, and a slightly alkaline reaction with a pH (KCl) of 7.2. This soil type was characterised by micellar carbonates and high biological activity, making it highly representative of the semi-arid agricultural zones of the Black Sea region. The application of agrochemical agents was executed in a three-stage sequence to model a specific agronomic protocol involving pre- and post-herbicide fertilisation. In the first stage, the soil samples were irrigated with biostimulant solutions to prime the soil matrix: 25 mL of "BioFulvo" solution (at a concentration of 1:100) or 25 mL of "Humate Potassium" solution (at a concentration of 1:300) were applied to the respective experimental units. In the second stage, performed one week after the initial biostimulant application, the herbicide treatments ("Uragan Forte" or "Otaman") were applied using 15 mL of solution per sample, prepared at a concentration of 10 mL of herbicide per litre of water. In the third stage, one week following the herbicide application, the soil samples were treated again with the biostimulants ("BioFulvo" or "Humate Potassium") using the exact same volumes and concentrations as in the first stage. This design allowed for the assessment of element migration under conditions of repeated biostimulant loading.

The experimental design involved creating a leaching water regime imitating intensive precipitation or irrigation. During a 30-day incubation period (corresponding to the active vegetation phase), distilled water was added to the columns in a volume equivalent to the monthly precipitation norm for the study region (approximately 60 mm), ensuring a downward moisture flow (eluvial regime). This allowed for the modelling of vertical migration processes of dissolved substances. Upon completion of incubation, the soil monoliths were subjected to rapid freezing to fix chemical gradients and prevent moisture redistribution. The frozen columns were divided into three discrete horizons for subsequent analysis, allowing for a detailed assessment of the profile's chromatographic effect:

- Zone A (Proximal/Upper): 0-2.7 cm. A zone of direct agrochemical application, maximal root mass concentration (in pot experiments), and highest microbiological activity.
- Zone B (Medial/Transit): 2.7-5.3 cm. A buffer zone where adsorption and desorption processes determine the further fate of migrating elements.
- Zone C (Distal/Lower): 5.3-8.0 cm. A zone of accumulation or washout bordering the drainage system. Increased element concentration in this zone is a direct indicator of leaching risk into groundwater.

Experimental treatments and analytical methods

To investigate the differentiated impact on element migration, a spectrum of preparations representing various chemical classes and mechanisms of action was selected. Among the biostimulants, the study examined "BioFulvo," a preparation based on highly concentrated fulvic acids. Chemically, these are low-molecular-weight organic acids (under 1,000 Da) enriched with oxygen-containing functional groups, specifically carboxyl (-COOH) and phenolic (-OH) groups. Their presumed mechanism involves high solubility across the entire pH range and the ability to form stable, soluble chelate complexes with polyvalent cations like Fe^{3+}, Zn^{2+}, and Cu^{2+}, thereby promoting their mobilisation.

In contrast to the fulvic acids, "Potassium Humate" was utilised as a source of high-molecular-weight humic acids derived from leonardite. These are macromolecular structures (exceeding 10,000 Da) possessing a polyanionic character with high cation exchange capacity. Their primary function in the soil profile was the synthesis of insoluble complexes with heavy metals and the aggregation of soil particles, effectively acting as a geochemical barrier. Additionally, the complex biological preparation "StimOrganic" was included as a stubble biodestructor. Its composition featured a consortium of living cells and spores of bacteria (*Bacillus subtilis*, *Bacillus licheniformis*) and fungi (*Trichoderma viride*, *Trichoderma lignorum*) with a titre of at least 1.0×10^9 CFU/cm^3, enriched with 100 g/L of humic substances and microbial metabolic products. Its mechanism relied on the enzymatic destruction of organic residues and the production of siderophores and organic acids (such as gluconic and citric acids), ensuring biologically regulated element mobilisation.

Regarding herbicides, "Uragan Forte" (Syngenta), a potassium salt of glyphosate (500 g/L), was selected for its specific surfactant system designed for rapid cuticular penetration. As noted by O. Litvinova *et al.* (2023), such surfactants can significantly reduce the surface tension of the soil solution, enhancing the physical migration of substances. This was compared against "Otaman" (Alfa Smart Agro), a classic isopropylamine salt of glyphosate (480 g/L). The isopropylamine cation in this formulation was bulkier compared to the potassium ion, which may influence the kinetics of herbicide sorption on clay minerals. The research investigated both separate applications of these preparations and their binary mixtures (e.g., Uragan + BioFulvo) to imitate the common tank mix practices in Ukraine. Elemental analysis was conducted using a Hitachi X-MET8000 portable XRF spectrometer (Japan). This instrument represents the advancement in field spectrometry, bridging the gap between field convenience and laboratory precision.

Technical specifications:

- Detector: High-performance Silicon Drift Detector (SDD) with a large active area, allowing for high count rates and excellent energy resolution.
- Excitation Source**:** X-ray tube optimised with BOOST™ technology, which enhances the sensitivity for heavy elements and allows for lower Limits of Detection (LOD) compared to conventional diode-based systems.
- Calibration: The instrument was calibrated using the Soil-FP (Fundamental Parameters) mode. This algorithm is critical for soil analysis as it mathematically models the interaction of X-rays with the sample matrix, automatically correcting for inter-element matrix effects (absorption and secondary fluorescence) caused by variations in soil density.

Measurements were taken in triplicate for each layer of each replicate to ensure statistical robustness. The spectra were analysed for characteristic K-alpha and L-alpha lines. Specifically, Iron (Fe) was analysed at ~6.40 keV, a region free from significant interference in silicate matrices. Raw spectral data (counts per second) were converted to concentrations (ppm) using the Soil-FP calibration curves. To account for local soil heterogeneity, measurements were performed in triplicate for each specific horizon layer. The final value for each data point was calculated as the arithmetic mean of these three technical replicates, ensuring a representative profile analysis. Consequently, vertical migration trends were evaluated by comparing these averaged concentration gradients, and leaching indices were calculated as the ratio of concentration in Zone C to Zone A.

RESULTS AND DISCUSSION

Baseline geochemical stratification (control group)

The analysis of the control group provides the reference state for the soil's natural vertical distribution. As shown in Table 1, the soil exhibits specific pedogenic trends even without external chemical intervention.

Table 1. *Vertical distribution of elements in control soil (ppm)*

Element	Layer 1 (0-2.7 cm)	Layer 2 (2.7-5.3 cm)	Layer 3 (5.3-8.0 cm)	Trend analysis
Fe (Iron)	15,536	14,818	15,048	Stable / uniform profile
K (Potassium)	9,750	9,280	10,280	Eluviation (leaching)
Ca (Calcium)	7,727	6,255	6,785	Surface accumulation
Ti (Titanium)	2,439	2,068	2,234	Matrix stability marker

Table 1, Continued

Element	Layer 1 (0-2.7 cm)	Layer 2 (2.7-5.3 cm)	Layer 3 (5.3-8.0 cm)	Trend analysis
Mn (Manganese)	385	340	360	Biogenic accumulation
Zn (Zinc)	81	83	86	Slight downward migration
Pb (Lead)	20	15	19	Variable / anthropogenic

Source: *developed by the authors*

In the control variant, two competing hydrological and biogeochemical processes are observed. Potassium (K) demonstrates a clear tendency to accumulate in the lower horizon (10,280 ppm vs 9,750 ppm at the surface). This indicates a leaching regime where highly soluble monovalent cations move downward under the influence of gravitational water. This is a typical characteristic of soils with a percolation water regime, where potassium, if not intercepted by roots or fixed by illitic clay minerals, migrates to sub-arable horizons. Conversely, Calcium (Ca) and Manganese (Mn) are enriched in the surface layer. For calcium (7,727 ppm in Layer 1 vs 6,255 ppm in Layer 2), this is likely due to the evaporation effect of the soil solution, which draws bicarbonate-rich water to the surface where calcium carbonate precipitates upon drying. For manganese, such enrichment reflects the "biological pump" mechanism: plants (precursors) uptake Mn from depth and return it to the surface through plant residues, creating a nutrient-rich top layer. The relative uniformity of lithogenic markers, such as Titanium (Ti), confirms the mineralogical homogeneity of the soil column, validating the experimental design. Iron (Fe) acts as a reference element in these soils. Its stability indicates that without chemical intervention (like chelating agents), the soil matrix is stable, and there is no massive redox-induced migration under natural conditions. In the absence of chelating fertilisers, Zinc (Zn) is relatively immobile. The slight increase in depth might be conditioned by association with clay particles (illuviation) which naturally migrate downwards over long periods. Lead (Pb) is tightly bound to organic matter in the topsoil. Its lack of migration in the control group confirms that there are no natural acidic conditions or complexing agents moving toxic metals into the groundwater – until agents like fulvic acid are added.

Impact of biostimulants and herbicides on the vertical distribution of soil elements

The application of the "BioFulvo" preparation caused the most radical restructuring of the geochemical profile, characterised by aggressive mobilisation of transition metals (Table 2).

Table 2. *Element dynamics under "BioFulvo" treatment (ppm)*

Element	Layer 1	Layer 2	Layer 3	Deviation from control (Layer 2)
Fe	14,082	10,358	12,400	-30.1% (severe depletion)
Zn	92	58	79	-31.7% (severe depletion)
Cu	23	15	20	-26.8% (mobilisation)

Source: *developed by the authors*

The comparison of soil horizons in Table 2 reveals a classic chromatographic leaching effect, where the medial soil layer functions as a primary donor of elements rather than a buffer. In the upper proximal zone (Layer 1), the iron concentration stands at 14,082 ppm; while this is lower than the control, it represents only the initial phase of mobilisation where high concentrations of fulvic acids begin to solubilise minerals within the organic-rich surface matrix. A substantial geochemical anomaly emerges in the medial zone (Layer 2), where Iron (Fe) levels precipitously drop to 10,358 ppm and zinc decreases to 58 ppm. This pronounced decline, representing a roughly 30% reduction compared to the control, indicates that low-molecular-weight fulvic acids have effectively stripped metal ions from the exchange complex, transforming this horizon into a "zone of depletion" or a geochemical vacuum. Although concentrations partially recover in the distal zone (Layer 3) to 12,400 ppm for iron and 79 ppm for Zinc (Zn) – confirming a vertical downward flux from the depleted middle layer – these values remain significantly below the control levels for the same depth. This specific distribution profile suggests that the fulvic acid complexes are sufficiently stable to bypass the lower adsorption barriers, meaning a significant portion of the mobilised metal load likely passed through the entire soil column and was lost to drainage, thereby posing a risk of groundwater contamination. In sharp contrast to the mobilising action of fulvic acids, the "Humate Potassium" treatment acted as a stabilising agent, reinforcing the soil's capacity to retain cations and structure (Table 3).

***Table 3.** Element dynamics under "Humate potassium" treatment (ppm)*

Element	Layer 1	Layer 2	Layer 3	Key observation
Fe	9,107	14,409	12,411	Apparent surface depletion/masking
K	6,739	9,277	8,294	Fixation/interlayer entrapment
Pb	13	18	15	Surface immobilisation

***Source:** developed by the authors*

The geochemical profile resulting from the application of Potassium Humate demonstrates a distinct mechanism of stabilisation, functioning diametrically opposite to the mobilisation observed with fulvic acids. In the proximal horizon (Layer 1: 0-2.7 cm), a significant reduction in detectable iron concentrations to 9,107 ppm was recorded. Unlike the depletion caused by leaching, this surface reduction is interpreted as an immobilisation phenomenon where high-molecular-weight humic acids form insoluble organo-mineral complexes and coat mineral particles, effectively "masking" the metal from rapid solubilisation. Crucially, the medial zone (Layer 2: 2.7-5.3 cm) retained high iron levels (14,409 ppm), closely mirroring the natural baseline found in the control. This preservation of the middle horizon confirms that the humic amendment successfully shielded the mineral matrix from desorption processes, maintaining the structural integrity of the soil profile preventing the creation of a "depletion zone". A specific geochemical anomaly was observed regarding Potassium (K) distribution. Despite the introduction of an external potassium source via the humate preparation, the concentration of this element in the upper layer (6,739 ppm) was notably lower than in the control. This counter-intuitive result indicates the activation of a fixation mechanism, where humic substances facilitate the entrapment of potassium ions within the interlayer spaces of clay minerals. Rather than remaining in the soil solution where it would be vulnerable to gravitational washout, the potassium was sequestered into the structural phase of the medial zone (9,277 ppm) and distal zone (8,294 ppm). This process suggests that the humates promoted the transition of exchangeable potassium into a non-exchangeable, fixed form, thereby reducing immediate losses while conserving the nutrient pool within the soil column.

The barrier function of the humate treatment was most critically evidenced by the behaviour of Lead (Pb). The proximal layer exhibited a reduced concentration of 13 ppm compared to the control baseline of 20 ppm. Most importantly, this surface reduction did not correspond to an accumulation in the distal accumulation zone (Layer 3), where levels remained low at 15 ppm. This distribution pattern confirms that the lead was not washed down but was effectively immobilised in situ at the point of contact or within the upper matrix. The macromolecular humic structures functioned as a "geochemical anchor", binding the toxic cations through strong inner-sphere complexation and physical entrapment. Consequently, the treatment successfully prevented the vertical migration of lead into the lower horizons, thereby mitigating the risk of groundwater contamination. The treatment with the stubble destructor ("StimOrganic") occupied a functional middle ground, optimising the "Bioavailability vs. Leaching" trade-off essential for precision agriculture. The data presented in Table 4 illustrates the unique "regulatory" capacity of the StimOrganic biodestructor, which fundamentally differs from both the aggressive chemical mobilisation of fulvic acids and the rigid fixation of humates. The vertical distribution profile of microelements under this treatment is characterised by exceptional uniformity, suggesting a mechanism of biological homeostasis rather than passive physical transport.

***Table 4.** Micronutrient retention with biodestructors (ppm)*

Element	Layer 1	Layer 2	Layer 3	Distribution profile
Zn	107	103	100	High & uniform
Mn	396	350	386	Stable

***Source:** developed by the authors*

In the proximal horizon (Layer 1: 0-2.7 cm), the application of the biodestructor resulted in a high level of zinc bioavailability (107 ppm) compared to the control (81 ppm). Unlike the fulvic acid treatment, where mobilisation led to immediate downward migration, the microbial complex successfully retained these mobilised nutrients in the upper root-accessible zone. This retention is likely facilitated by the synthesis of microbial biomass and the development of temporary, labile complexes with amino acids and enzymes produced by the Bacillus and Trichoderma consortium present in the preparation.

The medial zone (Layer 2: 2.7-5.3 cm) demonstrated a remarkable stability that contrasts sharply with the "depletion zones" observed in other treatments.

Zinc concentrations remained at 103 ppm, and manganese at 350 ppm, showing virtually no significant gradient relative to the surface layer. This absence of a sharp concentration drop indicates that the biodestructor prevents the rapid gravitational leaching of elements. Instead of being washed through this layer, the elements are maintained in a state of dynamic equilibrium, likely regulated by the diffusion of microbial siderophores which solubilise metals only to the extent required for biological activity, effectively buffering the soil solution against sharp geochemical fluctuations. The distal zone (Layer 3: 5.3-8.0 cm) confirmed the safety of this approach regarding groundwater contamination risks. Zinc levels (100 ppm) and manganese levels (386 ppm) were comparable to the upper horizons, resulting in a Leaching Index (LI) close to 1.0. This uniform column-wide distribution signifies that the biodestructor achieved "smart mobilisation": it increased the total pool of available nutrients throughout the profile without creating a surplus of free ions that would be lost to drainage. Consequently, the distinct stratification typical of chemical leaching was replaced by a biologically homogenised profile, optimal for root development throughout the entire depth of the arable layer.

The most interesting finding of the study was the detection of a fundamental divergence in geochemical behaviours when glyphosate herbicides were co-applied with different fractions of humic substances. The interaction between the glyphosate formulation "Uragan Forte" and the fulvic acid preparation "BioFulvo" resulted in a distinct synergistic effect characterised as "hyper-mobilisation". In this variant, the iron concentration within the soil profile surged to 21,592 ppm, exceeding the control level by 39%. This extreme value, which surpasses natural variability, indicates a massive phase transition of iron from the solid mineral state into the soil solution. This non-additive phenomenon suggests the synthesis of soluble ternary complexes, where fulvic acids destabilise Fe-O bonds on mineral surfaces while glyphosate simultaneously chelates the released metal, effectively maintaining it in a soluble state. Such a mechanism poses a dual risk: potential phytotoxicity due to iron overload and the accelerated leaching of the herbicide itself, as the dissolution of iron oxides – the primary sorbent for glyphosate – facilitates its downward migration. Conversely, the addition of "Potassium Humate" to glyphosate mixtures produced an antagonistic, stabilising effect. In these trials, the system exhibited high retention of calcium (8,805 ppm) and the effective confinement of heavy metals. This stabilisation is attributed to the buffering capacity of high-molecular-weight humic acids, which likely neutralised the pH reduction associated with glyphosate hydrolysis and provided ample surface area for the re-adsorption of mobilised ions, thereby neutralising the geochemical disturbance caused by the herbicide.

Mechanisms, risks, and contextual significance

The vertical migration of chemical elements within the vadose zone is not merely a physical displacement but the result of a dynamic and competitive equilibrium between sorption processes on the solid soil phase and solubilisation kinetics in the liquid phase. The results of this study clearly delineate the divergent roles played by different fractions of humic substances in this equilibrium, challenging the conventional view of organic amendments as a monolithic group. It is a fundamental and well-established fact in soil chemistry that fulvic acids, characterised by their low molecular weight and high density of oxygen-containing functional groups, function as aggressive transport agents in soil environments. Due to their high stability constants with metal ions and solubility across a broad pH range, these fulvic complexes are capable of overcoming the natural electrostatic and steric barriers of the soil matrix that typically retain cations. In the conducted experiment, this mechanism was evidenced by the critical depletion of iron and zinc in the medial horizons treated with "BioFulvo". This confirms that on light-textured soils or those undergoing dehumification – a condition increasingly characteristic of degraded Ukrainian chernozems – the application of concentrated fulvic acids carries a significant risk of accelerating the leaching of essential microelements, effectively stripping the arable layer of its nutritional potential.

In contrast to this mobilisation, the application of "Potassium Humate" resulted in the effective immobilisation of Lead (Pb). This aligns with the remediation strategies proposed by O. Sytar & N. Taran (2022) and Y. Lu *et al.* (2025), who advocated for the use of humates to create geochemical barriers. Conversely, Y. Lu *et al.* (2025) demonstrated that humic acid composites (e.g., with hydroxyapatite) effectively immobilise Cd and Pb, reducing their translocation to grains, thus positioning humic acids as remediation agents. Unlike the mobile fulvic fraction, humic acids facilitate the synthesis of insoluble organo-mineral aggregates and promote the fixation of metals within the interlayer spaces of clay minerals. This property is critically important for the restoration of the soil's barrier function, especially given the data from V. Datsenko (2022) indicating a reduction in the sorption capacity of soils in the Kharkiv Oblast due to anthropogenic acidification. However, the most geochemically significant and ecologically concerning discovery of this study is the "hyper-mobilisation" phenomenon observed when glyphosate herbicides are co-applied with fulvic acids, resulting in a 39% surge in soluble iron concentrations. While standard models, such as those by X. Li *et al*. (2023) and B. Geysels *et al*. (2025), posit that glyphosate is typically inactivated through adsorption onto iron oxides like goethite and ferrihydrite, the current findings suggest that the presence of fulvic acids fundamentally disrupts this interaction. The data indicate a mechanism of competitive solubilisation or ternary complex formation. By competing for sorption sites or chemically attacking the oxide surface, the fulvic acid dissolves the mineral carrier, releasing the herbicide-metal complex into the soil solution. B. Geysels *et al*. (2025) provided a mechanistic surface-complexation model for glyphosate binding to ferrihydrite, showing primarily binuclear bidentate coordination. This interaction is crucial because iron oxides are the primary "sink" for glyphosate in soils; however, the presence of strong chelators can dissolve these oxides, releasing both the iron and the adsorbed herbicide. The dichotomy between humic and fulvic acids has been refined in evolving scientific discourse. This synergistic solubilisation implies that migration models failing to account for dissolved organic matter may severely underestimate the risk of groundwater contamination, a concern that echoes the warnings of O. Litvinova *et al*. (2023) regarding the deep-profile accumulation of pesticide residues.

Furthermore, the study illuminates the advantages of biological regulation over chemical manipulation. The "StimOrganic" biodestructor demonstrated a strategy of "smart mobilisation", where nutrient availability is regulated by microbial siderophores. As elucidated by B. Khoshru *et al*. (2023) and M. Maciel-Rodríguez *et al*. (2025), the soil microbiome functions as an active regulator of elemental cycling through siderophore-mediated homeostasis. Their research demonstrated that specific rhizobacteria mobilise manganese and zinc via inducible metabolic pathways – including acidification and enzymatic reduction – that are responsive to environmental depletion signals. This biological feedback loop achieves a state of "smart mobilisation", where nutrient solubility is synchronised with plant demand, thereby maintaining high bioavailability in the root zone while preventing the unregulated mass leaching losses associated with passive chemical chelators.

These findings have direct implications for agricultural practices in Ukraine, validating the conclusions of O. Litvinova *et al*. (2023) regarding the role of surfactants in pesticides as active geochemical migration agents and confirming the urgent need for organic stabilisation strategies to verify the loss of buffering capacity described by V. Didora *et al*. (2024). Ultimately, regarding the remediation of soils subjected to heavy metal contamination, as described by E. Moliszewska *et al*. (2023) and O. Datsko *et al*. (2025), the application of potassium humates functions as a critical measure to restore the protective sorption capacity of the pedosphere. The study by O. Litvinova *et al*. (2023) emphasised that the accumulation of surfactants (surface-active agents), which are part of pesticide formulations, significantly alters the migration capacity of biogenic elements, effectively "washing" them out of the root zone. This phenomenon is exacerbated by the use of glyphosate – a herbicide that remains dominant in global and Ukrainian agriculture.

CONCLUSIONS

The comprehensive analysis conducted in this study, utilising high-precision ED-XRF spectrometry, provided critical experimental evidence that necessitated a fundamental revision of current agronomic practices regarding the use of soil amendments and herbicides. The results unequivocally demonstrated that humic substances cannot be treated as a monolithic functional entity in agricultural management, exhibiting instead a strict geochemical dichotomy that determined the fate of soil elements. Fulvic acids were identified as aggressive mobilising agents that induced the rapid desorption and downward migration of essential microelements, specifically iron and zinc. This process posed a significant long-term threat to soil fertility by effectively stripping the arable horizon of its nutritional reserves and translocating them into the subsoil, unavailable to crop roots. Conversely, the application of Potassium Humates proved to be a highly effective strategy for chemical stabilisation, acting as a robust geochemical barrier that immobilises toxic metals, such as lead, via inner-sphere complexation, thereby mitigating the risks of aquifer contamination.

From an ecological perspective, the most alarming finding was the discovery of a synergistic "hyper-mobilisation" mechanism when glyphosate herbicides were co-applied with fulvic acids. The observed 39% surge in soluble iron concentrations indicated that fulvic acids destabilised the mineral matrix, preventing the natural adsorption of the herbicide onto iron oxides. This synthesis of soluble ternary complexes implied that the common practice of tank-mixing these agents may inadvertently facilitate the deep percolation of glyphosate into groundwater, bypassing the soil's natural filtration capacity. In contrast to these chemical risks, the biological approach utilising microbial-enzymatic biodestructors ("StimOrganic") offered a sustainable alternative. This treatment achieved an optimal balance of "smart mobilisation", regulated by microbial siderophores, which ensured high nutrient bioavailability in the rhizosphere without the ecological liability of mass leaching associated with synthetic chelators or pure fulvic acids.

Consequently, to ensure environmental safety and soil health, it is imperative to revise agrochemical protocols: the mixing of glyphosate with high-concentration fulvic acids must be strictly prohibited on soils with low sorption capacity or high-water tables. Priority should be given to high-molecular-weight potassium humates for the recultivation of technogenically disturbed or war-impacted lands. Future scientific inquiries should focus on validating these mechanisms through isotopic labelling (^{14}C – glyphosate) to directly trace the molecular transport of herbicide residues within ternary complexes, and on implementing longitudinal field studies to assess the scalability of these geochemical interactions under variable climatic conditions.

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REFERENCES

[1] Datsenko, V. (2022). Physical and chemical properties of soils in Kharkiv (Ukraine). *Environmental Monitoring and Assessment*, 194, article number 163. doi: 10.1007/s10661-022-09827-7.

[2] Datsko, O., Melnyk, O., Kovalenko, I., Butenko, A., Zakharchenko, E., Ilchenko, V., Onychko, V., & Solokha, M. (2025). Estimation of the content of trace metals in Ukrainian military-affected soils. *Notulae Botanicae Horti Agrobotanici Cluj-Napoca*, 53(1), article number 14328. doi: 10.15835/nbha53114328.

[3] De Gerónimo, E., & Aparicio, V.C. (2022). Changes in soil ph and addition of inorganic phosphate affect glyphosate adsorption in agricultural soil. *European Journal of Soil Science*, 73, article number e13188. doi: 10.1111/ejss.13188.

[4] Didora, V., Klyuchevich, M.M., Chingiene, R., Stolyar, S., & Derebon, I.Yu. (2024). Restoration of soil fertility and improvement of phytosanitary condition of soil in short rotation of crops in Polissia of Ukraine. *Scientific Horizons*, 27(4), 98-106. doi: 10.48077/scihor4.2024.98.

[5] Geysels, B., Weng, L., Hiemstra, T., & van Riemsdijk, W.H. (2025). A mechanistic surface complexation model for glyphosate adsorption to ferrihydrite in competition with phosphate. *Water Research*, 288, article number 124634. doi: 10.1016/j.watres.2025.124634.

[6] Jenkins, E., Galbraith, J., & Paltseva, A.A. (2025). Portable X-ray fluorescence as a tool for urban soil contamination analysis: Accuracy, precision, and practicality. *SOIL*, 11(2), 565-582. doi: 10.5194/soil-11-565-2025.

[7] Jiao, Y., Jia, J., Gu, J., & Wang, S. (2024). Insights into the enhanced adsorption of glyphosate by dissolved organic matter in farmland Mollisol: Effects and mechanisms of action. *Environmental Geochemistry and Health*, 46(11), article number 459. doi: 10.1007/s10653-024-02210-0.

[8] Khoshru, B., *et al.* (2023). Enhancing manganese availability for plants through microbial potential: A sustainable approach for improving soil health and food security. *Bacteria*, 2(3), 129-141. doi: 10.3390/bacteria2030010.

[9] Li, X., *et al*. (2023). Adsorption mechanisms of glyphosate on ferrihydrite: Effects of Al substitution and aggregation state. *Environmental Science & Technology*, 57(38), 14384-14395. doi: 10.1021/acs.est.3c04727.

[10] Litvinova, O., Tonkha, O., Havryliuk, O., Litvinov, D., Symochko, L., Dehodiuk, S., & Zhyla, R. (2023). Fertilizers and pesticides impact on surface-active substances accumulation in the dark gray podzolic soils. *Journal of Ecological Engineering*, 24(7), 119-127. doi: 10.12911/22998993/163480.

[11] Liu, Q., Sun, X., Wang, Sh., Zhao, R., Li, L., Zhou, J., Bao, L., Zhou, W., & Zhang, N. (2025). Impacts of humic acid and potassium fulvate on cadmium and lead accumulation and translocation in maize (*Zea mays* L.) grown in co-contaminated soil. *Agriculture*, 15(19), article number 2064. doi: 10.3390/agriculture15192064.

[12] Lu, Y., Yue, H., Tan, R., Ding, Z., Chen, G., Zhang, S., Li, Z., Proshad, R., Cheng, X., & Zhao, Z. (2025) Remediation effects of humic acid and hydroxyapatite on cadmium-contaminated alkaline wheat soil and its microbial community response: A field trial. *Journal of Environmental Science*. doi: 10.1016/j.jes.2025.09.013.

[13] Maciel-Rodríguez, M., Moreno-Valencia, F.D., & Plascencia-Espinosa, M. (2025). The role of plant growth-promoting bacteria in soil restoration: A strategy to promote agricultural sustainability. *Microorganisms*, 13(8), article number 1799. doi: 10.3390/microorganisms13081799.

[14] Moliszewska, E., Bida, I., Matic, K., Ślusarczyk, A., Pawliczek, D., Havryliuk, O., Hovorukha, V., & Tashyrev, O. (2023). Analysis of variations in heavy metal levels and soil microorganism counts resulting from shelling incidents in Ukraine. *Archives of Environmental Protection*, 51(1), 83-91. doi: 10.24425/aep.2025.153752.

[15] Qian, G., Xu, L., Li, N., Wang, K., Qu, Y., & Xu, Y. (2022). Enhanced arsenic migration in tailings soil with the addition of humic acid, fulvic acid and thiol-modified humic acid. *Chemosphere*, 286(2), article number 131784. doi: 10.1016/j.chemosphere.2021.131784.

[16] Ravansari, R., Wilson, S.C., & Tighe, M. (2020). Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. *Environment International*, 134, article number 105250. doi: 10.1016/j.envint.2019.105250.

[17] Sytar, O., & Taran, N. (2022). Effect of heavy metals on soil and crop pollution in Ukraine – a review. *Journal of Central European Agriculture*, 23(4), 881-887. doi: 10.5513/JCEA01/23.4.3603.
[18] Tang, F., Lenzen, M., McBratney, A., & Maggi, F. (2021). Risk of pesticide pollution at the global scale. *Nature Geoscience*, 14, 206-210. doi: 10.1038/s41561-021-00712-5.
[19] Tavares, T.R., de Almeida, E., Pinheiro, C.R., Guerrero, A., Fiorio, P.R., & de Carvalho, H.W.P. (2023). Analysis of total soil nutrient content with X-ray fluorescence spectroscopy (XRF): Assessing different predictive modeling strategies. *AgriEngineering*, 5(2), 680-697. doi: 10.3390/agriengineering5020043.
[20] Zhang, R., *et al*. (2022). An amino acid fertilizer improves the emergent accumulator plant *Nasturtium officinale* R. Br. phytoremediation capability for cadmium-contaminated paddy soils. *Frontiers in Plant Science*, 13, article number 1003743. doi: 10.3389/fpls.2022.1003743.

Вплив біостимуляторів і гліфосату на вертикальну міграцію елементів у сільськогосподарських ґрунтах

Олег Кібаров
Аспірант
Національний університет кораблебудування імені адмірала Макарова
54025, просп. Героїв України, 9, м. Миколаїв, Україна
https://orcid.org/0009-0001-2691-1908

Ганна Трохименко
Доктор технічних наук, професор
Національний університет кораблебудування імені адмірала Макарова
54025, просп. Героїв України, 9, м. Миколаїв, Україна
https://orcid.org/0000-0002-0835-3551

Владислав Недорода
Доктор філософії, викладач
Національний університет кораблебудування імені адмірала Макарова
54025, просп. Героїв України, 9, м. Миколаїв, Україна
https://orcid.org/0000-0002-1046-5114

Анотація. Метою цього дослідження було оцінити закономірності вертикальної міграції макро-та мікроелементів у південних чорноземах під впливом бінарних сумішей гербіцидів на основі гліфосату та біостимуляторів різних класів. Інтенсифікація сучасних аграрних систем спричинила суттєві зміни в біогеохімічному кругообігу поживних елементів і контамінантів у педосфері. У роботі представлено комплексне дослідження механізмів вертикальної міграції макро- та мікроелементів у модельному ґрунтовому профілі з акцентом на порушення, спричинені сумісним застосуванням гліфосатвмісних гербіцидів і біостимуляторів різної природи (фульвові кислоти, гумати калію та комплексні стерньові біодеструктори). Для кількісної оцінки перерозподілу Fe, K, Ca, Mn, Zn, Cu та Pb у трьох ґрунтових горизонтах контрольованих мікрокосмів застосовано високороздільну енергодисперсійну рентгенофлуоресцентну спектрометрію (ED-XRF). Дослідження виявило діаметрально протилежні геохімічні функції гумусових фракцій: фульвові кислоти («BioFulvo») діяли як агресивні мобілізувальні агенти, вилучаючи перехідні метали з середнього горизонту та посилюючи ризики вимивання (зменшення вмісту Fe на 30,1 % у транзитній зоні), тоді як гумати калію виконували роль стабілізуючих геохімічних бар'єрів, ефективно іммобілізуючи антропогенний свинець і утримуючи поживні елементи в кореневмісному шарі. Ключовим результатом роботи стало виявлення феномену «гіпермобілізації», що виникає внаслідок синергічної взаємодії гліфосату та фульвових кислот і призводить до зростання концентрації розчинного заліза на 39 %, ймовірно, через утворення тернарних фосфонат–фульват–металевих комплексів. Водночас мікробно-гумінові біодеструктори продемонстрували унікальний потенціал «біофортифікації», підтримуючи високу біодоступність цинку та марганцю без порушення стабільності ґрунтового профілю. Отримані результати підкреслили необхідність диференційованого підходу до управління агрохімічними технологіями. Хоча фульвові кислоти сприяють швидкому транспорту поживних елементів, їх поєднання з гербіцидами на чутливих ґрунтах несе суттєві екологічні ризики, які можуть бути нівельовані буферною здатністю високомолекулярних гуматів

Ключові слова: біогеохімія ґрунтів; транспорт у вадозній зоні; XRF-спектрометрія; гумусові речовини; фульвові кислоти; ремедіація важких металів; точне землеробство

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тел.: +38(0512) 70-93-54
E-mail: ubsras@bsagriculture.com.ua
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