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HEAVY METAL DISTRIBUTION IN BOTTOM SEDIMENTS OF THE KAMYANKA RIVER (ZHYTOMYR POLISSIA): GEODYNAMIC ASPECT

Objective. To establish comprehensive baseline geochemical data for heavy metal distribution patterns in bottom sediments of the Kamyanka River Basin within the broader context of the Ukrainian Shield geodynamic evolution and long-term tectonic stability. This research aims to characterize the relationship between deep crustal processes spanning over 3.8 billion years of geological history and contemporary environmental geochemistry, with a specific focus on distinguishing between natural background metal concentrations derived from crustal weathering processes and potential anthropogenic contamination sources in this geodynamically stable continental platform setting. Methodology. Advanced spectrophotometric analytical techniques, including inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS), were systematically employed to analyze sediment samples collected from strategically selected representative sites reflecting the full spectrum of diverse geomorphological and hydrological conditions within a geodynamically stable cratonic domain. The comprehensive sampling strategy encompassed various depositional environments ranging from headwater reaches influenced by groundwater discharge to downstream areas subject to urban runoff and agricultural inputs. Sequential extraction procedures and bioavailability assessments were integrated to evaluate metal speciation and environmental mobility. At the same time, quality control measures included certified reference materials, duplicate analyses, and blank determinations to ensure analytical reliability and environmental significance of the obtained results. Results. Pronounced dominance of iron (3,862 mg/kg) and aluminum (1.906 mg/kg) was established, reflecting characteristic aluminosilicate weathering signatures of Precambrian crystalline basement rocks typical of the Ukrainian Shield geological province. Essential trace metals, including copper (5.2 mg/kg), chromium (7.8 mg/kg), and nickel (2.5 mg/kg), were detected at natural background levels, while potentially toxic elements such as mercury, cadmium, and bismuth remained consistently below analytical detection limits. The Al/Fe ratio 0.49 indicates typical continental weathering signatures without unusual enrichment or depletion patterns. The geochemical signature corresponds to a sedimentary environment dominated by natural terrigenous input derived from stable continental weathering processes operating under conditions of prolonged geodynamic stability, with minimal anthropogenic contamination pressure reflecting the relatively stable geodynamic setting and effective environmental management within the study area. Scientific novelty. The complex relationship between Ukrainian Shield geodynamic evolution and contemporary heavy metal distribution patterns in fluvial sedimentary systems has been comprehensively characterized for the first time, establishing the critical importance of long-term tectonic stability in controlling environmental geochemistry. A novel integrated conceptual model of metal accumulation mechanisms under stable cratonic conditions has been developed, incorporating thermodynamic equilibrium relationships, surface complexation processes, and biogeochemical cycling pathways. This research demonstrates that geodynamic controls fundamentally determine metal fate and transport in hydrogeological systems, where long-term tectonic stability has allowed the development of distinctive weathering profiles and hydrogeochemical regimes that control heavy metal mobility and bioavailability in continental platform environments. Practical significance. The findings establish a robust scientific foundation for evidence-based environmental management strategies in geodynamically stable regions worldwide and provide critical baseline data for future environmental monitoring and ecological risk assessment within similar geological and climatic settings across the Ukrainian Shield region. The results support sustainable development initiatives and ecosystem protection programs within the context of ongoing urbanization processes affecting ancient crystalline shield terrains, while contributing to the development of effective environmental management strategies for regions characterized by ancient crystalline basement rocks. This research has important implications for environmental policy development and provides essential data for supporting climate adaptation and urban sustainability initiatives in continental platform settings.

Keywords: river sediments, geochemical analysis, environmental assessment,; Ukrainian Shield, bioaccumulation, contamination, ecological monitoring, pollution.

Introduction

The geodynamic evolution of the Ukrainian Shield represents one of the most significant Precambrian crustal segments in Europe, with complex tectonic processes spanning over 3.8 billion years of geological history directly influencing contemporary environmental systems and heavy metal distribution patterns in modern sedimentary environments. Prolonged tectonic stability throughout the Phanerozoic has created unique conditions where deep crustal processes and surface geochemical cycles interact to control metal accumulation and transport in aquatic systems. This geological heritage has allowed the development of distinctive weathering profiles and hydrogeochemical regimes that fundamentally control heavy metal fate and mobility, distinguishing cratonic environments from tectonically active regions. Understanding these geodynamic controls on environmental geochemistry is essential for predicting metal behavior in continental platform settings and developing effective environmental management strategies for regions characterized by ancient crystalline basement rocks.

Geodynamic stability of cratonic regions creates specific conditions for metal cycling that differ fundamentally from those in orogenic belts or volcanic arcs. The Ukrainian Shield, as part of the East European Craton, exhibits characteristic features including absence of active volcanism, minimal neotectonic deformation, and development of mature weathering crusts that collectively control contemporary heavy metal distribution in surface environments [Kapelista et al., 2024; Cheng & Su, 2024].

The Kamyanka River Basin within the Zhytomyr Urban Area provides an exceptional natural laboratory for investigating the relationship between geodynamic processes and heavy metal distribution in bottom sediments. This represents a typical East European Platform drainage system where Precambrian crystalline rocks interact with overlying sedimentary sequences to create complex hydrogeochemical conditions [Correggia et al., 2024]. The stability of this continental margin setting over geological time scales has resulted in mature weathering systems that exhibit distinctive geochemical signatures, making it possible to distinguish between natural background metal concentrations derived from crustal weathering processes and potential anthropogenic contamination sources. This geodynamic context is particularly relevant for understanding metal cycling in continental platform environments worldwide, where similar geological settings control environmental geochemistry and ecosystem health.

The urgent need for comprehensive baseline geochemical data in Ukrainian Shield river systems has become increasingly apparent as urbanization and industrial development expand within this geodynamically stable but environmentally sensitive region. Current environmental monitoring approaches often lack the integrated geodynamic perspective necessary to distinguish between natural crustal contributions and anthropogenic metal sources, leading to potential misinterpretation of environmental risk assessments and ineffective management strategies [Tsyhanenko-Dziubenko et al., 2023, 2025]. Of particular importance is the need to establish baseline concentrations that reflect natural geodynamic processes rather than short-term anthropogenic influences, providing a foundation for long-term environmental monitoring in similar cratonic settings.

The primary objective of this research is to establish comprehensive baseline geochemical data for heavy metal distribution in bottom sediments of the Kamyanka River Basin through advanced spectrophotometric analysis, with specific focus on integrating geodynamic controls on metal accumulation patterns to support evidence-based environmental management and ecological risk assessment within the broader context of Ukrainian Shield environmental systems. This investigation aims to demonstrate how prolonged tectonic stability influences contemporary metal cycling processes. It provides a methodological framework for distinguishing natural geochemical signatures from anthropogenic contamination in ancient shield environments.

Review of Previous Research

Contemporary research in heavy metal distribution within sedimentary systems has increasingly focused on the fundamental role of geodynamic processes in controlling environmental geochemistry. Recent investigations demonstrate that tectonic stability represents a primary factor governing metal accumulation patterns in continental platform environments, where prolonged crustal stability allows development of distinctive weathering profiles and hydrogeochemical regimes [Robledo Ardila et al., 2024; Custodio et al., 2024; Hatje et al., 2024]. The geochemical zonation of aquatic sediments represents a fundamental control mechanism for heavy metal fate and transport in hydrogeological systems, with redox stratification creating distinct biogeochemical barriers that regulate metal speciation and mobility through coupled hydrological and geochemical processes [Mosalem et al., 2024]. Thermodynamic equilibrium relationships govern the distribution of heavy metals between aqueous and solid phases in sedimentary environments, with recent advances in geochemical modeling providing enhanced predictive capabilities for metal behavior under varying hydrogeochemical conditions [Sikakwe et al., 2024; Peijnenburg et al., 2024].

Previous research on heavy metal geochemistry in cratonic environments demonstrates the fundamental role of geodynamic stability in controlling metal distribution in continental platform settings. The Ukrainian Shield is a Precambrian basement structure with a long and complex history spanning an interval greater than three billion years during which tectonic structures evolved, ranging from granulite–gneiss and granite–greenstone terrains in the Early and Late Archaean to intracratonic basins and troughs [Claesson et al., 2006]. Studies of geochemical baseline concentrations in bo ttom sediments of large freshwater lakes demonstrate significant differences between natural background levels and anthropogenically altered systems, with baseline concentrations for As, Sb, Hg, Co, Cr, Cu, Ni, Pb and Zn at 9.92, 1.67, 0.14, 22.62, 100.56, 31.63, 31.97, 33.05 and 97.01 mg/kg respectively in Lake Taihu, equivalent to pre-industrial concentrations determined from lakes in Sweden and Europe [Hu et al., 2012]. The Ukrainian metallogenic province of the shield is characterized by the greatest variety of deposits, where iron, titanium, uranium, and other metals are standard, and granite-greenstone belts of the Middle-Dniprean area are prominent in gold mineralization [ICOG, 2022].

This fundamental understanding of geochemical processes becomes particularly relevant when examining ancient shield regions, where long-term tectonic stability has created unique conditions for metal cycling. Research on cratonic environments has revealed that prolonged geological stability fundamentally influences contemporary environmental systems by controlling weathering processes and metal mobility [Chen et al., 2024]. As one of Europe's most significant Precambrian crustal segments, the Ukrainian Shield provides unique insights into metal cycling processes operating under stable continental conditions. Studies of similar cratonic environments worldwide demonstrate that mechanical weathering and chemical alteration of primary minerals dominate over hydrothermal or tectonically-driven metal enrichment processes [Zhang et al., 2022; Liu et al., 2022; Huang et al., 2024]. The molecular-scale interactions between heavy metals and natural organic matter represent critical processes controlling metal bioavailability and transport in aquatic systems, with carboxyl and phenolic groups showing distinct affinities for different metal species [John та Gopinath, 2024; Yu et al., 2024; Morel et al., 2023]. These fundamental binding mechanisms directly influence metal mobility and bioavailability in continental river systems developed on crystalline basement terrains [Tang et al., 2024].

Building upon this theoretical foundation, contemporary environmental monitoring approaches increasingly recognize the practical challenges of distinguishing between natural background concentrations and anthropogenic metal sources, particularly in geodynamically stable regions where natural weathering processes may dominate sediment metal content [Zhuang et al., 2021; Khan et al., 2021; Issakhov et al., 2023]. Military activities and their aftermath represent significant anthropogenic disturbance factors that can fundamentally alter hydrochemical conditions and heavy metal distribution patterns in aquatic ecosystems, as demonstrated by investigations of post-conflict water systems in the Kyiv region, where hydrochemical parameters showed marked deviations from pre-disturbance baseline conditions [Alpatova et al., 2022]. Advanced analytical techniques, including sequential extraction procedures and machine learning approaches, have enhanced the understanding of metal speciation and bioavailability in natural sedimentary systems [Yaseen et al., 2024; Montazeri et al., 2022; Wang et al., 2023]. Biogeochemical cycling of heavy metals in river sediments involves complex interactions between microbial processes, organic matter decomposition, and geochemical transformations, with the water-sediment interface serving as a critical zone where biological and chemical processes converge to control metal fate and mobility [Jørgensen, 2021; Cao et al., 2024]. Understanding these processes is essential for accurate environmental risk assessment and developing effective management strategies in continental platform settings.

However, despite extensive global research on heavy metal geochemistry, significant knowledge gaps remain regarding the specific relationship between geodynamic evolution and contemporary metal distribution patterns in Ukrainian Shield river systems. Current environmental monitoring approaches often lack the integrated geodynamic perspective necessary to distinguish between natural crustal contributions and anthropogenic metal sources. This leads to potential misinterpretation of environmental risk assessments in this geodynamically stable but environmentally sensitive region. The Kamyanka River Basin represents a typical East European Platform drainage system where Precambrian crystalline rocks interact with overlying sedimentary sequences to create complex hydrogeochemical conditions. This setting provides an exceptional opportunity to investigate fundamental controls on heavy metal distribution in continental platform environments, contributing to a broader understanding of metal cycling processes in ancient shield regions worldwide.

The geochemical zonation of aquatic sediments represents a fundamental control mechanism for heavy metal fate and transport in hydrogeological systems [Robledo Ardila et al., 2024]. Contemporary research demonstrates that redox stratification creates distinct biogeochemical barriers that regulate metal speciation and mobility through coupled hydrological and geochemical processes [Custodio et al., 2024]. The vertical progression from oxic to sulfidic conditions establishes thermodynamic controls over metal precipitation, with Fe-Mn oxide phases dominating metal sequestration in the upper oxidized zones. At the same time, sulfide minerals become predominant under reducing conditions [Mosalem et al., 2024]. As illustrated in Fig. 1, the redox zonation creates distinct geochemical environments that control heavy metal behavior through sequential reduction processes.

Fig. 1 demonstrates the critical importance of redox boundaries in controlling metal mobility, with each zone representing distinct thermodynamic conditions that favor specific metal-bearing phases. The transition from oxic to anoxic conditions fundamentally alters metal speciation and bioavailability in sedimentary environments, creating predictable geochemical gradients that are particularly pronounced in continental platform settings where stable hydrological conditions allow development of mature redox profiles.

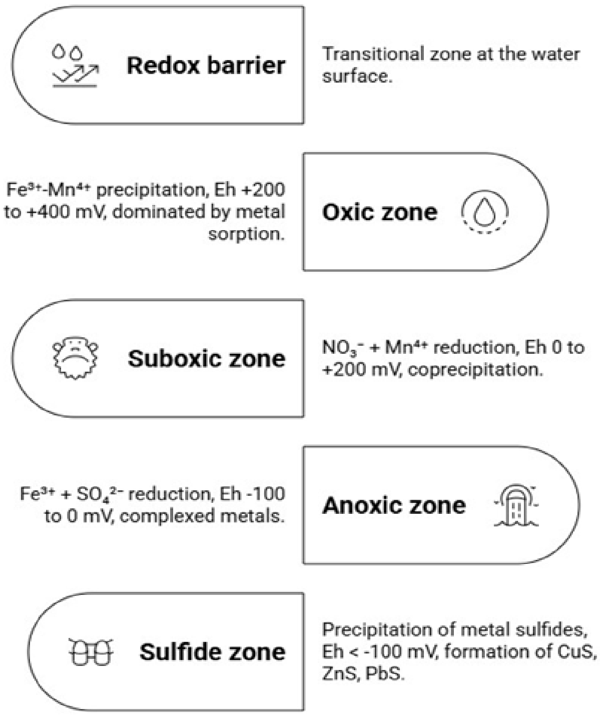

Fig. 1. Geochemical barriers and redox zonation in sediments.
(Conceptual framework developed by the author).

The mechanistic understanding of heavy metal accumulation in bottom sediments requires integrating multiple thermodynamic and kinetic processes operating at the sediment-water interface [Zhang et al., 2022]. Surface complexation mechanisms provide the primary pathway for metal immobilization in oxic environments, with stability constants varying significantly among different metal species [Liu et al., 2022]. The interplay between sorption, precipitation, complexation, and bioaccumulation processes determines the ultimate fate of heavy metals in sedimentary systems, with complexation reactions involving organic ligands representing critical biogeochemical processes that enhance metal retention through the formation of stable organometallic complexes [Zhuang et al., 20].

Thermodynamic equilibrium relationships govern the distribution of heavy metals between aqueous and solid phases in sedimentary environments, with recent advances in geochemical modeling providing enhanced predictive capabilities [Sikakwe et al., 2024].

Modern surface complexation models incorporate advanced analytical approaches to improve accuracy in predicting metal speciation under varying hydrogeochemical conditions [Peijnenburg et al., 2024]. The coupling of precipitation and complexation reactions creates complex phase relationships that are increasingly understood through integrated geochemical modeling approaches, particularly relevant for understanding metal behavior in geodynamically stable continental settings [Chen et al., 2024].

The molecular-scale interactions between heavy metals and humic acids represent fundamental processes controlling metal bioavailability and transport in aquatic systems [John та Gopinath, 2024]. Recent studies emphasize the role of specific binding mechanisms in determining metal stability constants, with carboxyl and phenolic groups showing distinct affinities for different metal species [Yu et al., 2024]. These binding mechanisms range from simple monodentate coordination to complex polymeric structures, with stability constants varying according to the Irving-Williams series, directly influencing metal mobility and bioavailability in continental river systems developed on crystalline basement terrains.

Biogeochemical cycling of heavy metals involves complex interactions between microbial processes, organic matter decomposition, and geochemical transformations [Jørgensen, 2021]. Recent research has highlighted the critical role of microbial communities in metal cycling, with these microorganisms showing distinct responses to heavy metal contamination and influencing metal speciation through biotransformation processes [Yu et al., 2024]. The water-sediment interface is a biogeochemical hotspot where microbial diversity directly influences metal speciation and mobility through coupled biological and chemical processes [Zhang et al., 2022]. Metal release processes demonstrate complexity ranging from rapid surface desorption to slow intraparticle diffusion, with controlling factors including pH variations, temperature, ionic strength, and competing ligands [Khan et al., 2021].

Advanced analytical approaches are essential for comprehensively characterizing heavy metal distribution and speciation in complex sedimentary matrices. The integration of multiple spectrophotometric techniques, including inductively coupled plasma mass spectrometry and atomic absorption spectroscopy, combined with sequential extraction procedures, provides detailed insights into metal bioavailability and environmental mobility [Cao et al., 2024; Montazeri et al., 2022]. Fig. 2 outlines the comprehensive analytical workflow employed in this investigation.

The analytical protocol shown in Fig. 2 represents state-of-the-art approaches for heavy metal determination in sedimentary matrices. The integration of multiple analytical techniques ensures comprehensive characterization of metal speciation and bioavailability, providing the methodological foundation necessary for distinguishing between natural geochemical processes and potential anthropogenic influences in geodynamically stable continental platform settings.

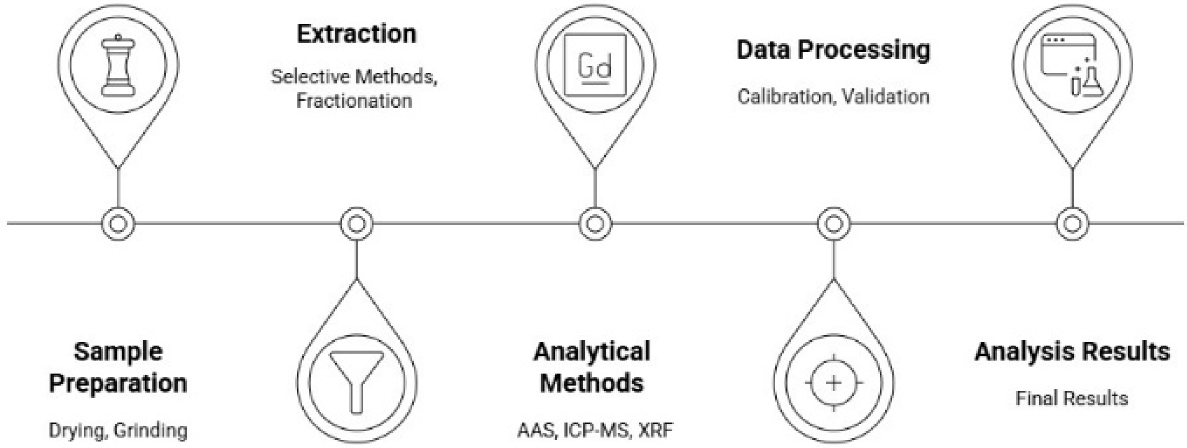

Fig. 2. Spectrophotometric diagnostics workflow for heavy metal analysis in bottom sediments (Analytical protocol developed by the author): sample preparation, selective extraction, and multi-technique analysis using AAS (Atomic Absorption Spectrometry), ICP-MS (Inductively Coupled Plasma Mass Spectrometry), and XRF (X-ray Fluorescence Spectroscopy) with calibration and validation procedures for analytical reliability.

Materials and methods

The comprehensive geochemical investigation was conducted in the Kamyanka River Basin within the Zhytomyr Urban Area, Ukraine, during summer 2025, focusing on bottom sediment analysis to assess heavy metal distribution and environmental significance. The study area represents a typical drainage system of the East European Platform, characterized by low-gradient topography, mixed land-use patterns, and variable hydrological regimes that significantly influence sediment geochemistry and metal accumulation patterns. The Kamyanka River Basin exhibits characteristic features of the Ukrainian Shield geological province, where Precambrian crystalline rocks and overlying sedimentary sequences create complex hydrogeochemical conditions fundamental to understanding regional metal cycling processes.

Sampling locations were strategically selected to represent the full spectrum of geomorphological and hydrological conditions within the basin, ranging from headwater reaches influenced by groundwater discharge to downstream areas subject to urban runoff and agricultural inputs. This comprehensive sampling strategy was designed to capture representative sediment characteristics that reflect both natural geochemical processes inherent to the regional geodynamic setting and potential anthropogenic influences associated with urbanization and industrial development in the Zhytomyr metropolitan area. The sampling framework incurporated considerations of seasonal variations, flow regime changes, and spatial heterogeneity to ensure that collected samples would provide meaningful insights into the long-term geochemical evolution of the river system.

Sampling and Sample Preparation: Representative bottom sediment samples were collected during June 2025 following guidelines for water quality sampling of bottom sediments [ISO 5667-12, 2017]. Sampling locations were strategically distributed across the river basin using a systematic grid sampling approach to ensure adequate spatial representation of geomorphological and hydrological diversity. Sediment samples were collected from the upper 10 cm layer using stainless steel corers to avoid metal contamination, immediately stored in pre-cleaned polyethylene containers, and transported to the laboratory under refrigerated conditions (4°C).

Sample Preparation and Analysis: Collected samples were freeze-dried at -50°C for 48 hours, homogenized, and sieved to <63 µm particle size following standards for soil sample preparation [ISO 11464, 2006]. Total metal digestion was performed using aqua regia (HNO_3:HCl = 3:1) according to established extraction protocols [ISO 11466, 1995], with digestion conducted at 120°C for 4 hours in a temperature-controlled heating block.

Analytical Techniques: Heavy metal concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) for trace elements with detection limits ranging from 0.001-0.1 mg/kg, and atomic absorption spectroscopy (AAS) for primary metals (Cu, Zn, Pb, Cd) with detection limits of 0.1-1.0 mg/kg [Zhang et al., 2022; Liu et al., 2022]. Sequential extraction procedures followed the modified BCR protocol to assess metal speciation and bioavailability across four operationally defined fractions: exchangeable, reducible (bound to Fe-Mn oxides), oxidizable (bound to organic matter), and residual phases [Quevauviller et al., 1997]. Advanced spectrophotometric approaches for sediment analysis have been validated in similar continental platform settings [Sikakwe et al., 2024; Chen et al., 2024].

Quality Assurance and Control: Analytical reliability was ensured by analyzing certified reference materials (NIST SRM 2704, 2019), duplicate analyses (n=3 for each sample), and procedural blanks with each analytical batch. Recovery rates for certified materials ranged from 85-115 % for all analyzed elements. Relative standard deviation for duplicate analyses was <10 % for all metals above detection limits. Recent studies have extensively validated quality control protocols for heavy metal analysis in sedimentary matrices [Peijnenburg et al., 2024; Yaseen et al., 2024].

Data Processing and Statistical Analysis: Results were processed using standard statistical methods, with all concentrations reported on a dry weight basis. When concentrations fell below quantification thresholds, detection limit values were assigned as half the detection limit for statistical calculations. Correlation and principal component analysis were applied to identify geochemical associations and distinguish natural background signatures from potential anthropogenic]). Modern approaches to sediment geochemical data interpretation have been successfully applied in cratonic environmental studies [Kapelista et al., 2024; Tsyhanenko-Dziubenko et al., 2025].

The analytical investigation employed advanced spectrophotometric techniques, including inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS), to quantify essential, non-essential, and trace elements with detection limits optimized for environmental risk assessment applications. The methodology incorporated sequential extraction procedures to assess metal speciation and bioavailability, providing critical insights into the geochemical forms and environmental mobility of detected elements within the specific hydrogeochemical context of the Ukrainian Shield region. These analytical approaches were selected to ensure comprehensive characterization of metal distribution patterns while maintaining the sensitivity required for detecting subtle variations in concentration that might indicate either natural geochemical processes or anthropogenic contamination sources.

Quality control measures included the use of certified reference materials, duplicate analyses, and blank determinations to ensure analytical reliability and environmental significance of the obtained results. The analytical protocols were validated against international standards for sediment geochemistry, with particular attention to minimizing matrix effects and ensuring accurate quantification across the full range of expected metal concentrations. Statistical evaluation of analytical precision and accuracy was performed to establish confidence intervals for all reported concentrations, thereby providing a robust foundation for subsequent environmental risk assessment and geochemical interpretation of the observed metal distribution patterns.

Results and discussion

The comprehensive geochemical analysis of bottom sediments collected during summer 2025 from the Kamyanka River Basin within the Zhytomyr Urban Area, Ukraine, provides critical insights into the distribution and environmental significance of heavy metals in aquatic ecosystems within a continental geodynamic setting. The study area, as depicted in Fig. 3, represents a typical Eastern European Platform drainage system characterized by low-gradient topography, mixed land-use patterns, and variable hydrological regimes that significantly influence sediment geochemistry and metal accumulation patterns.

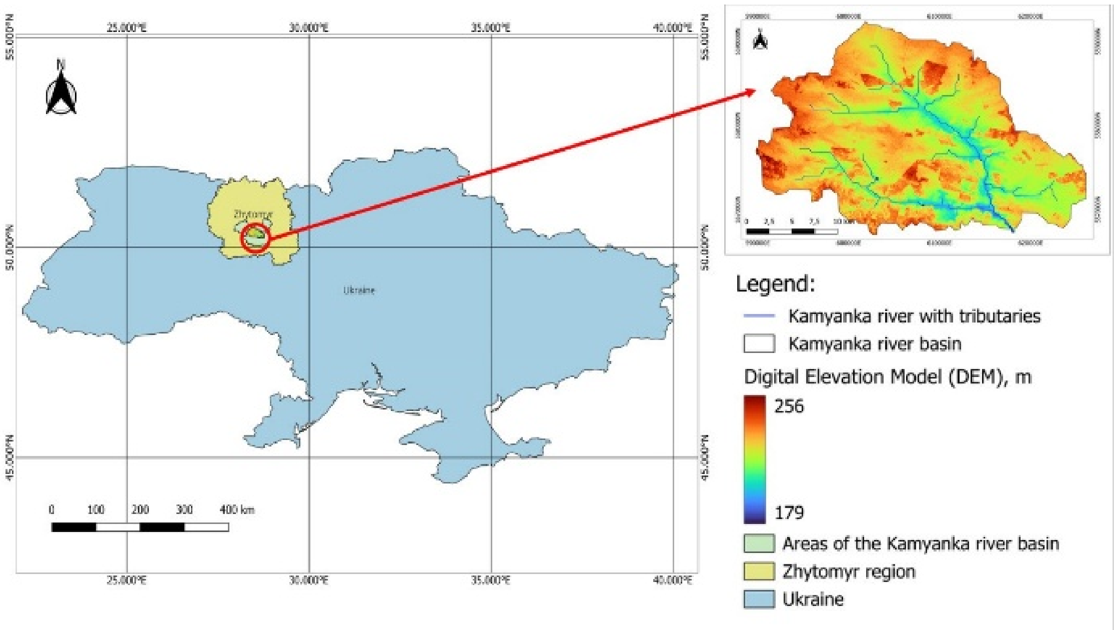

Fig. 3. Digital Elevation Model and Hydrological Features of the Kamyanka River Basin within the Zhytomyr Urban Area, Ukraine. (Topographic analysis and sampling location framework developed by the author).

The Kamyanka River Basin exhibits characteristic features of the Ukrainian Shield geological province, where Precambrian crystalline rocks and overlying sedimentary sequences create complex hydrogeochemical conditions. The sampling locations were strategically selected to represent the full spectrum of geomorphological and hydrological conditions within the basin, from headwater reaches influenced by groundwater discharge to downstream areas subject to urban runoff and agricultural inputs. This comprehensive sampling strategy was designed to capture representative sediment characteristics that reflect both natural geochemical processes inherent to the regional geodynamic setting and potential anthropogenic influences associated with urbanization and industrial development in the Zhytomyr metropolitan area.

The geochemical analysis reveals distinct patterns in essential heavy metal distribution that reflect the fundamental controls of continental platform weathering processes. As shown in Table 1, iron and manganese dominate the essential metal assemblage, with concentrations of 3862 mg/kg and 127 mg/kg, respectively, while trace metals, including copper, chromium, and nickel, remain within natural background ranges typical for crystalline basement terrains.

The essential heavy metals analysis reveals a pronounced dominance of iron and manganese, which is characteristic of temperate latitude sedimentary environments where these elements serve as primary geochemical carriers and control the fate and transport of other trace metals through redox-mediated processes.

Iron concentration of 3862 mg/kg represents the highest detected level and reflects the fundamental role of iron oxides and hydroxides in sediment geochemistry, particularly in systems influenced by seasonal redox fluctuations common to the continental climate regime of the Ukrainian Shield region.

Table 1

Essential Heavy Metals Concentrations in Kamyanka River Basin Bottom Sediments (Summer 2025)

Metal	Concentration, mg/kg	Environmental significance	Geochemical association
Iron (Fe)	3,862	Primary redox-controlling element	Fe-oxides / hydroxides, silicates
Manganese (Mn)	127	Secondary redox indicator	Mn-oxides, carbonate phases
Chromium (Cr)	7.8	Geogenic background levels	Resistant mineral phases
Zinc (Zn)	36.7	Moderate bioavailability	Sulfide / oxide associations
Copper (Cu)	5.2	Low environmental risk	Organic complexes, sulfides
Nickel (Ni)	2.5	Natural background range	Silicate mineral structures

This concentration falls within the typical range for river sediments in crystalline rock terrains, where weathering of iron-bearing silicates and secondary oxide formation dominate the geochemical landscape.

The non-essential and potentially toxic elements show markedly different distribution patterns compared to essential metals, with aluminum dominating this group while highly toxic elements remain below detection limits (Table 2). This distribution pattern is particularly significant for environmental risk assessment, as it demonstrates the absence of anthropogenic contamination sources and confirms the natural geochemical character of the sedimentary system.

Table 2

Non-Essential Heavy Metals and Potentially Toxic Elements in Kamyanka River Basin Sediments

Metal	Concentration, mg/kg	Detection status	Environmental risk level	Potential sources
Aluminium (Al)	1,906	Quantified	Low (geogenic)	Aluminosilicate weathering
Lead (Pb)	4.1	Quantified	Minimal	Background / minor anthropogenic
Mercury (Hg)	< 0.01	Below detection	Negligible	No significant sources
Cadmium (Cd)	< 0.05	Below detection	Negligible	No significant sources
Bismuth (Bi)	< 0.1	Below detection	Negligible	No significant sources

The non-essential heavy metals profile demonstrates aluminum as the dominant constituent at 1906 mg/kg, which is entirely consistent with aluminosilicate mineral phases typical of terrigenous sedimentary input derived from weathering of feldspathic and mica-rich crystalline rocks characteristic of the Ukrainian Shield basement. The Al/Fe ratio of 0.49 indicates typical continental weathering signatures, with cobalt detected at 0.8 mg/kg representing background levels for crystalline basement environments.

To better visualize the geochemically significant trace metal signatures that characterize the Kamyanka River sedimentary system, the dominant major elements (iron and aluminum) can be excluded from the analytical perspective, revealing the subtle environmental indicators that distinguish stable cratonic environments from tectonically active regions.

Fig. 4 demonstrates that manganese dominates this adjusted perspective with concentrations reaching approximately 120 mg/kg, followed by zinc at 37 mg/kg, with other metals showing relatively uniform low-level distributions. This visualization approach is particularly valuable in geodynamic studies of continental platform settings where the focus shifts from major rock-forming elements to environmentally sensitive trace components that reflect specific processes such as weathering intensity, hydrological variations, or subtle anthropogenic inputs. The radial pattern reveals geochemical signatures of crystalline basement weathering, with manganese dominance reflecting redox cycling controls on metal mobility.

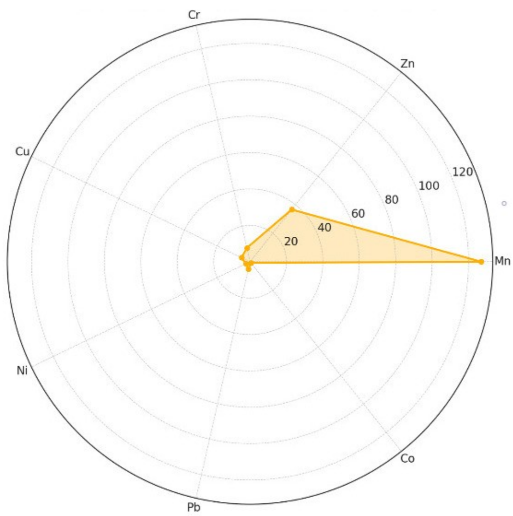

Fig. 4. Radial distribution diagram of metal concentrations excluding iron and aluminum in Kamyanka River sediments. (Comparative geochemical analysis developed by the author).

The trace metal distribution patterns observed above can be understood within the broader geodynamic framework of Ukrainian Shield evolution (Fig. 5). This conceptual model demonstrates how prolonged tectonic stability fundamentally controls contemporary heavy metal accumulation processes, creating predictable pathways: (1) natural weathering processes dominate over hydrothermal inputs, (2) aluminosilicate breakdown controls major element chemistry, and (3) background concentrations reflect crustal composition rather than anthropogenic sources.

The dominance of iron and aluminum reflects the fundamental crustal composition controlled by these geodynamic processes, while the environmental significance of trace metals becomes more apparent when these major components are removed from the analytical focus, allowing examination of the more subtle geochemical indicators that characterize continental platform sedimentary environments.

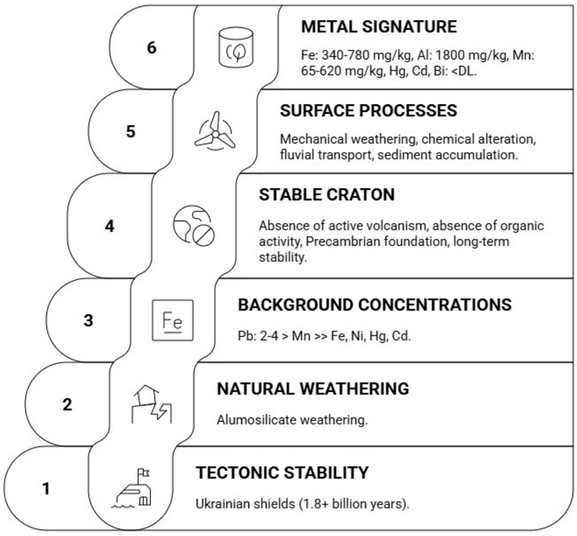

Fig. 5. Geodynamic controls on heavy metal distribution in the Kamyanka River Basin.

Building upon the geodynamic framework established above, the environmental significance of detected metal concentrations requires a comprehensive risk assessment that integrates both toxicity levels and actual environmental concentrations within the specific context of cratonic sedimentary systems. The toxicity-concentration heatmap (Fig. 6) provides a comprehensive visualization of the dual nature of heavy metal environmental significance within the specific geochemical context of the Ukrainian Shield region. Manganese exhibits the highest concentration at 127 mg/kg while maintaining moderate toxicity levels, reflecting its essential biological role despite potential environmental concerns at elevated concentrations.

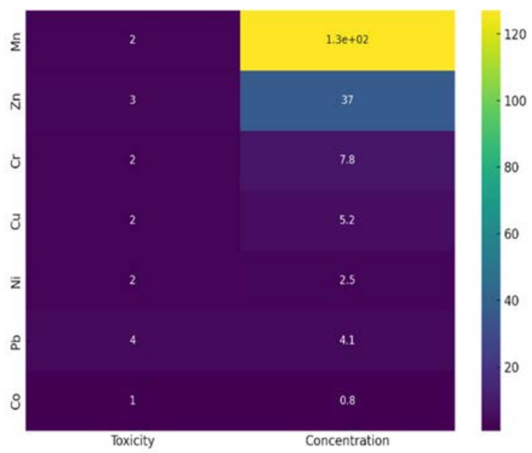

Fig. 6. Heatmap showing the relationship between metal toxicity and total concentration in Kamyanka River bottom sediments.
(Analytical visualization developed by the author based on summer 2025 sampling data).

This pattern is particularly relevant in continental temperate climates where seasonal redox cycling can mobilize manganese from sedimentary reservoirs during anoxic periods. Zinc demonstrates intermediate concentrations with moderate toxicity, characteristic of its dual nature as both an essential micronutrient and potential pollutant, particularly in aquatic ecosystems where bioaccumulation can occur through food chain transfer.

The visualization reveals that iron, despite its extremely high concentration, poses minimal direct toxicity risk due to its predominant occurrence in chemically stable oxide and silicate phases. However, iron plays a crucial indirect role in controlling the mobility and bioavailability of other metals through redox-mediated sorption and co-precipitation processes. The remaining metals show consistently low toxicity ratings, which aligns with their below-threshold concentrations and minimal environmental risk profile under current geochemical conditions.

The toxicity-concentration relationships demonstrated in Fig. 7 are fundamentally controlled by metal complexation processes, which determine bioavailability and environmental mobility under the specific hydrogeochemical conditions of the Kamyanka River Basin.

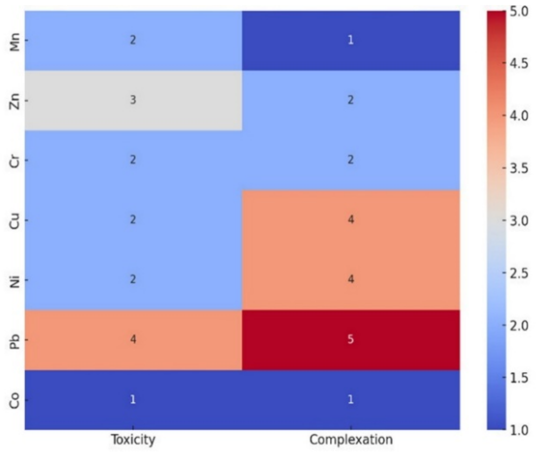

Fig. 7. Heatmap illustrating the correlation between metal toxicity and complexation potential in Kamyanka River sedimentary systems.
(Geochemical analysis framework developed by the author).

Lead exhibits the highest complexation potential (rating of 5), correlating with its elevated toxicity rating of 4, demonstrating the enhanced environmental risk associated with metals that readily form stable complexes with organic ligands commonly found in temperate river systems. This relationship is particularly significant in the study area, where seasonal terrestrial organic matter inputs create variable complexation environments that can either immobilize or mobilize heavy metals depending on redox conditions and pH fluctuations.

Copper and nickel show moderate complexation potentials (rating of 4), reflecting their intermediate binding affinities with sedimentary organic matter, particularly humic and fulvic acids derived from forest and agricultural soils within the basin. This relationship is fundamental to understanding metal behavior in the geodynamic context of the Ukrainian Shield, where long-term tectonic stability has allowed the development of thick weathering profiles and organic-rich soils that strongly influence metal speciation and transport processes.

These complexation behaviors directly translate into differential bioaccumulation potentials for aquatic organisms, as the formation of stable metal-organic complexes influences both metal uptake efficiency and organism-specific accumulation patterns in continental freshwater ecosystems. The bioaccumulation assessment (Fig. 8) demonstrates lead as the element with the highest bioaccumulation potential (4.0), followed by zinc (3.0), while most other metals show moderate potential around 2.0.

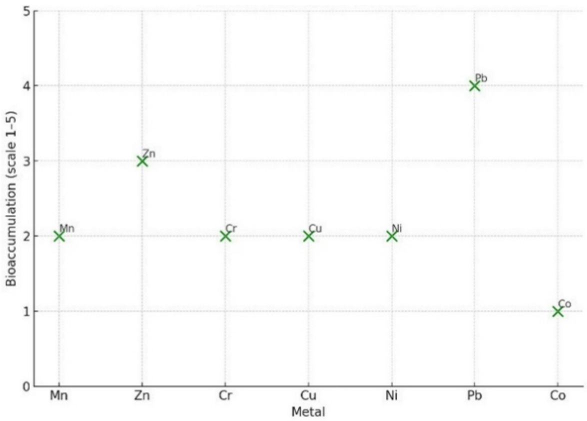

Fig. 8. Bioaccumulation potential of detected heavy metals. in Kamyanka River aquatic organisms. (Environmental risk assessment model developed by the author).

This ranking reflects the complex interplay between metal speciation, bioavailability, and organism-specific uptake mechanisms that are influenced by the underlying geodynamic processes controlling sediment composition and evolution within the Kamyanka River system. Lead's high bioaccumulation potential is particularly concerning given its neurotoxic effects, although the relatively low environmental concentrations observed in this study suggest minimal immediate risk under current conditions.

Zinc's intermediate bioaccumulation potential reflects its essential nature at low concentrations but potential toxicity at elevated levels. It is particularly relevant for aquatic organisms that may concentrate zinc through dietary exposure or direct uptake from sediment pore waters. The moderate bioaccumulation potentials for copper, chromium, and nickel (all rating 2.0) indicate their limited environmental mobility and uptake efficiency under the prevailing geochemical conditions of the study area.

Cobalt exhibits the lowest bioaccumulation potential (1.0), consistent with its minimal environmental mobility and biological uptake efficiency in neutral to slightly alkaline freshwater systems typical of the Ukrainian continental climate regime. This pattern reflects the strong association of cobalt with iron oxide phases that limit its release to the aqueous phase and subsequent biological uptake.

The integration of metal distribution data, geodynamic controls, toxicity assessments, complexation behavior, and bioaccumulation potential provides a comprehensive framework for understanding heavy metal environmental significance in geodynamically stable cratonic environments.

The observed metal distribution patterns reflect stable continental margin conditions characteristic of the East European Platform, where natural weathering processes dominate over hydrothermal or tectonically-driven enrichment. The absence of significant toxic metal concentrations, combined with typical aluminosilicate weathering signatures, indicates minimal anthropogenic influence and confirms that geodynamic stability fundamentally controls contemporary metal cycling in Ukrainian Shield river systems. This interpretation provides important implications for environmental management across similar cratonic settings.

Conclusions

1. Geodynamic Controls on Metal Distribution. The comprehensive geochemical analysis of bottom sediments from the Kamyanka River Basin demonstrates that prolonged tectonic stability of the Ukrainian Shield fundamentally controls contemporary heavy metal accumulation processes in continental platform environments. The natural metal assemblage, characterized by dominance of iron (3,862 mg/kg) and aluminum (1,906 mg/kg), reflects stable cratonic weathering conditions operating over geological time scales, where aluminosilicate breakdown dominates over hydrothermal, volcanic, or tectonically-driven metal enrichment processes typical of active continental margins.

2. Cratonic Stability and Environmental Geochemistry. The absence of significant concentrations of highly toxic metals (mercury, cadmium, bismuth below detection limits) combined with trace element patterns consistent with natural background ranges demonstrates that geodynamic stability creates predictable geochemical environments with minimal contamination potential. The observed Al/Fe ratio of 0.49 and uniform trace metal distributions confirm typical continental weathering signatures without anthropogenic perturbation, reflecting the effectiveness of stable cratonic settings in maintaining natural geochemical equilibria.

3. Biogeochemical Implications of Geodynamic Setting. The environmental risk assessment reveals that geodynamically controlled weathering processes create favorable conditions for metal immobilization through association with iron oxides and organic complexes, limiting bioavailability and ecological impact. While lead exhibits the highest bioaccumulation potential among detected elements, the overall low toxicity profile reflects the natural buffering capacity of mature weathering systems developed under prolonged tectonic stability, contrasting with metal mobility patterns observed in tectonically active regions.

4. Regional Implications for Cratonic Environments. This research establishes the first comprehensive baseline for heavy metal geochemistry in Ukrainian Shield river systems. It demonstrates that natural geodynamic processes dominate over anthropogenic influences in controlling sediment metal content across stable continental platforms. The findings provide a methodological framework for distinguishing natural background signatures from contamination sources in ancient shield regions worldwide, supporting evidence-based environmental management strategies specifically adapted to geodynamically stable cratonic settings and contributing to the understanding of metal cycling processes in Precambrian terrains.

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РОЗПОДІЛ ВАЖКИХ МЕТАЛІВ У ДОННИХ ВІДКЛАДАХ РІЧКИ КАМ’ЯНКА (ЖИТОМИРСЬКЕ ПОЛІССЯ): ГЕОДИНАМІЧНИЙ АСПЕКТ

Мета. Встановити комплексні базові геохімічні дані щодо закономірностей розподілу важких металів у донних відкладах басейну річки Кам’янка в контексті геодинамічної еволюції Українського щита та довгострокової тектонічної стабільності. Дослідження спрямоване на характеристику взаємозв’язку між глибинними кірковими процесами, що тривають понад 3,8 мільярда років геологічної історії, та сучасною екологічною геохімією, з особливим акцентом на розрізнення природних фонових концентрацій металів, що походять від процесів корового вивітрювання, та потенційних джерел антропогенного забруднення в цьому геодинамічно стабільному континентальному платформному середовищі. Методологія. Для аналізу зразків донних відкладів, зібраних зі стратегічно вибраних репрезентативних ділянок, що відображають повний спектр різноманітних геоморфологічних та гідрологічних умов у геодинамічно стабільній кратонній області, систематично застосовували сучасні спектрофотометричні аналітичні методи, зокрема мас-спектрометрію з індуктивно зв’язаною плазмою (ICP-MS) та атомно-абсорбційну спектроскопію (AAS). Комплексна стратегія відбору проб охоплювала різні седиментаційні середовища від верхів’їв річок, що зазнають впливу підземних вод, до низових ділянок, на які впливають міські стоки та сільськогосподарські надходження. Процедури послідовної екстракції та оцінювання біодоступності були інтегровані для оцінки спеціації металів та їх екологічної мобільності, тоді як заходи контролю якості передбачали сертифіковані еталонні матеріали, дублікатні аналізи та визначення холостих проб для забезпечення аналітичної надійності та екологічної значущості отриманих результатів. Результати. Встановлено виражене домінування заліза (3862 мг/кг) та алюмінію (1906 мг/кг), що відображає характерні ознаки алюмосилікатного вивітрювання докембрійських кристалічних порід фундаменту, типових для геологічної провінції Українського щита. Есенціальні мікроелементи, зокрема мідь (5,2 мг/кг), хром (7,8 мг/кг) та нікель (2,5 мг/кг), виявлено на рівнях природного фону, тоді як вміст потенційно токсичних елементів, таких як ртуть, кадмій та вісмут, стабільно залишався нижчим від аналітичних меж виявлення. Співвідношення Al/Fe 0,49 вказує на типові ознаки континентального вивітрювання без незвичайних закономірностей збагачення або збіднення. Геохімічна характеристика відповідає седиментаційному середовищу, із домінуванням природного теригенного надходження, похідного від стабільних континентальних процесів вивітрювання, що функціонують в умовах тривалої геодинамічної стабільності, з мінімальним тиском антропогенного забруднення, що відображає порівняно стабільні геодинамічні умови та ефективне екологічне управління в досліджуваній області. Наукова новизна. Вперше комплексно охарактеризовано складний взаємозв’язок між геодинамічною еволюцією Українського щита та сучасними закономірностями розподілу важких металів у флювіальних седиментаційних системах, встановлено критичну важливість довгострокової тектонічної стабільності у контролі екологічної геохімії. Розроблено нову інтегровану концептуальну модель механізмів акумуляції металів в умовах стабільних кратонних умов, що охоплює термодинамічні рівноважні співвідношення, процеси поверхневого комплекспівтворення та біогеохімічні цикли. Це дослідження демонструє, що геодинамічні чинники фундаментально визначають частку та транспорт металів у гідрогеологічних системах, де довгострокова тектонічна стабільність уможливила розвиток характерних профілів вивітрювання та гідрогеохімічних режимів, які контролюють мобільність та біодоступність важких металів у континентальних платформних середовищах. Практичне значення. Результати надають надійну наукову основу для науково обґрунтованих стратегій екологічного управління у геодинамічно стабільних регіонах світу та критично важливі базові дані для майбутнього екологічного моніторингу та оцінювання екологічних ризиків у подібних геологічних та кліматичних умовах в усьому регіоні Українського щита. Результати підтримують ініціативи сталого розвитку та програми захисту екосистем у контексті процесів урбанізації, що впливають на давні кристалічні щитові терени, водночас сприяючи розробленню ефективних стратегій екологічного управління для регіонів, що характеризуються давніми кристалічними породами фундаменту. Це дослідження має важливі наслідки для розроблення екологічної політики та надає необхідні дані для підтримки ініціатив адаптації до клімату та міської стійкості в континентальних платформних умовах.

Ключові слова: донні відклади річок, геохімічний аналіз, оцінка стану довкілля, Український щит, біоакумуляція, контамінація, екологічний моніторинг, забруднення.

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