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Geochemical evaluation of trace metals and rare-earth elements in soils and sediments from a legacy copper mining site in Kongo Central, Democratic Republic of the Congo

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Abstract

This study assessed trace metals, metalloids, and rare earth elements (REEs) in soils and sediments around an abandoned artisanal copper mine in Madimba Territory, Kongo Central Province (DR Congo). Trace metals and REEs in soils and sediments were quantified following complete acid digestion and analysis by ICP-MS, using collision-cell technology to minimize spectral interferences. Total mercury was determined independently using a DMA-80 direct analyzer, which measures Hg via thermal decomposition, catalytic reduction, gold amalgamation, and CV-AAS detection without chemical digestion. The Enrichment Factor (EF), Geoaccumulation Index (Igeo), and Potential Ecological Risk Index (RI) were used to evaluate contamination levels and ecological risks. The EF and Igeo results highlighted anthropogenic inputs, explicitly confirming that historical mining activities were the main source of Cu, Pb, As, and Hg contamination. Sediments showed high concentrations of Cu (591.75 mg kg⁻¹ dw), Pb (179.54 mg kg⁻¹ dw), As (8.57 mg kg⁻¹ dw), and Hg (0.36 mg kg⁻¹ dw), largely exceeding international guidelines on sediment quality. Furthermore, the EF and Igeo values indicated extreme enrichment and strong pollution from anthropogenic sources mainly linked to historical mining activities. The total ecological risk (RI = 287.8–2655.7) classified the area as from considerable to very high ecological risk, with Hg and Cu as the main contributors to environmental contamination. The sum of REEs (4.08–72.92 mg kg⁻¹ dw) showed minor enrichment but displayed distinct Ce, Eu, and Gd anomalies. Negative Ce–Eu anomalies reflected redox-controlled fractionation, whereas positive Gd anomalies suggested interactions with organic matter, promoting metal co-mobility and sediment accumulation. The Principal Component Analysis (PCA) was applied to integrate physicochemical parameters, trace metals, and REEs. The first two principal components explained 73.1% of the total variance. PC1 correlated strongly with mining-related metals (Cu, Pb, Zn, Co) and ΣREE, highlighting anthropogenic contamination and ore-derived enrichment. PC2 was associated with organic matter, CaCO₃, and sediment texture, reflecting geochemical controls of soil and sediment



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composition. PCA effectively distinguished contaminated sites from less-impacted areas and elucidated relationships between REEs, heavy metals, and sediment properties. Overall, Cu, Pb, As, and Hg emerged as the key pollutants of concern, posing significant ecological threats. The results underscore the urgent need for remediation and long-term environmental monitoring to protect local ecosystems and communities.

Keywords Abandoned mining site, Trace metals, REEs, Ecological risk, REE anomalies, Principal component analysis

1 Introduction

Mining activities, including exploration, extraction, and post-closure phases, are well-known sources of long-term environmental degradation. They particularly affect soils and sediments, which act as sinks for trace metals, metalloids, and other contaminants released during ore processing and mining waste disposal. Accumulation of metals in soils and sediments can result in persistent ecological risks, including toxicity to terrestrial and aquatic organisms, disruption of biogeochemical cycles, and potential transfer of contaminants through the food chain [1–3]. The extent of contamination depends on mineralogy, ore processing methods, waste management practices, and local environmental conditions. Historically, artisanal and early industrial mining in many African regions occurred with minimal environmental oversight, leading to widespread pollution in soils, sediments, and surface waters [4–7].

In the Democratic Republic of the Congo (DRC), mining regions such as Lubumbashi and Kolwezi have been extensively studied for metal contamination [4, 5, 8]. Soils and sediments in these areas frequently exhibit elevated concentrations of Cr, Cu, Pb, Zn, and As, with riverbed sediments often exceeding Sediment Quality Guidelines for the protection of aquatic life. For example, in such areas Cu level in riverbed sediments reached 2768 mg.kg⁻¹ [8], reflecting strong contributions from ore extraction, tailings, and smelting residues. Enrichments of rare earth elements (REEs) have also been observed in sediments near mine wastes [4], although they are commonly less assessed than heavy metals. These contaminants pose ecological and human health hazards through chronic exposure pathways, such as ingestion and inhalation of soil dust, dermal contact, and consumption of locally grown crops.

Copper-bearing ores, such as sulfides, oxides and carbonates, are prone to oxidation upon exposure to air and water. Oxidation of sulfide minerals generates acid mine drainage (AMD), which mobilizes metals and metalloids in surrounding soils and sediments. Sulfuric acid formed during AMD increases metal solubility, often leading to concentrations in soils and sediments that exceed environmental safety thresholds [9–11]. Sediments, due to their adsorption capacity and role in biogeochemical cycling, often retain elevated levels of metals, serving as indicators of historical mining contamination.

In assessment of contamination the commonly used indices, such as enrichment factor (EF) and geoaccumulation index (Igeo), compare measured metal concentrations to background values in order to evaluate contamination levels [4]. However, in copper-rich lithologies or mineralised terrains, natural trace metal concentrations can be significantly higher than in unmineralised soils, potentially leading to overestimation of anthropogenic enrichment if background values are not carefully selected [5]. For example, soils developed on Cu-sulfide-bearing rocks may naturally exhibit high Cu, Zn, or

Pb concentrations, influencing EF and Igeo calculations. This index sensitivity highlights the need for site-specific reference values derived from local geochemical baselines rather than generic crustal averages, allowing for more accurate discrimination between natural lithogenic enrichment and mining-related contamination [12].

Rare earth elements, including the lanthanides plus yttrium and scandium, provide valuable insights into geochemical processes in soils and sediments. The REE distribution patterns, fractionation between light and heavy REEs (LREE/HREE), and specific anomalies (Ce, Eu, Gd) can distinguish natural lithogenic signatures from anthropogenic inputs and reflect redox conditions, mineral weathering, and sediment deposition processes [13, 14]. Unlike metals such as Cu, Pb, or Hg, the REEs are relatively conservative, and their anomalies can reveal subtle geochemical changes resulting from mining activities and organic matter interactions.

The abandoned copper mine at Mbamba Kilenda, Madimba Territory, is located near human settlements and surface waters, soils and river sediments are the support to local agriculture and water supply for human consumption. Therefore, the understanding of contamination status of soils and sediments is crucial for evaluating ecological and human health hazards and guiding remediation efforts. While water analyses can provide supporting information on the physicochemical environment and potential mobility of dissolved metals, soils and sediments serve as primary reservoirs and archives of past contamination events.

This study aimed at providing a geochemical assessment of soils and sediments around the abandoned copper mine at Mbamba Kilenda. Furthermore, through integrating REE analysis with conventional heavy metal assessment this study aimed also at providing a more comprehensive evaluation of legacy mining impacts on soils and sediments in Kongo Central Province, DRC, capable to support environmental management actions with evidence-based recommendations. The key objectives were set as: (1) Identify and compare trace metals enrichment relative to natural background levels in soils and sediments, (2) Evaluate environmental contamination and ecological risks using EF, Igeo, and RI indices to determine whether they indicate consistent dominant factors, (3) Investigate REE patterns and anomalies (Ce, Eu, Gd) to discern natural versus anthropogenic influences. These objectives address the overarching questions of which metals pose the greatest enrichment risk, whether contamination indices align, and whether REE signatures are an helpful diagnostic of mining impacts.

2 Materials and methods

2.1 Description of the study area and sampling procedure

This research was conducted in the Kongo Central Province (formerly Lukaya District), in the Democratic Republic of the Congo, Central Africa (Fig. 1). In this province, the subsoil is rich in the so-called “documented and known” mineral resources, which have already been the subject of thorough techno-economic studies and are only awaiting capital investment to be developed. This is the case for the polymetallic copper-family ore deposits located by the village of Mbamba Kilenda, in the Territory of Madimba. This village is at 60 km distance from Kinshasa [15] and the site’s geographical coordinates are : 15°30′ East longitude and 4°56′ South latitude (Table 1).

The Mbamba Kilenda ore deposits (Fig. 2) were exploited during the colonial era through artisanal mining operations that ended in the 1960s, when the DR Congo

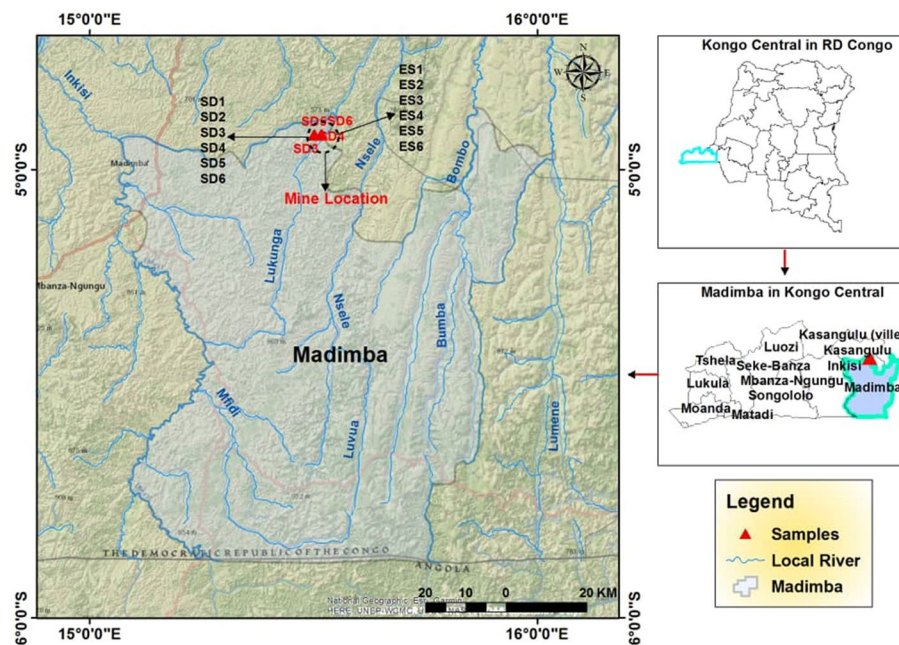


Fig. 1 Geographical location of Madimba in Kongo-Central province including sampling stations

independence was achieved. In 2013, the company KWANGO Mines SARL, which holds three Exploration Permits for these deposits, signed an option agreement with private investors, leading to the creation of a new mining company, the « Compagnie Minière de Mbamba Kilenda », abbreviated as CMMK SARL, for the economic development of these deposits. However, mining operations have not re started yet (Fig. 3).

Since the years of the artisanal mining at Mbamba Kilenda, the polymetallic ore deposit has been partially exposed to weathering such as the uncovered legacy mining waste piles around the site. The mine site bears a water source initiating a creek. The Lukunga River and several creeks flow across the area and receive surface runoff from the mine site, which is particularly abundant during the rainy season because of the heavy rainfall (1273.9 mm per year). Local communities use the groundwater from a borehole and surface water from rivers as drinking water and grow their foods in the agricultural areas nearby.

Sampling of sediments, soils, and water was conducted in May 2024, at the end of the rainy season, along the Masungu 1 and 2 streams and the Lukunga River (Fig. 1).

A total of six sediment samples from rivers, labelled from SD1 through to SD6, and six soil samples, labelled from ES1 through to ES6, were collected in the area. Seven water samples labelled from W1 through to W7 were collected also in rivers and boreholes (Table 1).

At each sampling site, 250 to 300 g of surface soil or sediment from the top layer (0–3 cm depth) were collected using a plastic shovel and stored in plastic sampling bags duly identified. Riverbed sediment samples were taken at 3 to 5 m from the shoreline. Water samples were collected directly into 75 mL plastic bottles at a depth of approximately one meter below the water surface and at a distance of 3 to 5 m from the shore in the streams. A groundwater sample was collected from the borehole. All samples were stored at 4 °C for preservation and transported to the analytical platform laboratories of the University of Geneva for analyses.

Table 1 Identification and description of soil (ES), sediment (SD) and water (W) samples collected at the Mbamba Kilenda area

N°	Sample ID	Geographic Coordinates	Site description and human activities nearby
1	ES1	X : 04°55'27" Y : 015°30'5"	Abandoned pit from the Belgian colonial era, fenced off in 2014, located within a palm plantation.
2	ES2	X : 04°55'25" Y : 015°30'6"	Cassava field and palm tree plantation.
3	ES3	X : 04°55'25" Y : 015°30'2"	Cassava, lemon tree, palm tree, mango tree plantation.
4	ES4	X : 04°55'27" Y : 015°30'58"	Three exploration pits from the Belgian colonial era cassava field and palm trees.
5	ES5	X : 04°55'21" Y : 015°31'7"	Cassava plantation.
6	ES6	X : 04°55'19" Y : 015°30'57"	Cassava plantation.
7	SD1	X : 04°55'24" Y : 015°30'6"	Downstream of the Masungu stream. Reddish water because of dissolved metal salts.
8	SD2	X : 04°55'24" Y : 015°30'4"	Upstream of the Masungu stream branch 2. Reddish water because of dissolved metal salts.
9	SD3	X : 04°55'27" Y : 015°30'2"	Upstream of Masungu stream branch 1. Reddish water because of dissolved metal salts. Banana tree, palm tree, cassava plantation.
10	SD4	X : 04°55'21" Y : 015°30'5"	Around a slab closing a former ventilation pit, where water is gushing out.
11	SD5	X : 04°55'25" Y : 015°30'10"	Lukunga river, by the bridge crossing to Kasangulu sector. Blackish river water due to decaying organic matter.
12	SD6	X : 04°55'21" Y : 015°31'8"	Downstream of the basin formed by the water from a borehole drilled in the Belgian colonial era and used as a bathing site. Cassava plantation, and cassava soaking and washing.
13	W1	X : 04°55'27" Y : 015°30'5"	Water gushing from a recent exploration pit : reddish water.
14	W2	X : 04°55'24" Y : 015°30'6"	Masungu stream : reddish water because of dissolved metal salts.
15	W3	X : 04°55'27" Y : 015°30'2"	Upstream of Masungu stream branch 1 : reddish water : banana tree, palm tree, cassava plantation.
16	W4	X : 04°55'20" Y : 015°31'5"	Drinking water from a Belgian-era borehole gushing from a metal pipe : colorless with salty taste (hard water).
17	W5	X : 04°55'21" Y : 015°31'5"	Water gushing from under a slab closing a former ventilation pit. Water colorless.
18	W6	X : 04°55'21" Y : 015°31'8"	Water gushing from an exploitation pit near a footpath. Water colorless.
19	W7	X : 04°55'25" Y : 015°31'10"	Lukunga River by the bridge crossing to Kasangulu sector. Blackish river water due to decaying organic matter.

2.2 Determination of physicochemical parameters and concentrations of dissolved ions in water samples

The physicochemical characteristics of the water samples, such as temperature (T), hydrogen potential (pH), and electrical conductivity (EC), were measured directly in the field using a calibrated multi-parameter probe (Model 340i, WTW, Weilheim, Germany). The concentrations of dissolved ions including phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), and chloride (Cl^-) were analyzed by ion chromatography using a Dionex ICS-3000 system (Canada), following the protocol outlined in Graham et al. [16]. Dedicated chromatographic columns from Thermo Fisher Scientific were employed for determination of cations and anions.



Fig. 2 The abandoned mining sector at the village Mbamba Kilenda: **A** Mining gallery from the Belgian colonial era; **B** Recent artisanal exploitation of the site and **C** Masungu River (Photos by P. Kutakimina)

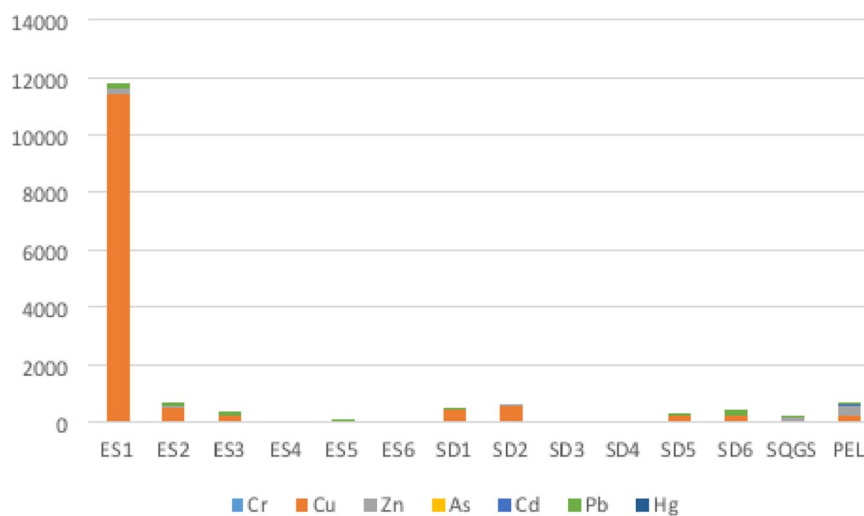


Fig. 3 Histogram comparing Cr, Cu, Zn, As, Cd, Pb and Hg concentrations in the samples with SQG and PEL values

As an analytical quality control, the certified reference material (CRM) for water Ontario-99 (Water Research Institute, Canada) was used. The measurements obtained for this CRM were within the range of certified values, confirming the precision and accuracy of the analytical method [17].

2.3 Determination of physicochemical characteristics of soil and sediment samples

The collected soil and sediment samples were homogenized, and aliquots were extracted as needed for subsequent analyses. The particle size distribution, comprising the mean diameter and the relative proportions of clay, silt, and sand was assessed using a Laser

Coulter® LS-100 particle size analyzer (Beckman Coulter, Fullerton, CA, USA), following the method outlined in Banze wa Mutombo et al. [5].

As per the classification criteria established by Blott and Pye [18], sediments with an average particle diameter below 2 µm are dominated by clay. Silt is predominant when grain sizes range between 2 and 63 µm, while sand is the major component when particles fall within the 63 µm to 2 mm range.

The contents of organic matter (OM) and calcium carbonate (CaCO₃) in the sediments were determined by measuring the weight loss of dry subsamples after combustion in a muffle furnace (Salvis AG, Lucerne, Switzerland) at 550 °C and 1000 °C for one hour, respectively, in accordance with the procedure described in Mabidi et al. [19].

2.4 Determination of trace metals and rare-earth elements in soil and sediment samples

Soil and sediment samples were freeze-dried, finely milled into a uniform powder, and sieved through a 2 mm mesh screen, following the methodology described in Poté et al. [20]. Total digestion of samples was conducted according to procedures modified from Thevenon et al. [21]. Briefly, 10 mg of the powdered sediment was fully digested using high-purity acids in Teflon vessels placed on a ceramic hotplate. The digestion in acids was performed in three successive steps : (i) addition of 1 mL of suprapur nitric acid (65%), (ii) a second step combining 0.5 mL of perchloric acid (70%) with 0.5 mL of hydrofluoric acid (40%), and (iii) a final step using 0.5 mL of nitric acid. Between each step, samples were heated to dryness. The dry residues were dissolved with 10 mL of 1% nitric acid before instrumental analysis.

Elemental quantification was performed via Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x), optimized for samples with complex matrices. A helium collision cell and correction equations were employed to reduce spectral interferences. Calibration curves were established using multi-element standard solutions at concentrations of 0, 0.02, 1, 5, 20, 100, and 200 µg L⁻¹.

The analytical accuracy was checked and validated using the certified reference material STSD-1 (Stream sediment) from the National Research Council, Canada. Results of the laboratory analysis for the CRM were within ± 10% of the certified concentrations. The results for metal concentrations in the CRM, compared to the certified values, indicated elemental recovery rates above 92.5% for all elements analyzed by triple quadrupole ICP-MS. The limit of detection was calculated as 3 times standard deviation of the blanks. Spike recoveries were performed on representative soil and sediment samples, with elemental recovery rates above 92.5%, demonstrating method reliability. The elements rhenium (Re) and rhodium (Rh) at the concentration of 50 ppb were used as internal standards (ISTD). The recovery values of ISDT were more than 98% for all analyzed. Results were expressed in mg kg⁻¹ on a dry weight basis. Analytical precision was high, with relative standard deviations for triplicate analyses below 2.5%, and blank values below 1% of the sample signal. Additional methodological details are provided in the Supplementary Information (SI).

2.5 Determination of total mercury in sediment samples

Total mercury (Hg) concentrations in soil and sediment samples were quantified using a Direct Mercury Analyzer (DMA 80-III, MWS GmbH), based on the cold vapor atomic absorption spectroscopy (CV-AAS) technique. The method involves sample combustion,

trapping of elemental mercury in a gold amalgamator, and subsequent detection via atomic absorption. The approach yielded excellent recovery, reaching 99%.

As an analytical quality control of mercury determinations, the certified reference material SRM 2702 (Inorganics in Marine Sediment) from the National Institute of Standards and Technology, USA, was analyzed alongside the samples, following the Feststoff Schnell protocol, which involves direct combustion at 750 °C without prior drying. The estimated relative uncertainty of measurement was around 4%. The detection limit of this method, calculated as the mean blank signal plus three standard deviations, was 0.003 µg g⁻¹. The reproducibility of the measurements was satisfactory, with variation among replicates below 5%. Mercury concentrations were reported in mg kg⁻¹ on a dry weight basis [22].

2.6 Assessment of soil and sediment contamination and associated ecological risk

To evaluate the extent of soil and sediment contamination, two widely used geochemical indices were applied the Enrichment Factor (EF) and the Geoaccumulation Index (Igeo) [23]. These indices were designed to distinguish natural geochemical background levels from anthropogenic contributions to trace metal concentrations.

The EF was calculated by normalizing each metal concentration to scandium (Sc) concentration. The EF was computed using the formula :

$$EF = \frac{(Metal/Sc)_{sample}}{(Metal/Sc)_{background}}$$

Sc was selected as the normalizing element because it is a conservative, lithogenic, and immobile element, largely unaffected by weathering processes, grain-size effects, or anthropogenic inputs. Its stable geochemical behavior makes it a reliable proxy for detrital material, allowing for a more accurate identification of true metal enrichments. This practice is consistent with numerous geochemical studies where Sc has been demonstrated to be an appropriate and robust normalizer.

Background concentrations for both trace metals and Sc were based on the average Upper Continental Crust (UCC) values as reported by McLennan [24]. UCC values are widely used when site-specific pristine background data are unavailable or when local lithological variability prevents establishing a consistent regional baseline. Using UCC ensures a standardized, globally recognized geochemical reference, facilitating meaningful comparisons with other contaminated or mining-impacted systems.

The contamination levels of soils and sediments were assessed using the Geoaccumulation Index (Igeo), defined as:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right)$$

where C_n is the observed concentration of the metal in the sample, B_n is the background value, and the factor 1.5 accounts for natural variability of elements in background levels [25].

The combined use of EF and Igeo provides a robust framework for assessing the degree of anthropogenic metal enrichment and evaluating associated ecological risks in the study area.

To evaluate contamination at the individual metal level, the Contamination Factor (CF) was calculated as: $CF = \frac{C_n}{B_n}$

with C_n representing the concentration of the metal in the sample and B_n the corresponding background concentration, following Rubio et al. [26] and Förstner et al. [27].

The cumulative level of metal contamination was represented by the Contamination Degree (CD), calculated as the sum of all CF values :

$$CD = \sum CF_i$$

The analysis focused on key potentially toxic metals including Hg, Cd, As, Co, Cu, Pb, Cr, and Zn [28].

To further characterize ecological threats posed by these metals, the Ecological Risk Index (Eri) was computed using :

$$Er_i = Tr_i \times CF_i$$

where Tr_i denotes the toxic-response factor (in parenthesis) for each element : Hg (40), Cd (30), As (10), Co (5), Cu (5), Pb (5), Cr (2), and Zn (1) [29, 30].

The overall ecological risk, combining all investigated metals, was estimated using the Potential Ecological Risk Index (RI), given by :

$$RI = \sum Er_i$$

This index integrates metal toxicity, concentration levels, and ecological vulnerability of the studied area [31].

Moreover, soil and sediment metal concentrations were compared against Canadian Sediment Quality Guidelines (SQGs) and Probable Effect Levels (PELs) to assess potential ecological impacts on aquatic life, following the CCME standards [32].

2.7 Determination of Ce, Eu and Gd anomalies

The anomalies of Ce, Eu, and Gd in the studied sediments were calculated following the standard approach based on North American Shale Composite (NASC)-normalized REE concentrations. These anomalies quantify deviations from the expected REE pattern, assuming a smooth, log-linear trend across neighboring elements [14, 33–35]:

The Ce, Eu and Tm anomalies were calculated using the following formulas [36, 37] :

$$\frac{Ce}{Ce^*} = \frac{Ce_N}{\sqrt{La_N \times Pr_N}} ; \frac{Eu}{Eu^*} = \frac{Eu_N}{\sqrt{Sm_N \times Gd_N}} ; \frac{Gd}{Gd^*} = \frac{Gd_N}{\sqrt{Sm_N \times Tb_N}}$$

where X_N represents the NASC-normalized concentration of element X.

The anomalies values are interpreted as follows: (1) $Ce/Ce^* = 1$ indicates no Ce anomaly; values < 1 or > 1 indicate negative or positive anomalies, respectively; (2) Eu/Eu^* and Gd/Gd^* are interpreted in the same way.

These calculations provide a quantitative assessment of local enrichments or depletions of specific REEs relative to the expected trend, which can be linked to mineralogical or redox controls in the sedimentary environment [13].

2.8 Statistical treatment of data

Heavy metal concentrations were determined in triplicate for each sample, and the results were averaged to enhance representativeness of results with better accuracy and reproducibility. Statistical analysis, including Spearman correlation, was conducted using the XLSTAT version 2021.1 (Addinsoft, New York, USA; <https://www.xlstat.com>, accessed on May 2025).

The Principal Component Analysis (PCA) was performed using Python (version 3.11) with the scikit-learn and matplotlib libraries). Before PCA, metal and REE concentrations were log₁₀-transformed to reduce skewness and limit the influence of highly enriched samples. The variables were then mean-centered and scaled to unit variance to ensure equal contribution to the multivariate structure. Non-detects were replaced by half of the detection limit (DL/2) prior to transformation. Although the data are compositional, the use of absolute concentrations (mg/kg) together with log-transformation and standardization sufficiently reduced closure effects, so no additional compositional treatment was applied. The standardized log-transformed dataset was subsequently used to generate the PCA outputs.

3 Results and discussion

3.1 Physico-chemical characteristics of water samples

Results for physico-chemical parameters measured in water samples (temperature, pH, electrical conductivity) are summarized in Table 2. These values were compared to the World Health Organization (WHO) drinking water quality guidelines [38].

Water temperature (T) values for all samples, with measurements ranging from 27.7 °C to 28 °C, exceeded the recommended WHO range of 12–25 °C for drinking water. These findings align with previous studies conducted in tropical environments. For instance, Ngandote et al. [20] reported values between 22.9 and 26.1 °C, Nienie et al. [39] found ranges of 24.5–25.6 °C during the rainy season and 24.7–29.2 °C during the dry season, while Kapembo et al. [40] observed values between 25.8 and 28.8 °C in the rainy season and 23.9–26.9 °C in the dry season.

Samples W1, W2, and W3 exhibited acidic pH levels ranging from 4.47 to 4.76, which fall below the WHO acceptable range of 6.5–9.5 for drinking water. Similar low pH values were reported by Ngandote et al. [17], with ranges of 4.43–5.1 in the dry season and 4.49–5.77 in the rainy season, and by Kapembo et al. [40], who observed pH values

Table 2 Mean values of physicochemical parameters and soluble ion concentrations in water samples

Sample	T° (°C)	pH	EC (μS cm ⁻¹)	Cl ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	PO ₄ ³⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	NO ₂ ⁻ (mg L ⁻¹)
W1	27.7	4.47	15.7	112.18	205.7	2.53	43.9	0.07
W2	27.9	4.67	26.4	112.18	205.7	4.90	59.75	0.03
W3	28	4.76	27.2	168.27	205.7	6.31	66.61	0.09
W4	28	6.20	197.1	168.27	205.7	5.92	46.92	0.02
W5	27.9	6.27	199.3	145.83	411.4	4.02	51.79	0.05
W6	27.8	6.49	201	168.27	411.4	6.71	89.91	0.09
W7	27.9	6.81	14.5	145.83	205.7	7.71	79.21	0.12
^a WHO	12–25	6.5–9.5	200–800	250	500	≤ 0.5	50	< 3

^aRecommended values according to WHO drinking water quality guidelines [40];

Note : Values that do not fall within the WHO guidelines limits are shown in bold

between 4.6 and 7.8 during the rainy season and 5.2–6.9 in the dry season across the Kinshasa metropolitan area. Several factors may contribute to the observed low pH values, such as the mineral composition of geological formation.

Electrical conductivity (EC) values ranged from 14.5 to 199.3 $\mu\text{S cm}^{-1}$, which are below the WHO recommended range for potable water (200–800 $\mu\text{S cm}^{-1}$), except for the sample W6 (201 $\mu\text{S cm}^{-1}$) suggesting a generally low mineralization of the water.

Concentrations of dissolved ions including Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , and NO_2^- are shown also in Table 2. Overall, most water samples met WHO guidelines for Cl^- , SO_4^{2-} , and NO_2^- . However, phosphate concentrations in all samples exceeded the WHO recommended threshold, with values ranging from 2.53 to 7.71 mg L^{-1} . Similarly, nitrate concentrations were generally above the WHO recommended limit of 50 mg L^{-1} , except for sample W1, which displayed a concentration of 43.9 mg L^{-1} .

The elevated levels of phosphate and nitrate in water were attributable to inputs from agricultural fertilizers rich in phosphorus and nitrogen, as well as to the breakdown of organic matter in the aquatic environment. In the groundwater sample collected from a borehole, the presence of phosphate may also suggest a geological source. Conversely, the low levels of nitrite observed in the samples can be explained by its rapid oxidation to nitrate under aerobic conditions, a process facilitated by nitrifying bacteria such as *Nitrobacter*.

3.2 Physico-chemical characteristics of soil and sediment samples

Table 3 summarizes the results for total organic matter content, calcium carbonate concentration, and mean particle grain size in soil and sediment samples.

The organic matter (OM) content of samples varied significantly across sampling points. In sediment samples, OM ranged from 3.01% to 28.88%, while in soil samples, values were lower, ranging from 2.45% to 6.83%. The relatively higher organic matter content in sediments was likely due to the natural accumulation of organic residues from vegetation in aquatic environments and slower degradation under anoxic conditions. In contrast, soil samples are more susceptible to oxidation, high microbial activity, and anthropogenic disturbance, all of which contribute to faster organic matter breakdown.

Calcium carbonate (CaCO_3) content showed only slight variation among samples. In sediments, values ranged from 1.10% to 3.76%, while in soils the CaCO_3 concentrations varied from 0.73% to 4.53%.

Table 3 Physico-chemical parameters of soil (ES) and sediment (SD) samples

Sample ID	OM (%)	CaCO_3 (%)	Clay (%)	Silt (%)	Sand (%)	Grain size (μm)
ES1	3.85	3.39	1.73	25.89	72.38	107.
ES2	6.25	4.53	3.32	54.15	42.53	31.32
ES3	3.18	1.44	2.46	25.74	71.8	86.01
ES4	2.45	0.73	3.51	19.63	76.86	102.6
ES5	6.83	2.92	4.52	50.02	45.46	32.36
ES6	3.93	1.16	2.28	17.68	80.04	119.3
SD1	13.14	3.28	2.3	50.31	47.39	44.56
SD2	28.88	3.7	2.81	69.26	27.93	25.78
SD3	4.92	1.1	1.33	18.81	79.86	129.9
SD4	6.62	2.79	5.05	53.05	41.9	29.08
SD5	6.49	3.76	3.22	39.66	57.12	51.47
SD6	3.01	1.33	1.7	26.23	72.07	86.82

The grain size distribution analysis revealed a dominance of sand in both sediment and soil samples. Sand content ranged from 27.93% to 79.86% in sediments and from 45.46% to 80.04% in soils. Silt content varied from 18.81% to 69.26% in sediments and from 17.68% to 54.15% in soils. Clay was present in lower proportions, with values ranging from 1.33% to 5.05% in sediments and from 1.73% to 4.52% in soils. According to the classification by **Blott and Pye [18]**, samples are considered sand-dominated when their mean grain size falls between 63 μm and 2 mm, whereas silt-dominated samples typically have grain sizes between 2 μm and 63 μm .

3.3 Concentration of heavy metals in soil and sediment samples

The results obtained for certified reference materials (CRMs), when compared with their certified values indicated good analytical accuracy in the determination of heavy metals and REEs. Recovery rates exceeded 94% for all elements analyzed using triple quadrupole ICP-MS in CRM STSD-1, and reached 99% for mercury (Hg) in CRM SRM 2702.

The concentrations of fourteen heavy metals measured in soil and sediment samples are summarized in Table 4. In general, the data showed minor variations in metal concentrations across the samples. For instance, the following concentration ranges (mg kg^{-1}) were recorded across sampling points (in parentheses): scandium (Sc) ranged from 0.09 (SD3) to 0.58 (ES5); titanium (Ti) from 0.49 (ES2) to 16.63 (ES6); vanadium (V) from 2.57 (SD3) to 25.55 (ES1); cobalt (Co) from 0.13 (ES4) to 60.35 (ES1); nickel (Ni) from 0.25 (SD5) to 18.61 (ES1); selenium (Se) from 0.02 (ES4) to 1.26 (ES2); and barium (Ba) from 0.89 (ES4) to 475.5 (ES1).

When compared to Sediment Quality Guidelines (SQGs) established for the protection of aquatic life, certain sediment samples exceeded the SQG threshold values. Elevated concentrations were noted for chromium (Cr) in sediment samples SD6; copper (Cu) in SD1, SD2, SD5 and SD6; arsenic (As) in SD1; lead (Pb) in SD5 and SD6; and mercury (Hg) in SD1 and SD2.

Sample ES1 generally exhibited the highest metal concentrations among all the sites. This location corresponds to an open pit historically exploited as a copper mine during the Belgian colonial period and officially closed in 2014 (Table 1; Fig. 2A). The metal concentrations observed at this site are consistent with those previously reported by Atibu et al. [8] and Banze wa Mutombo et al. [5] in both active and abandoned copper mining areas in Katanga, southeastern DR Congo.

Regarding potential toxicity to aquatic organisms, concentrations of copper in the analyzed sediments exceeded the Probable Effect Level (PEL) by factors ranging from 1.1 to 3 times the threshold of 197 mg kg^{-1} . Similarly, lead concentrations surpassed the PEL of 91.3 mg kg^{-1} by 2 times (Table 4). These elevated levels of Cu and Pb pose a substantial ecological risk and may significantly impact aquatic life and ecosystem health.

3.4 Concentration of rare earth elements in soil and sediment samples

The total concentrations of rare earth elements (ΣREE) in soils (ES) and surface sediments (SD) showed significant variations, ranging from 4.08 to 72.92 $\text{mg}\cdot\text{kg}^{-1}$ in soils and from 4.54 to 20.35 $\text{mg}\cdot\text{kg}^{-1}$ in sediments, which can be compared to 172.85 $\text{mg}\cdot\text{kg}^{-1}$ in the NASC reference (Table 5). This indicates a general depletion of REEs in the studied samples relative to the average upper continental crust. The highest ΣREE was observed

Table 4 Metal concentrations (mg kg⁻¹ dry weight) in soil (ES) and surface sediment (SD) samples analysed by ICP-MS and AAS. Values for the CRMs are included

Sample ID	Sc	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Ba	Pb	Hg
LOD		0.098	0.024	0.000	0.025	0.000	1.516	2.033	0.049		0.063		1.091	0.005
ES1	0.43	2.04	25.55	25.08	60.35	18.61	11423.82	179.28	3.75	0.58	0.45	475.5	210.45	0.17
ES2	0.41	0.49	7.64	37.23	15.83	5.11	470.78	60.48	10.97	1.26	0.03	18.01	173.03	0.08
ES3	0.33	8.41	6.34	25.02	0.43	0.50	246.05	6.66	0.90	0.29	0.03	5.36	111.11	0.07
ES4	0.16	8.76	3.63	10.96	0.13	0.36	1.76	2.85	0.21	0.02	0.00	0.89	2.02	0.07
ES5	0.58	7.24	11.64	50.55	0.40	0.85	14.03	8.59	4.74	0.94	0.01	15.75	19.28	0.08
ES6	0.26	16.63	5.80	44.98	0.22	0.67	4.07	4.21	0.47	0.24	0.01	3.78	3.84	0.04
SD1	0.20	2.31	5.35	20.24	4.71	2.01	418.96	38.47	8.57	0.37	0.04	13.22	13.35	0.33
SD2	0.30	4.88	6.66	25.82	0.52	1.41	591.75	21.95	0.87	0.23	0.02	9.16	4.77	0.36
SD3	0.09	4.86	2.57	11.59	0.45	0.52	6.07	15.59	1.16	0.09	0.01	3.3	3.49	0.17
SD4	0.24	4.70	5.39	20.96	0.93	0.47	33.21	15.98	3.13	0.37	0.08	9.75	10.98	0.10
SD5	0.15	3.83	3.23	20.87	0.53	0.25	209.61	10.08	1.55	0.19	0.06	5.79	89.27	0.12
SD6	0.21	11.96	5.98	40.15	0.66	0.66	234.19	14.99	2.75	0.29	0.10	7.96	179.54	0.04
STSD-1	-	-	47	28	14	18	36	165	17	-	0.8	-	34	-
	Ref. values													
	Det. values	101.79	47.08	27.93	12.96	17.77	36.39	162.58	18.11	0.59	0.74	28.27	35.24	-
SRM 2702	-													0.4474
	Ref. values													
	Det. values													0.4434
SQGS			37.3				35.7	123.0	5.9		0.6		35.0	0.17
PEL			90.0				197.0	315.0	17.0		3.5		91.3	0.486

In bold, values of heavy metal's concentration higher than the recommended probable effect concentration according to International Sediment Quality Guidelines (SQG) for the Protection of Aquatic Life recommendation [34]; PEL—probable effect levels (sediment dry weight)

in the soil sample ES2 (72.92 mg·kg⁻¹), while the lowest occurred in ES4 (4.08 mg·kg⁻¹). Sediments exhibited narrower variations, with the highest value in SD6 (20.35 mg·kg⁻¹).

The light rare earth elements (LREE: La–Sm) are more abundant than heavy rare earth elements (HREE: Gd–Lu), consistent with natural crustal patterns. However, normalization to NASC reveals specific anomalies (Fig. 4). The calculated Ce anomaly (Ce/Ce*) (Table 6), based on La–Pr interpolation, ranges from negative anomalies (< 1, e.g., ES1, ES2, SD4) to positive anomalies (> 1, e.g., ES3, SD2), reflecting variable redox conditions. The Eu anomaly (Eu/Eu*) (Table 6), computed relative to Sm–Gd, is generally negative (< 1) in most soils and sediments, suggesting feldspar depletion or plagioclase fractionation. In contrast, the Gd anomaly (Gd/Gd*) (Table 6), calculated relative to Sm–Tb, shows occasional deviations: some samples (e.g., SD1, SD2, SD3 and SD5) exhibit positive anomalies, while others show depletion.

Overall, soils (ES) displayed greater variability in REE patterns and anomalies compared to sediments (SD), which in the environment generally are more homogenized than soils.

The lower Σ REE values relative to NASC indicate overall depletion of REEs in both soils and sediments, which may result from intense weathering, leaching, or sedimentary dilution processes [41]. The higher REE contents in some soils (e.g., ES2 and ES5) suggested localized enrichment, possibly linked to lithological differences or anthropogenic inputs [42].

The Ce anomaly is an important redox indicator. Positive anomalies observed in some soils and sediments (e.g., ES3, SD2) could be attributed to oxidative scavenging of Ce⁴⁺ onto Fe–Mn oxyhydroxides, while negative anomalies (e.g., ES2, ES4, SD4) may reflect reducing conditions that prevent Ce oxidation. This highlights the influence of redox conditions on REE geochemistry in the studied environment [43].

The negative Eu anomaly observed in most samples suggests feldspar weathering, as Eu²⁺ is preferentially incorporated into plagioclase, leading to Eu depletion in the residual phases [44]. This pattern is consistent with the weathering history of continental crustal material [45].

A positive Gd anomaly observed in certain sediment samples, particularly SD3 and SD5 (Table 6), can result from several natural geochemical processes, including preferential mobilization of middle REEs during weathering, adsorption–desorption reactions involving Fe–Mn oxyhydroxides, or subtle mineralogical contributions from Gd-bearing accessory phases. Given the absence of known local anthropogenic sources of Gd (e.g., medical contrast agents), the anomaly observed here is most likely linked to natural fractionation processes rather than external inputs.

Overall, the Gd anomaly remained weak and should be interpreted cautiously, as its magnitude falls within the range commonly attributed to natural variability in sedimentary REE patterns. Additional mineralogical or speciation analyses would be required to discriminate more precisely among possible mechanisms.

The REE distribution patterns in soils and sediments from the studied area are controlled by a combination of lithology, weathering intensity, redox conditions, and potential anthropogenic influences, with soils reflecting more pronounced geochemical heterogeneity than sediments.

The concentrations of thorium and uranium, ranging from 0.41 to 2.68 mg kg⁻¹ and from 0.03 to 1.69 mg kg⁻¹ respectively, were much lower than those reported for the

Table 5 Concentrations of rare Earth elements ($\text{mg}\cdot\text{kg}^{-1}$ dry weight) in soils (ES) and surface sediments (SD) analyzed by ICP-MS. NASC, North American shale composite

Sample ID	ES1	ES2	ES3	ES4	ES5	ES6	SD1	SD2	SD3	SD4	SD5	SD6	NASC
LOD	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	
La	7.44	16.99	2.69	0.84	11.28	2.19	2.68	1.72	0.86	4.33	2.53	4.9	32
Ce	14.05	31.74	6.54	1.81	21.65	3.68	6.3	5.71	2.05	8.27	4.99	9.07	73
Pr	1.92	4.4	0.71	0.19	2.68	0.5	0.7	0.49	0.22	0.98	0.57	1.14	7.9
Nd	7.01	14.98	2.42	0.64	9.02	1.64	2.5	1.91	0.79	3.28	1.93	3.92	33
Sm	1.26	2.43	0.44	0.12	1.5	0.3	0.44	0.39	0.14	0.54	0.32	0.68	5.7
Eu	0.39	0.38	0.09	0.02	0.27	0.06	0.09	0.09	0.03	0.1	0.06	0.12	1.24
Gd	0.47	0.97	1.66	0.31	0.11	1.03	0.34	0.34	0.32	0.12	0.39	0.23	5.2
Tb	0.09	0.14	0.03	0.01	0.09	0.02	0.04	0.04	0.01	0.03	0.02	0.04	0.85
Dy	0.36	0.47	0.14	0.07	0.3	0.09	0.15	0.2	0.06	0.12	0.07	0.15	5.8
Ho	0.06	0.07	0.02	0.01	0.04	0.01	0.03	0.04	0.01	0.02	0.01	0.02	1.04
Er	0.15	0.19	0.05	0.03	0.1	0.03	0.07	0.1	0.03	0.04	0.03	0.05	3.04
Tm	0.02	0.02	0.01	0	0.01	0	0.01	0.01	0	0	0	0	0.5
Yb	0.11	0.12	0.04	0.03	0.06	0.02	0.04	0.08	0.02	0.03	0.02	0.03	3.1
Lu	0	0.02	0	0	0.01	0	0.01	0.01	0	0	0	0	0.48
ΣREE	33.33	72.92	14.84	4.08	47.12	9.57	13.4	11.13	4.54	17.86	10.94	20.35	172.85
Th	1.18	1.86	1.57	0.87	2.68	1.29	1.2	0.9	0.41	1.24	0.72	1.1	
U	1.69	0.15	0.08	0.03	0.19	0.05	0.09	0.09	0.04	0.09	0.06	0.14	

NASC: North American Shale Composite (Haskin et al. 1968)

Ulindi River sediments, a site in DR Congo characterized by intensive semi-industrial gold mining [46]. In that region, Th and U concentrations reached values between 10.3 and 526 mg kg⁻¹ and 2.37–124 mg kg⁻¹, respectively. Therefore, the levels of uranium and thorium in soils and stream sediments in the Mbamba Kilenda area do not pose a significant radiological risk to the members of the population.

3.5 Evaluation of environmental pollution and ecological risk parameters

The Geo-accumulation Index (Igeo) and the Enrichment Factor (EF) were calculated to distinguish between anthropogenic and geogenic sources of the analyzed metal elements, as well as to classify the degree of metal and metalloid contamination in the samples [5]. Igeo and EF values are presented in Table 7. Results show that all samples fall into Class 0 (Igeo = 0), indicating they are practically unpolluted with respect to Ti, V, Cr, Ni, Zn, Se, and Ba. Some samples are categorized as Class 1 ($0 < \text{Igeo} < 1$), corresponding to unpolluted to moderately polluted conditions for Co, Zn, As, and Hg; others fall within Class 2 ($1 < \text{Igeo} < 2$), indicating moderate contamination by Co, As, Cd, Pb, and Hg. Samples in Class 3 ($2 < \text{Igeo} < 3$) exhibit moderate to heavy pollution levels for Cu, As, Pb, and Hg; samples in Class 4 ($3 < \text{Igeo} < 4$) indicates heavy contamination by Cu, and samples in Class 6 reflects extremely high pollution levels for Cu.

The EF values, also summarized in Table 7, indicated no enrichment ($\text{EF} < 1$) for Ti and Se across all samples. However, a range of enrichment from minor ($\text{EF} < 3$) to extremely severe was observed for elements such as V, Cr, Co, Ni, Cu, Zn, As, Cd, Ba, Pb, and Hg, depending on the sample. These findings suggest significant anthropogenic inputs of these elements, likely related to industrial and other human activities.

Ecological risk parameters, including the Contamination Factor (CF), Degree of Contamination (CD), Potential Ecological Risk Factor (Eri), and the Ecological Risk Index (RI) are shown in Table 8. Some samples exhibited low contamination levels ($\text{CF} < 1$) for Cr, Co, Cu, Zn, As, Cd, Pb, and Hg, while others displayed moderate to very high contamination levels for the same elements. The Contamination Degree varied from moderate ($8 \leq \text{CD} < 16$), to considerable high ($16 \leq \text{CD} < 32$), and very high ($\text{CD} \geq 32$).

Based on Eri values, the majority of samples posed a low ecological risk ($\text{Eri} < 40$) for Hg, Cd, As, Co, Cu, Pb, Cr, and Zn. However, several samples exhibited moderate ($40 < \text{Eri} < 80$), considerable high ($80 < \text{Eri} < 160$), high ($160 < \text{Eri} < 320$), or very high ecological risk ($\text{Eri} > 320$) for Hg, Cd, As, Cu, and Pb. Regarding the RI, samples SD1, SD2, ES1, and ES2 indicated considerable ecological risk ($300 < \text{RI} < 600$) or very high risk ($\text{RI} > 600$), while the remaining samples showed low ecological risk ($\text{RI} < 150$).

The selection of background values (Upper Continental Crust and Sc) may not fully capture local geochemical variability in highly mineralised terrains. While these benchmarks provide a baseline, naturally elevated metal concentrations in the Kongo Central region could influence enrichment factors. Therefore, interpretations of contamination levels should consider both background variability and site-specific geological context.”

3.6 Statistical correlations

The Spearman correlation coefficients calculated for metal and metalloid concentrations are presented in Table 9. The table shows several statistically significant positive correlations ($p < 0.05$), particularly between OM/Hg ($R^2 = 0.705$), CaCO_3/Co ($R^2 = 0.657$), CaCO_3/Cu ($R^2 = 0.755$), CaCO_3/Zn ($R^2 = 0.657$), CaCO_3/As ($R^2 = 0.594$), CaCO_3/Ba (R^2

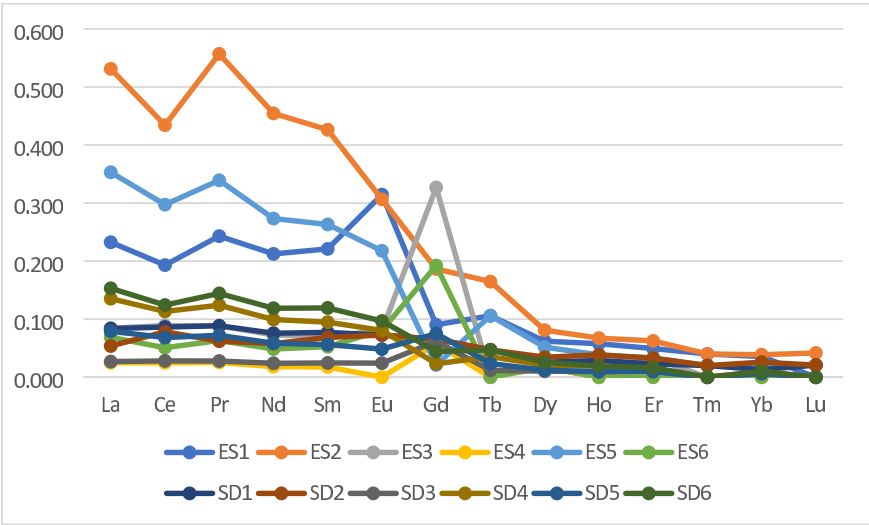


Fig. 4 NASC-normalized rare earth element patterns

Table 6 Ce, Eu and Gd anomalie values in soils (ES) and sediments (SD) from the study area

Sample ID	Ce/Ce*	Eu/Eu*	Gd/Gd*
ES1	0.81	2.23	0.59
ES2	0.80	1.09	0.70
ES3	1.03	0.53	-
ES4	0.98	0.00	-
ES5	0.86	2.92	0.13
ES6	0.77	0.80	-
SD1	1.00	1.02	1.08
SD2	1.35	1.09	1.15
SD3	1.03	0.62	3.62
SD4	0.87	1.72	0.40
SD5	0.91	0.75	2.06
SD6	0.84	1.33	0.59

Table 7 Results for EF and Igeo indices for metals in soil and sediment samples

Igeo	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Ba	Pb	Hg	Igeo classification
SD1	-10.9	-4.1	-1.4	-1.7	-3.9	-3.2	-1.5	1.9	-7.7	-1.9	-6.0	-1.2	2.0	Igeo < 0 Class 0 – practically unpolluted
SD2	-9.5	-3.8	-1.0	-4.9	-4.4	4.0	-2.3	-1.4	-8.3	-2.9	-6.5	-2.7	2.1	
SD3	-9.9	-5.1	-2.2	-5.1	-5.9	-2.6	-2.8	-1.0	-9.7	-3.9	-8.0	-3.1	1.0	
SD4	-9.9	-4.1	-1.3	-4.0	-6.0	-0.2	-2.7	0.5	-7.7	-0.9	-6.4	-1.5	0.3	
SD5	-10.2	-4.8	-1.3	-4.8	-6.9	2.5	-3.4	-0.5	-8.6	-1.3	-7.2	1.6	0.5	1 < Igeo < 2 Class 2 – moderately polluted
SD6	-8.6	-3.9	-0.4	-4.5	-5.5	2.6	-2.8	0.3	-8.0	-0.6	-6.7	2.6	-1.1	
ES1	-11.1	-1.8	-1.1	2.0	-0.7	8.8	0.8	0.7	-7.0	1.6	-0.8	2.8	1.0	2 < Igeo < 3 Class 3 – moderately to heavily polluted
ES2	-13.2	-3.6	-0.5	0.1	-2.6	3.7	-0.8	2.3	-5.9	-2.3	-5.5	2.5	-0.1	
ES3	-9.1	-3.8	-1.1	-5.1	-5.9	2.7	-4.0	-1.3	-8.0	-2.3	-7.3	1.9	-0.3	3 < Igeo < 4 Class 4 – heavily polluted
ES4	-9.0	-4.6	-2.3	-6.9	-6.4	-4.4	-5.2	-3.4	-11.9	-	-9.9	-3.9	-0.3	
ES5	-9.3	-3.0	-0.1	-5.2	-5.1	-1.4	-3.6	1.1	-6.3	-3.9	-5.7	-0.6	-0.1	4 < Igeo < 5 Class 5 – heavily to extremely polluted
ES6	-8.1	-4.0	-0.2	-6.1	-5.4	-3.2	-4.7	-2.3	-8.3	-3.9	-7.8	-2.0	-4.1	
EF	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Ba	Pb	Hg	EF interpretation values
SD1	0.0	4.9	31.9	25.5	3.5	221.2	29.6	214.2	0.4	22.4	1.3	96.7	224.1	EF < 1 : no enrichment
SD2	0.1	4.1	27.0	1.9	2.6	867.9	11.3	21.3	0.2	7.5	0.6	8.7	235.1	
SD3	0.2	5.2	40.3	5.5	3.2	29.7	28.8	94.5	0.2	12.5	0.7	21.3	271.0	
SD4	0.1	4.1	27.4	4.3	1.1	66.9	10.3	95.6	0.3	27.4	0.8	28.2	31.8	
SD5	0.1	3.9	43.2	3.9	0.9	614.9	10.4	78.5	0.3	24.0	0.8	322.1	137.7	EF 5-10 : moderate to severe enrichment
SD6	0.2	5.2	60.1	3.5	1.7	490.7	11.1	96.0	0.3	53.4	0.8	450.2	35.4	
ES1	0.0	10.9	18.3	184.4	23.8	11689.5	64.6	64.0	0.3	117.5	22.1	269.2	77.7	EF 25-50 : very severe enrichment
ES2	0.0	3.4	28.5	47.5	6.9	503.2	22.9	196.1	0.7	8.2	0.9	213.1	18.3	
ES3	0.1	3.5	23.8	1.4	0.8	28.1	3.1	20.0	0.2	10.2	0.3	188.2	41.7	EF > 50 : extremely severe enrichment
ES4	0.2	4.2	21.5	0.9	1.2	4.8	2.8	9.6	0.0	0.0	0.1	6.9	35.9	
ES5	0.0	3.7	22.4	0.8	0.8	10.6	2.3	58.9	0.4	1.9	0.5	18.3	22.1	
ES6	0.2	4.1	54.4	0.9	1.4	6.9	2.5	13.3	0.2	4.3	0.3	8.1	30.2	

= 0.741), and CaCO₃/Pb (R² = 0.552). These strong associations indicate that organic matter (OM) and calcium carbonate (CaCO₃) may play a pivotal role in the mobility and transport of these elements within soils and sediments.

In addition, several significant positive correlations were observed among various metal pairs, suggesting that these elements may share similar sources and migration

Table 8 Results for CF, CD, Eri, RI indices calculated for soil and sediment samples

Sample ID	CF								DC	Sample ID	Eri								RI
	Cr	Co	Cu	Zn	As	Cd	Pb	Hg			Hg	Cd	As	Co	Cu	Pb	Cr	Zn	
SD1	0.6	0.3	16.8	0.5	5.7	0.4	0.7	5.9	31.0	SD1	235.7	12.2	57.1	2.4	83.8	3.3	1.2	0.5	396.3
SD2	0.7	0.1	23.7	0.3	0.6	0.2	0.2	6.4	32.2	SD2	257.1	6.1	5.8	0.3	118.4	1.2	1.5	0.3	390.7
SD3	0.3	0.0	6.2	0.2	0.8	0.1	0.2	3.0	4.9	SD3	121.4	3.1	7.7	0.2	1.2	0.9	0.7	0.2	135.4
SD4	0.6	0.1	1.3	0.2	2.1	0.8	0.5	1.8	7.5	SD4	71.4	24.5	20.9	0.5	6.6	2.7	1.2	0.2	128.1
SD5	0.6	0.1	8.4	0.1	1.0	0.6	4.5	2.1	17.4	SD5	85.7	18.4	10.3	0.3	41.9	22.3	1.2	0.1	180.3
SD6	1.1	0.1	9.4	0.2	1.8	1.0	9.0	0.7	23.3	SD6	28.6	30.6	18.3	0.3	46.8	44.9	2.3	0.2	172.1
ES1	0.7	6.0	457.0	2.5	2.5	4.6	10.5	3.0	486.9	ES1	121.4	137.8	25.0	30.2	2284.8	52.6	1.4	2.5	2655.7
ES2	1.1	1.6	18.8	0.9	7.5	0.3	8.7	1.4	40.0	ES2	57.1	9.2	73.1	7.9	94.2	43.3	2.1	0.9	287.8
ES3	0.7	0.0	9.8	0.1	0.6	0.3	5.6	1.3	18.4	ES3	50.0	9.2	6.0	0.2	49.2	27.8	1.4	0.1	143.9
ES4	0.3	0.0	0.1	0.0	0.1	0.0	0.1	1.3	1.9	ES4	50.0	0.0	1.4	0.1	0.4	0.5	0.6	0.0	53.0
ES5	1.4	0.0	0.6	0.1	3.2	0.1	1.0	1.4	7.8	ES5	57.1	3.1	31.6	0.2	2.8	4.8	2.9	0.1	102.6
ES6	1.3	0.0	0.2	0.1	0.3	0.1	0.2	0.7	2.9	ES6	28.6	3.1	3.1	0.1	0.8	1.0	2.6	0.1	39.3

CF classification

CF<1	Low contamination
1<CF<3	Moderate contamination
3<CF<6	Considerable contamination
6<CF	Very high contamination

RI Classification

RI<150	Low ecological risk or low ecological level
150<RI<300	Moderate ecological pollution level or moderate ecological risk
300<RI<600	Considerable ecological risk or severe ecological pollution level
RI>600	Very high ecological risk or serious ecological pollution level

Eri classification

Eri < 40	Low ecological risk
40 < Eri < 80	Moderate ecological risk
80 < Eri < 160	Considerable ecological risk
160 < Eri < 320	High ecological risk
Eri > 320	Very high ecological risk

CD Classification

8<CD<16	Moderate contamination
16<CD<32	High contamination
32<CD	Very high contamination

pathways. No statistically significant negative correlations were detected between the analyzed elements.

3.7 Principal component analysis (PCA)

The Principal Component Analysis (PCA) was applied to the dataset combining physico-chemical parameters, trace metal concentrations, and rare earth element (REE) contents in soils and sediments collected from the Mbamba–Kilenda area. The objective was to identify the main geochemical associations and to discriminate the sources of variability among the sampling sites.

Figure 5A (Scree plot) shows that the first two principal components (PC1 and PC2) account for 73.1% of the total variance (51.7% and 21.4%, respectively), indicating that most of the data variability can be explained in a two-dimensional space. The subsequent components contribute marginally to the overall variance and were therefore not considered for further interpretation. The biplot of PC1 vs. PC2 (Fig. 5B) clearly separates soil samples (ES) from sediment samples (SD), reflecting the influence of both lithogenic and anthropogenic processes. PC1 is strongly and positively correlated with heavy metals such as Cu, Pb, Zn, and Co, together with the REE sum (Σ REE), suggesting that this component mainly represents the metal enrichment factor related to historical mining activities and weathering of ore-rich formations. In contrast, PC2 is associated with variables such as organic matter (OM), CaCO_3 , and clay content, indicating that it reflects sediment texture and organic geochemistry. Samples ES1, ES2, and SD6 are positioned on the positive side of PC1, showing the highest metal accumulation, while ES4 and SD3 plot negatively, corresponding to less contaminated or more natural materials. The correlation circle (Fig. 5C) confirms these associations. Metals of anthropogenic or ore-related origin (Cu, Pb, Zn, Co, As) cluster closely along PC1, whereas geochemical background indicators (CaCO_3 , sand, grain size) are oriented in the opposite direction. The REE variables (La, Ce, Nd, Sm, and Gd) are positioned between these two groups,

Table 9 Spearman ranks correlation for some parameters analyzed in soil and sediment samples

Cr	Co	Ni	Cu	Zn	As	Se	Cd	Ba	Pb	Hg	Grain size	CaCO ₃	OM
	0.000	0.462	0.182	0.007	0.224	0.556	0.082	0.427	0.420	-0.309	-0.213	0.238	0.112
Co		0.524	0.769	0.916	0.748	0.587	0.823	0.755	0.657	0.484	-0.325	0.657	0.252
Ni			0.657	0.692	0.552	0.664	0.194	0.734	0.399	0.365	-0.164	0.455	0.294
Cu				0.797	0.490	0.510	0.638	0.713	0.685	0.526	-0.416	0.755	0.294
Zn					0.685	0.538	0.596	0.762	0.455	0.694	-0.374	0.657	0.434
As						0.850	0.505	0.853	0.608	0.299	-0.416	0.594	0.399
Se							0.430	0.895	0.657	0.052	-0.423	0.524	0.280
Cd								0.558	0.767	0.227	-0.173	0.467	0.023
Ba									0.664	0.386	-0.542	0.741	0.455
Pb										-0.037	-0.129	0.552	-0.133
Hg											-0.288	0.519	0.705

Statistically significant coefficients ($p < 0.05$) are shown in bold

indicating an intermediate geochemical behavior possibly controlled by both detrital input and secondary adsorption on Fe–Mn oxides. The strong positive correlation between ΣREE and Cu or Pb suggests a common mineralogical source (e.g., sulfide-bearing rocks or alteration zones).

Overall, the PCA results reveal that the first component reflects contamination gradients driven by mining-related metals and REE enrichment, while the second component reflects sedimentary and organic controls. These findings support the interpretation that the soils and sediments of Mbamba–Kilenda are geochemically influenced by both natural lithology and anthropogenic inputs from former mining activities.

Although PCA clearly separated contamination-related variables (PC1) from natural geochemical controls (PC2), some methodological limitations must be considered. Because metal and REE concentrations are compositional, PCA may introduce artefacts linked to closure; thus, the ordination should be viewed as exploratory. Sensitivity tests (removal of enriched samples and alternative treatments of non-detects) showed that the structure of PC1 and PC2 remained stable, confirming that the main gradients are robust. Standardization also helped balance high-variance metals with physicochemical variables. Given potential effects of closure and collinearity, PCA patterns should be interpreted together with EF/Igeo, RI and REE signatures to ensure reliable environmental inferences.

4 Conclusions

This study provides a comprehensive geochemical assessment of soils and sediments in the vicinity of the abandoned artisanal copper mine of Mbamba Kilenda, Madimba, Kongo Central Province, DR Congo. The findings revealed distinct contamination patterns in soils and sediments, reflecting both natural lithology and historical mining activities.

Soil samples exhibited highly variable metal concentrations, with maxima observed for Cu (up to 11,424 mg kg⁻¹ dw), Pb (210 mg kg⁻¹ dw), Zn (179 mg kg⁻¹ dw), As (11 mg kg⁻¹ dw), and Hg (0.36 mg kg⁻¹ dw). The Geoaccumulation Index (Igeo) reached values up to 5 for Cu, classifying soils as extremely polluted. Similarly, the Enrichment Factor (EF) showed extremely severe enrichment for Cu (EF ≈ 11,689) and Pb (EF ≈ 470), while As and Hg also displayed substantial anthropogenic contributions. The Potential Ecological Risk Index (RI) indicated very high ecological risk for soils, predominantly driven by Cu and Hg. These results highlight that the mining legacy has left open pits and uncovered highly contaminated waste piles that overtime have contaminated agriculture soils in the vicinity. Therefore, this site requires urgent attention for stabilization of mining waste in order to prevent further soil and water contamination and soil remediation measures, as adequate.

Riverbed sediment samples displayed also elevated metal levels in specific locations along Masungu 1, Masungu 2, and the Lukunga River. Certain samples exceeded the Sediment Quality Guidelines (SQGs) and Probable Effect Levels (PELs) established for aquatic ecosystems, notably for Cu (up to 3× PEL), Pb (up to 2× PEL), As, Cr, and Hg. The calculated geochemical indices corroborated these observations: the Igeo and EF indicated moderate to extremely severe enrichment in sediments for Cu, Pb, As, and Hg, while the ecological risk parameters (Eri, RI) confirmed considerable to very high potential risk to aquatic life in sites SD1, SD2, and SD6. These findings suggest that riverbed

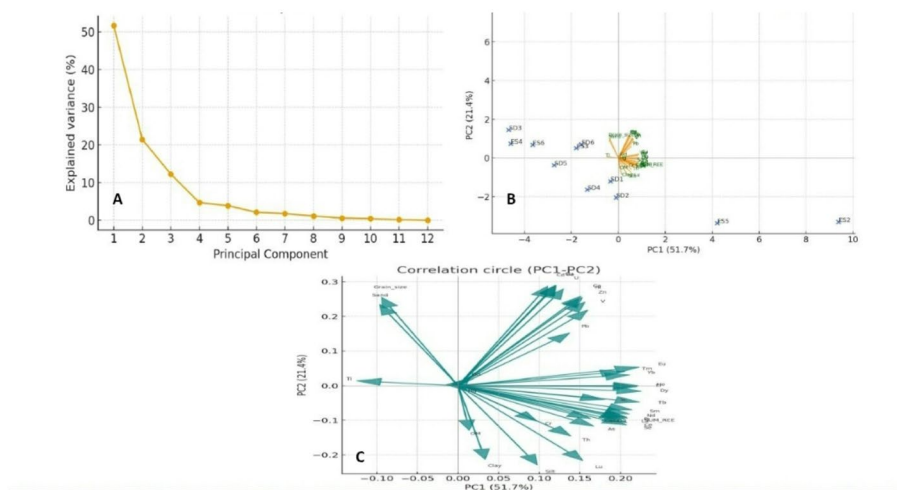


Fig. 5 Principal Component Analysis (PCA) of soils and sediments from the Mbamba–Kilenda area. **A** Scree plot of explained variance. **B** PCA biplot (PC1–PC2) showing sample distribution and variable contributions. **C** Correlation circle (PC1–PC2) illustrating relationships among physicochemical parameters, metals, and REEs

sediments serve as both a sink and, later on, a potential secondary source of contaminants to aquatic ecosystems with implications for ecological health and bioaccumulation in the food chain up to human beings.

Both soils and sediments exhibited overall REE depletion relative to NASC, with soils showing greater variability. Ce and Eu anomalies suggest redox-controlled fractionation, while occasional positive Gd anomalies in sediments likely reflect natural fractionation processes influenced by organic matter and mineralogical heterogeneity rather than direct anthropogenic inputs.

The legacy of artisanal copper mining at Madimba has left a significant imprint on local soils and sediments, with Cu, Pb, As, and Hg representing the main pollutants of concern. Soils in the vicinity of the mining area are heavily contaminated compared to background levels, while riverbed sediments exceed the SQGs and PELs at several locations, indicating substantial ecological hazards. These results underscore the urgent need for targeted remediation strategies, including mining waste piles stabilization, containment of mine wastes, and long-term monitoring of both terrestrial and aquatic environments. Future studies should focus on metal speciation and bioavailability to better quantify ecological and human health risks.

Supplementary Information

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Supplementary Material 1

Author contributions

The conceptualization, methodology and validation were carried out by P.B.K., J.-A.L.M., E.K.A., C.K.M., F.P.C. and J.P. The calculation was carried out by P.B.K. and E.K.A. The first draft of the manuscript was written by E.K.A. and F.P.C. and J.P. improved and consolidated the initial version of the manuscript. All authors read and approved the final manuscript.

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Data availability

All data underlying the results presented in this study are included in the article. Additional raw data can be obtained from the corresponding author upon justified request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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