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Trace metals and rare earth elements in sediments along the Muanda River estuary and coastal ocean continuum in an oil exploitation area

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Abstract

This study evaluated the distribution and ecological risks of trace metals and rare earth elements (REEs) in surface sediments along the river–estuary–coastal continuum of Muanda, Democratic Republic of the Congo (DRC), a region under strong environmental pressure by oil exploitation. Fifteen sediment samples were analyzed by ICP-MS, AAS, and DMA. Sediments were mainly sandy, with variable organic matter (1.75–10.30%) and CaCO₃ (0.26–9.14%) contents, which significantly influenced metal retention. Elevated concentrations of Zn (up to 523.6 mg·kg⁻¹), Pb (311.2 mg·kg⁻¹), Cr (253.6 mg·kg⁻¹), and Cu (165 mg·kg⁻¹) exceeded international Sediment Quality Guidelines (SQGs) and Probable Effect Levels (PELs) on aquatic life, especially near industrialized estuarine sites. Geoaccumulation Index (I_{geo}) and Enrichment Factor (EF) indices confirmed moderate to severe anthropogenic pollution, while contamination and ecological risk indices (CF, CD, Eri, RI) indicated localized moderate ecological risk, despite overall low cumulative risk due to sedimentary buffering. Total REEs ranged from 3.28 to 6.72 mg·kg⁻¹, markedly lower than shale standards, with slight negative Ce (0.91–0.93) and Eu (0.70–1.17) anomalies, reflecting primarily natural geochemical control. Statistical correlations revealed that organic matter and CaCO₃ acted as key scavengers, enhancing retention of Cu, Zn, Pb, and Hg. Spearman rank correlation analysis confirmed oil industry-related discharges as the dominant source of trace metal enrichment. Spearman correlations highlighted the role of organic matter (OM) and calcium carbonate (CaCO₃) as major binding phases for metals, while PCA confirmed their clustering with REEs in fine sediments and distinguished metals from anthropogenic sources (V, Ni, Cu, Pb, Zn, As, Cd) from metals of geogenic origin. Petroleum exploitation was identified as the main source of contamination, with additional contributions from agriculture, industrial effluents, and maritime activities.

Keywords Muanda, Oil industry, Trace elements, REE, Ecological risk factor



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1 Introduction

Petroleum exploitation is widely recognized as a significant source of environmental degradation, primarily through hydrocarbon spills, toxic waste discharges, and inadequate waste management [1, 2]. Such activities contribute to the degradation of water resources, degradation of ecosystems, and pose hazards to human health. These concerns are particularly acute in developing countries, where regulatory oversight and institutional capacities are often limited [3–6]. Coastal oil-producing areas in Central and West Africa, including Nigeria, Angola, and Gabon, already face chronic soil and water pollution, increasing the vulnerability of local populations [7–9].

In Democratic Republic of the Congo (DRC), the Muanda coastal basin in Kongo-Central province has been affected by oil exploitation since 1968. Historical and current activities include crude-oil leaks, improper disposal of drilling muds, and informal fuel trafficking which pollute aquatic ecosystems and freshwater resources [10–12].

The Muanda area is the only DRC coastal basin currently in active exploitation [12]. Oil operations began without baseline environmental studies, and no systematic operational or post-operational monitoring has been implemented, thus limiting our understanding of long-term impacts. Recent industrial expansion, including the presence of Perenco oil company and the set up of a new oil refinery, has intensified the potential for environmental contamination [12]. Although, some decommissioned wells are assumed to have currently a minimal impact with new releases of organic pollutants and due to the natural degradation of oil from old spills, still trace elements and rare-earth elements (REEs) are chemically stable and may persist in the environment [13, 14].

Rare earth elements (REEs) are emerging contaminants of increasing environmental concern due to their extensive use in industrial applications, including oil refining, electronics, and as catalysts in industrial processes [15–17]. In aquatic systems, REEs are chemically stable, mobile, and have the potential to bioaccumulate in sediments and organisms, raising ecological and health concerns. Despite their growing relevance, the environmental behavior of REEs in sediment–water systems, especially in areas impacted by hydrocarbon pollution, remains unstudied [18]. Environmental pollution by trace elements is systematically associated with oil exploitation, and these metals are both persistent and toxic to biota [21–25]. Rare-earth elements, such as lanthanum and cerium, are nowadays used as catalysts in oil refining processes and oil spills from refineries may spread these elements into the environment [26]. Despite their mobility and bioaccumulation potential, REEs in petroleum contexts remain largely understudied [27, 28]. Therefore, investigating REEs together with traditional trace elements provides a more comprehensive assessment of sediment contamination, allowing identification of anthropogenic inputs, their co-accumulation patterns, and potential ecological risks [19, 20].

Over five decades of industrial oil activities, combined with informal hydrocarbon trafficking, have raised concerns among local communities regarding their environmental impacts [10, 12]. Preliminary studies in Muanda and other DRC coastal areas have documented elevated Pb, As, and Cd concentrations exceeding WHO recommended thresholds [29, 30]. Particularly in the Ramsar-listed Mangrove Marine Park, significant metal contamination and low dissolved oxygen levels, likely linked to petroleum hydrocarbon pollution, have been observed [6, 31].

This study aimed to provide a comprehensive assessment of sediments contamination in Muanda, focusing on trace elements and REEs across the river-estuary-coastal continuum. It also aimed to evaluate ecotoxicological risks using established indices, and to identify the role of oil related activities in metal enrichment in sediments. Furthermore, by delivering the first integrated evaluation of trace metals and REEs in this region, this study established a baseline for future environmental monitoring and management strategies.

2 Materials and methods

2.1 Study area and sampling description

This study was conducted in the Muanda coastal basin (Fig. 1), located in Kongo-Central Province, Democratic Republic of Congo (DRC), between longitudes 11°15'–12°40' E and latitudes 05°00'–06°05' S [32, 33]. Figure 1 shows the geographical setting of the Muanda coastal basin together with the distribution of the sediment sampling sites along the river, estuary, and coastal zones.

In order to assess the contamination by trace elements and REEs, in July 2024 surface sediment samples were collected from seven representative areas encompassing the main aquatic compartments, i.e., river, estuary, coastal zone, and included also aquatic areas near urban and industrial spots.

The investigated areas, illustrated in Fig. 2, included: (1) the Yacht-SOCIR-Perenco area, a heavily industrialized zone (represented by six sediment samples collected at OT01 Jetée, OT02 Sewer, OT03 P, OT04 Incat, OT05 Yacht, OT06 PK); (2) the Banana area, located in the Congo River (represented by one sediment sample, FC01 Banana); (3) the Baku Yanga area within the estuary (represented by one sediment sample, FC02 BY); (4) the Tshiende River (represented by one sediment sample, R01 RTh.); (5) the Port of Mibale on the coast (represented by one sediment sample, R02 RM); (6) the Konde

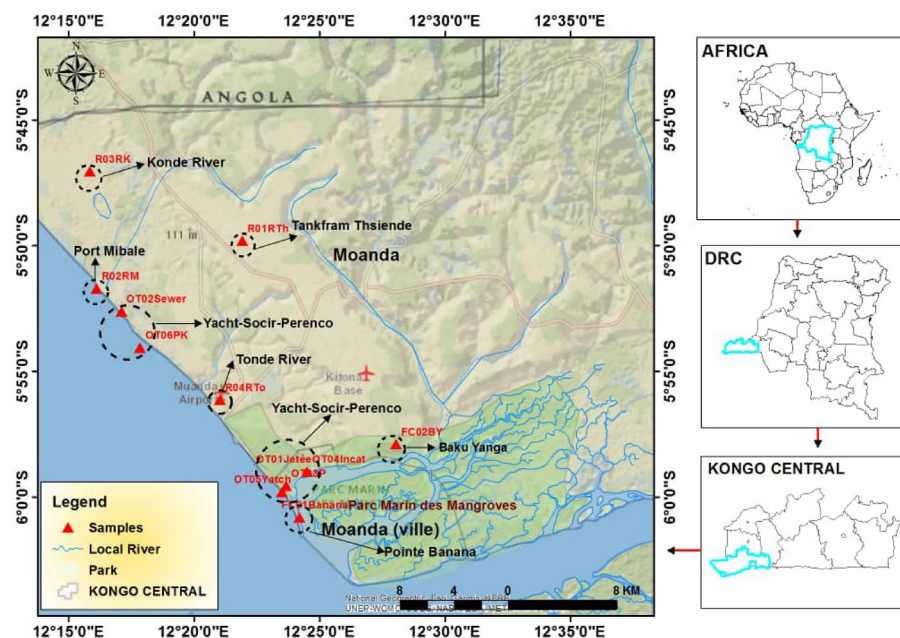


Fig. 1 Map of sampling area showing the geographical location of the DR Congo in Africa; the location of the Kongo Central province within DR Congo and the view of the Atlantic Coast in the Muanda region. Sampling stations are indicated with solid triangles



Fig. 2 Photographs of selected sampling sites **a** Yacht (decommissioned site); **b** Crude oil transfer station for off-shore shipping; **c** Incat (active oil facility); **d** Atlantic Ocean estuarine area (Yacht-Socir-Perenco). Photos by G. Nsiala (July 2024)

River (represented by one sediment sample, R03 RK); and (7) the Tonde River (represented by one sediment sample, R04 RTo). Figure 2 complements this spatial overview with photographs of selected sites, illustrating both legacy and ongoing petroleum-related activities: the decommissioned Yacht site, the crude oil transfer station for off-shore shipping, the active Incat oil facility, and the Atlantic Ocean estuarine area around Yacht-Socir-Perenco oil facilities.

All investigated areas have been impacted by past or current oil related activities. The Yacht, SOCIR, and Perenco area is located within the Muanda estuarine zone, forming a significant hotspot of petroleum-related activities. Yacht was previously an informal site for hydrocarbon trafficking and was active until 2022. SOCIR, the national crude oil refinery, has been operational since 1968, while Perenco is the primary oil extraction company in the region, with its main terminal situated also within the estuarine area. The concentration of infrastructures and operations within such a confined section of the estuary makes this zone one of the most heavily impacted by petroleum activities, with both legacy and current sources of hydrocarbon pollution. The Tankfarm Tshiende, in the Tshiende River, is an artisanal fishing port hosting also several industrial oil facilities, with visible traces of hydrocarbons in the water and soils. Detailed information on the sediment sampling location, sediment characteristics, and description of anthropogenic activities by the sampling areas is provided in Table 1.

At all sampling sites the sediments were collected from nearshore, at 1–3 m from the bank. At each site, sediment samples were collected in triplicate, and the three replicate samples were merged in one composite sample, totalizing approximately 250–300 g, in order to provide an enhanced representativeness of the sediment. Sediment samples were taken from the top sediment layer (0–3 cm sediment depth) using a sterile glass

Table 1 Sample labels, GPS coordinates, and site description, including human activities in the study area in Muanda, Atlantic coast of the DRC

Sam- pling site	Sample Label	Longitude	Latitude	Description
Yacht- Socir- Perenco in the Estuary	OT01Jetée	12.418	– 5.9805556	Transit zone, with oil drilling and hydrocarbon (HC) warehouses. Operational since the 1960s. Maritime and river transport of HCs. Presence of artisanal fishing activities
	OT02Sewer	12.437722	– 5.9799444	Discharge of industrial effluents from SOCIR into a branch of the Congo River. Traces of HCs observed in water. No aquatic life
	OT03P	12.390276	– 5.994315	Presence of multiple oil terminals for crude oil transfer for offshore shipping. Heavy traffic. Operational since 1981. Artisanal fishing takes place there
	OT04Incat	12.437722	– 5.9811389	Transit site for informal HC traffic from Soyo (Angola). Heavy traffic, with about 30,000m ³ of HCs handled every day. Operational since 2022. HC discharges into water and oil pollution visible in soils and water
	OT05Yatch	12.396493	– 5.999127	Site for HC transfer with over 1,000 m ³ handled every day. It was active from 2010 to 2022; currently decommissioned. Traces of HCs in soils and water. Artisanal fishing and vegetable farming activities are carried out there
	OT06PK	12.26751	– 5.860283	Artisanal fishing port. Several industrial facilities. Traces of HCs in water and soils
Tankfarm Tshiende	R01RTh	12.33834	– 5.794352	Temporary HC storage site. River basin occupied by oil facilities, in operation for over 40 years. Multiple HC spills reported. Traces of HCs in soils and water. Vegetable farming and artisanal fishing activities nearby
Port Mibale	R02RM	12.236361	– 5.8084444	Industrial and artisanal fishing port. Gas flaring. Off-shore oil exploitation. Discharge of oil waste; Traces of HCs visible in water and in some fishery products
Konde River	R03RK	12.260556	– 5.7608056	Recreational site with fishing and vegetable farming activities. Presence of wells and pumpjacks. HC discharges into the river
Tonde river	R04RTo	12.33834	– 5.925645	Onshore oil exploitation. Oil spills on land and traces of HCs visible in the water. Artisanal fishing and vegetable farming activities nearby
Pointe Banana on the Congo River	FC01Banana	12.406372	– 6.024859	Downstream the Yacht site and at the junction of SOCIR, Perenco, and Incat ports. Site currently used for informal oil trafficking. It is a major transit hub for hydrocarbons coming from Soyo (Angola). Operational since 2022. Visible hydrocarbon discharges into water and visible contamination of soils and water. Dumping ground for various HC discharges. Artisanal fishing and tourism practiced
Baku Yanga in the Estuary	FC02BY	12.438435	– 5.982231	Artisanal fishing port. River transport of HCs. Traces of HCs on fishing products

spatula, transferred into 0.5 L glass containers, stored at 4 °C, and transported to the analytical platform of the University of Geneva for physical and chemical analyses.

2.2 Physicochemical characteristics of sediments

Sediment samples were carefully homogenized and, as needed, aliquots were taken for the several analyses carried out. The grain size distribution, including the mean grain size and proportions of clay, silt, and sand, was assessed using a Laser Coulter®

LS-100 diffractometer (Beckman Coulter, Fullerton, CA, USA), following the procedure described by Banze wa Mutombo et al. [34].

As outlined by Blott and Pie [35], regarding sediment grain size the sediment samples composition may vary widely but, for classification purposes, samples with an average grain size below 2 μm are predominantly clay, while those with average grain size between 2 μm and 63 μm are mainly composed of silt, and samples with average grain sizes ranging from 63 μm to 2 mm can be classified as sandy.

The sediment water content (WC) was assessed through the determination of the weight loss of sediment aliquots after oven drying at 105 °C for about 24 h until constant weight. The sediment organic matter (OM) content was quantified based on the weight loss of dry sediment aliquots following ignition of aliquots in a muffle furnace (Salvis AG, Luzern, Switzerland) for one hour at 550 °C [21, 36]. The carbonate content (expressed as CaCO_3 equivalent) of the sediments was determined using the loss-on-ignition method. Dried sediment samples were ignited in a muffle furnace (Salvis AG, Luzern, Switzerland) at 1000 °C for one hour, and the resulting weight loss was recorded. The mass loss corresponding to CO_2 release was converted to CaCO_3 content using the calcite conversion factor (2.273), as the exact carbonate mineralogy (calcite or dolomite) was not determined.

2.3 Trace metals and rare-earth elements analysis in sediments

Aliquots of sediment samples were first freeze-dried, then finely ground to achieve a homogeneous powder, and subsequently sieved using a 63 μm mesh, following the method described by Thevenon et al. [37]. The digestion of sediments followed protocols developed by Thevenon et al. [38]. Briefly, accurately weighed aliquots, each with approximately 10 mg of dry sediment powder, were subjected to complete acid digestion in Teflon digestion vessels placed on a ceramic hotplate for solution heating. The digestion process involved three successive heating and dissolution stages: (i) 1 mL of nitric acid (HNO_3 , suprapur, 65%), (ii) a mixture comprising 0.5 mL of perchloric acid (HClO_4 , suprapur, 70%) and 0.5 mL of hydrofluoric acid (HF , suprapur, 40%), and (iii) an additional step with 0.5 mL of HNO_3 (65%). Between each stage, samples were evaporated to dryness and the dry residue dissolved with the acid used in the next stage of the procedure. The final sample dry residues were dissolved in 10 mL of a 1% HNO_3 solution in preparation for chemical analysis.

Trace metal concentrations, including Ti, V, Cr, Co, Ni, Cu, Zn, As, Se, Ba, Cd, Pb, Sc and Hg, and REEs concentrations, including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, were determined using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Agilent 7700 $\times$ series), and a technique optimized for the analysis of complex matrices. The helium (He) collision mode and interference correction equations were applied to mitigate spectral interferences. The calibration of the instrument was carried out using a series of multi-element standards at concentrations of 0, 0.02, 1, 5, 20, 100, and 200 $\mu\text{g L}^{-1}$. The method exhibited high precision, with standard deviations of triplicate measurements remaining below 2.5%, and procedural blanks accounting for less than 1% of the analytical signal.

As an analytical quality control the certified reference material (CRM) stream sediment STSD-1 from the National Research Council, Canada, was included in the batch

of samples being analyzed. The results of the CRM analyses were in good agreement, within $\pm 10\%$, with the certified values.

The results for metal concentrations in the CRM, compared to the certified values, indicated elemental recovery rates above 97.5% for all elements analyzed by triple quadrupole ICP-MS.

Results for element concentrations are reported in milligrams per kilogram (mg kg^{-1}) on a sediment dry weight basis.

2.4 Mercury analysis in sediments

The concentration of total mercury (Hg) in sediment samples was determined using a Direct Mercury Analyzer (DMA 80-III, MWS GmbH), which operates on the principle of cold vapor atomic absorption spectroscopy (CV-AAS). The analytical procedure included sample combustion, mercury amalgamation in a gold trap, and quantification of gaseous mercury via atomic absorption. The method demonstrated a high recovery rate, exceeding 99%.

The relative measurement uncertainty was approximately 4%. The method's detection limit, calculated as the mean of the blank plus three standard deviations, was $0.003 \mu\text{g g}^{-1}$. Reproducibility was high, with variation between replicates remaining below 5% [39].

As an analytical quality control for the determination of total mercury in sediment samples, the certified reference material for inorganics in marine sediment SRM 2702, from the National Institute of Standards and Technology, USA, was prepared and analyzed alongside the samples. This was done following the Feststoffe Schnell protocol (no drying stage, combustion temperature set at 750°C) [40]. The concentration result obtained for total mercury in the CRM SRM 2702, compared to the certified value, and indicated a Hg recovery rate of 99%. Mercury and trace element concentrations in all analyzed samples were reported in milligrams per kilogram (mg kg^{-1}) on a sediment dry weight basis.

2.5 Evaluation of sediment pollution

The assessment of sediment pollution was carried out using two widely recognized geochemical indicators: the Enrichment Factor (EF) and the Geoaccumulation Index (Igeo) [41]. These indices allow differentiating between the natural geochemical background levels and the anthropogenic input of trace elements into sediments. The Enrichment Factor (EF) was calculated using the following equation:

$$\text{EF} = (\text{Metal}/\text{Sc})_{\text{Sample}} / (\text{Metal}/\text{Sc})_{\text{Background}}$$

where Metal represents the concentration of the target trace element, and Sc (scandium) is employed as a reference element for normalization due to its conservative geochemical behavior. Background values for both metals and Sc were based on the Upper Continental Crust (UCC) metals composition, as reported by McLennan [42].

The degree of sediment contamination was further evaluated using the Geoaccumulation Index (Igeo), calculated according to the formula:

$$\text{Igeo} = \text{Log}_2 [(C_n) / 1.5 (B_n)]$$

where C_n is the concentration of metal « n » in the sediment, B_n is the corresponding background concentration, and the constant 1.5 is used as a safety factor to account for lithogenic variations in natural background values [43].

2.6 Determination of Ce, Eu and Tm anomalies

The anomalies of cerium (Ce), europium (Eu), and thulium (Tm) in the studied sediments were calculated following the standard approach based on NASC-normalized REE concentrations. These anomalies quantify deviations from the expected REE pattern, assuming a smooth, log-linear trend across neighboring elements [44–47]:

The Ce, Eu and Tm anomalies were calculated using the following formulas [48, 49]:

$$\frac{Ce}{Ce^*} = \frac{Ce_N}{\sqrt{La_N \times Pr_N}}; \frac{Eu}{Eu^*} = \frac{Eu_N}{\sqrt{Sm_N \times Gd_N}}; \frac{Tm}{Tm^*} = \frac{Tm_N}{\sqrt{Er_N \times Yb_N}}$$

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 Tm/Tm^* 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 [50, 51].

2.7 Ecological risk assessment

To quantify the contamination levels of individual trace elements in sediment samples, the Contamination Factor (CF) was used, and it is defined as follows:

$$CF = (C_n/B_n)$$

where C_n is the concentration of the trace element « n » in the sample and B_n is its background concentration (UCC value) [52, 53].

The overall load of polymetallic contamination was evaluated using the Contamination Degree (CD), computed as:

$$CD = \sum CF_i$$

where CF_i is the contamination factor for metal i. For computing the CD value the following trace elements were considered: Hg, Cd, As, Co, Cu, Pb, Cr, and Zn [54].

To assess the ecological impact of individual metals, the Ecological Risk Index (Eri) was applied. This index incorporates both the contamination level and the toxicological significance of each metal [55], and it was calculated as:

$$Eri = Tr_i \times CF_i$$

where Tr_i is the toxic-response factor for each metal: Hg (40), Cd (30), As (10), Co (5), Cu (5), Pb (5), Cr (2), and Zn (1) [56].

The cumulative ecological threat posed by all investigated metals was assessed through computation of the Potential Ecological Risk Index (RI), which sums the individual risk indices:

$$RI = \sum Eri$$

where Eri is the ecological risk index for the metal « i ». This parameter reflects the combined effects of metal toxicity, concentration, and ecological sensitivity of the receiving environment [57].

Additionally, the ecotoxicological risk of metal contamination of sediments was evaluated by comparing the measured metal concentrations with the Sediment Quality Guidelines (SQG) and Probable Effect Levels (PEL) established for the protection of aquatic life, as recommended by Canadian environmental authorities [58].

2.8 Data analysis

Heavy metal concentrations were determined in triplicate for each sample, and the results were averaged to ensure 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 scikit-learn (Python v3.10) after standardizing variables (zero mean, unit variance). Results were visualized with matplotlib and seaborn to assess sample clustering and variable contributions.

3 Results and discussion

3.1 Physicochemical characteristics of sediment samples

The physicochemical characteristics of the sediment samples, including total organic matter (OM), calcium carbonate (CaCO₃), grain size distribution, and average particle size, are summarized in Table 2.

Organic matter (OM) ranged from 1.75% (OT01Jetée) to 10.30% on dry weight basis (R04To), with higher values near industrial and estuarine sites. Elevated OM at sites such as R04To may reflect both natural inputs and hydrocarbon-derived residues from oil exploitation (see Table 1). OM is known to act as a natural scavenger for metals, forming complexes with cationic species such as Cu, Zn, Pb, and Co, thereby reducing their mobility [59]. Nevertheless, these values are comparable to those reported by Mabidi et al. [60] for sediment samples collected along the Congo River at the Maluku, Gombe, and Kinsuka sites, but lower than those observed in the Mai-Ndombe River, a location with limited anthropogenic influence. This indicates that the OM levels recorded in

Table 2 Organic matter (OM), calcium carbonate (CaCO₃), particle size classes and particle mean grain size in the sediment samples

Sample	OM (%)	CaCO ₃ (%)	Clay (%)	Silt (%)	Sand (%)	Mean grain size (µm)
OT01Jetée	1.75	0.26	0.515	11.565	87.92	127.6
OT02Sewer	2.19	0.30	0.488	14.282	85.23	114.7
OT03P	4.53	2.36	1.47	16.92	81.61	104.3
OT04Incat	4.20	4.06	1.33	13.01	85.66	135.4
OT05Yatch	4.05	9.14	0.678	10.262	89.06	189.2
OT06PK	4.66	1.44	0.730	19.94	79.33	132.6
R01RTh	2.54	1.72	0.742	9.328	89.93	209.9
R02RM	3.83	1.40	0.825	21.035	78.14	132.6
R03RK	3.47	1.29	0.413	11.347	88.24	120.8
R04To	10.30	2.75	0.754	18.476	80.77	136.5
FC01Banana	3.13	1.84	1.05	10.45	88.5	149.7
FC02BY	3.22	1.76	0.331	10.029	89.64	127.6

the present study may primarily originate also from natural sources, and are not solely attributable to anthropogenic discharges.

The calcium carbonate (CaCO_3) content (in % dry weight) also varied significantly across sites, ranging from 0.26% at OT01Jetée to 9.14% at OT05Yatch. A significant positive correlation was observed between OM and CaCO_3 contents ($R^2 = 0.622$, $p < 0.05$, $n = 12$), suggesting their co-accumulation. This relationship may be explained by organic carbon stabilization through complexation with Ca^{2+} ions, or by co-precipitation under conditions favorable to carbonate formation [61]. In petroleum-impacted systems, this mechanism may increase retention of metals associated with hydrocarbon residues, providing a partial natural attenuation process.

In terms of granulometry, all samples were predominantly composed of sand, with proportions ranging from 78.14% (R02RM) to 89.93% (R01RTh), consistent with previous observations in coastal estuarine systems [62, 63]. Silt and clay fractions, which ranged from 9.33% (R01RTh) to 21.04% (R02RM) and 0.33% (FC02BY) to 1.47% (OT03P), respectively, are minor but play a disproportionate role in trace element retention due to their high surface area and cation exchange capacity [61, 64]. According to the descriptive terminology defined by the GRADISTAT program [35], the sediment samples were mainly classified as very fine to fine sand.

3.2 Metal and rare earth element concentrations in surface sediments

Concentrations of the fourteen trace elements analyzed in sediment samples are shown in Table 3. The following concentration ranges were observed across the sampling points (in parentheses): 110.24 (OT06PK)–314.90 (R04RTo) for Ti; 8.74 (OT02Sewer)–13.23 (R02RM) for V; 0.06 (OT01Jetée)–20.45 (R04RTo) for Co; 0.30 (OT02Sewer)–5.19 (OT04Incat) for Ni; 0.03 (OT04Incat)–0.12 (R04RTo) for Se; 0.89 (OT02Sewer)–3.66 (OT03P) for Ba; and 0.03 (OT01Jetée)–0.17 (R04RTo) for Se. Overall, these results for the Muanda region fall within the range of those reported by Suami et al. [29] in fluvial, estuarine, and marine sediments from the Atlantic coast of the Democratic Republic of the Congo (Table 3) and demonstrate the consistency of both studies in the assessment of current levels of metals in sediments.

Compared to the values established by the Sediment Quality Guidelines (SQGs) for protection of aquatic life, almost all sediment samples from the Muanda area displayed concentrations exceeding the SQG limits, except for Cu in samples OT01Jetée and OT02Sewer, and Pb in sample OT06PK. The concentrations of As, Cd, and Hg were below the SQG thresholds.

Regarding the potential toxicity of sediments to aquatic biota, the sediment samples exhibited concentrations above the Probable Effect Levels (PELs) for Cr, Zn, and Pb in at least one sample, with maximum values of $253.58 \text{ mg kg}^{-1}$, $523.61 \text{ mg kg}^{-1}$, and 311.2 mg kg^{-1} , respectively (Table 3 and Fig. 3). Therefore, the elevated concentrations of these metals in the sediments pose a threat to aquatic life and may compromise the health of the ecosystem.

The spatial distribution of metal concentrations highlighted hotspots in the Yacht-SOCIR-Perenco estuarine area (OT03P, OT04Incat, OT05Yatch), consistent with their proximity to oil terminals, crude oil transfer points, and refinery discharge zones (Table 1). The observed pattern aligns well with global reports linking hydrocarbon-related activities to elevated trace metals in sediments [64–66]. Cr and Pb enrichments

Table 3 Metal concentrations (mg kg^{-1} dry weight sediment) in surface sediments from Muanda aquatic system

Sample Label	Concentration (mg kg^{-1})												
	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Ba	Cd	Pb	Hg
OT01Jettee	258.23	8.96	163.00	0.06	0.39	0.39	523.61	0.14	0.10	1.05	0.00	146.96	0.03
OT02Sewer	269.31	8.74	175.17	0.08	0.30	0.22	465.11	0.19	0.09	0.89	0.00	140.20	0.03
OT03P	192.34	11.74	112.76	1.09	2.71	99.74	477.65	1.03	0.07	3.66	0.02	184.07	0.11
OT04Incat	186.26	11.62	137.84	1.59	5.19	165.12	486.71	1.23	0.03	3.58	0.03	206.55	0.08
OT05Yatch	314.90	11.64	194.41	2.38	4.21	148.14	426.43	1.38	0.05	3.64	0.05	215.42	0.08
OT06PK	110.24	11.83	62.00	0.25	0.57	61.41	310.39	0.25	0.10	1.29	0.01	11.21	0.12
R01RTh	255.67	11.38	253.58	0.99	4.01	104.45	291.18	0.96	0.09	2.11	0.05	311.20	0.08
R02RM	112.68	13.23	84.37	0.29	0.65	51.80	315.39	0.49	0.08	1.66	0.01	71.48	0.14
R03RK	118.85	11.37	80.75	0.39	0.81	63.57	312.89	0.26	0.10	2.47	0.02	42.94	0.10
R04RTo	114.03	12.51	120.70	20.45	1.07	150.81	337.35	0.49	0.12	2.89	0.02	82.98	0.17
FC01Banana	203.86	11.47	133.27	1.60	4.78	138.10	427.57	0.91	0.04	2.75	0.02	160.04	0.08
FC02BY	110.96	11.01	80.38	0.31	0.86	63.10	313.01	0.23	0.10	1.49	0.01	62.38	0.07
Suami et al. [29]	–	–	186.64	17.73	29.93	216.84	686.79	23.68	–	–	0.30	125.12	10.36
STSD-1	–	47	28	14	18	36	165	17	–	–	0.8	34	–
Ref. values	–	47.08	27.93	12.96	17.77	36.39	162.58	18.11	0.59	28.27	0.74	35.24	0.63
Det. values	–	–	–	–	–	–	–	–	–	–	–	–	–
SRM 2702	–	–	–	–	–	–	–	–	–	–	–	–	–
Ref. values	–	–	–	–	–	–	–	–	–	–	–	–	–
Det. values	–	–	–	–	–	–	–	–	–	–	–	–	–
SQG	–	–	37.3	–	–	35.7	123.0	18.11	–	–	0.60	35.0	0.17
PEL	–	–	90.00	–	–	197.0	315.0	17	–	–	3.50	91.3	0.49

In bold, values of the trace element's concentration high than the recommended probable effect concentration according to International Sediment Quality Guidelines (SQG) for the Protection of Aquatic Life recommendation [58] adopted by Canada; PEL—probable effect levels (sediment dry weight)

may originate from corrosion of drilling and transfer infrastructure, whereas Zn and Cu could derive from lubricant residues and refinery effluents [67, 68]

The concentrations of fourteen rare earth elements (REEs), namely La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, plus thorium (Th) and uranium (U) determined in sediment samples are shown in Table 4. The low REE concentrations in sediment samples were not surprising considering that most of the sediment material was sand (silica) and, thus, REE concentrations in this material were significantly lower than those reported for the Post-Archean Average Australian Shale (PAAS) [69] and the North American Shale Composite (NASC) [70]. The total REE concentrations in sediments from the study area ranged from 3.28 to 6.72 mg·kg⁻¹, which is substantially lower than the values reported for surface soils and sediments from other regions of the DR Congo, such as Lubumbashi River and Tshamilemba Canal which ranged from 66.3 to 219.7 mg·kg⁻¹ [43]. The concentration of REEs in sediments seems to be influenced by grain size. Fine-grained fractions, such as clays and silts (<63 µm), generally exhibit higher ΣREE values compared to coarser, sandy fractions. This trend is primarily due to the greater surface area and adsorption capacity of fine particles, which preferentially bind REE-bearing minerals, Fe–Mn oxides, and OM. In contrast, sandy sediments, dominated by quartz and feldspar, typically displayed lower ΣREE [71, 72].

Similarly, the concentrations of primordial radionuclides thorium and uranium in sediments, ranging from 0.18 to 0.48 mg·kg⁻¹ and from 0.04 to 0.34 mg·kg⁻¹ respectively, were lower than the worldwide Th and U average values in soils, 5 and 1 mg·kg⁻¹ respectively [73]. Concentrations of Th and U in the Muanda region were also considerably lower than those reported in sediments from the Ulindi River in DR Congo, where those primordial radionuclides occur in association with gold [74]. In the Ulindi River, Th and U concentrations ranged from 10.3 to 526.3 mg·kg⁻¹ and from 2.37 to 123.52 mg·kg⁻¹, respectively, much higher than worldwide average values and were considered as susceptible to originate a significant radiation exposure of human beings, which is not the case in Muanda.

3.3 Determination of Ce, Eu and Tm anomalies

The shale-normalized REE patterns of all studied sediment samples are presented in Fig. 4, normalized to NASC, which allows a direct comparison of relative abundances across the lanthanide series. To further quantify deviations from the expected smooth REE trends, the anomalies of Ce, Eu, and Tm were calculated for each sample and are summarized in Table 3. These tables provide a comprehensive overview of both the overall REE distribution and the specific enrichments or depletions of Ce, Eu, and Tm, serving as a basis for the subsequent interpretation of geochemical and redox controls in the sedimentary environment (Fig. 5).

Overall, Ce exhibited moderate negative anomalies ($Ce/Ce^* \approx 0.91\text{--}0.93$) (Table 5), consistent with oxic conditions in the sedimentary environment [75]. Eu anomalies were slightly negative on average ($Eu/Eu^* \approx 0.7\text{--}1.17$), reflecting relative plagioclase depletion with some local variability [76]. Tm anomalies showed unrealistic values ($Tm/Tm^* = 0$ or > 3) and, therefore, were considered non-robust, likely due to analytical artifacts [77].

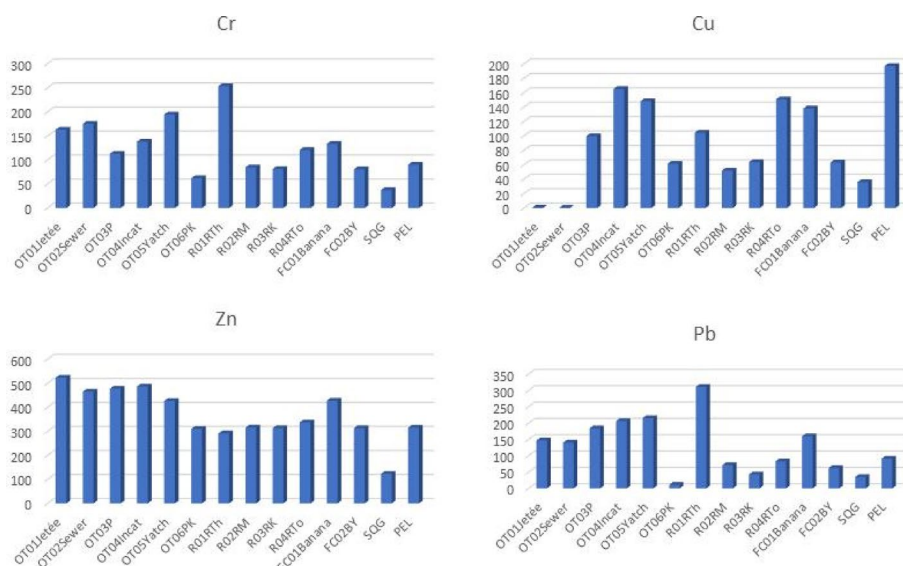


Fig. 3 Histogram comparing Cr, Cu, Zn, and Pb concentrations in the samples with SQG and PEL values

3.4 Assessment of pollution by metals and ecological risk parameters

The Geoaccumulation Index (Igeo) and Enrichment Factor (EF) indices were calculated to differentiate metal and metalloid concentrations of geogenic origin from those of anthropogenic sources and to classify pollution levels and the degree of elemental enrichment in sediment samples [40]. The calculated Igeo and EF values are presented in Table 5. All sediment samples did fall into class 0 ($I_{geo} \leq 0$), indicating that they were mostly unpolluted with respect to Ti, V, Co, Ni, As, Se, Ba, Cd, Sc, and Hg. A few samples ranked in class 1 ($0 < I_{geo} < 1$) and can be classified as unpolluted to moderately polluted, and in class 2 ($1 < I_{geo} < 2$) classified as moderately polluted, and in class 3 ($2 < I_{geo} < 3$) classified as moderately to heavily polluted and displayed enhanced concentrations of Cr, Cu, Zn, and Pb. One sample (R01RTh) ranked into class 4 ($3 < I_{geo} < 4$), indicating strong pollution by Pb.

The calculated EF values shown in Table 5 revealed no enrichment ($EF < 1$) for Se and Ba in all samples, whereas a minor enrichment to extremely severe enrichment ($EF < 3$) of Ti, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg was observed in several samples. The moderate to heavy pollution for Cr, Cu, Zn, and Pb, confirmed anthropogenic influence. Notably, EF values > 5 for Pb at R01RTh and R04RTo suggested extreme enrichment, likely due to cumulative deposition of contaminants during decades of oil handling and accidental spills, which is consistent with findings in oil-impacted estuaries in the same area indicated by Suami et al. [29]. The observed low enrichment of Ti, V, Co, Ni, As, Se, Ba, Cd, Sc, and Hg, indicated lithogenic origins primarily.

The results for ecological risk parameters, including the Contamination factor (CF), Contamination Degree (CD), Ecological Risk Factor for individual potentially toxic elements (Eri), and potential ecological Risk Index (RI), are shown in Table 6. All samples exhibited low contamination factors ($CF < 1$) for Ti, V, Co, Ni, As, Se, Ba, Cd, Sc, and Hg, while a few samples showed moderate ($1 < CF < 3$), considerable ($3 < CF < 6$), and very high contamination ($CF > 6$) levels for Cr, Cu, Zn, and Pb. Furthermore, the same samples showed Contamination Degrees ranging from moderate ($8 \leq CD < 16$) to high ($16 \leq CD < 32$) and to very high values ($CD \geq 32$) (Table 7).

Table 4 Rare earth element concentrations (mg kg⁻¹ dry weight sediment) in surface sediments from Muanda aquatic system

Sample Label	REEs Concentration (mg.kg ⁻¹)														ΣREEs	Th	U
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
OT01Jetée	1.11	2.14	0.23	0.77	0.13	0.02	0.12	0.01	0.05	0.01	0.02	0.00	0.01	0.00	4.62	0.31	0.04
OT02Sewer	1.08	2.1	0.24	0.81	0.14	0.02	0.11	0.01	0.04	0.01	0.02	0.00	0.01	0.00	4.59	0.37	0.04
OT03P	0.8	1.77	0.21	0.78	0.14	0.03	0.14	0.02	0.09	0.02	0.05	0.01	0.04	0.00	4.1	0.25	0.28
OT04Incat	0.69	1.55	0.18	0.67	0.12	0.03	0.11	0.02	0.08	0.02	0.04	0.00	0.03	0.00	3.54	0.18	0.29
OT05Yatch	0.88	1.85	0.21	0.77	0.14	0.03	0.13	0.02	0.09	0.02	0.05	0.01	0.04	0.00	4.24	0.21	0.27
OT06PK	0.93	2.08	0.26	0.97	0.19	0.04	0.15	0.02	0.1	0.02	0.05	0.00	0.04	0.00	4.85	0.25	0.22
R01RTh	0.94	1.94	0.25	0.84	0.14	0.03	0.14	0.02	0.09	0.02	0.04	0.01	0.04	0.00	4.5	0.28	0.22
R02RM	0.99	2.21	0.28	1.05	0.19	0.04	0.17	0.02	0.1	0.02	0.05	0.01	0.04	0.01	5.18	0.31	0.24
R03RK	1.38	2.84	0.36	1.32	0.26	0.04	0.22	0.03	0.12	0.02	0.06	0.01	0.05	0.01	6.72	0.48	0.16
R04To	1.19	2.7	0.31	1.14	0.21	0.05	0.2	0.03	0.14	0.03	0.08	0.01	0.06	0.01	6.16	0.32	0.34
FC01Banana	0.65	1.42	0.17	0.62	0.12	0.03	0.11	0.01	0.07	0.01	0.04	0.00	0.03	0.00	3.28	0.18	0.24
FC02BY	0.9	1.79	0.23	0.83	0.14	0.02	0.13	0.02	0.08	0.01	0.04	0.00	0.03	0.00	4.22	0.27	0.12
PAAS	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.12	2.85	0.43	184.51		
NASC	32	73	7.9	33	5.7	1.24	5.2	0.85	5.8	1.04	3.4	0.17	3.4	0.5	173.2		

PAAS: Post Archean Average Australian Shale [69]. NASC: North American Shale Composite [70]

Regarding the Ecological Risk Factor for metals (Eri), most samples displayed a low ecological risk for Hg, Cd, As, Co, Cu, Pb, Cr, and Zn, except four samples (OT03P, OT04Incat, OT05Yatch, and R01RTh), which exhibited a moderate ecological risk ($40 < \text{Eri} < 80$). The cumulative ecological risk (RI) remained low across sites, suggesting that, despite elevated metal concentrations, overall ecological threats are mitigated by sediment characteristics (e.g., sand dominance, organic matter stabilization) (Table 8).

These results are consistent with global studies in petroleum-impacted estuarine systems, where metals exhibit localized hotspots with moderate ecological risk, often mitigated by sedimentary buffering and natural attenuation processes [78, 79]

3.5 Statistical correlations and principal component analysis

Spearman correlation analysis revealed several significant positive associations ($p < 0.05$) between organic matter (OM) and trace metals, including OM–V ($R^2 = 0.825$), OM–Co ($R^2 = 0.517$), OM–Cu ($R^2 = 0.510$), OM–Ba ($R^2 = 0.580$), OM–Sc ($R^2 = 0.809$), and OM–Hg ($R^2 = 0.630$). Similarly, CaCO_3 exhibited strong positive correlations with Co ($R^2 = 0.888$), Ni ($R^2 = 0.846$), Cu ($R^2 = 0.888$), As ($R^2 = 0.827$), Ba ($R^2 = 0.846$), Cd ($R^2 = 0.745$), and Hg ($R^2 = 0.725$). The positive relationship between OM and CaCO_3 suggests that organic matter may promote carbonate precipitation or stabilization, thereby enhancing their joint role as scavengers of trace metals [80]. In petroleum-impacted environments, OM likely originates both from natural biological inputs and from hydrocarbon residues, reinforcing its ability to retain metals in association with CaCO_3 [81].

In contrast, a significant negative correlation was observed between OM and Ti ($R^2 = -0.531$), consistent with the lithogenic origin of Ti and its distinct geochemical behavior compared to OM-associated elements. Positive associations among metals such as Cu–Ni, Zn–Pb, and As–Cd point to shared anthropogenic sources [82], particularly petroleum exploitation, refinery discharges, and lubricant residues [29]. Other metals displayed multiple origins, including lithogenic contributions (Ti, Cr, Sc), petroleum-related sources (V, Ni, Cu, Pb), and additional anthropogenic inputs such as agriculture, urban effluents, and maritime traffic (Zn, As, Cd) [83].

The Principal Component Analysis (PCA) provided a multivariate confirmation of these relationships. The first three principal components (PC1, PC2, and PC3) explained 95% of the total variance (72%, 15%, and 8%, respectively). PC1 grouped OM and REEs (Nd, Sm, Gd, Dy, Er, Pr, Tm, Yb, Sc), while showing negative loadings with Ti, Zn, Pb, and Cr, indicating the natural geochemical control of fine-grained, organic-rich sediments enriched in REEs. This finding is consistent with the positive OM–REE correlations from Spearman analysis. PC2 was dominated by anthropogenic metals (Cu, As, Ni, U, Cd) and strongly associated with silt and clay fractions, reflecting localized pollution inputs and their affinity for fine sediments. This corroborates the significant correlations observed among Cu, Ni, As, and Cd, and supports their linkage to petroleum-derived contamination. PC3 highlighted carbonate-related variability, with CaCO_3 and associated metals (Ba, Hg, Cd), confirming the role of carbonate phases as metal scavengers.

Overall, the convergence between correlation analysis and PCA underlined two main controls on sediment geochemistry in the Muanda estuarine system: (i) natural processes, including lithogenic inputs, organic matter accumulation, and carbonate associations, and (ii) anthropogenic influences, primarily from petroleum exploitation, but also supplemented by agriculture, urban discharges, and maritime activities.

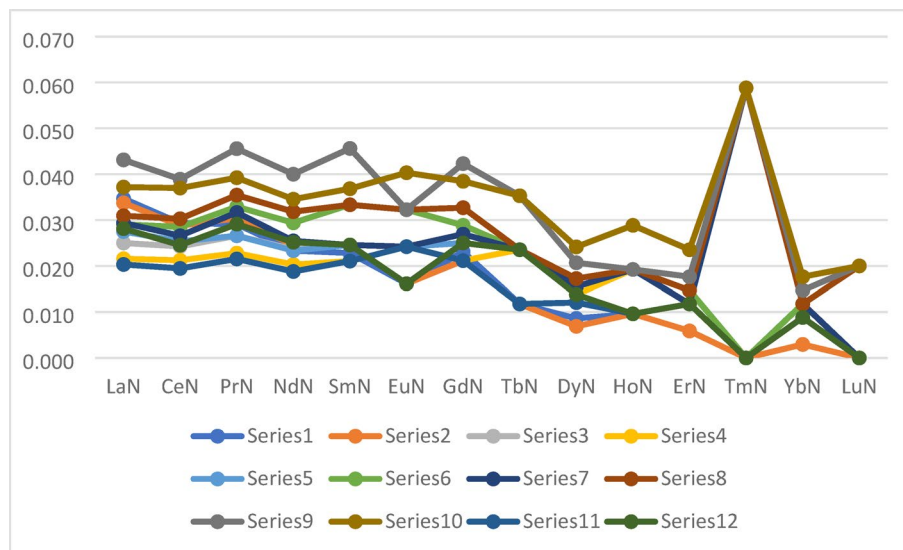


Fig. 4 NASC-normalized rare earth element patterns

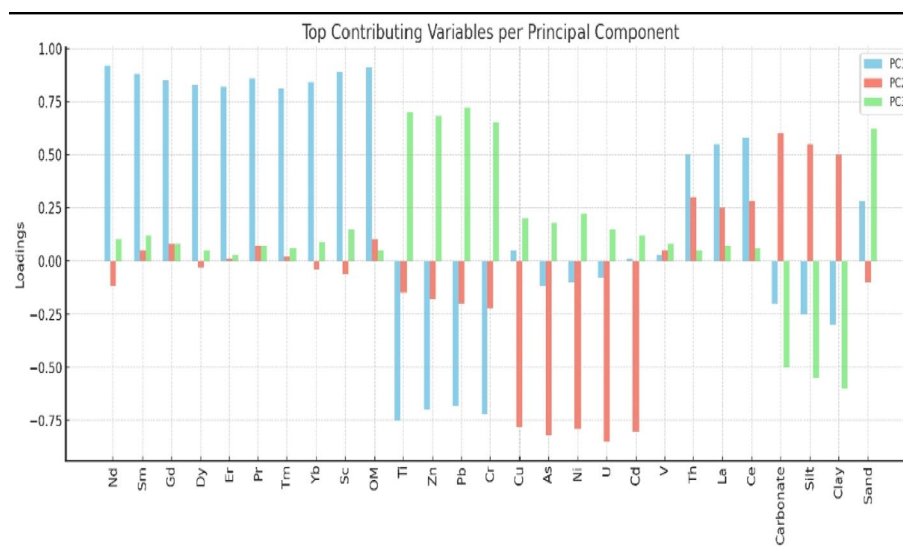


Fig. 5 Top contributing variables for the first three principal components (PC1, PC2, PC3)

4 Conclusions

This study highlighted significant contamination of surface sediments along the Muanda river–estuary–coastal continuum, primarily linked to historical and ongoing oil exploitation. Sediments were mainly sandy but enriched in organic matter (1.75–10.30%) and carbonates (0.26–9.14%), which modulated metals retention. Elevated levels of Zn (up to 523.6 mg·kg⁻¹), Pb (311.2 mg·kg⁻¹), Cr (253.6 mg·kg⁻¹), and Cu (165 mg·kg⁻¹) exceeded Sediment Quality Guidelines (SQGs) and Probable Effect Levels (PELs), particularly in estuarine and industrial zones, confirming strong anthropogenic inputs. Geoaccumulation Index (I_{geo}) values for Pb and Zn reached 2.1–2.5, while enrichment factors (EF) exceeded 5 for Cu and Zn, classifying several sites as moderately to heavily polluted. Contamination factor (CF) values ranged from 2.0 to 5.1, and the ecological risk index

Table 5 Calculated anomaly values

Sample Label	Ce/Ce*	Eu/Eu*	Tm/Tm*
OT01Jetée	0.91	0.7	0.0
OT02Sewer	0.91	0.7	0.0
OT03P	0.92	0.92	4.4
OT04Incat	0.93	1.14	0.0
OT05Yatch	0.91	0.96	4.4
OT06PK	0.92	1.11	0.0
R01RTh	0.92	0.94	4.4
R02RM	0.91	0.98	4.4
R03RK	0.92	0.78	4.1
R04To	0.93	1.04	3.2
FC01Banana	0.92	1.17	0.0
FC02BY	0.93	0.7	0.0

Table 6 Geoaccumulation Index (Igeo) and Enrichment Factor (EF) values calculated for metals and metalloids in soil samples

Sample	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Ba	Cd	Pb	Sc	Hg	Igeo Classification
OT01Jetée	-4.1	-3.3	1.6	-8.0	-6.3	-6.6	2.3	-4.0	-9.6	-9.6	-	2.3	-9.1	-3.4	Igeo ≤ 0 Classe 0 – pratiquement non pollué
OT02Sewer	-4.1	-3.4	1.7	-7.6	-6.6	-7.4	2.1	-3.6	-9.7	-9.9	-	2.2	-9.1	-4.4	0 < Igeo < 1 Classe 1 – non pollué à modérément pollué
OT03P	-4.5	-2.9	1.1	-3.8	-3.5	1.4	2.2	-1.1	-10.1	-7.8	-2.9	2.6	-7.2	-1.7	1 < Igeo < 2 Classe 2 – modérément pollué
OT04Incat	-4.6	-3.0	1.4	-3.2	-2.5	2.1	2.2	-0.9	-11.3	-7.8	-2.3	2.8	-7.7	-1.7	2 < Igeo < 3 Classe 3 – modérément à fortement pollué
OT05Yatch	-3.8	-3.0	1.9	-2.7	-2.8	2.0	2.0	-0.7	-10.6	-7.8	-1.6	2.8	-7.7	-1.9	3 < Igeo < 4 Classe 4 – Fortement pollué
OT06PK	-5.4	-2.9	0.2	-5.9	-5.7	0.7	1.5	-3.2	-9.6	-9.3	-3.9	-1.4	-7.1	-2.9	4 < Igeo < 5 Classe 5 – Fortement à extrêmement pollué
R01RTh	-4.1	-3.0	2.3	-3.9	-2.9	1.5	1.5	-1.2	-9.7	-8.6	-1.6	3.4	-7.7	-3.1	5 < Igeo Classe 6 - Extrêmement pollué
R02RM	-5.3	-2.8	0.7	-5.7	-5.5	0.5	1.6	-2.2	-9.9	-9.0	-3.9	1.3	-6.9	-2.9	
R03RK	-5.2	-3.0	0.6	-5.3	-5.2	0.8	1.6	-3.1	-9.6	-8.4	-2.9	0.5	-7.4	-2.1	
R04To	-5.3	-2.8	1.2	0.4	-4.8	2.0	1.7	-2.2	-9.3	-8.2	-2.9	1.5	-6.6	-1.3	
FC01Banana	-4.5	-3.0	1.3	-3.2	-2.6	1.9	2.0	-1.3	-10.9	-8.2	-2.9	2.4	-7.7	-2.3	
FC02BY	-5.3	-3.0	0.6	-5.6	-5.1	0.8	1.6	-3.3	-9.6	-9.1	-3.9	1.1	-7.9	-1.3	

Sample	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Ba	Cd	Pb	Hg	EF interpretation values
OT01Jetée	31.6	54.8	1707.6	2.2	7.2	5.7	2704.1	34.2	0.7	0.7	0	2694.3	52.4	FE < 1 Pas d'enrichissement
OT02Sewer	32.9	53.4	1835.1	2.9	5.5	3.2	2402	46.4	0.7	0.6	0	2570.3	26.2	FE < 3 enrichissement mineur
OT03P	6.4	19.6	322.2	10.9	13.6	399	672.7	68.7	0.1	0.7	20.4	920.4	46.4	FE 3-5 enrichissement modéré
OT04Incat	8.5	26.6	541.5	21.9	35.7	908.2	942.6	112.8	0.1	0.9	42.1	1420	61.4	FE 5-10 enrichissement modérément sévère
OT05Yatch	14.4	26.7	763.8	32.7	28.9	814.8	825.8	126.5	0.1	0.9	70.2	1481	54	FE 10-25 enrichissement sévère
OT06PK	3.4	18.1	162.4	2.3	2.6	225.2	400.7	15.3	0.2	0.2	9.4	51.4	18	FE 25-50 enrichissement très sévère
R01RTh	11.7	26.1	996.2	13.6	27.6	574.5	563.9	88	0.2	0.5	70.2	2139.5	24.6	FE > 50 enrichissement extrêmement sévère
R02RM	3	17.3	189.4	2.3	2.6	162.8	349	25.7	0.1	0.2	8	280.8	15.4	
R03RK	4.4	20.8	253.8	4.3	4.5	279.7	484.8	19.1	0.2	0.5	22.4	236.2	37.3	
R04To	2.5	13.5	223.1	132.3	3.5	390.3	307.4	21.1	0.2	0.3	13.2	268.5	38.1	
FC01Banana	0	0.1	2.7	0.1	0.2	3.9	4.2	0.4	0	0	0.1	5.6	0.2	
FC02BY	5.8	28.8	360.9	4.9	6.8	396.6	692.8	24.1	0.3	0.4	16	490.1	98.2	

(RI) reached up to 160 at hotspot sites, indicating localized moderate ecological risks for benthic organisms.

In contrast, REE concentrations were very low ($\Sigma\text{REEs} = 3.28\text{--}6.72 \text{ mg}\cdot\text{kg}^{-1}$), far below shale standards ($65\text{--}110 \text{ mg}\cdot\text{kg}^{-1}$), with only slight negative Ce (0.91–0.93) and Eu (0.70–1.17) anomalies, reflecting limited anthropogenic influence.

Spearman correlations and PCA consistently revealed the co-occurrence of OM, CaCO_3 , and REEs, while separating petroleum-related metals (V, Ni, Cu, Pb, Zn, As, Cd) from other sources such as agriculture, industrial effluents, and maritime activities. Overall, the findings highlight petroleum exploitation as the dominant contamination source, with OM and carbonates acting as key natural scavengers regulating metal mobility.

Table 7 CF, CD, Eri and RI values in sediment samples

CF														CD	Eri								
Sample	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Ba	Cd	Pb	Sc		Hg	Sample	Hg	Cd	As	Co	Cu	Pb	C
OT01Jetée	0.1	0.1	4.7	0.0	0.0	0.0	7.4	0.1	0.0	0.0	0.0	7.3	0.0	0.1	19.6	OT01Jetée	5.7	0.0	0.9	0.0	0.1	36.7	
OT02Sewer	0.1	0.1	5.0	0.0	0.0	0.0	6.6	0.1	0.0	0.0	0.0	7.0	0.0	0.1	18.8	OT02Sewer	5.7	0.0	0.9	0.0	0.1	35.1	10
OT03P	0.1	0.2	3.2	0.1	0.1	4.0	6.7	0.7	0.0	0.0	0.2	9.2	0.0	0.5	24.6	OT03P	18.6	6.1	6.9	0.5	19.9	46.0	6
OT04Incat	0.1	0.2	3.9	0.2	0.3	6.6	6.9	0.8	0.0	0.0	0.3	10.3	0.0	0.4	29.5	OT04Incat	17.9	9.2	8.2	0.8	33.0	51.6	7
OT05Yatch	0.1	0.2	5.6	0.2	0.2	5.9	6.0	0.9	0.0	0.0	0.5	10.8	0.0	0.4	30.3	OT05Yatch	15.7	15.3	9.2	1.2	29.6	53.9	1
OT06PK	0.0	0.2	1.8	0.0	0.0	2.5	4.4	0.2	0.0	0.0	0.1	0.6	0.0	0.2	9.6	OT06PK	7.9	3.1	1.7	0.0	12.3	2.8	3
R01RTh	0.1	0.2	7.2	0.1	0.2	4.2	4.1	0.6	0.0	0.0	0.5	15.6	0.0	0.2	32.5	R01RTh	7.1	15.3	6.4	0.5	20.9	77.8	1
R02RM	0.0	0.2	2.4	0.0	0.0	2.1	4.4	0.3	0.0	0.0	0.1	3.6	0.0	0.2	13.2	R02RM	7.9	3.1	3.3	0.1	10.4	17.9	4
R03RK	0.0	0.2	2.3	0.0	0.0	2.5	4.4	0.2	0.0	0.0	0.2	2.1	0.0	0.3	12.2	R03RK	13.6	6.1	1.7	0.2	12.7	10.7	4
R04To	0.0	0.2	3.4	2.0	0.1	6.0	4.8	0.3	0.0	0.0	0.2	4.1	0.0	0.6	21.5	R04To	23.6	6.1	3.3	10.2	30.2	20.7	6
FC01Banana	0.1	0.2	3.8	0.2	0.2	5.5	6.0	0.6	0.0	0.0	0.2	8.0	0.0	0.3	24.6	FC01Banana	12.1	6.1	6.1	0.8	27.6	40.0	7
FC02BY	0.0	0.2	2.3	0.0	0.0	2.5	4.4	0.2	0.0	0.0	0.1	3.1	0.0	0.6	12.8	FC02BY	5.7	3.1	1.5	0.2	12.6	15.6	4

CF classification

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

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

RI classification

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

CD classification

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

Although limited to a single sampling campaign, this research provided the first comprehensive geochemical and ecotoxicological baseline for Muanda. It demonstrated that petroleum exploitation is the main source of trace metal enrichment, creating metal hotspots with measurable ecological risks, while REEs remain largely at background levels. These results are critical for guiding future monitoring, regulatory enforcement, and the design of mitigation strategies to preserve biodiversity and safeguard public health in this oil-producing coastal region.

Table 8 Spearman's rank-order correlation for selected parameters analyzed in the sediments

Variables	CaCO ₃	Grain size	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Ba	Cd	Pb	Sc	Hg
OM	0.622	0.091	− 0.531	0.825	− 0.455	0.517	0.287	0.510	− 0.140	0.452	0.029	0.580	0.331	− 0.182	0.809	0.630
CaCO ₃		0.502	0.014	0.490	0.133	0.888	0.846	0.888	0.105	0.827	− 0.456	0.846	0.745	0.483	0.292	0.725
Grain size			0.312	0.435	0.565	0.607	0.618	− 0.291	0.525	− 0.249	0.288	0.648	0.474	0.138	0.018	
Ti				− 0.462	0.895	0.091	0.147	0.042	0.483	0.214	− 0.406	0.105	0.216	0.734	− 0.592	− 0.420
V					− 0.322	0.448	0.266	0.385	− 0.196	0.501	− 0.118	0.497	0.302	− 0.070	0.902	0.350
Cr						0.196	0.280	0.217	0.343	0.322	− 0.389	0.112	0.371	0.846	− 0.489	− 0.403
Co							0.846	0.937	0.014	0.792	− 0.342	0.874	0.810	0.455	0.385	0.648
Ni								0.909	0.084	0.872	− 0.642	0.818	0.867	0.650	0.118	0.522
Cu									0.035	0.806	− 0.371	0.839	0.864	0.503	0.307	0.620
Zn										0.053	− 0.410	0.175	− 0.194	0.378	− 0.385	− 0.011
As											− 0.704	0.890	0.896	0.683	0.329	0.398
Se												− 0.496	− 0.451	− 0.653	0.147	0.005
Ba													0.799	0.503	0.421	0.658
Cd														0.641	0.248	0.382
Pb															− 0.300	− 0.053
Sc																0.350

Correlation coefficients have been calculated using the log value of the parameter contents to normalize their distribution (statistically significant coefficients (p < 0.05) are in bold)

Author contributions

The conceptualization, methodology and validation were carried out by Gurvitch O. Nsiala, Emmanuel K. Atibu, Emmanuel M. Biey and John Poté. The calculation was carried out by Gurvitch O. Nsiala and Emmanuel K. Atibu. The first draft of the manuscript was written by Gurvitch O. Nsiala and Emmanuel K. Atibu. Fernando P. Carvalho provided consulting and contributed with the writing of final manuscript. Emmanuel M. Biey, and John Poté commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability

All data generated or analysed during this study are included in this published article [and its supplementary information files].

Declarations

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