Heliyon 9 (2023) e18866

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Trace metal geochemistry sediments from the Dibamba River, SW Cameroon: Implication for heavy metal assessment and origin

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ARTICLE INFO

Keywords:
Trace metals
Ecological assessment
Environmental assessment
Dibamba River
Cameroon

ABSTRACT

Sediment quality and trace metal accumulation are two of the most pressing issues facing the aquatic ecosystem around the world. Twenty-four (24) samples of stream sediments were collected along the Dibamba River, in the economic and industrial capital of Cameroon, to judge the trace metal levels in this river flowing near the city of Douala. Trace metal concentrations were disclosed with an ICP-MS on two different grain size fractions (very fine-grained sand and clay). The sediments indicate possible adverse effects of trace metals on surrounding biota as elements like Cr, Cu, Ni, Zn, Pb, and Hg show positive enrichment of greater than 1 when compared to background values from the upper continental crust (UCC) and sediment quality factors such as TEL (threshold effects level), PEL (probable effects level), ERL (effects range low), and ERM (effects range medium) values. The sediments show values of Degree of contamination (DC = 2–4), Pollution load index (PI = 1–2), and individual potential risk (EI = 92–219) indicating moderate pollution and ecological risk. Statistical and multivariate analyses point to both anthropogenic and geogenic sources for the heavy metals in the Dibamba stream sediments. The geogenic origin of the heavy metals is linked to the weathering of gneiss and migmatite found in the river banks. This study found low to mild levels of metal pollution and toxicity in the sediment, but it also warned that the continued development of nearby industries and businesses, the provision of transportation services, and waste disposal activities could result in a gradual outflow and accumulation of metals in the sediment, endangering the aquatic ecosystem.

1. Introduction

Trace metals are natural components in soil, as it contains various types of minerals inherited from their parent rocks. The significant accumulation of trace metals in soils and sediments results in pollution. Heavy metal pollution in the soil is linked to anthropogenic activities such as waste from industries, power production, mining, fisheries, petroleum exploration activities, agriculture, and mining actions. According to Refs. [1,2], and [3], trace metal accumulation in sediments is triggered when companies dump garbage and refuse directly into the water in city environments, as well as indirectly through urban water flow.

Rapid urbanization, industrial development, and changes in land use (animal husbandry and crop production) have resulted in

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https://doi.org/10.1016/j.heliyon.2023.e18866
Received 16 February 2023; Received in revised form 28 July 2023; Accepted 31 July 2023
Available online 2 August 2023

increased pollution, especially near the estuaries, rivers, streams, and coastal areas. According to Ref. [4] these sediments, which act as potential sinks for trace (trace) metals, also serve as a habitat for many aquatic organisms and as such this may affect the aquatic ecosystem by allowing these trace metals to infiltrate the food chain and finally poses danger to humans. Consequently, it is vital to examine the danger of trace metal accumulation in sediments, to judge environmental hazards, and to appraise likely sources of contaminants in riverine areas [5]. The conservation of biodiversity in riverine and estuarine areas is potentially related to aquatic environment control which has a clear connection to the checking of trace metal pollution testing and quality of sediments in rivers. Trace metals distribution in sediment are tools used to evaluate the effect of natural and anthropogenic factors on the biological aquatic ecosystem. According to Ref. [6], trace metal proxies have become powerful tools used to convert chemical data into logical values, which enables the establishment of suitable classifications used in monitoring trace metal enrichment and effect in a particular study area. This information plays a vital role in influencing decision-makers and local authorities to educate locals and inhabitants in such areas about controlling or preventive measures of the river to soil pollution.

The Dibamba area is drained by the Dibamba River which acts as the main collector of other rivers coming from the southern, northern, western, and eastern sectors. This river acts as the main useable source to the inhabitants around the vicinity for drinking, bathing, cooking, and fishing. The inhabitants and population of the neighboring areas feed on the fishes from this river. Smaller tributaries of the Dibamba River are fed with gutter, septic tanks, toilets, and from company activities. The recent building of the Japoma Stadium (2009–2020) on the Eastern outskirts of Douala led to the development of many new businesses and companies in the Dibamba locality. The newly constructed roads and gutter channels are used as pathways for the discharge of waste products from commercial activities into the river. The Dibamba River site stands as one of the most prominent beaches for artisanal sand mining and fishing for the indigenes in that locality. Also, urban run-off from settlements, mechanical workshops, welding workshops, agricultural land activities, and direct municipal waste flushes in this river. Several households found on the shores around this river use it during the rainy season to empty their toilet waste.

This study intends to: (1) investigate the content of selected trace metals (As, Cd, Cr, Cu, Ni, Pb, Hg, and Zn) in riverine sediments, (2) assess the degree of trace metal enrichment and finally, (3) appraise the ecological risks of trace metals. The outcome of this research will offer insights on a national level and act as a reference manual for the Cameroon Environmental Protection Agency to identify rivers with excessive levels of pollution.

2. Methodology

2.1. Site selection, description and geologic setting

This study took place along the Dibamba river, found in the Sanaga-Maritime division located in the littoral region of Cameroon

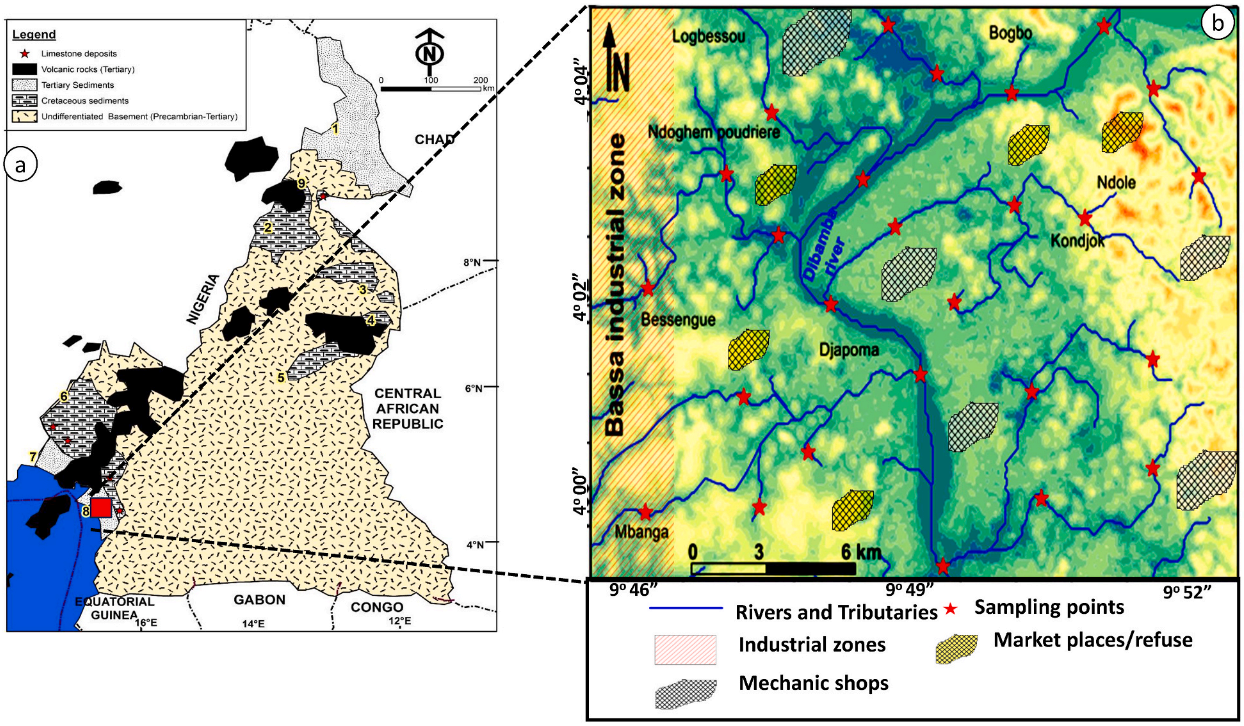

Fig. 1. (a) Map of Cameroon showing the Douala Basin, (b) Sample location map of Dibamba showing the Dibamba main river, tributries and sample location points.

(Fig. 1). This river drains through mangrove vegetation and empties into the Douala estuary towards the south. This rivers length is 150 km with the main tributary being river Ebo stream (ES), flowing South East. According to Ref. [7], this river has a length in the neighborhood of 40 km with a mean discharge of 480 m^3 per second. This river acts as a collector to small tributaries and gutters run-off from the city. This area encloses a lot of garages, local markets where waste is poorly disposed of, and welding garages. Most of the drainage systems in this area of the city empty into the Dibamba River. The study area is chiefly constituted of rocks of sedimentary and metamorphic origins. According to Refs. [8,9], the metamorphic lithologies are made up of Neoproterozoic migmatite, gneisses, and migmatitic gneisses, and migmatites of about 620 and 540 Ma known as the Pan African age. To authors like [10,11], the sedimentary formations are mostly of Cretaceous to Paleogene age consisting of sandstones, clays, marly to calcareous limestones, and alluviums.

2.2. Sampling

Surface sediment samples were collected with a hard rubber plate in shallow waters, and a PVC tube when the water depth is greater than 2 m. The pipes were fit into the sediments using the local gravity method. The chosen sites were suspected to be areas characterized by anthropogenic activities. The collected samples were air-dried, then sealed in plastic bags and transported to the Eawag laboratories in Switzerland. The samples were sieved into different fractions of sand and clay using a Retsch sieving tower. Twenty-four (24) samples collected from the field were used for geochemical analyses.

2.3. Geochemical analyses

The geochemical method used in this work was the inductively coupled plasma-mass spectrometry (ICPMS). Samples were measured with an Agilent 7900 ICP-MS at Eawag for trace and rare earth elements. A multi-element standard (Kraft 32,195) as well as standards for Ti (Baker: 5787) and Ni (Baker: 6936) were used at different concentrations. The digestion of the powdered samples was achieved by adding 6 mL of 65% of HNO_3 dropwise and 18 mL of 30% of HCl to 250 mg sample in a Teflon tube. The samples were heated up to 230 °C in a microwave (ETHOS 1) for 90 min before being diluted with nanopure water. The consistency of the analyses was tested by the blank technique using three certified reference materials (INTL 15–23810, DUP-17-41,709, and BLANK-17-28,360).

Table 1
Trace elements concentration of the Dibamba Stream sediment in ppm and sediment quality guidelines (SQGs) for heavy metals in marine sediments Adapted from Refs. [16,17], and [18].

	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb
Sand								
D1	687	128	451	796	0.6	0.5	0.3	187
D2	268	95	111	337	0.5	0.3	0.2	72
D3	300	99	439	448	0.6	0.4	0.3	37
D4	351	105	261	330	0.5	0.4	0.3	71
D5	455	105	78	330	0.6	0.3	0.1	70
D6	376	110	47	434	0.5	0.2	0.3	31
D7	748	137	311	828	0.5	0.6	0.3	53
D8	522	112	729	121	0.5	0.4	0.3	74
D9	546	109	133	345	0.6	0.3	0.3	34
D10	111	222	308	201	0.6	0.5	0.2	86
D11	462	119	940	203	0.6	0.5	0.2	99
D12	316	105	637	131	0.6	0.3	0.2	70
D13	338	98	168	857	0.6	0.4	0.2	46
D14	412	105	114	322	0.5	0.3	0.2	35
D15	417	96	432	2.5	0.5	0.5	0.2	69
D16	806	343	101	8	0.6	0.2	0.2	111
D17	702	181	222	3	0.7	0.3	0.2	171
D18	396	132	158	801	0.5	0.4	0.2	58
D19	293	102	600	1.5	0.5	0.4	0.3	202
Clay								
D20	355	99	320	323	0.9	0.6	0.4	165
D21	543	109	841	4	0.8	0.5	0.3	65
D22	705	418	254	311	0.8	0.5	0.3	105
D23	523	536	684	1	0.6	0.4	73	99
D24	332	98	111	1	0.8	0.5	0.4	85
BGV	92	47	50	175	15	0.3	0.3	70
SQGs								
UCC	92	47	28	67	4.8	0.08	0.05	17
TEL	52	15.9	18.7	124	7.2	0.68	0.13	30.2
PEL	160	42.8	108	271	41.6	4.2	0.7	112
ERL	81	21	34	150	8.2	1.2	0.15	47
ERM	370	52	270	410	70	9.6	0.71	218

TEL (threshold effects level), PEL (probable effects level), ERL (effects range low), ERM(effects range medium), UCC (Upper continental Crust).

The exactness of this technique is 5%.

2.4. Pollution indices

2.4.1. Sediment quality guidelines (SQGs)

It is wise to evaluate if trace elements in the host sediments pose an ecological threat to aquatic life. Multiple sediment reference standard materials have been used to evaluate the consistency of analysed data. Though many sediment criteria and standards have been created in China and other parts of the world, Cameroon hasn't any suitable sediment quality guidelines. To blend the guideline, the risk potential associated with the observed metals in this work will be judged using standard SQGs proposed by Refs. [12,13] known as TEL (threshold effects level), PEL (probable effects level), ERL (effects range low), and ERM (effects range medium) values and UCC (Upper continental; crust) (Table 1). When a metal's content is below the TEL, detrimental consequences are unlikely; however, when the level is beyond the PEL, harmful effects are common [14,15]. In our study, most background values were taken from the upper continental crust (UCC).

2.4.2. Contamination factors (CF) and degree of contamination (DC)

Coefficient of contamination determines the degree to which trace metals have contaminated the sediment. It employs a single pollution index that measures the pollution of environmental indicators directly. The contamination factor (Cf) for each pollutant was calculated using the formula below proposed by [19].

$$Cf = \frac{Cs}{Cb} \quad \text{(eq1)}$$

Where Cs and Cb represent the mean value of the studied element in the samples and background value, respectively from UCC.

Degree of Contamination (DC) measures how polluted an environment is. It sums up the Cf values for many trace elements while considering separate Cf [19]:

$$\mathrm{DC} = \sum_{i=1}^{n=1} Cf \quad \text{(eq2)}$$

The revised formula for a widespread method of calculating the DC is seen below:

$$\mathrm{mDC} = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad \text{(eq3)}$$

The quantity of element analysed is represented as n and with Eq (2) providing the $C^i f$ values. The widespread method to calculate mDC used the integration of numerous analysed elements.

2.4.3. Pollution load index (PLI)

This index a well-known approach for assessing simultaneous contamination implications [20,21] and it was used to decipher the pollution level of the 08 selected trace metals in our study:

$$\mathrm{PI} = \frac{C_n}{B_n} \quad \text{(eq4)}$$

$$\mathrm{PLI} = \sqrt[8]{PI_{Cr} \times PI_{Cu} \times PI_{zn} \times PI_{Ni} \times PI_{Pb} \times PI_{As} \times PI_{Cd} \times PI_{Hg}} \quad \text{(eq5)}$$

Cn represents the trace metal value and Bn is the trace metal background value.

2.4.4. Potential ecological risk index (RI)

[22] introduced the prospective ecological risk factor RI, which is used in analysing overall contamination levels and environmental effects with toxicology. It is computed using the equation derived from Refs. [22,23]:

$$EI = T_i \times PI_i \quad \text{(eq6)}$$

$$RI = \sum_{i=1}^{n=1} EI \quad \text{(eq7)}$$

With values of Hg, Cd, As, Pb, Cu, Ni, Cr, and Zn being 40, 30, 10, 5,5,5,2 and 1 respectively. The toxicity effect coefficient is Ti and the individual potential risk is called EI. The ecological hazard risk of trace metals in sediments is abbreviated as RI.

3. Results and discussion

3.1. Trace metal distribution in sediments

The trace metals concentration in stream sediments for both sandy and clay fractions from the Dibamba commercial and pre-industrial zone is listed in Table 1. The sediments were grouped into very fine-grained sand and clay fractions. The elemental concentration of the trace metals in the study area shows that Cu is concentrated at the centre and NE section of the study area with the highest concentrations observed at the centre (Fig. 2a). For Zn, four sections are seen concentrated with two points seen in the NW, and one point each in both the SW and SE. The highest point of Zn concentration occurs towards NW and SW (Fig. 2b). Ni is concentrated towards the northeastern part of the study area and occupies a large surface area as compared to Cu and Zn (Fig. 2a,b,c). Cr is concentrated towards the NW and SW sections of the study area with its high points seen in the NE (Fig. 2d). As show a high concentration with its highest point in the SSE (Fig. 2e). Cd concentration is basically in the SSE and SSW of the study area with a large surface area and point of contamination seen in the SSE (Fig. 2f). Pb (Fig. 2g) and Hg (Fig. 2h) show two points of concentration, which are the NNW and SSE with the highest concentration towards NNW. The similarities in the concentration of Pb and Hg (in the same vicinity suggest that both would have originated from the same source. As and Cd show high concentration in the NNE portion of the study area, indicating a similar source for the trace metals with the source of contamination pointing to the same direction. Most of the trace metal concentration found at the centre of the study area may have been transported by smaller tributaries which empty themselves into the main Dibamba River.

The trace metals in this study were compared with those of sediments Guidelines (UCC, TEL, PEL, ERL, and ERM). The upper continental crust was considered as the background concentration for the geogenic origin of the trace metals and anything greater than this baseline is considered as an addition from an external source. The average proportion of the metals in both the very fine-grained sand and the clay fractions show an enrichment in all the metals except for As, which shows a strong negative anomaly indicating no external contribution from the surrounding environmental activities.

Except for As, all the trace metals show concentration above the normal UCC as seen in Fig. 3a indicating their average to moderate enrichment in the study area. Comparing the trace metals under investigation with the SQG shows that Cr, Cu, Zn, Ni, Pb, and Hg are above TEL and ERL (Fig. 3b,d), while only Cr, Cu, Zn and Ni are above the PEL (Fig. 3c), and only Ni is above the ERM (Fig. 3e). Interestingly, As is significantly below each of these potential effects level. The fact that several trace metals are above the PEL indicates that the aquatic ecosystem in this area may be affected by the pollution. Elements below the UCC threshold are of Geogenic

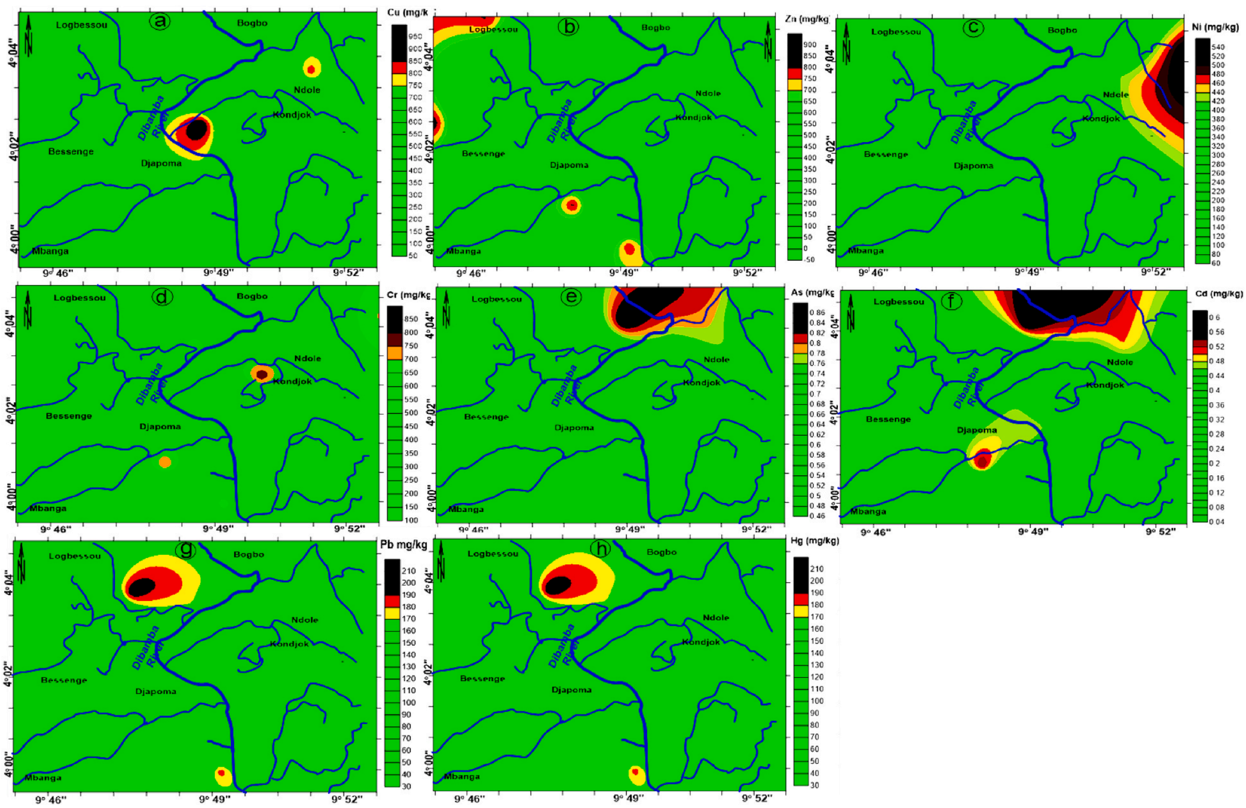

Fig. 2. Heavy metal concentration spatial distribution maps of the study area (a) Cu distribution, (b) Zn distribution, (c) Ni distribution, (d) Cr distribution, (e) As distribution, (f) Cd distribution, (g) Pb distribution, (h) Hg distribution.

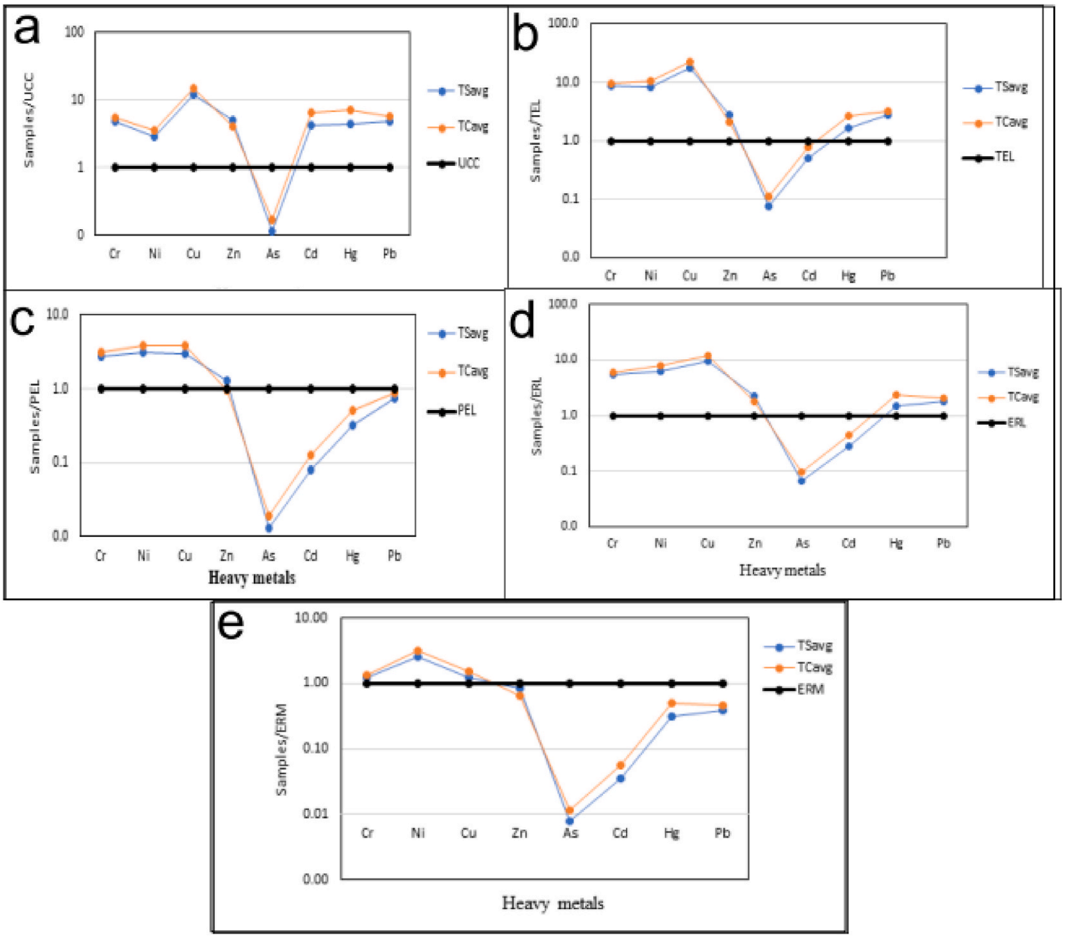

Fig. 3. Heavy metal normalization with SQG (Sediment quality Guide lines) parameters and standards. (a)UCC (Upper continental Crust), (b) TEL (threshold effects level), (c)PEL (probable effects level), ERL (effects range low), (d) ERM(effects range medium). ***TSav(Average total sand), TCav (Average total clay)***.

origin. The elements above the UCC threshold indicate an addition of anthropogenic activities to their enrichments in the studied sediments as seen in Fig. 3a.

The enrichment of these elements in the sediments indicates mixing of felsic-intermediate sedimentary source rocks and anthropogenic source materials from riverine or industrial effluents by the Dibamba River. The lithology of the river catchment consists mainly of metamorphic and sedimentary rocks [24]. The outcrops along the river are composed of metamorphic rocks comprising gneisses, migmatitic gneisses, and migmatites of the Neoproterozoic Pan-African age. The Dibamba River transports sediments mixed with materials from industries, companies, and commercial activities to the Wouri River and the Atlantic Ocean. A high content of some metals namely; Cr, Ni, Zn, Cd, Hg, and Pb in the Dibamba sediments are above the UCC threshold indicating an anthropogenic input while As below the UCC threshold indicates a geogenic origin.

3.2. Sediments contamination indices

3.2.1. Factor of contamination (CF)

The sediment contamination indices discussed in this work to evaluate the pollution level of the Dibamba River are; contamination factor (CF., ***eq (1)***), degree of contamination (DC., ***eq2***), and pollution load index (PLI., ***eq5***). The factor of contamination determined for sediments gives clear information on the contamination level of the Dibamba stream (Table 3) with the highest point seen at the middle of the study area (Fig. 4f). According to Ref. [25], the CF has been classified using the following expressions: $CF < 1$, $1 \leq CF < 3$, $3 \leq CF < 6$, and $CF \geq 6$, representing low contamination factor; moderate contamination factors; considerable contamination factors; and very high contamination factor respectively. In the very fine-grained sand fractions, As and Hg show low contamination, while Zn, Al, Ni, Pb, and Cd show moderate contamination. Cr shows moderate to considerable contamination (4.9). Cu with a CF value of 7.3 shows a very high contamination. The picture is very similar in the clay fractions. As falls in the low contamination range, while Zn, Al, Ni, Pb, and Cd fall under moderate contamination. Cr shows considerable contamination and Cu, with a CF value of 8, shows a very

Table 2
Correlation matrix of selected heavy metals with Ti and Al.

Clay	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb	Al	Ti
Cr	1.00									
Ni	**0.64**	1.00								
Cu	0.31	0.19	1.00							
Zn	0.21	0.01	−0.46	1.00						
As	−0.36	−0.82	−0.56	0.51	1.00					
Cd	−0.52	−0.80	−0.61	0.55	0.97	1.00				
Hg	0.11	**0.76**	0.44	−0.41	−0.94	−0.83	1.00			
Pb	−0.32	−0.07	−0.39	**0.77**	0.35	0.53	−0.07	1.00		
Al	0.13	**0.70**	−0.20	−0.38	−0.67	−0.63	**0.66**	−0.28	1.00	
Ti	0.38	**0.89**	0.33	0.07	−0.80	−0.69	**0.87**	0.24	0.50	1.00
Sand	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb	Al	Ti
Cr	1.00									
Ni	0.43	1.00								
Cu	−0.08	−0.21	1.00							
Zn	0.07	−0.27	−0.28	1.00						
As	0.36	0.52	0.05	−0.29	1.00					
Cd	−0.03	−0.12	0.55	0.20	−0.20	1.00				
Hg	0.12	−0.15	0.32	0.21	0.06	0.15	1.00			
Pb	0.28	0.27	0.33	−0.30	0.27	0.19	−0.08	1.00		
Al	−0.13	0.03	0.28	−0.07	0.02	0.16	−0.41	−0.07	1.00	
Ti	0.19	0.20	0.37	0.12	0.18	0.35	−0.09	0.46	0.32	1.00

Bold: significant at $P \leq 0.05$ $0 \leq r < 0.5$ = low; $0.5 \leq r < 0.7$ = moderate; $0.7 \leq r < 0.9$ = strong; $0.9 \leq r < 1$ = very strong correlation.

Table 3
Pollution indices: (CF) contamination factor, (DC) degree of contamination, (mDC) average degree of contaminatio and (PLI) pollution load indices.

	Concentration factor (CF)								PLI	DC	mDC
VFS	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb			
D1	7.5	2.7	10.0	4.6	0.0	1.5	1.0	2.7	1.9	31.8	3.5
D2	2.9	2.0	2.5	1.9	0.0	1.1	0.6	1.0	1.0	13.8	1.5
D3	3.3	2.1	9.8	2.6	0.0	1.5	1.0	0.5	1.3	23.6	2.6
D4	3.8	2.2	5.8	1.9	0.0	1.2	1.0	1.0	1.2	18.2	2.0
D5	4.9	2.2	1.7	1.9	0.0	0.8	0.2	1.0	0.9	15.2	1.7
D6	4.1	2.3	1.1	2.5	0.0	0.1	1.2	0.4	0.8	14.2	1.6
D7	8.1	2.9	6.9	4.7	0.0	1.8	1.3	0.8	1.8	30.3	3.4
D8	5.7	2.4	16.2	0.7	0.0	1.5	1.2	1.1	1.5	31.7	3.5
D9	5.9	2.3	3.0	2.0	0.0	0.8	1.2	0.5	1.2	18.9	2.1
D10	1.2	4.7	6.8	1.2	0.0	1.5	0.9	1.2	1.2	19.5	2.2
D11	5.0	2.5	20.9	1.2	0.0	1.5	0.9	1.4	1.7	37.4	4.2
D12	3.4	2.2	14.2	0.8	0.0	0.9	1.0	1.0	1.3	27.2	3.0
D13	3.7	2.1	3.7	4.9	0.0	1.2	0.8	0.7	1.3	20.1	2.2
D14	4.5	2.2	2.5	1.8	0.0	0.9	0.8	0.5	1.2	19.7	2.2
D15	4.5	2.0	9.6	0.0	0.0	1.5	0.6	1.0	0.8	21.9	2.4
D16	8.8	7.3	2.3	0.1	0.0	0.7	0.7	1.6	0.9	23.4	2.6
D17	7.6	3.9	4.9	0.0	0.0	0.8	0.8	2.4	0.9	23.0	2.6
D18	4.3	2.8	3.5	4.6	0.0	1.2	0.7	0.8	1.4	21.6	2.4
D19	3.2	2.2	13.3	0.0	0.0	1.3	1.0	2.9	0.9	27.7	3.1
Clays											
D20	3.9	2.1	7.1	1.9	0.1	2.0	1.6	2.4	1.9	27.0	3.0
D21	5.9	2.3	18.7	0.0	0.1	1.6	1.2	0.9	1.1	37.1	4.1
D22	7.7	8.9	5.6	1.8	0.1	1.7	1.2	1.5	1.9	31.5	3.5
D23	5.7	2.4	11.9	3.9	0.1	1.8	1.6	1.0	1.9	31.0	3.4
D24	3.6	2.1	2.5	0.0	0.1	1.8	1.4	1.2	0.8	17.5	2.0

high contamination.

The degree of contamination (DC) was calculated using eight elements. For sand sediments, the DC values ranged between 15 and 32 with an average of 23 (Table 3). The clay sediments show DC values ranging from 17 to 37 with an average of 27 (Table 3). The DC concentration is seen in two points at the centre of the study area (Fig. 4b). The DC < 12 signifies a low contamination degree while values between 12 and 24 stand for a moderate degree of contamination [25]. The mean values for the two fractions exceed 24 indicating accumulation of trace metals within the studied sediments. According to Refs. [26,27], the DC can be modified by dividing the summation of DC by the number of studied or analysed trace metals (see methodology) to give a new factor denoted as mDC (***eq (3)***). For the sand sediments, the mDC is 1.5–4.0 with a mean value of 3.0 (Table 3). The clay sediments show mDC values ranging from 2.0 to 4.0 with an average of 3.0 (Table 3). Just like the DC, the mDC is seen concentrated in two points at the centre of the study area (Fig. 4c). According to Ref. [28], the mDC, are described as follows: mDC values < 1.5; 1.5 to 2, 2 to 4; 4 to 8; 8 to 16; 16 to 32 and > 32

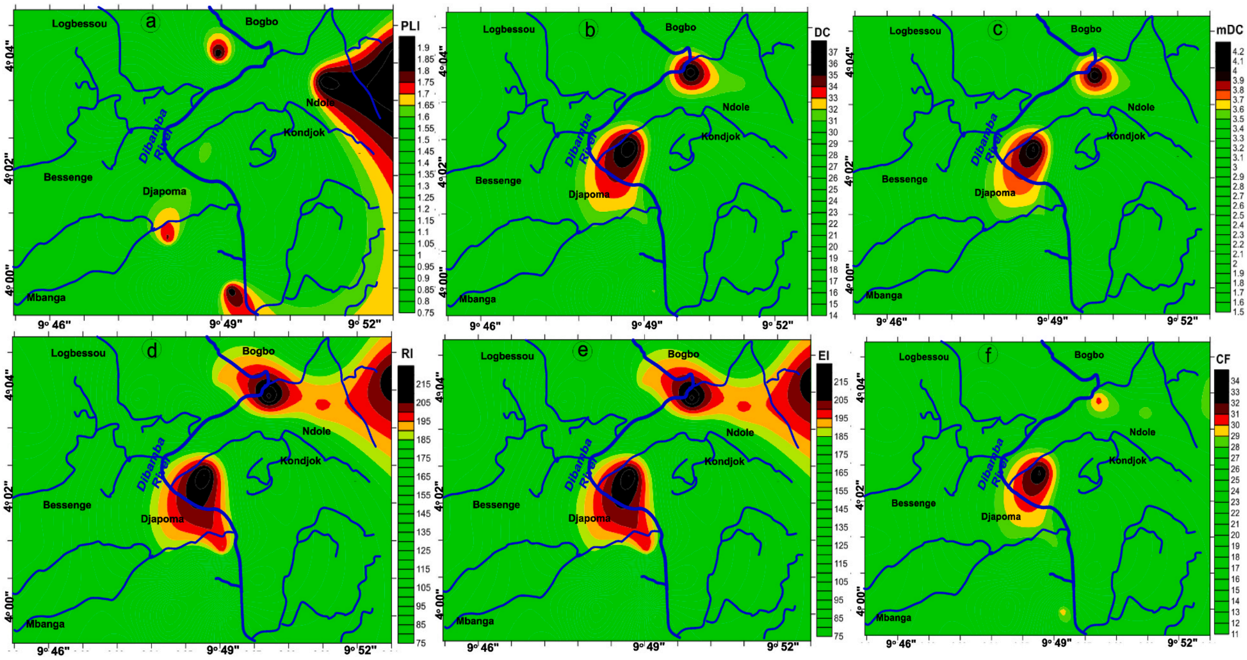

Fig. 4. Spatial distribution maps for indices of pollution in the study area. (a) Pollution load index (PI), (b) Degree of contamination (DC), (c) Average degree of contamination (mDC), (d) probable ecological risk index (RI), (e)ecological risk factor (EI), (f) contamination factor (CF).

corresponds to; no to very small, small grade, modest grade, high grade, very high, enormously high and ultra-high grade respectively. Following the average values of the mDC of the studied fractions, both sediment fraction shows a moderate degree of contamination. Specifically, within a very fine-grained sand fraction, about 20% of the samples fall within the low contamination while 80% falls within the moderate contamination level. A nearly similar picture emerges for the clay fraction as 90% of the samples show moderate contamination level while only 10% show low contamination.

The calculated PLI from PI (***eq (4)***) from the two different fractions from the Dibamba River is listed in Table 3. PLI shows a high concentration in the eastern part of the study area (Fig. 4a). Conferring to Ref. [29], PLI can be grouped into 6 categories as follows;

Table 4
Ecological risk assessment (EI.), and potential ecological risk index (RI).

	EI								
Sand	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb	**RI**
D1	14.9	13.7	50.2	4.6	0.4	44.7	41.1	13.4	182.9
D2	5.8	10.1	12.3	1.9	0.3	33.7	23.5	5.2	92.9
D3	6.5	10.5	48.8	2.6	0.4	43.7	39.5	2.6	154.6
D4	7.6	11.2	29.0	1.9	0.4	34.7	41.1	5.1	130.9
D5	9.9	11.1	8.6	1.9	0.4	24.7	9.1	5.0	70.7
D6	8.2	11.7	5.3	2.5	0.4	2.7	47.5	2.2	80.4
D7	16.3	14.6	34.6	4.7	0.4	54.7	50.7	3.8	179.7
D8	11.3	11.9	81.0	0.7	0.4	43.7	47.5	5.3	201.8
D9	11.9	11.6	14.8	2.0	0.4	24.7	49.1	2.4	116.9
D10	2.4	23.6	34.2	1.2	0.4	45.8	34.7	6.2	148.5
D11	10.1	12.7	104.4	1.2	0.4	44.7	36.3	7.1	216.8
D12	6.9	11.2	70.8	0.8	0.4	25.8	37.9	5.0	158.7
D13	7.4	10.4	18.7	4.9	0.4	34.7	33.1	3.3	112.9
D14	9.0	11.1	12.7	1.8	0.3	25.8	31.5	2.5	94.8
D15	9.1	10.2	48.0	0.0	0.3	44.8	25.1	5.0	142.4
D16	17.5	36.5	11.3	0.1	0.4	21.6	26.7	7.9	122.0
D17	15.3	19.3	24.7	0.0	0.4	24.8	29.9	12.2	126.6
D18	8.6	14.0	17.6	4.6	0.3	35.7	28.3	4.1	113.2
D19	6.4	10.9	66.6	0.0	0.3	38.7	39.5	14.5	176.9
Clays									
D20	7.7	10.6	35.6	1.9	0.6	58.7	63.5	11.8	190.3
D21	11.8	11.6	93.4	0.0	0.5	48.7	47.5	4.7	218.2
D22	15.3	44.5	28.2	1.8	0.5	49.7	49.1	7.5	196.6
D23	11.4	11.9	59.5	3.9	0.6	54.7	63.5	5.2	210.7
D24	7.2	10.5	12.4	0.0	0.5	53.7	55.5	6.1	145.9

≤0, 0–1, 1–2, 2–4, 4–8, and 8–16 representing null, small, modest, high, very high and extremely high degree of pollution respectively. For the sand fraction, the values range between 0.78 and 1.85 with an average of 1.31. Specifically, out of the 19 samples analysed for the sand fraction, 72% of the samples show values ranging between 1.2 and 1.9, while 28% of the samples show values between 0.8 and 0.9. For the clay fraction, generally, the values are between 0.8 and 1.9 with a mean value of 1.4. About 90% of samples within this fraction have PLI values ranging between 1.1 and 1.9, and 10% represent one sample display value of 0.8. Following the above classification of PLI, a smaller proportion (28% and 10%) of the studied samples for both fractions fall in the low degree of pollution domain, while the greater proportion (72% and 80%) falls within the domain of moderate pollution degree.

3.3. Ecological risk assessment

Beyond measuring trace metal concentrations, an EI (***eq (6)***) assessment is necessary to understand their probable negative consequences. The results of the individual ecological risk factor (EI., ***eq (6)***) used for 8 elements were summed up to determine the probable ecological risk index (RI., ***eq7***) as seen in Table 4. The highest concentrations for both the EI and RI are seen in different portions of the study area with the high points indicated by a black dot (Fig. 4d&e). For sand sediments, the average EI values of all the trace metals are less than 40 posing no risk at this level. For the clay fraction, Cd and Hg show the highest risks in areas of the river, as they show an average EI value of greater than 40. The high value of EI in the clay fraction may be due to their dominant deposition in low energy (quiet water) depositional environments.

The very fine-grained sand show values of RI ranging between 70 and 216 with an average of 145 (Table 4). The clay fraction sediments show values ranging between 145 and 218 with an average of 192.3 (Table 4). From 19 sand sediments samples analysed, 32% show values of RI greater than 150, and 68% of the samples show values lower than 150. From 06 clay samples analysed, 90% show values of RI greater than 150, and 10% show values of RI lower than 150 [19]. proposed a classification for the description of the RI based on the calculated values. To them, RI < 150 denotes small ecological risk, RI (150 and 300) indicates modest ecological risk, RI (300 and 600) indicates considerable ecological risk, and RI (≥600) signpost very high ecological risk. Following the above groupings made by Ref. [19] in corroboration to the present study, both the very fine-grained sand and clay sediments fall within the categories of low ecological risk, and moderate ecological risk with a high (90%) clay fraction sediments falling with the moderate ecological risk. The ecological effects of the heavy metals within the Dibamba river are noticed from the disappearance of plants around the banks of the river in areas where commercial drainage is active.

3.4. Multivariate statistical analyses and heavy metal origin

The geochemical elements used in this work from the Pearson correlation matrix show substantial relationships at a rate of $p<0.05$ (Table 2). In this work, Aluminium and Ti are considered to be elements from geogenic origins. Aluminium and Ti moderately correlate in the clay fraction (0.5) and correlate poorly for sand (0.3) fractions indicating they were derived from the same geogenic source for the clay fractions and may show variable origin for the sand fractions. The low correlation of Al and Ti in the sand fraction may be a result of the unstable nature of Al within a sedimentary system as this is proven by the high weathering rate in the Dibamba sand by Ref. [24].

For the clay fractions, the trace metal shows strong correlations for elements Cr and Ni (0.64), Zn and Pb (0.76), Ni and Hg (0.75), As and Cd (0.96) while correlations of 0.5 are seen in Zn and Cd, Pb and Cd. Ti and Al show significant correlation with Ni (0.89 and 0.70 respectively) and Hg (0.87 and 0.66 respectively). The PCA analyses for the clay fractions show the heavy metals falling in 03 different quadrants (Fig. 5a.) with As, Cd, Pb, and Zn in quadrant 2, Hg, Ni, and Cr in quadrant 3 alongside Al and Ti and only Cu falls in quadrant 4. The cluster (CL) analyses show trace elements such as Zn, Pb, As, and Cd on CL2 while Cr, Cu, Ni, Ti, Hg, and Al on the cluster CL1 (Fig. 5b). The CL1 shows that the heavy metals Cr, Cu, Ni, and Hg may have derived from weathering of the source area while the CL2 indicates anthropogenic influence. The weathering of the source area which may have resulted in the CL1 elements is reported in Ref. [24] while the anthropogenic sources may have resulted from commercial waste including mechanic workshops and companies. Though Cr, Cu, and Hg fall within the geogenic Cluster, one cannot eliminate the minor contribution of anthropogenic effect to their concentration in the clay fraction of the sediments.

For the sand fractions, significant correlations above 0.5 are seen in Ni and As, Cu and Cd. Same like in the clay fraction, the PCA analyses show the metals falling within the 03 quadrants, with Zn and Hg in quadrant 2, Cd, Cu, and Pb couple with Al and Ti in quadrant 3, while As, Cr, and Ni in quadrant 4 (Fig. 5c). The cluster analyses show trace elements such as Zn, and Hg on CL2 while all the other elements alongside Ti and Al fall on cluster CL1 (Fig. 5d). The CL2 cluster of Zn and Hg are derived from anthropogenic activities such as the discharge of company's waste such as AZUR (soap making company), discharge from local mechanic shops and Artisanal sand mining. Cluster 1 (CL1) shows Pb and Ti on a subcluster signifying a geogenic origin. The other elements in cluster 1 such as Cr, Ni, As, Cu, and Cd were derived from both anthropogenic and geogenic sources. Their presence in the same main cluster 1, proves that at least part of the concentrations logged in the sediments would have a lithogenic origin. The lithogenic origin of the cluster 1 elements are linked to the weathering of the gneiss and migmatites found in the banks of the Dibamba River. Studies published by Ref. [30] have shown that rocks enclose a small portion of heavy metals and are found in the interstices between major elements. According to Ref. [31], heavy metals concentration in sediments is a result of weathering of parent rocks and contribution from external sources. Most of the heavy metal in the Dibamba sediments comes chiefly from industrial activities, mineral fertilizers, especially phosphate fertilizers, where they are present as impurities from septic tanks, metal waste from mechanic workshops, batteries waste from households, and insecticides from farms.

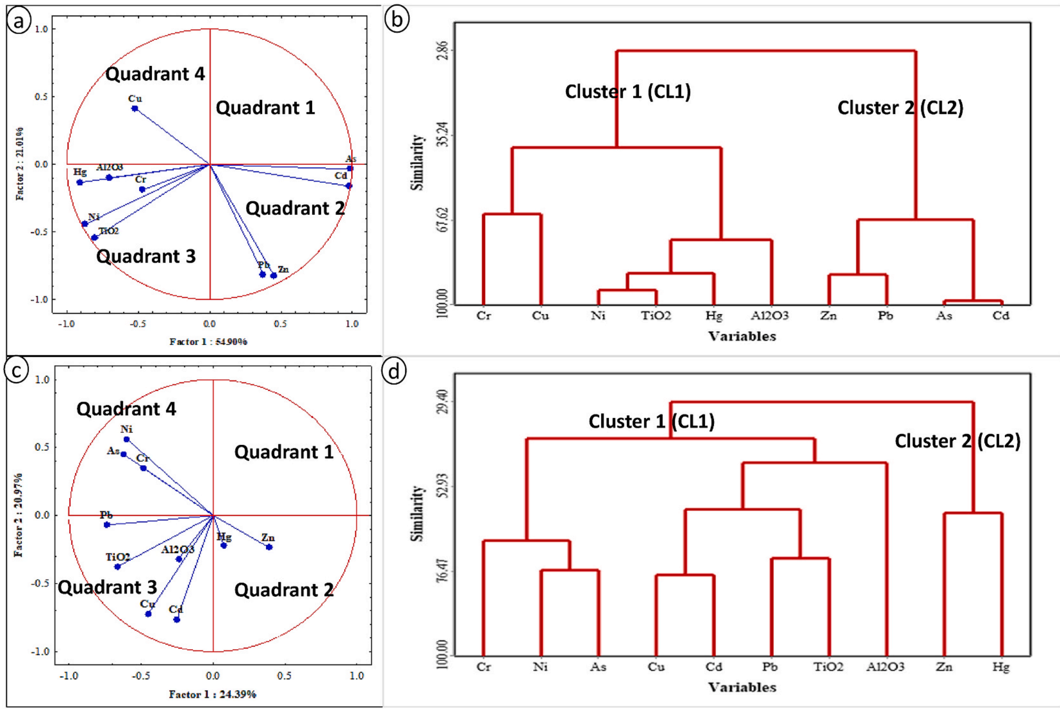

Fig. 5. Principal component analysis classifying trace elements in the Dibambariver (a) Clay fraction, (c) sand fraction and Dendogramof the hierarchical ascending cluster (b) clay fraction, (d) sand fraction.

4. Conclusion

An ICP-MS was used to quantify the trace metal content of sediment samples taken from the Dibamba River, and different indices were used to assess the quality and level of contamination. As had the highest median concentration of all the observed trace metals in all the sampling locations. While Cd, As, and Hg displayed low to moderate contamination, Cr, Cu, Zn, Pb, and Cd displayed extremely high enrichment. The amount of trace metals in the studied sediment was normalized to the SQG value, which suggested possible negative impacts on aquatic species. As, Cr, Cu, Zn, Ni, and Pb had low to moderate ecological levels based on their EI values. In general, low to moderate contamination was suggested by the results of the contamination indices, sediment quality, and toxicity evaluation related to trace metals. The trace metals in the Dibamba sediments were derived from geogenic and anthropogenic sources. Despite this, there is a chance that the concentration of trace metals in the sediment will gradually rise. The continual monitoring of trace metals in the sediment along the shore in the study region is suggested for the preservation of other aquatic animals, the preservation and protection of faunal and floral species, and especially endo-faunal species or organisms that live in sediments.

Author contribution statement

Bokanda Ekoko Eric: Mary Ewokolo Molua Mbua Etutu: Amaya Adama: BISSE Salomon Bertrant: ANYEKU Njeck Rexon: Mokake Fedelis Esue: Emmanuel Eseya Mengu: Conceived; And designed the experiments; Performed the experiments; Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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