Research

# Distribution, source apportionment and ecological risk assessment of heavy metals in Limbe River sediments, Atlantic Coast, Cameroon Volcanic Line

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# Abstract

The objective of this research was to assess sediments contamination, provenance and metal pollution using single and complex pollution indicators. Limbe River sediment samples were analysed using Inductively Coupled Plasma—Mass Spectrometry. The Limbe River sediments exhibit high content in Fe<sub>2</sub>O<sub>3</sub> sourced from haematization of basaltic rocks. The concentration of Cd, Co, Cr, Mn, Ni, Pb, Sn, Sr, V and Zn exceed upper continental crust and local baseline values for heavy metals. Correlation matrix analysis indicates the presence of common input sources and similar geochemical characteristics of heavy metals. Contamination factor (CF: 0.01–10.34), contamination degree (C<sub>deci</sub>: 14.91–36.57), pollution load index (PLI: 0.84–1.77), and nemerow integrated pollution index (NIPI: 0.2–1.7) indicates significant to high levels of contamination. The enrichment factor (EF: 0-5.67) and geo-accumulation index (Igeo: -7.55-2.59), suggests moderate to significant metal pollution of the Limbe River ecosystem, suggesting potential ecological effects. Modified hazard quotient (mHQ: 0.082-6.35) and toxic risk index (TRI: 10.49-27.43), indicates low to extreme pollution severity and high toxicity risks of heavy metals to the aquatic ecosystem fauna and flora. Primarily anthropogenic activities and secondary lithogenic provenance is attributed to sediments contamination and metals pollution. This study suggests that a greater emphasis should be placed on monitoring various provenances of metals entering the aquatic ecosystem from anthropogenic practices. The study emphasizes the significance of continual protection of aquatic ecosystem and biological resources and adaptive management. The development of reasonable goals for monitoring and remedial programmes can be aided by this data.

Keywords Atlantic Coast · Contaminant · Heavy metals · Sediments · Toxicity

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# 1 Introduction

Heavy metal pollution in coastal areas and cities is a common environmental problem worldwide due to urbanization, industrialization, agricultural activities and domestic practices [1–11]. The prevalence of rivers in cities is not only features of the landscape but are of significant cultural importance and components of urban ecosystems. Rivers provide a range of economic and social benefits, including flood control and drainage, water supplies and sources of recreation, a living ecosystem in their own right. Rivers also are of significance wider ecological ecosystem. However, rivers are under threat, especially from the acceleration of urbanization, rapid population growth, agricultural runoff which has a propensity for large amounts of industrial sewage and domestic wastewater to be discharged into them, resulting in the pollution of rivers with metals [12]. River sediments act as an ultimate receptor of pollutants from anthropogenic practices in many coastal areas and cities, especially in developing countries such as Cameroon [5, 13, 14]. Trace metals contamination of river ecosystems has gained the increased attention of many environmental scientists over the past decades [15-21]. From the findings of these scientists, it can be noted that heavy metals migrate into sediments which play a role of sinks [22–24]. In aquatic ecosystems, heavy metals such as As, Cd, Co, Cu, Pb, Hg and Zn which are listed as priority pollutants by the United States Environmental Protection Agency [25] originate from natural sources including weathering of rocks, erosion, forest fires, volcanic eruptions, and anthropogenic activities like industrial effluents, mining, agricultural practices, domestic activities and atmospheric deposition [24–26]. Therefore, heavy metals are natural constituents of sediments from weathering and erosion of pre-existing rocks, but they can also be derived from anthropogenic sources, and incorporate into sediments as pollutants [27].

Investigations of pollution in aguatic ecosystems have emerged, due to the toxicity of these metals and their accumulation in the food web [28–34]. These metals, also known as potentially toxic elements (PTEs) are not removed from the water as a result of self-purification, and for this reason, they can accumulate in reservoirs by biological and geochemical mechanisms and enter the biological chain. Therefore heavy metals constitute a serious and pressing concern in terms of their pollution in aquatic ecosystems [28, 35]. Due to their non-degradability, toxicity, and resistance to metabolization [36], PTEs in sediments can harm aquatic organisms, as well as human health, through bioaccumulation and bioamplification [37]. PTEs also exhibit toxic chronic health effects of various intensity which are dangerous to humans [17, 38–40]. Urbanization, agriculture and industrialization are the most common human practices responsible for metal pollution in the environment. Ecological risk assessment is a vital parameter to determine the impact of pollutants on aquatic ecosystems [41]. Consequently, the analysis of sediments is a useful tool to determine the contamination status of heavy metals in river sediments. Although some studies on the possible impact of metal contamination have been carried out along the Atlantic coast of Limbe in Cameroon [5], little or no studies have been conducted using single and complex pollution and ecological indicators in the evaluation of pollution, ecological and toxicity risks of metals in Limbe River sediments, a tributary of the Atlantic Ocean. It is necessary to perform a comprehensive study for assessing the concentrations, pollution status, toxicity and sources of heavy metals in the sediments of Limbe River. The effective evaluation of sediments contamination focuses on the use of pollution and ecological indicators. Therefore, the aim of this study is to evaluate the pollution, ecological risks and toxicity of metals in Limbe River sediments. The study emphasizes the significance of continuous evaluation and management for preserving aquatic ecosystem and biological resources. This data provide vital information, and an acceptable base for the management of pollution issues in coastal areas in Cameroon, protection of human health and maintenance of ecosystems. The use of pollution indicators in this research also provides a more efficacious method for metal analyses that can be employed in future monitoring exercises of sediments in coastal areas.

# 2 Location of the study area and geological setting

The study area is found along the coast of the Atlantic Ocean, situated between latitudes 4°00'00"–4°02'30"N and longitudes 9°11'30"–9°13'30"E, in the Southwest Region of Cameroon. It is bordered by the Atlantic Ocean to the south and Mount Etinde and numerous volcanic cones of Mount Cameroon to the north and northeast. Limbe River is found at the boundary between the oceanic and the continental sectors of the Cameroon Volcanic Line (CVL; Fig. 1). The area is dominated by irregular relief made up of highlands of pyroclastic cones and lowlands. It is also characterized by a long rainy season from March to October with rain peaks usually occurring between July and





Fig. 1 Map of CVL with Limbe situated at the SE foot slope of Mount Cameroon, on landward of the ocean-continent boundary (adapted from [51]



August [42]. The Limbe coastal area has as main activity fishing which is done on a large scale by companies and local population. Other human activities carried out along the Atlantic Coast of Limbe include domestic practices, offshore drilling, transportation of petroleum products, quarrying activities, mining and agro-industrial activities etc. Discharge of solid and liquid waste and effluents from these human practices along the Atlantic Coast of Limbe releases significant amount of pollutants (heavy metals) into the Limbe River and other surrounding water bodies. The study area is located at the SE foot slope of Mount Cameroon and forms part of the CVL. The CVL like many other volcanic provinces on the African plate is a distinguished Tertiary to recent volcanism associations [43]. It forms one of the African plate's major geologic lineaments and it is describes as a unique and distinct example of an active intraplate alkaline tectonic magmatic alignment simultaneously developed into oceanic and continental domains [44]. The CVL is made up of plutonic orogenic and anorogenic complexes of granitic to syenite with alkaline and peralkaline compositions [44, 45], and islands (e.g., Pagalu, Sao Tome, Principe, Bioko) and continental volcanic massifs (e.g., Mounts Cameroon, Manengouba, Bamboutos, Oku, etc.). The study area lies on a metamorphic substratum of pan-African fold belt which is covered by Tertiary to recent alkali basaltic lavas and Quaternary age sediments. The lava flows of the lower dark series are mainly basanite, tephrite, hawaiite and mugearite that resulted from the eruptions of Mount Cameroon, an active-type of volcano [46–48], and olivine melanephelinite to noseanleucitenephelinite found at Mount Etinde [49, 50]. The upper dark series on the other hand is of Quaternary to recent, and it is composed of vesicular to scoriaceous pyroclasts.

# 3 Materials and methods

Eighteen (18) river sediment samples (Fig. 2) were collected from the riverbank with the help of a stainless-steel shovel and auger at depth to avoid contamination and their coordinate values listed in Table 1 of Supplementary material. River sediment samples were collected according to the existing possible pollution provenance from 200 and 250 m. In the dry season, when there was no flooding and minimal river flows, sediments were collected, which is conducive to high concentration of metals in sediments found in the channel bed [39, 52]. The locations of all sampling points were determined using the global positioning system. The collected sediments were put in the polythene bags and labelled neatly. After being transported to the laboratory, they were air dried at 25 °C and passed through a plastic sieve (1 mm) to remove plant materials, debris and gravel-sized materials; and then sieved through a nylon sieve (aperture 125 μm). Precautions were taken to prevent contamination during drying, sieving and storage. The eighteen (18) sediment samples were subjected to chemical analysis for various element concentrations. Each sediment sample weighed 0.5 g was digested with aqua regia (9 ml HNO<sub>3</sub>, 3 ml HCl) in a Perkin Elmer Multivalve 3000 Microwave unit. The temperature of the microwave was raised to 160 °C for 10 min and held for 15 min at a power of 800 W and pressure of 30 bar. The digestion was carried out for 35 min at a rate of 0.5 bar s<sup>-1</sup>. After the microwave-assisted digestion, the samples were filtered, transferred into 50 mL volumetric flask and made to volume using distilled deionized water. The contents of elements in each digest were then determined using a Perkin Elmer Nexion 300Q ICP-MS. ICP-MS analysis and digestion of various sediment samples were done at the Activation Laboratories Ltd., Ontario in Canada. For quality control procedures, triplicates, method blanks and reference standards were employed. In this study, analytical-grade chemicals and reagents were used. Glassware and vessels were washed with 20% HNO<sub>3</sub> and air-dried after rinsing with deionized water. Rigorous validation of the ICP-MS method was conducted to ensure accuracy, precision, recovery, and determination of the limit of detection. Quality control and assurance was achieved using the certified reference materials (UME EnvCRM 03) supplied by Tübitak Ulusal Metroloji Enstitüsü (UME), Ankara, Türkiye. The relative standard deviations (RSDs) for triplicate samples were within ± 15% of the mean. For heavy metals, recoveries between 95 and 105% were obtained. Calibration curves were generated utilizing standard stock solutions (Agilent 8500–6940 2A, 27-element mix). Multivariate parameter like Pearson's correlation matrix was applied to define the provenance of toxic metals. The correlation coefficient which represents the degree of linear relationships between two variables is displayed in the correlation matrix. The correlation coefficient has a value between – 1 and + 1. The statistical analysis was done using shuttle radar topography mission (SRTM), ArcGIS, Microsoft Excel and Statistical Package for Social Science (SPSS 16.0) software.

#### 3.1 Contamination and pollution assessment

Contamination factor (CF) describes the contamination of a given metal in sediments of Limbe River which was calculated using Eq. 1 [53]:





Fig. 2 Sample location map showing eighteen sampling sites

$$CF = \frac{Content of each metal}{Background content of metal}$$
(1)

where the background content of metal is a reference value for the maximum allowable concentration of metals in the Upper Continental Crust (Table 1) after [54], and CF is classified as: Low contamination (CF < 1); moderate contamination (1 < CF < 3); considerable contamination (3 < CF < 6) and very high contamination (CF > 6).

Contamination degree (C<sub>dea</sub>) is the sum of all the CF for various metals and it was computed using Eq. 2 [53]:

$$Cdeg = \sum_{i=1}^{8} CF$$
<sup>(2)</sup>

where CF is contamination factor;  $C_{deg} < 8$  denotes low contamination degree;  $8 < C_{deg} < 16$  suggests moderate contamination degree;  $16 < C_{deg} < 32$  indicates significant contamination degree and  $C_{deg} > 32$  signals high contamination degree.

Modified contamination degree helps in the assessment of overall metal contamination in the sediment samples. It is computed using Eq. 3 [53]:

$$mC_{deg} = \frac{\sum C_F}{n} \tag{3}$$



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Table 1	Descriptive Statistics
of majo	r oxides (%) and trace
elemen	ts (mg/kg) in Limbe
River Se	diments

Variables	Min	Max	Mean	StDev	Variance	Coef Var	UCC values
Al <sub>2</sub> O <sub>3</sub> (%)	2.06	5.65	3.61	0.87	0.76	24.19	15.4
CaO	0.32	2.27	0.92	0.48	0.23	52.17	3.59
Fe <sub>2</sub> O <sub>3</sub>	6.59	21.87	14.98	4.47	19.96	29.82	5.04
K <sub>2</sub> O	0.02	0.14	0.07	0.03	0	41.43	2.8
MgO	2.42	6.63	4.73	1.42	2.02	30.11	2.48
MnO	0.08	0.25	0.17	0.04	0	27.24	0.1
Na <sub>2</sub> O	0.06	0.48	0.17	0.11	0.01	63.73	3.27
$P_2O_5$	0.01	1.42	0.24	0.3	0.09	127.08	0.15
TiO <sub>2</sub>	0.83	2.82	1.92	0.63	0.4	32.72	0.64
Ag (mg/kg)	0.02	0.09	0.07	0.02	0	27.48	53
Cd	0.11	0.31	0.17	0.05	0	32.02	0.09
Со	32.6	84.1	64.57	14.78	218.6	22.9	17.3
Cr	123	858	456.70	215.6	46484.8	47.21	92
Cu	0.2	58.7	9.47	14.11	198.96	149	28
Hg	0.02	0.07	0.04	0.02	0	42.25	0.05
Mn	648	1950	1272.20	351.1	123,273	27.6	0.1
Ni	100	248	168.61	42.11	1773.66	24.98	47
Pb	4.6	75.8	21.55	18.57	344.91	86.18	17
Sn	1.26	16.9	5.71	5.19	26.94	90.93	2.1
Sr	40.4	173	78.20	31.49	991.69	40.27	320
V	123	492	329.8	120.9	14,615.8	36.65	97
Zn	92.1	339	235.70	64.1	4107.7	27.2	67

UCC values (Upper continental crust values by [54]

where  $C_F$  is the contamination factor and n is the number of elements analysed. Modified contamination degree were classified as follows:  $mC_{deg} < 1.5$  is nil to low,  $1.5 < mC_{deg} < 2$  is low,  $2 < mC_{deg} < 4$  is moderate,  $4 < mC_{deg} < 8$  is high,  $8 < mC_{deg} < 16$  is very high,  $16 < mC_{deg} < 32$  is extremely high and  $mC_{deg} > 32$  is ultra-high contamination [19].

Pollution load index (PLI) serves to determine the cumulative pollution impact at various constitutes in sediments at different locations and it was computed using Eq. 4 [55]:

$$PLI = \left(CF_1 \times CF_2 \times \dots \times CF_n\right)^{1/n} \tag{4}$$

where PLI > 1 implies polluted; PLI < 1, shows not polluted and PLI = 1, denotes base level of pollution.

Nemerow integrated pollution index (NIP) evaluates amount of metal pollution and determine the effects of various metals on the sediments. The index is calculated using Eq. 5 [56]:

$$NIPI = \frac{\sqrt{\left(\frac{1}{m}\sum_{i=1}^{m}P_{i}\right)^{2} + \left(P_{imax}\right)^{2}}}{2}$$
(5)

where P<sub>i</sub> is the single pollution index of heavy metal i; P<sub>imax</sub> is the maximum value of the single pollution indices of the investigated heavy metal(s) and m is the count of the heavy metal species.

Enrichment factor (EF) evaluate the degree of metals contamination in sediments. It was calculated using Eq. 6 [57]:

$$EF = \frac{(C_x/C_{Fe})_{sample}}{(C_x/C_{Fe})_{background}}$$
(6)

where the ratio of metals to iron oxide in the sample is  $(C_x/Fe)_{sample}$  and the background ratio of metal to iron oxide concentration is  $(C_x/Fe)_{background}$ , which is unpolluted and not impacted by pollution. Enrichment Factor was interpreted as follow: EF < 2 = deficiency to minimal mineral enrichment; 2 < EF < 5 = moderate enrichment; EF 5 < EF < 20 = significant enrichment; 20 < EF < 40 = very high enrichment; EF > 40 = extremely high enrichment.



Geo-accumulation index (Igeo) was used to evaluate the contamination level in sediments through a comparison of the existing concentrations of each metal to that of the reference standard [53]. Igeo was calculated using Eq. 7 [58]:

$$g_{geo} = \log_2(C_n/1.5B_n) \tag{7}$$

where, Cn = measured concentration of metal ion in sample; Bn = background concentration value for metal [54] and 1.5 represents the background matrix correction factor due to lithogenic effects. Igeo  $\leq 0$  = uncontaminated;  $0 \leq$  Igeo < 1 = uncontaminated to moderately contaminated;  $1 \leq$  Igeo < 2 = moderately contaminated;  $2 \leq$  Igeo < 3 = moderately to strongly contaminated;  $3 \leq$  Igeo < 4 = strongly contaminated;  $4 \leq$  Igeo < 5 = strongly to extremely contaminated; Igeo > 5 = extremely high contaminated.

#### 3.2 Ecological and ecotoxicity risks assessment

Ecological risk factor (Er) is used to quantify possible ecological risks connected to a certain specific pollutant. It was obtained using Eq. 8 [53]:

$$Er = Tr^i \times CF^i \tag{8}$$

where Tr is toxic response factor of a metal (Pb=5, Zn=1, Cd=30, Cr=2, Ni=5, Hg=40, Cr=2, Cd=30, As=10 and Cu=5). CF is the contamination factor. Er is define as Er < 40 denotes low Er, Er = 40–80 implies moderate Er, Er = 80–160 signify considerable Er, Er = 160–320 indicate high Er and Er > 320 suggest very high Er.

Potential ecological risk index (PERI) accounts for cumulative impacts of metals under consideration. It is the sum of all Er variables in a given study area. It was calculated using Eq. 9 [53]:

$$PERI = \sum_{i=1}^{n} T_r^i \times C_r^i$$
(9)

where, Er is the ecological risk factor, n is the number of elements studied and  $C_r^i$  is the contamination factor (Eq. 9). The following terminologies have been used for the potential ecological risk index: < 150, low potential ecological risk index; 150 < PERI < 300, moderate potential ecological risk index; 300 < PERI < 600, high potential ecological risk index; and  $\geq$  600, significant potential ecological risk index.

Modified hazard quotient (mHQ) was used to assess biological impact in sediments-related chemical states on microbial species of the study area. It was calculated using Eq. 10 [59]:

$$mHQ = \sqrt{\frac{C_i}{TEL_i} + \frac{C_i}{PEL_i} + \frac{C_i}{SEL_i}}$$
(10)

where, Ci stands for the measured concentration of metal I (Eq. 10). TEL = Threshold Effect Level (As = 5.9, Cr = 37.3, Cu = 35.7, Ni = 18, Zn = 123), PEL = Probable Effect Level (As = 17, Cr = 90, Cu = 197, Ni = 36, Zn = 315), SEL = Severe Effect Level (As = 33, Cr = 110, Cu = 110, Ni = 75, Zn = 820).

Probability of toxicity index (mERMQ) method determines the harmful effects of metals on sediment and water environments. It was computed using Eq. 11 [60]:

$$mERMQ = \frac{\sum_{i=1}^{n} \frac{C_i}{ERMi}}{n}$$
(11)

where, Ci = concentration of the metal i, ERM is the effects range median, and n is the number of metals (Eq. 11). Low risk level are designated as mERMQ < 0.1 with 9% probability of toxicity; 0.1—0.5, medium risk level with 21% probability of toxicity; 0.5 to 1.5, high risk level with 49% probability of toxicity; and > 1.5 very high risk level with 76% probability of toxicity.

Multiple probable effect concentration quality (mPECQ) was used for ecological risk assessment of metals in sediments. It was determined using Eq. 12 [61]:



$$mPEC_Q = \frac{\sum_{i=1}^{n} \frac{C_i}{PEC_i}}{n}$$
(12)

where, Ci = content of element i in sediments (mg/kg). PEC is the probable effect concentration of individual metal based on consensus. The PEC values of Cr, Ni, Cu, As, Cd, Pb, Zn, and Hg were 111, 48.6, 149, 33, 4.8, 129, 459 and 1.06 mg/kg respectively, n is the number of heavy metals.

Toxic risk index (TRI) was used to assess the potential toxic risk of heavy metals in fresh and marine water environment to biota. It is computed using Eq. 13 [62]:

$$TRI_{i} = \sqrt{\frac{(C_{i}/TEL_{i})^{2} + (C_{i}/PEL_{i})^{2}}{2}}$$
(13)

where, C<sub>i</sub> denotes concentration measured metal in sample (Eq. 13). TEL = Threshold Effect Level (As = 5.9, Cr = 37.3, Cu = 35.7, Ni = 18, Zn = 123). PEL = Probable Effect Level (As = 17, Cr = 90, Cu = 197, Ni = 36, Zn = 315). TRI < 5 implies no toxic risk; TRI: 5–10 signify low toxic risk; TRI: 10–15 indicate moderate toxic risk; TRI: 15–20 denotes significant toxic risk and TRI > 20 correspond to very high toxic risk.

# 4 Results and discussion

The pollution, ecological and toxicity risk assessment using stochastic techniques offers a strong framework for assessing the build-up of heavy metals in Limbe River sediments, Atlantic Coast, Cameroon. Our understanding of heavy metals dynamics is enhanced by the integrated use of single and complex pollution indices and statistical methods, which also lays the groundwork for wise decision to be made in environmental and remediation projects. This study establishes the foundation for further investigation and focused intervention in Cameroon freshwater and marine water settings while also advancing our understanding of the ecological and eco-toxicity dangers related to metallic pollution in aquatic ecosystems.

# 4.1 Distribution of major and trace elements

#### 4.1.1 Distribution of major elements

Major elements chemistry of Limbe River sediments are shown in Table 1, with the concentration of each element expressed in wt. % and compared with UCC values. The concentrations of Fe<sub>2</sub>O<sub>3</sub> (6.59 to 21.87 wt. % with a mean of 14.98 wt. %), MgO (2.42 to 6.63 wt. % with a mean of 4.73 wt. %), MnO (0.08 to 0.25 wt. % with a mean of 0.17 wt. %) and TiO<sub>2</sub> (0.83 to 2.82 with a mean of 1.92 wt. %) are greater than those of the Upper Continental Crust (UCC) proposed by Rudnick and Gao (2014), while Na<sub>2</sub>O, CaO, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O contents are less than those proposed by the same authors. Al<sub>2</sub>O<sub>3</sub> (2.06 to 5.65 wt. %) display low contents when compared with threshold values. This variation in major elements concentration is displayed in the box plot to indicate their distribution in sediment samples (Fig. 3). The chemical composition of the sediment samples studied is reported in the enrichment-depletion plot (Fig. 4) in which samples show enrichment for Fe<sub>2</sub>O<sub>3</sub> MgO, MnO and TiO<sub>2</sub> and depletion for the other major elements. Elevated concentration of Fe<sub>2</sub>O<sub>3</sub> in sediment samples suggest that the sediments are ferruginous and are sourced from haematization of the parent rocks, mostly basaltic rocks. High contents of MgO and MnO in sediments suggest the presence of mafic minerals in relation to the parent rocks. Moderate content of TiO<sub>2</sub> indicates that rutile and illmenite continued to form during parent rocks alteration [39]. Alkali and alkali-earth oxides (K<sub>2</sub>O, CaO, MgO and Na<sub>2</sub>O) and P<sub>2</sub>O<sub>5</sub> have low concentrations probably because of their high mobility during weathering or sorting of parent materials (Table 1).

# 4.1.2 Distribution of trace elements

The selected trace elements or trace metals in Limbe River sediment samples are presented in Table 1. The Limbe River sediments displayed high contents in Cd (0.11–0.31; average 0.17 mg/kg), Co (32.60–84.10; av = 64.87 mg/kg), Cr (123–858; av = 456.67 mg/kg), Mn (648–1950; av = 1272.17 mg/kg), Ni (125–248; av = 168.61 mg/kg), Pb (4.60–75.80;



Fig. 3 Box plot for major

**River sediments** 

oxides distribution in Limbe



**Fig. 4** Enrichment/depletion plot for major oxides in Limbe River sediments

av = 21.55 mg/kg), Sn (1.26–16.90; av = 5.71 mg/kg), Sr (40.40–173; av = 78.20 mg/kg), V (133–492; av = 329.83 mg/kg) and Zn (92.10–339; av = 235.67 mg/kg), which generally exceed the standard values of the upper continental crust (Fig. 4) [54]. Ag (0.05–0.09; av = 0.07 mg/kg) and Hg (0.02–0.07; av = 0.04 mg/kg) concentrations were below the reference standards (Fig. 5). The high contents of trace metals in Limbe River sediments is sourced from intense alteration of basaltic lavas, atmospheric deposition and human input such as agricultural runoff and practices (phosphate fertilizers, animal manure, pesticides, herbicides, fungicides), agro-industrial and quarrying activities, sewage sludge, municipal solid and liquid wastes, household effluents, garbage and waste water irrigation. It was noticed that Limbe River drains through the agricultural areas, thus increase in heavy metal concentration sources from agricultural practices. This is similar to the findings of other authors along the continental sector of the CVL [37]. Low Ag and Hg content are probably sourced from volcanoes, atmospheric deposition and chemical weathering of source rocks. Comparing heavy metals concentrations are higher than those of other metals (Table 1). This reveals that, besides geogenic influence as the source of these metals in sediments, there are other human input sources in Limbe River sediments. The high concentrations of these metals are attributed to geologic materials, mainly basaltic lava flows that characterized the study area and anthropogenic metal inputs due to agricultural practices from palm plantations on the flanks of Mount Cameroon, industrial discharge,

0.001







domestic activities and other human inputs from mid-course to down course of the river profile. The variation of heavy metals concentration in Limbe River sediments are higher than those earlier reported in beach sediments of Limbe [5], in Bambui sediments [52], and in Pouma sediments [12]. These concentrations are lower than those recently reported in sediments of Mari and Mbal located within pull apart Lom basin in Cameroon [25, 26] and in Nkwen River sediments situated in the continental sector of the CVL [41]. The varying anthropogenic impacts may be responsible for the spatial changes in heavy metal pollution. These variations in heavy metals concentrations highlight the diverse contamination levels within the study area, necessitating comprehensive assessment and management strategies to mitigate potential risks to environmental and human health. The significant differences in Co, Cr, Mn, Ni, Pb, Sr, V and Zn concentration highlight their importance in environmental assessment, with implications for ecosystem health and human well-being. Hazardous toxic metals can harm both the environment and health. The presence of these contaminants in sediments can indicate contamination from anthropogenic sources. Vigilant monitoring and management strategies are necessary to mitigate associated risk [63-65].

# 4.2 Source apportionment

# 4.2.1 Pearson's correlation matrix

Pearson correlation analysis (Table 2) was performed to identify possible sources of the heavy metals in the sediments of the Limbe River. Previous studies reported that heavy metals with strong correlations originate from the same source [39]. Pearson's correlation matrix (Table 2) display positive correlations for major oxides, except  $Al_2O_3$ ,  $Pe_2O_3$ , MgO and  $Na_2O$ . Positive correlation exists between CaO/K<sub>2</sub>O,  $Na_2O$  and  $K_2O/Na_2O$ . This is associated with the presence of feldspar, zircon and apatite in parent rocks within the study area (basaltic rocks). In this area, the correlation between CaO and  $K_2O$ ,  $Na_2O$  is due to mafic and felsic minerals. The majority of heavy metals also display positive correlations with r > 0.5and this is linked to the geologic materials in the area and also to human activities (Table 2). Negative correlation is also observed between most of the heavy metals. Positive correlation indicates their similar origin from geogenic sources and human input such as mining, agro-industrial and quarrying activities, fishing, sewage sludge, garbage, animal manure, municipal solid waste, agricultural activities and waste water irrigation [26], which are probably governed by the same or similar physicochemical processes. A significant correlation between two metals may indicate an incidence of strong dependency of both metals on the same causal factor, most likely due to their similar genesis from underlying basement complex.

# 4.2.2 Sediment contamination and metal pollution indices

4.2.2.1 Contamination factor (CF), contamination degree (C<sub>deq</sub>), modified contamination degree (mC<sub>deq</sub>) and pollution load index (PLI). Results of CF of metals are listed in Table 3 and Fig. 6. Contamination factor varies from 0.01 (Cu) to 10.34 (Cr)



Table 2	Correlati	on matrix	of major	oxides (%)	and trace	metals (m	J ui (gy/gu	imbe Rive	er sedimer	nts									
	$AI_2O_3$	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	Ag	Cd	Co	C	Cu	Hg	Mn	Pb	Sn	Sr	>	Zn
$AI_2O_3$	1									-									
CaO	0.24	-																	
$Fe_2O_3$	0.05	-0.57	-																
K <sub>2</sub> O	0.36	0.93	-0.46	-															
MgO	0.07	-0.01	-0.28	-0.03	-														
MnO	-0.32	-0.40	-0.04	-0.52	0.00	-													
$Na_2O$	0.10	0.88	-0.61	0.72	0.22	-0.28	-												
Ag	0.09	-0.05	-0.24	-0.01	0.43	-0.05	0.11	-											
Cd	0.04	-0.09	0.18	0.07	0.01	0.01	-0.11	-0.06	-										
°C C	-0.50	-0.52	0.08	-0.52	-0.16	0.66	-0.34	0.28	0.00	-									
ۍ	-0.46	-0.36	0.25	-0.37	-0.33	0.50	-0.32	0.14	-0.25	0.79	-								
Cu	0.60	0.18	-0.05	0.29	0.14	-0.40	0.16	-0.06	0.21	-0.58	-0.67	-							
Hg	-0.03	0.10	0.16	0.27	-0.02	-0.38	-0.06	0.14	0.29	-0.31	-0.25	0.16	-						
Чn	-0.44	-0.44	-0.10	-0.55	-0.13	0.93	-0.30	-0.02	0.02	0.69	0.51	-0.36	-0.36	-					
Рb	-0.32	-0.14	0.11	-0.10	-0.32	-0.27	-0.25	-0.31	0.22	-0.20	-0.31	0.08	0.32	-0.04	-				
Sn	-0.10	-0.10	-0.10	-0.07	0.12	-0.05	0.06	0.03	0.60	0.01	-0.33	0.06	0.28	0.02	0.18	-			
Sr	0.48	0.19	-0.07	0.35	0.24	-0.58	0.23	-0.02	0.27	-0.52	-0.65	0.88	0.16	-0.53	0.14	0.22	-		
>	-0.45	-0.39	0.28	-0.40	-0.22	0.59	-0.27	0.25	-0.14	0.84	0.94	-0.62	-0.23	0.60	-0.30	-0.26	-0.61	-	
Zn	-0.50	-0.53	0.17	-0.61	-0.26	0.87	-0.48	-0.06	0.04	0.67	09.0	-0.48	-0.20	0.92	0.04	-0.08	-0.68	0.69	-
Bold n	umber rep	resents siç	gnificant p	oositive co	rrelation,	$r^2 = 0.50 - 0$	3boM) 69.0	erate corre	elation), r <sup>2</sup>	=0.70-0.7	'9 (Strong	correlatic	on) and r <sup>2</sup>	= 0.80-0.9	9 (Very sti	ong corre	lation		



Table 3 Contamination factor, contamination degree, modified degree of contamination and pollution load index of heavy metals in Limbe River sediments

	Ag	Cd	Со	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sn	Sr	V	Zn	Cdeg	mCdeg	PLI
S1	1.78	3.16	0.54	4.23	0.37	2.12	0.89	1.95	4.70	0.53	3.07	0.25	2.82	2.93	29.35	2.10	1.49
S2	1.72	2.14	0.66	6.02	0.21	2.80	1.25	2.45	5.64	4.46	1.32	0.24	3.76	3.92	36.57	2.61	1.77
S3	1.46	1.94	0.56	5.51	0.01	2.28	1.07	1.73	4.41	0.27	0.23	0.18	3.38	3.10	26.13	1.87	0.87
S4	1.20	1.33	0.55	6.87	0.16	2.32	0.71	1.63	3.50	2.11	0.44	0.21	3.46	3.13	27.63	1.97	1.24
S5	1.46	1.33	0.52	3.88	0.93	2.26	1.07	2.18	4.59	0.85	2.27	0.29	2.75	3.04	27.42	1.96	1.54
S6	1.60	2.04	0.35	1.48	2.35	1.24	1.07	1.32	3.39	0.96	0.42	0.49	1.36	1.92	19.99	1.43	1.20
S7	0.96	1.12	0.28	1.93	0.70	1.02	0.36	1.08	2.84	1.54	0.24	0.32	1.24	1.30	14.91	1.06	0.84
S8	1.58	1.22	0.65	6.52	0.01	2.62	0.89	2.23	5.32	0.33	0.67	0.16	3.56	3.39	29.17	2.08	0.98
S9	0.80	2.35	0.52	5.90	0.28	1.77	1.16	2.05	5.00	1.75	2.51	0.24	3.36	3.65	31.33	2.24	1.54
S10	0.40	2.24	0.59	4.34	0.67	2.56	0.45	2.45	2.73	2.35	1.07	0.26	2.50	3.80	26.41	1.89	1.36
S11	1.38	1.12	0.56	8.54	0.01	2.56	0.89	2.17	3.30	0.62	0.39	0.21	4.00	3.30	29.05	2.07	0.97
S12	1.52	1.73	0.60	2.41	0.35	2.18	0.54	2.33	2.27	1.59	2.73	0.29	1.57	2.82	22.93	1.64	1.31
S13	1.08	1.63	0.72	10.34	0.01	3.37	0.54	3.25	3.70	0.49	0.33	0.12	4.60	4.77	34.94	2.50	0.99
S14	1.68	1.43	0.62	5.86	0.36	3.08	0.36	2.93	3.27	0.44	0.29	0.17	4.21	4.46	29.16	2.08	1.21
S15	1.66	1.43	0.69	9.04	0.01	3.27	0.36	2.68	3.95	0.45	0.31	0.12	4.58	4.21	32.76	2.34	0.95
S16	1.60	1.22	0.67	7.82	0.01	2.98	0.36	2.48	4.30	0.62	0.69	0.17	4.16	4.10	31.17	2.23	1.01
S17	1.72	1.33	0.56	6.75	0.01	1.17	1.07	1.12	2.95	0.76	0.82	0.19	3.03	2.11	23.58	1.68	0.89
S18	1.08	1.53	0.30	1.61	0.38	2.10	1.25	2.12	3.11	2.70	0.89	0.12	1.15	3.80	22.16	1.58	1.15

**Fig. 6** Contamination factors (CF) of heavy metals in Limbe River sediments



in sample S13. Co, Cu, Pb and Sr show low contamination (CF < 1). Ag, Cd, Fe, Hg, Mn, Pb, Sn, V and Cu in sample S6 are moderately contaminated (CF = 1–3). Cr, Ni, Zn and Cd in sample S1 are considerably contaminated (CF = 3–6) and Cr in samples S2, S4, S8, S11, S13, S15-17 is highly contaminated (CF > 6) in Limbe River sediments. Therefore, the Limbe River sediments show low to very high contamination by these heavy metals. This contamination is attributed to offshore drilling, transportation of petroleum products, quarrying activities, and agro-industrial activities, agricultural practices and runoff, domestic activities, industrial activities and other human practices as reported elsewhere in Cameroon [5, 39]. These findings suggest minimal contamination for Co, Cu, Hg, Sr, Sn and Pb as their CF values were < 1, moderate contamination levels for Ag, Cd, Fe, Mn and V ( $1 \le CF < 3$ ), significant contamination for Cr, Ni, Zn and Cd, as CF were 3 to 6 in some samples. Cr in majority of samples was in the class of high contamination (CF > 6). Some factors responsible



for metal contamination include physical and chemical weathering and erosion of nearby rock. However, it is imperative to acknowledge the role played by additional elements like productivity, pH, cation exchange capacity, atmospheric conditions, and sediments texture. Remobilization of metals can occur due to internal geochemical processes and these phenomena needs to be considered when evaluating contamination.

The  $C_{deg}$  varies from 14.91 (sample S7) to 36.57 (sample S2) (Table 3). The  $C_{deg}$  is as follows: S2 > S13 > S15 > S9 > S16 > S1 > S8 > S14 > S11 > S4 > S5 > S10 > S3 > S17 > S12 > S18 > S6 > S7. Samples S6, S7, S12 S18 and S17 are in the category of significant contamination ( $C_{deg}$  12–24), accounting for 27.77%. The other 13 sampling sites are in the class of very high contamination ( $C_{deg}$  > 24) and accounts for 72.22%. This suggests considerable to extreme contamination rate of heavy metals in Limbe River sediments, sourced from anthropogenic (agricultural practices, offshore drilling, transportation of petroleum products, fishing, quarrying activities, domestic activities, industrial activities, household effluents, municipal solid and liquid waste) and geogenic (volcanic eruption, alteration of minerals and parent rocks) pollutants [5, 11, 24].

The modified contamination degree  $(mC_{deg})$  is an integrated index utilized for the purpose of evaluating the degree of pollution in sediments; it provides a numerical representation of the quantity of contaminants present in comparison to regulatory standards or background concentrations [12, 25, 39, 64, 65]. This index is highly advantageous due to its incorporation of various heavy metals assessed in the aquatic ecosystem, thereby providing a holistic viewpoint on environmental contamination [63–65]. The modified contamination degree (mC<sub>deg</sub>) varies between 1.06 insample S7 to 2.61 insample S2 (Table 3). The whole area is in the class of low degree of contamination (mC<sub>deg</sub> 1.5–2) except samples S2, S7, S8, S11 and S13-S16 that are in the class of moderate degree of contamination, accounting for 544.44% of the study area. This study suggests that proper focus should be taken on monitoring the point sources of heavy metals entering the Limbe River from domestic activities, industrial activities, offshore drilling, transportation of petroleum products, quarrying activities, and agro-industrial activities and agricultural practices such as phosphate fertilizers applications, pesticides, fungicides, herbicides and waste water irrigation. Thus, this study found a mean mCd value of 1–2, indicating low contamination, as per the criterion of mC<sub>deg</sub> 1.5–2. This classification held true across all stations, with mCd values consistently below 3, reaffirming low contamination levels in the study area.

The pollution load index assesses the degree of correlation between heavy metals and river sediments, serving as a tool to evaluate potential impacts on sediment micro flora and fauna [12, 39, 52, 63–65]. This index compares heavy metals concentrations in sediment samples to reference values, guiding remediation strategies and efforts to protect sediment ecosystems [25, 26, 39]. The computed PLI for each sampling sites are shown in Table 3. The PLI varies from 0.84 (sample S7) to 1.77 (sample S2). Samples S3, S7, S8, S11, S13, S15 and S17 display minimal pollution status (PLI < 1) and accounts for 38.88% of the study area. The other sampling sites have PLI values greater than 1 (PLI > 1) indicating pollution of the study area, accounts for 55.55%. The high degree of PLI values in some sampling sites is probably due to the effects of human activities. PLI (PLI > 1) suggests that these sites have been subjected to serious anthropogenic pollution. Metals sourced from human provenance display higher biological availability than those from natural sources; hence, the latter might be easier to transfer along the food chain. The occurrence of metals in Limbe River sediments is sourced from offshore drilling, transportation of petroleum products, agro-industrial and quarrying activities, agricultural practices, domestics and industrial activities, household effluents into the river and other anthropogenic inputs [24, 25, 52]. Therefore, the area of study is at risk of pollution and this need preservative and remediation methods for domestic, industrial and agricultural practices, indiscriminate dumped of household and municipal solid and liquid waste into the Limbe River.

**4.2.2.** Nemerow integrated pollution index (NIPI), enrichment factor (EF), geo-accumulation index (Igeo) The NIPI is an essential tool in environmental research, providing valuable insights into pollution levels in different ecosystems, such as surface sediments of river systems [26, 39, 52]. It combines measurements of contaminants and their toxicity weights, assisting experts in assessing environmental health, pinpointing pollution sources, and devising strategies for sustainable development and pollution reduction [12, 24, 25, 65]. The computed NIPI varies from 0.38 (Sr) to 8.28 (Cr) for Limbe River sediments (Table 4; Fig. 7). The NIPI follows the trend: Cr (8.28) > Ni (4.82) > Zn (4.11) > V (3.91) > Pb (3.28) > Fe (2.89) > Mn (2.74) > Cd (2.53) > Sn (2.29) > Cu (1.68) > Ag (1.59) > Hg (1.05) > Co (0.64) > Sr (0.38). The NIPI values for Co and Sr indicates that the Limbe River sediments have minimal pollution in these heavy metals (NIPINemerow < 1), while Ag, Cd, Cu, Fe, Hg, Mn and Sn display light pollution (NIPINemerow 1–2). Cr, Ni, Pb, V and Zn is in the category of serious pollution (NIPINemerow > 3). The presence of metals in the sediments studied could be linked to human activities such as offshore drilling, transportation of petroleum products, fishing, mining, quarrying activities, agro-industrial activities, domestic waste and effluents and agricultural practices along the Atlantic coast of Limbe [11]. In this study, the NIPI values of Co, Sr, Ag, Cd, Cu, Fe, Hg Mn and Sn fall between 1 and 2, indicating that the area is classified as low polluted in



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Table 4Nemerow integratedpollution index of heavy	Variables	Cfmax	Cfav	(Cfmax)^2	(Cfav) <sup>2</sup>	NIPI
metals in Limbe River	Ag	1.78	1.37	3.17	1.88	1.59
sediments	Cd	3.16	1.68	10.01	2.83	2.53
	Со	0.72	0.55	0.52	0.30	0.64
	Cr	10.34	5.50	106.86	30.27	8.28
	Cu	2.35	0.38	5.51	0.14	1.68
	Fe	3.37	2.32	11.38	5.37	2.89
	Hg	1.25	0.79	1.56	0.63	1.05
	Mn	3.25	2.12	10.56	4.50	2.74
	Ni	5.64	3.83	31.77	14.68	4.82
	Pb	4.46	1.27	19.88	1.61	3.28
	Sn	3.07	1.04	9.44	1.08	2.29
	Sr	0.49	0.22	0.24	0.05	0.38
	V	4.60	3.08	21.14	9.50	3.91
	Zn	4.77	3.32	22.80	11.02	4.11





these metals while Cr, Ni, Pb, V and Zn values fall above 3, suggesting serious pollution degree. This conclusion holds true for other pollution indicators use above across all. It suggests that overall pollution levels remain consistently significant throughout the study area, reflecting a relatively unhealthy environmental condition in the studied area [63–65]. The CF, C<sub>dea</sub>, mC<sub>dea</sub>, and PLI values as well as those that attest to the inherent contribution of the mineral assemblage and alteration processes, all firmly support this. According to these findings, the metals in the river constitute pollutants since their current state and quantity, as indicated by computed indices, suggest that they are harmful.

The enrichment factor analysis conducted in this study offers valuable insights into the sources and levels of metal enrichment in the river ecosystem. Enrichment factor for heavy metals in Limbe River sediments varies from zero (Cu) in most of the samples to 5.76 (Cr) in sample S17 (Table 5; Fig. 8). The EF follows the decending order: Cr (0.77–5.76) > Ni (1.04-2.83) > V (0.55-2.59) > Zn (1.29-2.07) > Cu (0-1.89) > Pb (0.12-1.59) > Cd (0.53-1.49) > Sn (0.09-1.45) > Mn (0.70–1.16) > Hg (0.11–0.92) > Ag (0.38–0.84) > Sr (0.03–0.40) > C0 (0.13–0.34). Limbe River sediments enriched in Ag, Cd, Co, Cu, Hg, Mn, Pb, Sn and Sr show no enrichment factor (EF < 1). Cd (samples S9-10, S12), Cu (sample S6), Mn (samples S6-7, S9, S12, S18) and Cr are in the class of minimal enrichment (EF = 1-2) in the sediments studied. These sediments rich in Cr (samples S9, S11, S13) are moderately enriched (EF = 2–5). Cr (sample S17) display significant enrichment

(EF) of heavy metals in Limbe		Ag	Cd	Со	Cr	Cu	Hg	Mn	Ni	Pb	Sn	Sr	V	Zn
River sediments	S1	0.84	1.49	0.25	1.99	0.17	0.42	0.92	2.22	0.25	1.45	0.12	1.33	1.38
	S2	0.81	1.01	0.31	2.15	0.08	0.45	0.88	2.01	1.59	0.47	0.09	1.34	1.40
	S3	0.69	0.91	0.26	2.41	0.00	0.47	0.76	1.93	0.12	0.10	0.08	1.48	1.36
	S4	0.57	0.62	0.26	2.96	0.07	0.31	0.70	1.51	0.91	0.19	0.09	1.49	1.35
	S5	0.69	0.62	0.24	1.72	0.41	0.47	0.97	2.03	0.38	1.00	0.13	1.21	1.34
	S6	0.75	0.96	0.17	1.19	1.89	0.86	1.06	2.73	0.78	0.34	0.40	1.09	1.54
	S7	0.45	0.53	0.13	1.90	0.69	0.35	1.06	2.80	1.51	0.23	0.31	1.22	1.28
	S8	0.74	0.58	0.31	2.49	0.00	0.34	0.85	2.03	0.13	0.26	0.06	1.36	1.30
	S9	0.38	1.11	0.24	3.34	0.16	0.66	1.16	2.83	0.99	1.42	0.13	1.91	2.07
	S10	0.19	1.06	0.28	1.69	0.26	0.17	0.96	1.07	0.92	0.42	0.10	0.98	1.49
	S11	0.65	0.53	0.26	3.34	0.00	0.35	0.85	1.29	0.24	0.15	0.08	1.56	1.29
	S12	0.72	0.82	0.28	1.10	0.16	0.25	1.07	1.04	0.73	1.25	0.13	0.72	1.29
	S13	0.51	0.77	0.34	3.06	0.00	0.16	0.96	1.10	0.14	0.10	0.03	1.36	1.42
	S14	0.79	0.67	0.29	1.90	0.12	0.12	0.95	1.06	0.14	0.09	0.06	1.37	1.45
	S15	0.78	0.67	0.33	2.76	0.00	0.11	0.82	1.21	0.14	0.09	0.04	1.40	1.29
	S16	0.75	0.58	0.31	2.63	0.00	0.12	0.83	1.44	0.21	0.23	0.06	1.40	1.38
	S17	0.81	0.62	0.26	5.76	0.01	0.92	0.95	2.52	0.65	0.70	0.16	2.59	1.80
	S18	0.51	0.72	0.14	0.77	0.18	0.59	1.01	1.48	1.28	0.42	0.06	0.55	1.81



**Fig. 8** Box Plot of EF of metals in Limbe River sediments

(EF = 5–20). Minimal to significant enrichment of some toxic metals are sourced from human activities such as offshore drilling, transportation of petroleum products, agro-industrial and quarrying activities, agricultural practices (application of phosphate fertilizers, pesticides, animal manure, fungicides, herbicides for high crop yield), sewage, waste water irrigation, household effluents, agrochemicals, municipal waste and industrial waste as previously reported elsewhere [5, 67–69]. These results indicates that Limbe River sediments contain significant amounts of hazardous metals. Regulating and adjusting agronomic measures, indiscriminate dumped of household effluents and industrial wastes into the river and land-use types in sites where hazardous metals contents are elevated, could reduce human health risk by controlling the point sources of pollutants. The minimal to significant enrichment of Cd, Cu, Cr and Mn related to sediment minerals, leaching in irrigation water of rocks present in the Cameroon volcanic line which are enriched in the transition metals and other elements reflecting their mantle origin. This enrichment could also be control by several anthropogenic influences as earlier mention and mineralogy (olivine, pyroxene, amphiboles, augite, kaolinite, feldspars and goethite) which are



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Table 6	Geo-accumulation	index (Igeo) of h	eavy metals in	Limbe River sediments
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	Ag	Cd	Со	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sn	Sr	V	Zn
S1	0.25	1.08	-1.47	1.50	-2.03	0.50	-0.75	0.38	1.65	-1.50	1.03	-2.59	0.91	0.97
S2	0.20	0.51	-1.19	2.01	-2.82	0.90	-0.26	0.71	1.91	1.57	-0.19	-2.65	1.32	1.38
S3	-0.04	0.37	-1.43	1.88	-7.55	0.61	-0.49	0.21	1.56	-2.47	-2.71	-3.05	1.17	1.05
S4	-0.32	-0.18	-1.44	2.19	-3.19	0.63	-1.07	0.12	1.22	0.49	-1.78	-2.81	1.20	1.06
S5	-0.04	-0.18	-1.54	1.37	-0.69	0.59	-0.49	0.54	1.61	-0.81	0.60	-2.38	0.87	1.02
S6	0.09	0.44	-2.08	-0.02	0.65	-0.27	-0.49	-0.19	1.17	-0.64	-1.85	-1.60	-0.15	0.35
S7	-0.64	-0.42	-2.43	0.36	-1.11	-0.56	-2.07	-0.47	0.92	0.03	-2.65	-2.24	-0.27	-0.21
S8	0.07	-0.29	-1.20	2.12	-7.55	0.80	-0.75	0.57	1.83	-2.19	-1.16	-3.22	1.25	1.18
S9	-0.91	0.65	-1.53	1.98	-2.44	0.24	-0.37	0.45	1.74	0.22	0.74	-2.66	1.17	1.28
S10	-1.91	0.58	-1.35	1.53	-1.17	0.77	-1.75	0.71	0.86	0.65	-0.48	-2.54	0.74	1.34
S11	-0.12	-0.42	-1.42	2.51	-7.55	0.77	-0.75	0.53	1.14	-1.27	-1.94	-2.83	1.42	1.14
S12	0.02	0.21	-1.31	0.68	-2.09	0.54	-1.49	0.64	0.60	0.08	0.86	-2.39	0.07	0.91
S13	-0.47	0.12	-1.06	2.78	-7.55	1.17	-1.49	1.12	1.30	-1.62	-2.20	-3.70	1.62	1.67
S14	0.16	-0.07	-1.27	1.96	-2.04	1.04	-2.07	0.97	1.13	-1.78	-2.37	-3.12	1.49	1.57
S15	0.15	-0.07	-1.12	2.59	-7.55	1.13	-2.07	0.84	1.40	-1.75	-2.27	-3.64	1.61	1.49
S16	0.09	-0.29	-1.17	2.38	-7.55	0.99	-2.07	0.73	1.52	-1.28	-1.12	-3.13	1.47	1.45
S17	0.20	-0.18	-1.42	2.17	-7.55	-0.36	-0.49	-0.43	0.98	-0.98	-0.87	-3.01	1.01	0.49
S18	-0.47	0.03	-2.33	0.11	-1.97	0.49	-0.26	0.50	1.05	0.85	-0.75	-3.61	-0.38	1.34

**Fig. 9** Graphical inspection of Igeo of metals in Limbe River sediments



characteristic of source rocks and sediments along the CVL. Therefore, the EF analysis underscores the predominance of anthropogenic sources in contributing to the presence of heavy metals in river environment, with minor lithogenic contributions [63–65]. These findings have significant implications for environmental management and highlight the importance of distinguishing between natural and human-induced sources of metal pollution in aquatic ecosystems [64, 65]. Furthermore, EF values offer valuable information on the underlying factors responsible for the occurrence of metal deposition in sedimentary environments. Enrichment is most likely attributed to human causes when the EF surpasses 1.5. Metals with an EF ranging from 0.05 to 1.50 are classified as having a lithogenic origin [63–65]. Therefore, outcome of EF for this study indicated that heavy metals in the sediments had anthropogenic and to a lesser extent lithogenic origin.

Geo-accumulation (Igeo) index of metals in Limbe River sediments show a variation from -7.55 (Cu) to 2.59 (Cr) in sample S15 (Table 6 and Fig. 9). The geo-accumulation index shows that majority of heavy metals are in the category of virtually unpolluted (Igeo < 0) in the sediment samples. This shows minor anthropogenic pollution in the Limbe River

sediments, suggesting that these sediments are in background values. Sediments rich in iron are unpolluted to moderately polluted (0 < Igeo < 1), while sediments enriched in Cr, Ni, V and Zn are moderately polluted (Igeo 1–2). Cr in samples S2, S4, S11, S13 and S15-17 are moderately to strongly polluted (Igeo 2–3). Moderately to strong pollution degree are attributed to agro-industrial and guarrying activities, agricultural practices, domestic activities, industrial activities, household effluents into the river, indiscriminate dumped of municipal waste into the river, agrochemicals and animal manure in crop production and agricultural runoff from farmlands into Limbe River. These human inputs are responsible for metal pollution of the Limbe River sediments in Atlantic coast of Cameroon, suggesting the presence of contamination within the sediments of the Limbe River System. This finding emphasises the moderate pollution levels and potential toxicity that the sediments ecology of Limbe River may experience. Thus, it is imperative to take the required precautions to prevent any environmental contamination.

#### 4.3 Potential ecological risk (PERI) and ecotoxicity assessment

PERI is pivotal in environmental assessments, particularly for evaluating ecological risks in aquatic environments. It systematically evaluates pollution levels of various metals, facilitating the identification of regions with heightened pollution [12, 24, 25]. This enables targeted interventions by policy makers and experts to mitigate ecological risks effectively, advancing environmental sustainability efforts [26, 39, 52, 63, 65]. The process involves assessing the ecological hazard linked to specific metals by taking into account both pollution and toxicity aspects [64]. The ecological risk factor (Er) varies from 0.04 (Cd) to 4.77 (Zn) (Table 7). The study area display low ecological risk index with Er < 40 for Cr, Cu, Hg, Ni, Cd, Co, Pb and Zn, indicating less ecological impact on living biota and humans for these metals [52]. This clearly suggests low ecological and chronic risks of metals to biological resources in Limbe River. The potential ecological risk index (PERI) for the samples analysed is compiled in Table 7. The PERI varies from 4 (sample S7) to 13.29 (sample S13). The study area shows low ecological risk index (PERI < 150) for metals in Limbe River sediments. These results suggest less ecological risk for metals in the water ecosystem [52]. This means that the environmental quality is usually acceptable. In general, a low PERI level indicates a favorable assessment of the ecological health in the study area, implying that the existing pollution

Table 7Potential ecologicalrisk and Eco-toxicity indices of	Samples	Cd	Со	Cr	Cu	Hg	Ni	Pb	V	Zn	PERI	TRI
heavy metals in Limbe River	S1	0.11	0.11	2.11	0.07	0.02	0.94	0.11	1.41	2.93	7.81	18.59
sediments	S2	0.07	0.13	3.01	0.04	0.03	1.13	0.89	1.88	3.92	11.1	25.22
	S3	0.06	0.11	2.75	0	0.03	0.88	0.05	1.69	3.1	8.68	19.89
	S4	0.04	0.11	3.43	0.03	0.02	0.7	0.42	1.73	3.13	9.62	18.05
	S5	0.04	0.1	1.94	0.19	0.03	0.92	0.17	1.37	3.04	7.8	11.98
	S6	0.07	0.07	0.74	0.47	0.03	0.68	0.19	0.68	1.92	4.84	10.5
	S7	0.04	0.06	0.96	0.14	0.01	0.57	0.31	0.62	1.3	4	23.4
	S8	0.04	0.13	3.26	0	0.02	1.06	0.07	1.78	3.39	9.76	22.99
	S9	0.08	0.1	2.95	0.06	0.03	1	0.35	1.68	3.65	9.9	27.42
	S10	0.07	0.12	2.17	0.13	0.01	0.55	0.47	1.25	3.8	8.58	18.91
	S11	0.04	0.11	4.27	0	0.02	0.66	0.12	2	3.3	10.52	17.17
	S12	0.06	0.12	1.2	0.07	0.01	0.45	0.32	0.79	2.82	5.84	23.93
	S13	0.05	0.14	5.17	0	0.01	0.74	0.1	2.3	4.77	13.29	21.06
	S14	0.05	0.12	2.93	0.07	0.01	0.65	0.09	2.1	4.46	10.49	22.7
	S15	0.05	0.14	4.52	0	0.01	0.79	0.09	2.29	4.21	12.1	15.95
	S16	0.04	0.13	3.91	0	0.01	0.86	0.12	2.08	4.1	11.26	10.87
	S17	0.04	0.11	3.37	0	0.03	0.59	0.15	1.51	2.11	7.93	18.86
	S18	0.05	0.06	0.81	0.08	0.03	0.62	0.54	0.57	3.8	6.57	12.15
	TEL	0.59	-	37.3	35.7	0.17	18	35	-	123		
	PEL	3.35	-	90	197	0.48	36	91.3	-	315		
	EML	5	-	80	70	0.15	30	35	-	120		
	SEL	10	-	110	110	2	75	250	-	820		
	ERM	9	-	145	390	1.3	50	110	-	270		
	Metal contents	0.17	-	456.70	9.47	0.04	168.61	21.55	-	235.7		



levels are mostly within the acceptable thresholds [64, 65]. Consistent with the Er results, the study site is a low ecological risk environment with respect of heavy metals. The values of Er and PERI indicate the ecological risk associated with each element, with Cr exhibiting the highest Er value and Ag with lowest Er value. From the findings, it can be inferred that there is no significant risk associated with any heavy metal since all projected Er and PERI values remained below 40 and 150 respectively [63–65]. This classification aligns with the typical understanding of Er and PERI values, where values below 40 and 150 indicate minimal ecological risk factor and potential ecological risk index. Therefore, based on the Er and PERI values obtained, it can be highlighted that the investigated heavy metals do not pose a substantial ecological hazard, as their Er and PERI values fall within the low-risk category [63–65].

To determine the biological effects of heavy metals for this study, five sediment quality guidelines (SQGs) parameter were used: threshold effect level (TEL), probable effect level (PEL), Effect range median (ERM), effect range low (EML) and severe effect level (SEL). The values of TEL, PEL, ERM, EML and SEL were compared with the mean content of heavy metals in sediments of Limbe River (Table 7). The results indicated that Cd, Cu, Hg and Pb had no biological effect on the water ecosystem as their concentrations were below the TEL, PEL, ERM, EML and SEL values, indicating low toxicity impact of these metals to the aquatic ecosystem. Cr concentrations were above the TEL, PEL, ERM, EML and SEL values, suggesting that adverse effects of Cr are expected to occur in the aquatic ecosystem thus, significant toxicity of Cr in water ecosystem. Ni and Zn contents were above the TEL, ERM and EML, which indicates that adverse effects would occur frequently. This suggests high toxicity impact with adverse biological effects on humans, aquatic organisms and biota in the water ecosystem [70]. Ni and Zn contents were below SEL and PEL values, and adverse effect rarely occurs in the water ecosystem. These results indicate that Cr, Ni and Zn have the greatest impact on biological resources and their toxicity is of great concern. These results also point out that benthic organisms inhabiting the sediments may have developed toxic responses to these heavy metals. Therefore, it can be highlighted that the elevated levels of various heavy metals in the sediments of the Limbe River System suggest a concerning environmental scenario. In other words, benthic organisms in this habitat are likely experiencing toxic stress due to the accumulation of elements like Cr, Ni and Zn beyond safe levels [64].

The toxic risk index (TRI) aims to inform about potential environmental impacts stemming from detected heavy metals levels in the study area. This index provide information regarding the potential ecological damage caused by the total amount of measured metals in the research area [65]. Understanding TRI assessment results is vital for informed decision-making across government, industry, government, non-governmental organizations, and the general public and academia [63–65]. In the study area, the toxic risk index (TRI) values range from 10.49 in sample S6 to 27.42 in sample S9 (Table 7; Fig. 10). Samples S5, S6, S16 and S18 are in the class of moderate toxicity risk of heavy metals (TRI, 10–15) and



**Fig. 10** Histogram of toxic risk index of heavy metals in Limbe River sediments



account for 22.22% of the study area. Samples S1, S3-4, S10-11, S15 and S17 are in the category of significant toxicity risk of heavy metals (TRI, 15–20), accounting for 38.88% of the study area, while samples S2, S7-9 and S12-14 fall in the class of very high toxicity risk of metals (TRI > 20), and accounts for 38.88%. The moderate to very high toxicity risk indicates ecological, chronic and biological effects of metals to the water ecosystem and human through food chain [71–73]. Therefore, the outcome suggests that the combined presence of quantified metals in the study regions poses a level of risk to the environment that falls within a moderate to very high range of pollution. This classification is indicative of a potential impact on ecological health, which may not be severe [63–65]. Consequently, this indicator demonstrated that ecological risks were identified from heavy metals found in the sediments of Limbe River.

The Modified Hazard Quotient (mHQ) is a method utilized to control the degree of severity by metals to aquatic organisms. The method utilized in this study is determined by analyzing the distribution of adverse ecological synoptic impacts for guantitative thresholds including TEL, PEL, and SEL, which are utilized to assess the metal content in sediments [39]. Modified hazard quotient (mHQ) in the study area varies from 0.08 (Cu) in sample S17 to 6.35 (Cr) in sample S9 (Table 8; Fig. 11). In ascending order, the measurements of mHQ were as follows: Cr > Ni > Zn > Pb > Cu > Hg > Cd > As. This ranking indicates the relative severity of contamination, with As exhibiting the lowest and Cr the highest contamination levels. The study area displayed no severity of pollution (mHQ < 0.5) for As and Cd, and very low severity of pollution for Cu, Pb and Hg (mHQ = 0.5-1). Cu in sample S5 shows low severity of pollution (mHQ = 1-1.5) and Zn is in the category of moderate severity of pollution (mHQ = 1.5-2). Cr and Ni in most of the samples show extreme severity of pollution of heavy metals (mHQ > 3.5). Notably, As, Cd, Cu, Pb and Hg demonstrate minimal contamination severity, Zn show moderate contamination severity while Ni and Cr show extreme contamination. This is generally due to anthropogenic activities associated with crop production, domestic activities, industrial activities and other human inputs [19]. Previous study in Limbe beach sediments shows low ecological risks [5]. Thus, severity of pollution might vary according to location and anthropogenic practices [71]. These findings underscore the importance of monitoring and assessing heavy metals contamination in sediment environments, particularly focusing on metals such as Cr and Ni, to inform effective environmental management strategies aimed at safeguarding aquatic ecosystems [63–65]. The computed mPECQ in Limbe River sediments range from 0.62 (sample S7) to 1.51 (sample S13; Table 8). Samples S6, S7, S10, and S12 were all less than 1 indicating minimal toxic effects (mPECQ < 1) which are < 25% toxicity incidence in the study area. The rest of the sampling sites had values greater than one (mPECQ = 1-1.5), which represents 25 to 75% toxicity incidence in the study area. The distribution in mPECQ of heavy metal concentrations base on sites in the study area required more focus and attention due to their toxicity effects to biota and humans [72].

Probability toxicity index (mERMQ) determine the ecological pollution degree of metals in each sample. The results of probability of toxicity index are listed in Table 8. The mERMQ varies from 0.71 in sample S7 to 1.75 in sample S13. Twelve

	As	Cr	Cu	Ni	Zn	Cd	Pb	Hg	mPECQ	mERMQ
S1	0.15	4.06	0.62	4.47	1.61	0.45	0.63	0.64	1.08	1.25
S2	0.14	4.85	0.47	4.90	1.87	0.37	1.82	0.76	1.45	1.70
S3	0.14	4.64	0.09	4.33	1.66	0.36	0.45	0.71	1.15	1.32
S4	0.16	3.89	0.99	4.42	1.64	0.29	0.79	0.71	1.17	1.37
S5	0.16	2.40	1.57	3.80	1.31	0.37	0.84	0.71	1.06	1.22
S6	0.12	2.74	0.86	3.48	1.07	0.27	1.07	0.41	0.70	0.78
S7	0.16	5.04	0.09	4.76	1.74	0.28	0.49	0.64	0.62	0.71
S8	0.14	5.77	0.09	3.74	1.71	0.27	0.68	0.64	1.36	1.57
S9	0.13	6.35	0.09	3.97	2.06	0.33	0.60	0.50	1.31	1.51
S10	0.14	4.78	0.62	3.73	1.99	0.31	0.57	0.41	0.88	1.05
S11	0.13	5.94	0.09	4.10	1.94	0.31	0.58	0.41	1.27	1.47
S12	0.16	5.52	0.09	4.27	1.91	0.28	0.68	0.41	0.62	0.74
S13	0.12	5.18	0.42	3.86	1.67	0.29	1.25	0.58	1.50	1.76
S14	0.13	4.80	0.54	4.61	1.80	0.39	1.14	0.73	1.06	1.25
S15	0.13	4.11	0.84	3.41	1.84	0.38	1.32	0.46	1.41	1.64
S16	0.16	3.07	0.61	3.11	1.58	0.34	1.08	0.50	1.35	1.57
S17	0.14	5.13	0.08	3.54	1.37	0.29	0.75	0.71	1.04	1.20
S18	0.16	2.51	0.64	3.64	1.84	0.32	1.41	0.76	0.71	0.86





**Fig. 11** mHQ of heavy metals in Limbe River sediments



sample sites (S1, S3-S7, S10-S12, S15, S12-S18) are in the class of medium risk level (mERMQ = 0.1–0.5) which account for 66.66% and represents 21% of probability toxicity index of heavy metals. The other sampling sites (S2, S8-S9, S13, S15 and S16) are in the class of very high risk levels (mERMQ > 1.5), accounting for 33.33% and represents 76% of probability toxicity index for heavy metals. This indicates that the Limbe River sediments have 97% probability of toxicity in heavy metals and this clearly indicate anthropogenic metal sources in the Limbe River ecosystem. The high risk levels with 97% probability of toxicity in heavy metals is attributed to agro-industrial and quarrying activities, domestic and industrial activities, municipal solid and liquid waste, wastewater irrigation and agricultural practices as reported in other studies in Cameroon [5, 24, 72, 73].

To assess the heavy metals contamination status of the sediments of Limbe River, the metal concentrations obtained from this study were compared with those reported by previous studies (Table 9). The mean concentrations of most heavy metals in the Limbe River sediments in this study were comparably lower than those found in river sediments of other study sites in Cameroon [26, 39]. In addition, the mean concentrations of Co, Cr, Mn, Ni, and Zn in the sediments of the Limbe River were higher than those of river sediments from Pakistan and Turkey [71, 74], while the other mean content of other heavy metals were lower. These results revealed that the heavy metal contents in the sediments of the different river sediments varied greatly due to the existing spatial heterogeneity in the sediments as a result of human activities and natural sources such as rock weathering [72–75].

	Cd	Со	Cr	Cu	Hg	Mn	Ni	Pb	Zn	References
Limbe River sediments (Cameroon)	0.17	64.57	456.7	9.47	0.04	1272	168.61	21.55	235.7	This study
Nkwen River sediments (Cameroon)	1.25	33.55	121	1131	849	414.16	43	508.13	1123.58	[39]
Mari stream sediments (Cameroon)	0.08	5.28	25	31.94	7.62	1836.1	5.11	200.88	1636.73	[26]
Keban dam reservoir (Turkey)	1.5	24	144	34	-	588	107	11	77	[71]
Samana stream (Pakistan)	1.3	-	21	37	-	900	33	16	45	[74]
Bahmanshir River (Iran)	0.22	-	133	86.5	-	425	84.4	28.8	113	[75]

Table 9 Comparison of the mean contents of heavy metals in this study with those of other aquatic water (mg/kg)



#### 4.4 Environmental implications

The results of this study reveal various perceptions of heavy metals in Limbe River sediments, emphasizing the need for site-specific assessment and management strategies that account for both natural and anthropogenic inputs. High concentration of Co, Cr, Mn, Ni, Pb, Sr, V and Zn, may indicates environmental stress actions in the Limbe coastal area, Atlantic Ocean. Several sediment samples exhibit pollution levels, highlighting the importance of tailored sustainable development measures. Each study area is considered, taking into account both rural and urban inputs. Anthropogenic activities prevalent in major urban areas and cities appear as plausible subsurface sources of heavy metals contamination in the study area. Further research on historical conditions, migration patterns, biological efficiency, toxicity and potential environmental impacts of heavy metals highlight the need for a thorough understanding of long-term environmental threats, including both input from urban areas and cities. Increased concentration of heavy metals proximity to urban areas and cities reaffirms the role of anthropogenic practices in contributing to sediments pollution in both urban areas and cities, emphasizing the need for evaluation of both natural and anthropogenic input in environmental assessment.

#### 4.5 Remediation strategies of heavy metals

The Limbe River sediments reveal significant contamination of sediments by Co, Cr, Mn, Ni, Pb, Sr, V and Zn. It is necessary for the concentration of these heavy metals to be remediated in river sediments so as to prevent extreme toxicity and also prevent health hazards to humans and biota. It is also necessary that the population should be educated about negative consequences of indiscriminate anthropogenic practices such as mining, agro-industrial activities, quarrying operations, domestic activities and agricultural practices (fertilizers, herbicides, bio-solids, sewage, pesticides and other agrochemicals) which further lead to build-up of some of these metals in sediments of water ecosystem [39]. Furthermore, it is important to note that sediments and soils are treated either by dilution, adsorption, biodegradation, volatilization, thermal treatment, phytoremediation, electrokinetic remediation, washing, chlorination, ion exchange, or bioleaching in order to reduce the concentration of these heavy metals in sediments or soils [76, 77].

# 5 Conclusions

The sediments display high contents in Fe<sub>2</sub>O<sub>3</sub>, Ni, Pb, Sn, Cd, Co, Cr, Mn, Sr, V and Zn. The enrichment of Fe<sub>2</sub>O<sub>3</sub> suggests that the sediments are ferruginous and are sourced from haematization of the parent rocks (basaltic rocks) and composed of ferromagnesian minerals. The elevated contents of heavy metals is attributed to geogenic sources (intense alteration of basaltic rocks, volcanic eruptions and atmospheric deposition) and human inputs such as agricultural practices (phosphate fertilizers, agrochemicals, insecticides, pesticides and herbicides), agro-industrial activities, guarrying activities, domestic and industrial activities. Correlation matrix revealed evidence of common provenance linked to the occurrence of basaltic rocks and anthropogenic activities. According to single and complex contamination indicators, the Limbe River sediments are significantly contaminated due to geogenic influences and anthropogenic practices. Pollution indicators: PLI = (0.84 - 1.77), NIPI: (0.30 - 8.28), and EF = (0 - 5.67) revealed metallic pollution of the Limbe River ecosystem. Potential ecological risk index (ER = 0.04-4.77; PERI = 4-13.29) suggests low ecological risk index. Modified hazard quotient (mHQ = 0.082-6.35) and Toxic risk index (TRI = 10.49-27.42) indicates significant pollution severity and high toxicity risks levels of heavy metals in the aquatic ecosystem. Sediment quality guidelines show biological effects of various metals to the river ecosystem. This study is vital to ensure efficient wastewater treatment, regulating excess fertilizers and pesticides usage in agricultural farms, and restricting the discharge and dumping of solid and liquid waste into rivers. Further training is required for city dwellers for a sustainable waste management and environmental contamination through domestic, agricultural and industrial activities. Therefore, this serves as an early warning of sediments contamination and heavy metal pollution in riverine ecosystem of Atlantic coast, Limbe, Cameroon. Firstly it is recommended that the water and sediment samples of the river should be monitored regularly to avoid any metal pollution in the aquatic ecosystem in the future. Further studies are also required to investigate the interaction of heavy metals between sediments and water and the associated environmental factors. Furthermore, research efforts could explore the long-term trends in heavy metals accumulation, assess the effectiveness of remediation strategies, and investigate the influence of climate change on heavy metals dynamics in aquatic ecosystems. Although the findings obtained in this



study suggested that anthropogenic activities have important effect on the contents of heavy metals in the sediments of the Limbe River, it is recommend that the water and sediment samples of the river should be monitored regularly to avoid any heavy metal pollution in the river in the future.

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#### Declarations

Competing interest The authors declare no competing interests.

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