

Potential Ecological Risk of Heavy Metals in Sediments from the Ivory Coastal Areas (Toukouzou Hozalem-Assinie)

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ABSTRACT

The level and the ecological risk assessment of heavy metals were evaluated in surface sediments of 72 samples from 12 stations located in the Toukouzou Hozalem-Assinie zone along the Ivorian coast using X-ray fluorescence spectroscopy. The heavy metals contamination was assessed using pollution indices: Modified degree of contamination (mCd), potential acute toxicity (TU), and potential ecological risk index (RI). The results revealed that they are ranked in descending order: Fe>Cr>Mn>V>Zn>Ni>Pb>As>Cu>Cd and the mCd values are between 4.15 and 7.86 which reflect a high degree of contaminations. The highest total toxic units (Σ TUs) were calculated in sediment samples with Cr and Cd presenting the higher TUs compared to the rest of heavy metals and contributed the most (80%) to the overall TUs. It reveals a high potential toxicity for the marine ecosystems in the Ivorian coast. Comparison with sediment quality guidelines (TEC, PEC, PEL, and mPECq) showed that Cr, Cd, and As are 75% toxic to most species of aquatic organisms living in sediments. Potential ecological RI values indicate moderate ecological risk for Cr, considerable for As, and very high for Cd for most sites.

Key words: Contamination, Heavy metals, Ivorian coast, Sediments, Ecological risk assessment, Toxic.

1. INTRODUCTION

Industrial and urban activities have contributed during the past few decades to the increase in metal contamination in marine ecosystems and directly influencing the coastal areas through sewage rejection and/or deposition of contaminated atmospheric particulate matter [1,2]. Heavy metals are considered dangerous to the aquatic ecosystem or humans because of their non-biodegradability, bioaccumulation, persistent, ubiquitous, and toxic character [3]. Once they reached the aqueous systems, they are adsorbed and accumulate on suspended particles that sink rapidly to the bottom and strongly attach to sediments as final reservoirs [4]. Environmental factors, such as sediment properties (e.g., organic matter [OM] and clay content), are important in explaining the sources and distribution of heavy metals. Thus, the ability of sediments to adsorb both organic and inorganic contaminants makes sediment analysis a valuable tool for the assessment of the quality of aquatic environment [5]. Lead and cadmium have been included in the regulations of the European Union for hazardous metals [5], while chromium and nickel are listed as hazardous metals by the United States Food and Drug Administration [6]. In the Ivory Coast, the coastline covers an area of 23.253 km² or 7% of the area [7]. It produces about 41 million m³ of gas per year and experiences intense maritime traffic [7]. It is the seat of industrial, commercial, tourist, and fishing activities [7]. The dynamism of its activities is supported by the proximity of the port of Abidjan and maintained by the important migratory flow from the Central and Northern regions. In addition, the Ivorian coastal area is full of numerous oil platforms. All these activities are likely to pollute it. Studies carried out in the Ebré Lagoon Rodrigue *et al.*, Wognin *et al.*, Toure *et al.*, Konan and Albert,

Coulibaly *et al.*, and Keumean *et al.* [8-13] with (Cd, Cu, Pb, and Zn); (Ni, Cu, Cd, and Zn); (Cd, Zn, Fe, Cu, Mn, and Hg); (Cd, Co, Cu, Ni, Pb, and Zn); (Cd, Zn, Fe, Cu, Mn, and Hg); (Pb, Zn, Cu, Cd, and Cr), respectively, have shown the presence of certain heavy metals in the sediments. However, in Ivory Coast, very few studies have been carried out with a multitude of heavy metals as in this study, namely, Zn, Cr, Ni, Pb, Cu, Cd, V, Mn, Fe, and As at the level of the Ebré Lagoon but mainly on the coastal area. Studies on heavy metals pollution in coastal areas of Cote d'Ivoire are still limited [13]. Furthermore, studies on metal pollution in coastal sediments, and their ecological impacts on natural ecosystems, have increased in the past few decades Ngeve *et al.*, El Zrelli *et al.*, Jamshidi and Bastami, Ahmed *et al.*, Goher *et al.*, Mirzaei *et al.*, and Wang *et al.* [14-20]. For this reason, it is necessary to point out that ecological studies are paramount to help managing the local environment. In the present study, we aimed to (1) investigate the current pollution status of heavy metal (Zn, Cr, Ni, Pb, Cu, Cd, V, Mn, and As); (2) evaluate the ecological risks of heavy metals in an integrated system by comparing the present data with those of sediment quality guidelines (SQG).

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2. MATERIALS AND METHODS

2.1. Sampling

The study area is located in a coastal strip with about 204 km long from Toukouzou (TKZ)-Hozalem to Assinie. The region is extended between latitude 5°15'0" N and 5°00'0" N and longitude 4°35'0" W and 3°20'0" W (Figure 1). Superficial sediment samples were collected in November 2017–February 2019, from 12 different stations: TKZ, Addah, Adjué, Jacquville (JAC), Adjouffou (ADJ), Bassam-Modeste Plage (BMP), Bassam-Modeste Lagune (BML), Azurety (AZT), Assinie-Plage, Assinie-Lagune (AL), Assinie Canal Droite (ACD), and Assinie Canal Gauche. Sampling activities were carried out in six campaigns over four seasons (GSS: Long dry season from January to March, GSP: Long rainy season from April to June, PSS: Short dry season from July to September, and PSP: Short rainy season from October to December), for a total of 72 samples.

2.2. Sediment Characterization

The clay, silt, and sand contents of the sediment samples were determined using laser particle size analyzer (Mastersizer 2000, Malvern, UK). Before analysis, all samples were treated with 37% H₂O₂ and 10% HCl to remove OM and carbonates. The carbonate concentration on the sediment was determined by Bernard calcimeter method [21].

For total OM (TOM) determination, 4 g of samples were combusted in an oven at 550°C for 4 h and 950°C for 2 h. TOM was determined by the following equation:

$$\text{TOM}(\%) = \left(\frac{B - C}{B} \right) * 100 \quad (1)$$

Where, B and C are the weights of dried sediment before and after combustion in the oven, respectively.

2.3. Sample Analysis

Samples collected were dried in a room at ambient temperature (about 23°C), ground with a vibratory ball mill (RETSCH GmbH, Type MM400; 42781 Haan, Germany), and sieved at 63 µm. Subsequently, the samples

were mixed with 10% of binder (Fluxana BM-0002-1-CEROX) and 5 g pellets were made using 15-ton pressure (Specac; Atlas TM manual 15 Ton Hydraulic Press, England) before metals analysis by the X-ray fluorescence (XRF) method (energy-dispersive XRF spectrometry: EDXRF; Spectro-XEPOS, AMETEK, France).

The accuracy and precision of the XRF analyses were verified by repeated measurements of reference materials to the STANDARD IGGE IRMA, GSR-5 (Geochemical Standard Reference sample rock) for standardization and to monitor the performance of the instrument with known elementary compositions.

2.4. Evaluation of the Sediment Contamination

Modified degree of contamination (mCd), potential acute toxicity (TU), SQGs, and potential ecological risk index (RI) have been used to determine the levels of metal contamination in the sediments [19-22]. These tools can provide valuable information to elucidate different aspects of pollution.

2.5. mCd

The mCd was introduced to assess the overall contamination degree at a given site caused by multimetals. The mCd value can be calculated by Equation (2), [23].

$$mCd = \frac{\sum_{i=1}^n C_f^i}{n} \quad (2)$$

Where, n refers to the number of metals and contamination factor (C_f), the C_f suggested by Hakanson [24]. Based on mCd values, seven categories have been proposed to reflect the degree of contamination by heavy metals [23]:

- mCd < 1.5: Very low degree of contamination;
- 1.5 ≤ mCd < 2: Low degree of contamination;
- 2 ≤ mCd < 4: Moderate degree of contamination;
- 4 ≤ mCd < 8: High degree of contamination;
- 8 ≤ mCd < 16: Very high degree of contamination;
- 16 ≤ mCd < 32: Extremely high degree of contamination and;
- mCd ≥ 32: Ultra-high degree of contamination.

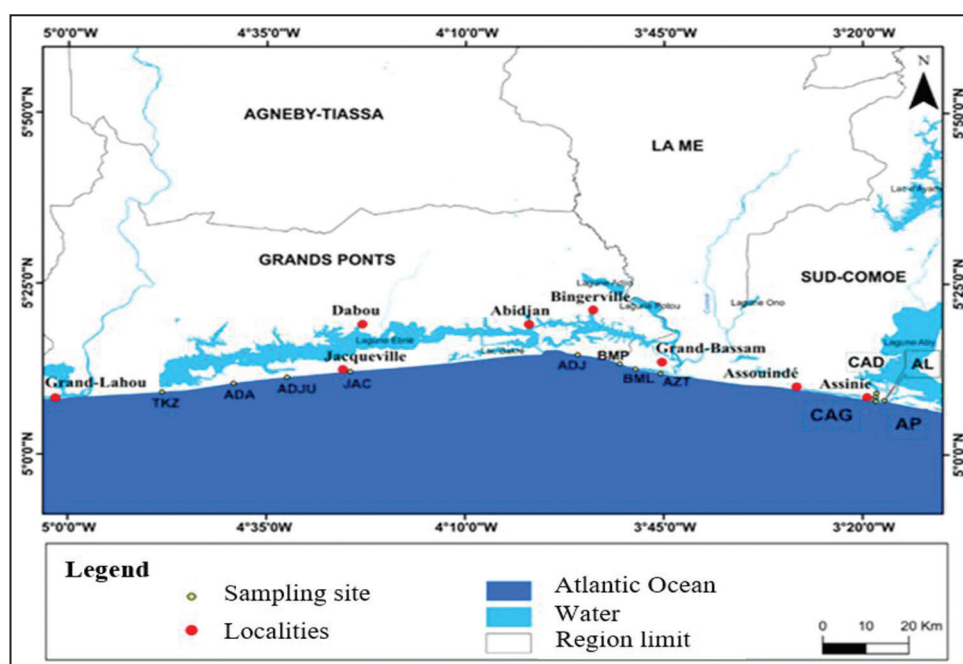


Figure 1: Location map of the coastal zone (Toukouzou Hozalem-Assinie)

2.6. Potential Acute Toxicity (TU)

For assessing the extent to which the aquatic organisms may be influenced by sediment pollution, potential acute toxicity can be estimated [6]. Potential acute toxicity of contaminants in sediment samples is the sum of the toxic units (ΣTU) defined as the ratio of the determined concentration of element i (C_i) to the probable effect level (PEL) value of element i (PEL_i) [25].

$$TU_{st} = \frac{C_i}{PEL_i} \quad (3)$$

If the ΣTU s value is lower than 4, it indicates low toxicity; whereas if the ΣTU s value exceeds 4, it indicates moderate toxicity to an ecosystem [25].

2.7. SQG Method

Several indicators have been developed to evaluate sediment quality. Long and MacDonald [26] proposed four parameters to predict the potential biological threat to benthic organisms:

- TEC: Threshold effect concentration;
- PEC: Probable effect concentration;
- mPEC: Mean PEC quotient;
- PEL: Probable effect level.

The SQGs are important screening tools to investigate trace metal toxicities in freshwater aquatic ecosystems [27].

Adverse effects are expected to occur when contents are below consensus-based TEC, and adverse effects more commonly occur when contents are above the PEC.

However, if $TEC \leq \text{Mean concentrations} \leq PEC$, the potential risk cannot be ascertained from heavy metal concentrations alone. In addition, cumulative toxicities of the metals can be estimated by mPECq [28] and calculated as in Equation (4). Sediment is defined as toxic if $mPECq > 0.5$ and non-toxic if $mPECq < 0.5$ [27]:

$$mPECq = \sum_{n=1}^n \left(\frac{C_i}{PEC} \right) \quad (4)$$

Where, n is number of heavy metals, C_i is the heavy metal concentration in sediment, and PEC is the PEC of each metal.

2.8. Potential Ecological RI

Potential ecological RI is used to estimate the heavy metals pollution degree in sediments [29]. RI is the sum of potential ecological risk of an individual metal i (E_r^i). It represents the sensitivity of a biological community to toxic substance and illustrates the potential ecological risk caused by contaminants.

The potential ecological RI of the multielements (RI) can be calculated through formulas:

$$RI = \sum_{i=1}^n E_r^i \quad (5)$$

$$E_r^i = T_r^i \times C_f^i \quad (6)$$

$$C_f^i = \left(\frac{C_s^i}{C_n^i} \right) \quad (7)$$

T_r^i is the biological toxic factor of an individual element i , with Cd = 30; Ni = 6; Pb = Cu = 5 and Zn = 1 [30]; As = 10; Cr=2 (Xu *et al.*, 2020); V=2; Mn=1.

C_f^i , C_s^i , and C_n^i are the C_f , the concentration in the sediment, and the background reference value for element i , respectively.

According to Hakanson [29], RI caused by heavy metals in surface sediments in coastal areas, could be classified into four categories:

- Low ecological risk: $E_r^i < 40$, $RI < 150$;
- Moderate ecological risk: $40 \leq E_r^i < 80$, $150 \leq RI < 300$;
- Considerable ecological risk: $80 \leq E_r^i < 160$, $300 \leq RI < 600$;
- Significantly high ecological risk: $160 \leq E_r^i < 320$, $RI \geq 600$.

3. RESULTS AND DISCUSSION

3.1. Metal Concentrations in Coastal Sediments (TKZ Hozalem-Assinie)

Comparative table of the contents of metal levels (mg/kg per dry weight) in the Ivorian coastal zone with those recorded in other areas of the world is presented in Table 1. The abundance order of these metals was found to be Fe>Cr>Mn>V>Zn>Ni>Pb>As>Cu> and Cd with mean concentrations of 19144.23; 431.30; 249.12; 54.59; 28.82; 17.37; 8.39; 7.93; 7.57; and 3.08 mg/kg dry weight, respectively.

The means concentrations in the sediments of Cr (140.42–883.42 mg/kg per dry weight), (Cd 1.08–3.88 mg/kg per dry weight), Fe (4510–89,730 mg/kg per dry weight), and As (0.25–18.37 mg/kg per dry weight) were higher than the values (Cd = 0.25 ± 0.20 mg/kg and As = 1.13 ± 0.66 mg/kg); (Cr = 83.92 mg/kg and Cd = 1.45 mg/kg) reported by Coulibaly *et al.*, Keumean *et al.* [12,13] in the Ebrie Lagoon, respectively. These low concentrations of metals in the areas might be due to less agro-chemical usage around the study areas and less industrial activities which are the major sources of heavy metal contamination in aquatic environments [13].

Furthermore, the comparison of heavy metals contents recorded herein with those reported in sediments from different regions of the world showed that the Cr, Cd, and Fe concentrations in surface sediments of Ivorian coastal are remarkably high (Table 1). This could be due to anthropogenic activities, petroleum, refineries, fuel, fossil fuel burning, and industrial waste [8].

In contrast, the concentrations of the other heavy metals analyzed (i.e., Zn, Ni, Cu, V, and Mn) were found to be low compared to those reported in other regions of the world and in the Ivorian coastal zone with the exception of the Persian Gulf coast (Table 1). These low concentrations of metals in the areas could be due to less agro-chemical usage around the study areas and less industrial activities which are the major sources of heavy metal contamination in aquatic environments [12].

On the other hand, the values of Pb obtained were close to those obtained at Caspian Sea and Cameroon coast.

3.2. Sediment Classification

Clay, silt, and sand contents of sediment samples are presented in Table 1. Effects of TOM and grain size on the spatial variation of metals in the sediment are shown in several studies [30]. TOM is another parameter affecting heavy metal amount of sampled sediment. The content of TOM is increasing with decreasing grain size. Sediments enriched by OM react with metals and create metal complexes. Particle size analysis indicated that sandy sediment is dominant in the majority of sampling sites. Sand, clay+silt ranged from 92.09 to 98.51% and 0.6 to 1.36% respectively. The TOM was generally low. It ranged from 0.33% to 1.17% with an average of 0.51% (Table 2). In general, higher values of TOM are observed at sites AL and AP. It may be due to the lower turbulence of

Table 1: Comparative table of the contents of metal levels (mg/kg per dry weight) in the Ivorian coastal zone with those recorded in other areas of the world

Locations	Zn	Cr	Ni	Pb	Cu	Cd	V	Mn	Fe	As	References
Ivorian coastal zone	8.57–185.25	140.42–883.42	13.7–24.53	1.93–46.43	5.58–17.33	1.08–3.88	25.33–250.5	25.4–2148.05	4510–89730	0.25–18.37	Present study
Mean	28.82	431.3	17.37	8.39	7.57	3.08	54.59	249.12	19144	7.93	
Nador Lagoon (Morocco, Mediterranean coast)	554.9	71.6	-	135	150.8	1.6	-	-	-	-	[33]
Coast of Cameroon	7.9–212	5.13–328	1.59–457	1.14–21	1.0–64	0.01–0.21	-	-	3473.9–136.762	-	[34]
Caspian Sea	88.07	102.02	43.27	11.9	39.33	0.55	117.84	-	4.32%	11.01	[35]
Algerian coast	101.3	97.9	32.3	27.3	19.7	0.2	124.1	365.6	3.09	21.8	[17]
Nasser Lake (Egypt)	26.9–98.36	-	-	-	19.22–41.82	0.13–0.349	-	92.8–619.7	6.17–21.05	-	[18]
Persian Gulf Coastal (Iran)	1.35	1.11	0.89	0.73	2.03	0.04	-	-	1.86	-	[19]

Table 2: General characteristics of the sediments

Sampling sites	TOM (%)	Carbonate (%)	Sand (%)	Clay+Silt (%)
TKZ	0.43	0.75	98.14	1.86
ADDA	0.46	0.88	97.5	2.5
ADJUE	0.36	0.78	98.51	1.49
JACQ	0.46	0.7	97.82	2.18
ADJ	0.34	0.6	92.09	7.91
BML	0.55	0.67	98.35	1.65
BMP	0.43	0.7	98.32	1.68
AZT	0.6	0.64	97.87	2.13
ACD	0.4	0.67	97.67	2.33
ACG	0.33	0.71	98.06	1.94
AL	1.17	1.36	96.94	3.06
AP	0.65	1.35	97.6	2.4
Average±SD	0.51±0.23	0.82±0.26	98.48±1.76	1.51±1.73

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water that allows sedimentation of fine-grained particles. Carbonate levels at the sampling sites range from 0.6% to 1.36%, with an average value of $0.82 \pm 0.26\%$. The highest carbonate levels were observed at sites AL and AP, respectively (Table 1). The highest average values for CaCO_3 and TOM were observed because these sites do not receive any wave's energy from Ivorian Coast. Most organic materials are finally deposited in seabed sediments through a series of physical, chemical, and biological processes [30]. It may be due to the lower turbulence of water that allows sedimentation of fine-grained particles

3.3. mCd

The mCd values for the studied metals in the Ivorian coastal zone in sediments are listed in Figure 2. The mCd values of Zn, Cr, Ni, Pb, Cu, Cd, V, Mn, Fe, and As at 12 stations are between 4.15 and 7.86. Three sampling locations (TKZ, BML, and ADJ) could be categorized as having a highly mCd. The high mCd value at TKZ was due to the highest Cf values, with major contributions from Cd (Cf= 30.78) and Cr (Cf= 12.32). A high Cf of the trace metal implies a high-risk degree to the aquatic environment [31,32]. These results obtained confirm those obtained by Konan and Albert [11]. This state of Vridi channel is essentially due to

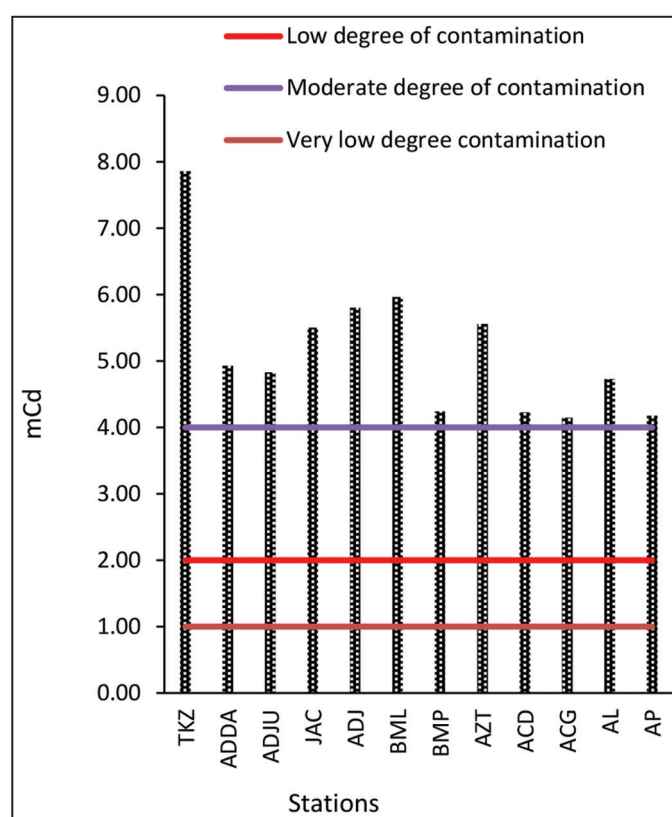


Figure 2: Modified degree of contamination based on contamination factors of costal sediments from the Ivorian

high anthropogenic pressures doing on this estuary. Other elements, such as V, Zn, and As, also significantly contributed to the mCd values at TKZ. This appears to be due to refining fuel releases, oil, industrial and chemical waste, shipping, and oil traffic. Overall, all stations can be interpreted high degree of contamination using mCd classification.

3.4. Potential Acute Toxicity

The sums of the toxic units (ΣTU) for each of the sampling sites based on heavy metal concentrations are shown in Figure 3. ΣTU for all stations followed the descending order of $\text{Cr} > \text{Cd} > \text{Ni} > \text{As} > \text{Zn} > \text{Pb} > \text{Cu}$. The contribution of Cd and Cr to ΣTU was the highest (81.87%) compared to the other heavy metals. The moderate toxic risks of As and

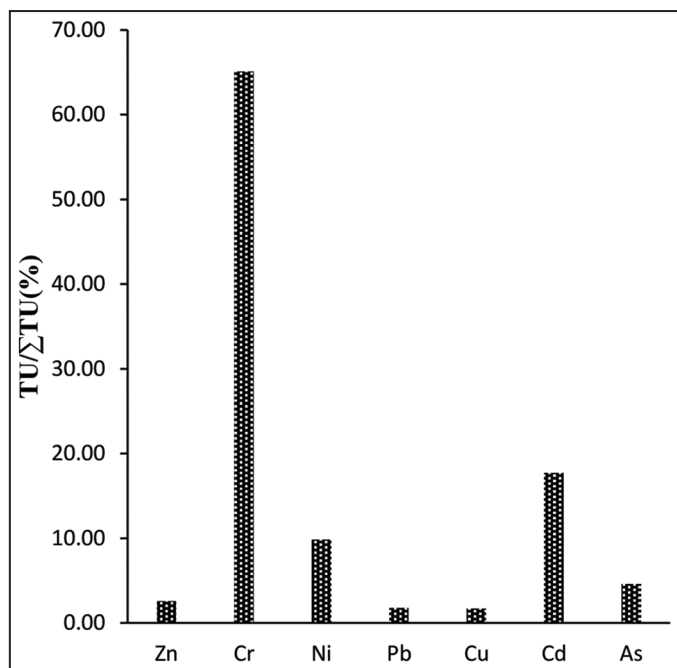


Figure 3: Contribution of respective heavy metals to the sum of the toxic units from the Ivorian

Ni were observed as the ΣTUs values exceeded than 4 comparatively to Zn, Pb, and Cu where the ΣTUs value was lower than 4, indicating low toxicity, Pedersen *et al.* [25]. In addition, the contamination may cause toxicity to other benthic organisms, in particular molluscs [15], crustaceans, and fishes, of which many species are widely consumed in Ivorian Coast and may. Therefore, it would present a serious risk for human health. These observations indicate that the protection of the coastal ecosystems in the Ivorian is still possible with the provision of stopping any type of industrial wastes at sea.

3.5. SQG Method

3.5.1. TEC and PEC approach

To evaluate the environmental quality of sediments, we compared the average concentrations of heavy metals to the American SQG of Macdonald *et al.* [27]. The TEC and the PEC established by Macdonald *et al.* [27] are used to assess the quality of marine and freshwater sediments. The TEC identifies contaminant concentrations below which sediment-dwelling organisms are not affected, while the PEC identifies contaminant concentrations above which adverse effects on sediment-dwelling organisms are observed. The concentrations of heavy metals in the sediment samples were compared to the TEC and PEC values of seven heavy metals (Zn, Cr, Ni, Pb, Cu, Cd, and As) and are recorded in Table 3. Compared to the results of the present study: As, Zn, Ni, Pb, and Cu are lower than the TEC 75%, 91.67%, and 100% in the samples, respectively. Therefore, these metals do not represent a hazard for most samples. Between the TEC and PEC, the concentrations of Zn, Ni, Pb, and As are 8.33% and 25% of the samples. Zn, Ni, and Pb are toxic to the coastal zone environment at the TKZ, JAC, and BML sites, respectively. As is toxic at the BMP, AZT, and AP sites. However, Cd is 100% toxic for all stations. Cr is very toxic for the 100% stations. These results indicate that the concentrations of Zn, Ni, Pb, As, Cd, and Cr at the level of the Ivorian coastal zone are likely to cause adverse effects on organisms living in the sediments. Furthermore, according to Rodrigue *et al.* [8], only Pb, Cd, and Zn are harmful to the environment of the Vridi Canal because of the intense industrial activities that take place there

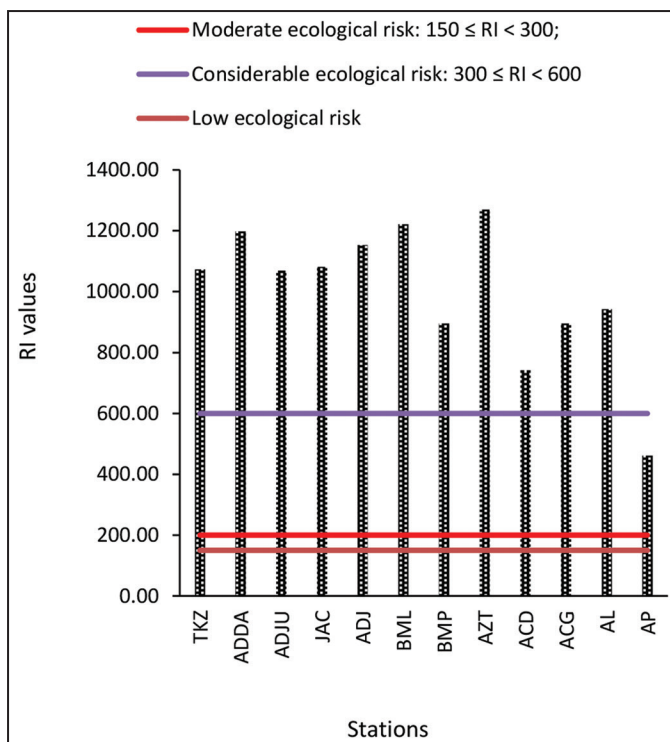


Figure 4: Potential ecological risk index based on contamination factors of surface sediments from the Ivorian Coast

Table 3: Sediment quality at stations

	Zn	Cr	Ni	Pb	Cu	Cd	As
TEC	121.00	43.30	22.70	35.80	31.60	0.99	9.79
PEC	459	111	48.6	128	149	4.98	33
Mean	28.82	431.3	17.37	8.39	7.57	3.08	7.93
Minimum	8.57	140.42	13.7	1.93	5.58	1.08	0.25
Maximum	185.25	883.42	24.53	46.43	17.33	3.88	18.37
% of samples <TEC	91.67	—	91.67	91.67	100	—	75
% of samples between TEC and PEC	8.33	—	8.33	8.33	—	100	25
% of samples >PEC	—	100	—	—	—	—	—

Table 4: Biological toxicity values for metals in sediment

	m-PECq <0.5	m-PECq >0.5
Percentage (%)	25	75%

3.5.2. Assessment of the biological toxicity of metals in sediments

To evaluate the biological toxicity of all the metals studied in the sediments, the m-PECq initiated by Macdonald *et al.* [27] was evaluated. The results of this assessment (Table 4) indicate that 75% of the sediment samples have m-PECq values >0.5 while 25% of the sediment samples have m-PECq values <0.5. Consequently, the littoral zone (TKZ Hozalem-Assinie) would be 75% toxic to most species of aquatic organisms living in the sediments while the Vridi Canal zone would be 57.17% toxic to one or more species of aquatic organisms living in the sediments [8].

3.5.3. Potential ecological RI

Figure 4 presents the potential ecological RI in sediments from the Ivorian Coast. As a consequence of the calculated RI values for Mn,

Zn, V, Pb, Cu, and Ni through the whole study area, these metals present a low potential ecological hazard. Of the 12 sampling sites, 11 sites have RI values greater than 600, indicating very high ecological hazards ($741.56 < RI < 1269.80$) for these stations. Only the AP station is subject to a considerable ecological risk with $RI = 462.09$. The potential ecological risks caused by metals ranked in a decreasing order of $Cd > As > Cr > Ni > Cu >$

$Pb > V > Zn > Mn$. The results showed that Cd ($RI = 11079$), As ($RI = 475.65$), and Cr ($RI = 295.65$) had the highest single potential ecological risk indices in the sediment. These high values of RI are likely caused by anthropogenic inputs (such as offshore oil production, oil refinery, discharged ballast water from oil tanker and other ships, high maritime traffic, transit of oil carriers, port areas, industrial units, and discharge wastewater) [35].

4. CONCLUSION

The results of this study indicated that the mean heavy metal concentrations, in the sediments of Ivorian Coast zone, exhibited a decreasing order: $Fe > Cr > Mn > V > Zn > Ni > Pb > As > Cu > Cd$. From a qualitative point of view, the comparative analysis of metal contents to TEC, PEC, PEL, and m-PEC quality reference and potential ecological RI values indicates that most sites present very high ecological risks. Arsenic (As) is toxic at the BMP, AZT and AP sites. However, Cd and Cr are 100% toxic for all stations. These results indicate that the concentrations of heavy metals are likely to cause adverse effects on organisms living in the sediments. ΣTU for all stations followed the descending order of $Cr > Cd > Ni > As > Zn > Pb > Cu$. The contribution of Cd and Cr to ΣTU was the highest (80%). The mCd values reflect a high degree of contaminations for all stations.

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6. CONFLICTS OF INTEREST

The authors have indicated that they have no conflicts of interest regarding the content of this article.

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