Assessment of Heavy Metals Contamination in Sediments of the Vridi Canal (Côte d'Ivoire)

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Abstract

The concentrations of cadmium, copper, lead and zinc in sediment samples from the Vridi Canal (Harbour area of economic capital of Cote d'Ivoire) were determined to evaluate the level of contamination. All metal concentrations in sediment samples, except Cu, were greater than the concentration of Upper Continental Crust (UCC). Sediment pollution assessment was undertaken by using Enrichment Factor (EF), geoaccumulation index (I_{geo}) and Pollution Load Index (PLI). The enrichment factor (Cd: EF = 20.04; Pb: EF = 3.43; Zn: EF = 1.56) and géoaccumulation index (Cd: I_{geo} = 4.29; Pb: I_{geo} = 1.81) showed that the sediments were polluted. The Pollution Load Index (PLI > 1) indicated that the sediments of the studied area were heavily contaminated. Based on the comparison with sediment quality guidelines, the concentrations of cadmium, lead and zinc would be toxic to one or more species of aquatic organisms living in the sediments.

Keywords

Heavy Metals, Vridi Canal, Contamination

1. Introduction

Aquatic ecosystems are often impacted by heavy metals which represent serious environmental threats. High levels of Pb, Zn, Cd, Cu in aquatic ecosystems are known to adversely affect aquatic organisms. Sediments are important sinks for heavy metals and play a significant role in enrichment and remobilization of heavy metals in aquatic systems [1]. The transfer of metals from sediments to organisms has been reported as an important metal source for many species [2] [3]. Therefore, the evaluation of metal

contamination in sediments is especially vital in the aquatic environment.

In Côte d'Ivoire, the Vridi Canal has a great socio-economic potential. A large number of other economic activities such as fishing and maritime traffic pose an increasing threat of heavy metals. This canal, which links Ebrie lagoon to the Gulf of Guinea, is the only canal which allows one to enter and exit the harbour area of Abidjan. However, an assessment of metal contamination has never been conducted in the Vridi Canal. Different assessments of metal contamination in sediments have been focused in the Ebrie lagoon [4] [5] [6]. These studies have reported high levels of metal contamination in sediments

The objective of this study is to assess the contamination level of cadmium, zinc, copper and lead in sediments of the Vridi Canal by using pollution indices and sediment quality guidelines. This work represents the first multi-metal assessment of sediments from the Vridi Canal.

2. Materials and Methods

2.1. Study Area

Vridi Canal which is an artificial watercourse, is located in the southern part of Cote d'Ivoire and situated between 5˚15'23"N and 4˚0'50"W (**Figure 1**). It was selected for its proximity to most of the industrial and maritime activities taking place such as maritime transport and fishing. This canal is 2.7 km long and 370 m wide and a navigable depth of 15 m. It receives domestic raw sewage, household waste, and industrial wastes from it neighbourhood.

2.2. Sampling and Sample Conservation

Sediment samples were collected by using plastic container. Then sediment samples were put into small plastic bags and kept in a cooler at 4˚C. All samples were transported to laboratory and subsequently stored in a freezer at −20˚C. Upon analysis, samples were defrosted and air-dried in an oven at 60˚C to constant weight, then ground to a powder using an agate mortar. These samples were sieved through a 2 mm mesh and sealed in a clean polyethylene bags then stored until further use. Every precaution was taken to avoid contamination during sampling, drying, grinding, sieving and storage.

2.3. Sediment Analysis

A mass of 0.2 g of each of the homogenized sediment was digested in closed Teflon bomb with a mixture of 1 mL of aqua regia (HNO_3: HCl; 1:3, V/V) and 3 mL of HF, heated to 100˚C for 3h in a water bath. After cooling, a volume of 20 mL of H_3BO_4 (140 g/L) was added to each Teflon bomb to mask free fluoride ions in solution and re-dissolve fluoride precipitates[3]. The final volume was made up to 50 mL with 2% ultrapure HNO_3. The solutions were filtered and stored in polyethylene flasks for later determination of metal content.
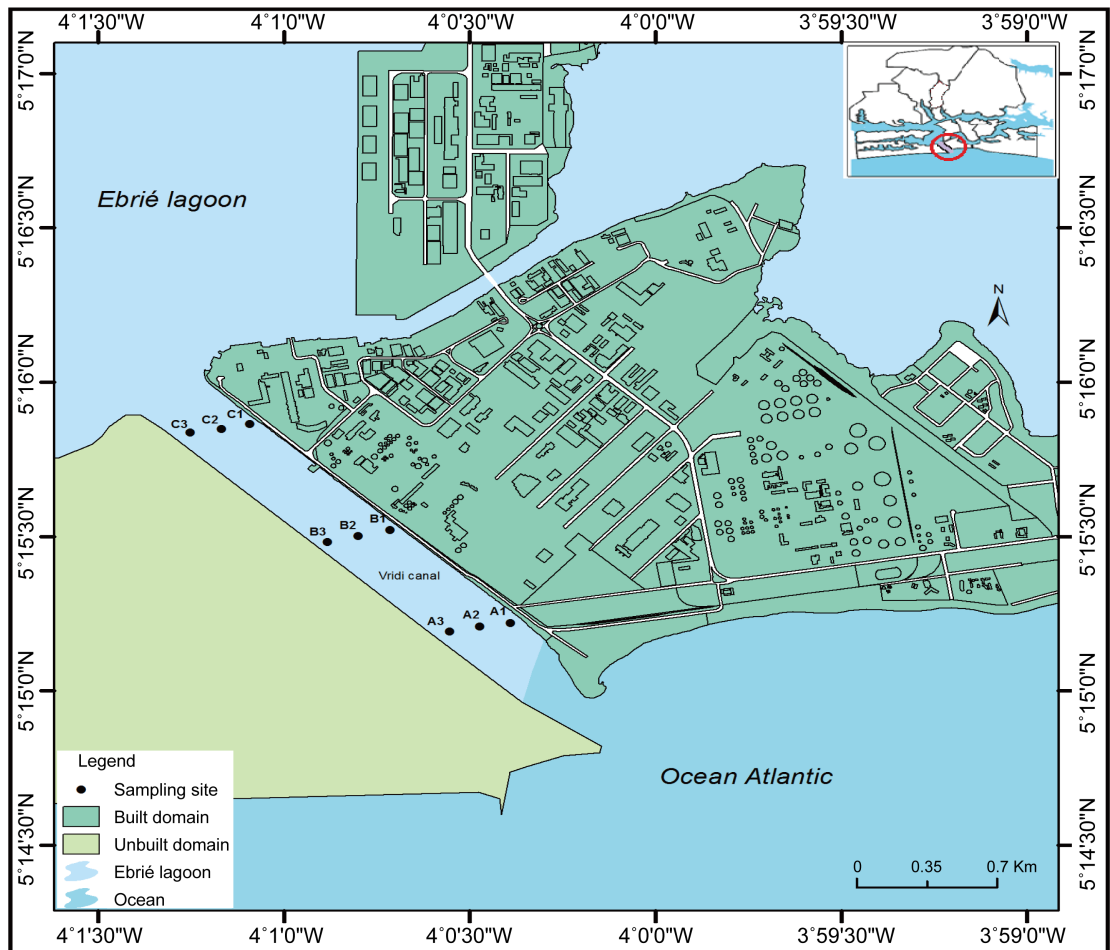
Figure 1. Map of the study area showing sampling sites.

2.4. Determination of Metal Concentration

Metals were determined by using an air-acetylene flame atomic adsorption spectrometer (**Varian SpectrAA 20**). The detection limit was 0.003 mg/kg for Cd, Pb, Cu and Zn. In addition, accuracy and precision of analysis was checked by replicate measurements of standard reference materials (BCSS-1, National Research Council Canada). The measured concentrations fell within the range of certified values, and the recoveries varied between 94% and 108%.

2.5. Statistical Analysis

The analysis of variance (ANOVA one way) was used to evaluate the difference between sites. Differences were considered significant at p values <0.05. Statistical analyses (mean value, minimum, maximum) were carried out with Statistica 7.1 software.

2.6. Sediment Assessment

The following pollution indices were used to determine the level of contamination: contamination factor (CF), pollution load index (PLI), géoaccumulation index (I_{geo})

and enrichment factor (EF).

2.6.1. Contamination Factor (CF)

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or background value [7] [8].

$$CF_i = C_{metal(i)} / C_{background(i)} \qquad (1)$$

where $C_{metal(i)}$ is the concentration of metal (i) in the sediment is sample and $C_{background(i)}$ is the background value of the metal (i). CF values were interpreted as suggested by [7], where: CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination.

2.6.2. Pollution Load Index (PLI)

For the entire sampling site, PLI has been determined as the nth root of the product of the n CF [9]:

$$PLI = \left(CF_1 \times CF_2 \times \cdots \times CF_n \right)^{1/n} \qquad (2)$$

CF_1, CF_2, $\cdots$, CF_n are contamination factors of the sediment sample with respect to element 1, 2, and n, respectively; n is the number of metals investigated.

This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When PLI > 1, it means that a pollution exists; otherwise, if PLI < 1, there is no metal pollution [10].

2.6.3. Geoaccumulation Index (I_{geo})

The degree of contamination from the trace metals could be assessed by determining the geoaccumulation index (I_{geo}). The index of geoaccumulation (I_{geo}) has been widely applied to the assessment of sediment contamination [11]. In order to characterize the level of pollution in the sediment, I_{geo} values were calculated using the equation,

$$I_{geo} = \log_2 \left(C_n / (1.5 b_n) \right) \qquad (3)$$

In this equation, C_n is the total content of the individual element n and b_n is its geochemical background concentration, while 1.5 is the background matrix correction factor due to lithogenic effects. The geoaccumulation index consists of seven classes. Class 0 (practically unpolluted): $I_{geo} \leq 0$; Class 1 (unpolluted to moderately polluted): 0 < I_{geo} < 1; Class 2 (moderately polluted): 1 < I_{geo} < 2; Class 3 (moderately to heavily polluted): 2 < I_{geo} < 3; Class 4 (heavily polluted): 3 < I_{geo} < 4; Class 5 (heavily to extremely polluted): 4 < I_{geo} < 5; Class 6 (extremely polluted): 5 > I_{geo}.

2.6.4. Enrichment Factor (EF)

Enrichment factor (EF) is considered as an effective tool to evaluate the magnitude of contaminants in the environment [12]. The EF for each element was calculated to evaluate anthropogenic influences on heavy metals in sediments using the following formula [13]:

$$EF = \left(C_M / C_{Fe} \right)_{sample} / \left(C_M / C_{Fe} \right)_{background} \qquad (4)$$

where $(C_M/C_{Fe})_{sample}$ is the ratio of concentration of heavy metal (C_M) to that of iron (C_{Fe}) in the sediment sample, and $(C_M/C_{Fe})_{background}$ is the same reference ratio in the background sample. EF values were interpreted as suggested by Sakan *et al*. (2009), where: EF < 1 indicates no enrichment; <3 is minor enrichment; 3 - 5 is moderate enrichment; 5 - 10 is moderately severe enrichment; 10 - 25 is severe enrichment; 25 - 50 is very severe enrichment; and >50 is extremely severe enrichment.

2.6.5. Sediment Quality Guideline

The consensus-based sediment-quality guidelines (CBSQGs) were used in this study to assess possible risk that arises from the heavy metal contamination in sediments of the study area. These synthesized guidelines consist of a threshold effect concentration (TEC) below which adverse effects are not expected to occur and a probable effect concentration (PEC) above which adverse effects are expected to occur more often than not [14].

3. Results and Discussion

3.1. Heavy Metals in Sediments

Results for the levels of Cd, Cu, Pb and Zn in the sediments are shown in Table 1. The range of mean concentrations were: 2.41 ± 2.10 - 4.85 ± 3.31 mg/kg for Cd, 75.65 ± 68.88 - 553.72 ± 437.04 mg/kg for Zn, 5.37 ± 2.42 - 6.29 ± 2.52 mg/kg for Cu, 83.29 ± 34.12 - 115.04 ± 47.44 mg/kg for Pb. During the study period, Cd, Cu, and Pb did not show any significant spatial variations (ANOVA, $p > 0.05$), while, Zn showed significant spatial variation. The highest concentrations of Zn were found at site C2 (near to the Ebrié lagoon). In this study Pb, Zn, and Cd in the Vridi Canal sediments have greater concentrations than those of upper continental crust (UCC). The opposite was observed for Cu. The concentration order found was Zn > Pb > Cu > Cd. Results indicated that Vridi Canal has been affected by activities take place in this area such as, the

Table 1. The mean concentration values of heavy metal (mg/kg dry weight) in sediment of the Vridi Canal.

Site	Cd	Cu	Pb	Zn
A1	3.14 ± 2.63	6.19 ± 2.33	83.29 ± 34.12	117.67 ± 92.42
A2	2.41 ± 2.10	5.52 ± 2.54	98.83 ± 44.02	93.74 ± 62.63
A3	3.12 ± 2.74	5.72 ± 2.27	104.94 ± 47.57	106.64 ± 97.84
B1	3.95 ± 2.72	5.41 ± 2.92	94.29 ± 42.65	101.42 ± 69.65
B2	3.77 ± 2.78	5.87 ± 1.92	115.04 ± 47.44	83.69 ± 58.11
B3	3.69 ± 2.51	6.29 ± 2.52	88.25 ± 30.63	75.65 ± 68.88
C1	4.61 ± 2.38	5.64 ± 2.06	100.47 ± 19.15	190.67 ± 117.09
C2	4.85 ± 3.31	5.37 ± 2.42	97.28 ± 37.93	553.72 ± 437.04
C3	4.46 ± 3.00	5.69 ± 2.73	86.59 ± 26.20	97.53 ± 80.39
Upper Continental Crust (UCC)	0.1	14.3	17	52

oil refinery in the vicinity of the area and maritime traffic. However, this information alone is not sufficient to indicate the level of metal contamination and the sediment metal quality.

3.2. Assessment of Metal Pollution in Sediments

3.2.1. Contamination Indices

Table 2 presents CF, EF and I_{geo} of the metals studied. The mean CF value of Cd was >6 in the sediment samples, which denotes a "very high contamination" by this metal. The mean CF values of Pb and Zn in sediments showed a "considerable contamination". While, the mean CF values for Cu indicated a "low contamination". Overall, the CF for all metals were the descending order of Cd > Pb > Zn > Cu.

Enrichment factor has been used to assess anthropogenic contributions of the metals in sediments [15]. The mean values of enrichment factor of the sediments are shown in Table 2. The mean EF value of Cu was 0.24 ± 0.11, indicated no enrichment. The mean EF value of Zn (1.56 ± 2.01) showed minor enrichment, and the mean EF value of Pb (3.43 ± 1.48) manifested moderately enrichment. Among the selected metals, the mean EF value of Cd (20.04 ± 9.82) demonstrated severe enrichment in the sediments. The EF for all metals were the descending order Cd > Pb > Zn > Cu.

I_{geo} is the quantitative measure of the contamination index in the sediments. Any increase in the current levels is envisaged to be anthropogenic [16]. The mean I_{geo} value of Cd (4.29 ± 1.07) revealed that the studied sediments were characterized as heavily to extremely contaminated by this metal. The sediments were uncontaminated to moderately contaminated by Pb, and uncontaminated by Cu and Zn. Among the studied metals, the I_{geo} values showed the decreasing order of Cd > Pb > Zn > Cu.

The calculated pollution load index (PLI) values of metals in sediment are summarized in Figure 2 which were ranged from 2.90 ± 1.45 to 4.95 ± 2.51 confirming that the sediment of the studied area was heavily contaminated (PLI > 1). However, the higher PLI values indicated that Cd is the major contributors to the sediment pollution. The PLI can provide some understanding to the inhabitants about the quality of the environment. In addition, it also provides valuable information to the decision makers on the pollution status of the area (Suresh *et al.*, 2012). Higher PLI values were observed in sediments samples, which might be due to the effects of harbour activities.

CF, EF and I_{geo} showed the same decreasing order of contamination by the metals

Table 2. The Mean values of CF, EF, and I_{geo} in sediments of the Vridi Canal.

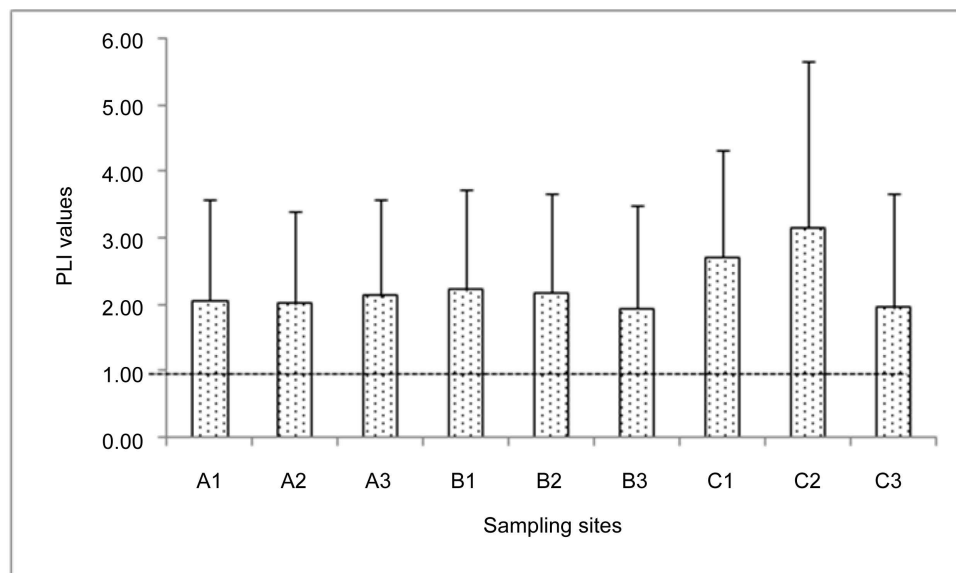|	CF	EF	I_{geo}
	Mean ± SD	Mean ± SD	Mean ± SD
Cd	37.78 ± 26.58	20.04 ± 9.82	4.29 ± 1.07
Cu	0.40 ± 0.16	0.24 ± 0.11	−2.03 ± 0.65
Pb	5.68 ± 2.17	3.43 ± 1.48	1.81 ± 0.59
Zn	3.04 ± 4.09	1.56 ± 2.01	−0.12 ± 2.04

Figure 2. Pollution load index (PLI) value of heavy metals in sediment of Vridi Canal.

studied but I_{geo} showed a different order. However, these indices showed that the sediments were contaminated by Cd and Pb while they were less contaminated by Cu. However, sediment quality guidelines are helpful in screening heavy metal contamination.

3.2.2. Sediment Quality Guide Lines

Concentrations of heavy metal in sediment samples were compared with consensus-based TEC and PEC values (Table 3). Cd, Pb, Zn and Cu were lower than the TEC in 2.78%, 4.17%, 50%, and 100% of samples, respectively. Cu and Zn were lower than the TEC in 100% and 50% of samples, respectively. Pb, Cd and Zn were between the TEC and PEC in 76.39%, 70.83% and 43.06% of samples, respectively. Cd, Pb and Zn exceeded the PEC in 26.39%, 19.44% and 6.94 of samples, respectively. These results indicate that the concentrations of Cd, Pb and Zn are likely to result in harmful effects on sediment-dwelling organisms which are expected to occur frequently.

The toxicity to organisms living in the sediment of all metals in sediments was evaluated by determining the mean quotient PEC (m-PECQ). The m-PECQ values were calculated using the methods of [14]. Sediment samples are predicted to be not toxic if mPECq are below 0.5. In contrast, sediment samples are predicted to be toxic [14]. The results of this assessment (Table 4) indicate that 45.83% of sediment samples have m-PECQ values below 0.5, while, 57.17% of sediment samples have mPECq values greater than 0.5. Consequently, more than half of the sediment samples in the Vridi Canal would be toxic to one or more species of aquatic organisms living in the sediments.

4. Conclusion

The purpose of this study was to assess levels of Cd, Cu, Pb and Zn in sediment samples

Table 3. Comparison between sediment quality guidelines (CBSQGs) with heavy metals concentrations (mg/kg) of all sites in the Vridi Canal.

		Cd	Cu	Pb	Zn
SQGs	TEC	0.99	31.60	35.80	121.00
	PEC	4.98	149.00	128.00	459.00
Values in this study	Mean	3.78	5.74	96.55	157.86
	Minimum	0.40	2.11	33.52	1.77
	Maximum	9.90	9.70	202.19	891,91
	% of samples< TEC	2.78	100	4.17	50.00
	% of samples between TEC and PEC	70.83	0	76.39	43.06
	% of samples>PEC	26.39	0	19.44	6.94

Table 4. Predictive ability of mean PEC quotients in sediment samples of the Vridi Canal.

Mean PEC Quotient (m-PECQ)	m-PECQ < 0.5	m-PECQ > 0.5
Percentage (%)	45.83	57.17

from the Vridi Canal. The results indicated that concentrations of Cd, Pb, Zn, except Cu, in sediment samples were higher than their corresponding concentration of Upper Continental Crust (UCC) due to anthropogenic activities. The metal Enrichment Factor (EF) and geoaccumulation index (I_{geo}) of Cd, Pb and Zn showed that the sediments were polluted, whereas Cu was generally unpolluted. The heavy metal concentrations in assessed sediment samples were compared with consensus-based sediment quality guidelines. The results indicated that the concentrations of Cd, Pb and Zn were likely to result in harmful effects on sediment-dwelling organisms which were expected to occur frequently. An index of toxicity risk, mean PEC quotients, was evaluated in this study. According to mean PEC quotients, more than half of sediment samples were predicted to be toxic to sediment-dwelling organisms. These results demonstrate the high ecological risk and the need of an environmental monitoring, supporting the development of an efficient remediation strategy to reduce local pollution and contamination.

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