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Contribution to the Assessment of Heavy Metal Contamination in Fish and Shrimp from the Continental and Marine Areas of Cameroon

Raoul Polycarpe Tuekam Kayo[1,2*], Fils Mamert Onana[3], Antoine Tamsa Arfao[4,5], Alexandra Geordie Ngaldeu Noupoue[3], Paul Alain Nana[6], Ledna Lendira Lefoume[3]

[1]Department of Zoology, Faculty of Science, University of Bamenda, Bambili, Cameroon
[2]International Centre of Environment Studies and Research for Development (ICERD), Yaoundé, Cameroon
[3]Department of Aquatic Ecosystems Management, Institute of Fisheries and Aquatic Sciences, University of Douala, Douala, Cameroon
[4]Laboratory of Hydrobiology and Environment, Department of Animal Biology and Physiology, Faculty of Science, University of Yaoundé 1, Yaoundé, Cameroon
[5]Medical Analysis and Application Laboratory, Higher Institute of Health Science, Technician and Management of Garoua (ISSTSM), Garoua, Cameroon
[6]Department of Oceanography, Institute of Fisheries and Aquatic Sciences, University of Douala, Douala, Cameroon
Email: *tuekamkayo@yahoo.fr

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Abstract

Heavy metals occur naturally in the environment. However, human activities such as industry, agriculture, and mining are responsible for a significant increase in their concentrations in ecosystems, including waterways and marine environments. This study aims to assess heavy metal contamination in fish and shrimp from Cameroon's continental and marine areas. Fish were sampled *in situ* in the Wouri, Nkam, and Dibamba rivers. The shrimp were collected from local fishermen at the landing sites in Youpwé and Kribi. Water samples for laboratory analysis of trace metals were collected upstream in the rivers using 1,000 mL polyethylene bottles and then analyzed in the laboratory using standard methods. The trace metal content was measured using mass spectrometry. The results for water show that the highest average concentrations of zinc (5.325 mg/L) are observed at Youpwé, while the Nkam station has the highest average mercury concentration (7 mg/L). The sediments of Kribi have high concentrations of lead (10.39 mg/kg), those of Dibamba have high concentrations of cadmium (119.7 mg/kg) and nickel (0.6182 mg/kg), those in Youpwé have high concentrations of zinc (7.7 mg/kg), and those in Wouri have high concentrations of mercury (166.2 mg/kg). The most abundant traces of heavy metals in the two fish species (*Oreochromis niloticus* and *Chrysichthys nigrodigitatus*) were lead and cadmium, particularly at the Wouri and Dibamba sites, with values exceeding the permitted limits (0.01 µg/g). However, in the Kribi area, there is contamination (CF > 1) of the shrimp species *Penaeus notialis* by lead and high contamination (CF > 6) of all shrimp species by mercury. The fish species *Oreochromis niloticus* bioaccumulates zinc in the Dibamba River, and the shrimp species *Penaeus notialis* bioaccumulates lead in Kribi (BCF > 1). The study found that the concentrations of trace metals in the water exceed the WHO guidelines for the ecological status of surface water. The water at urban stations (Wouri and Dibamba) shows very high levels of cadmium, lead, and mercury contamination, which could be due to the presence of various industries. Sediments at all stations are extremely polluted with mercury, while only sediments at the Wouri and Dibamba stations are extremely polluted with cadmium.

Keywords

Contamination, Fish, Shrimp, Heavy Metals, Water, Sediment

1. Introduction

Heavy metals occur naturally in the environment. However, human activities such as industry, agriculture, and mining are responsible for a considerable increase in their concentrations in ecosystems, including waterways and marine environments. As a result, aquatic organisms are directly exposed to these metals, either through water or food [1]. Fish and crustaceans, particularly shrimp, can accumulate these substances to potentially toxic levels. For the general population, the consumption of these aquatic products is a major route of exposure to heavy metals throughout life. The adverse health effects of consuming contaminated food or water vary depending on the dose, duration of exposure, and age of the individual. Mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As) are among the most toxic metals and are highly bioaccumulative in aquatic organisms and the food chain. In some ecosystems, the presence of these pollutants can cause the disappearance of animal and plant species, leading to the dysfunction of the food chain [2]. The bioaccumulation of heavy metals within the food chain is indeed a threat that can lead to health disasters. Certain organisms, such as shrimp and fish, are powerful bioaccumulators, capable of bioconcentrating these molecules [3]. In humans, accumulation through food is associated with serious diseases and severe physiological disorders, which can even lead to death [4] [5]. Work carried out by [6] in Asia revealed very high contamination with heavy metals in aquatic fauna in rural and urban rivers in the Pearl River Delta. In Africa, several studies have also highlighted the bioaccumulation of TMMs in various species of edible fish [7] [8]. In Cameroon, research on heavy metal contamination of coastal and littoral ecosystems remains limited. To date, only a few data are available on the study of contamination of aquatic organisms in coastal ecosystems [9] [10]. These preliminary studies have already revealed the accumulation of heavy metals in aquatic gastropods and the presence of cadmium in *Macrobranchium macrobranchium* shrimp. In order to contribute to a better understanding of this issue in Cameroon, the main objective of this work is to assess heavy metal contamination in fish and shrimp from the Wouri, Dibamda, Nkam, Kribi, and Youpwé rivers. Specifically, this study aims to: determine the concentrations of heavy metals in water, sediments, and two species of fish and four species of shrimp; assess the degree of contamination of water, fish, shrimp, and sediments; determine the level of accumulation of heavy metals in fish and shrimp.

2. Materials and Methods

2.1. Study Site and Sample Collection

Fish were collected *in situ* from the Wouri, Nkam, and Dibamba rivers. Shrimp were collected from local fishermen at the landing sites of Youpwé and Kribi (**Figure 1**). The Wouri watershed covers an area of 11,700 km^2. Samples were taken at the geographical coordinates 4˚05′00″N and 9˚42′00″E. This site is mainly characterized by its proximity to a large industrial port area, which is an important factor in assessing the risk of contamination. The Dibamba watershed covers an area of 2,400 km^2. Sampling was carried out at the geographical coordinates 3˚94′90″N and 9˚82′40″E. According to data from Olivry (1974), the Nkam watershed covers an area of 8,250 km^2. Samples were collected in this basin at the geographical coordinates 4˚45′11″N and 9˚96′64″. Water samples for laboratory analysis of trace metals were collected upstream in rivers using 1,000 mL polyethylene bottles. Sediments were collected using a core sampler; approximately 200 g of sediment was collected and stored in plastic freezer bags. Fish and shrimp samples were collected in collaboration with fishermen working in the various rivers. These samples were then placed in a cooler and brought back to the laboratory.

2.2. Laboratory Sample Analysis

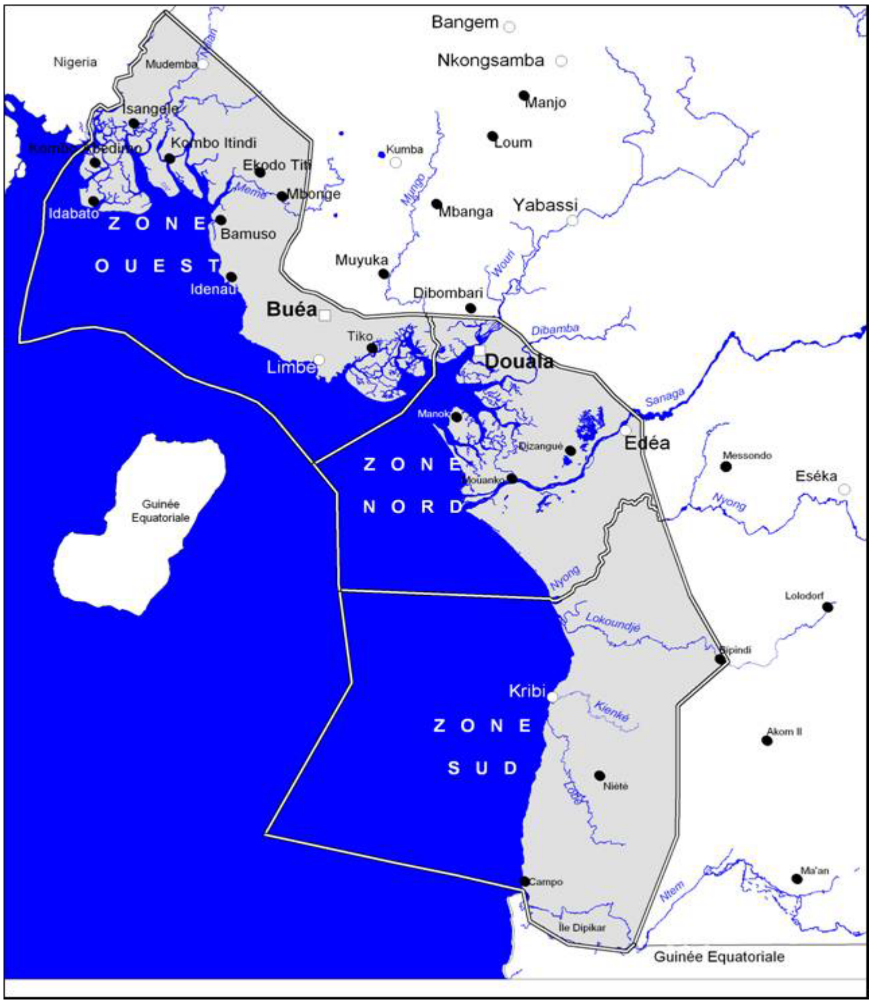
Water samples intended for heavy metal analysis were stabilized at pH < 2 by adding concentrated nitric acid (5 mL of concentrated HNO_3 per liter of sample). The samples were filtered through a 0.45 μm pore size membrane; then the membrane was washed with 1 mol/L nitric acid and thoroughly rinsed. The samples were then stabilized by adding acid and stored in a refrigerator at a temperature between 1 and 5˚C.

2.2.1. Mineralization of Fish, Shrimp, and Sediment Samples

Heavy metals were extracted from fish, shrimp, and sediments after drying and grinding in a mortar as follows: To 0.2 g of powder obtained after drying in an oven and grinding in a mortar, 4 ml of 95% concentrated sulfuric acid (H_2SO_4) was added, and the mixture was placed in mineralization cells. These solutions were then incubated for approximately 5 minutes in a Hach Digesdahl mineralizer. Mineralization was carried out gradually from low temperatures to high temperatures until reaching approximately 440˚C. A lightening of the mixture was observed. During incubation at rest, more precisely between the third and fourth minute (after boiling), 10 ml of hydrogen peroxide (H_2O_2) was gradually added using a syringe. The mineralized solution thus obtained (4 - 5 mL) was brought back to 70 ml in a volumetric flask with distilled water.

2.2.2. Measurement of Heavy Metals

Heavy metals were measured using X-ray fluorescence spectrometry, with a Bruker XRF spectrometer, type Pioneer S4, at WDS (Wavelength Dispersive Spectrometry) wavelength. The heavy metal content of lead (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), and mercury (Hg) was expressed in mg/L and mg/kg.



Note: Source: SNH/CPSP-ENVIREP: Study on monitoring the protection of the coastal zone and marine environment as part of the CAPECE project—Cameroon: Final report (June 2007).

Figure 1. A map showing the boundaries of Cameroon's marine and coastal zone.

3. Data Analysis

The contamination factor (CF), used to determine the degree of environmental contamination by a trace metal element, was calculated using the following formula: $CF = \frac{\text{metal content in wet tissue in mg/kg}}{\text{metal content in water in mg/L}}$ [11].

The bioconcentration factor (BCF) for each metal was calculated using the following formula:

$$BCF = \frac{\text{Concentration of heavy metal } X\left(Cx\right)}{\text{Concentration of heavy metal } Y\left(Cy\right)}$$

where BCF is the bioaccumulation factor, Cx and Cy are the concentrations of heavy metals [9].

The geo-accumulation index (Igéo) was calculated using the formula:

$$Igeo = Log2\frac{Cn}{1.5 \times Bn}$$

where: Cn: concentration measured in the sediment for the element; Bn: geochemical background noise for element n; 1.5: constant taking into account natural fluctuations in the content of a given substance in the environment as well as anthropogenic influences [12] [13].

4. Results and Discussion

Figure 2 shows the variations in the values of the various trace metals (lead, cadmium, nickel, zinc, and mercury) measured in the water during this study. Although occasional peaks were recorded, the concentrations measured are generally higher than the environmental quality standards for surface water (NEQS) applicable to watercourses for all five stations examined (**Table 1**). It should be noted that zinc levels are below the recommended standards at the Dibamba and Nkam stations. Similarly, mercury concentrations are below the regulatory thresholds at the Kribi and Youpwé stations. **Table 1** presents the descriptive statistics for the heavy metals measured. The waters of the Wouri River show the highest average concentrations of lead (86.5 mg/L), cadmium (251.3 mg/L), and nickel (35.3 mg/L). The highest average concentrations of zinc (5.325 mg/L) are observed at Youpwé, while the Nkam station has the highest average mercury concentration (7 mg/L). Analysis of variance (ANOVA) reveals no statistically significant differences ($p > 0.05$) between the concentrations of heavy metals measured in the waters of the different study locations. With the exception of zinc, all average concentrations of heavy metals exceed the World Health Organization (WHO) guidelines for good ecological status of surface waters. These high concentrations could have negative impacts on aquatic organisms. The significant concentrations of lead and cadmium observed in the Wouri and Dibamba rivers could be attributed to industrial activities in both watersheds. These activities include the manufacture of phosphate fertilizers, plant protection products, and chemicals (SOLEVO), the production of storage batteries (BOCOM and CAMI TOYOTA), the manufacture and coating of construction materials (COMETAL), and cement production. These levels remain higher than those obtained by [13] in the waters of Oued

Bouhamra in Algeria.

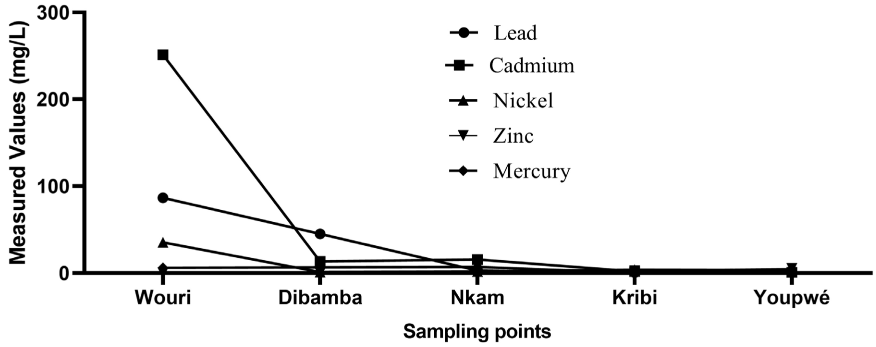


Figure 2. Average variation in heavy metals values in water from different study areas.

Table 1. Descriptive statistics for heavy metals measured in water and sediments from different study areas.

		Pb	Cd	Ni	Zn	Hg
Min	Water (mg/L)	0.6795	0.938	1.15	0.009667	0.0005
	Sediments (mg/kg)	0.000647	0.1263	0.005319	0.01494	3.05
Max	Water (mg/L)	86.5	251.3	35.3	5.325	7
	Sediments (mg/kg)	10.39	119.7	0.6182	7.7	166.2
Moy ± SD	Water (mg/L)	27.29 ± 38.1	56.65 ± 109	9.112 ± 14.68	1.695 ± 2.36	3.9 ± 3.577
	Sediments (mg/kg)	3.437 ± 4.839	46.93 ± 60.73	0.2397 ± 0.2349	1.919 ± 3.321	54.78 ± 66.32
Permissible limit values	Water	10 µg/L	5 µg/L	20 µg/L	20 µg/L	1 µg/L
	Sediments	100 mg/Kg	3 mg/Kg	100 mg/Kg	200 mg/Kg	1 mg/Kg

Figure 3 illustrates the variations in heavy metals concentrations (lead, cadmium, nickel, zinc, and mercury) measured in sediment samples during this study.

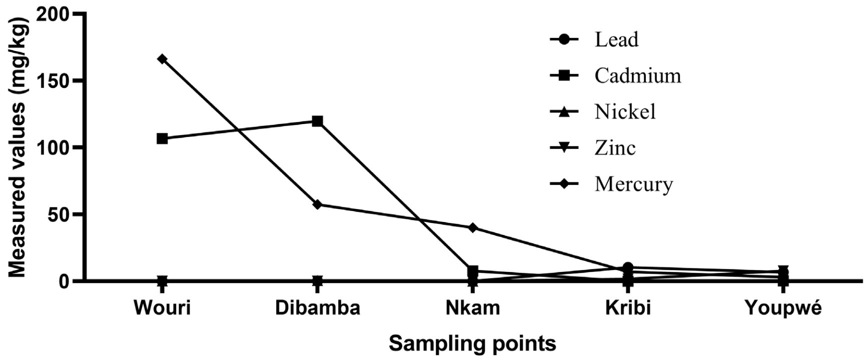


Figure 3. Average variation in heavy metals values in sediments from different study areas.

Although there are peaks, the values remain below the environmental standards associated with sediments at the sites studied (**Table 1**). However, cadmium values exceed the recommended environmental standards for sediments. Sediments from the Wouri, Dibamba, and Nkam rivers have high cadmium values, while mercury values in sediments from all study sites exceed standards. The descriptive statistics for the metals measured in the sediments of the study areas are presented in **Table 1**. It appears that the sediments of Kribi have high concentrations of lead (10.39 mg/kg), those of Dibamba have high concentrations of cadmium (119.7 mg/kg) and nickel (0.6182 mg/kg), those in Youpwé have high concentrations of zinc (7.7 mg/kg), and those in Wouri have high concentrations of mercury (166.2 mg/kg). However, the ANOVA test shows no significant difference ($p > 0.05$) between the heavy metal values in the sediments of the study sites. The high heavy metal values in sediments could be explained, on the one hand, by natural inputs, and on the other hand, by industrial effluents or discharges, or indirectly after the leaching of waste deposits along watersheds by rainwater. Moreover, [13] [14], in a similar study, show that the main source of heavy metal contamination in sediments is anthropogenic. The cadmium, lead, and nickel levels obtained for this study in sediments are all higher than those obtained in Ghana [15]. This result could be explained by differences in the geological composition of the areas studied [6], differences in the type and extent of anthropogenic pressures on the areas studied, and differences in industrial and household waste management in the two countries. The values obtained remain lower overall than those found in sediments from the Ebrié lagoon in Côte d'Ivoire [13]. **Table 2** shows the average values of heavy metals in fish and shrimp from the different study areas in this work. The most abundant traces of heavy metals in the two fish species (*Oreochromis niloticus* and *Chrysichthys nigrodigitatus*) were lead and cadmium, particularly at the Wouri and Dibamba sites, with values exceeding the permitted limits. However, the values for nickel, zinc, and mercury remained below the limits overall. All shrimp species harvested in Kribi and Douala had mercury levels above the standard. However, in the city of Kribi, the species *Penaeus monodon*, *Kerathus*, and *Penaeus notialis* had high lead concentrations, while in the city of Douala, Penaeus notialis had levels above the standard.

Table 2. Average values of heavy metals measured in the various organisms collected.

Organism		Pb	Cd	Ni	Zn	Hg
Fish (*Oreochromis niloticus*)	Wouri	1.056	1.062	0.002771	0.010375	0.005
	Dibamba	0.196	0.125799	0.000607	0.940525	0.001
	Nkam	0.0892	0.0462	0.000284	0.00004	0
Fish (*Chrysichthys nigrodigitatus*)	Wouri	0.555	0.364	0.000776	0.000413	0.002
	Dibamba	0.043	0.105	0.002113	0.00225	0.001
	Nkam	0.0278	0.052	0	0.00125	0
Permissible limit value (mg/kg)		0.1	0.05		50	0.5
Shrimp (*Penaeus monodon*)	Kribi	0.52	0.0695	0.4675	/	6.6
	Douala	0.67	0.0675	0.4305	/	9.5

Continued

Shrimp (*Kerathus*)	Kribi	0.57	0.073	0.235	/	5.1705
	Douala				/	
Shrimp (*Penaeus notialis*)	Kribi	0.999	0.074	0.0565	/	11.7
	Douala	0.021	0.62	0.1455	/	3.1
Shrimp (*Parapenaepsis*)	Kribi	0.091	0.0405	0.487	/	5
	Douala	/	/	/	/	/
Permissible limit value (mg/kg)		0.5	0.5			0.5

Table 3. Concentration factors for heavy metals in water, sediments, fish, and shrimp in the study areas.

		Fish (*Oreochromis niloticus*)	Fish (*Chrysichthys nigrodigitatus*)	Shrimp (*Penaeus monodon*)	Shrimp (Kerathus)	Shrimp (*Penaeus notialis*)	Shrimp (Parapenaepsis)
Lead	Wouri	0.0122081	0.006416	0	0	0	0
	Dibamba	0.0043411	0.000952	0	0	0	0
	Nkam	0.0307586	0.009586	0	0	0	0
	Kribi	0	0	0.765269	0.838852	1.470199	0
	Youpwé	0	0	0.546939	0	0.017143	0.074286
Cadmium	Wouri	0.0042255	0.001448	0	0	0	0
	Dibamba	0.0094349	0.007875	0	0	0	0
	Nkam	0.0029489	0.003319	0	0	0	0
	Kribi	0	0	0.035473	0.037259	0.03777	0
	Youpwé	0	0	0.071962	0	0.660981	0.043177
Nickel	Wouri	0	0	0	0	0	0
	Dibamba	0.0005275	0.001838	0	0	0	0
	Nkam	0.0001575	0	0	0	0	0
	Kribi	0	0	0.119374	0.060006	0.014427	0
	Youpwé	0	0	0.126804	0	0.042857	0
Zinc	Wouri	0.0393738	0.001565	0	0	0	0
	Dibamba	97.29569	0.232759	0	0	0	0
	Nkam	0.0035294	0.110294	0	0	0	0
	Kribi	0	0	0	0	0	0
	Youpwé	0	0	0	0	0	0
Mercury	Wouri	0.0008333	0.000333	0	0	0	0
	Dibamba	0.0001538	0.000154	0	0	0	0
	Nkam	0	0	0	0	0	0
	Kribi	0	0	8800	6894	15600	6666.667
	Youpwé	0	0	19000	0	6200	0

Table 3 shows the factors contributing to heavy metal contamination in fish and shrimp from the different study areas. However, in the Kribi area, there is contamination (CF > 1) of the shrimp species *Penaeus notialis* by lead and high contamination (CF > 6) of all shrimp species by mercury. In the Youpwé area, high mercury contamination was found in the shrimp species *Penaeus monodon* and *Penaeus notialis*. With the exception of lead and cadmium, all trace metal levels found in fish were below WHO guidelines. These high levels in fish could have negative impacts on the health of the population that consumes them.

Lead and cadmium contamination in fish could be explained by the fact that these elements accumulate in the food chain. These heavy metal levels remain higher overall than those found in certain fish in Côte d'Ivoire [16] and those found by [15] in marine fish from the Togolese coast at Agbodrafo (0.24 to 0.38 mg/kg). Lead levels in fish remain lower overall than those in bivalve species (2.9 mg/kg) obtained in the Togolese lagoon system by [17]. Our results could be explained by the fact that demersal and benthopelagic species are closer to sediments, which are reservoirs or sinks for many chemical pollutants [18] [19]. Species that are in contact with sediments will be the most contaminated in accordance with their lifestyle, as they feed on benthic organisms and even mud.

Table 4. Bioconcentration of heavy metals in water, fish, and shrimp.

Water-Fish	Sampling area	Pb	Cd	Ni	Zn	Hg
Water-*Oreochromis niloticus*	Wouri	0.012	0.004	0.000	0.039	0.000
	Dibamba	0.004	0.009	0.000	97.295	0.000
	Nkam	0.030	0.002	0.000	0.003	0.000
Water-*Chrysichthys nigrodigitatus*	Wouri	0.006	0.001	0.000	0.001	0.000
	Dibamba	0.000	0.007	0.001	0.232	0.000
	Nkam	0.009	0.003	0.000	0.110	0.000
Water-Shrimp						
Water-*Penaeus Monodou*	Kribi	0.765	0.035	0.119		0.000
	Youpwé	0.546	0.071	0.126		0.000
Eau-*Kerathus*	Kribi	0.838	0.037	0.060		0.000
Water-*Penaeus notialis*	Kribi	1.470	0.037	0.014		0.000
	Youpwé	0.017	0.660	0.042		0.000
Water-*Parapenaepsis*	Kribi	0.133	0.020	0.124		0.000

Table 4 shows the level of accumulation of heavy metals in water, fish, and crustaceans in the different study areas. It shows that the fish species *Oreochromis niloticus* bioaccumulates zinc in the Dibamba River, and the shrimp species *Penaeus notialis* bioaccumulates lead in Kribi (BCF > 1). The other heavy metals cadmium, nickel, and mercury are not bioaccumulated in any fish or shrimp species. The concentration factor revealed that fish and shrimp in the areas studied are contaminated with lead and cadmium. This contamination could be due to the bioaccumulation, biomagnification, and bioconcentration of trace metals along the food chain. With regard to bioaccumulation in organisms, it appears that the fish species Oreochromis niloticus in Dibamba bioaccumulates zinc, and the shrimp species Penaeus notialis bioaccumulates lead in Kribi.

5. Conclusion

The objective of this study was to assess the contamination by certain trace metals in the water, sediments, and two fish species (*Chrysichthys nigrodigitatus* and *Oreochromis niloticus*) of the Nkam, Wouri, and Dibamba rivers. The study found that the concentrations of trace metals in the water exceeded the WHO guidelines for the ecological status of surface water. The water at urban stations (Wouri and Dibamba) showed very high levels of cadmium, lead, and mercury contamination, which could be due to the presence of various industries. Sediments at all stations were extremely polluted with mercury, while only sediments at the Wouri and Dibamba stations were extremely polluted with cadmium.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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