

# Heavy Metal Concentration of Surface Water, Sediment and Fishes Impacted by Crude Oil Pollution in Bodo/Bonny River, Nigeria

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## Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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## ABSTRACT

Heavy metals can be released into the aquatic environment through storm-water run-off and wastewater discharges and reprocessing from various industrial and anthropogenic activities. They have the potential to be toxic to biota above certain threshold concentrations while sediments in the marine ecosystems act as long-term sinks for many anthropogenic contaminants such as these organic pollutants. This study was therefore aimed at determining the heavy metal contents in the surface water, sediments and fishes from the Bodo/Bonny river. Sampling was done according to standard protocols. Surface water, sediment and fish samples were collected from 5 stations (BBW1, BBW2, BBW3, BBW4 and LFPW5) with LFPW5 serving as control. Sediment was collected from 0-15 and 15-30 cm. The fish gills, liver, kidney etc. were excised from the rib for heavy metals (Pb, Fe, Zn, Cr, Cd etc) analysis using sterile scalpel. The results of heavy metal in surface water samples show that Zinc had a range of 173.1±10.21 to 179.3±11.01 mg/kg in all sampling locations above the permissible limit of DPR limit of 5 mg/kg for Brackish/ Saline water. The sediment samples were loamy. The concentrations of trace metals in sediments revealed that Pb had the highest concentration of 48.61mg/kg at 0-15cm depth while Chromium had highest concentration of

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41.54mg/kg at 15-30cm depth. Chromium, Cadmium and Copper increased with increase in depth at 15-30cm while Lead, Zinc and Iron took the reverse trend at 0-15cm depth. Heavy metal content of fish samples from the river water show that the mean concentration values in the fresh fish was in the increasing order of Copper < Cadmium < Nickel < Lead < Iron < Zinc. The data generated from this study showed that there were actually heavy metals accumulations in fish tissues that were above the WHO permissible limits. The increased heavy metals concentration from all sites suggest that fishes that inhabit polluted areas risk bioaccumulation, which go on to affect the overall health of the human population that depend on such rivers for fishing, drinking or irrigation.

*Keywords: Heavy metals; surface water; sediment; fish; bodo/bonny river; pollution.*

## 1. INTRODUCTION

Heavy metals are metallic elements with a relative density at least five times that of water [1]. These elements have several toxic effects in humans, and their toxicity is inter-related with their heaviness [1]. Although these metals occur naturally and are found throughout the earth's crust at low quantities. However, human exposure generally results from anthropogenic activities such as smelting, mining, and agricultural and industrial activities [2,3] Once released into the environment, heavy metals may be taken into the body by inhalation and ingestion through the food chain. Rapid accumulation in body tissues greater than the detoxification pathways in the body can cause a gradual build-up of these metals [4]. The toxicity of heavy metals varies from one heavy metal to another and in the same element may have different toxic effects depending on its chemical form and its speciation [1].

Oil spills are a source of heavy metal contamination of aquatic and terrestrial environments, especially in oil-producing regions [5]. Crude oil is a complex mixture of hydrocarbon and non-hydrocarbon compounds (including heavy metals) found in subsurface deposits worldwide. Their presence have negative socioeconomic impacts on the surrounding environment such as a decrease in agricultural productivity due to farmland degradation, pollution of traditional fishing grounds and destruction of aquatic life, as well as negative effects on soils, forests and water bodies [5]. However, few of these impacts have health hazards because of their toxicity both in the immediate and long-term on the environment and the inhabitants of the affected communities [6]. In water bodies these group of trace elements Cr, Cd, Ni, Zn, Cu, Pb and Fe have been known to create definite health hazards when taken up by aquatic biota. The contamination of river water and biota by heavy

metals is one of the major concerns especially in many industrialized countries because of their toxicity persistence and bioaccumulation [7]. Many rivers receive flux of sewage, domestic waste, industrial effluents and agricultural waste as major sources which contain substances varying from simple nutrients to highly toxic chemicals [8]. Heavy metal pollution of wastewater is a significant environmental problem and has a negative impact on human health and agriculture and on the environment in which the organism lives [9, 10]. However, it has been reported that oil pollution in coastal ecosystems by human mediated activities can adversely alter the ecological integrity of fragile aquatic systems, resulting in bioaccumulation of chemical contaminants by zoobenthos [11-14] sediment enrichment [15] and impact on species abundance and biomass [12]. Other causes of ecological imbalance aside from oil pollution, may also include human disturbance, physical habitat alteration, other pollution, fishing, alteration of predation patterns, weather and climate.

Fishes ingest heavy metals from the surrounding waters, planktons, other feeding diets and sediments resulting to their accumulation in reasonable amounts [16] Metals such as Copper and Zinc are essential for metabolism in fish at low concentrations while some others such as Lead, Cadmium are toxic to living organisms [17] When present at high concentrations, these metals impose serious damage to metabolic, physiological and structural systems of organisms in the aquatic environment. Sediments are an important sink and long-term store of a variety of pollutants, particularly heavy metals, and may serve as an enriched source of food for benthic organisms in estuarine ecosystems [18,19] because they are in constant flux with the overlying water column [20-22] Some of the sediment-bound metals may be remobilized and released into water as a result of changes in environmental conditions that leads

to acidification and reduction/oxidation and impose adverse effects on living organisms [23]. The occurrence of increased concentrations of heavy metals in sediments can be a good indicator of man-induced pollution rather than natural enrichment of the sediment by geological weathering [24,25] leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecological communities [26]. It will also cause changes in the nutrient concentrations of water which may lead to harmful effects on humans and aquatic life. The coastal waters of Nigeria is under increasing pressure from industrial pollution, oil spills, anthropogenic activities and agricultural wastes. These pressures pose potential threat to the entire ecosystems and human well-being. Therefore, there is the need for this study with a view to help the problems of environmental pollution to provide salient data which will assist in the coastal waters quality evaluation. This study was therefore aimed to determine the heavy metal contamination of the surface water, fishes and sediment samples from Bodo/Bonny river.

## 2. MATERIALS AND METHODS

### 2.1 Sampling Location

Samples were collected from five different stations in Bodo/Bonny River in Gokana Local Government Area of Rivers State. Control samples were collected from link fish pond located 50m away from the location where there was no record of crude oil pollution within the river environment. Surface water, sediment and fish samples were collected from 5 stations (BBW1, BBW2, BBW3, BBW4 and LFPW5) with LFPW5 serving as control (Table 1). The sampling stations were chosen based on an experimental scheme design following ecological settings and human activities in the area. Bodo Creek is characterized by low tidal energy current, making its swamps and canals exceptional breeding grounds for a vast variety of fish and shellfish. It also provides an excellent habitat for periwinkles (*Tympanotonus fuscatus*; *Tympanotonus fuscatus varradula*; *Pachymelania aurita*; *Pachymelania fusca*) [27]. The original diversity of shellfish found in the Creek included bloody cockle (*Senilia senillis*), oyster (*Crassostrea gasar*), swimming crab (*Callinectes amnicola*), razor clam (*Tagelus adansonii*), land crab (*Cardisoma amatum*), and mangrove purple hairy crab (*Goniopsis pelli*) [27]. The Bodo/Bonny River meet several socio-

economic needs including aquaculture, fishing, sand dredging and drainage of the various towns and villages bordering it.

### 2.2 Sample Collection

Samples used for this study are surface water, sediment and fishes (*Pseudotolithus elongatus*) from the river and Fish Link pond as control (Plates 1 and 2). Dead floating fishes were collected from the seashore during the sampling period. Sampling was done in the mornings between 10 am-12 noon each day for a period of 12 months covering both wet and dry seasons, at an interval of once a month. Sample were collected in duplicates from each location, monthly. Collection of the samples was done in the hours when tide in the river was at its peak in duplicates

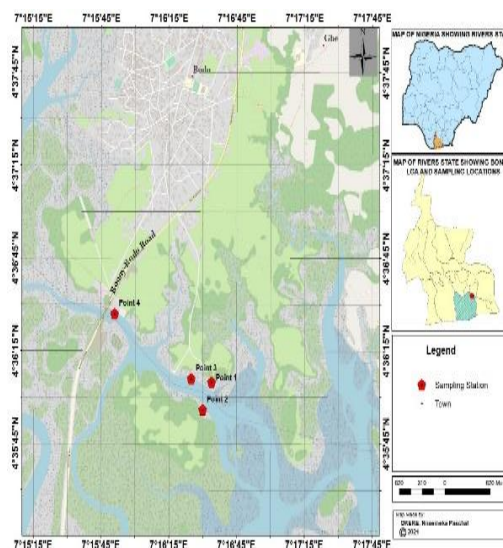


Fig. 1. Map indicating sampling stations (Bodo/Bonny River)



Plate 1. Fish (*Pseudotolithus elongatus*) Samples from the Bodo/Bonny River



**Plate 2. Dead Fishes (*Pseudotolithus elongatus*) in the Bodo/Bonny River due to asphyxiation**

### **2.3 Heavy Metal Analyses of Water Samples**

The following heavy metals (Cadmium, Chromium, Iron, Nickel, Zinc, Lead, Mercury, Arsenic and Barium) present in the respective surface water were analyzed using atomic absorption spectrophotometer (UNICAM 929 AAS). The equipment absorbs the water sample and gives the concentration of the metals in the sample; this is done by using the respective cathode lamp for each heavy metal [28].

#### **2.3.1 Surface water samples**

For surface water from the river and link fish pond, 20 ml was measured into 250 ml beaker to which 1:10 v/v mixture of HNO<sub>3</sub> and HCl was added. The mixture was concentrated to 5ml by boiling on hot plate at 95<sup>o</sup>C

#### **2.3.2 Sediment samples**

Two grams (2g) of the sediment samples from the river and link fish pond was weighed into 250ml beaker, 50ml of 1:10 v/v mixture of HNO<sub>3</sub> and HCl was added and digested according to the method adopted by Inengite [28].

#### **2.3.3 Fish samples**

Two grams (2g) of the Fish samples from the river and link fish pond was weighed into 250ml beaker, 50ml of 1:10 v/v mixture of HNO<sub>3</sub> and HCl was added and digested according to the method adopted by Inengite(2015).

### **2.3.4 Sediment samples**

Sediment samples were collected using a grab sampler. The grab sampler was thoroughly rinsed with wastewater along the same water course to remove any visible sediment before and after use. At each sampling point, the sampler was lowered to the water bed and the topmost layer of the sediment heaved out. The sediment sample was scooped from the grab's cup and transferred into sterile sample container. The sample was labelled and then transported to the laboratory in a cooler packed with ice blocks for analysis.

#### **2.4.1 Spectrophotometric analysis**

The concentration obtained (5ml each) above was allowed to cool to room temperature after which the solution was filtered and quantitatively transferred into 50 ml volumetric flask while diluting with deionized water to 50ml for solid matrix digest and 20ml for surface water digest. A hollow cathode lamp for the desired metal was installed in the Atomic Absorption Spectrophotometer and the wavelength was properly set. The slit width was set for the element being measured. The current was readjusted as required after warm up and wavelength was optimized by adjusting the wavelength dial unit until optimum energy gain was obtained, the lamp was aligned accordingly. Heavy metals concentration values were read by desolvation by the chemical flame and the particles absorb the light beam from the light source while the concentration of ground state atoms in the flame is directly proportional to the concentration of heavy metal of interest.

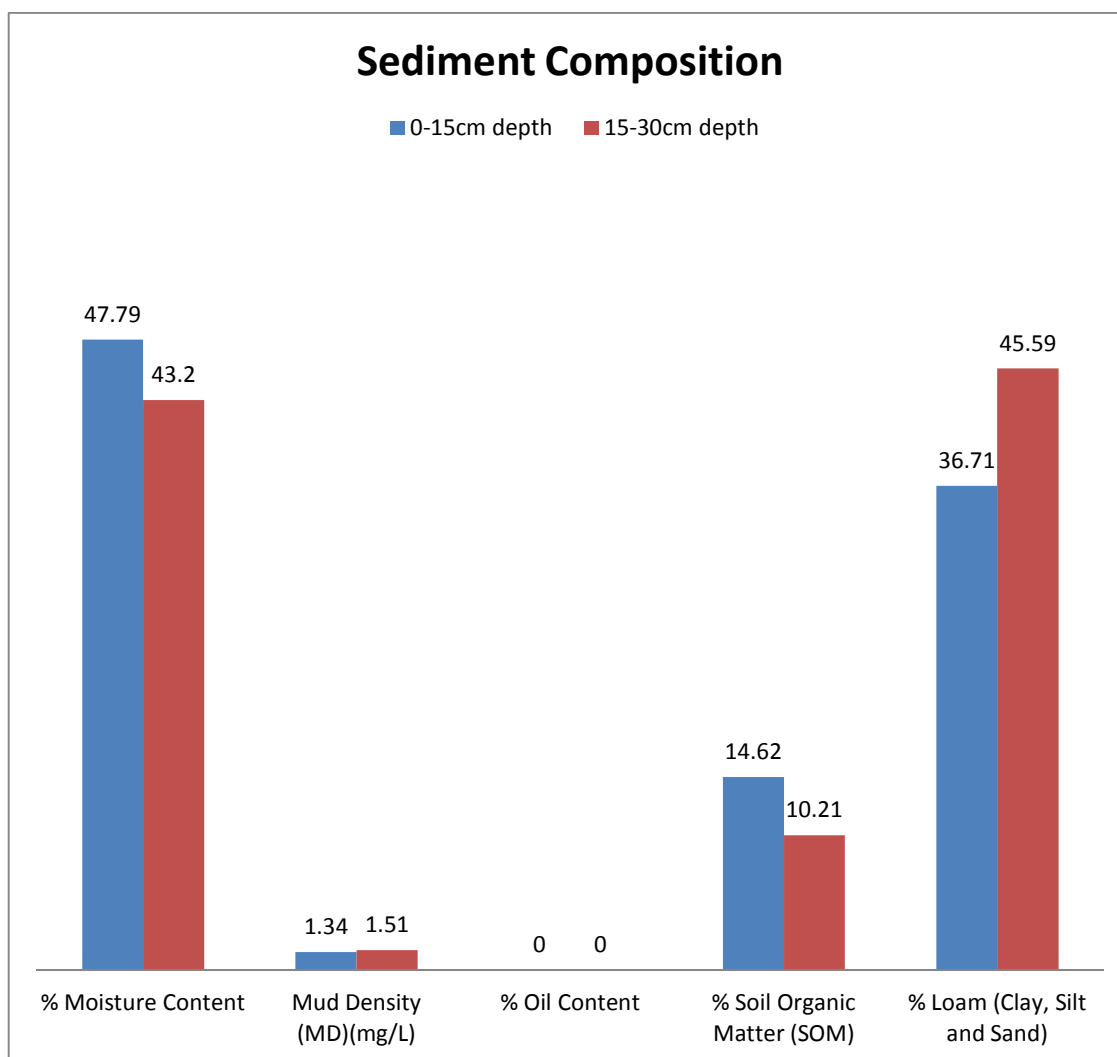
## **3. RESULTS**

### **3.1 Surface Water and Sediment Characteristics**

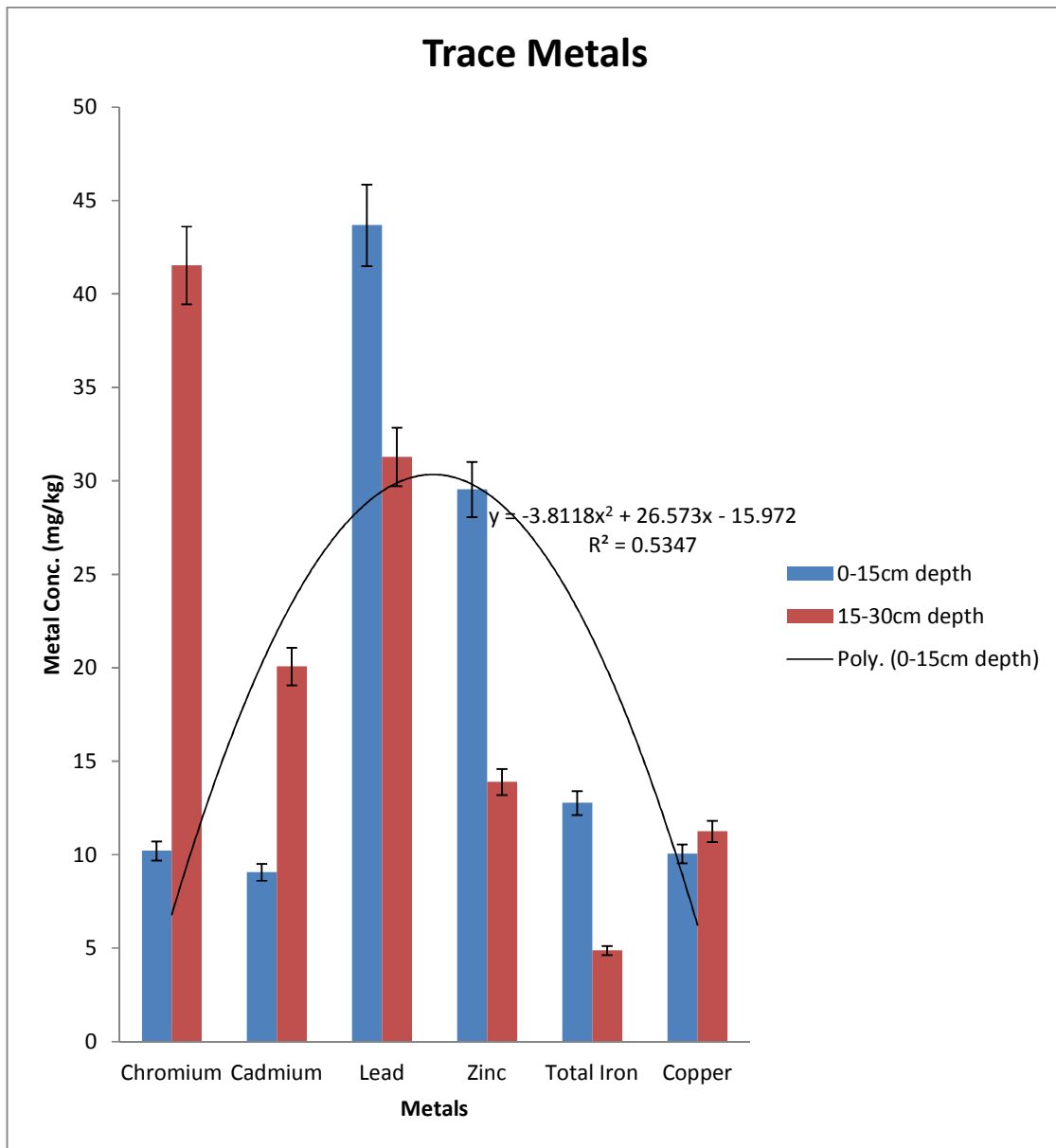
Results of surface water and Link fish pond samples showed wide significant differences at (P < 0.005) of heavy metal concentrations with the exception of Mercury, Arsenic, Barium, and Chromium which had an insignificant values during the sampling periods. Zinc recorded a range of 173.1±10.21 to 179.3±11.01 mg/kg while Iron had a range of 58.6±8.01 to 63.0± 8.01mg/kg in all sampling locations above the permissible limit of DPR limit of 5mg/kg for Brackish/ Saline water.

The sediment analysis obtained from Bodo/Bonny River at different depths are presented in Fig 2 which revealed it to be loamy. Moisture content decreased with increase in depth (47.79 – 43.20%) while Mud Density (MD) increased from 1.34mg/l at 0-15cm depth to 1.51mg/l at 15-30cm depth. Percentage Soil Organic Matter (%SOM) decreases with increase in depth from 14.62 – 10.21%. Alternate range was observed in Percentage Loam (Clay, Silt and Sand), as it increases with increase in depth from 36.71 – 45.59%. (Fig 2).

The concentrations of trace metals in sediments are presented in Fig 3. The result revealed that Pb had the highest concentration of 48.61mg/kg at 0-15cm depth while Chromium had highest concentration of 41.54mg/kg at 15-30cm depth. It was observed that all trace metals analyzed, showed differences in depth with variation in the concentrations of metals in the aquatic sediments. Chromium, Cadmium and Copper increases with increase in depth at 15-30cm while Lead, Zinc and Iron increased in this order at 0-15cm depth (Fig 3).



**Fig. 2. Sediment composition of Bodo/Bonny River at different depth**



**Fig. 3. Trace metal concentration of sediment at different depths along Bodo/Bonny River**

### 3.3 Heavy Metal Content of Fish Samples of River Water and the Link Fish Pond

The results of Heavy metal analysis for the Bodo /Bonny surface bwater and Link Fish Pond are presented in Table 3. The surface water and Link fish pond samples showed significant differences at  $P < 0.005$  in heavy metal concentrations. Zinc was shown to have values above the DPR standard limits. Heavy metal content of fish samples from the river water show that the mean concentration values in the fresh

fish was in the increasing order of Copper < Cadmium < Nickel < Lead < Iron < Zinc for the Intestines while Mercury, Arsenic, Barium, and Chromium had insignificant low values in the fish samples across the sampling points as well as the Link fish pond (Table 3). Results for Gills show that Cu had 4.9, Cd 7.8, Ni 23.42, Pb 28.44, Zn 142.0 mg/kg while smoked fish recorded Cd 5.12, Pb 9.65, Ni 42.34, Fe 50.20, Cu 83.24, and Zn 163.1 mg/kg. The dry fish recorded 42.34 mg/kg for Ni, 3.24 mg/kg for Cu while Fe content had 50.20



**Table 2. Heavy metal concentration of the Surface River water and the Link fish pond**

Heavy Metals (mg/Kg)	STATIONS					DPR Limit for Brackish/ Saline water
	BBW1	BBW2	BBW3	BBW4	LFPW5	
Cadmium	5.12±1.03 <sup>a</sup>	5.3±2.03 <sup>a</sup>	4.9±1.06 <sup>a</sup>	5.0±1.06 <sup>a</sup>	0.10±0.00 <sup>b</sup>	-
Chromium	<0.001	<0.001	<0.001	<0.001	<0.001	1
Copper	8.34±2.00 <sup>a</sup>	8.34±2.00 <sup>a</sup>	8.26±1.01 <sup>a</sup>	8.44±2.01 <sup>b</sup>	1.30±0.01 <sup>ab</sup>	No Limit
Iron	60.2±8.01 <sup>a</sup>	60.2±8.01 <sup>a</sup>	58.6±8.01 <sup>a</sup>	63.0±8.01 <sup>a</sup>	28.7±8.01 <sup>a</sup>	No Limit
Nickel	42.34±8.01 <sup>a</sup>	42.34±8.01 <sup>a</sup>	45.84±8.01 <sup>a</sup>	50.00±8.01 <sup>ab</sup>	2.00±1.02 <sup>abc</sup>	Nickel
Zinc	173.1±10.21 <sup>a</sup>	173.1±10.21 <sup>a</sup>	179.3±11.01 <sup>b</sup>	177.6±22.00 <sup>a</sup>	28.22±8.01 <sup>abc</sup>	5
Lead	30.65±5.21 <sup>a</sup>	30.65±5.21 <sup>a</sup>	32.38±6.22 <sup>ab</sup>	32.98±7.20 <sup>ab</sup>	6.20±1.0abc	No Limit
Mercury	<0.001	<0.001	<0.001	<0.001	<0.001	-
Arsenic	<0.001	<0.001	<0.001	<0.001	<0.001	-
Barium	<0.001	<0.001	<0.001	<0.001	<0.001	-

**BBW1=Bonny; BBW2=Bodo; BBW3= Andoni; BBW4= Finima; LFPW5 = Link Fish Pond Water**

Results are means of three replicates. Means of the same superscript are not significantly different at ( $p \geq 0.05$ ) while means in the same column not followed by the same superscript are significantly different

**Table 3. Heavy Metal Content Analysis of Fish samples from River water and the Link Fish Pond**

HEAVY METALS (mg/Kg)	River Water FRESH FISH			Link Fish pond (CONTROL)	FRESH FISH		River Water Smoked FISH	Link Fish pond Smoked FISH
	GILL	INTESTINE	MUSCLE	GILL	INTESTINE	MUSCLE		
Cadmium	7.80	6.86	6.10	0.002	0.001	<0.001	5.12	<0.001
Chromium	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Copper	4.94	4.34	4.02	1.00	0.87	0.56	83.24	16.56
Nickel	23.42	22.64	21.91	3.00	2.60	2.00	42.34	5.00
Zinc	142.0	122.2	120.6	23.00	21.00	16.46	163.1	18.46
Lead	28.44	23.48	23.12	<0.02	<0.02	<0.02	9.65	<0.02
Mercury	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Arsenic	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Barium	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Iron	60.72	60.04	58.04	5.74	4.34	4.44	50.20	20.44

## 4. DISCUSSION

### 4.1 Heavy Metal Concentrations of Sediment and Surface River Water

In aquatic ecosystems, sediments play important roles in the growth, evolution and establishment of aquatic organisms. They are also a sink for pollutants. Consequently, sediment represents one of the ultimate sinks for heavy metals released into the aquatic environment [10,29]. The ability of sediment to act as a sink for pollutants arises from a combination of processes, which include river hydrodynamics, biogeochemical processes, and environmental conditions. Consequently, heavy metals in sediments are useful markers of environmental changes in the aquatic ecosystem and give an indication of the ability of natural mechanism to eliminate them while in their compartment [30]. Within the aquatic food chain, the presence of heavy metals can lead to a wide range of effects ranging from molecular alterations to deaths in local fish populations [31]. In this study, Pb had the highest concentration of 48.61mg/kg at 0-15cm depth while Chromium had highest concentration of 41.54mg/kg at 15-30cm depth. The highest concentrations of the heavy metal especially the hazardous metal such Lead, Cadmium etc recorded in this study from the surface water samples can result to exposures of aquatic flora and fauna to unacceptable effects. Apart from its vital role in carbohydrate metabolism (i.e glucose tolerance and glycogen synthesis), trivalent chromium is also believed to play an important role in cholesterol and amino acid metabolism and acts as a cofactor for the hormone insulin. However, high intake beyond the permissible limit is carcinogenic to man and other mammals and this is possible through the food chain. From the result of all trace metals analyzed it shows that differences in depth had great variation in the concentrations of metals in aquatic sediments. Trace metals occurring in aquatic ecosystems at varying concentrations may be due to biogeochemical cycling and anthropogenic inputs [32].

Metal pollution of the sea is known to be less visible and direct than other types of marine pollution, but with profound impacts on marine ecosystems [33]. The most potentially harmful of these elements are heavy metals, such as lead, mercury, cadmium etc. Studies on heavy metal levels in benthos, water and sediment of coastal waters have been a major environmental focus especially in the last decades [7,34-37].

However, the significant difference between link fish pond and the surface water indicates serious pollution of the surface water. In the present study Zinc had a range of 173.1±10.21 to 179.3±11.01 mg/kg, Iron ranged from 58.6±8.01 to 63.0± 8.01mg/kg, Nickel value was 42.34±8.01 to 50.00±8.01 mg/kg while Copper recorded 8.26±1.01 to 8.44±2.01 mg/kg in all sampling locations above the permissible limit of DPR limit of 5mg/kg for Brackish/ Saline water while Mercury, Arsenic, Barium, and Chromium concentrations were below detection limit of 0.001 mg/kg across the stations. Metals such as Copper and Zinc are essential for metabolism in fish at low concentrations while some others such as Lead and Cadmium are toxic to living organisms [17]. When present at high concentrations, these metals impose serious damage to metabolic, physiological and structural systems of organisms in the aquatic environment. Sediments are an important sink and long-term store of a variety of pollutants, particularly heavy metals, and may serve as an enriched source of food for benthic organisms in estuarine ecosystems [18] because they are in constant flux with the overlying water column [16,21,22] The occurrence of increased concentrations of heavy metals in sediments can be a good indicator of man-induced pollution rather than natural enrichment of the sediment by geological weathering [24,25] Some of the sediment-bound metals may be remobilized and released into water as a result of changes in environmental conditions that leads to acidification and reduction/oxidation and impose adverse effects on living organisms [23]. The coastal waters of Nigeria is under increasing pressure from industrial pollution, oil spills, anthropogenic activities and agricultural wastes. These pressures pose potential threat to the entire ecosystems and human well-being. It also shows that the accumulation of heavy metals is predominant in sediments rather than of surface water which can be linked to the fact that sediments act as an important host for all toxic metals, contaminants and dead organic matter descending from the ecosystem. This therefore shows the impact of anthropogenic and industrial activities to the concentration of heavy metal in Rivers.

### 4.2 Heavy Metals in Fishes

Fishes are major faunal components of aquatic environments and are usually used as excellent environmental biomarkers of the health of aquatic systems. Fishes are continuously exposed to waterborne and particulate heavy



metals due to continuous flow of water through gills and through food sources. Metals bioaccumulate in different tissues follow different patterns of bioaccumulation factors [38]. The most commonly found heavy metals in water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment [39]. Fishes ingest heavy metals from the surrounding waters, planktons, other feeding diets and sediments resulting to their accumulation in reasonable amounts [16]. This study revealed the concentrations of different heavy metals in the fishes in this order: Copper 4.34 < Cadmium 6.86 < Lead 23.48 < Nickel 22.64 < Iron 60.04 < Zinc 122.2 mg/kg for the Intestines while Mercury, Arsenic, Barium, and Chromium had insignificant low values in the fish samples across the sampling points as well as the Link fish pond. The dry fish recorded 42.34 mg/kg for Nickel, 83.24 mg/kg for Copper while Iron content had 50.20 mg/kg. The heavy metals, obtained in this study as contaminants, are not necessarily bound to sediment, but may also be released into the water column through various remobilization processes. Thus, in water bodies, sediment can be both a vector and a potential source of pollutants [40,41]. Depending on environmental conditions and hydrodynamic features, metallic trace elements, especially heavy metals, tend to adsorb from the water column onto the surfaces of fine particles and generally move with the sediment, and can affect benthic, pelagic and even planktonic organisms and, to some extent, the food chain if toxic levels are reached, thus posing a health risk [38,42,43]. This therefore poses severe health risk for consumption of seafoods especially fish from such sources.

## 5. CONCLUSIONS

The present study reveals the concentration of metals like Iron, Zinc, Chromium, Copper, Cadmium and Lead in sediment were generally high when compared with recommended values, indicating pollution. It also shows that the accumulation of heavy metals is predominant in sediments rather than of water and organisms, which can be linked to the fact that sediments act as an important host for all toxic metals, contaminants and dead organic matter descending from the ecosystem above. This therefore shows the impact of anthropogenic and industrial activities to the concentration of heavy metal. Mangrove ecosystems provide ideal habitats for many marine organisms and the

impact of crude oil pollution/contamination on these fragile inter-tidal estuarine wetlands present potential ecological risks to the ecosystems. Therefore, proper monitoring and continuous environmental assessment is highly essential along the coastal zones as indiscriminate discharge of effluents from various sources must be stopped or treated appropriately before being discharged into surface river waters.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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