Distribution of Toxic Metals in Biota, Sediments and Water from a Polluted Mangrove Swamp in Rivers State

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Concentrations of Pb, Cd, and As were investigated in the tissues of mudskippers (*Periophthalmus papilio*), water, and sediments from Isaka-Bundu mangrove swamp in the Upper reach of Bonny Estuary, Niger Delta, Nigeria. The samples were collected from three stations every week for three months. The trace metals and physicochemical parameters were determined according to APHA 2000 methods. The concentration of trace metals by stations followed the order: station III (Dockyard) > station II (Bundu-Ama) > station I (Isaka). The trace metal distribution sequence in the fish, water and sediment according to their stations followed this sequence: Dockyard (Sediment = Pb > Cd > As; Water = Pb > Cd > As; Fish = Pb > As > Cd); Isaka (Sediment = Pb > Cd > As; Water = Pb > Cd > As; Fish = Pb > As > Cd); Bundu Ama (Sediment = Pb > Cd > As; Water = Pb > Cd > As; Fish = Pb = As > Cd). The overall, trace metal concentrations by samples followed this sequence; (Sediment = Pb > Cd > As; Water = Pb > Cd >As; and the mudskippers (*P. papilio*) = Pb > As > Cd) across the stations. The study revealed that all sampled sites in the Isaka-Bundu mangrove swamp had heavy metal values within Joint FEPA/WHO recommended biota load limits. High significant values of Pb and Cd were observed in sediment and water across the three

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stations, while tissue concentration of all three metals was relatively low and uniform. If proper measures are not taken to curb the excess discharges into the river given the activities in the catchment, the condition of the river will deteriorate badly and become a menace to its inhabitants and the host community which depends on it directly or indirectly.

1. INTRODUCTION

Environmental pollution, natural or man-made, is assuming enormous proportions, increasing considerably by the day since the advent of civilization, industrialization, and urbanisation. The most often polluted environment is the aquatic systems' surface water and sediment, with the sediment serving as the repository. This is because contaminants in the air, soil, or on land ultimately end up in water bodies via local precipitation, surface water runoffs and leaching of rocks, and solid waste deposition [1]. Sewage, industrial wastes, agricultural chemicals such as fertilizers and pesticides, mineral and petroleum exploration, and exploitation, all contribute enormously to surface water pollution [2]. Furthermore, the aquatic ecosystem is one singular receptacle to the terrestrial ecosystem for various contaminants generated through the unfettered release of effluents from mines, smelters, industries, excessive usage of agrochemicals, and aerial deposition [3].

It is rapidly becoming common in the country for people to dump pollutants in water systems. It is a common assumption that aquatic systems: inland waters, estuaries, and even the world oceans have a limitless capacity to absorb an increasing amount and variety of waste substances and energy from our civilization, but on the contrary. Despite the global abundance of water and the mainly renewable property of water resources, its carrying capacity has been overwhelmed by anthropogenic discharges of unprecedented quality and quantity of waste deposits since the last century.

Water pollution has remained a puzzling issue, with the attendant food chain transfer of pollutants metal contaminants especially. Heavy metals: As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, and Zn have been studied as major environmental pollutants with well-established toxicity records [4]. Trace metal contamination and the trophic transfer along aquatic food chains have been a major concern in the past half-century. More so, the coastlines pose a high risk to aquatic habitats as they are inclined to significant effluents discharge and agrochemical runoffs.

Metals are different from other toxic contaminants because they are neither created nor destroyed by man. They are present in the aquatic environment naturally, but man's activity increases their level causing environmental issues in coastal areas and rivers [5]. Pollution by heavy metals in aquatic environments is growing globally, with worrisome tendencies worldwide due to their toxicity, durability, non-biodegradability, and biotransformation potential [6]. Rapid population development and growth in industrialisation, urbanisation, farming, and the rest of the world have caused serious global contamination of heavy metals, in particular in developed countries [7]. Significant quantities of metals from these human activities are released into water sources and can be heavily concentrated and biomagnified [8].

2. MATERIALS AND METHODS

2.1 Study Area

The Isaka-Bundu mangrove swamp is a tidal soft-bottom mangrove ecosystem that is often exposed to a wide range of mudflats. It is a tributary of the upper Bonny Estuary in the Niger Delta, Nigeria. The sampling stations were at least 1,000 meters apart along the tributary of the upper Bonny Estuary. The sampling stations were geo-referenced and selected specifically to cover study areas of the creek receiving effluents and wastes from different anthropogenic activities of the area; Isaka (Station I: $N04^0 45'03.05''$, $E007^0 00'45.51''$); Bundu-Ama (Station II: $N04^0 44'55.35''$, $E007^0 00'38.40''$); and Dockyard (Station III: $N04^0 45'03.58''$, $E007^0 00'57.75''$) as shown in (Fig. 1). This section of the river is constantly bombarded with human, animal, domestic wastes, and runoffs and is visible on the shorelines by residents for artisanal fishing, while various water-related activities such as commercial water transportation, industrial/manufacturing activities,

and oil and gas logistics operations are equally deployed either within or on the shores of this section of Bonny River.

In general, the study area is subject to effluents discharged from Industries sited along its banks and a densely populated coastal settlement. The vegetation present in the area is the red mangrove *Rhizophora mangles* and white mangrove *Laguncularia racemose.* Some of the dominant fish families in this ecosystem include the Lutjanidae, Clupeidae, Cichlidae, and the Claroteidae, but the most abundant are the Claroteidae (silver catfish) and Cichlidae (tilapias) [9]. Whereas the tidal mudflats species include the gobies, periwinkles, crabs, and mudskippers, only to mention a few.

2.2 Samples Collection

The water samples were collected in pre-cleaned high-density Schott glass bottles while the sediments were collected using an 'Ekman grab' sampler. Sediment and water samples for heavy metal analysis were aseptically collected from approximately 20 cm below the water surface near shore at both low and high tide in new, clean screw-capped bottles, acidified and clearly labeled. Freshly caught live mudskippers (*Periophthalmus papilio*) were collected from the catch of local fisher folks at the three sampling stations at the interval using a locally made fishing traps and stored in an ice pack in the field to maintain the freshness and then transported to the laboratory, where they were stored at 10°C until analysis. A total of sixty representative fish samples with mean length (9.5±0.56cm) and

weight (10.32±0.91g), five per station at each sampling campaign were obtained within a sampling period of six months to provide for statistical variation. All procedures followed the basic COVID-19 protocol while working on this research in the laboratory. The Mudskipper (*Periophthalmus papilio*) was chosen because they are closely linked to mangrove and adjacent soft bottom peri-tidal ecosystems. All samples were clearly labeled and transferred to the laboratory the same day on an ice chest to preserve sample integrity. The samples were then measured and refrigerated pending analysis. Analyses of heavy metal content were done using standard methods [10].

2.3 Physicochemical Parameters

The physicochemical parameters were analysed using an in-situ Handheld Multimeter. The pH, Temperature, Salinity (ppt), and Total Dissolved Solids (TDS) (ppt) of the water were measured using an in-situ Handheld Multimeter (Milwaukee Model pH600 and Laboratory Benchtop meter 860033-model). while the Dissolved Oxygen (DO) was measured using Winkler's method. A water sample for the Biochemical Oxygen Demand (BOD) was collected with a BOD bottle and then taken to the laboratory for analysis using the 5-day BOD test [11]. Precautions were taken to ensure the monitoring device was properly charged with an appropriate charger. An appropriate gas sensor (probe) was fixed before the test. Protective gears were used in case of environmental hazards. All procedures followed the basic COVID-19 protocol while working on this research in the field and laboratory.
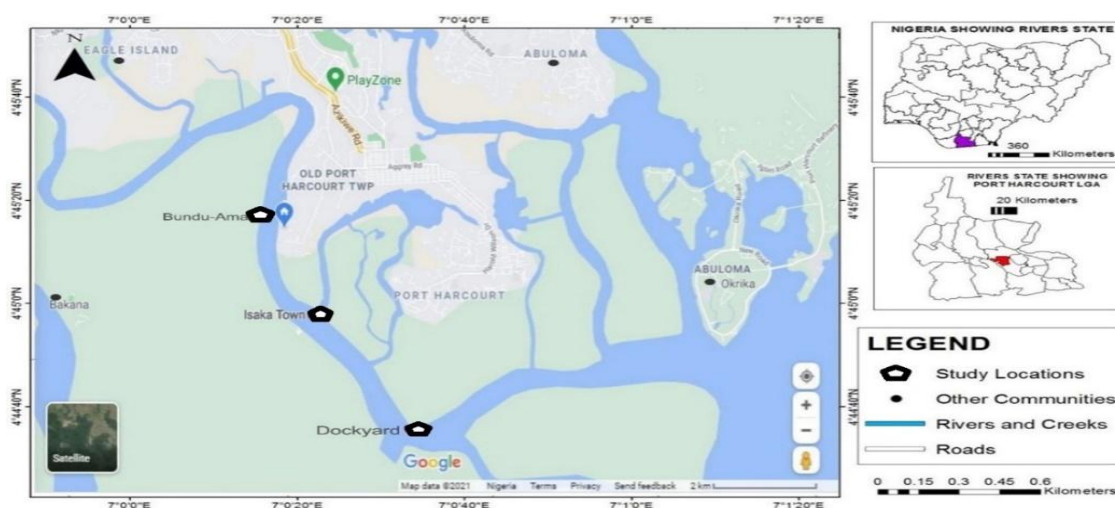

Fig. 1. Map showing the study area

2.4 Determination of Heavy Metals

The heavy metal analysis was done using APHA (3111B) modified method [12]. The trace metals analyzed were Pb, Cd, and As. The instrument setting and operational conditions were done following the manufacturer's specifications with the use of an Atomic Absorption Spectrophotometer (AAS) [10].

2.5 Evaluation of Tissue Concentration

Bio-Transfer Factor (BTF) and Bioaccumulation Factor (BAF) were calculated using the formular as proposed by [13] and [14]. The ratio between the accumulated concentration of a given pollutant in the organ and its dissolved concentration in water. It was calculated using the formular below;

$$BTF = M_{tissue} / M_{water}$$

The bioaccumulation information for sediment and biota. The equation which relates the heavy metal transfer from sediment in biota is thus;

$$BAF = M_{biota} / M_{sediment}$$

The tissue concentration was determined using dry weight concentrations.

2.6 Statistical Analysis

Descriptive statistics and Analyses of Variance (ANOVA) were done using SPSS version 16. Significant means were separated with Duncan Multiple Range Test at 0.05. Fish tissue concentration was calculated with the mean values generated. Microsoft Excel software was used to interpret the data presented. Mean, standard deviation, and standard error of the mean were the statistical quantities employed to manage the data, and Pearson's Product Correlation was used to examine the relationship among the parameters analysed.

3. RESULTS AND DISCUSSION

3.1 Physical and Chemical Parameters

The results show the variation in physicochemical parameters across stations (Figs 1a and 1b). The pH value was the only significantly different parameter ($p<0.05$) across the stations. Dockyard (6.31±0.05) recorded the higher pH value followed by Isaka (6.11±0.03)

while the least value was observed in Bundu-Ama (6.09±0.08). The highest temperature value was observed at Dockyard (28.77±0.58^{o}C) followed by Bundu-Ama (28.60±0.47^{o}C) and the least value at Isaka (27.70±0.31^{o}C). However, no significant ($p>0.05$) difference was reported in the Temperature value. Furthermore, Bundu-Ama had the highest electrical conductivity (12495.00±4127.80µS cm^{-1}) and the least value was observed in Dockyard (11010.0±2842.3µS cm^{-1}). The highest Total Dissolved Solids value was observed at Bundu-Ama (6240.0±2059.91mgL^{-1}) followed by Isaka (5715.00±1489.62mg L^{-1}) and the least value (5495.00±1417.77mgL^{-1}) was observed at Dockyard. Salinity was highest in Bundu-Ama (2174.80±688.16mgL^{-1}) followed by Isaka (2145.00±693.89mgL^{-1}) and the least value of salinity was recorded in Dockyard (2130.90±554.29mgL^{-1}). However, the highest Dissolved Oxygen was observed at Isaka (4.99±0.08mgL^{-1}). This was followed by Dockyard (4.97±0.02mgL^{-1}) and the least value was observed at Bunda-Ama (4.87±0.09mgL^{-1}). A similar trend was observed for Biological Oxygen demand where the highest value was observed at Isaka (2.54±0.34mgL^{-1}). The values for Bundu-Ama and Dockyard were 2.40±0.20mg L^{-1} and 2.40±0.26mg L^{-1} respectively.

The water quality observed during this study along the Isaka-Bundu mangrove swamp was compared with World Health Organization [15] guideline set for the maximum tolerable limit and other related research finds.

3.1.1 Temperature

The water temperature obtained from surface water from this study is also similar to the report of [16,17] who recorded water temperatures ranging from 27.7 to 31 ^{o}C from water bodies in the Niger Delta, Nigeria. This was on the average as compared to the values observed in the Niger Delta waters as reported by [18] with a similar trend also recorded in Bonny/New Calabar Estuary as reported by [19]. The variation of water temperature recorded could be attributed to high atmospheric temperature and exposure to direct solar radiation, low relative humidity, and reduction in the number of suspended particles which occurred as a result of high-water transparency and heat from sunlight increasing [20]. [17] stated that the aquatic organisms can be adapted to such changes in temperature and can even withstand changes outside this range.
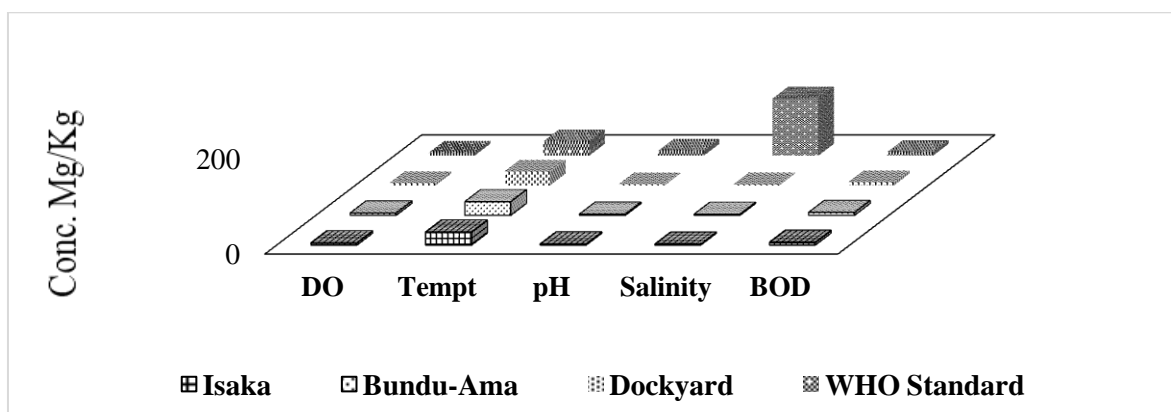
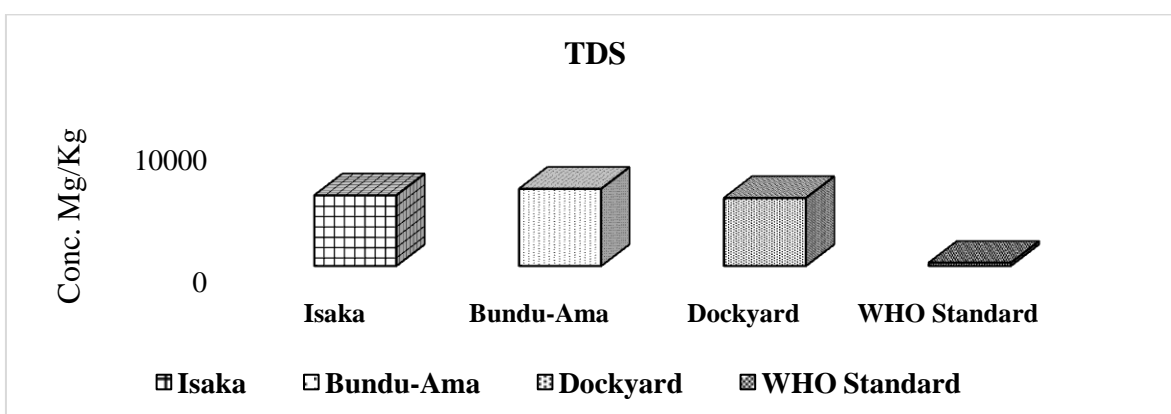**Fig. 1a. Variation in physicochemical parameters across stations**

Fig. 1b. Variation in physicochemical parameters across stations

3.1.2 Hydrogen ion concentration (pH)

The hydrogen ion concentration (pH) of water is an important parameter that is evident in the manner in which it affects the chemical reactions and biological activities in the aquatic environment [17, 21]. In this study, the pH concentration observed was slightly acidic and the range fell above the standard acceptable range for drinking waters of 6.5–8.5 [15]. This finding is in agreement with [16] who reported a similar range for pH of water sources in Isaka-bundu waterfront in Rivers Nigeria [22] reported lower values for pH at Ibiekum River, Ekpoma, and Adofi River [23] reported lower pH in Ogun as well. The mean pH values recorded may be considered to be too acidic for human consumption and can cause health concerns such as acidosis infections, and the low pH has synergistic effects on heavy metal toxicity in waterbodies.

The pH value range indicates that the Isaka-Bundu swamp water is slightly acidic. However, it falls above the range of pH of natural waters [24].

3.1.3 Electrical conductivity

Electrical conductivity is the measurement of the degree of ions in water, which affects the taste and has a significantly great impact on the user's acceptance of the water [17]. The mean value recorded for all underground water samples was within the WHO permissible limit. Findings were related to the report of [25]. This range of electrical conductivity values (11010 to 12495 µS/cm) recorded from the Isaka-Bundu swamp is generally higher than the permissible limit by [15] for normal natural water bodies. higher conductivity indicates that the water receives a high amount of dissolved inorganic substances in ionized form their surface catchments [26]. Higher conductivity values have been reported in many water bodies in the Niger Delta. - Bonny/New Calabar. Estuary showed higher values and variation with the season in a study reported by [18]. However, the total dissolved solids mineral load of the water, as observed to be higher in a station this study constantly fed with domestic and sewage wastes daily from a

densely populated settlement may also be attributed to the level. These could also be linked to be due to large volumes of water from the sea.

3.1.4 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) observed in this study were higher as compared to the ranged report by [27] who classified the amount of TDS per liter for brackish water to be between 1500 to 5000 mg L^{-1} TDS and saline water to be >5000 mg L^{-1}. The result is an indication that water in the mangrove swamps can switch between fresh and brackish waters. The high value of TDS recorded from Isaka-Bundu creeks might be due to agricultural runoff, and other human activities like domestic washing [16]. High levels of TDS can influence the taste and durability of plumbing and associated equipment. According to [28], the concentration and relative abundance of ions in waters is highly variable and depends mainly on the nature of the bedrock, precipitation, and evaporation crystallization processes. It is also known to show some correlation with water conductivity [16,29] recommends that water containing more than 2000 mg L^{-1} of dissolved solids should not be used if other less mineralized supplies are available.

3.1.5 Salinity

From this study, the salinity ranges between 2.13- 2.17%o. This gradient was not in conformity with the situation obtainable by [29]. The salinity values were also within the [15] guideline set for the maximum tolerable limit of salinity for brackish water. The concentration of salt may have resulted from the oceanic waters and decreasing influence of the river and runoff-derived freshwater [30]. The Isaka-Bundu swamp backed by the inundated tides may not be unconnected to the tidal influence given the proximity to Bonny River which receives a large amount of seawater [16] (Odekina *et al.,* 2021). An earlier study by [32] also reported a deviation in salinity from the usual downstream increase in salinity in brackish water. Studies on other water bodies in the Niger Delta have also reported a similar trend in the salinity variations [33, 34] recorded seasonal change in the salinity with low dry season values to wet season values and attributed it to a higher rate of surface water evaporation due to extreme sunshine. High precipitation could cause estuarine waters to dilute and thereby reduce salinity at a different time interval [35] (Okonkwo *et al.,* 2021). However, the range reported in the current in this

study fall below the limit of 10,000ppm (0.1%) set by [36,37] reported similar salinity values during the reconnaissance survey carried out at Amadi Creek, Port Harcourt, Nigeria. Although other research like [38,39] also reported a contrarily higher salinity value of 13,000%o) from Gwagwalada. [40] Mclusky (1989) concluded that precipitation could cause estuarine waters to dilute and thereby reduce salinity concentration.

3.1.6 Dissolved Oxygen (DO)

The observed DO values in this study ranged between (4.9 to 4.5mg/L) which were lower compared to [15] acceptable standards for drinking water and others documented by several researchers for some polluted water bodies in Niger Delta [41]. The values were lesser than the [15] WHO acceptable limit of 6mg/L. Decreased DO values observed may be indicative of too many bacteria that may use up the dissolved oxygen in it. The temperature may influence the amount of dissolved oxygen because only lesser oxygen is dissolved in warm water than in cold water [30]. Therefore, the high temperature of the water sources could be a major factor for the low DO values recorded in the current study. Dissolved oxygen may not have a direct health hazard to humans, but it could have effects on other chemicals in the water thereby affecting the aquatic environment [17]. High organic content from human feces, decayed domestic, sawmill wastes, and plant materials that found their way into these swamps have also been reported for the low DO record. Furthermore, DO also may have been consumed from the study area by the oxidation of nitrogenous material in water [34].

3.1.7 Biochemical Oxygen Demand (Bod)

The BOD measures the amount of oxygen utilized by microorganisms such as bacteria to oxidize organic matter available within the water [30]. The BOD values recorded in this study were within the range of 2.40 to 2.54mg/L. However, there range obtained from this study was below [15] WHO guideline set for the maximum tolerable limit of BOD in drinking water, for fisheries and aquatic life. The variations in the BOD values could be attributed to the effect of higher temperature, salinity, and putrefaction of substances deposited in the river [19]. The values of BOD obtained in this study were less than 10 mg/L as stipulated by [42,15], implying that the water body was fairly useful. The variations observed could be attributable to the dump heap within the area. However, the values

of the DO record were higher than those reported on the Bonny/New Calabar River by [43].

3.2 Heavy Metal Concentrations in Water, Sediment and Fish

The concentration of heavy metals by stations in order of magnitude followed: Station III (Dockyard) >Station II (Bundu-Ama) > Station I (Isaka). Heavy metal distribution sequence in sediment, water and fish by stations: Dockyard (Sediment = Pb>Cd>As; Water= Pb>Cd> As; Fish = Pb>As>Cd), Isaka (Sediment = Pb>Cd>As; Water = Pb>Cd>As; Fish= Pb>As>Cd); Bundu-Ama (Sediment = Pb>Cd> As; Water = Pb>Cd>As; Fish = Pb = As > Cd). Pb had the highest concentration in sediment at Dockyard (6.155-12.067mgkg^{-1}) while As recorded the lowest value (0.001mgL^{-1}) in water at Isaka and Dockyard. As was not found in water at Bundu-Ama. The concentration of trace metals observed in the water column in this study ranged between Pb (0,058-0.094 mgL^{-1}); Cd (0.051-0.054 mgL^{-1}) and As (0.001 m L^{-1}). Concentrations differ widely by station and for each heavy metal in the fish tissue. However, the Sequence of trace metal distribution in the tissue of fish by station followed the same trend: Dockyard **(**Fish = Pb > As > Cd**)**; Isaka **(**Fish = Pb > As > Cd**)**; Bundu-Ama **(**Fish = Pb = As > Cd**)**. Accumulation patterns were the same in all stations, however, accumulation rates of all metals varied between stations except for Cd (Figs 2 to 4).

Table 1 shows the variation in heavy metals in Isaka, Bundu-Ama, and Dockyard. All parameters were significantly (p<0.05) different across stations except for As. It was observed that Pb was highest in Dockyard with 4.055mgkg^{-1} concentration and Isaka and Bundu-Ama had the values of 2.072mgkg^{-1} and 2.862mgkg^{-1} respectively. Contrary to the trend, Bundu-Ama had the highest Cd concentration of 1.298mgkg^{-1}. This was followed by Dockyard (0.881mgkg^{-1}) and Isaka (0.795mgkg^{-1}). The concentration of As was 0.008 mgkg^{-1} at Dockyard and 0.007 mgkg^{-1} at Isaka and Bundu-Ama.

Table 2 shows the variation in heavy metals in water, sediment, and fish. All heavy metals were significantly different in water, sediment, and fish. For all the heavy metals considered in this study, the highest consecration for all the parameters is seen in sediment. Pb was highest in sediment (8.910mg kg^{-1}). This was followed by water (0.076mg L^{-1}) and then fish (0.004mg kg^{-1}). Cd

was also highest in sediment (2.920mg kg^{-1}) and least in fish (0.001mg kg^{-1}). Water had 0.053mg L^{-1} Cd concentrations. As was highest in sediment (0.017mg kg^{-1}) and least in fish (0.001mg kg^{-1}).

The correlation between heavy metals in the study area is seen in Table 3. All the relationships were positive. Also, all the heavy metals were significantly correlated except when correlated with the station. Very high relationships were observed between all the heavy metals. The correlation between Pb and AS was 0.888, Pb and Cd were 0.900 while Cd and As were 0.875 respectively.

Table 4 shows the variation in tissue concentration of heavy metals in water by *Periophthalmus papilio* in Bund-Ama, Isaka. and Dockyard. The highest tissue concentration ranges were observed in AS (2.00 mg kg^{-1}) followed by Pb (0.02702 -0.068966 mg kg^{-1}) and the least was seen in Cd (0.018519-0.019608 mg kg^{-1}across the heavy metals. However, the tissue concentration value for Cd (0.018519 mg kg^{-1}) was the same for Dockyard and Isaka. The sequence of tissue concentration readings from highest to lowest across the stations was As>Pb>Cd. Also, it was observed that the tissue concentration values of heavy metals in water were highest in Isaka, followed by Dockyard, and least in Bundu-Ama for all the metals under study. Meanwhile, As recorded a parallel value of 2.00 mg kg^{-1} across the stations.

Table 5 shows the variation in tissue concentration of heavy metals in sediment by *Periophthalmus papilio* in Bundu-Ama, Isaka, and Dockyard. The concentration deferred widely across heavy metals and between stations, with the highest value being AS in Isaka while the least was Cd which was recorded at Bundu-Ama. A similar trend was also observed in Cd values across the stations. The sequence of tissue concentration of heavy metals in sediment from highest to lowest across the stations was As>Pb>Cd.

3.2.1 The trend in metal concentrations across the stations

The study shows that metal concentrations in the Water, Sediment, and Fish were significantly different across the three stations. The concentration of metals observed in water in this study ranged between Pb (0,058-0.094 mgL^{-1}); Cd (0.051-0.054 mgL^{-1}) and As (0.001 m L^{-1}).

High significant values of Pb and Cd were observed in sediment and water across the three stations ranging from 6.155 to 12.067mgkg^{-1}) while tissue concentrations of all three metals were relatively different by stations and for each metal in the fish tissue. The high significant values of Pb and Cd observed in sediment and water across the three stations could be attributed to an avenue for the recontamination of the water channel as a result of turbulence or bioturbation in the sediment [34]. The level of these metals suggests varied intense anthropogenic influence due to industrial and urban advancement within the catchments of the Isaka-Bundu mangrove swamp [16].
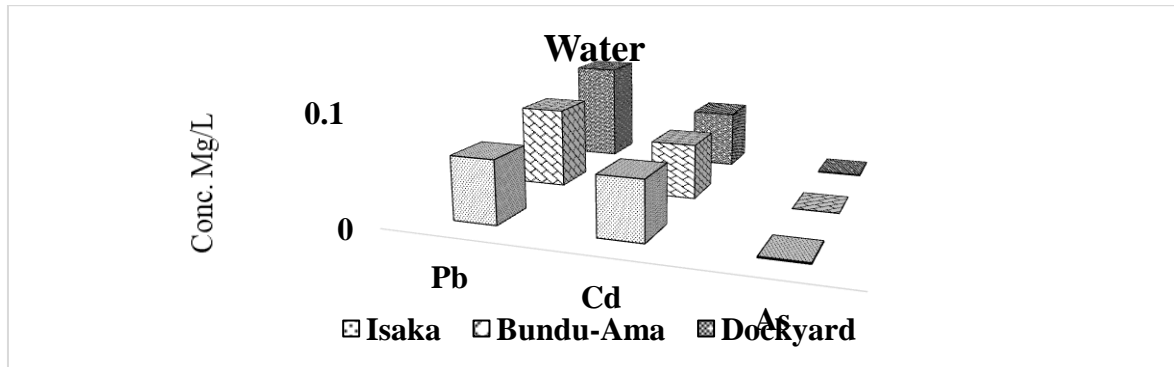

Fig. 2. Show the mean concentration of heavy metals in the water across the stations.
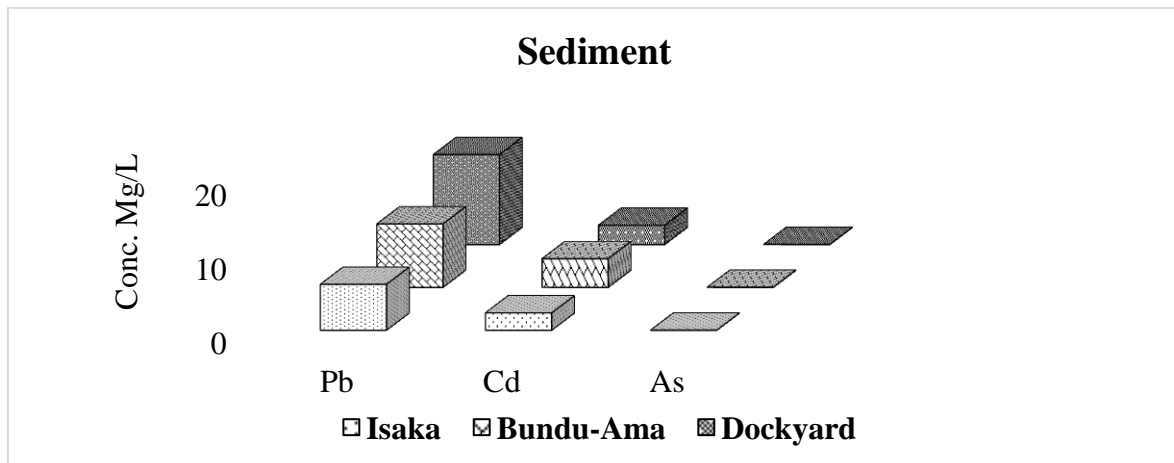

Fig. 3. Show the mean concentration of heavy metals in the sediment across the stations
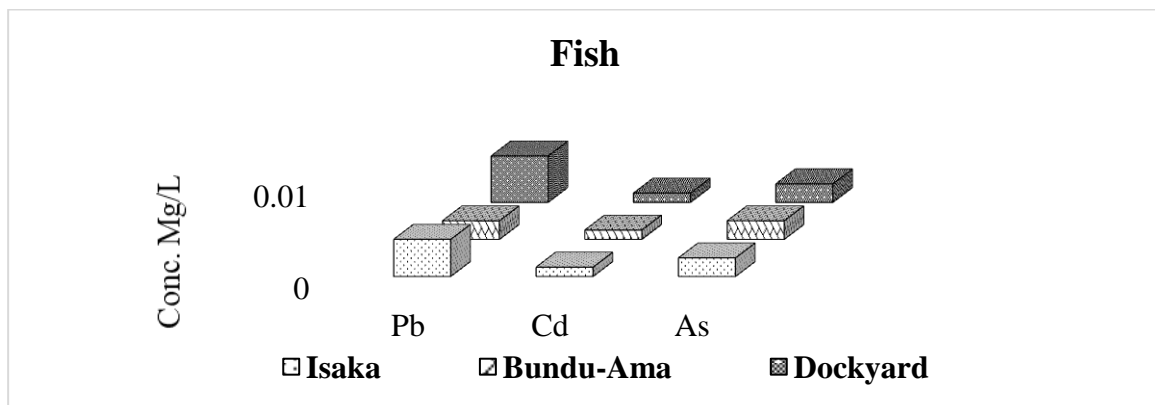

Fig. 4. Show the mean concentration of heavy metals in the Fish (*Periophthalmus papillio*) across the station. NB: The heavy metal concentrations in water were in mgL^{-1}

Table 1. Variation in heavy metals in Isaka, Bundu-Ama, and Dockyard

Station	Pb	Cd	As
Isaka	2.072[b]	0.795[b]	0.007[a]
Bundu-Ama	2.862[b]	1.298[a]	0.007[a]
Dockyard	4.055[a]	0.881[b]	0.008[a]
SEM	0.286	0.073	0.001
WHO 2011	0.1	0.003	10 µg/l
FEPA limit	2.0	2.0	1–10 µg/l

a, b: Means with different superscripts in the same column are significantly different (p<0.05); values with the same superscripts in the same column are not significantly different (p>0.05)

Table 2. Variation in heavy metals in water, sediment, and fish

Source	Pb	Cd	As
Water	0.076[b]	0.053[b]	0.004[b]
Sediment	8.910[a]	2.920[a]	0.017[a]
Fish	0.004[b]	0.001[b]	0.001[b]
SEM	0.286	0.073	0.001
WHO 2011	0.1	0.003	10
FEPA limit	2.0	2.0	1–10

a, b, c: Means with different superscripts in the same column are significantly different (p<0.05)

Table 3. Correlation between heavy metals in the study area

	Pb	Cd	As
Pb	1		
Cd	0.900[**]	1	
As	0.888[**]	0.875[**]	1

*NB: ** significant at 0.01 (p<0.01)*

Table 4. Tissue concentration of heavy metals in water by *P. papilio*

Station	Pb	Cd	As
Bundu-Ama	0.027027	0.019608	2.000
Dockyard	0.053191	0.018519	2.000
Isaka	0.068966	0.018519	2.000

NB: Concentration in (mg kg^{-1})

Table 5. Tissue concentration of heavy metals in sediment by *Periophthalmus papillio*

Station	Pb	Cd	As
Bundu-Ama	0.000235	0.000260	0.153846
Dockyard	0.000414	0.000386	0.125000
Isaka	0.000650	0.000429	0.166667

NB: Concentration in (mg kg^{-1})

These levels of chemical distribution in interstitial waters in the Niger Delta may influence the diversity of life present or adapted to the water channels, while the sediment act as a sink for contaminants in the aquatic ecosystem [30]. Pb and Cd were higher than the acceptable limit for heavy metals stipulated limits by [15] in the aquatic environment except for As and therefore require continuous monitoring to detect malicious increases as a result of anthropogenic input and avert possible public health implications of these metals on consumers of water and seafood from the study area. Other studies on trace metal level of the Bonny/New Calabar River Estuary, Niger Delta, Nigeria recorded lower As concentrations and opined that although the results of water concentrations of heavy metals observed in his study agrees with the general opinion of low-level heavy metal concentrations in other parts of the Niger Delta [19, 30].

Cd concentrations in this study ranged from 0.051 to 0.054 mg/L^{-1}. These values were above the Maximum Contaminant Level (MCL) of 0.005 mg L^{-1} [42]. This is an indication that the water from the mangrove swamps showed pollution of Cd. Sources of Cd in water include discharge of domestic effluents, weathering of minerals and soils, and urban storm-water runoffs containing Cd-laden materials [44]. The possible accumulation of Cd in man is mainly in the kidney and liver. Its high concentrations cause chronic kidney dysfunction, inducing cell injury and death by interfering with calcium (Ca) regulation in biological systems in man, fish, and other aquatic organisms [45].

The elevated levels of Pb in the current study could be traced to anthropogenic activities including illegal oil refining activities while human activities such as the discharge of industrial and household waste are non-natural sources of Cd [46]. Cd above certain concentrations (0.005-0.15 ppm) has been reported to be lethal for some aquatic biota such as crustaceans [47], however, this is minimized by the mangrove ecosystem via root absorption and binding. Mangrove in the research area is under constant attack by artisanal refining activities and land developments, and this can increase the effect of Cd pollution [48]. The high values recorded in this study can be attributed to pollution of the environment as a result of intense domestic, commercial, and industrial activities discharging their wastes into this water body indiscriminately [49].

As suggested in previous studies, most anthropogenic influences such as mining, agricultural wastes, disposal of untreated and partially treated industrial effluents, fossils fuels, petroleum exploration, indiscriminate use of heavy metal-containing fertilizer, pesticides in agricultural fields and oil spillage can play a relevant role and have been implicated in the metal contamination of rivers in this region [50]. All these studies provided general baseline information while some attempted to explain the possible effects of industrial discharges on this aquatic environment.

Sources of Cd in water include discharge of domestic effluents, weathering of minerals and soils, and urban storm-water runoffs containing Cd-laden materials [16]. The possible accumulation of Cd in man is mainly in the kidney and liver. Its high concentrations cause chronic kidney dysfunction, inducing cell injury and death by interfering with calcium (Ca) regulation in biological systems in man, fish, and other aquatic organisms [45]. Its involvement in endocrine disrupts activities, which could pose serious health problems. However, its concentrations in water are only likely to be of health concern in environments where pH is less than 4.5 [15].

A study on metal levels in Water, Sediment, and fish tissues of *Sarotherodon melanotheron* from the Upper Bonny Estuary in Nigeria and their human health implications reported low heavy metal concentration in sediment [19]. However, the elevated levels of Pb in the current study could be traced to anthropogenic activities including artisanal refining of crude oil because human activities such as the discharge of industrial and household waste are non-natural sources of Cd (Oguwenmo *et al.,* 2004). Mangrove in the research area is under constant attack by illegal refining of crude oil and land developments and this can increase the effect of Cd pollution.

The high values recorded in this study can be attributed to pollution of the environment as a result of intense domestic, commercial, and industrial activities discharging their wastes into this water body indiscriminately. As suggested by past studies, anthropogenic influences such as mining, partially treated industrial effluents, fossils fuels, petroleum exploration, indiscriminate use of heavy metal-containing fertilizer, pesticides in agricultural fields and oil spillage can play a relevant role and have been implicated in the metal contamination of rivers in this region [50]. All these studies provided general baseline information while some attempted to explain the possible effects of industrial discharges on this aquatic environment.

Comparing the levels of the heavy metal in sediments of the Isaka-Bundu mangrove swamp with other areas of the world, it was found that similar high concentrations of Cd and Pb were reported in the sediment of Lake Balaton in Central Europe [51]. Furthermore, very high levels of Cd and Pb were recorded in sediments of Lake Hannah in Canada [52]. In this study, the sites near the Dockyard and active dredging facility showed higher values than sites near clusters of settlements and the dump heap. The slightly lower values of Arsenic (As) across all media recorded may be due to their distance away from the source of the pollutant. Also,

some sort of relationship has been said to relate heavy metal concentration to sediment type.

This study observed that As accumulated in the tissue of the fish more than they are present in the water. This singular potential should qualify the mudskipper as a bioindicator species just like other benthos e.g., crabs, shrimps, and bivalves well-known as standard bioindicators of aquatic pollution owing to their capability to bioaccumulate organic pollutants in tissues organs at levels higher than background bioconcentration [53]. The characteristic soft bottom nature of the mangrove swamps may be responsible for the high chances of metal enrichment as observed in the study area.

4. CONCLUSION

The results showed high metal concentration in the sediments followed by the water and the least was reported in fish tissue. As was considerably higher than the other two metals and may have bioaccumulated in the sediments which act as a sink for heavy metals that absorbs and accumulates toxic pollutants and permits the detection of heavy metals that may be in low concentration in the water and fish. However, the metals were within the Joint [15] [36] permissible limits for this study but the irregular monitoring of these deteriorating aquatic environment may lead to the bioaccumulation of these metals in the edible component fish tissue thereby leading to hazard to one's health.

5. RECOMMENDATION

In conclusion, the major source of these heavy metals in Isaka and Bundu mangrove swamps is anthropogenic in nature, which includes effluents from the illegal refinery, construction and reclamation, and agricultural/domestic waste. These tidal creeks are not overwhelmingly burdened with these heavy metals at present but have led to a significant variation in the physicochemical parameters. However, with the current trajectory, there are high prospects for elevation over time due to changes observed in the fluctuation of physicochemical parameters especially as seen in the level of dissolved oxygen as compared to the standard guideline set by WHO for the maximum tolerable. Therefore, relevant agencies may need to protect these water bodies and make them safe for aquatic life and human.

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