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EVALUATION OF PHYSICOCHEMICAL PARAMETERS AND HEAVY METAL CONCENTRATIONS IN SHRIMP (*Penaeus monodon*), SEDIMENT AND SURROUNDING WATER OF THE MANGROVE SWAMPS, RIVERS STATE, NIGERIA

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ABSTRACT

The study focused on the evaluation of the physiochemical and heavy metal concentration in shrimp (P. monodon), sediments and surface water of Ikpukulu, Kalio, and Ogoloma swamps in Okrika Local Government Area, Rivers State, Nigeria. The following parameters were examined: temperature, potential hydrogen, electrical conductivity, salinity, dissolved oxygen, biochemical oxygen demand, total dissolved oxygen, temperature, and the content of heavy metals (Cd, Cu, and Cr) in surface water, sediments, and shrimp. The pH values (p > 0.05) did not significantly differ amongst the stations. The three sampling station readings of pH were below WHO and FEPA (standards). The temperature data from the three stations did not show any significant differences (p > 0.05), but when compared to the standards, all of the readings were much lower. Result from Ogoloma showed that it had lowest electrical conductivity ratings of the three stations, although overall, the values were higher than the norms. At Kalio, the highest Total Dissolved Solids value (9348.6 ± 67 mg/L) was recorded. When compared to the standards, the salinity values of the three stations were noticeably higher. For Biological oxygen demand, there was no significant (p>0.05) difference between the three stations, but comparing the values to the standards they were all significantly (p>0.05) lower. Heavy metal analysis showed that in the sediment, Copper concentration at Ogoloma was significantly (p>0.05) higher among the three metals in the three stations. Copper and chromium concentrations in the three stations were much higher than the standard. Among the three metals found in the water at the three stations, copper had the highest quantities; the content of copper in Ogoloma was noticeably greater than the standard. Of the three locations, Ogoloma exhibited a noticeably greater concentration of copper for Shrimp. The findings highlight the necessity for preventative action by pointing to an increase in heavy metal concentrations in the Mangrove swamp area.

Keywords: Heavy metals; Shrimps (*P. monodon*); physicochemical parameters; sediment; Niger Delta

INTRODUCTION

Water bodies are essential to plant, animal, and human life everywhere in the world. Since water is the most important component for climate adaptation, it acts as a vital link between human existence and the environment (Zahra et al., 2020; Rathi et al., 2020). Because of this, health authorities are often emphasizing the importance of having a sufficient supply of high-quality water to provide the best possible agricultural, industrial, and household practices; nevertheless, water pollution is becoming a bigger concern (Miebaka, 2017; Boretti and Rosa, 2019).

Both man-made and natural factors can contaminate water. This involves the unintentional release of biological, chemical, and physical contaminants into water bodies from the environment of humans (Ngoka et al., 2021). Through runoff that carries toxic chemicals into adjacent water bodies, agricultural practices such as the application of synthetic fertilizers and pesticides to increase food production and stop food hunger also contribute to the contamination of the aquatic environment. Once in the environment, these toxic compounds can cause major harm to the ecology and public health by entering the food chain (Duruibe et al., 2017; Shittu et al., 2023).

Because heavy metals are so dangerous, environmentalists, chemists, and biologists are particularly drawn to them among all the contaminants (Orororo et al., 2018; Isiuku and Enyoh, 2019; Ekakitie et al., 2021; Orororo et al., 2023; Kpomah and Orororo, 2023). According to Kpomah and Orororo (2023), heavy metals are naturally occurring elements with large bulk densities and atomic masses, including arsenic, lead, chromium, mercury, cobalt, cadmium, nickel, and selenium. Furthermore, even when present in extremely low concentrations in water sources, these toxins constitute a major threat to aquatic life and human health due to their non-biodegradability through bioaccumulation and biomagnification (Akankali and Davies, 2021; Orororo et al., 2022; Orororo and Udi, 2023).

While there are various natural and human-caused ways that metals can get up in water bodies, one significant one is oil spills, which frequently happen in Nigeria's oil and gas producing region, the Niger Delta (UNDP 2006; UNEP 2011). Researchers in the Niger Delta region have found alarmingly high levels of heavy metal contamination in water and even food samples (Vincent-Akpu et al., 2015; Woke and Ndaage, 2017; Akankali and Davies, 2021; Kpomah and Orororo, 2023). Particularly, fish species are excellent and easily accessible biomarkers for identifying heavy metal contamination in water. Excessive concentrations of heavy metals in water have detrimental effects on the ecological health of aquatic animal species and are primarily the cause of declines in aquatic species populations (Ahmed et al., 2015; Javed and Usmani, 2019). Due to the threat to shrimp as well as the noncarcinogenic health hazards associated with consuming shrimp, heavy metal pollution in shrimp has gained international attention (Javed and Usmani, 2019).

Additionally, sediments containing heavy metals have the potential to become short- or long-term sinks in aquatic systems and sources of additional contamination. The granular makeup of the sediments and the physico-chemical characteristics of the water regulate the accumulation of metals (Akankali and Davies, 2021). It is crucial to comprehend the current state of heavy metal contamination in water from both an environmental and economic standpoint. This makes a significant contribution to the creation of laws, regulations, and management guidelines for businesses that produce large volumes of heavy metal-contaminated wastewater. Furthermore, it can guide researchers so that state-of-the-art technologies can be created and developed, not only for treating wastewater before release but also for recovering valuable heavy metals from waste streams.

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This study provides baseline environmental data on pollution status within the sample region

MATERIALS AND METHODS

Study Area

The Okrika Mainland study area is situated in Rivers State, Nigeria, and is part of the South-West Niger Delta coastal region. It is distinguished by its beaches, mangroves, swamps, and barrier bars (Fig.1). The region is located between latitudes 04^o 43.842 and 04^o 45.050 N and longitudes 7o.00' to 7o.50' E. Eleme Local Government Area borders Okrika on the north; Ogu/Bolo borders it on the east; Bonny Local Government Area borders it on the south; Degema borders it on the south-west; and Port Harcourt City borders it on the north-west (Mbaneme and Okoli, 2012). The Nigerian National Petroleum Corporation (NNPC) owns the Port Harcourt Refinery Company (PHRC) and Pipeline Product Marketing Company (PPMC), both of which are located in the region. The Okrika jetty and port, which is utilized for the loading and unloading of oil and gas products as well as associated operations, are also located in this area. Due to these, the area has seen a constant influx of related businesses and residents, which has increased anthropogenic activity and the consequent release of pollutants into the environment.

The sampling stations were deliberately chosen and georeferenced to encompass research regions of the creek that receive wastes and effluents from various anthropogenic activities in the vicinity.

Station 1 (Okpulu)

It has a coordinate of N04^{0}44’3.671” E007^{0}1’30.214”. The station is near the village of Akubiakiri; this area is dominated by mudflat piles that resemble a dumping place for tidal currents. Discarded home rubbish and refuse, fishing, an abandoned artisanal refining operation visible, and a heavily strewn area tarnished by an oil slick.

Station 2 (Kalio)

It bears coordinate N04^{0}45’42.440” E007^{0}4’6.715” and is located at the mouth of Abuloma Creekdirectly across from Kali-Ama. The intertidal feeder channel is primarily home to black and red mangroves (Avicennia Germinans and Rhizophora mangle) as well as a few stands of Nympapalm (*Nypa Fruiticans*). There were more visible industrial wastes, effluents from bunkering operations, and human and animal wastes, together with clearly visible runoff trails.

Station 3 (Ogoloma)

It bears coordinate N04044’11.797” E00704’38.520”. The location of the site is at the intersection of the Woji Elelewo Creek System and the Bonny River. The mangrove forest border is interspersed with a few stands of Nympa palm. The bottom is distinguished by a large mudflat that emerges at low tide, bordering a lush mangrove swamp that is primarily made up of red mangrove (R. recemosa), and by a densely populated coastal town with a clear landing area for illegally refined products.

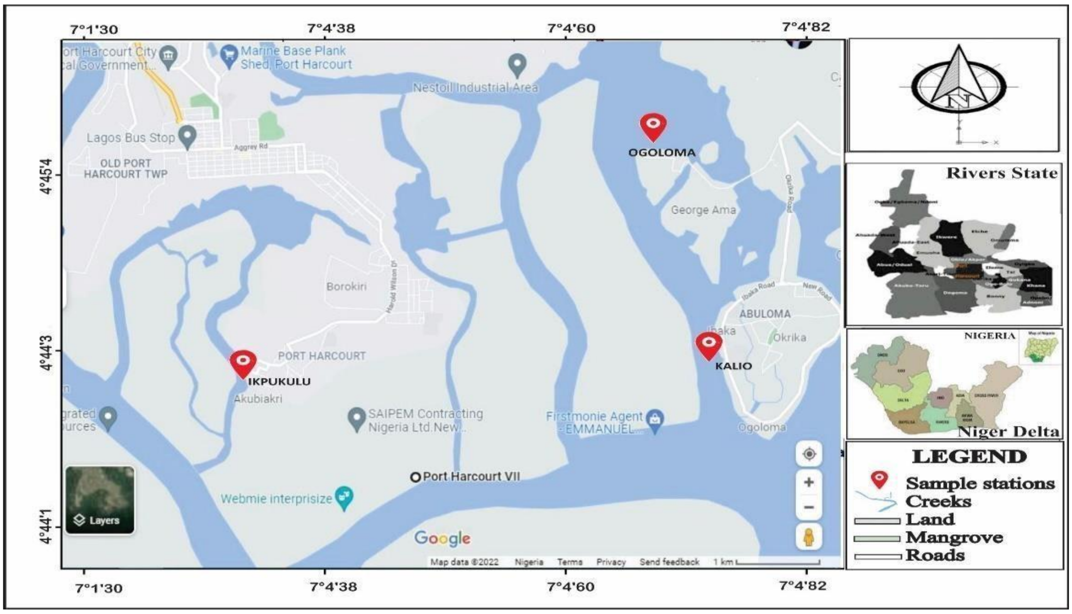

Figure 1: Map of Port Harcourt Showing Study Area

The samples were collected from the section of the river bombarded with human, animal, and domestic waste and run-off and it is visible on the shoreline.

Samples Collection

The sediments were gathered using a "Ekman grab" sampler, and the water samples were taken in high-density Schott glass bottles that had been previously cleaned. In new, clean screw-capped bottles that were acidified and clearly labelled, sediment and water samples for heavy metal analysis were aseptically collected from a depth of about 30 cm below the water's surface near shore during both low and high tide. Freshly captured live giant tiger shrimp (*Penaeus monodon*) were gathered from the harvest of nearby fishermen at three separate sampling stations, employing locally manufactured fishing traps. To preserve their freshness, the shrimp were kept in the field in an ice pack before being brought to the laboratory and kept at 10°C until analysis. Fifteen representative fish samples totaling 9.5 ± 0.56cm in length and 10.32 ± 0.91g in weight were collected throughout a 24 hour sampling period at each station during each sampling session. This allowed for statistical fluctuation. The selection of the Giant Tiger Shrimp arises from their strong relationship to neighbouring soft bottom peri-tidal ecosystems and mangroves. To maintain sample integrity, each sample was properly labelled and brought to the lab on an ice chest the same day. After that, the samples were measured and placed in the fridge to await analysis. Standard procedures were used to analyze the level of heavy metals (APHA, 2000).

Determination of Physiochemical Parameters

The physicochemical characteristics of water were examined using an in-situ handheld multimeter. A laboratory benchtop meter (860033-model) and a Milwaukee Model pH600 handheld multimeter were used to test the water's pH, temperature, salinity (ppt), and total dissolved solids (TDS) (ppt). Winkler's method was utilized to measure the Dissolved Oxygen (DO). A 5-day BOD test was used to analyze a water sample for the Biochemical Oxygen Demand (BOD) in the laboratory after it was collected using a BOD bottle (APHA, 2000). To make sure the monitoring equipment was correctly charged using the right charger, precautions were taken. Before the test, the proper gas sensor (probe) was fixed. When there were environmental risks, protective clothing was utilized.

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Determination of Heavy Metals

The modified APHA (3111B) method was utilized for the analysis of heavy copper, cadmium, and chromium. Using an Atomic Absorption Spectrophotometer (AAS), the instrument settings and operating conditions were completed according to the manufacturer's instructions (APHA, 2000).

Procedure for Heavy Metals Determination in Water

1 millilitre of nitric acid was added to 50 millilitres of sample, which was then heated with a heating mantle. WhatmanNo. 42 filter paper was used to filter 1/3 of the 50 ml volume into a 50 ml standard flask after it was allowed to cool. A 100 ml plastic container held 50 ml of fluid and was analyzed using AAS (Shimadzu model AA 6300).

Procedure for Heavy Metal Analysis in Biota/Sediment

Ten millilitres of thoroughly combined perchloric, nitric, and sulfuric acid were added to one gram of biota/sediment. To introduce metals into the solution, it was heated further using a heating mantle for 10 to 20 minutesand then allowed to cool before adding 20 ml of deionized water. Whatman filter paperNo. 42 was used to filter the mixture before filling a 100 ml standard flask. The supernatant was analyzed using AAS (AA 6300).

Statistical Analysis

SPSS version 21 was used for both descriptive statistics and analyses of variance (ANOVA). Duncan Multiple Range Test was used to differentiate significant means at 0.05.

RESULTS AND DISCUSSION

Physicochemical Properties

The results in Table 1 show the spatial variations in the physicochemical parameters of the water samples. The pH values ($p>0.05$) did not significantly differ amongst the stations. As seen in Figure 2, the pH values reported in the three sample locations were below FEPA and WHO (standards). As illustrated in Figure 3, Ikpuluku and Ogoloma recorded the greatest temperature (29.1±0.21^{o}C), while Kalio recorded the lowest temperature (28.8±0.21). That being said, there was no statistically significant ($p>0.05$) variation in temperature values reported among the three stations, and all of the results were marginally below the WHO and FEPA requirements.

In Figure 4, Ikpuluku had the highest electrical conductivity (1917.6±47µS cm^{-1}) followed by Kalio (1824.6±47µS cm^{-1}) and the lowest value was observed in Ogoloma (1245.6±47µS cm^{-1}). The highest Total Dissolved Solids value was observed at Kalio (9348.6±67mg L^{-1}) followed by Ikpuluku (7300.7±67mg L^{-1}) and the lowest value (9348.6±67mgL^{-1}) was observed at Ogoloma (Figure 5).

Salinity was highest in Kalio (333.3±43.1mg/L) followed by Ogoloma (315.0±43.1mg/L) and the lowest value of salinity was recorded in Ikpuluku (233.3±43.1mg/L) all values where higher when compared to the standards (Figure 6).Conversely, the highest Dissolved Oxygen was observed at Ikpukulu (5.6±0.06mg/L). This was followed by Kalio and Ogoloma having the same values of (3.2±0.06mg/L) (Figure 7).

For Biological Oxygen Demand as seen in Figure 8, there was no significant difference between the three stations, but comparing the values to the standards they were all significantly lower.

Table 1: Variation in Physico-chemical Parameters Across Stations

Stations	**pH**	**Tempt (°C)**	**EC (μS/cm)**	**TDS (mg/L)**	**Salinity (ppm)**	**DO (mg/L)**	**BOD (mg/L)**
Ikpukulu	5.6±0.07[a]	29.1±0.21[a]	1917.6±47[a]	7300.7±67[b]	233.3±43.1[c]	5.6±0.06[a]	3.3±0.11[a]
Kalio	5.6±0.07[a]	28.8±0.21[a]	1824.6±47[a]	9348.6±67[c]	333.3±43.1[b]	3.4±0.06[b]	3.2±0.11[a]
Ogoloma	5.6±0.07[a]	29.1±0.21[a]	1245.6±47[a]	3856.3±67[a]	315.0±43.1[a]	3.2±0.06[c]	2.9±0.11[a]
FEPA (2017)	6.5-8.5	24.8-30	400	2000	-	7.5	5.7
WHO (2011)	6.5-8.5	27-30	200-1000	1000-2000	120	6	10

**a, b: Means with different superscripts in the same column are significantly different (p<0.05);*
**Values without superscripts in the same column are not significantly different (p>0.05)*
**Biological Oxygen Demand (BOD), Dissolved Oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC).*

This study assessed the levels of heavy metals in the water, sediments, and shrimp of the Okrika Local Government Area, Rivers, Nigeria's Ikpuluku, Kalio, and Ogoloma swamps. The metal contamination of the waters in the three stations (Ogoloma, Kalio, and Ikpuluku) has been linked to several anthropogenic factors, as previous studies have indicated (Efekemo et al., 2024). These include mining, agricultural wastes, the disposal of untreated and partially treated industrial effluents, fossil fuels, petroleum exploration, the careless use of fertilizer containing heavy metals, pesticides in agricultural fields, and oil spills.

Physicochemical Properties of Water

The pH values ($p > 0.05$) did not significantly differ amongst the stations. The pH values seen in the three sample stations were below the FEPA and WHO guidelines. All three stations had a very low pH of 5.5. Anthropogenic activities such as oil spills, home garbage, and artisanal refining could be the cause of this low pH. Low pH can affect the availability of nutrients, metabolic rates, and the success of reproduction in aquatic life. Fish and other creatures acclimated to a particular pH range might suffer damage from acidic environments. There is a chance that ecosystem health may be weakened and biodiversity will decline. The physiological functions of fish and the dynamics of the population as a whole may be adversely affected by acidic circumstances.

Numerous studies have documented the adverse effects of oil spills on water quality parameters, including pH levels. For example, research by Ifelebuegu et al. (2017) investigated the impact of oil spillage on water quality parameters in the Niger Delta region, highlighting how oil contamination can lead to decreased pH levels in affected water bodies. Studies have shown that low pH levels resulting from anthropogenic activities can have detrimental effects on aquatic life. For instance, research by Menon et al. (2023) explored the effects of acidic pH on the physiology and behaviour of fish species in polluted aquatic environments, emphasizing how exposure to acidic conditions can impair metabolic rates, reproductive success, and overall health in fish populations. The link between low pH and declines in ecosystem health and biodiversity has been extensively studied. For example, work by Ezenwa et al. (2023) investigated the impact of acidic conditions on aquatic biodiversity in the Niger Delta region, highlighting how decreased pH levels can lead to declines in species richness and abundance, as well as alterations in community composition. Research has also focused on understanding how fish and other aquatic organisms respond physiologically to changes in pH levels. Studies by Mariu et al.

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(2020) explored the mechanisms of pH regulation and acid-base balance in fish species exposed to acidic environments, shedding light on the physiological adaptations that enable some species to tolerate or mitigate the effects of low pH conditions.

This result is consistent with Hart and Zabbey's (2005) findings of 27 to 28°C from a few Niger Delta creeks. Additionally, it supports research by Akankali and Davies (2018), who also noted temperature readings ranging from 26.7 to 27.18 degrees Celsius.The temperature of the water obtained is also comparable to that reported by Adefemi and Albert (2012), who found that water bodies in the Nigerian Niger Delta had temperatures ranging from 27.7 to 31 ^{o}C. The observed fluctuations in water temperature can be explained by elevated air temperatures and direct solar radiation exposure, low relative humidity, and a decrease in suspended particles due to increased water transparency and solar heat generation (Davies and Okonkwo, 2021). According to Adefemi and Albert (2012), aquatic species are capable of adapting to temperature variations and can even endure variations outside of this range. All of the sampling stations had identical temperatures, with no discernible change. This is consistent with the findings of Ezeonye (2009), who linked the lack of microclimatic temperature variations to the small temperature range between stations.

The study's results show significant differences in electrical conductivity between the locations examined. Specifically, Ikpuluku had the highest electrical conductivity at 1917.6 ± 47 µS cm^{-1}, followed closely by Kalio at a slightly lower level of 1824.6 ± 47 µS cm^{-1}. In contrast, Ogoloma had the lowest electrical conductivity among the sites, measuring 1245.6 ± 47 µS cm^{-1}. These findings indicate a varied distribution of water quality parameters in the research area, potentially impacting ecological processes and ecosystem well-being.

All subterranean water sample mean values were, on average, greater than the allowable limit (WHO, 2011). Greater conductivity is a sign that surface catchments provide the water with a significant amount of dissolved inorganic compounds in ionized form. A similar result was reported by Vincent-Akpu et al. (2015).

These numbers were higher than the FEPA/WHO recommended limits in 2003. According to Ngah et al. (2017), the Niger Delta's reputation for heavy rainfall may be linked to the turbulent effect of variations in TDS. The elevated TDS measurement seen throughout the study stations is indicative of contamination by human activities such as soil and agricultural runoff, household washing, etc. (Akankali and Davies, 2020, Odekina et al., 2021).

Salinity varies throughout the stations, much like other characteristics. All results were greater than the norms. The number of industrial effluents released into rivers may be the cause of this (Adekunle et al., 2009). According to Davies and Ekpenusi (2021), the concentration of salt might have been caused by the marine waters, the diminishing impact of the river, and runoff generated freshwater.

The result of dissolved oxygen shows that at Ikpukulu, the maximum level of dissolved oxygen was recorded (5.6 ± 0.06 mg/L). The next highest result was recorded at Ogoloma (3.2 ± 0.06 mg/L), followed by Kalio (3.4 ± 0.06 mg/L). Environmental variables may be the cause for this (Akankali and Davies 2020). This was consistent with DO levels reported by Chindah (2004), Okeke and Adinna (2018), and Duru and Nwanekwu (2019) for a comparable aquatic body (estuary) and season in the Niger Delta region. A comparable pattern was noted for the biological oxygen requirement, with Ikpuluku recording the highest value at 3.3 ± 0.11 mg/L. The values for Kalio and Ogoloma were 3.2 ± 0.11 mg/L and 2.9 ± 0.11 mg/L respectively. The concentration of biological oxygen recorded in the sample stations was very low compared to the standards.

Given that DO has been demonstrated to rise with temperature (Moss, 2000), it makes sense that Ikpuluku, which likewise had the highest water temperature of the three test sites, would have the highest DO. Reduced DO readings could be a sign that there are too many bacteria present, depleting the dissolved oxygen. Because less oxygen dissolves in warm water than in cold water, temperature may have an impact on the amount of dissolved oxygen (Davies and Ekperusi, 2021).Thus, one of the main possible causes of the low DO values found in the current study could be the water sources' high temperatures. While dissolved oxygen could not directly endanger human health, it might have an impact on other compounds in the water, which could change the aquatic ecosystem (Adesakin et al., 2020; Olawale, 2021).

The BOD levels found in this investigation fell between 2.9 and 3.33 mg/L. The study's range, however, fell short of the WHO standard for the highest acceptable level of BOD in drinking water for aquatic life and fisheries. The influence of increased temperature, salinity, and putrefaction of materials deposited in the river could be responsible for the fluctuations in BOD values Onojake et al. (2017).

Heavy Metals Concentration in Water, Sediments and Shrimp

Heavy metal concentrations in Water, Sediments and Shrimp (*P. monodon*) in the sample stations was depicted in Figures 2 to 4 respectively.

For sediment, the Copper concentration at Ogoloma was significantly higher among the three metals in the three stations, it was followed by Kalio and then Ikpukulu. Comparing the concentration in the three stations to the standard, copper and chromium were significantly higher.

In water, copper was the highest among the three metals of the three stations followed by chromium and then cadmium. When comparing the values to the standard, copper concentration in Ogoloma had significantly higher concentrations but was lower for Kalio and Ikpukulu. For chromium, the concentration for Kalio and Ogoloma was significantly higher than the standards. Cadmium had no significant difference across all the stations and the standards.

For Shrimp (*P. Monodon*), of the three stations, Ogoloma had a significantly higher concentration of copper, while Kalio and Ikpukulu were similar. Comparing the values to the standards, the three stations were significantly higher in copper and chromium concentration than the standards

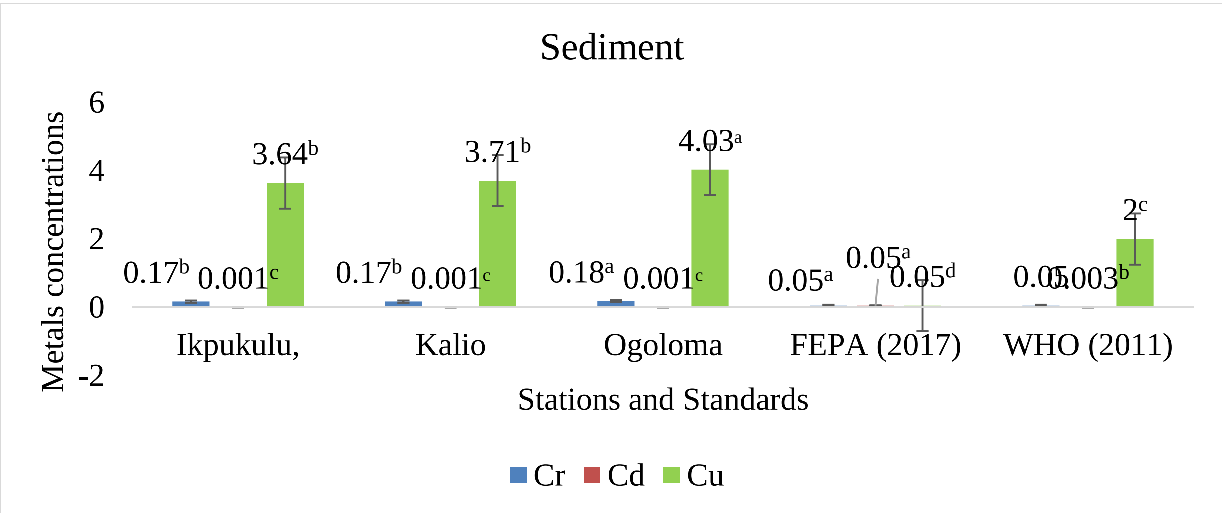

Fig. 2: Mean concentrations of heavy metal from sediment across the stations (mg kg^{-1})
a, b, c: Means values with different superscripts on the same bar color are significantly different (p<0.05)

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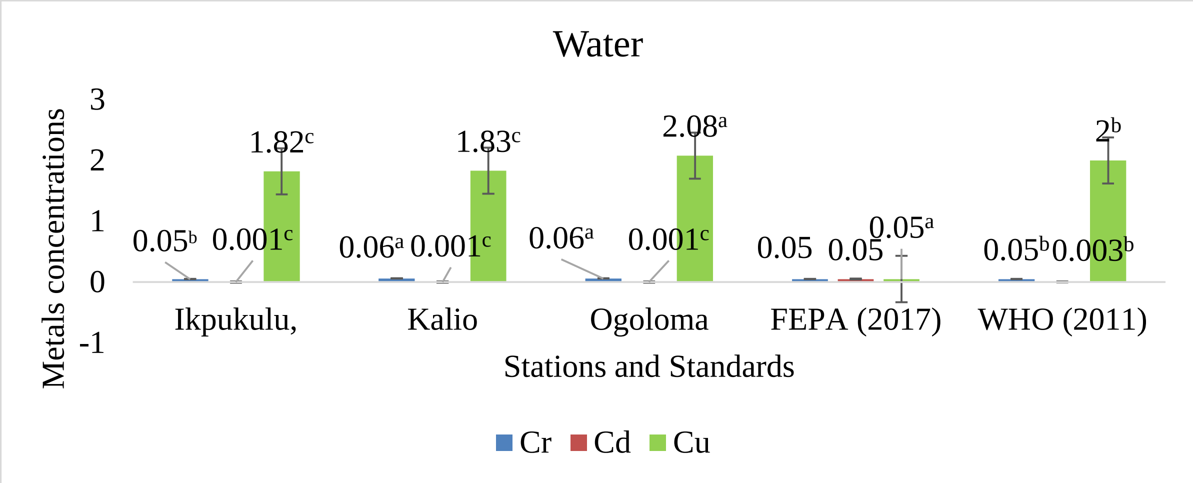

Fig. 3: Mean concentrations of heavy metal in water across the stations (mg kg^{-1})
a, b, c: Means values with different superscripts on the same bar color are significantly different (p<0.05)

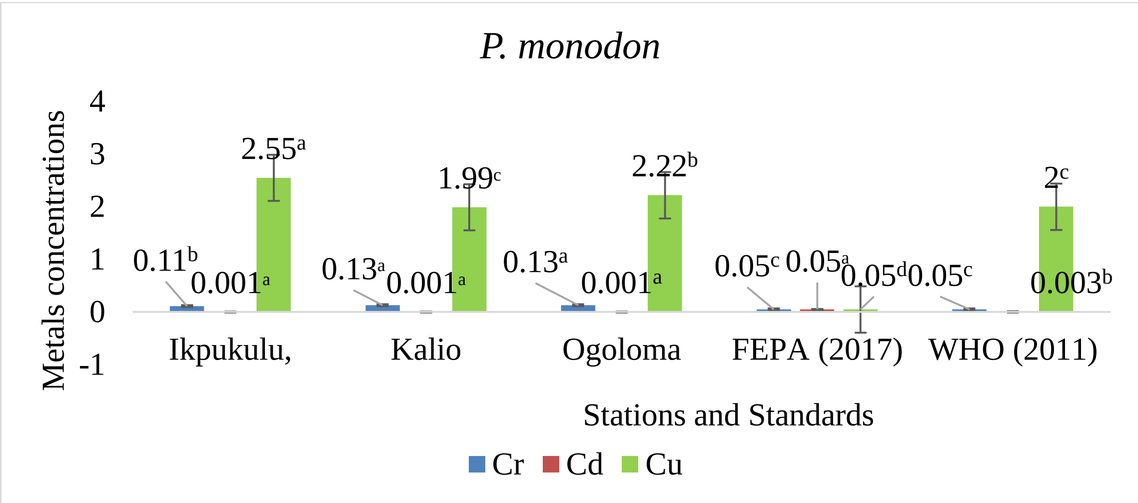

Fig. 4: Mean concentrations of heavy metals in *P. monodon* across the stations (mg kg^{-1})
a, b, c: Means values with different superscripts on the same bar colour are significantly different (p<0.05)

Heavy Metals Concentration in Shrimp, Sediments, and Water

The order of magnitude for the heavy metal concentration in shrimp by station: Station I (Ogoloma) > Station III (Ikpukulu) > Station II (Kalio). Cu has the highest concentration among the three sites, followed by Cr, while Cd has the lowest concentration.

The heavy metal concentration in the sediments at each site was listed in the following order of concentration: Site I (Ikpukulu) > Station II (Kalio) > Station III (Ogoloma). Cu has the highest concentration among the three sites, followed by Cr, while Cd has the lowest concentration.

The order of magnitude for the concentration of heavy metals in water by station: Station III (Ogoloma) > Station II (Kalio) > Station I (Ikpukulu). Cu has the highest concentration among the three sites, followed by Cr, while Cd has the lowest concentration.

The concentration of these metals indicates varying degrees of severe human influence as a result of urbanization and industrialisation in the catchments around the creeks. While the sediment serves as a sink for pollutants in the aquatic ecosystem, the chemical distribution levels in the Niger Delta's interstitial waters may have an impact on the variety of species present or have adapted to the water channels (Davies and Ekperusi, 2021). The WHO (2015) and FEPA's permissible limits for all heavy metals were exceeded.

The release of industrial and household effluents, the weathering of minerals and soils, and urban stormwater runoffs containing these heavy metals were some of the sources of Cd, Cr, and Cu in water (Odekina et al., 2021). Due to its interference with the regulation of calcium (Ca) in biological systems, high concentrations of cadmium (Cd) cause chronic kidney dysfunction, injuring and killing cells in fish and other aquatic creatures (Odekina et al., 2021). The environment downstream may suffer from high copper concentrations (Herbst et al., 2018).

CONCLUSION

This study shows that human activities like household and agricultural waste, construction and reclamation debris, effluents from illegal refineries, etc., were the main sources of heavy metals in the mangrove swamps of Ikpuluku, Kalio, and Ogoloma. As a result, the physiochemical parameters and levels of heavy metals were adversely affected compared to the standards set by the Federal Environmental Protection Agency (FEPA) and the World Health Organization (WHO). Consumption of samples from the investigated sites could pose health risks, as the metals that accumulate in shrimp can act as carcinogens, mutagens, and other harmful substances when ingested by humans. The physiochemical properties and heavy metal concentrations in these tidal creeks display significant variations. The study suggests that anthropogenic activities in the area should be restricted, as there is a high probability that they will increase over time and harm the aquatic ecosystem.

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