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Research Article

Seasonal Assessment of Pollution Status, Bioaccumulation and Potential Human Health Risk of Heavy Metals in Shrimps (*Penaeus monodon*) and Water from the Great Kwa River in Calabar, Nigeria

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ABSTRACT

The deterioration of water quality in rivers is caused by various factors, with heavy metals contamination being a significant contributor. Human activities are identified as the main cause of this contamination. This research evaluated the pollution levels, bioaccumulation, and potential health risks associated with heavy metals presence in Shrimps (*Penaeus monodon*) and the water from Great Kwa River in Calabar, Nigeria. Shrimp and water samples were collected for both wet and dry season at four designated locations along the river. The physical characteristics of the water were assessed in-situ. The concentrations of heavy metals, namely lead, cadmium, chromium, cobalt, iron, and copper were determined through wet digestion and analyzed using an Atomic Absorption Spectrophotometer. To validate the method, standard reference materials (Lichens coded IAEA - 336) were utilized. The physical properties of water were found to be within the established standards. In the shrimp, the Fe and Pb were significantly higher ($p < 0.05$) during the wet season compared to the dry season. Similarly, the occurrence of Fe, Cr, and Pb in the water samples was significantly higher ($p < 0.05$) during the wet season compared to the dry season. The Estimated Daily Intake of all the assessed metals in both seasons were within the recommended upper tolerable limits for heavy metals in seafoods. The Target Hazard Quotients for metals under investigation were also within safe limits for both seasons. The Hazard Indices of these metals in both seasons were less than one (<1), indicating minimal or no significant health risks. The individual Incremental Lifetime Cancer Risks for Chromium, Cadmium, and Lead ranged from 10^{-7} to 10^{-4}, which are considered acceptable. Therefore, the consumption of shrimps from Great Kwa River is unlikely to pose a significant carcinogenic risk associated with the examined metals.

Keywords: *heavy metals pollution status, bio-accumulation, health risk assessment, great kwa river, biomonitoring*

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INTRODUCTION

Heavy metals naturally occur in aquatic environment in very low concentration, but their concentration can increase due to incursion of anthropogenic pollutants over time (Kargin et al., 2001). Industrial, agricultural, and mining activities create a potential source of heavy metals pollution in aquatic environment. Pollution of aquatic ecosystems by heavy metals is of utmost concern to the environment as it constitutes most dangerous toxicants that can bioaccumulate (Benson et al., 2007). Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological

damage also posing a threat to human health due to biomagnifications over time (Yilmaz and Yilmaz, 2007). Aquatic organisms have been reported to accumulate heavy metals in their tissues several times above ambient levels (Canli and Atli, 2003). In Nigeria, over 80% of the industries discharge their waste containing toxic metals such as Cd, Cu, Zn, Hg, and Cr into the environment without any prior treatment (Sobvha et al., 2007). While just only 18% of industries undertake rudimentary recycling prior to disposal. These pollutants including agricultural wastes find their way into the water bodies through runoff (Cempel and Nekel, 2006). The problem is further amplified when rivers carry their pollutant to estuaries and finally to oceans, while during the transition from the terrestrial to the ocean harmful substances enter into the food chain and subsequently become bioaccumulated in marine organisms (Schmitt et al., 2006).
This research work was designed to assess the pollution status, bioaccumulation and potential human health risk of heavy metals in Shrimps (*Penaeus monodon*) and Water from the Great Kwa River in Calabar, Nigeria.

MATERIALS AND METHODS

Study area: This study was carried out at the Esuk Atu beach of the Great kwa River drainage. The area is located between latitude 80 15’E and 80 30’E and longitude 40 45’N and 50 15’N. It has an estimated length of 56km and is about 2.8km wide at the mouth where it empties into the Cross-river Estuary (Okorafor *et al.,* 2012). Two climatic seasons are prevailing in the study area (wet season and dry season). The wet season is usually characterized by heavy rainfalls while the dry season experiences occasional downpours. The shorelines are lined with dark plates usually exposed during low tides and the shore is brackish and rich with zooplankton. The banks are also surrounded by lush and evergreen, forest vegetation with different species of trees, shrubs and grasses. The part of the river that was chosen for the study represents one of the most active fishing terminals and is known to support substantial Shrimp fishery, crab, fish and local periwinkle. The university of Calabar and the teaching Hospital covers a large hectare site between this part of the river where apart from natural processes, anthropogenic activities also discharge tons of wastes into the water, which tends to increase the contaminants level.

Sample collection: Shrimp and water samples were collected from four (4) locations along the course of the water body (Great Kwa River) with at least 500metres away from each collection point. Sampling was located upstream, downstream, and two from the midstream on opposite ends of the river. The breadth of the river at this length was crossed by means of a canoe and the measurements were taken with a measuring tape. Shrimp samples were collected into polythene bags while the water sample were collected into a pre-acid rinsed plastic sample bottles. As a criterion for proper identification, samples were labeled S1-4 and W1-4 for shrimps and water samples respectively. Sampling was carried out in wet and dry season from the creek between 7.00am and 9.00am. For safety concerns the voyage required the services of two guides: mainly fishermen and canoe paddlers from the beach to lead the movement across the breadth of the river. Fresh Shrimp samples caught by artisanal shrimpers using stow net were preserved in ice from where both samples were transported to the laboratory.

Sample digestion: One (1) gram of the shrimp muscle was taken and put in a 100 ml capacity digestion beaker and subsequently 30 ml aqua regia solution (20ml HNO3 and 10ml HCL) was added. The product was gently boiled for 30 to 45 min to ensure complete dissolution and allowed to cool, according to the method of Udiba et al, (2023). Following cooling, the solution was filtered through Whatman filter paper and transferred into a volumetric flask via addition of distilled water to make up to 50ml. The digest was kept in a labelled plastic bottle until analysis.
Water sample digestion was conducted with the aid of aqua regia solution (20ml HNO3 and 10ml HCL). The obtained water sample (20ml) was poured into a beaker, to which 30ml of aqua regia solution was included. The resulting product was placed on a hot plate and allowed to gently boil. The volume of the solution was reduced to about 30ml through evaporation. The digest was diluted to 50ml in volumetric flask and transferred into a plastic container that was acid-washed and ready for analysis.

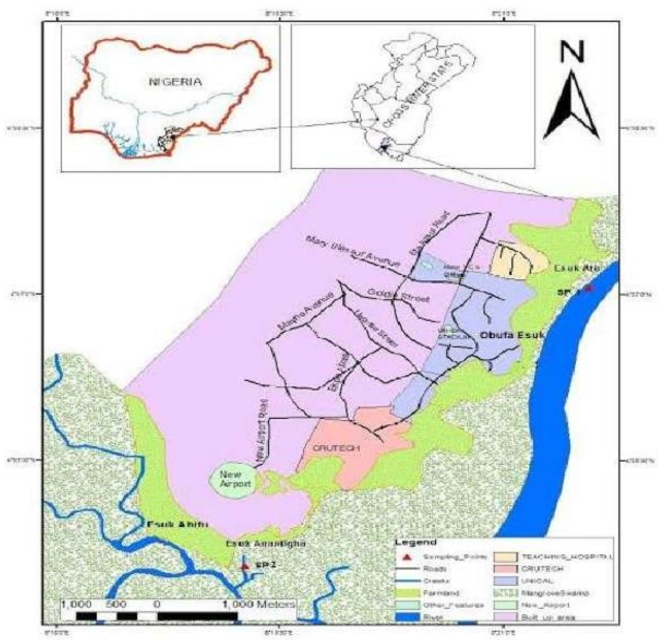

Figure 1:
Map of study area

Atomic absorption spectroscopic analysis: The digest of samples was analyzed for selected heavy metals using Buck 211VGP Atomic Absorption Spectrophotometer. The digest solution was washed into 100ml volumetric flask with deionized water and made up to mark. This diluent was aspirated into the Buck 211VGP Atomic Absorption Spectrophotometer (AAS) through the suction tube. Each of the trace mineral elements was read at their respective wavelengths with their respective hollow cathode lamps using appropriate fuel and oxidant combination.

Health risk assessment: Health risk assessment involves estimating the probable occurrence and impact of a potentially harmful contaminant over a given period. The potential health risk of each contaminant is based on the estimated risk level; and thus, non-carcinogenic and carcinogenic health risk were calculated using the estimated daily intake (EDI) of metals, the target hazard quotient (THQ), the hazard index (HI), and the incremental life cancer risk (ILCR).

Estimated daily intake: The estimated daily intake (EDI) of the different metals was evaluated based on the tissue concentrations of each metal in the shrimp and the average daily shrimp ingestion rate (Santos *et al*. 2004). The EDI represents the estimated daily intake of metal through the consumption of shrimp by an adult human (in mg kg−1 day−1). The following relationship was used to calculate the EDI (Liu *et al*., 2018):

$$EDI = C \times FIR/BWa$$

where EDI is the estimated daily intake, FIR is the Food ingestion rate (g day−1), C is the concentration of metal in the shrimp (mg kg−1 dw), BWa is the average adult body weight (kg). The daily consumption rate was set at 20.67 g person−1 day−1 as per the report of the Statistics for the shrimp rates of consumption, while the average adult body weight in was assumed to be 57.7 kg (Walpole *et al.*, 2012).

Target hazard quotient: The target hazard quotient (THQ) is defined as the maximum tolerable daily intake of a specific metal that does not result in any deleterious health effects. In the present study, we used the THQ to assess the human health risk level due to pollutant exposure from consuming metal-contaminated shrimp. The THQ was calculated as the ratio of the average daily intake of a specific chemical over a lifetime to the oral reference dose (RfD) of the trace metal. The following equation was used to determine the THQ (Anandkumar *et al*., 2018; Liu *et al*., 2018):

$$THQ = EDI/RfD$$

THQ values of < 1 indicate that adverse health effects are unlikely to occur, and THQ values of > 1 indicate that the consumer population has potential health risks.

Hazard index: Since exposure is usually not associated with a single toxicant, the hazard index (HI) was developed from the THQs and expressed as the sum of the hazard quotients (USEPA, 2018). The hazard index derived for the shrimp was determined according to the following equation:

$$HI = \sum THQs$$

where THQ is the target hazard quotient of an individual metal and HI is the total hazard index for all metals. In the present study, HI is the total hazard index for ten metals (Cd, Cr, Co, Cu, Mn, Pb, As, Ni, Fe Hg). HI > 1 indicates a potential for an adverse effect on human health.

Carcinogenic risk: The carcinogenic risk was estimated as the incremental probability of an individual developing cancer over a lifetime of exposure to a potential carcinogen by employing a target cancer risk value. The carcinogenic health risks related to the consumption of seafood were measured based on the incremental life time cancer risk (ILCR), which was calculated as follows:

$$ILCR = EDI \times CSF \times 10^{-3}$$

Where, CSF is the cancer slope factor and is defined as the risk generated by a lifetime average amount of one mg/kg/day of carcinogen chemical and is contaminant specific. According to the New York State Department of Health (NYSDOH), the threshold ILCR values for categorizing risk are as follows: ILCR $\leq 10^{-6}$, lowrisk;10^{-4} to 10^{-3}, moderate risk; 10^{-3} to 10^{-1}, high risk; and $\geq 10^{-1}$, very high risk.

Statistic and Data Analysis

Data were subjected to statistical analysis to determine significant differences among groups by independent T-test. Graph Pad Prism and Microsoft (MS) excel software`s were used. Data was presented as Mean ± SD (Standard Deviation). At $p< 0.05$, the results were deemed statistically Significant.

RESULTS

Analytical quality assurance: In order to check the reliability of the analytical methods employed for the determination of lead in the samples, standard reference materials, Lichens coded IAEA-336 was also digested and then analyzed following the same procedure, (Table 1). The values determined and the certified values of the element determined were compared to ascertain the reliability of the analytical method employed.

Table 1

Result of analysis of reference material (Lichen International Atomic Energy Agency code, IAEA -336) compared to the certified reference value (mg/kg).

Element	Pb	Cd	Cu	Mn	Zn
A Value	29.18	5.25	0.140	4.00	55.78
R Value	4.2-5.5	0.1-2.34	3.1-4.1	56-70	37-33.80

A Value = Analyzed value; R Value = Reference value

Physco-chemical analysis of water: The physio-chemical parameters obtained from the analysis of water samples from four different points on the course of the water body of the Great Kwa river are presented in Table 2a and 2b. The water was slightly acidic in the wet season with Ph values ranging from 6.20 at point one (1) to 6.90 at point four (4) with a mean of 6.63±0.30. Meanwhile, for dry season, Ph ranged from 7.50-7.90 with a mean of 7.70±0.18. The temperature ranged from 30.00°C at point one (1) to 32.50°C at point four (4) for wet season, with a mean of 31.70±1.63°C, and ranged from 30.20-30.70°C for the dry season with a mean of 30.45 ± 0.23. Electrical conductivity ranged from 1.30 in point one (1) to 1.82 in point four (4) for wet season, with a mean of 1.45±0.24, and ranged from 0.10 – 0.25 for the dry season with a mean of 0.16±0.07. Total dissolved solid ranged from 946.0 in point one (1) to 1341 in point four (4) with a mean of 106±188.4 for the wet season, and ranged from 77.00-186 with a mean of 119.5±51.0.

TABLE 2a
Physio-chemical parameters of water from great kwa river during wet season

Sampling P.	Temperature(°C)	pH	Conductivity (ppm)	TDS (mg/I)
Point 1	30.0	6.20	1.32	958
Point 2	32.5	6.80	1.30	946
Point 3	32.4	6.90	1.37	996
Point 4	31.9	6.60	1.82	1341
Mean ± SD	31.70±1.63	6.63±0.30	1.45±0.24	106±188.4
Range	30.00-32.50	6.20-6.90	1.30-1.82	946.0-1341.0
***WHO**	30-35	6.5-8.5	1.00-1.90	500
****NSDWQ**	30-35	6.5-8.5	1.00-1.90	500

**World Health Organization*
***Nigerian Standard for Drinking Water Quality*

Table 2b
Physio-chemical parameters of water from great kwa river during dry season

Sampling P.	Temperature (°C)	pH	Conductivity (ppm)	TDS (mg/I)
Point 1	30.0	6.20	1.32	958
Point 2	32.5	6.80	1.30	946
Point 3	32.4	6.90	1.37	996
Point 4	31.9	6.60	1.82	1341
Mean ± SD	31.70±1.63	6.63±0.30	1.45±0.24	106±188.4
Range	30.00-32.50	6.20-6.90	1.30-1.82	946.0-1341.0
***WHO**	30-35	6.5-8.5	1.00-1.90	500
****NSDWQ**	30-35	6.5-8.5	1.00-1.90	500

**World Health Organization*
***Nigerian Standard for Drinking Water Quality*

Heavy metals concentrations: The heavy metals levels of water from great kwa river are presented in figures 1 to 3. Cadmium (Cd) level in water in the wet season was 0.02 ± 0.01, while that of dry season was 0.11±0.00. The lead (Pb) level in wet season was 0.28 ± 0.09, and was significantly higher ($P<0.05$) than the dry season, 0.09 ± 0.06. Chromium (Cr) level in wet season was 0.09 ± 0.03, and was significantly higher ($P<0.05$) than the dry season 0.01 ± 0.00.

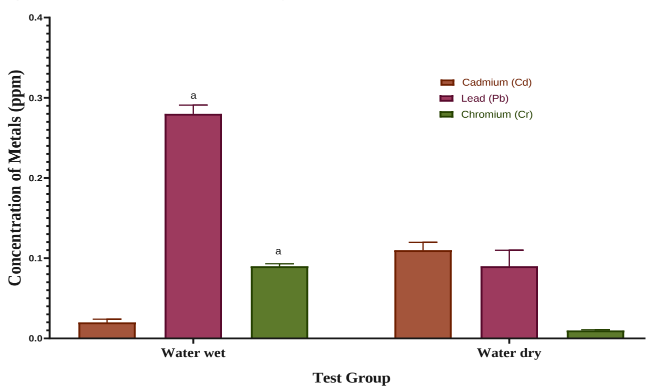

Figure 2:
Result showing concentration of Cadmium, Lead and Chromium and in water from Great Kwa river, for wet and dry season.
a = significantly different from dry season (p<0.05), n = 4.

The Iron (Fe) level in water in the wet season was 1.94 ± 0.36, and was significantly higher ($P<0.05$) than that of the dry season 0.56 ± 0.24. Copper (Cu) level in wet season was 0.18 ± 0.11, while that of dry season was 0.05 ± 0.02.

The heavy metals levels of shrimp from great kwa river are presented in figure 4 to 7. The cadmium levels in shrimp in the wet season was 0.09 ± 0.03, while that of dry season was 0.11 ± 0.06. lead levels in shrimp in the wet season was 0.27 ± 0.06, and was significantly higher ($P<0.05$) than the dry season 0.11 ± 0.02. Chromium levels in the wet season was 0.03 ± 0.26, while that of the dry season was 0.02 ± 0.00.

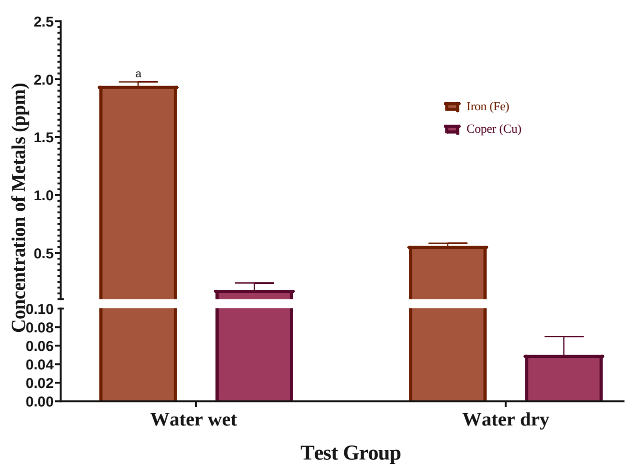

Figure 3:
Result showing concentration of Iron and Copper in water from Great Kwa river, for wet and dry season.
a = significantly different from dry season (p<0.05), n = 4.

The iron level in shrimps in the wet season was 1.94 ± 0.36, and was significantly higher ($P<0.05$) than that of the dry season 0.61 ± 0.02. Copper level in shrimps in the wet season was 0.37 ± 0.20, while that of dry season was 0.06 ± 0.00.

Lead (Pb) levels in water and shrimps for the wet season was 0.28 ± 0.09 and 0.27 ± 0.06 respectively, while that of the dry season was 0.09 ± 0.06 and 0.11 ± 0.02. Cadmium (Cd) levels for water and shrimps in the wet season was 0.02 ± 0.01 and 0.09 ± 0.03 respectively, significantly lower ($P<0.05$) levels were observed in water than in shrimps. While the level of cadmium in water and shrimps in the dry season was 0.11 ± 0.00 and 0.11 ±0.06. Chromium (Cr) levels in water and shrimp for wet season was 0.09 ± 0.03 and 0.03 ± 0.26 respectively, significantly higher ($P<0.05$) levels were observed in water than in shrimps. During the dry season, the levels of chromium in water and shrimp was 0.01 ± 0.00 and 0.02 ± 0.00.

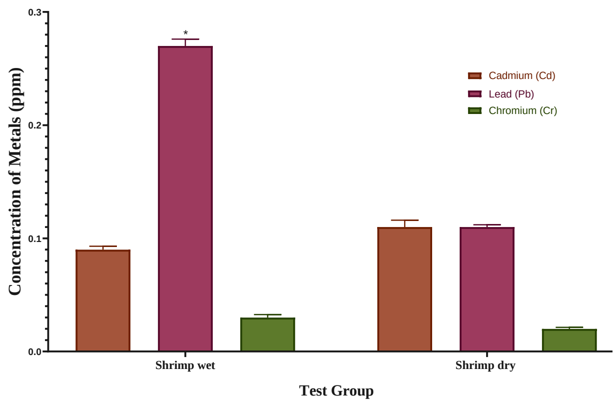

Figure 4:
Results of the concentration of Cadmium, Lead and Chromium in shrimp from great Kwa river, for wet and dry season.
** = significantly different from dry season (p<0.05), n = 4.*

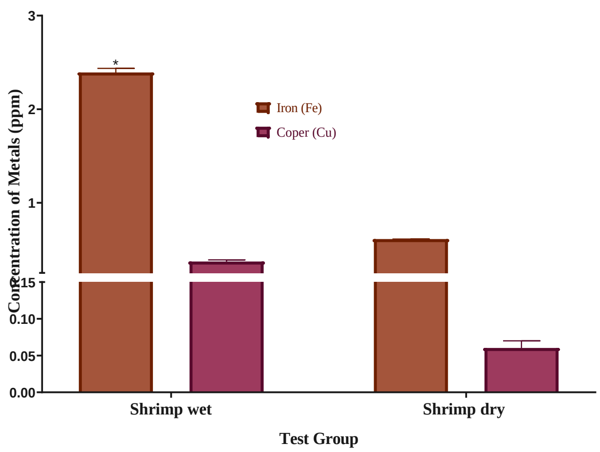

Figure 5:
Result showing concentration of Iron and Copper in shrimp from great Kwa river, for wet and dry season.

* = significantly different from dry season (p<0.05), n = 4.

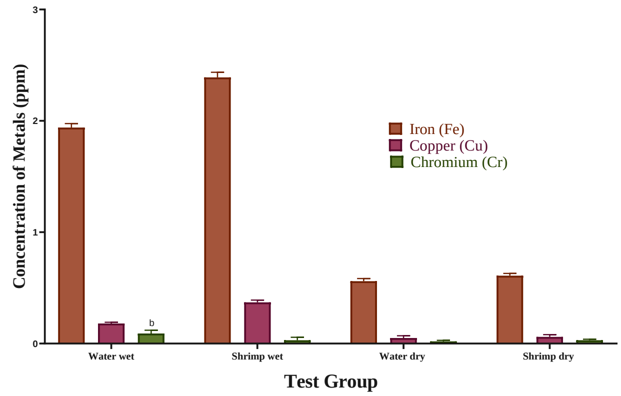

Figure. 6:
Result showing concentration of Iron, Copper and Chromium in water and shrimp from great Kwa river, for wet and dry season.
b= significantly different from shrimp sample for wet season (p<0.05), n = 4.

The lead (Pb) levels in water and shrimps for the wet season was 0.28±0.09 and 0.27±0.06 respectively, while that of the dry season was 0.09±0.06 and 0.11±0.02. Cadmium (Cd) levels for water and shrimps in the wet season was 0.02±0.01 and 0.09±0.03 respectively, significantly lower ($P<0.05$) levels were observed in water than in shrimps. While the level of cadmium in water and shrimps in the dry season was 0.11±0.00 and 0.11±0.06.

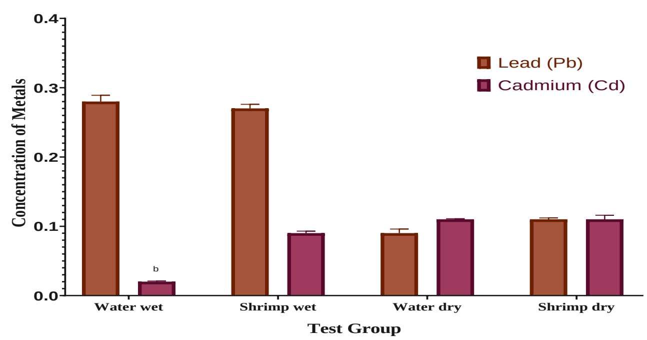

Figure 7:
Result showing concentration of Lead and Cadmium in water and shrimp from great Kwa river, for wet and dry season.
b = significantly different from shrimp sample for wet season (p<0.05), n = 4.

Table 3
Estimated Daily intake of heavy metals in shrimps harvested from the great Kwa river.

Wet season				Dry season			
Metal	Mean	EDI	UL	Metal	Mean	EDI	UL
Cr	0.03	0.00000988	0.20	Cr	0.02	0.00000658	0.20
Cd	0.09	0.0000297	0.06	Cd	0.11	0.0000362	0.06
Pb	0.27	0.000088	0.21	Pb	0.11	0.0000362	0.21

EDI = Estimated daily intake, UL = upper tolerable daily intake, RDI = Recommended daily intake, Values are expressed as mg/kg body weight/day

Table 4
Target Hazard Quotient (THQ) of heavy metals in shrimps harvested from the great Kwa river.

Wet season				Dry season			
Metal	EDI	RFD	THQ	Metal	EDI	RFD	THQ
Cr	0.00000988	1.5	0.0000067	Cr	0.00000658	1.5	0.00000439
Cd	0.0000297	0.001	0.02965	Cd	0.0000362	0.001	0.0362
Pb	0.000088	0.004	0.02224	Pb	0.0000362	0.004	0.00905

∑THQ =HI= 0.052 ∑THQ =HI= 0.045
RFD=oral reference dose for the metal in mg/kg/day (USEPA Regional studies, 2017); THQ values (mg/kg wet weight/day)

Table 5
Incremental Lifetime Cancer Risk for Carcinogens

Wet season				Dry season			
Metal	EDI	CFS	ILCR	Metal	EDI	CSF	ILCR
Cr	0.00000988	$5x10^{-1}$	$4.9x10^{-5}$	Cr	0.00000658	$5x10^{-1}$	$3.29x10^{-6}$
Cd	0.0000297	6.1	$1.8x10^{-4}$	Cd	0.0000362	6.1	$2.2x10^{-4}$
Pb	0.000088	$8.5x10^{-3}$	$8.0x10^{-7}$	Pb	0.0000362	$8.5x10^{-3}$	$3.1x10^{-7}$

Values are in mg/kg/day
Iron (Fe) and Copper (Cu) has no CSF and is not considered to create cancer (WHO,2011); CSF= Cancer Slope Factor (mg/kg/day)

DISCUSSION

The results of the physico-chemical analysis showed a slight variation in temperature between locations. This could be attributed to time of sampling, river gradient, rate of flow of the river and weather condition. Temperature plays a vital role in controlling chemical reactions in water and metabolic processes in seafood (Udosen, 2006). Increase in temperature leads to growth of algae, with consequent depletion in oxygen concentration which suffocates aquatic organisms, with increase solubility of substances. The temperature effect on oxygen concentration in water is very significant as solubility of oxygen in water decrease from 14.74 mg/l at 0OC to 7.03 mg/l at 40C (Odey et al., 2022). The, values of temperature recorded in this study were within USEPA and WHO recommended limits of 30 0C to 35 0C.

pH values obtained for the wet season were close to those reported by Akpan, (2012) for Qua Iboe river. The lower pH values as shown in the wet season can increase corrosion in water and make metal bioavailability higher. The values of pH from this study are however within the WHO, (2008) recommended pH values (6.50 – 8.50) for drinking and fishing water. A good knowledge of pH of water is important. According to Udosen, (2006), processes such as water softening, corrosion control, coagulation, acid-base neutralization, precipitation and disinfection are pH dependent. Even aquatic organism metabolic activities and osmotic effects largely depend on pH.

Electrical conductivity in water defines the capacity of water to conduct electricity and this varies both with number and types of ions the solution contains. In this study, a mean conductivity value of 1.45 ± 0.24 Scm-1 for the wet season and 0.16 ± 0.07Scm-1 was recorded in dry season. The electrical conductivity values determined between locations in wet season were higher than the WHO limit of 250Scm-1for drinking water. This high conductivity values obtained in this study could be linked to ions containing wastes dumped into great Kwa river. Electrical conductivity measurements of 0 – 1,990 indicates fresh water, thus, great Kwa river could be classified as fresh water. Similarly, electrical conductivity measurements of 1,990 – 19,900 indicates brackish water, hence, great Kwa river could also be classified as both fresh in dry season and brackish water in wet season based on results recorded for them (Bessie et al., 2021). The little disparity in seasonal values may be due to high volume of water and dilution effect caused by heavy rainfall.

Total dissolved solids provides information on the aesthetic value, turbidity status and density of water. The contributors to the total dissolved solids in water are bicarbonate, sulphate, phosphate, nitrate, magnesium, calcium, sodium, heavy metals and organic ions. Total Dissolved solids therefore influences water used for drinking, irrigation, industrial and recreational purposes. The TDS obtain for the dry season was below the recommended limits of 500 by WHO, while the values obtained for the wet season were higher than the maximal allowable limit of 500 by WHO. According to Taiwo et al. (2012) high TDS could cause a reduction in the development and survival of salmond eggs, and larva and clogging of fish gills. Therefore, cations and anions containing wastes should not be dumped into these rivers again.

Humans are exposed to harmful heavy metals through a variety of pathways, but one of the most worrisome is the regular consumption of food from river habitats that are contaminated with a wide range of dangerous and toxic metals. Particularly in the Nigerian region of the Niger Delta, pollution concerns are caused by urbanization, uncontrolled solid waste disposal, oil drilling and a variety of other natural and manmade factors. It has been determined that this ongoing water pollution poses a risk for the bioaccumulation of metals in seafood and may thus, have toxicological effects on both aquatic life owing to bio-magnification and bio-accumulation at higher trophic levels in the food chain.

Heavy metals are not biodegradable yet highly bioavailable and then toxic at even very small concentration. WHO, US-EPA and FAO as well as other food standards and safety agencies have established permissible limits in water, seafood, fruits, processed foods for adults and children as guidelines for toxicity concerns. In polluted waters, seafoods, including shrimp accumulates heavy metals from their respective niche in the habitat. The purpose of this study was to evaluate the level of pollution in the great kwa river and to forecast any potential health impacts that could result from prolonged exposure to one or more heavy metals, such as Cr, Fe, Cu, Pb and Cd. Fe and Cu are trace element but extremely hazardous when concentrations are higher than the permissible levels needed by the body for metabolic activities. In contrast, heavy metals such as Cd, Cr and Pb are very toxic and have no known biological function (Udiba et al., 2023).

A suitable bio indicator, such as shrimp which is more associated with surface water was selected in order to efficiently analyze the heavy metals contamination status of great kwa river.

The seasonal variations of the analyzed heavy metals was such that the concentrations in the wet season decreased in the following trend Fe > Pb> Cu> Cr> Cd, while that of dry season was Fe> Cd > Pb> Cu> Cr. The higher concentrations of Fe could be due to anthropogenic activities around the river. Prolonged exposure to excess iron levels in water can result in iron overload in the body, a condition known as hemochromatosis (). Iron accumulation in organs such as the liver, heart, and pancreas can cause damage to their tissues and impair their normal functions. The values recorded for Cr and Pb were significantly higher ($P< 0.05$) in the wet season than the values obtained from the dry season. This values also exceeded the recommended limits by WHO and FAO as shown in figure 7. The disparity in the concentration of heavy metals between these seasons could be due to higher pollutants load in wet season. Solid garbage and industrial pollutants are frequently dumped into water bodies during the wet season. The water becomes turbid as a result, allowing for an increased dose of pollutant in the water. Cd exceeded the WHO permissible limits of 0.05mg/kg in both seasons. Cadmium is a non-essential metal and considered a serious contaminant with adverse effects on living organisms, particularly the skeletons and kidney (). Cu was also higher in the wet season when compared to the dry season with mean values exceeding the permissible limit of metals as recommended by WHO/FAO. The high concentration of this metals recorded could be due to the mining and other anthropogenic activities in the community. The result of this investigation is consistent with the concentration of heavy metals from Qua iboe river as reported by of Bessie et al., (2021).

The distribution pattern of heavy metals concentrations in shrimps was observed to be slightly different from that of water in the wet season but similar in the dry season. The metals decreased accordingly, in the order; Fe > Cu > Pb >Cd > Cr in the wet season, and Fe > Cd > Pb > Cu > Cr for dry season. This trend could be due to the intense discharges of organic pollutants from surface runoffs and drainage channels into the river during the wet season. Similar observations were reported by Bessie et al., (2021) who reported higher concentration of Pb, Cr, and Cu in the wet season from Qua Iboe river. In contrast to this, the mean concentration of Cd in shrimps was higher in the dry season than the wet season. This could be as a result of discharges from industrial and municipal waste into the great kwa river when diluting water was reduced due to lack of rain. The concentration of all metals under study in shrimps for both seasons were found to exceed the permissible limits as recommended by WHO (2003) and FAO (2007). Iron was the most concentrated metal in shrimps with maximal value observed in the wet season, with concentrations for both seasons much higher than the recommended limit by WHO of 0.5mg/kg. This indicates that shrimps from great kwa river were contaminated with heavy metals.

Consumption of seafood from contaminated water can pose a range of human health risks, which are grouped into carcinogenic and non- carcinogenic. The estimation is based on calculation and assumptions that cooking does not have any effect on the concentration of the metal absorbed and bio available in the body. Some heavy metals have no biological function and toxic at low concentration, while some have no recommended daily allowance. There are others who have known biochemical functions but above their recommended or upper tolerable limits, will be toxic.

The indicators of toxicity for non-carcinogenic health effects are; first, computation of the estimated daily intake (EDI). The EDI of all the metals were low (<1). This indicates safe consumption rate in comparison to the recommended daily intake (RDI) and the upper tolerable limit of the metal in seafood as established by WHO/FAO (2007). Toxic heavy metals like Cd and Pb are not required in any concentration in the body. FAO/WHO recommended 0.00mg/kg of these metals because of the dangers of toxicity they possess. The EDI computed for these metals were within the UL. The next indicator of toxicity is the Total Hazard Quotient (THQ). The THQ is estimated, to show the effect of a single metal in the food consumed and the possible human risk expected. For the study, THQ of individual heavy metals through shrimp consumption by average adult followed a descending order Cd>Pb>Cr for both seasons. THQ <1 is considered safe for consumption without potential risk (Udiba et al., 2023). Conversely, THQ>1 or 1 indicates a potential health risk and will require related intervention and protective measures taken (Martin and Griswold, 2009). In this study, the THQ of all the metals was less than one, in both seasons.

To evaluate the combined toxicity of multiple heavy metals, another metric called TTHQ (Total Target Hazard Quotient) or HI (Hazard Index) is used. The HI takes into account the combined effects of all the metals consumed through shrimp consumption. It provides a more comprehensive assessment of the potential health risks associated with the ingestion of multiple metals simultaneously (). Trace elements play a significant role in the cellular interactions of toxic substances, contributing to the expression of toxicity observed in human health conditions. For instance, the excessive intake of copper, zinc, and lead has been associated with Alzheimer's disease. Similarly, iron, in close association with zinc, has been implicated in Parkinson's disease (Soghra, 2018).

From a nutritional standpoint, the HI and THQ values below 1 indicate that the food provides quality and nutritional benefits. However, when the value exceeds 1, it suggests a potential threat to health (Ahmed et al., 2016). The HI of the heavy metals in both seasons was less than 1, indicating minimal or no significant health risks. However, when considering the relative contribution of each metal to the potential development of non-carcinogenic risks due to exposure, Iron stood out. Iron (Fe) accounted for 67% of the risk during the dry season and 20% during the wet season.

These findings support the notion that the river is being increasingly polluted by natural and anthropogenic sources, such as flooding during heavy rainfall and the discharge of industrial chemicals and effluents into the water.

Incremental Lifetime Cancer Risk (ILCR) provideS an estimate of the lifetime potency of carcinogens. In this particular study, the average life expectancy of a Nigerian, which is 55 years, was utilized to calculate the EDI (Estimated Daily Intake), along with the average body weight of an adult, which is 60.7 kg. The ILCR value was obtained by multiplying the EDI by the CSF (Cancer Slope Factor) of the metal. If the calculated value exceeds 10-4, it suggests potential carcinogenic risks. The individual ILCR values for Cr, Cd, and Pb in this study ranged from 10-7 to 10-4, which are considered acceptable. These results align with the findings of Bessie et al, (2021).

In conclusion, consumption of shrimp with elevated levels of heavy metals may lead to high level carcinogenic risks to human health. Therefore, it is strongly recommended to regularly monitor the presence of heavy metal in shrimp species thriving at contaminated waters to ascertain the food safety. This research study was conducted to examine the build-up of certain heavy metals (Cd, Fe, Cu, Cd and Pb) in shrimps and water from the Great Kwa River in Cross River State, Nigeria. The aim was to address pollution concerns. The findings of the study indicate that consuming shrimps is unlikely to pose any significant health risks associated with the investigated metals. As a result, it is recommended to include shrimps in the diet for its nutritional benefits. However, the study emphasizes the importance of adhering to regulations that ensure water quality and the implementation of effective waste management practices in the Calabar metropolis. Additionally, regular biomonitoring is suggested to monitor pollution levels in the river. To maintain the safety of consuming shrimps in relation to human health risks from metal ingestion, it is crucial to prevent the introduction of heavy metals, particularly Fe, into the catchment area. Furthermore, future studies should focus on assessing toxic heavy metals such as Arsenic, Mercury, and Nickel to determine their potentials for cancer development over a lifetime.

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