



## **Evaluation of Pollution Load: Heavy Metal Contents and Physiochemical Properties of the Great Kwa River, Calabar, Cross River State, Nigeria**

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### **Authors' contributions**

*This work was carried out in collaboration among all authors. Author PBE design and supervised the research. Authors AJU and PBE executed the work, analyzed the data and wrote the first manuscript. Authors NGA, CJS and GA assisted in editing the manuscript, data analyses and interpretation of results. Author IPE assisted in samples collection and laboratory work. Author GA carried out literature search and reviews. All authors have read and approved the final version of the manuscript.*

### **Article Information**

DOI: 10.9734/IJECC/2021/v11i230356

Editor(s):

(1) Dr. Arjun B. Chhetri, Dalhousie University, Canada.

Reviewers:

(1) Georgios Sylaios, Democritus University of Thrace, Greece.

(2) Adams Sadick, CSIR-Soil Research Institute, Ghana.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/66295>

**Original Research Article**

**Received 12 January 2021**

**Accepted 16 March 2021**

**Published 12 April 2021**

### **ABSTRACT**

**Background and Objectives:** Human activities can increase the amount of pollutants in the environment leading to water pollution. The contamination of surface water and sediments by heavy metals can result in adverse health conditions of humans, due to the bioaccumulation of metals. This study seeks to assess the pollution load of some heavy metals and physiochemical

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properties in Great Kwa River.

**Methods:** Water samples were collected once a month from three stations within four selected months in wet and dry seasons. Samples were preserved by adding 10 ml of 6 N Nitric acid and stored at 5°C. Laboratory investigations were conducted and data analyzed statistically.

**Findings:** The mean pH, dissolved O<sub>2</sub>, biological O<sub>2</sub> demand, conductivity, NO<sub>3</sub>, NH<sub>4</sub> and temperature were 7.44±1.24, 5.58±0.92, 0.957±0.002, 32.84±2.941, 0.1030±0.1701, 0.113±0.018 and 28.2±1.48, respectively during wet season. Mean concentration of Cu, Fe, Cr, Mn, Zn, Ni are 0.225±0.003, 0.489±0.009, 0.068±0.016, 0.102±0.006, 0.794±0.003, 0.031±0.001, respectively during the wet season. Mean concentration of metals in the river during the wet season were ranked in descending order as Zn > Fe > Cu > Mn > Cr > Ni. Iron (0.489±0.009 mg/l and 0.438±0.003 mg/l), chromium (0.068±0.016 mg/l and 0.055±0.008 mg/l), nickel (0.031±0.001 mg/l and 0.025±0.002 mg/l) were higher than Nigerian standard for drinking water in both seasons. The contamination factor of heavy metals in station 3 were 2.14, 1.56, 1.09, 0.89 for Fe, Cr, Ni, Zn, respectively, indicating moderate contamination. The pollution load index in stations 1, 2, 3 were 0.262, 0.537, 0.981, respectively.

**Conclusion:** The present study provided base-line information on the pollution levels and physiochemical properties of the river. The river was not highly polluted by heavy metals except iron, chromium and nickel that were found above the recommended standards. However, drinking of water from the river over one's lifetime is not advisable due to detrimental health hazards.

*Keywords: Contamination; pollution load index; physiochemical properties; heavy metals; Kwa river.*

## 1. INTRODUCCION

Human activities increase pollutants in the environment, leading to land, water and air pollution. These activities by man have led to a rapid increase in the release of contaminants, such as heavy metals, into the terrestrial and aquatic environment [1-4]. However, the contamination of heavy metals in surface water, air and sediments can cause adverse health effects on humans and the environment [1,2]. Water pollution occurs due to the introduction of undesirable high amount of chemicals deposition in water bodies, thereby making it unhealthy for usage. The aquatic environment can be polluted either through point source or non-point source pollutants. Pollution incidents may arise from unidentifiable sources (non-point sources) being responsible for major part of contaminants present in the aquatic environment [1-4]. Pollution load is the amount of stress placed upon an ecosystem through contamination, either physically or chemically released into the environment by man-made or natural means. Water quality can be determined through pollutant concentration or pollution load index and physiochemical properties [1,2,5-7].

Heavy metals are metals having densities that are five times higher than water. They are dangerous because they tend to accumulate in living organisms like animals, man and some plants lacking the ability of phytoremediation [8]. Compounds accumulate in living things any time

they are taken up and stored faster than they are metabolized [1-3,5-8]. Geological weathering, soil erosion, airborne dust, atmospheric transportation, precipitation, and anthropogenic activities including fertilizer, leaching, sewage discharge, industrial waste/ wastewater, and urban construction are factors that enhance heavy metals entry into lakes, rivers, streams and other water bodies [9]. Hydrological cycles, physiochemical processes, and complex spatio-temporal variation enable remobilization of heavy metals from sediments into the surrounding water bodies [7]. An increase in the concentration of heavy metals increases the potential of adverse health effects to populace living in an environment [10]. The toxicity of heavy metals depends on their chemical form and the species of the elements. The degree a cell, organ or system is affected by heavy metals toxin depends not only on the toxin alone but also on the person's degree of exposure to the toxin [11]. The toxicity of heavy metals can be summarized in their order of decreasing toxicity as Hg>Cd>Cu>Zn>Ni>Pb>Cr>Al>Co [5,11]. This is only approximate because the vulnerability of species to individual metals varies [5,12]. The most common health risk associated with heavy metals poisoning include organ damage, breathing related problems and blindness [13,14]. Iron (Fe) is one of the biological essential element to living organisms, but excess quantity is detrimental to man. The body requires iron for the synthesis of its oxygen transport proteins; in particular hemoglobin and myoglobin, and for the

formation of heme enzymes and other iron-containing enzymes involved in electron transfer and oxidation-reductions [15,16]. It was documented that the effects of excess iron in human bodies include decreased growth (both linear growth and weight), increased illness (usually diarrhea), interactions with other trace elements, such as copper and zinc, altered gut microbiota to more pathogenic bacteria, increased inflammatory markers, and impaired cognitive and motor development [17]. Zinc plays a very important role in plant nutrition and has been a component of some metallo-enzymatic pathways [12]. It is an essential beneficial element to man but their salts produce undesirable taste in water. It is release into sewage and soils from the cosmetic industry, pharmaceutical paints, pigment and several insecticides. Even though zinc has been found to have low toxicity to man, prolonged consumption of large doses can lead to some health challenges and complications like fatigue, dizziness, and neutropenia [12]. Nickel is among the non-essential element needed for healthy growth of plants, animals and soil microbes. It interacts with iron present in hemoglobin and helps in oxygen transport, stimulate the metabolism as well as being regarded as a key metal in several plants and animal's enzymatic pathways [10]. However, higher concentrations of nickel can be toxic [5]. Excessive and prolonged inhalation of manganese particulate in welding, mining and industries leads to its accumulation in selected brain tissue, causing central nervous system (CNS) dysfunctions and an extrapyramidal motor disorder [18].

Toxicity varies according to the prevailing environmental conditions of a place coupled with the chemical speciation of metals. Water pollution is a common and significant problem globally [5-7,19-22]. Water is an essential natural resource for human life, developing economy and society in terms of agriculture, industry, etc. Water bodies required periodic assessment of the degree of contamination or pollution load. Additionally, they do not only supply water for human consumption but also receive waste materials from surrounding coastal environment. There is dearth of information on the pollution load of heavy metals in the river within Calabar metropolis based on literature search to the best of our abilities. Therefore, this study seek to assess the pollution load of some heavy metals and physiochemical properties in the Great Kwa River, Calabar, Nigeria.

## 2. MATERIALS AND METHODS

### 2.1 Research Location

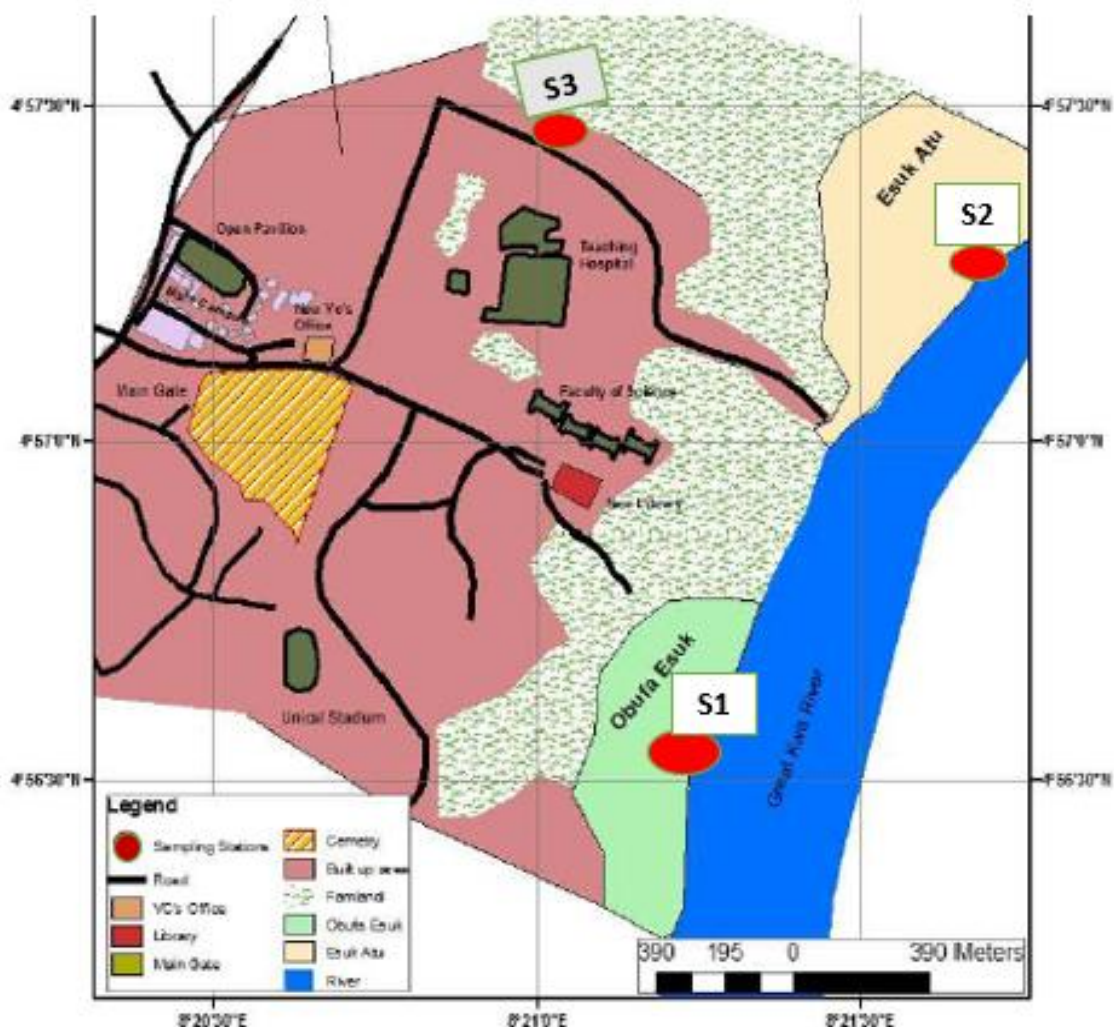
The research was carried out in the Great Kwa River, Cross River State. The area is located between latitude  $8^{\circ}15'E$  and  $8^{\circ}30'E$  and longitude  $4^{\circ}45'N$  and  $5^{\circ}15'N$ . It has an estimated length of 56km and is about 2.8km wide at the mouth where it empties into the Cross River Estuary [7,23]. 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.

### 2.2 Sampling Stations

Three sampling stations were mapped along the Great Kwa River bank. Station 1 (Obufa Esuk) was located between Latitude  $4^{\circ}94'N$  and Longitude  $8^{\circ}35'E$ , close to the Faculty of Biological Sciences and the University of Calabar Teaching Hospital. Station 2 (Esuk Atu) and Station 3 (outskirt of Esuk Atu beach) were located between Latitude  $4^{\circ}95'N$  and Longitude  $8^{\circ}36'E$  (Fig. 1) [23], with few modifications. Human activities take place in these selected locations and they are local settlements for fishermen, farmers and traders.

### 2.3 Samples Collection

Surface and subsurface water samples were collected once a month from the three stations with respects to two seasonal changes (wet season: February –March, and dry season: June and July) along the Great Kwa River. Surface water samples (approximately one meter) and subsurface water samples (approximately four meter) were obtained using a Nansen bottle water sampler. Upon retrieval, the water sample were emptied into sterile plastic bottles and one liter of each sample was preserved by the addition of 10 ml of 6 N Nitric acid and stored at  $5^{\circ}C$ . Three replicates were collected at each station and all samples were labeled accordingly reflecting each sample station and location.



**FIG. 1. Map showing the research area of S1 (Obufa Esuk), S2 (Esuk Atu) and S3 (outskirt of Esuk Atu)**

The samples were subsequently transported to the Institute of Oceanography Laboratory, University of Calabar, Calabar for further processing and laboratory analyses.

### 2.4 Physicochemical Parameters Determination

The samples were analyzed for Temperature (T), hydrogen ion concentration (pH), dissolved oxygen (DO), biological oxygen demand (BOD), conductivity, dissolved nutrients such as nitrite (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), phosphate (PO<sub>4</sub>), sulphate (SO<sub>4</sub>) and ammonium (NH<sub>4</sub>). Temperature (T) of the water sample was determined using mercury in glass thermometer (Model: Combo). Hydrogen Ion concentration (pH) was determined using the

pH- meter (PHS-3C Model) and the pH meter was calibrated with buffered solutions and the instrument was standardized before taken readings [24,25]. Dissolved oxygen measurement was done *in-situ* using digital portable analysis (Model JPB-607A) [26]. Biological oxygen demand was determined after the initial dissolved oxygen was measured. Water samples were stored in a 100 cl container in an ice pack to maintain normal microbial activities; and stored at 20°C for 120 hours (5 days). Then the oxygen content of the refrigerated sample was determined using dissolved oxygen analyzer, value was read and biological oxygen demand was calculated. Conductivity was measured using HANNA HI 991301 model device [24].

Dissolved nutrients were also determined using spectrophotometer – PRIM Light and Advance 70C10382 model. Phosphate (PO<sub>4</sub>) was analyzed using the Molybdenum blue method and the absorbance of the resultant blue color was measured at 88 nm. Nitrite (NO<sub>2</sub>) and Nitrate (NO<sub>3</sub>) were analyzed using the diazotization method. The reduction with cadmium granules, 2 ml of sulphuric acid was added to 50 ml of the sample and allowed for 5 minutes. 1 ml of 1-Naphthyl Ethylene-dihydrochloride (NED) was added and thoroughly mixed, then allowed for 20 minutes before filling into a cuvette. Then inserted into the spectrophotometer at 240 nm wave length and reading was taken. Ammonium (NH<sub>3</sub>) was analyzed by direct Nesslerization using comparator. 1 ml of Sodium Hexametaphosphate solution was added to 50 ml of sample, followed by 2 ml Nessler reagent. It was evenly mixed and kept for 10 minutes and then the extraction was read at 425 nm wave length of the spectrophotometer.

## 2.5 Heavy Metals Analysis for concentration

The samples were tested for heavy metals content and the heavy metals evaluated are Zinc (Zn), Copper (Cu), Chromium (Cr), Manganese (Mn), Nickel (Ni), Arsenic (As), Iron (Fe) and Lead (Pb) using ultra violet-Visible Spectrophotometer methods; the equipment model was UV-V spectrometry-VGP-210. The water samples for heavy metal analysis were filtered through Whatman filter paper number 1 and 100 ml of filtrates were acidified to pH 2 with 20 ml of 6N HNO<sub>3</sub>. Standard solution for Zn, Cu, Cr, Mn, Ni, As, Fe and Pb were prepared according to the analytical methods for atomic absorption spectrophotometry [27].

## 2.6 Estimation of Heavy Metals Pollution Load

Heavy metals contamination or pollution load were assessed using the Contamination factor (CF) and Pollution load index (PLI). The Contamination factor gives an indication of the degree of contamination in the environment; either in soil or water sample [28]. The level of contamination factor by metal is expressed by the equation below:

$$CF = \frac{C_{sample}}{C_{background}}$$

Where,

C<sub>sample</sub> and C<sub>background</sub> are the mean concentration of a pollutant in the surface water and the background (subsurface water) of the study area. Contamination factor values were interpreted as summarized: CF < 1 = low pollution, 1 ≤ CF < 3 = moderate pollution, 3 ≤ CF < 6 = considerable pollution and CF ≥ 6 = very high pollution [29].

Pollution load index (PLI) is used in evaluating the pollution level in an environment [29,30]. It is the square root of the multiplication of the contamination factor (CF) of metals in a given environment [30,31].

The equation is given below:

$$PLI = \frac{(CF_1 \times CF_2 \times CF_3 \times CF_4 \times \dots \times XCF_n)^{1/n}}$$

Where,

CF is the contamination factor and n is the number of metals investigated. When PLI value is greater than one, it implies polluted sample while PLI value is less than indicate no pollution [30,31].

## 2.7 Statistical Analysis

Microsoft Excel 2010 was used for coding of data and data was analyzed using Statistical Package for Social Sciences (SPSS) version 20.0. Results of heavy metals in the water and sediments were calculated by using mean and standard deviation.

## 3. RESULTS AND DISCUSSION

### 3.1 Heavy Metals Concentrations and Contamination Factor

The mean concentration of Cu, Fe, Cr, Mn, Zn, and Ni were 0.060±0.007, 0.438±0.003, 0.055±0.08, 0.075±0.012, 0.0271±0.005 and 0.025±0.002 respectively during the dry season. (Table 1). In wet season, the mean concentration of Cu, Fe, Cr, Mn, Zn, and Ni were 0.225±0.003, 0.489±0.009, 0.068±0.016, 0.102±0.006, 0.794±0.003 and 0.031±0.001 respectively (Table 2). Globally, anthropogenic contaminants are washed into surrounding water bodies and coastal environment from industries, untreated dump sites in developing and under-developed countries. Heavy metals are very serious contaminants to the aquatic ecosystem [1-3,18-21,32] and are finally deposited in human's system when they feed on these contaminated

aquatic animals like fish, crab, shrimps, lobsters, etc [19,33,34]. The mean values of heavy metal concentrations in water samples in this present study was lower than the standard set by Nigerian Standard for Drinking Water (NSDW) [35], World Health Organization (WHO) in 2017 [36] and Food and Agricultural Organization

(FAO) [37], except for Iron (0.489±0.009 mg/l and 0.438±0.003 mg/l), chromium (0.068±0.016 mg/l and 0.055±0.008 mg/l) and nickel (0.031±0.001 mg/l and 0.025±0.002 mg/l) in that were higher than the Nigerian standard for drinking water [35]. This implies that some level

**Table 1. Physiochemical parameters and heavy metals in the water samples during dry season**

Parameters	Minimum	Maximum	Mean	Maximum WHO (2017)	Permitted NDWS (2007)	FAO (1985)
pH	5.48	9.21	9.48±1.03	6.5-8.5	6.5-8.5	
DO(mg/l)	6.20	9.2	9.617±1.001	5-10	5-10	
BOD(mg/l)	0.19	0.32	0.319±0.006	<5.0	<5.0	
Cond(µS/cm)	20.3	40.1	26.68±1.046			
NO <sub>3</sub> (mg/l)	0.0921	0.1462	0.1135±0.26	<50	<10	
NO <sub>2</sub> (mg/l)	0.162	0.281	0.1811±0.92			
PO <sub>4</sub> (mg/l)	0.010	0.019	0.0186±0.61	<0.10	<0.10	
SO <sub>4</sub> (mg/l)	0.8699	0.1673	0.9223±0.029			
NH <sub>4</sub> (mg/l)	0.086	0.198	0.1247±0.013			
Temp(°C)	26	31	30.43±1.68			
Cu(mg/l)	0.41	0.63	0.060±0.007	2.0	1.0	0.2
Fe(mg/l)	0.61	0.73	0.438±0.003	0.3	0.3	
Cr(mg/l)	0.041	0.169	0.055±0.008	0.05	0.05	0.1
Mn(mg/l)	0.011	0.082	0.075±0.012	0.4	0.2	0.2-10
Zn(mg/l)	0.691	0.890	0.0271±0.005	3.0	3.0	2.0
Pb(mg/l)	BDL	BDL	BDL	0.01	0.01	
Ni(mg/l)	0.029	0.036	0.025±0.002	0.07	0.02	
As(mg/l)	BDL	BDL	BDL	0.01	0.01	

BDL= Below Detectable Limit; WHO= World Health Organization; NSDW= Nigerian Standard for Drinking Water; FAO= Food and Agricultural Organization

**Table 2. Physiochemical parameters and heavy metals in the water samples during wet season**

Parameters	Minimum	Maximum	Mean	Maximum WHO (2017)	Permitted NDWS (2007)	FAO (1985)
pH	5.48	6.19	7.44±124	6.5-8.5	6.5-8.5	
DO(mg/l)	4.90	5.80	5.58±0.92	5-10	5-10	
BOD(mg/l)	0.80	1.0	0.957±0.002	<5.0	<5.0	
Cond(µS/cm)	24.60	40.1	32.84±2.941			
NO <sub>3</sub> (mg/l)	0.1541	0.0983	0.1030±0.1701	<50	<10	
NO <sub>2</sub> (mg/l)	0.024	0.176	0.145±0.674			
PO <sub>4</sub> (mg/l)	0.036	0.013	0.0287±0.093	<0.10	<0.10	
SO <sub>4</sub> (mg/l)	0.214	0.01673	0.486±0.061			
NH <sub>4</sub> (mg/l)	0.011	0.163	0.113±0.018			
Temp(°C)	27	29	28.2±1.48			
Cu(mg/l)	0.030	0.520	0.225±0.003	2.0	1.0	0.2
Fe(mg/l)	0.231	0.730	0.489±0.009	0.3	0.3	
Cr(mg/l)	0.040	0.082	0.068±0.016	0.05	0.05	0.1
Mn(mg/l)	0.012	0.041	0.102±0.006	0.4	0.2	0.2-10
Zn(mg/l)	0.089	1.696	0.794±0.003	1.0-5.0	3.0	2.0
Pb(mg/l)	BDL	BDL	BDL	0.01	0.01	
Ni(mg/l)	0.016	0.033	0.031±0.001		0.02	
As(mg/l)	BDL	BDL	BDL	0.01	0.01	

BDL= Below Detectable Limit; WHO= World Health Organization; NSDW= Nigerian Standard for Drinking Water; FAO= Food and Agricultural Organization

of caution must be taken when considering drinking the water from Great Kwa River and for agricultural purposes. It was reported by WHO that the concentrations of iron in drinking water are normally less than 0.3 mg/l but may be higher in countries where various iron salts are used as coagulating agents in water treatment plants and where cast iron, steel, and galvanized iron pipes are utilized for water distribution [38]. In Calabar, iron salts are used as coagulating agents in some water treatment facilities and sometimes these water are channel back into the water bodies as wastewater.

Also in time past; steel, irons and galvanized pipes were used to distribute water to the populace, these might have brought an increased in the iron concentration over the years due to bioaccumulation before they were replaced with plastic pipes. It was documented that excess iron in human's body are detrimental (altering gut microbiota, increased inflammatory markers, impaired cognitive and motor development) and also interacts with other trace elements (like copper and zinc) [17], indicating that consumption of water with high concentration of iron may be hazardous to man's health. The mean concentration of iron was 2.0 mg/l in Choba section of the new Calabar river, Rivers State [5], 0.65 mg/l and 4.61 mg/l for Mbat-Abbiati Creek and Oberekkai Creek, respectively, in Odukpani section of the Great Kwa River, Cross River State [7], 10.68±1.91 and 7.37±0.24 mg/l for wet and dry season, respectively, in Qua Iboe river, Akwa Ibom State [6], 43.523 mg/l in one of the location in River Benue [1], which were higher than the mean concentration value (0.489±0.009 mg/l) observed in our present study in Calabar. Substantially higher ferrous compounds concentration in the aquatic environment may emanate from the precipitation of iron in alkaline and oxidizing conditions [39]. Also, exchangeable iron which usually relates to adsorbed metals on the sediment surface can easily be remobilized into the surrounding water bodies [40]. These reasons may have contributed to the higher concentrations reported in some water bodies. In contrast, lower mean concentration of iron was 0.229±0.01 to 0.042±0.01 mg/l in different locations within Orashi River along Engenni axis, Rivers State, Nigeria [22], which was lower than the mean value of iron (0.489±0.009 mg/l) observed in this present study. Several researches also documented lower average concentrations of iron in different water bodies; including River Nun in Bayelsa State [41], Bodo

creek water in Niger Delta [33], surface water bodies in Kaduna metropolis [42]; all in Nigerian water bodies and in lakes within Nagpur City, India [43].

The average concentration of zinc in this study were 0.794±0.003 mg/l and 0.0271±0.005 mg/l in wet and dry season respectively. The result of zinc concentration obtained during the dry season in our study was similar to the mean values (0.023±0.01 mg/l -0.026±0.01 mg/l) recorded in all the stations within the shores of Orashi River, Rivers State, Nigeria [22], although lower than our mean value during wet season. Also, our findings was in tandem with the mean values of 0.08±0.03 mg/l and 0.03±0.01 mg/l observed in Qua-Iboe river, Akwa Ibom state during wet season and dry season, respectively [6]. The levels of zinc detected in water samples of the Great Kwa River were slightly lower than those observed in Sagbama river, Bayelsa State, Nigeria [44], but much lower values documented for Wen-Rui Tang River in China using surface water [45], Bomu and Oginigba rivers in Rivers State, Nigeria [46], and in coastal marine sediments in Anantigha, Calabar, Cross River State [2]. Higher mean concentrations of zinc was documented in Mbat-Abbiati Creek and Oberekkai Creek (between 0.21 to 0.26 mg/l) in Odukpani area of the Great Kwa River [7], new Calabar river, Choba locations, Rivers State [5], River Benue [1] and hyporheic zone of the Weihe River, China [32].

Mean copper concentrations were 0.225±0.003 mg/l and 0.060±0.007 mg/l for wet and dry season respectively. The result obtained during the dry season was similar to the mean value documented in Mbat-Abbiati Creek (0.63±0.14 mg/l) in Odukpani area of the Great Kwa River [7]. On the other hand, the mean value recorded in Oberekkai Creek (0.28±0.11 mg/l) was similar to the value observed during wet season in the present study [7]. Lower mean concentrations of copper were documented in water samples collected in Qua-Iboe river, Akwa Ibom state [6], Udege Mbeki Mining District, North-Central Nigeria, [47], water bodies in Kaduna City [42], major rivers located in Penang, Malaysia [47] and coastal marine sediments deposited in Anantigha, Cross River State [2]. Previous studies documented higher mean concentrations of copper in different surface water, under-surface water and sediments including River Benue [1], new Calabar river, Rivers State [5], Weihe River, China [32], Cuba [48], and Nile Delta, Egypt [49].

The mean concentrations of manganese ranged from  $0.102 \pm 0.006$  mg/l to  $0.0075 \pm 0.012$  mg/l for wet and dry season respectively in this present study. These values were lower than the standard recommended by Nigerian standard for drinking water [35], WHO [36], and Food and Agricultural Organization [37]. This revealed that the Great Kwa River was not contaminated with manganese at the time of this research. This observation is in tandem with other findings conducted in Bayelsa State [44], Orashi River, Rivers State [22] and Ahoada-Ihuaba axis of Sombreiro River, Rivers State [50]. Manganese does not occur in the elemental form naturally, but exists in combination with other substances [7,51]. The sources of manganese in Great Kwa River might be anthropogenic activities like welding, mining, drilling of crude oil and untreated sewage discharges. Other studies reported higher mean concentrations of manganese in different surface water, under-surface water and sediments including River Benue [1], new Calabar river, Rivers State [5], Mbat-Abbiati Creek and Oberekkai Creek in Odukpani section of Great Kwa River [7], Weihe River, China [32], Cuba [48], and Nile Delta, Egypt [49] when compared with our present findings in Calabar.

The mean values recorded for chromium (Cr) was  $0.068 \pm 0.016$  mg/l in wet season and  $0.055 \pm 0.008$  mg/l in dry season. These values were higher than the FAO, WHO and SON standards for drinking water [35-37]. The slightly high concentration of chromium in Great Kwa River might be due to anthropogenic activities like painting, welding, wood work, untreated sewage, etc. Chromium is widely used as industrial chemicals, manufacturing of paints, metal finishing, steel (stainless steel manufacturing, alloy cast irons), chrome and wood treatment [52]. The inhalation and dermal routes entry of chromium is very toxic, causing lung cancer, nasal irritation, nasal ulcer, hypersensitivity reactions, contact dermatitis and cytotoxic and genotoxic reactions; affecting the immune system of man [52]. The surface water containing chromium seen in this study was lower than the reported values in Mbat-Abbiati Creek and Oberekkai Creek [7], River Gongola in Adamawa State [53], surface water in Kaduna metropolis [42] and Kosovo lakes [21]. Previous documented researches reported either higher or similar values as seen in this study; including Orashi River, Rivers State [22], Qua- Iboe river, Akwa Ibom state [6], Nun River in Gbarantoru and Tombia towns, Bayelsa State, Nigeria [41].

Additionally, much higher mean concentrations of chromium was recorded in different surface water samples, under-surface water or sediments in River Benue [1], new Calabar river, Rivers State [5], Weihe River, China [32], Cuba [48] Nile Delta, Egypt [49], Axios River, Greece [54] and Gomti river, India [55].

The average concentration values recorded for nickel were  $0.031 \pm 0.001$  mg/l and  $0.025 \pm 0.002$  mg/l for wet season and dry season, respectively. These values for nickel noted in this study was slightly higher than the recommended values by Nigerian standard for drinking water [35]. The concentrations of nickel reported in published researches in Choba region of new Calabar river, Rivers State [5], Qua- Iboe river, Akwa Ibom state [6], Udege Mbeki Mining District, North-Central Nigeria [56], Nun River, Bayelsa state [41], salt lakes in Romania [57], Weihe River, China [32], Nile Delta, Egypt [49], Axios River, Greece [54] and Gomti river, India [55] were higher than the records in our study. Generally, higher concentrations of heavy metals were mostly observed during wet season than dry season as noticed in our findings. This may be due to washing away of wastes and wastewater from dumps sites, fertilizer from farm land, pesticides, remains of photographic materials, mining areas (quarries sites) into the coastal and aquatic environment because of the topography nature of Calabar and its environs. The seasonal variations observed in the mean concentrations of heavy metals in this present study and other reported researches from different locations [1,6,19,58,59] were attributed to anthropogenic activities and surface run-off water; which collaborate with our findings.

The contamination factor of heavy metals in station 1 were 0.97, 0.99, 0.71 and 0.37 for Fe, Cr, Ni and Cu respectively in station 1, while Station 3 were 2.14, 1.56, 1.09 and 0.89 for Fe, Cr, Ni and Zn respectively (Table 3). The contamination factor revealed that the Great Kwa River is moderately contaminated in heavy metals like iron, chromium and nickel in station 3 (outshirt of Esuk Atu) and low contamination by copper and zinc. The maximum values of contamination factor at station S3 indicated that the site was moderately contaminated, while station S2 and S1 showed no contamination. This finding is similar to the documented results observed in Weihe River, China [32] and Orashi River, Rivers State [22] where the sites were either moderately contaminated or low



contamination. Also moderate contamination of heavy metals was documented in Qua- Iboe river, Akwa Ibom state [6] during dry season; but high contamination in wet season, whereas moderate to high contamination was reported in River Benue [1], North Central Nigeria. In contrast, high degree of heavy metals contamination was reported in new Calabar River, Port Harcourt [60]; which is not concomitant with our findings in Great Kwa River.

### 3.2 Pollution load index (PLI)

The pollution load index (PLI) of heavy metals in station 1, station 2 and station 3 of the Great Kwa River ranged from 0.262 – 0.981 (Table 4). The results indicate that the river is almost at threshold of contamination by the heavy metals, especially at station 3, which agrees with the PLI in Orashi River, Rivers State [22]. The pollution load index recorded in this study was lower than the PLI reported for surface water in Bonny River estuary [61]. Also lower pollution load index of 0.022 - 0.038 was previously recorded in Anantigha coastal marine sediment, Calabar South, Cross River State; revealing no pollution, although there was some degree of heavy metals contamination from those stations [2]. This published result is in harmony with our present findings in stations 1 (Obufa Esuk) and station 2 (Esuk Otu) located close to the Anantigha area in Calabar South, Cross Rivers state. Higher PLI was published in River Benue sediments [1], coastline of Erongo region, Western Namibia [28] and new Calabar River, Rivers State [5,60] were the water bodies are either severely polluted or excessively polluted in different locations. The high concentration of heavy metals and pollution load recorded in station 3 (Esuk Otu outskirt) may be attributed to the frequent flow or draining of untreated wastes and wastewater; especially during raining season from the central dump site in Calabar metropolis (located within "Parliamentary Extension") that lay in close proximity to station 3 of the Great Kwa River.

### 3.3 Estimation of Selected Physiochemical Parameters

The mean pH, dissolved O<sub>2</sub> (DO), biological oxygen demand (BOD), conductivity, NO<sub>3</sub>, NH<sub>4</sub> and temperature are 9.48±1.03, 9.617±1.001, 0.319±0.006, 26.69±1.060, 0.1135±0.026, 0.1247±0.013 and 30.43±1.68 respectively during dry season (Table 1), while 7.44±1.24, 5.58±0.92, 0.957±0.002, 32.84±2.941, 0.1030±0.1701, 0.113±0.018 and 28.2±1.48

respectively were recorded during wet season (Table 2).

The mean pH readings in dry and wet season depict alkalinity of the water. This finding was in harmony with the previous study in Qua- Iboe river, Akwa Ibom state [6], but disagree with the results in Mbat-Abbiati Creek and Oberekkai Creek, Odukpani section of the Great Kwa River where the water was mildly acidic [7]. The mean temperature, dissolved O<sub>2</sub> and BOD in both seasons implies that more metabolic and reproductive activities in the aquatic environment flourish more during the dry season based on the high temperature. It was documented that higher temperature in dry season increases metabolic activities in water resulting in depletion of dissolved oxygen in dry season [6], agreeing with our present findings where higher dissolved oxygen was observed in dry season than wet season (Table 1 and Table 2). Biological O<sub>2</sub> demand (BOD) is a measure of the biological activities in a water body, and it is used as a signal for organic load and pollution index in rivers, streams, lakes, etc. Biological O<sub>2</sub> demand mean values in this river was higher than the values documented in Mbat-Abbiati and Oberekkai creeks [7]. The high biological O<sub>2</sub> demand values observed in this study points to unlimited level of organic matter decomposition; sapping more oxygen from the river. This in-turn deprived oxygen availability for aquatic organisms like fishes, crabs, etc. The conductivity of water is a function of the concentration of dissolved ions and is one of the yard-stick for measuring water quality [6]. The high conductivity value observed in this research during wet season is in harmony with the findings in Qua- Iboe river [6]. Higher conductivity value was detected in Oberekkai Creek and Mbat-Abbiati Creek [7], disagreeing with this present finding in the Calabar section of the Great Kwa River. The SO<sub>4</sub> mean concentration in the surface water samples in this research was 0.9223±0.029 mg/l and 0.486±0.061 mg/l in dry and wet season respectively. High mean concentrations of SO<sub>4</sub> was documented in Mbat-Abbiati and Oberekkai Creeks, Odukpani area of the Great Kwa River [7] which is not similar with our present findings. In several natural water bodies, PO<sub>4</sub> concentrations range from 0.005 - 0.020 mg/l [62]. The mean levels of PO<sub>4</sub> in this study was 0.0186±0.61 mg/l in dry season and 0.486±0.061 mg/l in wet season. These values are above the levels in most natural water bodies [62]. High concentrations of phosphate are greatly responsible for eutrophic conditions in a

**Table 3. Contamination factor of heavy metals in the water samples during study period**

Heavy metals(mg/l)	Station 1(S1) Obufa Esuk	Station 2 (S2) Esuk Atu	Station 3 (S3) outskirts of Esuk Atu
Cu	0.37	0.60	0.98
Fe	0.97	0.98	2.14
Cr	0.99	0.75	1.56
Mn	0.34	0.51	0.93
Zn	0.43	0.63	0.89
Pb	BDL	BDL	BDL
Ni	0.71	0.96	1.09
As	BDL	BDL	BDL

**Table 4. Pollution load index (PLI) of heavy metals in the water samples during study period**

	Station 1(S1) Obufa Esuk	Station 2 (S2) Esuk Atu	Station 3 (S3) Outskirt of Esuk Atu
PLI	0.262	0.537	0.981

*PLI value  $\geq 1$  = polluted sample, PLI value  $< 1$  = no pollution*

water body and therefore enriches other nutrient in the river. Higher  $PO_4$  concentrations was previously documented in Oberekkai Creek and Mbat-Abbiati Creek, Odukpani section of the Great Kwa River, [7], harmonizing with our findings in the Calabar section of Great Kwa River, Cross River State, Nigeria.

#### 4. CONCLUSION

This present study therefore provides current base-line information on the pollution levels and physiochemical properties in the Calabar section of Great Kwa River, Cross River State. Physiochemical parameters had seasonal influences in the surface water. The findings offers reasonable evidence on the need for periodic assessment of heavy metals and other contaminants in order to secure the health of the community dwellers. Conclusively, the Great Kwa River was not highly polluted by some heavy metals. However, drinking of water from the river over one's lifetime is not advisable for obvious accumulation of heavy metals; which might be detrimental to health of the populace.

#### 5. LIMITATION OF THE STUDY

Geo-accumulation index and enrichment factor where not utilized in this study as a tool for predicting heavy metal contamination.

#### ACKNOWLEDGEMENTS

The authors wish to thank the management and staff of Cross Rivers State Waste Management

Authority, Institute of Oceanography, University of Calabar and Department of Genetics and Biotechnology, University of Calabar, undergraduate, post graduate students and all who provided data, information and contributed to the success of the research.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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