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Partition Coefficients and Metals Quality Index of Calabar and Great Kwa Rivers, Niger Delta, Nigeria

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ABSTRACT

Partitioning of toxic metals between suspended particulate matter (SPM) phase and dissolved phase in Calabar and Great Kwa rivers was investigated from October 2021 to August 2022, to determine the metals' mobility, bioavailability and potential toxicity. Metals in surface water were differentiated between dissolve and particulate matter forms, based on whether or not they passed through 0.45µm filters. Total and dissolved metals concentrations were determined using Atomic Absorption Spectrophotometer (Shemadzu, model 6800, Japan) after wetting. Total metal concentrations ranged from 0.212 mg/l - 0.494 mg/kg, 0.011-0.053 mg/kg, 0.004-0.008 mg/kg, and 0.014-0.049 mg/l for lead, cadmium, mercury and arsenic, respectively. The total metals concentrations of both rivers were above Nigerian Drinking Water Quality Standards (NDWQS) and World Health Organisation guidelines for drinking water quality, with mercury being the only exception. The percentage of lead, cadmium, mercury and arsenic concentrations in dissolved phase ranged from 14.80 – 23.54%, 8.88 - 20.00%, 16.67 – 20.00% and 6.45 – 17.24%, respectively. The total, dissolved and SPM concentrations of all the metals were significantly higher ($P \leq 0.05$) in Calabar River than the Great Kwa River. Heavy Metal Pollution index (HMPI) indicated that, both rivers are not fit for drinking and the status corresponds to high contamination. Partition coefficients revealed that cadmium and arsenic displayed affinity to bind and remain preferentially in suspended particulate matter phase, while lead and mercury showed tendency to be more easily mobilized from suspended particulate phase toward the dissolved phase. The study concluded that, studied metals were predominant in suspended particulate matter phase. Both rivers are not fit for domestic and agricultural purposes; however, filtering the water before application could reduce human health risk significantly. Further investigations into the chemical speciation of the metals in the two rivers is hereby recommended

INTRODUCTION

The Niger Delta is renowned as the third largest wetland globally, the largest river delta and mangrove ecosystem in Africa, and the hub of Nigeria's oil industry **(Adekola & Mitchell, 2011)**. With over 50% of the Delta consisting of water, it sustains a vast network of rivers, tributaries, creeks, and estuaries that support a diverse mangrove swamp ecosystem with extensive mudflats. Unfortunately, these estuarine ecosystems act as sinks for various contaminants like herbicides, pesticides, heavy metals, and plastics **(Adekola & Mitchell, 2011)**. Rapid ecological changes of the Niger Delta driven by pressures from oil

exploration/exploitation activities and their associated urbanization, industrialization, dredging of river channels and changing climates are raising serious concerns for the ecosystem and public health. **Chijioke *et al*. (2018)** reported that these anthropogenic activities have direct consequences on various components of the environment, including the atmosphere, soil, water (ground and surface water) and sediments. Heavy metals such cadmium, lead, mercury, manganese, vanadium, nickel, iron and copper have been associated with oil production activities including spillage **(Ubiogoro & Adeyemo, 2017)**. The Niger Delta has been identified as one of the five most polluted ecosystems in the world, with an estimated 3.1 million barrels of crude oil spilled between 1976 and 2014 in the region **(Ayuba, 2012; Chinedu & Chukwuemeka, 2018)**.

Metals have been reported as one of the most common environmental pollutants in the aquatic ecosystem **(Hamad *et al.,* 2012)**. They are natural component of the earth and are prevalent in aquatic environment. Additionally, large amounts produced from anthropogenic sources are released into aquatic habitats, where they travel down the overlaying water column and eventually settle and accumulate in sediments. While some of the trace and heavy metals are essential within certain thresholds, above these acceptable levels, they elicit deleterious effects on biota. Other metals such as cadmium, lead, arsenic and mercury which have no known bio-importance, exhibit extreme toxicity even at low concentrations. Metal concentrations in aquatic media can be a general indicator of pollution. Metals pollution indices (MPIs) highlight sites with high metals concentrations and are an excellent instrument that allows for comparison between site and monitoring over time. MPIs which are considered an excellent indicator of pollution level of each element and the overall pollution status of the site, however, provides no information regarding the metals' possible mobility between the liquid and solid phases, which are the two major components of the water body. The mobility, fate and bioavailability are directly related to the partitioning between water, suspended particulate matter and sediments **(Sedeno-Diaz *et al*., 2019)**.

The distribution processes between suspended particulate matter phase and the dissolved phase, which constitute a significant part of the metals geochemical cycle within rivers, estuaries and coastal oceans, are one of the major factors that determines the metals' mobility and toxicity. In aquatic ecosystem, both sediment and the overlying water are continuously exchanging materials and energy, thus maintaining a dynamic equilibrium of adsorption/absorption and release of contaminants. The distribution process depends on pH, redox reaction, temperature, salinity, and the composition of the suspended particulate matter (SPM). Sediments (suspended and bottom sediments) are recognized generally as the main sink for many contaminants such as heavy metals and as a potential source of dissolved and particulate bound contaminants to the overlying water column **(Alonso-Castilo *et al*., 2013; Zhu *et al*., 2017)**.

Metals that are present in aquatic media undergo reactions with ligands and solid materials in contact with the water. Reactions in which the metals are adsorbed or absorbed to the solid matrix are referred to as sorption reactions. In surface water system, sorption of metals to solid matrix brings about reduction in the dissolved concentration of the metal, hence its bioavailability **(Seidou *et al.,* 2022)**. The lower the bioavailability, the lower the

risk posed by the metal. In the absence of bioavailability, there is no exposure and the metals essentially pose no risk **(NGCERA, 1999)**. Sorption and desorption therefore play key role in determining the availability and associated risk of metals to biota.

The partition coefficient, also known as the sorption or distribution coefficient, is the most common parameter used to describe the solid-dissolved metal forms in water. It is an essential tool for estimating the migratory potentials and bioavailability of contaminants in water. While previous studies have assessed the concentrations of metals in the surface water and sediments of the Calabar and Great Kwa rivers **(Asuquo, 1999; Akpan *et al.*, 2002; Ewa *et al.*, 2013; Ephraim *et al.*, 2015; Ekpo *et al.*, 2021)**, no data have been reported on the distribution and partition coefficients of metals in the two rivers. The present study was designed to assess the current total metals concentrations, partitioning between the two major components of the water body (liquid and solid phases) and the heavy metals pollution indices of the rivers. Partition coefficient and metal quality indices improve the understanding of metals distribution and behavior in aquatic environment, provide unique and valuable insights into the pollution status and implications for ecosystem integrity and public health. Given the significance of the Niger Delta region in terms of biodiversity and ecosystem services, findings could also inform policies related to water quality management and pollution control.

MATERIALS AND METHODS

Study location

The studies were carried out in the lower tidal reaches of the Calabar and Great Kwa rivers (Fig. 1). The rivers originate from Oban Hills within Cross River State, Nigeria, flowing southward through the Oban massif and Cretaceous formations, draining the high rain forest and mangrove ecosystems before discharging into the Cross River Estuary, south of Calabar City. The two rivers drain the western and eastern coasts of Calabar City, respectively. The Calabar City which is the capital of Cross River State lies between longitudes 24°15' and 5°15'N and latitudes 8°15' and 8°25'E with a projected population of 579,000 for the year 2020 **(Populationstat, 2020)**. Considerable waste loads from the Calabar City find their way directly or indirectly into the rivers, particularly through surface run-off during the seasonal torrential rains.

The mangrove creek system of the two rivers serves as spawning grounds for shrimps, crabs, oysters, snails and many fin-fish species of commercial importance. Year-round semi-intensive farming is common within the flood plains. A number of municipal and industrial establishments located in the river basin contribute to waste discharges into the rivers including the University of Teaching Hospital, the United Cement Company (UNICEM) and associated quarries in Great Kwa River basin and the Nigeria Port Authority and Calabar Port in the Calabar River basin. Also located within close proximity of the Calabar Port are the Nigerian Export Processing Zone (NEPZ) and Free Trade Zone. Several oil and gas major marketers locate their tank farms in the river catchment, routing their cargo through the Calabar Port.

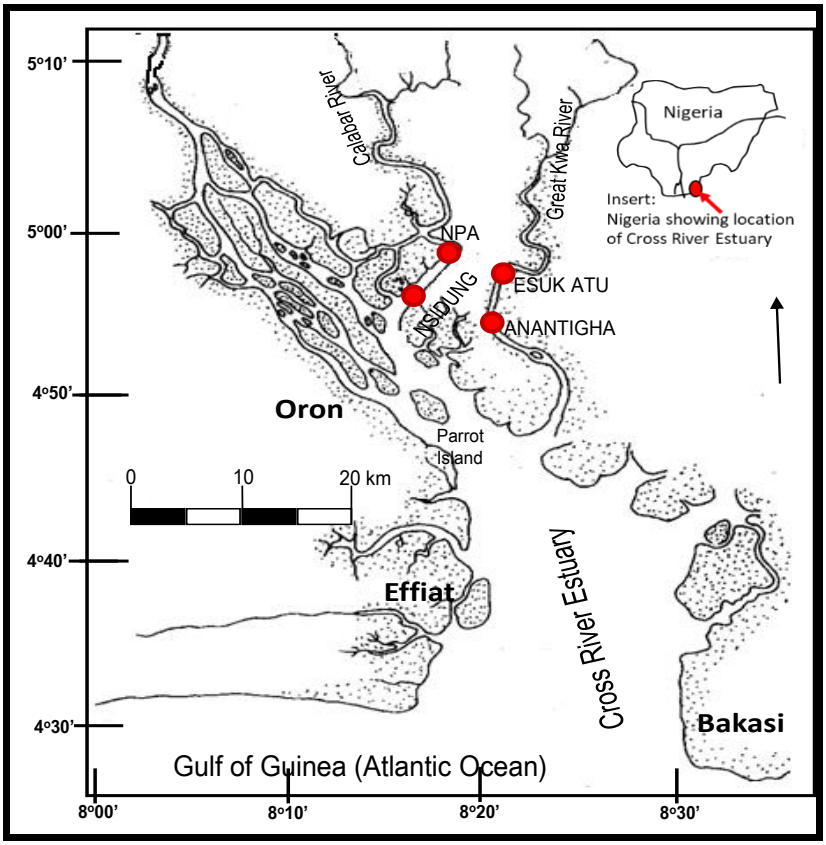

Fig. 1. Map of Cross River Estuary showing sampling points along Calabar and Great Kwa rivers

Samples collection

Sample collection and preparation was carried out following **APHA (2005)**. Two sampling points each (Esuk Atu and Esuk Anantigha for Great Kwa River, and Nigerian Port Authority Jetty and Nsidung beach for Calabar River) were established along the lower reaches of the two rivers. Surface water samples were collected at each of the established sampling point bimonthly from October 2021 to August 2022. Water samples were collected by grabs method into washed 1 liter plastic containers previously rinsed with the river water at the sampling site. To prevent sample contamination by surface microlayer, each container was opened and closed under water. Samples were collected during ebb tide at approximately 2 meters from the shore, transported to Lab 249, Zoology and Environmental Biology, University of Calabar in acid chess, and processed within 24 hours.

Sample preparation

The distribution of lead, chromium, cadmium, arsenic and mercury in surface water was studied according to **APHA (2005)**, using two methods. First is measurement method. This was used to measure the total and dissolved concentrations of the metals. The second is calculation method, and it involved the calculation of the particulate matter form and the partition coefficient of the metals. The metals in surface water were differentiated between

two operationally defined groups- dissolve and particulate matter forms, based on whether or not they went through 0.45µm filters **(Beltrame *et al.*, 2009)**. The surface water sample was well shaken to be mixed; 50ml was then filtered (Whatman filter Merck 0.45µm) using vacuum in all glass filtration system into 250ml acid washed conical flask. The filtered and 50ml of unfiltered surface water samples were each digested in 250ml acid washed conical flasks. Concentrated nitric acid (20ml) was added and brought to slow boiling before being evaporated on a hot plate to almost dryness. As needed, concentrated nitric acid was added to the mixture until the clear solution indicated that digestion was complete. The digest was filtered into a 50ml volumetric flask and was topped off with distilled deionized water **(Ewa *et al.*, 2013)**.

Sample analysis

Concentrations of lead, cadmium, mercury, arsenic, and chromium in the digested samples were determined using Atomic Absorption Spectrophotometry with a Shimadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) at the National Research Institute for Chemical Technology (NARICT) in Zaria, Nigeria.

Analytical quality assurance

Stringent quality control measures were implemented to ensure the accuracy and reliability of the obtained results. Throughout the study, samples were handled with care to prevent any cross-contamination. Glass wares were thoroughly cleaned, and distilled deionized water was employed consistently. Analytical grade HNO_3 (Riedel-deHaen, Germany) was used. To assess the reliability of the analytical method used for metal determination, a blank sample and a set of combined standards were run with each batch of samples. This allowed the detection of any background contamination and ensured consistency between batches. To further validate the accuracy of the results, Standard Reference Materials (Lichens coded IAEA-336) were also subjected to the same digestion and analysis procedure. The values obtained from the analysis were compared with the certified reference values of the elements determined, thus, verifying the reliability of the analytical method used.

Statistical analysis

A statistical test of significance was performed on the data collected. Independent t-test was used to compare metals levels in surface water between Calabar River and the Great Kwa River, as well as between wet and dry seasons. Probabilities less than 0.05 were considered to be significant. Statistical analysis was carried out using IBM SPSS version 23 for windows.

Metal pollution indices (MPIs)

Water quality index is essentially, a mathematical model used to calculate a single value from multiple water quality parameter analysis **(Edet & Offiong, 2002; Poshtegal & Mirbagheri, 2019)**. The index results represent the water quality status of the water body with respect to the parameters evaluated in the sample location. In this study, heavy metal

pollution index and heavy metal evaluation index, which provide an overview of water quality with respect to heavy metals levels, were used to estimate the water quality index.

- ***Heavy metal pollution index (HMPI)***

Heavy metal pollution index was determined following the method of **Poshtegal and Mirbagheri (2019)**, while quality parameters (Q_p) were calculated according to equation 1

$$Qp = \sum_{p-1}^{n} \left(\frac{Ap-Ip}{S-Ip}\right) x100 \quad \text{..... (1)}$$

Where, Ap is the average values of metals determined; S is the standard permissible value for the metals (In this study, WHO drinking water quality standards were used); and Ip is the ideal values for the metals (ideal values for toxic metals considered in this study were taken as zero). The unit weight (Wp) was determined by taking the reciprocal of the standard permitted value S of each metal under consideration. The subsequent calculation of the water quality index involved summing the products of the parameter qualities (Qp) and the unit weights (Wp), then dividing by the sum of the unit weights (Wp), as shown in equation 2

$$HMPI = \frac{\sum_{p-1}^{n} QpWp}{\sum_{p-1}^{n} Wp} \quad \text{..... (2)}$$

- ***Heavy metals evaluation index (HEI)***

Heavy metals evaluation index was determined according to **Igbemi *et al.* (2019)** using equation 3

$$HEI = \sum_{i=1}^{n} Hc/Hmac \quad \text{..... (3)}$$

Where, Hc is the concentration of each metal measured and Hmac the maximum admissible concentration of the metal under consideration.

Distribution of metals in surface water between dissolved phase and suspended particulate matter phase

The distribution of metals in surface water between dissolved phase and suspended particulate matter phase was done following **Hamad *et al.* (2012)**. Metals contents of filtered water (< 0.45µm) was used as proxy for dissolved metals concentration in surface water. Unfiltered digested water was used to estimate the total metal concentration in water. The particulate matter phase was calculated by subtracting the dissolved metal concentrations from the total metal concentrations

Partition coefficients of metals in surface water

The partition coefficient, which is defined as the ratio of heavy metals between the suspended particulate matter and dissolved concentrations in the water column, was calculated using Equation 4:

Kp (L/kg) = SPM (mg/kg) / W (mg/L)..... (4)

Where, Kp is the partition coefficient; SPM is the concentration of metals in the suspended particulate matter (a particulate form of the metals); and W is the concentration of metals dissolved in water (the dissolved form of the metal).

RESULTS

1. Analytical quality assurance

To ensure the accuracy and precision of the analytical process, a standard reference material (Lichen, IAEA-336) was analyzed in the same manner as the samples. The analyzed values were within the acceptable limits of the certified reference values of the elements, indicating the reliability of the method used (Table 1).

Table 1. Results of the analysis of the reference material (Lichen IAEA - 336) in comparison with the certified reference values

Metals mg/kg	Pb	Cd	Hg	As	Cr
Analyzed value	4.8	0.1046	0.19	0.63	1.00
Reference value	4.3-5.5	0.100-0.134	0.16-0.24	0.55-0.71	0.89-1.23

2. Metals concentration in surface water of Great Kwa River and Calabar River

Results obtained for dissolved, suspended particulate matter and total lead, mercury, cadmium and arsenic contents of the Great Kwa and Calabar rivers for and dry seasons are presented in Tables (2, 3), respectively.

2.1 Total metal concentration in surface water

Tables (2, 3) indicate that, the ranges of total metals concentrations were 0.212 mg/kg - 0.494 mg/kg, 0.011-0.053 mg/kg, 0.004-0.008 mg/kg, and 0.014-0.049 mg/kg for Pb, Cd, Hg and As, respectively. The total metal concentrations of the metals in the surface water of Calabar River were significantly ($P \leq 0.05$) higher than the Great Kwa River for both dry and wet seasons, total arsenic concentration during wet season being the only exception.

All the metals displayed significant ($P \leq 0.05$) seasonal variation in total metal concentrations in Calabar River, with dry season values being significantly higher than wet season values. Only total mercury and arsenic concentrations of the Great Kwa River displayed significant difference between dry and wet seasons at 95% confidence level.

2.2. Water quality index of surface water of Great Kwa and Calabar Rivers

2.2.1 Heavy metal pollution index (HMPI)

Table (4) indicates that the average HMPI of the surface water of the Great Kwa and Calabar rivers were 70.86 for Esuk Atu and 112.13 for Esuk Anantigha (Great Kwa River),

and 132.58 for NPA Jetty and 144.08 for Esuk Nsidung (Calabar River). The average heavy metals pollution index of Calabar River was significantly higher than Great Kwa River.

2.2.2 Heavy metal evaluation index (HEI)

The average HEI values (Table 4) were 34.815 for Esuk Atu and 49.045 for Esuk Anantigha (Great Kwa River), and 58.75 for NPA Jetty and 62.835 for Esuk Nsidung (Calabar River). The average HEI of Calabar River was significantly higher than Great Kwa River.

3. Distribution of metals concentration between dissolved phase and suspended particulate matter phase

The ranges of metal concentrations in dissolved phase of the surface water of the two rivers for both wet and dry season were 0.042-0.127 mg/l, 0.001- 0.009 mg/l, 0.001 – 0.002 mg/l and 0.001 – 0.009 mg/l for lead, cadmium, mercury and arsenic, respectively. The ranges of metal concentrations in the suspended particulate matter phase of the surface water of the two rivers for both wet and dry seasons were 0.175 -0.407 for lead, 0.010 – 0.044 for cadmium, 0.003 – 0.006 mg/l for mercury, 0.013 – 0.042 mg/l for arsenic (Tables 2 and 3).
The percentages of Pb, Cd, Hg and As in dissolved phase of the surface water of the two rivers ranged from 14.80 – 23.54%, 8.88 - 20.00%, 16.67 – 20.00% and 6.45 – 17.24%, respectively (Table 5).

4. Particulate coefficients (Kp) of metals in surface water

Partition coefficients (Log Kp) of the metals were of the ranges 3.27-5.76 for lead, 4.00-10.00 for cadmium, 2.5-5.00 for mercury and 4.80-14.5 for arsenic (Table 6).

Table 2. Dissolved, suspended particulate matter and total lead, cadmium, mercury, and arsenic concentrations of the surface water of Great Kwa River and Calabar River during dry season (mg/l)

Metal	Month	Total Metal Concentration				Dissolved Metal Concentration				Suspended Particulate Metal concentration			
		ESUK ATU	ESUK ANANTIGHA	NPA JETTY	ESUK NSIDUNG	ESUK ATU	ESUK ANANTIGHA	NPA JETTY	ESUK NSIDUNG	ESUK ATU	ESUK ANANTIGHA	NPA JETTY	ESUK NSIDUNG
Lead	October	0.231	0.354	0.467	0.467	0.046	0.054	0.069	0.102	0.185	0.300	0.407	0.374
	January	0.241	0.369	0.453	0.479	0.054	0.079	0.098	0.11	0.187	0.290	0.355	0.369
	March	0.343	0.387	0.481	0.494	0.065	0.072	0.091	0.126	0.278	0.315	0.390	0.368
	Mean±SD	0.272±0.05	0.370±0.013	0.467±0.01	0.480±0.01	0.055±0.01	0.068±0.01	0.086±0.01	0.113±0.01	0.217±0.01	0.302±0.01	0.384±0.02	0.370±0.01
	Range	0.231-0.494				0.046-0.127				0.185-0.407			
Cadmium	October	0.014	0.032	0.044	0.049	0.001	0.004	0.004	0.006	0.013	0.028	0.040	0.043
	January	0.023	0.039	0.048	0.053	0.004	0.004	0.007	0.009	0.019	0.035	0.039	0.044
	March	0.028	0.048	0.049	0.052	0.004	0.006	0.007	0.009	0.024	0.042	0.042	0.043
	Mean±SD	0.022±0.01	0.041±0.01	0.047±0.01	0.051±0.01	0.003±0.01	0.005±0.01	0.006±0.01	0.008±0.01	0.019±0.01	0.035±0.01	0.040±0.01	0.043±0.01
	Range	0.014-0.053				0.001-0.009				0.013-0.044			
Mercury	October	0.005	0.005	0.005	0.006	0.001	0.001	0.001	0.002	0.004	0.004	0.004	0.004
	January	0.005	0.005	0.006	0.007	0.001	0.001	0.001	0.002	0.004	0.004	0.005	0.005
	March	0.006	0.006	0.007	0.008	0.001	0.001	0.002	0.002	0.005	0.005	0.005	0.006
	Mean±SD	0.005±0.01	0.005±0.01	0.006±0.01	0.007±0.01	0.001± 0.00	0.001±0.00	0.013±0.01	0.002± 0.00	0.004±0.00	0.004±0.00	0.005±0.00	0.005±0.00
	Range	0.005-0.008				0.001-0.002				0.004-0.006			
Arsenic	October	0.022	0.028	0.038	0.042	0.002	0.002	0.005	0.006	0.020	0.026	0.033	0.042
	January	0.026	0.033	0.043	0.054	0.002	0.002	0.006	0.009	0.024	0.031	0.037	0.042
	March	0.034	0.033	0.049	0.058	0.005	0.002	0.007	0.009	0.029	0.031	0.042	0.042
	Mean±SD	0.027±0.01	0.031±0.01	0.043±0.01	0.051±0.01	0.003±0.01	0.002±0.00	0.006±0.01	0.008±0.01	0.024±0.01	0.029±0.01	0.037±0.01	0.042±0.01
	Range	0.022-0.049				0.002-0.009				0.020-0.042			

Table 3. Dissolved, suspended particulate matter and total lead, cadmium, mercury, and arsenic concentrations of the surface water of Great Kwa River and Calabar River during the wet season (mg/l)

Metal	Month	Total Metal Concentration				Dissolved Metal Concentration				Suspended Particulate Metal (SPM) concentration			
		ESUK ATU	ESUK ANANTIGHA	NPA JETTY	ESUK NSIDUNG	ESUK ATU	ESUK ANANTIGHA	NPA JETTY	ESUK NSIDUNG	ESUK ATU	ESUK ANANTIGHA	NPA JETTY	ESUK NSIDUNG
Lead	October	0.273	0.354	0.358	0.376	0.046	0.047	0.059	0.072	0.227	0.307	0.299	0.304
	January	0.231	0.321	0.325	0.356	0.042	0.054	0.048	0.061	0.189	0.267	0.277	0.295
	March	0.212	0.217	0.311	0.332	0.037	0.052	0.041	0.062	0.175	0.165	0.270	0.270
	Mean±SD	0.239±0.02	0.297±0.05	0.331±0.02	0.355±0.02	0.041±0.01	0.051±0.01	0.049±0.01	0.065±0.01	0.197±0.02	0.246±0.05	0.282±0.01	0.290±0.01
	Range	0.212-0.376				0.042-0.0.072				0.175-0.307			
Cadmium	October	0.021	0.039	0.044	0.049	0.004	0.004	0.005	0.005	0.017	0.035	0.039	0.044
	January	0.013	0.031	0.038	0.043	0.003	0.002	0.003	0.004	0.010	0.029	0.035	0.039
	March	0.011	0.028	0.034	0.042	0.001	0.002	0.003	0.004	0.010	0.026	0.031	0.038
	Mean±SD	0.015±0.01	0.033±0.01	0.039±0.01	0.045±0.01	0.003±0.01	0.003±0.00	0.004±0.00	0.004±0.00	0.012±0.01	0.030±0.01	0.035±0.01	0.040±0.01
	Range	0.011-0.049				0.001-0.005				0.010-0.044			
Mercury	October	0.004	0.005	0.005	0.005	0.001	0.001	0.001	0.002	0.003	0.004	0.004	0.003
	January	0.004	0.004	0.005	0.006	0.001	0.001	0.001	0.001	0.003	0.003	0.004	0.005
	March	0.004	0.004	0.004	0.006	0.001	0.001	0.001	0.001	0.003	0.003	0.003	0.005
	Mean±SD	0.004±0.00	0.004±0.00	0.005±0.00	0.006±0.00	0.001±0.00	0.001±0.00	0.001±0.00	0.001±0.00	0.003±0.00	0.0030.00	0.004±0.00	0.004±0.00
	Range	0.004-0.006				0.001-0.002				0.003-0.005			
Arsenic	October	0.025	0.028	0.036	0.034	0.002	0.002	0.005	0.006	0.023	0.026	0.031	0.028
	January	0.022	0.024	0.027	0.025	0.002	0.002	0.004	0.005	0.020	0.022	0.023	0.020
	March	0.014	0.023	0.023	0.028	0.001	0.001	0.003	0.004	0.013	0.022	0.020	0.024
	Mean±SD	0.020±0.01	0.025±0.01	0.029±0.01	0.029±0.01	0.002±0.00	0.002±0.00	0.004±0.00	0.005±0.00	0.019±0.01	0.023±0.00	0.025±0.00	0.024±0.00
	Range	0.014-0.036				0.001-0.006				0.013-0.031			

Table 4. Heavy metals pollution index (HMPI) of the surface water of Great Kwa and Calabar Rivers

	Heavy Metals Pollution Index (HMPI)				**Heavy Metals Evaluation Index (HEI)**			
	Great Kwa River		Calabar River		Great Kwa River		Calabar River	
	Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nsidung	Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nsidung
Dry Season	79.32	124.30	149.84	159.50	38.06	54.06	67.67	71.27
Wet Season	62.40	99.97	115.32	128.67	31.57	44.03	49.83	54.4
Average	70.86	112.13	132.58	144.08	34.815	49.045	58.75	62.835

Table 5. Percentage distribution of Pb, Cd, Hg and As in dissolved phase of the surface water of Great Kwa and Calabar Rivers

Metal	**Dry Season**								**Wet Season**							
	Esuk Atu		Esuk Anantigha		NPA Jetty		Esuk Nsidung		Esuk Atu		Esuk Anantigha		NPA Jetty		Esuk Nsidung	
	Dissolved	SPM	Dissolved	SPM	Dissolved	SPM	Dissolved	SPM	Dissolved	SPM	Dissolved	SPM	Dissolved	SPM	Dissolved	SPM
Lead	20.20	78.80	18.79	81.63	18.42	81.88	23.54	76.46	17.15	82.85	17.17	82.83	14.80	85.20	18.30	81.70
Cadmium	13.64	86.36	12.19	87.81	12.77	87.23	15.69	84.31	20.00	80.00	9.09	90.91	10.26	89.74	8.88	91.12
Mercury	20.00	80.00	20.00	80.00	21.66	78.34	28.57	71.43	25.00	75.00	25.00	75.00	20.00	80.00	16.67	83.33
Arsenic	11.11	88.89	6.45	93.55	13.95	86.05	15.69	84.31	10.00	90.00	8.00	92.00	13.79	82.21	17.24	82.76

Table 6. Partition coefficient (Log Kp) of heavy metal in the surface water of Great Kwa and Calabar Rivers

Metal	Dry Season				Wet Season			
	Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nsidung	Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nsidung
Lead	3.95	4.44	4.87	3.27	4.81	4.82	5.76	4.46
Cadmium	6.33	7.00	6.67	5.75	4.00	10.00	8.75	10.00
Mercury	4.00	4.00	5.00	2.50	3.00	3.00	4.00	4.00
Arsenic	8.00	14.50	6.17	5.25	9.50	11.50	6.25	4.80

DISCUSSION

1. Metals concentrations in surface water of Great Kwa and Calabar rivers

1.1 Total metal concentration in surface water

The total lead concentration of the surface water of both rivers were above the Nigeran Drinking Water Quality Standards (NDWQS), World Health Organization (WHO) guidelines for drinking water quality and the United State Environment Protection Agency (UN-EPA) drinking water standards/health advisories of 0.01mg/l **(NSDWQ, 2007; WHO, 2011; USEPA, 2011)**. Measured concentrations were also above toxicant guidelines for protecting aquaculture species in both fresh and marine water of between <1 and 7µg/ l, but below the Australia and New Zealand agricultural irrigation long term trigger value (LTV) of 5mg/ land short term trigger value (STV) of 2mg/ l **(ANZECC, 2000)**. The LTV is the maximum concentration of a given contaminant that can be tolerated for over a century of irrigation, determined by irrigation loading calculations. The STV, on the other hand, is the maximum concentration of a contaminant that can be tolerated for a short period (20 years). It is also based on the assumption of maximum irrigation loading to soil as in the case of LTV **(ANZECC, 2000)**. Higher ranges of mean total lead concentrations (0.72±0.002 - 0.99±0.002 mg/kg and 0.78±0.002 - 0.95±0.002 mg/kg) were reported for petroleum impacted river (Warri River) in Niger-Delta, Nigeria for dry and wet seasons, respectively **(Owamah, 2013)**. Lower ranges of mean total lead concentrations (0.17±0.001 - 0.20±0.001mg/kg and 0.10±0.001 - 0.18±0.001mg/kg) were also reported for non-petroleum impacted river (Ikpoba River) in Niger Delta, Nigeria for dry and wet seasons, respectively **(Owamah, 2013)**. **Ewa *et al.* (2013)** reported lead levels in surface water of Calabar River below detectable limit.

Total cadmium concentration of surface water of both Calabar River and Great Kwa River (0.014-0.053mg/ l) exceeded the Nigeran drinking water quality standards and world health organization drinking water quality guidelines of 0.003mg/ l and the US-EPA drinking water standards/health advisory of 0.005mg/ l **(NSDWQ, 2007; USEPA, 2011; WHO, 2011)**. The Australia and New Zealand long-term trigger value of 0.01mg/ kg and short-term trigger value of 0.005mg/ kg were also exceeded **(ANZECC, 2000)**. Measured concentrations were also above guidelines for the protection of aquaculture species for both fresh (0.2-1.8µg/ l) and marine (0.5-5.0µ/ l) waters **(ANZECC, 2000)**. Mean cadmium concentrations (0.49±0.001 - 0.52±0.001 and 0.22±0.001 - 0.39±0.002) were reported for petroleum impacted river (Warri River) in Niger-Delta, Nigeria, for dry and wet seasons, respectively **(Owamah, 2013)**. Mean cadmium concentrations ranging from 0.02±0.001 - 0.05±0.002 and 0.01±0.001 - 0.04±0.001 were also reported for non-petroleum impacted Ikpoba River in Niger-Delta Nigeria, for dry and wet seasons,

respectively **(Owamah, 2013)**. **Ewa *et al.* (2013)** reported that cadmium levels in surface water of Calabar River was below detectable limit.

Total mercury concentration of surface water of both rivers (0.005-0.008 mg/l) was also above the Nigeran drinking water quality standards of 0.001mg/ l and the acceptable limit of 1µg/ l for the protection of aquaculture species for both fresh and marine water, while being below world health organization drinking water quality guidelines of 0.006mg/ l for inorganic mercury and the US-EPA drinking water standards/health advisory of 0.2mg/ l **(ANZECC, 2000; NSDWQ, 2007; USEPA, 2011; WHO, 2011)**. Total mercury concentrations were above LTV and STV of 0.002mg/ kg **(ANZECC, 2000)**. Higher ranges of total mercury concentrations (0.12±0.001 - 0.13±0.001 and 0.10±0.003 - 0.12±0.001) were reported for petroleum impacted water (Warri River) in Niger-Delta, Nigeria for dry and wet seasons, respectively **(Owamah, 2013)**. Total mercury concentrations ranging from 0.17±0.001 - 0.20±0.001 and 0.10±0.001 - 0.18±0.001 were reported for non-petroleum impacted Ikpoba River in Niger-Delta Nigeria for dry and wet seasons, respectively **(Owamah, 2013)**. **Ewa *et al.* (2013)** reported that mercury levels in surface water of Calabar River was below detectable limit.

Moreover, total arsenic concentration of surface water of Great Kwa and Calabar rivers (0.022-0.049 mg/l) were above Nigerian drinking water quality standards, world health organization drinking water quality guidelines and the US-EPA drinking water standards/health advisory of 0.001 mg/l **(NSDWQ, 2007; USEPA, 2011; WHO, 2011)**. Total arsenic concentrations were found to be below the Australia and New Zealand agricultural irrigation LTV and STV of 0.0mg/ l and 2.0mg/ l, respectively **(ANZECC, 2000)**. Measured concentrations of total arsenic were within the acceptable limit of 50µg/ l and 30µg/ l for the protection of aquaculture species for both fresh and marine water, except in the dry season **(ANZECC, 2000)**. **Ewa *et al.* (2013)**, reported that arsenic levels in surface water of Calabar River was below detectable limits.

The findings of this study implies that the surface water of Great Kwa and Calabar rivers is not fit for domestic, aquaculture and agricultural irrigation purpose with respect to lead, cadmium, mercury and arsenic intoxication. The higher concentration of total metals observed at the Calabar River compared to the Great Kwa River could be attributed to higher anthropogenic activities. The Calabar River catchment is highly urbanized with most of the municipal surface run-off drained into it compared to the more prestine Great Kwa River catchment. Periodic dredging of the Calabar River in support of the Calabar Port may also contribute to remobilization of pollutants from sediment into the water column. The observed seasonal variation in metals concentrations with higher dry season values could be due to reduction in water levels resulting from low discharge of fresh water into the lower reaches of the rivers during dry season. The rivers are therefore more influenced by sea water during dry season.

1.2 Water quality index of surface water of Great Kwa and Calabar rivers

1.2.1 Heavy metal pollution index (HMPI)

Heavy metal pollution index was explained following the method of **Odiba *et al.* (2014)**. Ratings of water quality assigned for the water quality index values shown in Table (7) was used to explain heavy metals pollution index. The water quality index values indicate that, surface water of both Great Kwa and Calabar rivers ranged from bad to not fit for drinking purposes. This further stress the danger, exceedance of WHO, NDWQS and US-EPA drinking water quality standards by the toxic metal posed to public health.

Table 7. Water quality index and water quality status

Water Quality Index	Water Quality Status
0-25	Excellent
26-50	Good
51-75	Bad
76-100	Very bad
>100	Not fit for drinking

Source: **Odiba *et al.* (2014)**.

1.2.2 Heavy metal evaluation index (HEI)

The heavy metals evaluation index categorizes water quality into three distinct classes, according to the degree of contamination: low contamination (HEI < 10), medium contamination (10 < HEI < 20) and high contamination (HEI > 20) **(Maskooni *et al.*, 2020)**. Water quality status of Great Kwa and Calabar rivers, therefore, belongs to the class 'high contamination'. According to the classification system by **Maskooni *et al.* (2020)**, the water quality status of both rivers falls under the "high contamination" class, indicating a significant level of contamination.

2. Distribution of metals concentration between dissolved phase and suspended particulate matter phase

Table (6) shows that all the metals were predominant in suspended particulate matter phase. This indicates that, filtering surface water obtained from the two rivers before drinking could reduce human health risk significantly. It should be noted that metal toxicity and/or bioavailability is dependent mainly on chemical speciation. The specific physico-chemical form of the metals present in the dissolved phase should therefore, be

investigated to ascertain safety after filtration. The corresponding range of percentages of the metals in the suspended particulate matter phase were 76.21 – 85.20% for lead, 80.00 – 91.12% for cadmium, 71.43 – 83.33% for mercury and 82.76 – 93.55% for arsenic. These high percentages suggest that SPM could be a good indicator of Pb, Cd, Hg and As pollution and that it plays a vital role in the transport of the metals in both Calabar and Great Kwa Rivers. The study was carried out during ebb tide, which is usually associated with high total suspended solids (TSS). This may account for the high concentration recorded for metals in the SPM phase. Furthermore, the upper reaches of the two rivers are agriculturally dominated, and the areas just before the sampling points have significant industrial and other anthropogenic influence. The difference in the concentration of all the metals investigated in the dissolved phase between the surface water of Great Kwa and Calabar rivers were significant ($P \leq 0.05$) in the dry season, The Calabar River being significantly higher than Great Kwa River. The differences were, however, not significant at 95% confidence limit in the wet season. The higher levels of dissolved metals observed in Calabar River is in line with the higher levels of total metal concentration recorded for the river and attributed to higher anthropogenic influence. The difference was however not significant in the wet season due to the increased volume of water as a result of high precipitation and discharge from the upper reaches of the rivers and their tributaries. Both the Great Kwa and Calabar rivers displayed significant ($P \leq 0.05$) seasonal variations in the concentration of lead in the dissolved phase, dry season concentrations being higher than wet season. The two rivers did not display significant ($P \geq 0.05$) seasonal variation in the concentration cadmium, mercury and arsenic present in the dissolved phase of the surface water. Similarly, differences in concentrations of lead, cadmium and arsenic in the particulate matter phase between Calabar River and Great Kwa River were significant ($P \geq 0.05$) in the dry season, however, only the differences in lead and cadmium were significant in the wet season. Great Kwa River did not display significant seasonal variation in the concentration any of the metals in suspended particular phase while Calabar River displayed significant variation in the concentration of lead and arsenic.

3. Particulate coefficients (Kp) of metals in surface water

One of the key tools used to effectively assess potential migration of pollutant in the liquid phase that is in contact with suspended mater and sediment is a partition coefficient. It describes in quantitative terms, the partitioning of the pollutants in the water column between the dissolved phase and suspended particulate matter phase, and provides significant information for risk assessment. To better understand the potential mobilization of Pb, Cd, Hg and As between the liquid and solid phases of the surface water, the partition coefficients of the metals were calculated. The results of Kp were interpreted according to **Al-Obaidy *et al.* (2016)**, as follows: Log (Kp) > 5 indicates metal or compounds with the affinity to bind or remain in solid phase (suspended

particulate matter); values in the range of 3< log (Kp) < 4 corresponds to metals or compound more easily released from solid phase (towards the liquid phase) and Log (Kp) < 3 indicates metals present in the liquid phase preferentially. The values of partition coefficients in the study revealed that cadmium and arsenic displayed affinity to bind and remain preferentially in suspended particulate matter phase, while lead and mercury showed tendency to be more easily mobilized from suspended particulate matter phase towards the dissolved phase. This findings implies that, studied metals were predominant in suspended particulate matter phase and that, while cadmium and arsenic bind and remain preferentially in SPM phase, lead and mercury were relatively more mobile, bioavailable, and hence more toxic. The dominance of studied metals in suspended matter phase suggests that filtering the water before application could reduce human health risk significantly. However, the risk potential is a function of the chemical form of the metals under prevailing environmental conditions. Chemical speciation of these metals in the two rivers and a comparative study of the partition coefficients between ebb tide and flood tide conditions could further provide valuable insights.

CONCLUSION

The total metal concentrations in the surface water of the Great Kwa and Calabar rivers were found to be above the Nigeran drinking water quality standards and world health organization guidelines for drinking water quality, with mercury being the only exception. The percentages of lead, cadmium, mercury, and arsenic concentrations in the dissolved phase were relatively low, indicating that these metals were predominantly present in the suspended particulate matter phase. The total, dissolved and SPM concentration of all the metals were significantly higher in Calabar River compared to Great Kwa River. The partition coefficient revealed that cadmium and arsenic have affinity to bind and remain preferentially in suspended particulate matter phase while lead and mercury are more easily mobilized from suspended particulate phase towards the dissolved phase. The study concludes that, surface water from the two rivers is not fit for domestic and agricultural purposes. However, filtering the water before use could reduce human health risk significantly. Further investigations into the chemical speciation of the metals in the two rivers is hereby recommended.

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Conflict of interest

The authors affirm that they do not have any conflicting interests

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