Chemical Science International Journal
17(4): 1-10, 2016; Article no.CSIJ.28499
Previously known as American Chemical Science Journal
ISSN: 2249-0205

SCIENCEDOMAIN *international*
www.sciencedomain.org

Assessment of Contamination Status of Bomu and Oginigba Rivers, Rivers State, Nigeria, Using Some Trace Metals and *Callinectes gladiator* as Indices

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Authors' contributions

This work was carried out in collaboration between both authors. The experiment was designed by author ACM who equally drafted the manuscript which was read and corrected by author OSE. Both authors finally read and approved the final manuscript as presented.

Article Information

DOI: 10.9734/CSIJ/2016/28499
Editor(s):
(1) Zygadlo Julio Alberto, Professor of Chemistry, National University of Cordoba, Argentina.
(2) Marcelo Daniel Preite, Department of Organic Chemistry, Pontifical Catholic University of Chile, Chile.
Reviewers:
(1) E. P. Yesodharan, Cochin University of Science and Technology, India.
(2) Anonymous, California State University, USA.
(3) En-Chih Chang, I-Shou University, Taiwan.
Complete Peer review History: http://www.sciencedomain.org/review-history/17339

Original Research Article

Received 22nd July 2016
Accepted 11th October 2016
Published 24th December 2016

ABSTRACT

Two Rivers: Bomu in Ogoniland and Oginigba in Port Harcourt all in Rivers State, Nigeria were strategically chosen to represent rivers in Rivers State that are prone to ecological degradation due to industrial activities. Their contamination status was assessed using trace metals in water, sediment and *Callinectes gladiator* (swimming crab). Water, sediment and crab samples were collected following standard procedures (APHA, 1975). They were prepared by acid digestion using 1:3:1 mixture of $HClO_4$, HNO_3 and H_2SO_4 acids and Buck Scientific Atomic Absorption Spectrophotometer and air-acetylene flames were used for the trace metals analysis. The results of water analysis showed ranges of concentration (mgL^{-1}) of trace metals as follows: Cu (1.089-3.327), Ni (2.997-3.897), Cd (<0.001), Cr (2.728-0.291), Zn (0.853-3.123) and Pb (0.369-1.198) in Bomu; Cu (0.692-2.019), Ni (3.389-4.693), Cd (<0.001), Cr (0.872-5.771), Zn (1.748-2.621) and Pb (0.642-0.999) in Oginigba. In the sediment, concentrations (*ppm*, dry weight) were: Cu (91.028-

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119.275), Ni (145.175-161.025), Cd (ND), Cr (119.725-144.275), Zn (143.200-243.350) and Pb (52.353-117.350) in Bomu; Cu (62.350-146.050), Ni (108.775-193.700), Cd (ND) Cr (92.350-162.575), Zn (182.725-285.775) and Pb (30.900-117.158) in Oginigba. Tissue analysis of *C. gladiator* gave concentrations (*ppm*, dry weight) for egg, exoskeleton and flesh as follows: Cu (45.215, 37.217 and 64.372), Ni (47.301,16.824 and 51.973), Cd (ND) Cr (64.222, 13.874 and 54.354), Zn (19.823, 13.801 and 56.421) and Pb (ND, 44.036, and 31.120) in Bomu; Cu (40.411, 15.203 and 66.580), Ni (33.402, 41.053 and 101.620), Cd (ND) Cr (28.131, 21.333 and 78.442), Zn (197.783, 17.680 and 87.510) and Pb (5.555, 3.055 and 7.658) in Oginigba. There were no significant ($p>0.05$) variations in the heavy metal concentrations between the two rivers with regard to water and sediment. However, concentrations of heavy metals in the two rivers columns seemed to have been much depleted by rapid sedimentation in the bottom sediment. The water and sediment analyses revealed largely anthropogenic trace metal enrichment that exceeded both national and international limits in most of the cases with exception of Pb in Oginigba River, and Cu and Pb in the sediment. The observed heavy metal concentrations of Cu, Ni and Zn in the tissues of *C. gladiator* also classified the organism as a good bio-indicator for monitoring trace metals pollution of these waterbodies.

Keywords: Assessment; trace metals; contamination status; Oginigba; Bomu Callinectes gladiator.

1. INTRODUCTION

Trace metals are released into the environment as a result of wide range of industrial activities. These metals enter the aquatic environments through direct discharges into both freshwater and marine ecosystems or through indirect routes such as dry and wet discharges and land run-off. In assessing such metal loads in some environmental segments, [1] determined As, Au, Hg, Mn, Ni, Pb, Sb, and Zn in sediment and algae from River Niger and the Nigerian Atlantic Coastal waters. The measured concentrations of the metals were in both cases higher in the sediment than in the water. A similar trend was observed with algae.

The petroleum industry is major source of trace metals such as V, Ni, Fe, Al, Na, Cu and U in the Niger Delta area of Nigeria. Studies [2,3] have shown that metals such as cadmium, barium, lead, copper, vanadium, iron and mercury are commonly found in wastes generated from production operations in the petroleum industry. [4], reported that 5,500 tons of wastes was produced per year in Rivers State. The petroleum industry was the major contributor in the generated waste in the State. Thus, exposing rivers and creeks in these areas to risk of contamination from petroleum and associated pollutants. [5,6] have also identified incidences of oil spillages and seepages in addition to gas flaring as potential sources of heavy metals and mineral hydrocarbons (polyaromatic hydrocarbons, PAHs) to aquatic and terrestrial environments, which ultimately settle into sediment matrices. More so, there are air-borne particulates derived from fossil fuel combustion contain heavy metals [7]. These pollutants are potentially deleterious to fauna and flora as well as devalue the integrity of waterbodies.

However, quantification of contaminants in natural waters often faces difficulties. Apart from variations with time owing to certain natural and anthropogenic factors, there is the lack of useful connection between the concentrations of contaminants in the system and their bioavailability [8]. Nevertheless, the use of water, sediment and biota as indices has been key in evaluating environmental problems. As a result, these segments are periodically analyzed to assess, monitor and control aquatic pollution [9,10,11,12]. The greatest advantage of the use organisms to monitor pollution lies in the ability of such organisms to accumulate and sequestrate contaminants in such manner that they can be used as biomonitors without recourse to assumptions employed in water and sediment analyses [13].

Two rivers of interest (Bomu River in Ogoniland and Oginigba River in Port Harcourt) were strategically chosen for the present study for the following reasons:

- Shell entered Ogoniland, a rural community in the Niger Delta state of Rivers, Nigeria in the late 1950s. Among the numerous oil facilities established in Ogoniland for sucking the crude oil buried underneath the soil was, Bomu Oil Well 2 located in a landmass said to be jointly owned by Kegbara Dere and Beera in the

Gokana LGA of Rivers State. There had been oil spillages and seepages that have so destroyed land and crops that the entire Gokana people may feel the impact of the spillage as a result of the environmental or atmospheric and water pollution [14].

- Oginigba plays host to a number of industrial activities along the Trans-Amadi industrial layout. Some of these industries such as PABOD breweries, West African Glass Industries, Mitchelin Nigeria Ltd, Halliburton oil Servicing company Coca Cola bottling company etc, generate wastes that have the potentials to disturb the ecological balance of the ecosystem when discharged into the Oginigba River [15].

Although, because of the Ogoni struggle for self-determination over the years, Shell (SPDC) had since suspended operations, but their facilities continue to be a threat to both the people and their environment. Also, some of the companies in Trans-Amadi too, like Mitchelin have since folded up, but new ones are also springing up and the long term effects of the vestiges of the operations of those that have closed cannot be overemphasized.

Environmental pollution monitoring programmes are developed in relation to problems of increasing gross and specific pollution in the environment [16]. In some instances, there were warnings that specific pollutants be evaluated periodically to determine their impact on the environment. In other cases, recommendations have suggested that it is important to monitor pollutants in water, sediments, as well as the body burden of contaminants in key or sentinel biota. Environmental pollution monitoring has thus been considered to consist of repetitive data collection for the purpose of determining trends in environmental parameters [17]. The environment and resources form the basis for development for any country. Therefore, there is need for the assessment of the current contamination status of the two rivers using some trace metals (Cu, Ni, Cd, Cr, Zn & Pb) and *Callinectes gladiator* (swimming crab) as indices of pollution of the chosen environments.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

Water samples were collected below the surface film from the two rivers at different points once a month for eight months from October, 2014 to May, 2015 with pre-rinsed 1-Litre plastic containers, and homogeneously mixed to make a composite for analysis of trace metals. Samples were treated with nitric acid prior to storage in order to maintain stable oxidation states of the metals in frozen condition, and also to avoid adsorption of the metals on the container. Sediment samples were collected at low tide by the grab method [18] using Eckman Grab Sampler from 3 to 4 locations. The samples were placed in polythene bags previously leached with dilute acid, and stored in the laboratory by freezing. *Callinectes gladiator* samples were collected by means of traps locally known as *ikata*. They were washed and rinsed with distilled water before being taken to the laboratory. Various sizes were selected among the number caught and per boiled in order to separate the egg tissue and also have the fleshy part intact. The exoskeleton, egg and fleshy tissues were separately prepared for replicate analyses from which means were obtained.

2.2 Sample Analysis

Each water sample was treated with a 1:3:1 mixture of $HC1O_4$, HNO_3 and H_2SO_4 acids and digested at 60℃ in a 250 ml Teflon bottle to near dryness. The digest was then placed in a steam bath for about 30 minutes and later filtered into a 50 ml standard volumetric flask by means of a Whatman No.1 (11 µm) filter paper. The filtrate was then made up to mark with distilled water for analysis. The concentrations of the trace metals were determined against serially diluted standards on a Buck Scientific Model 200 Å Atomic Absorption Spectrophotometer (AAS) equipped with air-acetylene [19].

Sediment samples were thawed and air-dried for trace metals at ambient temperature and sieved through 0.5 mm sieve. Two grams (2 g) of the air-dried sediment samples were weighed using a high precision micro scale Technovetro balance in a 100 ml conical flask. The digestion process for sediment samples (as in water) was at 60℃ for 3 hours to near dryness. 20 ml deionized water were added after the digest was allowed to cool to room at temperature and it was then filtered into a 50 ml volumetric flask using Whatman No.1 (11 µm) filter paper. The digest was made up to mark with distilled water and the concentrations of the trace metals were determined by a Buck Scientific model 200 Å Spectrophotometer equipped with air-acetylene flame [20].

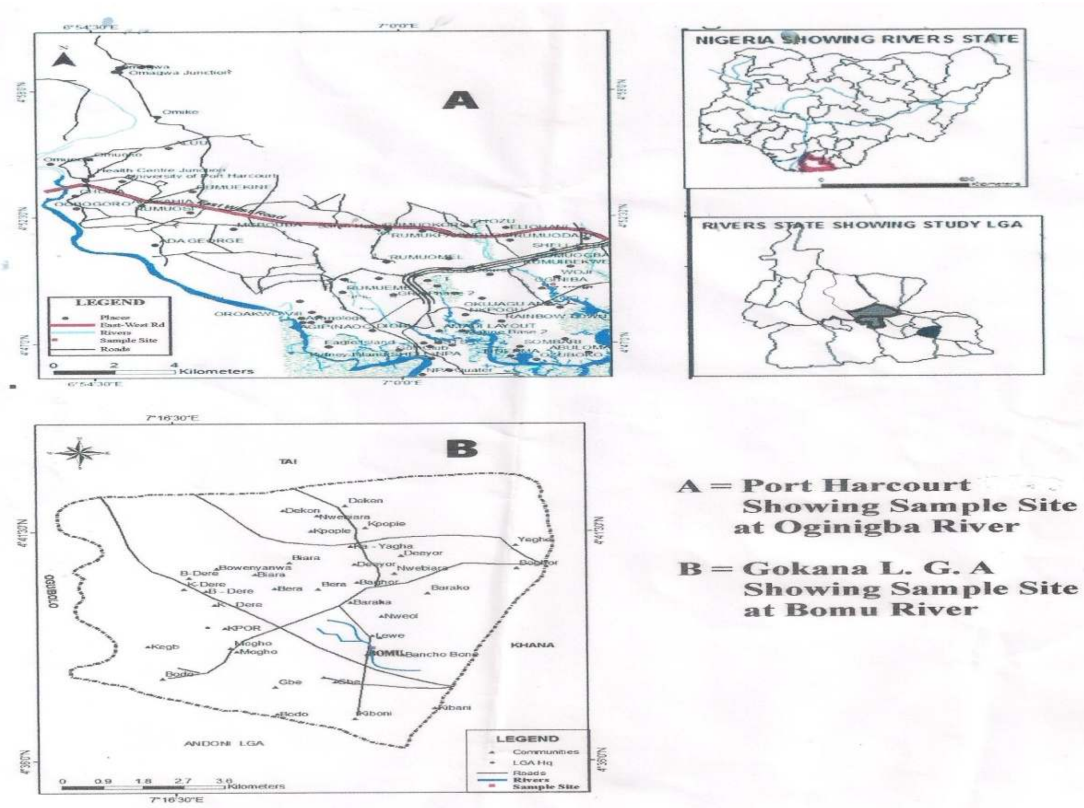

Fig. 1. Map showing Bomu and Oginigba Rivers

The exoskeletons of *Callinectes gladiator* samples were oven-dried to constant weight in an oven (Technicolor) at 105°C, crushed and homogenized. Two grams (2 g) of the oven-dried portion of the sample were weighed using high precision micro scale, placed in a digestion flask and also digested with acid mixtures employed for water and sediment samples at 60°C in a water bath until the content was near dryness. It was then set aside to cool, filtered as in the other cases into a 50 ml volumetric flask and made up to mark. The egg and flesh tissues were similarly prepared after dehydration to constant weight. The concentrations of Cu, Ni, Cd, Cr, Zn and Pb were then determined by AAS in same manner as for water and sediment.

Accuracy of sample manipulation was checked using samples of certified coastal marine sample (*CASS*-4) from sea water, marine sediment reference materials for trace metals and other constituents (*PACS*-2) from sediment and *DOLT*-2 (organism tissue) Matrix Certified Reference Material with known concentration for a certain metal [21]. For each batch of elemental analysis, an intra-run Quality Assurance Standard (1 mgL^{-1}, Multi-Element Standard Solution, Fisher Scientific) was checked for by reading deviation and accuracy of every 10 samples. Internal blanks were used to assess background noise interferences originating from sample manipulation and preparation. Blanks were processed exactly as respective regular sample. The recovery analysis using the reference standards gave results ranging from 89-95%.

In order to describe the data obtained, coefficients of variations in the metal concentrations in each river and paired sample *T*-test were performed on the platform of *SPSS* v 13.0 (*SPSS* Inc.).

3. RESULTS AND DISCUSSION

The results of detectable concentrations of trace metals are presented in their ranges, mean and coefficients of variation in Table 1, while those of the tissues of *Collinectes gladiator* and their legal limits are listed in Table 2. The bioaccumulation factors and percentage accumulations in the different tissues of *C. gladiator* are also shown in Tables 3 and 4 respectively.

Cadmium was not detectable in both water and sediment. However, chromium was found to have highest concentration of 3.164±0.075 mgL^{-1}, while lead was least with 0.472±0.053 mgL^{-1} in Oginigba River. The Oginigba sediment also recorded the highest concentration (213.315±60.214 ppm) for zinc and the least (60.301±29.122 ppm) came from lead at Bomu. In general, the concentrations of the trace metals were generally lower in the water than sediment. The standard deviations of the concentrations of the metal were expressed as percentages of the means. The coefficients of variations (CV) were calculated to describe their distribution pattern in the matrices of water and sediment of the two rivers and suggest plausible explanation to the observed trend. Paired sample *T*-test showed that there is no significant ($p>0.05$) variations between the metal concentrations from the two rivers with regard water and sediment. The result signifies somewhat similar characteristic features in the two rivers to mobilize these contaminants in quantity and quality. However, coefficients of variations of over 50% were obtained for copper, nickel and lead in Bomu sediment, and this may imply that these two metals are well dispersed in that column. The least coefficient of 2.37% was recorded in Oginigba River for chromium. With CV < 50% in the water column, it implies that the dispersion is lower in this column. The lower dispersion rate may have arisen from the rate of impute from the contamination channels.

Cadmium was not detected in all the tissues of *C. gladiator* (crab). Lead was not detected in the egg tissues of the crab of Bomu River. The highest (197.783 µg/g and lowest (3.033 µg/g) concentrations were found in egg and exoskeleton respectively in crab from Oginigba River. The exoskeleton generally had the least concentrations except for lead in the Bomu River crab and Ni in the Oginigba River crab (Table 2).

The bioaccumulation factors (BCF), which is ratio of metal level in tissue to metal levels in water were also calculated. The crab of Bomu River carried the highest body burden of 50.23 for copper in the flesh, representing 43.9% of the total accumulation of the tissues, and the exoskeleton recorded the least, 4.06, representing 10.5% for chromium (Tables 3 and 4). For the Oginigba crab however, the egg tissues had the highest and lowest BCF of 98.35 (65.3%) and 8.89 (22.0%) for zinc and chromium respectively. The accumulation factors are comparatively lower than those obtained by [22], who reported the factors in various tissues as ranging from 0.5-48.0 and attributed it to exposure of the species to high doses of the metals from industrial discharges.

Table 1. Ranges, means and coefficients of variation of concentrations (mgL^{-1}) in surface water and (ppm) in sediment of trace metals in Oginigba and Bomu, Rivers State, Nigeria

Trace metal	Bomu River	Oginigba River	Bomu sediment	Oginigba sediment
Cu	(1.089 – 3.327) 1.282 ± 0.557 43.45%	(0.692 – 2.019) 1.229 ± 0.083 6.75%	(91.025 -119.275) 66.301 ± 38.152 57.54%	(62.350 – 146.050) 74.610 ± 27.152 36.39%
Ni	(2.997 – 3.897) 3.069 ± 0.801 26.01%	(3.389 – 4.693) 3.119 ± 0.946 30.33%	(145.175 – 161.025) 148.919 ± 84.793 56.94%	(108.775 – 193.700) 151.219 ± 34.473 22.80%
Cd	<0.001 - -	<0.001 - -	<0.001 - -	<0.001 - -
Cr	(2.728 – 6.291) 3.106 ± 0.675 21.73	(0.872 – 5.771) 3.164 ± 0.075 2.37%	(119.725 – 144.275) 129.731 ± 30.483 23.50%	(92.350 – 162.575) 109.297 ± 21.843 19.98%
Zn	(0.853 – 3.123) 2.086 ± 0.999 47.89%	(1.748 – 2.621) 1.311 ± 0.092 7.02%	(143.200 – 243.350) 203.513 ± 63.101 31.01%	(182.725 – 285.775) 213.315 ± 60.214 28.23%
Pb	(0.369 - 1.198) 0.697 ± 0.134 19.22%	(0.642 – 0.999) 0.472 ± 0.053 11.23%	(52.353 – 117.350) 60.301 ± 29.122 57.54%	(30.900 – 117.158) 43.307 ± 21.521 49.70%

± Mean and Standard Deviation of 8 determinations

Table 2. Mean concentrations (24) of trace metals (µg/g) of tissue of *Callinectes gladiator* (Dry weight) and legal limits

Metals	Bomu River			Oginigba River			Legal Limits	
	Egg	Exoskeleton	Flesh	Egg	Exoskeleton	Flesh	FAO (2007)	WHO (2006)
Cu	45.215	37.217	64.392	40.411	15.203	66.580	20.00	30.0
Ni	47.501	16.824	51.973	33.402	41.053	101.620	-	0.5-1.0
Cd	ND	ND	ND	ND	ND	ND	-	-
Cr	64.222	13.874	54.354	28.131	21.333	78.442	13.00	50.0
Zn	19.823	13.807	56.421	197.783	17.680	87.510	75.00	100.0
Pb	ND	44.036	31.120	5.555	3.055	7.650	1.50	2.0

ND – No Detection

Table 3. Bioaccumulation factors of the metals in the tissues of *Callinectes gladiator*

Metal	Bomu River			Oginigba River		
	Egg	Exoskeleton	Flesh	Egg	Exoskeleton	Flesh
Cu	35.27	29.03	++50.23	32.88	12.37	54.17
Ni	12.95	45.59	14.17	10.71	13.16	32.58
Cd	-	-	-	-	-	-
Cr	18.80	+4.06	15.91	+8.89	6.74	24.79
Zn	9.50	6.62	27.05	++98.35	8.79	43.52
Pb	-	21.11	14.92	10.70	6.47	16.21

+ - Lowest accumulation; ++ - Highest accumulation

Table 4. Percentage accumulation of the metals in the tissues of *Collinectes gladiator*

Metal	Bomu River			Oginigba River		
	Egg	Exoskeleton	Flesh	Egg	Exoskeleton	Flesh
Cu	30.7	25.4	43.9	33.1	12.4	54.5
Ni	40.8	+14.5	44.7	19.0	23.3	57.7
Cd	-	-	-	-	-	-
Cr	48.5	10.5	41.0	22.0	16.7	61.3
Zn	22.0	15.3	++62.7	++65.3	+5.8	28.9
Pb	-	58.6	41.4	34.2	18.8	47.0

+ - Lowest percentage; ++ - Highest percentage

The concentrations of the metals in water (mg/L) and sediment (µg/g) were also compared with the results of the present study (Table 5). In the water column, copper, nickel chromium and zinc are above national standards [23,24], with exception of that of lead of Oginigba River. Similarly, nickel, chromium and zinc are above permissible limits in the sediment of both rivers, but copper and lead are below [25,26]. Table 2 compared the results of the present study with legal limits for the organism. Copper levels were higher than safe limits of 20-30 ppm [24,25] with exception of that in the exoskeleton of the Oginigba crab which recorded 15.203 ppm. Nickel and lead levels on the other hand, are higher than the standards in all the tissues. Chromium levels in the flesh of the crab of both rivers which were between 54.354 and 78.442 ppm are also above the 50 ppm recommended limits set) by [24]. Chromium in the egg of Bomu River was also above WHO limits. The concentration of zinc (197.783 ppm) in the egg of Oginigba crab was quite high judging from [25] limits of 75 ppm.

The results of the present study were also compared with similar studies in Nigeria (Table 6). The concentrations of the metals in the water of the present study are higher than those of other studies recently [27,28]. The concentrations of zinc which had a range of 0.2-12.7 mgL^{-1} in the report of [28] are however comparable. The trend is replicated in the sediment with exception of Pb which recorded 67.4 ppm [29,30]. Nevertheless, the concentrations in the organism are comparable with the findings of [31] and those of [32].

Table 5. Results of present study in surface water (mg/L) and sediment (µg/g) of the two rivers and legal limits

Metal	Surface water		Legal limits		Sediment		Legal limits	
	Bomu	Oginigba	WHO [24]	NESREA [23]	Bomu	Oginigba	FAO [25]	EWA [26]
Cu	1.282 ± 0.557	1.229 ± 0.083	1.000	-	66.301 ± 38.152	74.610 ± 27.152	250.0	-
Ni	3.069 ± 0.801	3.119 ± 0.946	-	1.000	148.919 ± 84.793	151.219 ± 34.473	-	45 - >210
Cd	<0.001	<0.001	-	-	<0.001	<0.001	-	-
Cr	3.106 ± 0.675	3.164 ± 0.075	0.050	-	129.731 ± 30.483	109.297 ± 21.843	11.0	-
Zn	2.086 ± 0.999	1.311 ± 0.092	0.010	-	203.513 ± 63.101	213.315 ± 60.214	123	-
Pb	0.697 ± 0.134	0.472 ± 0.053	0.050	0.050	66.301 ± 38.152	43.307 ± 21.521	-	>530

Mean ± SD; N = 8 determinations (October 2014- May 2015)

Table 6. Mean values of present study compared with those of other studies on water, sediment and *C. gladiator*

Metal	Water (mg/L)				Sediment (ppm)				*C. gladiator* (µg/g)			
	Present study		Others		Present study		Others		Present study		Others	
	Bomu	Oginigba	Marcus et al. [27]	Onojake et al. [28]	Bomu	Oginigba	Adekola & Saidu [29]	Marcus et al. [30]	Bomu	Oginigba	Patimah & Dainal [31]	Marcus et al. [32]
Cu	1.282	1.229	-	0.3-0.8	66.301	74.610	22.1	-	*48.941	*40.731	32-99	-
Ni	3.069	3.119	0.04	-	148.919	151.219	-	57.19	*38.766	*58.691	-	19.92
Cd	-	-	-	-	-	-	-	-	-	-	-	-
Cr	3.106	3.164	-	0.9-2.0	129.731	109.297	-	-	*44.150	*42.635	-	-
Zn	2.086	1.311	-	0.2-12.7	203.513	213.315	17.3	-	*30.017	*100.991	68-186	-
Pb	0.697	0.472	0.02	0.2	60.301	43.307	67.4	23.22	*37.578	*5.420	1.6-54	1.19

**- Means of the three tissues*

The choice of Bomu and Oginigba rivers for the present study was predicated on the possible long term effects of environmentally culpable activities that pervaded these areas over the years. Also, to ascertain if the effect of industrial activities in Port Harcourt can be comparable to those in the rural areas with regard to ecological degradation and contamination of the environment by pollutants. In this study, some trace metals and an organism, *Callinectes gladiator*, were used as indices. This trend which is usual with many studies in the past and present is attributable to the fact running natural waterbodies have capacity for self-purification due to constant renewal [33]. This is also in agreement with the observation of similar studies in Nigeria [34,35]. However, ecological perturbation [10,36,37] such as dredging activities, which are regular features in the studied area, are capable of remobilizing trace metals from the bottom sediment into the water column. This may account for the appreciable levels of the metals surpassing EPA maximum concentration limit.

The >50% coefficients of variations of the metals such as copper and nickel in the sediment signifying significantly wide dispersion underscores the role of sediment is the pollution scheme of rivers systems as repositories for physical debris that sink for contamination. According to [8] sediments can therefore be used to detect pollutants that escape water analysis, thereby providing information about critical sites of the river system. However, virtually all the detectable metals suggest a long time accumulation in the environment and therefore require regular monitoring to forestall or identify potential danger. The absence of significant ($p>0.05$) variations in the levels of the metals in the two river systems on the basis of the paired sample *T*-test is an indication of similarity in hydrodynamics and characteristic features of the studied area. Thus, the interplay of chemical and physical parameters in the two rivers may have resulted in physicochemical conditions that are capable of making it difficult to explain the effects on individual parameters.

Callinectes gladiator can feed deeper in water, and so, may be expected to pick up particulate trace metals by ingesting sediment particles, which are usually enriched with trace metals. The remarkable bioaccumulation factors for Cu in the flesh of the organism from the two rivers, Zn in the egg and flesh of the Oginigba crab and Ni in the exoskeleton of Bomu River crab imply that metal-laden particulates may have been ingested while feeding. This could be a further confirmation of a previous postulate that it is the dissolved forms of the trace metals that are effectively available to fish for bioaccumulation [38,39]. *Callinectes gladiator* can be considered not only as a good bioindicator of environmental pollution in these two rivers, but also the risk of its consumption (which is very common in the studied areas) could be potentially dangerous to the consumers.

4. CONCLUSION

The results obtained revealed similar patterns in the two rivers, with the concentrations higher in sediment than water. The water and sediments of Bomu and Oginigba Rivers in Rivers state are quite enriched with trace metals due especially to direct input of industrial and domestic wastes. Anthropogenic metal inputs are the major sources of trace metals in the sediment, water ad biota. Apart from the direct discharge of industrial and domestic wastes, immense volume of storm water runoff and tributary rivers entering the Bomu and Oginigba Rivers also play major roles in transporting metals originating from wastes discharge on land, especially during the rains, and these can lead to elevated levels. Rapid sedimentation seemed to have played major part too, in accumulating especially Ni, Cr and Zn in the bottom sediment thereby depleting the metals in the water column, even though in this study only Pb level in Oginigba River is below EPA maxima. The organism, *C. gladiator* appeared good for environmental pollution monitoring. However, it would be a better indicator for Cu, Ni and Zn. In general, all the metals point to pollution tendencies or implications except Cd in the water and sediment of both rivers and Cu and Pb in the sediment of both rivers.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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