

## Research Article

# Heavy Metals Concentrations in Shellfish and Sediments of Andoni River, Rivers State, Nigeria

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**Abstract**

The concentrations of seven heavy metals Fe, Zn, Mn, Cu, Pb, Cd and As were investigated in two aquatic organisms oyster (*Saccostrea cululata*) and cockle (*Andra granosa*) of Andoni Rivers system. Similar sizes of each species of the organisms were collected from five stations. The aquatic organisms were prepared and digested with a mixture of mineral acids, HNO<sub>3</sub> and HCl, while sediments by mixture of HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. They were analyzed with Atomic Absorption Spectrophotometer model 205. The results obtained showed that of the essential elements, Fe had the highest concentration of 2896.48±2083.11mg/Kg in sediment and the least concentration of 0.61 ± 0.302mg/Kg occurred in cockle. Of the non-essential elements Pb, Cd and As, As had the highest mean concentration of 0.7950 ±0.19mg/Kg, while Pb had the lowest concentration of 0.0680 ± 0.082mg/Kg in cockle. The results of ANOVA and Post Hoc Test (PHT) revealed significance difference at p<0.05 in the mean concentrations of some of the heavy metals. On the other hand, high pollution load index (PLI), were obtained at the stations. The consumer of shellfish in the area is at risk of being poisoned by heavy metals, as the values obtained were above standard set by WHO.

**Keywords:** Cockle, Oyster, Heavy metals, anthropogenic, shellfish**\*Correspondence**

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**Introduction**

The pathway and partitioning of toxic substances such as heavy metals and polyaromatic hydrocarbons (PAHs) into various environmental compartments has become a worldwide problem in recent years. This is due to increased industrialization, production of household and industrial wastes and construction of roads. The aquatic system is mostly affected due to transportation of these toxicants to aquatic environment, via erosion, deposition of particulate materials from atmosphere mining, and dumps leachates [1, 2].

The effluents from industries and household waste are carried in drains from the discharge point to the aquatic system. Among the environmental pollutants; heavy metals are of particular interest due to their potential toxic effect and ability to bio-accumulate in aquatic system. Some examples of metals are iron, magnesium, lithium, zinc, copper, chromium, nickel, cobalt, vanadium, arsenic, molybdenum, manganese, lead, mercury, and cadmium. All living organisms requires trace amount of some trace elements such as cobalt, copper iron, manganese, molybdenum, vanadium and zinc. However, excessive concentration of these metals can become detrimental to organisms [1, 3]. Metals in their natural or pure state do not cause any harm to life, the carcinogenic form of metals include; the hydroxide, oxides, silicates or sulfide which can be adsorbed to clay, silica or organic matter. Soluble form of metals is generally ions or unionized organometallic chelates or complexes [4, 5]. The solubility of trace metals in surface water is predominantly controlled by the water pH, the type and concentration of ligands on which the metal is adsorbed, oxidation state of the mineral component, and the redox environment of the system. According to [4] more than 90% of the trace metal load in the aquatic system is bound to suspended particulate matter and sediment. Sediment play a very important role in physico-chemical and ecological dynamics. Any change in toxic concentration of trace metal residues in sediments will affect the natural aquatic life support system.

Fish and other marine organisms contain protein and mineral salts that are essential for human life at low concentration. However, they become toxic at elevated concentrations, some other metals such as mercury, lead and cadmium are not required by humans at any known concentration. Heavy metals are non-biodegradable and can bio-accumulate along food chain producing their toxic effect at point far away from the source of pollution [6, 7]. The

adverse effect of heavy metals on human includes; hypertension, cancer, fatigue, depression, vomiting and mental disorder. In the Niger Delta area south-south Nigeria, there are lots of human activities such as vandalization of oil pipe line, loading and off loading of crude oil at wharfs, jetties and oil terminals. These activities in conjunction with effluents from industries pollute the environment with crude oil and other toxic substances [8]. Aquatic organisms such as oyster, periwinkle, fish, and crab are found in the area and the inhabitants of the area consume these aquatic organisms on daily bases. It has been recommended by [9] total diet studies (TDS) is one of the most effective method for assuring people that they are not exposed to unsafe levels of toxic chemicals through food. As a result, it becomes necessary to

- Determine the level of heavy metals Fe, Zn, Pb, Cd, As Cu and Mn in two species of aquatic organisms, oyster (*Saccostrea cucullata*), cockle (*Andra granosa*) and sediment.
- evaluate pollution load index (PLI), and contamination factor CF.
- Compare the results obtained with standard set by WHO in food.

## Materials and Methods

### *Study area*

Andoni is an urban area located in Rivers State, South-South Nigeria. It has an estimated area of 233km<sup>2</sup> and with a population of about 211,009 people. The area lies on the latitude 4<sup>0</sup>27<sup>1</sup>0<sup>1</sup>N and 4<sup>0</sup>35<sup>1</sup>0<sup>1</sup>N and longitude 7<sup>0</sup>29<sup>1</sup>0<sup>1</sup>E and 7<sup>0</sup>39<sup>1</sup>0<sup>1</sup>E. Andoni has 76 towns and villages and the occupation of the inhabitants is mainly fishing. The Andoni River system comprises of many creeks. However, the study was restricted to five locations that were carefully chosen. They were chosen to cover the entire area, the locations were Iwoma and Otukloko in North central, Egedem in North-East, Mbiaka in the West and Inyonkon in the South.

### *Sample collection*

Triplicate samples of the two species of shellfish cockle (*Andra granosa*) and oyster (*Sacrostrea cuculata*) were collected from five locations at intervals of three months namely; Iwoma, Otukloko, Egedem, Mbiaka and Inyonkon in a day with a speed boat. The cockles were handpicked from the surface and few centimeters below the surface of the sediment, while oysters were collected by cutting the red mangrove branches containing the organism. The oysters were placed in a different bagco sack bags while cockles were kept in basket that were labeled according to the location and were taken to the laboratory. On the other hand, sediment samples were collected with the help of a plastic hand trowel at about 5.0cm depth and were also placed in different containers and labeled according to sites.

### *Sample preparation and analysis*

Both cockle (*Andra granosa*) and oyster (*Saccostrea cuculata*) were opened at the groove with a sharp stainless knife and the entire fresh parts were taken and placed on a petri dish that were properly washed with distill water and labeled. They were oven dried at 105<sup>0</sup>C to ensure that all the water content was driven off until a constant weight was obtained. The sediment samples were air dried and then oven dried at 105<sup>0</sup>C. Each sample was homogenized with mortar and pestle. Thereafter, 5.0g of each sample was weighed, followed by adding 20ml of aqua regia prepared by mixing 30ml of hydrochloric acid and 70ml of trioxonitrate (v) acid (HNO<sub>3</sub>) and digested in a water bath. Thereafter, 10ml of de-ionized water was added to the content of each flask and was allowed to cool. The content of each flask was later filtered with Whatman 0.05µm filter paper. On the other hand, the sediment was digested by method of AOAC (1980) [10].

The filtrates were placed in sample bottles and preserved in a refrigerator overnight. The samples were analyzed the next day using Atomic Absorption Spectrophotometer model 205 made in Germany.

### *Statistical Analysis*

The results of the samples (shellfish and sediment) were subjected to analysis of variance (ANOVA).

### *Contamination factor (CF)*

The extent of pollution was determined using contamination factor (Cf), calculate as follows.

$$CF = \frac{Cn \text{ Sample}}{Cn \text{ background value}} \quad (1)$$

Where numerator (Cn sample) is the concentration of metals in the sample whereas the denominator is the (Cn background) is world average value of the metal in shale (mg/Kg) of metal. Contamination factor is classified into five classes, when  $CF < 0.1$  very slight contamination,  $0.10 - 0.25$  slight contamination,  $0.26 - 0.5$  moderate contamination,  $0.51 - 0.75$  severe contamination and  $0.76 - 1.00$  very severe contamination.

The background world average value in shale (mg/Kg) of metals were Fe, (47200), Zn (95), Pb (20), Co (19), Cu (45), Cr (90), Ni (68), Mn (850), As (13), Cd (0.3).

### Pollution Load Index (PLI)

The pollution load index at each site was determined using the expression

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF)^{1/n} \quad (2)$$

where n is the number of metal and CF is the contamination factor calculated from equation (1) above. When  $PLI < 1$ , indicate perfection,  $PLI = 1$  indicate that only baseline levels are present and  $PLI > 1$  indicate pollution of the site.

## Results and Discussion

The concentrations of heavy metals in oysters (*Saccostrea cucullata*), cockle (*Anadrara granosa*) and sediment samples are presented in **Tables 1-3**. **Table 4** showed the contamination/ pollution index of the sediment and **Table 5** showed the terminologies for the description of contamination and pollution indices, while **Tables 6 and 7** showed the descriptive statistics, one way analysis of variance (ANOVA) and post hoc test (PHT) respectively. The results in Tables 1-3 showed that the concentration of the heavy metals varied from one location to another and between the heavy metals in the samples. Two categories of metals were investigated, the essential and the non-essential metals. The results revealed that elevated levels of Fe, Zn, Mn and Cu were obtained in the samples except for Cu in cockle Table 6. Of the essential metals, iron (Fe) recorded the highest mean concentrations of  $2896.4 \pm 2083.11$  mg/Kg in sediment, while the lowest concentration of  $1676.05 \pm 2143.67$  mg/Kg was obtained in cockle (*Anadara granosa*) Table 6. However, the minimum concentrations of Fe 256.93 mg/Kg occurred in oyster at Egedem while the maximum 5710 mg/Kg occurred in the sediment at Iwoma. Elevated concentrations of iron in oyster (*Saccostrea cucullata*.) were obtained when compared to the levels in the sediment. This arises as a result of biomagnification of the heavy metals in the food chain. The results obtained in this study was similar to those reported by [5, 6, 11, 12], in the sediment and shellfish.

**Table 1** Concentration of heavy metals in oyster (*Saccostrea cucullata*) of selected sites of Andoni river system in mg/Kg

Location	Fe	Zn	Mn	Cu	Pb	Cd	As
Iwoma	5910	206.16	643.54	0.781	0.42	0.12	0.34
Mbiaka	2096	111.20	117.59	101.59	0.15	0.32	0.25
Egedem	256.93	105.11	214.06	6.811	0.31	0.19	0.41
Otukloko	246.02	175.11	205.02	5.38	0.12	0.01	0.72
Inyonkon	3041	138.24	430.21	6.05	0.23	<0.01	0.64

**Table 2** Concentration of heavy metal in cockle (*Anadara granosa*) of selected sites of Andoni river system

Location	Fe	Zn	Mn	Cu	Pb	Cd	As
Iwoma	5300	180.2	541.73	0.342	<0.01	0.38	0.79
Mbiaka	1982	142.0	127.63	0.705	0.20	1.01	1.03
Egedem	305.02	129.02	214.06	0.84	0.10	0.81	0.95
Otukloko	421.10	193.62	321.09	0.25	0.01	0.74	0.54
Inyonkon	372.15	175.67	273.12	0.93	0.02	0.35	0.67

**Table 3** Concentration of heavy metal in sediment of selected sites of Andoni river system in mg/Kg

Location	Fe	Zn	Mn	Cu	Pb	Cd	As
Iwoma	1051.33	1514	111.26	91.58	<0.01	0.35	0.27
Mbiaka	4610	4312	130.04	25.94	1.02	1.21	0.60
Egedem	5581	2796	327.49	18.66	1.01	0.72	0.52
Otukloko	2145	1456	127.04	75.26	0.01	0.52	0.82
Inyonkon	1095	1743	138.94	56.04	0.10	0.67	0.35

**Table 4** Contamination factor (CF) and pollution load index (PLI) of heavy metals in sediment (mg/Kg)

Location	Contamination factor (CF)							PLI
	Fe	Zn	Mn	Cu	Pb	Cd	As	
Iwoma	0.02	15.94	0.13	2.04	0.03	0.02	0.02	1.51
Mbiaka	0.10	45.38	0.15	0.58	3.4	0.06	0.05	1.75
Egedem	0.12	29.43	0.38	0.41	3.36	0.04	0.04	1.65
Otukloko	0.05	15.64	0.15	1.67	0.03	0.03	0.06	1.51
Inyonkon	0.02	18.35	0.16	1.24	0.33	0.03	0.03	1.53

**Table 5** Standard to describe contamination factor (Cf)

CF	Description
CF < 1	Low degree of contamination
1 < CF < 3	Moderate degree of contamination
3 < CF < 6	Consideration degree of contamination
CF > 6	Very high degree of contamination

**Table 6** the mean concentration of heavy metals in samples of Andoni River in mg/Kg

Metal	N	Mean	Std Deviation	Std Error	95% confidence interval mean		Minim um	maxim um	
					Lower Bound	Upper Bound			
Fe	Oyster	5	2309.9900	2346.02147	1049.173	- 602.9804	5222.9604	247.02	5910.00
	Cockle	5	1676.0540	2143.67657	958.68131	- 985.6720	4337.7800	305.02	5300.00
	Sediment	5	2896.4660	2083.11241	931.59619	309.9403	5482.9917	1051.33	5581.00
	Total	15	2294.1700	2095.56477	541.07250	1133.6849	3454.6551	246.02	5910.00
Zn	Oyster	5	147.1640	43.02061	19.23940	93.7469	200.58.11	105.11	206.16
	Cockle	5	164.1020	27.31081	12.21377	130.1911	198.0129	129.02	193.62
	Sediment	5	2364.2000	1215.92895	543.77996	854.4248	3873.9752	1456.00	4312.00
	Total	15	891.8220	1258.80510	325.02208	194.7190	1588.92.50	105.11	4312.00
Mn	Oyster	5	322.0840	213.43392	95.45055	57.0708	587.0972	117.59	643.54
	Cockle	5	295.5260	155.40085	69.49739	102.5703	488.4817	127.63	541.73
	Sediment	5	166.9340	90.29699	40.38204	54.8355	279.0725	111.26	327.49
	Total	15	261.5213	164.80806	42.55326	170.2537	352.7890	111.26	643.54
Cu	Oyster	5	24.1224	43.36941	19.39539	-29.7278	77.9726	.78	101.59
	Cockle	5	.6134	.30236	.13522	.2380	.9888	.25	.93
	Sediment	5	53.4960	31.23866	13.97035	14.7081	92.2839	18.66	91.58
	Total	15	26.0773	36.29983	9.37258	5.9751	46.1794	.25	101.59
Pb	Oyster	5	.2460	.12219	.05464	.0943	.3977	.12	.42
	Cockle	5	.0680	.08289	.03707	-0349	.1709	.01	.20
	Sediment	5	.4300	.53530	.23940	-2349	1.0947	.01	1.02
	Total	15	.2480	.33392	.08622	.0631	.4329	.01	1.02
Cd	Oyster	5	.1300	.13096	.05857	-0326	.2926	.01	.32
	Cockle	5	.6580	.28543	.12765	.3036	1.0124	.35	1.01
	Sediment	5	.6940	.32254	.14424	.2935	1.0945	.35	1.21
	Total	15	.4940	.35832	.09278	.2950	.6930	.01	1.21
As	Oyster	5	.4720	.20017	.08952	.2235	.7205	.25	.72
	Cockle	5	.7960	.19995	.08942	.5477	1.0443	.54	1.03
	Sediment	5	.5720	.21649	.09682	.2432	.7808	.27	.82
	Total	15	.5933	.29198	.06248	.4593	.7273	.25	1.03

**Table 7** One way analysis of variance for heavy metals

		Sum of square	df	Mean square	F	Sig.
Fe	Between Groups	3725391	2	1862695.334	.387	.687
	Within Groups	57754093	12	4812841.097		
	Total	61479484	14			
Zn	Between Groups	16259945	2	8129972.276	16.468	0.00
	Within Groups	5924319	12	493693.285		
	Total	22184264	14			
Mn	Between Groups	68835.672	2	34417.836	1.326	0.302
	Within Groups	311428.10	12	25952.339		
	Total	380263.70	14			
Cu	Between Groups	7020.085	2	3510.042	3.686	.057
	Within Groups	11427.404	12	952.282		
	Total	18447.489	14			
Pb	Between Groups	.328	2	.164	1.594	2.43
	Within Groups	1.233	12	.103		
	Total	1.561	14			
Cd	Between Groups	.997	2	.498	7.379	0.08
	Within Groups	.881	12	.068		
	Total	1.808	14			
As	Between Groups	.312	2	.156	3.688	0.56
	Within Groups	.508	12	.042		
	Total	.820	14			

The concentrations of Zn and Mn are also shown in Tables 1-6. Similar distribution trend of Zn and Mn were obtained in the samples, Zn recorded the highest concentration in the sediment particularly at Mbiaka, where 4312mg/Kg was obtained Table 3. However, in the two species of shellfish oyster and cockle, similar trend was also recorded except for Zn in oyster at Iwoma (station 1) where 206.16 mg/Kg was obtained which almost doubles the concentration at other stations (Mbiaka, Egedem, Otukloko and Inyonkon). Zn had the highest mean concentration of  $2364.2 \pm 1215$ mg/Kg in the sediment while the minimum and maximum concentration of Zn was 1456 and 4312.00mg/Kg as shown in Table 6. On the other hand, the range 111.26 to 327.49mg/Kg in sediment, whilst in cockle and oyster, the concentration occurred in the range of 127.67 to 541.78mg/Kg and 117.59 to 643.54mg/Kg respectively. Meanwhile, the mean and standard deviation of Mn in oyster is exceptionally high when compared to the mean levels in cockle and sediment which were  $3228 \pm 213.43$ ,  $295.52 \pm 155.4$  and  $166.95 \pm 90.29$ mg/Kg. Zinc and manganese are essential elements that occur naturally as mineral ores in the environment. However, elevated concentrations in organisms can pose threat to life. Elevated concentrations of Mn and Zn could result in neurological and neuromuscular control, mental and emotional disturbances, muscle stiffness, lack of coordination, difficulties with breathing or swallowing [3]. The concentration factor (CF) for Fe, Mn and Zn in Table 4 revealed that CF for Fe and Mn are less than one ( $CF < 1$ ) indicating low degree of contamination, while for Zn,  $CF > 6$  was obtained indicating very high contamination. The results of PLI obtained in the study were similar to those reported [5, 13, 14]. High PLI at the stations may be attributed to the fact that metals are distributed to the environment as a result of anthropogenic activities.

Copper concentrations are shown in Tables 1-6. The highest mean and standard deviation for Cu was obtained in sediment, while the minimum of 0.25mg/Kg was obtained in cockle while the maximum of 101.59mg/Kg was reported in oyster at station 4 (Otukloko) and station 2 (Mbiaka) respectively. A low concentration of Cu was obtained in cockle, oyster and sediments when compared to Fe, Zn and Mn. However, Cu occurs naturally and is distributed to the environment; aquatic, terrestrial and air through fuel, pigment and paints fertilizers and catalysts. Cu is among the essential elements that is required in trace amount for metabolism. However, elevated concentrations can be harmful to human resulting to irritation of the nose, mouth and eyes, nausea, vomiting, diarrhoea and stomach cramps. The concentration factor (CF) and pollution load index (PLI) for Cu indicates low degree of contamination at locations 2 and 3, while moderate degree of contamination occurred at locations 1, 3 and 5, as the CF values obtained is  $1 < CF < 3$ . On the other hand, the pollution load index (PLI) at the stations indicated that all the stations were polluted as the values of PLI in the stations were greater than one ( $PLI > 1$ ) Table 4. The results of one way analysis of variance (ANOVA) for Fe, Zn, Mn, Pb, Cd, Cu and As indicate no significance differences except for Zn and Cd at  $P < 0.05$ .

**Distribution of Pb, Cd and As in cockle, oyster and sediment**

The concentrations of the non-essential metals Pb, Cd and As are shown in Tables 1-6 while Table 4 presents contamination factor (CF) and pollution load index (PLI) at the stations. Low concentrations of Pb, Cd and As was reported in the samples. The results revealed that As recorded the highest concentration when compared to Pb and Cd as indicated in Tables 1-3. Table 6 showed the descriptive statistic for the elements, highest mean concentration of as  $0.7690 \pm 0.19\text{mg/kg}$  was obtained in cockle.

**Table 8** Post hoc tests for heavy metals in the samples

Dependent variable	(I) Samples	(J) Samples	Mean Difference (I-J)	Std Error	Sig.	95% confidence interval mean	
						Lower Bound	Upper Bound
Fe	Oyster	Cockle	633.93600	1387.493	.656	-2389.1512	3657.0232
		Sediment	-586.47600	1387.493	.680	-3602.8632	2436.6112
	Cockle	Oyster	6339.93600	1387.493	.656	-3657.0232	2389.1512
		Sediment	-1220.4120	1387.493	.396	-4243.4992	1802.6752
	Sediment	Oyster	586.47600	1387.493	.680	-2436.6112	3809.5632
		Cockle	1220.41200	1387.493	.396	-1802.6752	4243.4992
Zn	Oyster	Cockle	-16.93800	444.384420	.970	-985.1680	951.2920
		Sediment	-2217.0380*	444.384420	.000	-3185.2660	1248.8060
	Cockle	Oyster	16.93800	444.384420	.970	-951.2920	985.1680
		Sediment	-2200.0980*	444.384420	.000	-3168.3280	-1231.9680
	Sediment	Oyster	2217.03600*	444.384420	.000	1248.8060	3185.2660
		Cockle	2200.09800*	444.384420	.000	1231.8680	3168.3280
Mn	Oyster	Cockle	26.55800	101.88688	.799	-195.4344	248.5504
		Sediment	155.13000	101.88688	.154	-66.8624	377.1224
	Cockle	Oyster	-26.55800	101.88688	.799	-248.5504	195.4544
		Sediment	128.57200	101.88688	.231	-93.4204	350.5644
	Sediment	Oyster	-155.13000	101.88688	.154	-377.1224	66.8624
		Cockle	-128.57200	101.88688	.231	-350.5644	93.4204
Cu	Oyster	Cockle	23.50900	19.51700	.252	-19.0149	66.0329
		Sediment	-29.37360	19.51700	.158	-71.8975	13.1503
	Cockle	Oyster	-23.50900	19.51700	.252	-66.0329	19.0149
		Sediment	-52.88260	19.51700	.019	-95.4065	-10.3587
	Sediment	Oyster	29.37360	19.51700	.158	-13.1503	71.8975
		Cockle	52.88260*	19.51700	.019	10.3587	95.4065
Pb	Oyster	Cockle	.17800	.20276	.397	-2638	.6198
		Sediment	-.18400	.20276	.382	-6258	.2578
	Cockle	Oyster	-.17800	.20276	.397	-6198	.2638
		Sediment	-.36200	.20276	.099	-8038	.0798
	Sediment	Oyster	.18400	.20276	.382	-2578	.6258
		Cockle	.36200	.20276	.099	-0798	.8039
Cd	Oyster	Cockle	-.52800*	.16438	.007	-8861	-1699
		Sediment	-.56400*	.16438	.005	-9221	-2059
	Cockle	Oyster	.52800*	.16438	.007	-1699	.8861
		Sediment	-.03600	.16438	.830	-3941	.3221
	Sediment	Oyster	.56400*	.16438	.005	.2059	.9221
		Cockle	.03600	.16438	.830	-3221	.3041
As	Oyster	Cockle	-32400*	.13009	.028	-6074	-0406
		Sediment	-04000	.13009	.764	-3234	.2434
	Cockle	Oyster	.32400*	.13009	.028	.0406	.6074
		Sediment	.28400*	.13009	.050	.0006	.5674
	Sediment	Oyster	.04000	.13009	.764	-2434	.3234
		Cockle	-.28400*	.13009	.050	-5674	-0006

The concentration factor (CF) for Pb, Cd and As were less than 1 ( $CF < 1$ ) indicating that there was low degree of contamination of the three metals. The results of ANOVA for Pb, Cd and As indicated no significant differences in the mean concentration of As and Pb, while there was significant difference at  $P < 0.05$  for Cd in cockle, oyster and sediment Table 7. Cadmium and lead are potentially toxic to humans. These elements can cause irritation of the stomach, resulting in vomiting and diarrhea while Pb in human can damage the kidneys and reproduction system [5]. The Post hoc test (PHT) in **Table 8** showed the multiple comparisons of the samples for all the metals.

The (PHT) revealed that no significance difference occurred in As, Pb, Cu, Mn and Fe among the samples. However, there was significant difference between oyster and sediment, sediment and cockle, oyster and cockle at  $P < 0.05$  Table 8. The relative abundance of the metals in the samples occurred in the order  $Fe > Mn > Zn > Cu > As > Pb > Cd$ . The surface sediment recorded the highest concentration of the heavy metals followed by oyster and then cockle. Similar results were reported [12, 15].

## Conclusion

The relative abundance of the six heavy metals analysed in the samples occurred in the order  $Fe > Mn > Zn > Cu > As > Pb > Cd$ . The results of ANOVA at  $P < 0.05$  revealed significant difference for Zn and Cd, while no significant difference for Fe, Mn, Cu, Pb and As. The results revealed that the major source of pollution of the area was anthropogenic. Also, the contamination factor (CF) examined for essential metals showed that, there was low degree of contamination for Fe, Mn and Cu except at Mbiaka and Egedem, while Zn recorded very high degree of contamination. Of the non-essential elements Pb had considerate degree of contamination at Mbiaka, and Egedem where the CF was greater than three ( $CF > 3$ ) while at Iwoma, Otukloko, and Inyonkon recorded low degree of contamination. In addition, the CF for Cd and As showed low degree of contamination for the heavy metals at the stations Table 4. Table 4 also revealed that, the pollution load index (PLI) for the stations were greater than 1 ( $PLI > 1$ ) indicating that the stations were polluted with the heavy metals investigated. Based on the results obtained in this study, the inhabitants of the area should be informing about the status of these heavy metals. In addition, government should encourage companies and industries to recycle their waste before disposal.

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