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SOME HEAVY METALS CONTENT OF SEDIMENT AND TWO SPECIES OF CRABS OF THE LOWER REACHES OF NEW CALABAR RIVER, NIGERIA

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Abstract
This study surveyed heavy metals content (Cu, Se, Zn, Fe, BP, Mn, Cr, Cd, As, and Ni) in Surface sediment and two species of crab; Fiddler Ucapugnax and Portunus Trituberculatus of the lower reaches of New Calabar River. The two species of crab and surface sediments of about 0.5m depth were collected at three different locations in three different months August, September, and October 2021. The samples were analyzed using bulk scientific Atomic Absorption Spectrophotometry (AAS) model 200A. In the three sample locations the metal that had the highest and lowest concentrations in mg/kg were as follows in Sediment Fe (1.2005 + 0.00021), Ni (0.0295 ± 0.013); Portunus tissue Se (1.0983 ± 0.2993), Cr (0.012 ± 0.000); Portunus Shell As (1 .4668 ± 0.0009), BP (0.0004 ± 0.0004); Fiddler tissue Cu (0.0129 ± 0.0002), Cd (0.0006 ± 0.0002); Fiddler Shell Ar (0.0138 ± 0.0297), Cr (0.0002 ± 0.0000); The results revealed that Abonnema Wharf recorded the highest concentration of most of the metals. The order was Abonnema Wharf> Eagle Island> Iwofe. Analysis of Variance (ANOVA) was used to interpret the results, which shows the significant differences in various locations of the samples. The results of ANOVA revealed that there is no significant difference in the mean s of levels of heavy metals between the two species. The results obtained were within the permissible limit or standard set by WHO USEPA and NAFDAC.

Keywords: Heavy metals, sediment, crabs, New Calabar River.

Introduction

Heavy metals are any metallic compound component that has a somewhat high thickness and is harmful/noxious at low focuses. They are regular parts of the Earth's Crust Heavy metals as the name implies cannot be degraded or destroyed (Adekola et al., 2002). Some examples of heavy metals are Copper (Cu), Nickel (Ni), Arsenic (AS), Lead (Pb), Iron (Fe), Zinc (Zn), Manganese (Mn), Selenium (Se), and Cadmium (Cu), etc. Heavy metals to a "small extent enter our bodies through food, drinking water, and air. As trace elements, some heavy metals (for example copper, selenium, zinc) are essential to maintain the metabolism of the human body. At higher concentrations, heavy metals can lead to poisoning" (Lenntech, 2022).

Portunus is a genus of crab which includes several important species for fisheries, such as the blue swimming crab, portunus pelagicus, and the Gazami crab, P. trituberculatus" (Miers 1876). They live predominantly in water. A fiddler crab, in some cases known as cally crab, may be any of more than 100 types of semi-terrestial marine crabs in the group of ocypodidae. A more modest number of mangrove crab and apparition crab species are additionally found in the family ocypodidae. Fiddler crabs are found along ocean seashores and bitter intertidal mud pads, tidal ponds, and marshes (Levinton et al., 1995).

The residue is a characteristic happening material that is separated by cycles of enduring, disintegration and is hence moved by the activity of wind, or ice or by the power of gravity following up on the particles for example sand and residue can be conveyed in suspensions (Adekola et al., 2002). Heavy metals in silt assume a significant part in the contamination plan of a dreg and can be utilized to recognize toxins that getaway water examination and give data about the basic destinations of the river (Bender et al., 2009).

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Materials and Methods

Materials

The following materials were used: Volumetric flask, Oven, Funnel, Hydrochloric acid HC1, Trioxonitrate(IV) acid HNO_3, Perchioric acid $HC1O_4$, Weighing balance, Sieve, Heating mantle, Distilled Water, Whatman filter paper and Aluminum foil.

2.2 METHODS

Study area

The New Calabar River stretches from Igbo-Etche River through Iwofe River to Abonnema Wharf River and is located in the Niger Delta Area, South-South Nigeria.

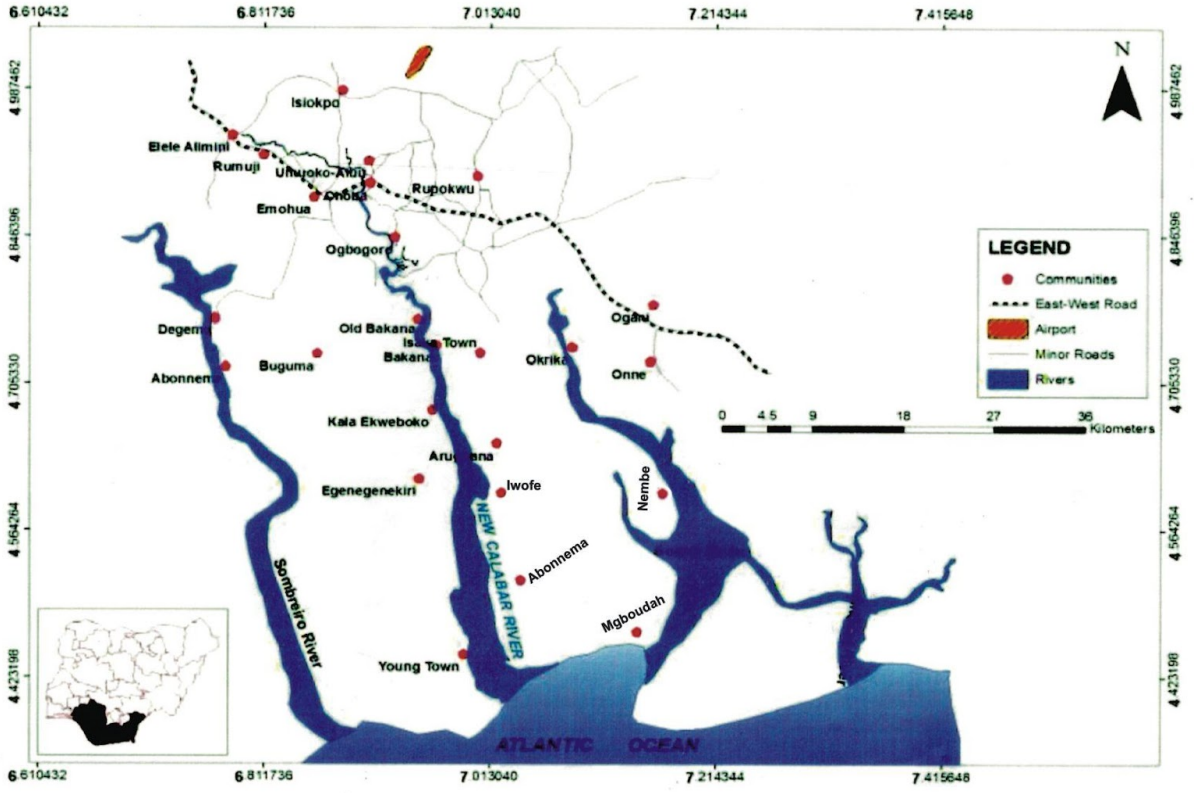

Figure 1a: Map of lower Niger Delta showing the New Calabar Rivers drainage system and study area.

Sample collection

Samples of sediments and two species of crab; Fiddler (Uca pugnax) and Portunus (*Trituber culatus*) were collected from the intertidal flat and in the water of New Calabar River. A triplicate samp1es were collected from three different locations in three months. 8th August, 11th September, and 22nd October 2021 namely: Iwofe River, Eagle Island, and Abonnema Wharf. Surface sediments were collected by scoping at 0-5cm and were wrapped with aluminum foil and were placed in a cooler packed with ice.

Sample storage

Immediately after collection samples were transferred in labelled sample containers (polythene bags), and aluminum foil to the laboratory for storage in a freezer (after washing crabs with deionized water).

Sample preparation

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A stainless knife was used to dissect the organisms and the gills, muscles, exoskeleton and legs were separated. The separated samples were oven-dried at 80-105°C then homogenized 5.0g of ground powder samples were weighed into conical flasks and then digested with aqua regia (HC1:HNO_3) and filtered with Whatman filter paper. The filtrate was made up to 50m1 with distilled water for further analysis.

Sample analysis

The samples were analyzed with the Atomic Absorption Spectrometer A.A.S. model- 200A, which enables the qualitative analysis of a sample. AAS is a technique used mostly for deciding the convergence of a specific metal component in a sample. The principle of A.A.S utilizes the nuclear ingestion range of a sample to evaluate the grouping of explicit analytes inside it. It requires guidelines with known analyte content to layout the connection between the deliberate absorbance and the analyte focus and depends thusly on the Beer-Lambert Law. The Instrumentation of A.A.S to investigate an example for its nuclear constituents must be atomized. The atomizers most normally utilized these days are blazes and electrothermal (graphite tube) atomizers. The particles should then be illuminated by optical radiation, and the radiation source could be a component explicit line radiation source or a continuum radiation source. The radiation then, at that point, goes through a monochromator to isolate the component of explicit radiation from some other radiation transmitted by the radiation source, which is at last estimated by a locator. (en.m.wikipedia.org).

Statistical tools:

The statistical tools were Mean, Standard deviation, and Analysis of Variance (ANOVA).

Results

The results of heavy metals analysis of Sediments and two species of crabs; Fiddler (*Uca pugnax*) and Portunus (*Trituber culatus*) in the three samples (Sediment, Fiddler, and Portunus) are presented in Table 1-5 and figures 1 - 5 showed the variations of heavy metals.

Table 1: Concentration of Heavy Metals in Sediment of Lower reaches of New Calabar River in mg/kg

S/N	Heavy Metals	Locations		
		Iwofe	**Eagle-Island**	**Abonnema Wharf**
1	Copper (Cu)	0.136±0.000	0.122± 0.079	0.143 ± 0.000
2	Nickel (Ni)	0.445± 0.000	0.030± 0.013	0.125 ± 0.002
3	Arsenic (As)	0.118± 0.048	0.134± 0.050	0.172 ± 0.002
4	Chromium (Cr)	0.094± 0.002	0.031± 0.001	0.754± 0.001
5	Lead (BP)	0.088± 0.000	0.063± 0.000	0.129± 0.000
6	Iron (Fe)	0.917± 0.000	0.923± 0.000	1.200 ± 0.002
7	Zinc (Zn)	0.179± 0.000	0.084± 0.000	0.059± 0.000
8	Manganese (Mn)	0.172± 0.000	0.107± 0.000	0.106 ± 0.000
9	Selenium (Se)	0.291± 0.009	0.421± 0.005	0.527 ± 0.071
10	Cadmium (Cd)	0.237± 0.001	0.063± 0.002	0.510 ± 0.000

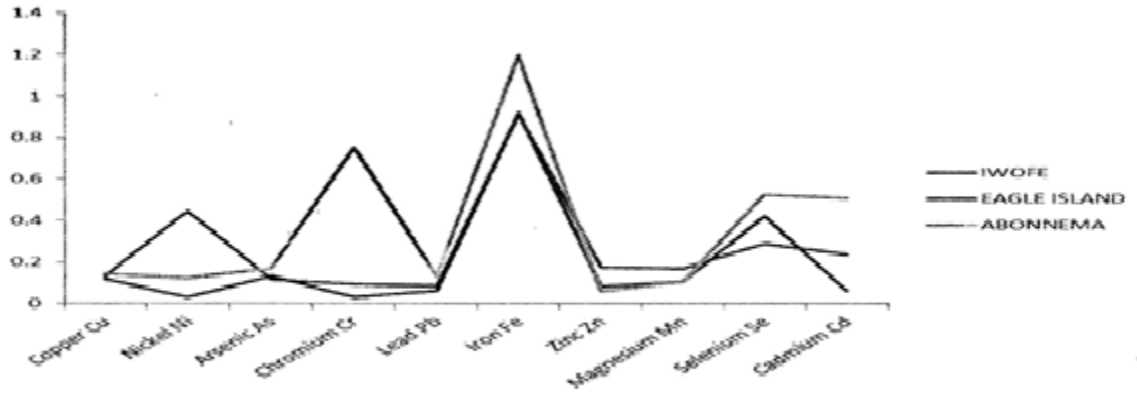

Fig. 1: Variation of Heavy Metals concentrations in sediment at various locations

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Table 2: Concentration of Heavy Metals in Muscle Tissue of Portunus Crab (Trituber culatus) in mg/kg.

S/N	Heavy Metals	Locations		
		Iwofe	**Eagle-Island**	**Abonnema Wharf**
1	Copper (Cu)	0.064 ± 0.001	0.049 ± 0.001	0.051 ± 0.000
2	Nickel (Ni)	0.029 ± 0.004	0.025± 0.006	0.042 ± 0.001
3	Arsenic (As)	0.076 ± 0.054	0.090 ± 0.004	0.188 ± 0.001
4	Chromium (Cr)	0.054 ± 0.001	0.012 ± 0.000	0.034 ± 0.001
5	Lead (BP)	0.042 ± 0.000	0.033 ± 0.000	0.059 ± 0.000
6	Iron (Fe)	0.378 ± 0.003	0.097 ± 0.000	0.893 ± 0.002
7	Zinc (Zn)	0.026 ± 0.000	0.020± 0.000	0.016 ± 0.099
8	Manganese (Mn)	0.793 ± 0.008	0.067± 0.017	0.026 ± 0.000
9	Selenium (Se)	0.355 ± 0.030	0.464 ± 0.019	1.098 ± 0.299
10	Cadmium (Cd)	0.070 ± 0.001	0.031 ± 0.002	0.043 ± 0.001

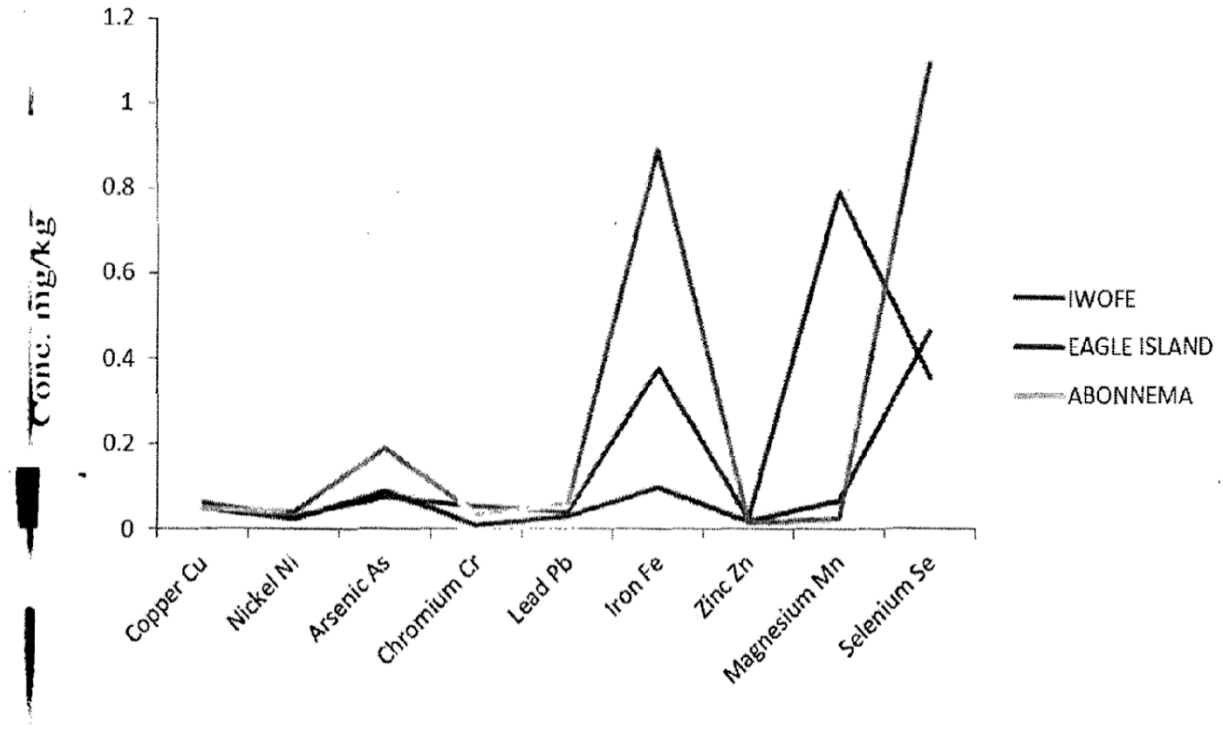

Fig 2: Variation of Heavy Metals concentration in Portunus Tissues at various Location

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Table 3: Concentration of Heavy Shell of Portunus Crab (Trituber culatus) in mg/kg.

S/N	Heavy Metals	Locations		
		Iwofe	**Eagle-Island**	**Abonnema Wharf**
1	Copper (Cu)	0.009 ± 0.000	0.008 ± 0.001	0.007 ± 0.005
2	Nickel (Ni)	0.015 ± 0.001	0.006 ± 0.001	0.005 ± 0.001
3	Arsenic (As)	0.095 ± 0.001	1.467 ± 0.002	0.207 ± 0.001
4	Chromium (Cr)	0.005 ± 0.001	0.002 ± 0.009	0.004 ± 0.001
5	Lead (BP)	0.002 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
6	Iron (Fe)	0.061 ± 0.002	0.029 ± 0.001	0.123 ± 0.002
7	Zinc (Zn)	0.011 ± 0.000	0.016 ± 0.025	0.010 ± 0.065
8	Manganese (Mn)	0.032 ± 0.000	0.002 ± 0.000	0.002 ± 0.000
9	Selenium (Se)	0.285 ± 0.020	0.658 ± 0.000	0.655 ± 0.004
10	Cadmium (Cd)	0.170 ± 0.002	0.037 ± 0.001	0.004 ± 0.000

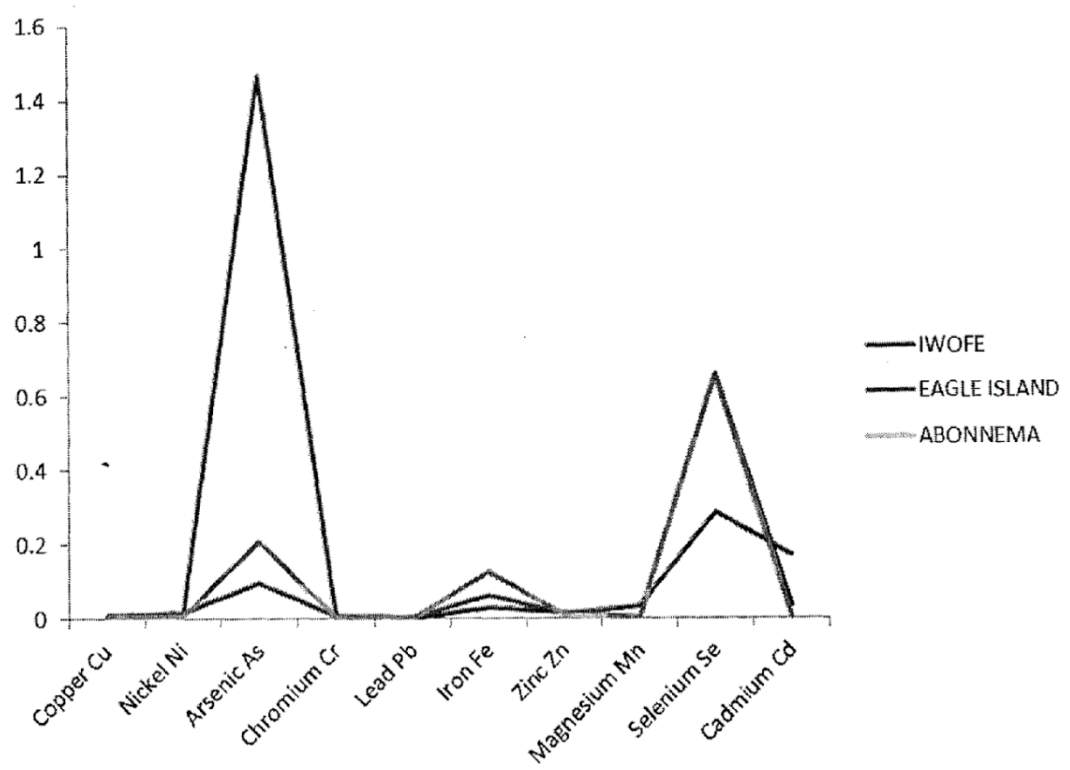

Fig 3: Variation of Heavy Metals concentration in Portunus Shell Various Location

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Table 4: Concentration of Heavy Metals Tissue of Fiddler (Uca pugnax) in mg/kg.

S/N	Heavy Metals	Locations		
		Iwofe	Eagle-Island	Abonnema Wharf
1	Copper (Cu)	0.013 ± 0.000	0.012 ± 0.000	0.009 ± 0.009
2	Nickel (Ni)	0.004 ± 0.004	0.011 ± 0.029	0.001 ± 0.000
3	Arsenic (As)	0.002 ± 0.000	0.002 ± 0.000	0.005 ± 0.001
4	Chromium (Cr)	0.004 ± 0.000	0.002 ± 0.002	0.004 ± 0.000
5	Lead (BP)	0.002 ± 0.000	0.002 ± 0.000	0.002 ± 0.000
6	Iron (Fe)	0.007 ± 0.000	0.002 ± 0.000	0.009 ± 0.003
7	Zinc (Zn)	0.009 ± 0.006	0.005 ± 0.000	0.004 ± 0.000
8	Manganese (Mn)	0.004 ± 0.000	0.002 ± 0.002	0.001 ± 0.001
9	Selenium (Se)	0.005 ± 0.000	0.004 ± 0.005	0.010 ± 0.006
10	Cadmium (Cd)	0.002 ± 0.000	0.001 ± 0.000	0.001 ± 0.000

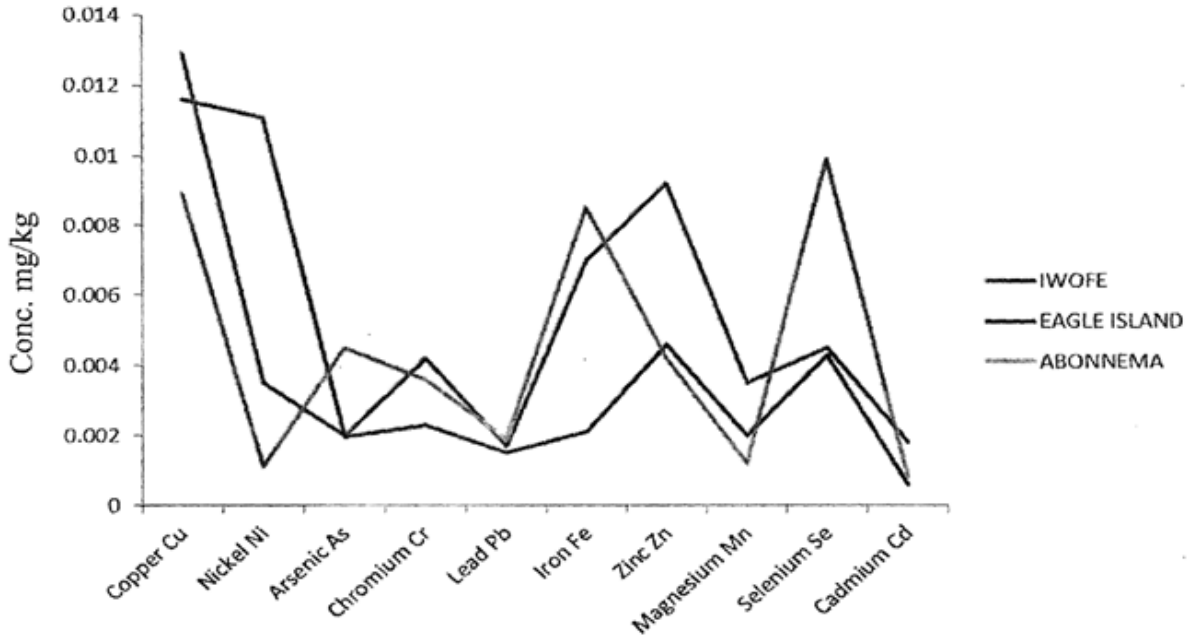

Fig. 4. : Variation of Heavy Metals concentration in Fiddler Tissues

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Table 5: Concentration of Heavy Metals in Shell of Fiddler (Uca pugnax) in mg/kg.

S/N	Heavy Metals	Locations		
		Iwofe	**Eagle-Island**	**Abonnema Wharf**
1	Copper (Cu)	0.003 ± 0.000	0.002 ± 0.002	0.002 ± 0.000
2	Nickel (Ni)	0.002 ± 0.035	0.001 ± 0.000	0.001 ± 0.000
3	Arsenic (As)	0.004 ± 0.003	0.013 ± 0.029	0.005 ± 0.000
4	Chromium (Cr)	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
5	Lead (BP)	0.004 ± 0.009	0.000 ± 0.000	0.000 ± 0.000
6	Iron (Fe)	0.002 ± 0.000	0.001 ± 0.000	0.007 ± 0.006
7	Zinc (Zn)	0.004 ± 0.000	0.001 ± 0.000	0.003 ± 0.001
8	Manganese (Mn)	0.003 ± 0.003	0.001 ± 0.000	0.001 ± 0.001
9	Selenium (Se)	0.004 ± 0.002	0.006 ± 0.000	0.006 ± 0.008
10	Cadmium (Cd)	0.004 ± 0.001	0.001 ± 0.000	0.001 ± 0.000

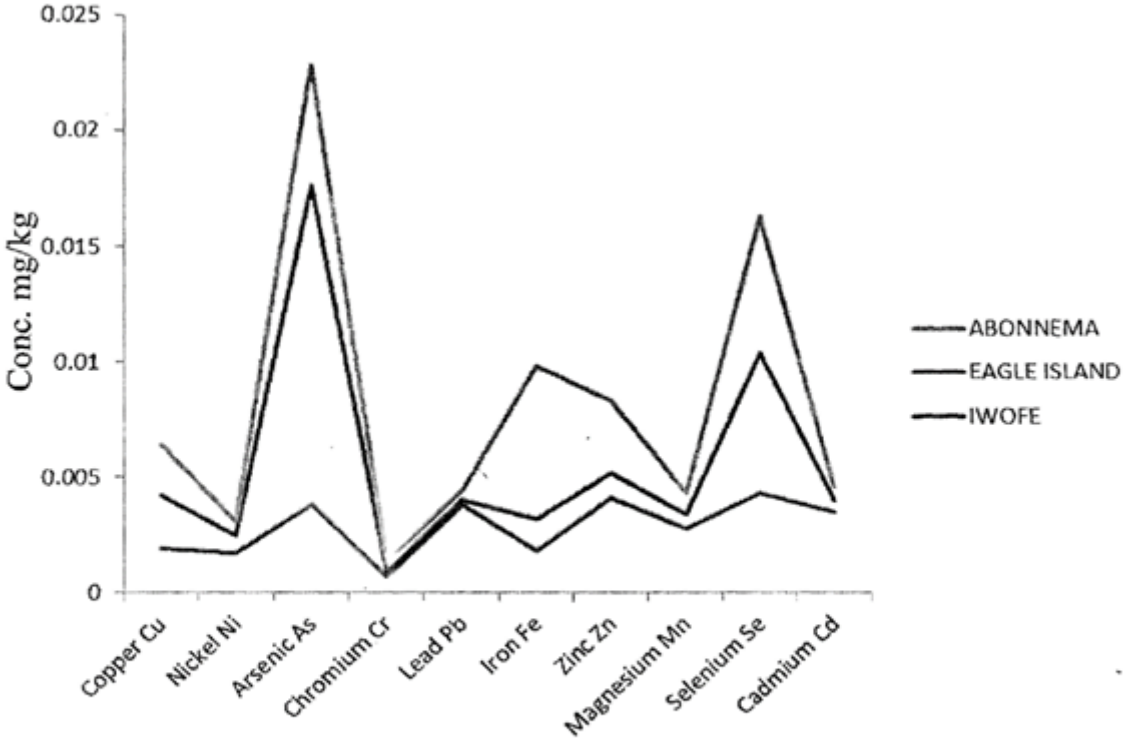

Fig. 5: Variation of Heavy Metals concentration in Fiddler Shell

Discussion

The results obtained revealed direct deposition, exploitation and accumulation of heavy metals into surface sediment due to anthropogenic activities including shipping, dredging, and urban wastewater discharges. Surface sediments had

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the highest mean values of heavy metals in all the three different locations (Iwofe, Eagle Island and Abonnema Wharf) than crabs muscle and shell, of the lower reaches of New Calabar River. The level of heavy metals in muscle Fiddler (Uca pugnax) is greater than the levels in the shell and the same applied to Portunus (Trituber culatus) muscle and shell. This is because of bioaccumulation of heavy metals or substance in muscle/tissue. Portunus (Trituber culatus) also known as the swimming crab or blue crab has higher mean concentrations of heavy metals in both muscle and shell, when compared to the Fiddler (Uca pugnax). Fiddler (Uca pugnax) is found on intertidal flat during low tide and can feed on solid particulate matter and waste dumped in the river, (Kpee & Marcus, 2017). On the other hand, the fiddler crab lives both on land and in water. It obtains its food by filtering water. Whereas Portunus (Trituberculatus) lives in water permanently (predominantly aquatic).

The concentration of heavy metals in sediments mg/kg, for the three locations; Iwofe, Eagle Island, and Abonnema Wharf, were Fe (0.917), Pb (0.088), 0.923mg/kg iron had the highest concentration of 1.2006mg/kg at Abonnema Wharf in the sediment than all the other metals Table I while lead had the least concentration of the heavy metals at Iwofe and Abonnema Wharf Table 1. Similar results were reported by Kpee and Ekpete (2014) and Horsfall and Spiff (2002) and in this study area. These could be attributed to the fact that Iron (Fe) is the most abundant element in the earth's crust, is used in many alloys, and is one of the constituents of crude oil. The results revealed that the concentrations of Fe in the locations are in the order Abonnerna Wharf > Eagle Island > Iwofe. Similar orders of results were obtained in Cu, As, Cr, Pb, Mn, and Cd except for Ni, Zn, and Mn Table 1. These high levels of heavy metals in Abonnema Wharf re could be attributed to the fact that more human activities such as bunkering, shipping of crude oil, and importation of other materials occurred at this location than, at Eagle Island and Iwofe.

Level of heavy metals in muscle tissues of Fiddler and Portunus

The results of the concentration of metabolism muscle tissue of the two species of crab are shown in Table 2 and Table 3. The results revealed the concentration of heavy metals in the two species was generally low when compared to the levels in the sediment of the three locations. The results revealed that Selenium (Se) recorded the highest mean concentration of 1.0983 ± 0.2993 at Abonnema Wharf in Portunus (Trituber culatus) which dwell predominantly in water when compared to 0.0099 ± 0.0055 mg/kg at the same location of Selenium in Fiddler (Uca pugnax) that is both aquatic and terrestrial. In the muscle tissue of Portunus (Trituber culatus) at Iwofe the heavy metals occurred in the order Mn>Fe>Se>As>Cd>Cu>Cr>Pb>Ni>Zn, in Eagle Island the order was Se>Fe>As>Mn>Cu>Pb>Cd>Ni>Zn>Cr, while at Abonnema the order of heavy metals was Se>Fe>As>Pb>Cu>Cd>Ni>Cr>Mn>Zn. The concentration of Heavy Metals in Portunus crab Shell (Trituber culatus) mg/kg, in the three locations: Iwofe, Eagle Island and Abonnema Wharf. Follows the order Se 0.285 > Pb 0.002, As 1.467 > Pb 0.0004 and Se 0.655 > Pb 0.0004. The concentration of Heavy Metals in fiddler Crab muscle (Uca pugnax) mg/kg, in the three different locations surveying which metal, is greater than in Iwofe, Eagle Island, and Abonnema Wharf, Cu 0.013> Pb 0.002, Cu 0.012>0.001, and Se 0.010> Cd 0.001. And these are the only elements. The concentration of heavy metals in fiddler Crab Shell (Uca pugnar) mg/kg, for the three locations, the results of analysis of variance (ANOVA) are in tables 1, 2, and 3 which revealed that there is no significant difference in the mean of levels of heavy metals between the two species of crab studied Portunus and Fiddler. Sediments are shown in different locations as P<O.05. However, table 3 showed that there is a significant interaction effect between the sample and heavy metals as P>0.05. This concludes that those contaminants may have the same or similar source input. Lower reaches of New Calabar River has a low to moderate potential ecological risk due to heavy metal contamination of sediments and the two species of crabs (Uca pugnax and Trituber culatus) of the New Calabar river. The level of heavy metals concentrations in this study are low and below the regulated level as recommended by USEPA.

Conclusion

The present study surveyed the extent of pollution of sediments and the two species of crabs (Uca pugnax and Trituber culatus) of the lower reaches of the New Calabar River. The results revealed that some traces of heavy essential and non-essential metals were reported in the samples of the three locations studied. Abonnema Wharf recorded the highest concentration of heavy metals in the two species of crab and the sediments samples. Iron was found to have the highest concentration at Abonnema Wharf while Nickel has the least concentration of all the analysed elements and this occurred at Eagle Island in Portunus (Trituber culatus), Abonnema Wharf also recorded the highest concentrations of all the metals in the tissue while in the shell of Portunus (Trituber culatus). As recorded the highest concentrations at Eagle Island. A similar trend of heavy metal also occurred at Abonnema Wharf for Fiddler (Uca pugnax) in tissues and the shell. Generally, there was a low level of heavy metals in all the samples examined in the study which was

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within the permissible limit set by WHO and USEPA. Contamination of the common habitat by weighty metals is a general issue because these metals are indestructible and the vast majority of them effectively affect living creatures when passable focuses are surpassed (Ogri, et al., 2011). The results obtained revealed that the concentration of all the heavy metals examined, was within the permissible limit set by WHO and USEPA. It could be concluded that the area is not polluted. This implies the safe consumption of aquatic crabs and other aquatic organisms from the New Calabar River.

Recommendations

1. The Federal Government through the Federal Ministry of Environment in collaboration with the National Agency for Food and Drug Administration and Control (NAFDAC) should establish guidelines.
2. The New Calabar River should be protected from contamination or pollution to minimize the potential associated with crabs and aquatic organisms in the areas.
3. It is evident from this study that exposure of aquatic organisms to a contaminated environment is to monitor the effects of other Heavy Metals on the early stages of life such as the eggs and Larvae of sea fishes and also on the reproductive stages in the New Calabar River of Niger Delta Area in Nigeria.

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