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Original Research Article

Trace Metals in Water, Bottom Sediment, Shrimp and Dependent Human Blood in Ukwuani Local Government Area of Delta State, Nigeria

ABSTRACT

Trace metals (Fe, Mn, Zn, Cu, Pb, Cd and Cr) levels were investigated in the water, bottom sediment, shrimp (*Macrobrachium vollenhovenii*) of Okumeshi River and blood of individuals that feed on the shrimps. The order of accumulation in the matrices studied was bottom sediment > shrimp > water > human blood. High level of zinc and copper in human blood can be attributed to their high concentrations in all environmental matrices. It can also be attributed to the high biological accumulation factors of the metals in the shrimp. Copper also has a high essentiality in the respiratory pigment haemocyanin of shrimps. These facts are buttressed by the significant correlations of copper and zinc concentrations in the shrimp with their concentrations in human blood. The observed insalubrity of the shrimps is a prognostic of chronic health hazards to the consumers.

Keywords: Trace metals; water; sediment; sorption capacity; biological accumulation; Macrobrachium vollenhovenii

1. INTRODUCTION

The study was conducted on Okumeshi River; within Uwuani Local Government area of Delta State. The river is a source of drinking water, finfish and shellfish to dwellers in near and far communities. Finfish and shellfish products from Okumeshi River serve as exotic local and foreign export products. However, despite its domestic, nutritional and economic values, the river is faced with incessant perturbations due to anthropogenic activities around it. The activities include oil exploration and exploitation, agricultural practices, discharge of domestic and industrial wastes, amidst others. Sadly, water and sediment matrices are receptors of these anthropogenic by-products; as well as they are habitats to aquatic organisms of high nutritional and economic values.

The indiscriminate dumping of refuse, discharge of industrial effluents, petroleum wastes and crude oil spills replete with heavy metals may culminate in serious health consequences on populace that

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consume the finfish and shellfish harvested from the river. The mechanism is by incorporation of the toxicants from anthropogenic perturbations such trace metals into the aquatic food; thereby biomagnifying up the pyramid of biomasses through alimentation (Mansour and Sidky, 2002; Jezierska and Witeska, 2006; Akintujoye et al., 2013). Variability in water and sediment properties is a function of a number of factors which have been enormously reported in previous studies. Generally, these factors can be categorized as authoctonous and allothonous factors working in tandem. Ogbeibu and Victor (1989) reported that perturbations from road and bridge construction across Ikpoba River, Benin City, Nigeria, had a significant impact on the bottom sediment which in turn had impacts on the vital benthic invertebrates. Benka-Coker and Ohiomian (1995) reported on the significant effect of slaughter house waste on the water and sediment qualities of Ikpoba River and warned against threats to the aquatic fauna which are of nutritional relevance to the dependent populace. Tukura et al., (2012) attributed variation of physico-chemical properties of water and sediment of Mada River, Nasarawa State, Nigeria to seasonal variation. The water matrix of an aquatic ecosystem is the first receptor of the contaminants released from anthropogenic activities. The sediment then serves as repository to the contaminants (Adams et al., 1992; Camusso et al., 1995). However, the rate of deposition of these contaminants is a function of their sorption capacities; which vary among contaminants. Ogbeibu et al., (2014) observed that manganese, zinc, copper, cadmium, lead and total hydrocarbons had very high sorption capacities from water into the sediment of Ikpoba River. Furthermore, the contaminants journey from these environmental matrices into the tissues of biota where they are stored indefinitely. Froese et al., (1998) reported bioaccumulation of polychlorinated biphenyls from sediments to aquatic insects in Saginaw Bay, Michigan, USA. Davies et al., (2006) reported accumulation of heavy metals in tissues of Tympanotomus var radula from sediment of Elechi Creek, Nigeria. Akan et al., (2012) attributed accumulation of metals in the gills, liver, stomach, kidney, bones and flesh tissues of *Tilapia zilli, Clarias anguillaris, Synodentis budgetti* and *Oreochronmis niloticus* from River Benue to the concentrations in the ambience. Isibor et al. (2016) attributed impermissible levels of trace metals in *Clarias gariepinus* of Osse River, Edo State, Nigeria to high levels observed in the water and sediment.

Palaemonid shrimps; particularly *Macrobrachium vollenhovenii* (Herklots, 1851) are very abundant in Okumeshi River in Uwkuani Local Government of Delta State, Nigeria. The shrimps serve as

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a cheap source of animal protein to dwellers in the nearby communities. They also serve as source income for the local fishermen and other buyers from far and near. Their high commercial value is partly due to their relatively large body size (Omoigberale and Ikponmwosa-Eweka, 2010) and tenacious nature (Isibor and Oluowo, 2016). Sadly, this species is highly notorious for accumulation of metals from polluted environments (De Silva and Anderson, 1995; Edema and Egborge, 1999; Omoigberale and Ikponmwosa-Eweka, 2010). This is due to their morphology and niche which maximize accumulation of contaminants from bottom sediments and overlying water (Isibor and Oluowo, 2016). Constant trace metals released into Okumeshi River are bound to remain the environmental matrices for long periods (Li et al., 2014, 2015, 2016) till they are accumulated in the biota.

The study was aimed at assessing the trace metals in the water, bottom sediment, *M. vellenhovenii* and blood of the dependent populace.

2. MATERIAL AND METHODS

2.1. The study area

The Study was conducted on a stretch of Okumeshi River from August, 2016 to January, 2017. The river lies between latitude 5° 28' - 5° 48' N and longitude 5° 31' - 5° 40' E; in Ukwuani Local Government Area of Delta State (Figure 1). The river serves as source of water, affordable animal protein and means of transportation to the surrounding communities. The river incessantly receives municipal wastes and industrial effluents (Ekeanyanwu et. al. 2010; Ekeanyanwu et. al.2011). It is a lotic freshwater with predominant vegetation such as palm trees (Elaeis guinensis), shrubs, floating Salvinia species, Lemnas pecies and water hyacinth (Eichorrnia crassipes). The study area is located in the Niger Delta area of Nigeria; with sediment which includes Benin, Agbada and Akata formations; ranging from Eocene to Recent age (Short and Stauble, 1967; Asseez, 1976). The study area is made up of the Benin formation which is of Miocene- recent age. The thickness is about 200 m (Kogbe et al., 1976).

For the purpose of the study water, sediment and *M. vollenhovenii* samples were collected from four (4) stations which were chosen along the stretch of the river. Station 1 was chosen as the control station. Stations 2 and 3 witnessed varied oil exploration activities over time, while Station 4 was disturbed with agricultural practices and domestic waste deposition. These activities were very severe as at the period of this study. Blood samples were collected from human volunteers who are residents of

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Ukwuani Local Government and they rely substantially on the supply of *Macrobrachium vollenhovenii* from the river as cheap source of animal protein. Occupations of the blood donors are basically farming and fishing.

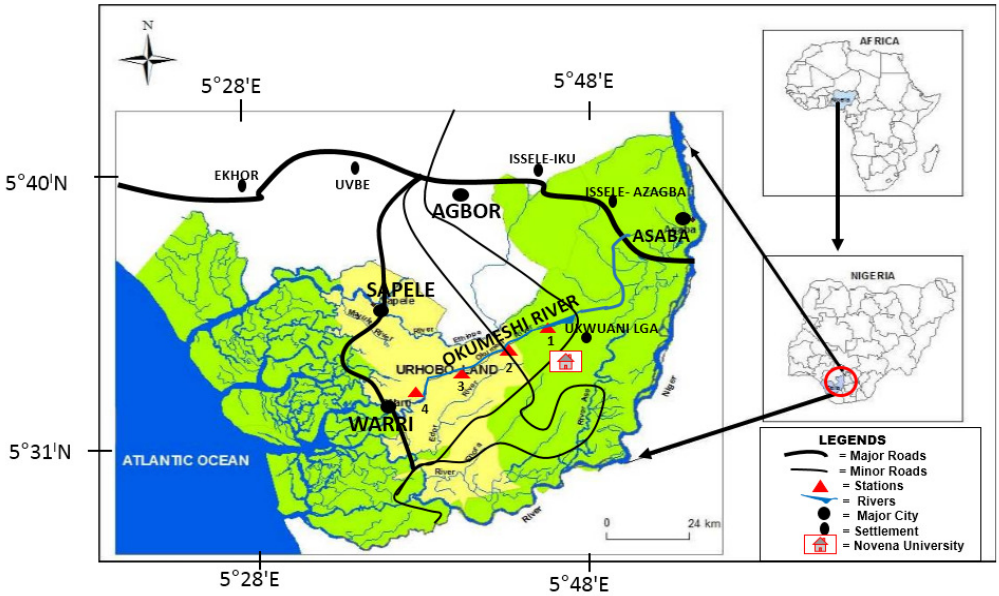

Figure 1. Map of the study area

2.2. Collection and analysis of samples

2.2.1. Blood samples

A total of 150 human volunteers (75 males and 75 females) were recruited into the research with their informed consent; in line with Helsinki Declaration guidelines. Prior to recruitment it was ascertained that they were all non-smokers. Their general health status was also verified through routine inquiries. The health screening procedures were taken due to the fact that health status influences mineral content of the blood (CDC, 2012; Harrington, 2014). 1 ml of blood samples was collected from donors in tubes containing lithium heparin anticoagulant; with lid. The tubes and their lids were thoroughly rinsed with de-ionized water and dried prior to use. The collected samples were taken immediately to the laboratory for analysis. Prior to digestion, all samples were vortexed thoroughly to provide a homogeneous matrix for digestion. Reagent blanks were prepared by addition of deionized water in place of the samples to monitor background concentrations of all analytes. 1 mL of HNO3 was added to each blood sample and was allowed to react for 30 minutes. Thereafter, 750 µL of non-stabilized 30% H_2O_2 solution was added to

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each sample. Once the addition of all reagents was complete, the tubes were sealed with lids and digested by microwave method using the Discovery SPD (CEM, Matthews, NC). After digestion, the samples were analyzed for trace minerals using the Thermo (Bremen, Germany) X-Series 2 ICP-MS equipped with a concentric glass nebulizer and peltier-cooled glass spray chamber. At the end of digestion, all samples were removed from the microwave and allowed to cool to room temperature. Samples were stored in a monitored refrigerator at a nominal temperature of 8 ℃ until analysis. Trace mineral calibration standards for ICP-MS analysis were prepared using NIST traceable 10 mg/L Fe, Mn, Zn, Cu, Pb, Cd, and Cr standards. Two sets of calibration standards were prepared for elements that were anticipated to be low-level elements (such as Pb, Cd, Cr, and Mn) and high-level elements (such Zn, Cu, and Fe). Samples were analyzed without dilution in the original storage containers to minimize the possibility of contamination. For the calibration, standards back-calculated concentrations was ensured to be within ±15% of the nominal concentration (±25% of the nominal concentration for the lowest concentration standard). Quality control checks was done to ascertain that concentration for all elements was found to be within ±15% of the nominal concentration.

2.2.2. Water samples

Surface water samples were collected at the four stations on monthly basis using 250 ~~ml~~ sampling bottles; and transported immediately to the laboratory for analysis of the trace metals. Water samples were pretreated and digested using the wet oxidation method described by Martin et al., (1992). Samples were fixed with 2 ~~ml~~ nitric acid (Martin et al., 1992) and then filtered through Whatman filter~~ed~~ paper no 1 and aspirated directly into an Atomic Absorption Spectrometer (Varian Techron Spectr AA – 10; serial number 902 1318) connected to an HP printer (Deskjet 2400 Printer series); for the quantitative determination of all trace metals. The blanks were prepared accordingly. For quality assurance purposes AAS was calibrated for each metal by dissolving 1 gram analar grade metal salt in 1 litre of distilled water. Standard and corresponding blanks were run with each set of experimental digest. The detection limits of iron (0.5 mg/L), manganese (0.5 mg/L), zinc (0.5 mg/L), copper (0.05 mg/L), lead (0.03 mg/L), chromium (0.05 mg/L) and cadmium (0.01 mg/L) were carefully observed.

To ascertain quality control and standardization measures, all laboratory procedures were repeated at least 3 times and mean values were compared with standard values supplied by FEPA (2003).

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2.2.3. Sediment samples

Bottom sediment samples were collected using a Birge-Ekman grab. The sediment samples were collected in foil papers and wrapped with labelled polythene. All samples were preserved in ice coolers and transported immediately to the laboratory for analysis. This routine was conducted repeated at all stations on monthly basis from August, 2016 to January, 2017.

1 gram air-dry sediment sample was placed in a 300 ~~ml~~ calibrated digestion tube. 3 mL concentrated nitric acid (HNO3) was added, swirled carefully and placed in a rack to settle. The mixture was slowly heat up by gradually increasing temperature to about 145 ℃ for 1 hour (Estefan et al., 2013). 4 ~~ml~~ concentrated Perchloric acid (HClO4) and heat it to 240 ^{o} C for another 1 hour. Mixture was allowed to cool to room temperature. It was filtered through Whatman No. 42 filter paper and the volume was made up to 50 ~~ml~~ with de-ionized water. Heavy metals were then determined by Atomic Absorption Spectrophotometer (model-analyst 200 PerkinElmer). For quality control and standardization measures, all laboratory procedures were repeated at least 3 times and mean values were compared with standard values supplied by FEPA (2003).

2.2.4. Shrimp samples

A total of 30 representatives (Isibor and Oluowo, 2016) of identified *Macrobrachium vollenhovenii* collected from each station on monthly basis were preserved for laboratory analysis. This was done at low tide regime during night periods using gears such as woven cylindrical non-return valve traps, baskets and scoop nets; in conjunction with coconut, cassava and earthworm baits. Some were procured from fishermen and sources of such samples were properly ascertained before procurement. The samples were preserved in four different coolers with ice; appropriately labeled to indicate the source stations. Whole shrimp was digested according to standard method illustrated by Benhard (1976). 10 grams of wet weight shrimp tissue was placed in silica flasks covered with a glass plate, 20 ~~ml~~ of HNO3: HClO4 mixture was added; ratio 5:1 respectively. Digestion process was carried out by heating the mixture at 105℃ for about 24 hours according to the illustrations of Turkmen (2012). The extract was made up to 25 ml with HNO3 (70%) and diluted with deionized water. For quality assurance, reagent blanks were processed simultaneously in triplicates. Each residue was filtered into volumetric flask with the aid of a Whatman filter paper. The solution was tested for metals concentrations using a Perkin Elmer

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3110 model Atomic Absorption Spectrophotometer (ASS) and recorded in mg/kg wet weight (Olaifa et al, 2004; Isibor and Oluowo, 2016). The ASS was calibrated for each metal by dissolving 1 gram analar grade metal salt in 1 litre of distilled and deionized water. Standard and corresponding blanks were run with each set of experimental digest. The detection limits of iron (0.5 µg/g), manganese (0.5 µg/g), zinc (0.5 µg/g), copper (0.05 µg/g), lead (0.03 µg/g), cadmium (0.01 µg/g) and chromium copper (0.05 µg/g) were carefully read.

The actual concentration of trace metals was calculated thus:

Actual concentration of metal = RD X Dilution factor (Olaifa et al, 2004)

Where RD = ASS reading of digest

$$\text{Dilution factor} = \frac{\text{Volume of digest used}}{\text{Weight of sample digested}}$$

2.3 Statistical analysis

The descriptive statistics of the trace metals in the water and sediment and blood of subjects were expressed as mean, standard error and range. The Analysis of Variance (ANOVA) was used to determine the significant differences at probability level of 0.05 using SPSS version 19.1. Furthermore, Duncan Multiple Range test (DMR) was employed to ascertain the actual locations of the significant differences.

In order to discern the major parameters of key importance i.e. active components in the matrices, the principal components were analyzed using descriptive statistics such as communalities, total variance, percentage variance and rotated component matrix. Parameters with communality values less than 0.75 were considered insignificant while components with Eigen values less than 1 were also considered insignificant (Chatfield and Collins, 1980); hence eliminated so that fewer components were further subjected to the Varimax rotation stage using Keiser normalization method (Hope, 1968; Chatfield and Collins, 1980; Mazlum, 1994).

Distribution coefficient (Kd) was used to determine the sorption capacity of the parameters into the sediment. Values less than 6 mg/L were considered insignificant.

$$\text{Distribution coefficient (Kd)} = \frac{M_{ads}}{M_{sol}} \quad \text{(Soares and Alleoni, 2006)}$$

Where M_{ads} = metals adsorbed into the soil and M_{sol} = metal concentration in water.

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The Biological Accumulation Factors (BAF) and Biota-Sediment Accumulation Factors (BSAF) of the trace metals in the *M. vollenhovenii* under study were calculated using the following methods;

$$BAF = \frac{CF\ (mg/kg)}{CW\ (mg/kg)}$$

Where BAF is the biological accumulation factor, CF is concentration of metals in the shrimp and CW is concentration of metals in water.

$$BSAF = \frac{CF\ (mg/kg)}{CS\ (mg/kg)}$$

Where BSAF is the biota-sediment accumulation factor, CS is the concentration of the metals in sediment and CW is the in water

3. RESULTS

Concentration of iron observed in water at Station 2 was sgnificantly higher than that of other stations ($P < 0.05$); which exhibited no significant difference (Table 1). However, the levels of iron across all stations were below the recommended limit by FEPA. The levels of manganese detected in the water of Stations 3 and 4 were higher than the regulatory limit, which was higher than the levels obtained at Station 2 and control. Copper concentration at was higher than the regulatory limit and other stations ($P < 0.01$). Generally, despite the spatial heterogenity in the levels of the trace metals in the water, levels of most of the metals were within regulatory limits throughout the study period.

Table 1: Summary of heavy metals (mg/L) in water of Okumeshi River

METALS	**STATION 1** MEAN±S.E(RANGE)	**STATION 2** MEAN±S.E(RANGE)	**STATION 3** MEAN±S.E(RANGE)	**STATION 4** MEAN±S.E(RANGE)	**P VALUE**	FEPA LIMIT
Fe	**1.81±0.16^{B} (0 – 2.4)**	**4.71±0.25^{A} (0 – 3.5)**	**1.50±0.19^{B} (0 – 2.9)**	**1.48±0.27^{B} (0.2 – 5.4)**	**P<0.05**	20
Mn	**0.31±0.01^{B} (0 – 0.1)**	**0.26±0.06^{B} (0 – 0.7)**	**0.97±0.22^{A} (0 – 2.3)**	**1.26±0.34^{A} (0 – 3.7)**	**P<0.001**	0.5
Zn	**0.7±0.03^{B} (0 – 0.4)**	**0.59±0.15^{A} (0.1 – 2.6)**	**0.92±0.3^{A} (0.2 – 5.2)**	**0.985±0.25^{A} (0 – 3.3)**	**P<0.05**	1
Pb	0.1±0.003(0 – 0.1)	0.08±0.01 (0 – 0.2)	0.03±0.24 (0 – 2.7)	0.33±0.26 (0 – 2.7)	P>0.05	< 1
Cu	**0.3±0.01^{C}(0 – 0.1)**	**0.14±0.03^{B} (0 – 0.5)**	**0.13±0.02^{B} (0 – 0.4)**	**1.05±0.26^{A} (0 – 2.76)**	**P<0.01**	< 1
Cd	**0.5±0.03^{B} (0 – 0.4)**	**0.08±0.02^{B}(0 – 0.3)**	**0.23±0.12^{B}(0 – 1.6)**	**0.4±0.16^{A}(0 – 0.7)**	**P<0.01**	<1
Cr	**0.02±0.01^{C}(0 – 0.2)**	**0.35±0.01^{B}(0 – 1.1)**	**0.71±0.18^{A}(0 – 2.1)**	**0.73±0.2^{A}(0 – 2.3)**	**P<0.01**	<1

Note: *Values with similar superscript letters have no significant difference Number of sample replicates (N) = 18. P>0.05 means there is no significant difference,* ***P<0.05*** *means there is significant difference,* ***P<0.01*** *means there is much significant difference, and* ***P<0.001*** *means there is very much significant difference. ND = Not Detected. FEPA (Federal Ministry of Environment, 2003)*

In the water matrix, only manganese had a significant communality extraction; which was 0.909 (Table 2). Components 1 (4.152) and 2 (1.232) had significant Eigen values and they contributed 51.898 and

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15.395 % respectively to the total percentage of variance. Varimax rotated matrix of water (Table 3) showed that manganese (0.947) > copper (0.883) > zinc (0.817) > chromium (0.759) > Pb (0.790) was the sequence of trace metal activity in component 1. While Cd (0.782) and Fe (0.812) were the only active metals in component 2.

Table 2: Principal components of water

Communality extractions						
Fe	Mn	Zn	Cu	Pb	Cd	Cr
0.680	0.671	0.699	**0.909**	0.555	0.478	0.544
Eigen values by principal components						
1	2	3	4	5	6	7
4.152	**1.232**	0.776	0.717	0.429	0.315	0.202
Percentage of total variance (%)						
51.898	15.395	9.698	8.958	5.263	4.932	2.527

Note: *Communality values from 0.75 and above are significant; hence emboldened*
Eigen values from 1 and above are significant; hence emboldened

Table 3: Varimax rotated component matrix of water

Component	Mn	Cu	Zn	Cr	Pb	Cd	Fe
1	**0.947**	**0.883**	**0.817**	**0.759**	**0.790**	0.675	0.144
2	0.112	0.054	0.061	0.318	0.070	**0.782**	**0.812**

Note: *Communality values from 0.75 and above are significant; hence emboldened*

The mean concentration of Fe in sediment at Station 2 was significantly higher than Station 3 > Station 4 > Station 1 ($P < 0.05$). Concentrations of all trace metals (except lead) in the sediment at all stations; except control exceeded the regulatory limit. The trend of manganese was Stations 2 and 3 > Station 4 > Station 1 ($P < 0.001$).

Table 4: Summary of heavy metals (mg/kg) in Sediment of Okumeshi River

METALS	**STATION 1** MEAN±S.E(RANGE)	**STATION 2** MEAN±S.E(RANGE)	**STATION 3** MEAN±S.E(RANGE)	**STATION 4** MEAN±S.E(RANGE)	**P VALUE**	FEPA LIMIT
Fe	**0.03 ± 0.06^{D} (0 – 2.4)**	**10.9 ± 2.2^{A} (9 – 63.8)**	**8.44 ± 0.19^{B}(0 – 2.9)**	**2.38 ± 0.27^{C}(0.2 – 5.4)**	**P<0.05**	1
Mn	**0.01 ± 0.003^{C} (0 – 0.1)**	**8.24 ± 0.6^{A}(2 – 10.7)**	**5.97 ± 0.22^{A} (1.2– 8.3)**	**4.26 ± 0.34^{B} (0 – 3.7)**	**P<0.001**	0.4
Zn	**0.35 ± 0.06^{D} (0 – 0.4)**	**7.59 ± 0.15^{A} (0.1 – 2.6)**	**4.92 ± 0.3^{B}(0.2 – 5.2)**	**1.99 ± 0.25^{C} (0 – 3.3)**	**P<0.05**	3
Pb	0.01±0.001(0 – 0.1)	0.04±0.01 (0 – 0.2)	0.03±0.24 (0 – 2.7)	0.03±0.26 (0 – 2.7)	P>0.05	0.05
Cu	**0.05 ± 0.015^{C}(0 – 0.1)**	**14.1 ± 0.3^{B}(6.3 –22.2)**	**21.11 ± 2^{A} (8.2 – 31.6)**	**12.01 ± 2^{B} (3.4 -22.7)**	**P<0.001**	0.3
Cd	**0.01 ± 0.001^{C}(0 – 0.3)**	**7.03 ± 0.02^{A}(1.2– 10.3)**	**3.13 ± 0.12^{B}(0 – 5.6)**	**4.8 ± 0.16^{B}(0.3 – 6.7)**	**P<0.01**	0.05
Cr	**0.01 ± 0.001^{D}(0 – 0.2)**	**0.3 ± 0.01^{C}(0 – 1.1)**	**8.33 ± 0.18^{A}(0 – 2.1)**	**4.73 ± 0.2^{B}(0 – 6.3)**	**P<0.01**	2

Note: *Values with similar superscript letters have no significant difference Number of sample replicates (N) = 18. P>0.05 means there is no significant difference,* ***P<0.05*** *means there is significant difference,* ***P<0.01*** *means there is much significant difference, and* ***P<0.001*** *means there is very much significant difference. ND = Not Detected. FEPA (Federal Ministry of Environment, 2003)*

Iron (0.784), manganese (0.745), copper (0.802), and cadmium (0.778) had significant communality extractions in the sediment. While only components 1 (3.954), 2 (1.373) and 3 (1.287) were of significant

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Eigen values (Table 5), and they constituted 49.426, 19.166 and 15.09 % respectively of the total variance. After subjecting only the significant components to further rotation to generate the rotated component matrix; copper (0.896) > cadmium (0.755) > Cr (0.756) was the sequence observed in component 1 (table 6). The sequence in component 2 was: Mn (0.871) > Pb (0.787) > Zn (0.771). Fe (0.812) was the only active metal in component 3.

Table 5: Principal components of sediment

Communality extractions						
Fe	Mn	Zn	Cu	Pb	Cd	Cr
0.784	**0.745**	0.699	**0.802**	0.555	**0.778**	0.544
Eigen values by principal components						
1	2	3	4	5	6	7
3.954	**1.373**	**1.287**	0.563	0.487	0.320	0.217
Percentage of total variance (%)						
49.426	19.166	15.090	5.037	4.087	2.999	1.710

Note: *Communality values from 0.75 and above are significant; hence emboldened*
Eigen values from 1 and above are significant; hence emboldened

Table 6: Varimax rotated component matrix of sediment

Components	Cu	Cd	Cr	Mn	Pb	Zn	Fe
1	**0.896**	**0.755**	**0.756**	0.687	0.656	-0.136	0.401
2	0.014	-0.174	0.447	**0.871**	**0.787**	**0.771**	0.064
3	0.022	0.334	0.142	0.456	0.675	0.056	**0.812**

Note: *Communality values from 0.75 and above are significant; hence emboldened*

Iron (3.28), manganese (6), copper (28.83), cadmium (12.35) and chromium (7.38) had significant sorption into the bottom sediment from the water medium (Table 7) i.e. their sorption capacities are above the significant level of 6 mg/L. Copper had an outstandingly high sorption into the bottom sediment: Cu > Cd > Cr > Mn.

Table 7: Distribution coefficients (Kd) of parameters in sediment and water (mg/L)

Fe	Mn	Zn	Cu	Pb	Cd	Cr
3.28	**6**	4.65	**28.83**	0.244	**12.35**	**7.38**

Note: *Values < 6mg/L are insignificant, = or > 6 mg/L are significant (Soares and Alleoni, 2006). Significant values are emboldened.*

Generally the levels of most metals observed in the *M. vollenhovenii* at the perturbed sections of the river were distinctively higher than the counterparts at the control station (table 8). The concentration of iron observed in *M. vellenhovenii* at Station 2 is significantly higher than that of Station 3 > 4 > Station 1 (P< 0.01). The levels of iron and in the shrimps at all stations exceeded the standard recommendation by

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FEPA. Most high concentrations of trace metals were detected in shrimps at Stations 2 > 3 > 4. The trend can be attributed to the respective extents of perturbations as observed around the stations. Only manganese, lead and chromium exhibited no significant difference shrimps across the stations. The levels of these trace metals in the shrimps were also below FEPA regulatory limit.

Table 8: Summary of heavy metals in *Macrobrachium vollenhovenii* of Okumeshi River

PARAMETERS	**STATION 1** MEAN±S.E(RANGE)	**STATION 2** MEAN±S.E(RANGE)	**STATION 3** MEAN±S.E(RANGE)	**STATION 4** MEAN±S.E(RANGE)	**P VALUE**	FEPA LIMIT
Fe (mg/L)	**0.3±0.06^{D} (0 – 1.2)**	**11.2±2.1^{A} (6.2 – 16.8)**	**8.44±1.19^{B}(2.2 –12.9)**	**1.78±0.27^{C}(0.2 – 3.4)**	**P<0.01**	100
Mn (mg/L)	0.001±0.001(0 –0.1)	0.23±0.01(0 -0.7)	0.35±0.01(0 –1.1)	0.32±0.04(0 –1.7)	P>0.05	1
Zn (mg/L)	**0.35±0.06^{C} (0 – 0.84)**	**4.99±0.15^{A} (0.1 – 8.6)**	**2.92±0.3^{B}(0.2 – 6.9)**	**0.99±0.2^{C} (0 – 1.5)**	**P<0.05**	75
Pb (mg/L)	ND	0.01±0.01 (0 – 0.2)	0.02±0.24 (0 – 2.7)	0.03±0.26 (0 – 2.7)	P>0.05	0.05
Cu (mg/L)	**0.05±0.015^{C}(0 – 0.1)**	**14.12±0.01^{A}(0 – 0.5)**	**12.3±0.02^{A} (0 – 0.4)**	**2.05±0.22^{B} (0 – 2.76)**	**P<0.001**	3
Cd (mg/L)	**ND^{c}**	**6.08±0.02^{A}(0 – 0.3)**	**2.23±0.12^{B}(0 – 1.6)**	**2.8±0.16^{B}(0 – 0.7)**	**P<0.01**	2
Cr (mg/L)	0.003±0.001(0 – 0.12)	0.04±0.01(0 – 0.9)	0.01±0.002(0 – 1.2)	0.03±0.2(0 – 0.7)	P>0.05	-

Note: *Values with similar superscript letters have no significant difference Number of sample replicates (N) = 18. P>0.05 means there is no significant difference,* ***P<0.05*** *means there is significant difference,* ***P<0.01*** *means there is much significant difference, and* ***P<0.001*** *means there is very much significant difference. ND = Not Detected. FEPA (Federal Ministry of Environment, 2003)*

Fe (0.772), Mn (0.945), Cu (0.784) had significant communality extractions (Table 9), while components 1 (4.054), 2 (2.973), 3 (1.887) and 4 (1.563) only had the significant Eigen values; hence were the only considered components. Varimax rotated component matrix showed that Cu (0.896) > Fe (0.725) > Zn (0.796) > Cd (0.887) were active in component 1. Cr (0.767) was the active metal in component 2, Pb (0.783) in component 3 and Mn (0.772) in component 4.

Table 9: Principal components of *Macrobrachium vollenhovenii*

Communality extractions						
Fe	Mn	Zn	Cu	Pb	Cd	Cr
0.772	**0.945**	0.223	**0.784**	0.251	0.278	0.223
Eigen values by principal components						
1	2	3	4	5	6	7
4.054	**2.973**	**1.887**	**1.563**	0.487	0.320	0.217
Percentage of total variance (%)						
39.426	21.166	17.090	14.037	3.087	2.999	2.195

Note: *Communality values from 0.75 and above are significant; hence emboldened Eigen values from 1 and above are significant; hence emboldened*

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Table 10: Varimax rotated component matrix of *Macrobrachium vollenhovenii*

Components	Cu	Fe	Zn	Cd	Cr	Pd	Mn
1	**0.896**	**0.785**	**0.796**	**0.887**	0.656	0.636	0.401
2	0.014	-0.174	0.447	0.559	**0.767**	0.271	0.541
3	0.023	0.561	0.334	0.243	0.012	**0.783**	0.472
4	0.455	0.056	0.667	0.451	0.042	0.402	**0.772**

Note: *Communality values from 0.75 and above are significant; hence emboldened*

As seen in Figure 2, significant Biological Accumulation Factors (BAF) were observed in iron (3.27), zinc (2.89), copper (17.6) and cadmium (9.17). The BAF of copper in the shrimp was outstandingly higher than others, while manganese, lead and chromium exhibited no significant BAFs. The high BAF of copper in *M. vollenhovenii* can be attributed to its threshold of essentiality in the respiratory pigment of the shrimp.

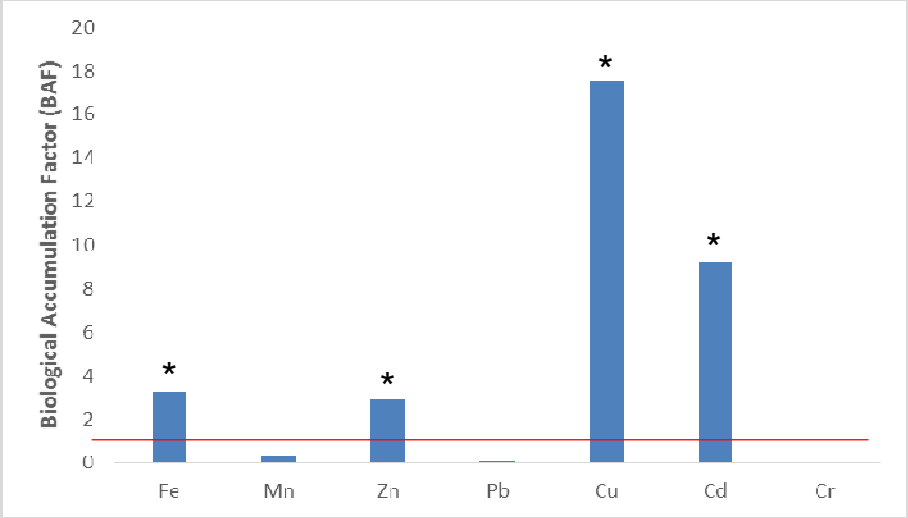

Figure 2- Biological Accumulation factors (BAF) of trace metals in *M. vollenhovenii*Note: *NOTE: BAF values of 1 and above signify significant values; indicated by the red line. Asterisked bars indicate trace metals of significant BAF.*

Significant Biota-Sediment Accumulation Factor (BSAF) was observed only in iron (1). Other trace elements exhibited non-significant BSAF (Figure 3). This implies that the shrimps accumulated more trace metals from the water matrix than from the sediment matrix.

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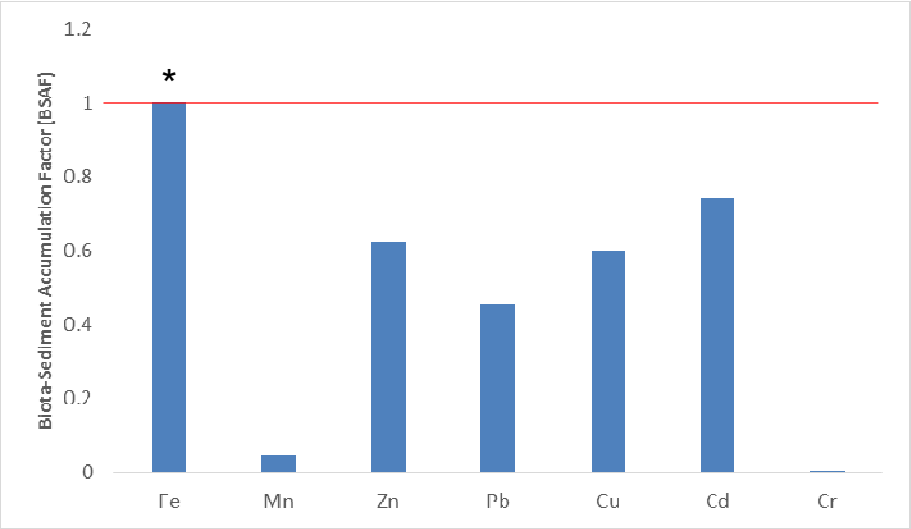

Figure 3- Biota-Sediment Accumulation factors (BSAF) of trace metals in *M. vollenhovenii*
NOTE: BAF values of 1 and above signify significant values; indicated by the red line. Asterisked bars indicate trace metals of significant BAF.

The levels of zinc (8864.68 ± 12.72) and copper (1387.48 ± 22.21) observed in the blood samples of the individuals who consume *M. vollenhovenii* of the river are higher than the recommended ranges; which are 4400- 8600 and 800- 1300 µg/ L respectively (Table 11). The levels of other trace metals in the blood samples of the subjects were within the acceptable range recommended by Iyengar and Woittiez (1988).

Having ascertained from results that significant concentrations of metals were accumulated only in shrimp samples obtained from the perturbed sections of the river, the need to trace these metals in the consumers became apparent. Therefore, at this juncture only *M. vollenhovenii* harvested from perturbed sections of the river were further assessed in the study. Significant correlations were observed between the trace metals in the *M. vollenhovenii* tissues and blood samples of subjects (Table 12). Level of iron in the blood samples highly correlated positively (0.81) with that in the *M. vollenhovenii* tissues. High correlations were also observed between the manganese (0.72) in the blood and that in the shrimp samples; zinc was 0.95, copper was 0.87 and cadmium was 0.67. Only chromium in the blood and the shrimp showed no significant correlation. The non-essential trace metals in the shrimps correlated negatively with the essential trace metals in the blood samples.

Table 11: Summary of trace metals in blood samples of Ukwuani residents; against recommended ranges

Metals	Mean ± S.E	Range	Certified Range (Iyengar and Woittiez, 1988)
Fe	221.5 ± 12	(172.4- 293.2)	309- 521
Mn	1.42 ± 0.04	(0.78- 2.76)	8- 18.7
Zn	**8864.68 ± 12.72***	(8542.3- 9012.2)	4400- 8600
Pb	0.031 ± 0.001	(0.01- 0.05)	8- 18.7
Cu	**1387.48 ± 22.21***	(1352- 1402)	800- 1300
Cd	0.029 ± 0.002	(0.006- 0.042)	0.3- 7
Cr	0.21 ± 0.004	(0.14- 0.34)	2.8- 45

NOTE: Values are expressed in µg/L and sample size is 156 individuals. Emboldened and asterisked values signify significant values; higher than certified range.

Table 12: Correlation of trace metals in *M. vollenhovenii* with the levels in Human blood samples

S- Fe	S- Fe	S- Mn	S- Zn	S- Pb	S- Cu	S- Cd	S- Cr	H- Fe	H- Mn	H- Zn	H- Pb	H- Cu	H- Cd	H- Cr
	1													
S- Mn	0.42	1												
S- Zn	0.53	0.55	1											
S- Pb	0.02	-0.02	0.01	1										
S- Cu	0.52	0.43	0.82	0.61	1									
S- Cd	0.17	0.01	-0.03	0.02	0.22	1								
S- Cr	0.31	0.34	0.58	0.04	0.44	**-0.67**	1							
H- Fe	**0.81**	0.52	0.04	0.22	0.47	0.41	0.33	1						
H- Mn	0.42	**0.72**	0.51	0.33	0.62	0.21	0.44	0.24	1					
H- Zn	0.02	0.29	**0.95**	0.44	0.02	0.34	**0.71**	0.47	**0.76**	1				
H- Pb	0.33	0.21	**-0.75**	0.29	0.02	0.07	0.09	0.02	**-0.78**	0.44	1			
H- Cu	0.03	-0.09	0.04	-0.06	**0.87**	**-0.82**	0.05	0.41	0.06	-0.22	0.36	1		
H- Cd	0.45	0.27	0.07	0.41	0.06	**0.67**	0.22	0.12	0.04	-0.01	-0.27	0.46	1	
H- Cr	0.04	0.08	0.49	0.06	0.02	0.33	0.35	0.24	0.17	0.02	**-0.71**	**-0.66**	0.19	1

NOTE: Values ≥ 0.5 signify significant correlations; hence emboldened, < 0.5 are insignificant. Prefix S= shrimps samples, while Prefix H= Human blood samples

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4. DISCUSSION

Spatially heterogeneous patterns of the trace metals in the river were apparent. The studies environmental matrices also accumulated the metals at different rates i.e. sediment > *M. vollenhovenii* > water > human blood. Concentrations of most of the metals analyzed in water of the river were higher at the perturbed stations than the control; although most of them were lower than the regulatory limit, except manganese and copper (Table 1) i.e. concentration of manganese at Stations 3 and 4 were significantly higher than the concentration at the control station and the regulatory standard limit ($P<0.001$). Manganese and copper were also the active components in the water medium (Table 3). This can be attributed to oil exploration activities around the stations. Although manganese is essential for healthy bones (Li *et al*., 2014); a constituent of mucopolysaccharides needed for healthy joint formation. Manganese is also essential for regulation of red blood cells and the reproductive cycle in vertebrates generally. It is a constituent of a number of metalloenzymes that occupy key roles in metabolism (Woolhouse, 1983; Burnell, 1988). Due to the high essentiality of manganese, there is little risk of exposure unless at extremely high concentrations; which is not the case in the current study area. High concentration of manganese in water at Gelegele section of Osse River was also attributed to oil exploration activities (Omoigberale and Ogbeibu, 2010; Oguzie and Ehigiator (2011).

Levels of trace metals were higher in the sediment (Table 2) than the water medium (Table 1) due to the repository nature of the sediment. This observation agrees with the findings of Cammuso et al., (1995). Through continuous biomagnification concentrations of copper could rise to attendant levels in organisms at the higher trophic levels and could ultimately culminate in tissue injury in vertebrates; due to its high oxidation potential i.e. excess copper may cause oxidative damage to biological systems, including peroxidation of lipids and other macromolecules.

The journey of the trace metals through all the matrices studied shows that movements of the metals are interactive. The sequence of active components in the water medium was Mn > Cu > Zn > Cr > Pb > Cd >Fe (Table 3), while that of sediment was Cu > Cd > Cr > Mn > Pb > Zn > Fe. This change in trend resulted from the complex interactions among the metals and with the matrices. This is quite evident in their respective sorption capacities which was: Cu (28.8) > Cd (12.35) > Cr (7.38) > Mn (6). There is a very high correlation between the sorption capacities and the component sequence in the

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sediment. Very high sorption capacities copper (141.76) and cadmium (400) were earlier observed at Ikpoba River, Benin City by Ogbeibu et al. (2014). Only sorption capacities of manganese, zinc and lead in the current study area were relatively low compared to the values obtained at Ikpoba River; there is somewhat correlation in the sorption capacities of the rest trace metals. The slight variability between the results obtained from the current study area and that of Ikpoba River can be attributed to the distinguished anthropogenic activities i.e. Ikpoba River was perturbed by effluents from a nearby brewery (Ogbeibu et al. 2014).

The levels of zinc and copper observed in the human blood were higher than the standard limits. This can be attributed to the sequence of components in the shrimps, which was: Cu (0.896) > Fe (0.785) > Zn (0.796) > Cd (0.887) > Cr (0.767) > Pb (0.783), Mn (0.772). The outstanding occurrence of copper in the sampled *M. vollenhovenii* can be attributed to bioavailability of copper in the matrices, particularly water; coupled with the fact that shrimps are notorious accumulators of copper due to the high essentiality of copper in their respiratory pigment haemocyanin (Van De Broek, 1979). Result indices show that only shrimps at the oil exposed Stations 2 and 3 accumulated copper beyond regulatory limit. This is due to the high bioavailability and affinity for copper (Table 8). Besides copper the shrimp exhibited affinity in the following order Cu > Fe > Zn > Cd > Cr > Pb > Mn (Table 10). High affinity of *M. vellenhovenii* for these metals necessitates stringent mitigation of the perturbing anthropogenic activities around the river. High bioavailability of the metals to the shrimps is enhanced by its feeding habit and niche i.e. they are detritivorous animals which feed on epibenthic organisms such as polychaetes, molluscs and other crustaceans (Isibor 2016). Also morphologically, their abdomen not being flexed beneath the thorax maximizes bioaccumulation of contaminants from the sediments and overlying water (Omoigberale and Ikponmwosa-Eweka, 2010). However Figures 2 and 3 show that most of the trace metals were accumulated more from the water than the sediment matrix. Significant bioaccumulation of some trace metals were earlier reported in the *M. vollenhovenii* of Ovia River, Nigeria (Oguzie and Ehigiator, 2011) and Egbokodo River, Nigeria (Isibor and Oluowo, 2016).

Zinc and copper were slightly above recommended limits in the human blood (Table 11). Excess zinc in consumers of the *M. vellenhovenii* may cause anaemia, damage to the pancreas and decrease levels of high density lipoprotein cholesterol (ATSDR, 2005). While impressible levels of copper observed

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in the blood of the consumers of *M. vollenhovenii* may elicit liver cirrhosis (ATSDR, 2010). These health consequences are liable to ensue of the trend in the aquatic environment is left unmitigated over an appreciable period of time. The high levels of the trace metals in the blood can be traced to their substantial availability in the shrimps. This is also buttressed by the fact very high positive correlations occurred between zinc (0.95) and copper (0.87) in the shrimp and blood samples of the dependent populace (Table 12).

5. CONCLUSION

Results shows that Okumeshi River was impacted by the anthropogenic activities which may have some health impacts on the consumers of the *Macrobrachium vollenhovenii* of the river. High level of zinc and copper in human blood necessitates a prompt bioremediation in the aquatic environment. The observed insalubrity of the shrimps is a prognostic of chronic health hazards to the consumers. The study has provided an early signal of likely impending catastrophe; necessitating a proactive regulation of trace metals released into the aquatic system through the prevalent anthropogenic activities.

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