

**HEAVY METALS IN SOME FISH SPECIES FROM OBOTIE RIVER ALONG THE  
NIGER DELTA ZONE OF NIGERIA, WEST AFRICA**

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**ABSTRACT**

The concentrations of Cadmium(Cd), Chromium(Cr), Copper(Cu) and Lead (Pb), were determined in Characid, Bagrid and Cichlid fish species from Obotie river, in the Niger Delta zone of Nigeria, by Atomic Absorption Spectrometric technique, in order to assess levels of potential risk to man who may eventually consume such fish. The mean concentrations of metals in fish ranged from 0.15 mg/kg (Cd) in *Brycinus nurse* to 12.32 mg/kg (Cu) in *Tilapia zillii*. The relative health factor (RHF), using fish as an integral component, ranged from 0.33 for Cu to 5.06 for Pb while the bioaccumulation quotient (BQ) ranged from 37.5 for Cd in *B. nurse* to 300.48 for Cu in *T. zillii*. The metals of ecological concern were Cd, Cr and Pb as their mean concentrations in fish and water surpassed established International thresholds. Such resources must therefore be consumed with caution in order to avert unwholesome health consequences over time.

**Key words:** Fish, Relative health factor, Bioaccumulation quotient

**INTRODUCTION**

Heavy metals are universally recognized as ubiquitous environmental pollutants. The increase of these metals in natural aquatic media has been linked to the rapid growth of economic activities particularly in developing countries (Ley et al. 2013). Food and water are the two main sources of essential metals and are also the media through which humans and fish are exposed to toxic metals (Amin et al. 2013). As heavy metals are not degradable, their effect on the environment can persist for a long time (Zhao and Marriott, 2013). Health Authorities in many parts of the world are becoming increasingly concerned about the effects of heavy metals on environmental and human health (Bolan et al. 2014). In addition, heavy metals are potential human health hazards especially when safe thresholds of exposure or absorption are exceeded (Zhao et al. 2014). On this premise, ecotoxicological research has been conducted worldwide using a host of environmental media, including fauna, flora, soil, sediment, and water, with a view of evaluating environmental integrity with regard to heavy metals. Obotie River, located in the Niger Delta belt of Nigeria, is under diverse anthropogenic perturbations along its course, which may conceivably introduce heavy metals

into the river in addition to natural background levels. It is in this realm that ecological risk assessments are carried out to provide a framework for estimating the possible toxic effects of pollutants on aquatic ecosystems (Quiroz et al. 2010). The present risk assessment was carried out to ascertain the level of heavy metal contamination in this aquatic ecosystem against the backdrop that there is paucity of ecotoxicological data regarding heavy metal pollution in the river. Furthermore, the river is a source of water and fish to people living around the area which underscores the relevance of the study. The heavy metals of interest (HMI) were Cd, Cr, Cu and Pb. The aforesaid HMI were determined in water, sediment and selected commercially important fish species. The specific bioindicators used were *Tilapia zillii* (Gervais, 1848), belonging to the family Cichlidae, *Chrisichthys nigrodigitatus* (Lacepede, 1803), belonging to the family Bagridae, and *Brycinus nurse* (Ruppel, 1832), belonging to the family Characidae. These species were purposely selected based on their commercial appeal. Data generated from the study have been compared to environmental media thresholds established by the World Health Organization (WHO), United States Environmental Protection Agency (USEPA), United States Department of Energy (USDOE) and the Wisconsin Department of Natural Resources (WDNR). Findings from the study are expected to serve as a reference point for future studies especially on this particular river ecosystem and could assist relevant ecological risk managers in executing risk mitigation and containment processes.

## **MATERIALS AND DETAILS**

### **Description of the study area**

Obotie River is located in Delta state, Nigeria and is gridlocked within Latitude 5.84092 °N and Longitude 5.57207 °E (Figure 1). The rainfall pattern of the area is typically bimodal, peaking usually in July and September yearly. Within the Obotie community, farming and fishing are the major occupations of the people. Three stations (Ale-Obite, Egbemeji- Odo and Odo), were established along the course of the river for the study, based on observed human activities and the characteristics of effluents entering the river. At Ale-Obite, observable activities include laundry, swimming and fishing while at Egb emeji- Odo, activities such as lumbering, sawmilling and palm oil production take place. At the Odo station, fishing is the main activity and several local water crafts (canoes) and boats fitted with outboard engines can be found in operation at this point. The study was carried out between August, 2016 and January, 2017.

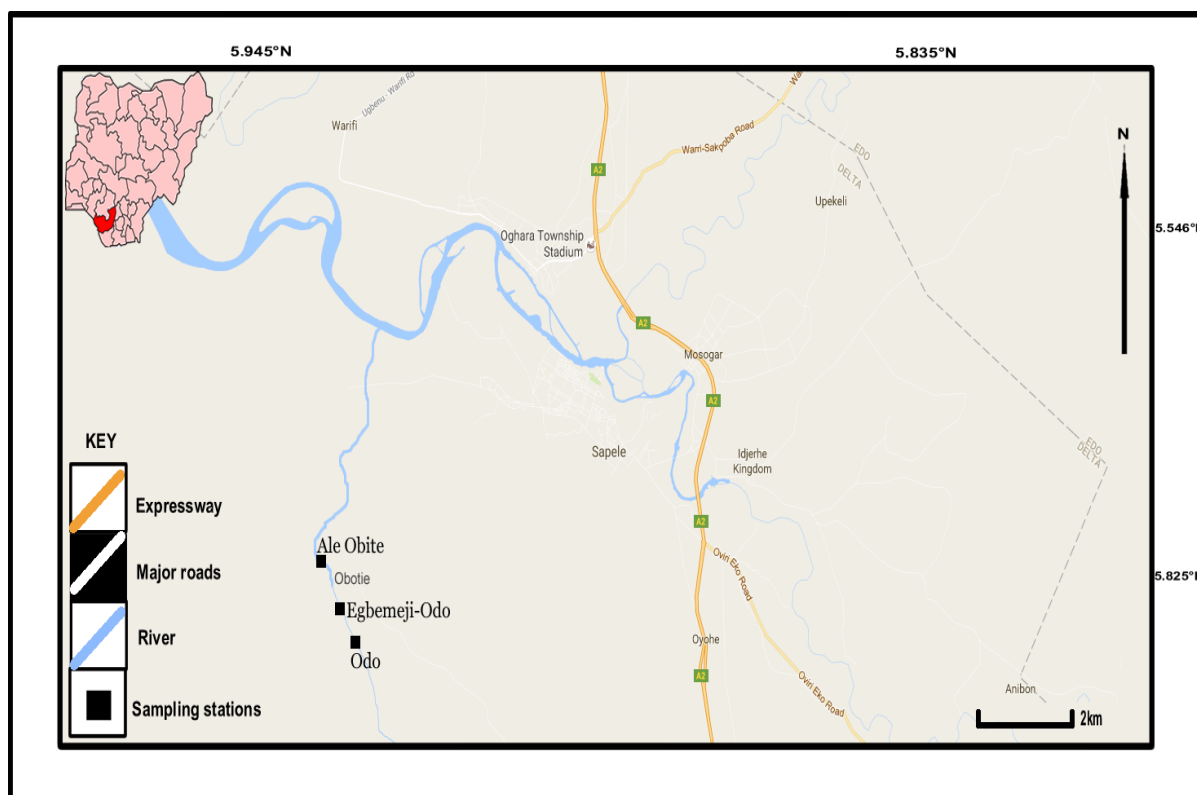


Fig.1: Satellite map of study area; Source: Google maps (2017)

### Collection of fish samples

Fish samples were captured with the assistance of artisanal fishermen using local fish traps, cast nets and baited hooks. Fish were washed in flowing water to remove adhering debris before they were transported to the laboratory within 24 hours in a Thermolineo® ice chest. A total of eighteen (n=18) *T. zillii* species (mean wet weight  $88.45 \pm 1.46$ g; mean total length  $18.76 \pm 1.33$  cm), twenty (n=20) *C. nigrodigitatus* species (mean wet weight  $92.09 \pm 3.42$ g; mean total length  $19.53 \pm 2.61$  cm) and eighteen (n=18) *B. nurse* species (mean wet weight  $69.38 \pm 2.15$ g; mean total length  $17.97 \pm 1.83$  cm) were collected.

### Collection of water samples

Surface water samples were collected randomly at approximately 30 cm depth into polyethylene bottles of 500 ml capacity. The bottles were pre-conditioned with 10% nitric acid (HNO<sub>3</sub>) and later rinsed with distilled water, 24 hours prior to use. The water samples were acidified to pH 1.5 with 10% nitric acid to ensure that heavy metals did not adhere to the walls of the bottles during storage. The samples were thereafter transported to the laboratory within 24 hours and stored at -4 °C in a Polystar® PV-CF 300L freezer.

### Collection of sediments

Eckman grab samples of sediment were collected from the river bed at approximately 20 cm depth and were placed in polythene containers which had earlier been washed out with detergent and rinsed with distilled water. Collected samples were transported to the laboratory on ice within 24 hours prior to further studies.

### Preparation and digestion of fish samples

Myonematic tissues were excised with a stainless steel lancet from the flanks of fish and oven dried at 80 °C for 72 hours using a Uniscope® SM 9023 Laboratory oven (Surgifield medicals, England), until a constant weight was attained. Each sample was milled separately for homogeneity using a porcelain mortar and pestle. Digestion of fish samples was achieved by organic extraction method as described by Endo et al. (2004). Blanks were prepared using the same quantity of mixed acids but without the samples. All reagents used were of analytical grade (BDH, England).

### Digestion of water samples

Water samples were digested using the pre-concentrated acid method (Parker, 1972; Wangboje and Ekundayo, 2015). Each sample was stored in plastic reagent containers prior to analysis. Blank samples were prepared using the same quantity of acid.

### Preparation and digestion of sediment samples

Sediment samples were sundried for 48 hours and sieved through a mesh net to remove coarse particles. The sieved sediment was oven dried at 75 °C for 72 hours until a constant weight was attained. Digestion was carried out as previously mentioned for fish.

### Analysis of fish, water and sediment digests for heavy metals

All digests were analysed thrice for Cd, Cr, Cu and Pb by means of a Unicam® 929 Series Atomic Absorbance Spectrophotometer (Unicam, England) with solar software using air acetylene flame. Heavy metal values in fish and sediment were expressed in mg/kg while heavy metal values in water were expressed in mg/L. A GENSTAT® computer software (Version 13.1 for Windows) was used for statistical analysis. Analysis of variance (ANOVA) was used to test for significant differences ( $P < 0.05$ ) between mean values of metals while Duncan Multiple Range Test was used to separate significant means. Microsoft Excel (for Windows 2010), was used for all graphical presentations.

### Bioaccumulation quotient (BQ)

The BQ expresses the ability of fish to accumulate heavy metals to levels above that of water or sediment.

$$BQ = \frac{\text{Heavy metal concentration in fish}}{\text{Heavy metal concentration in water or sediment}}$$

### Relative health factor (RHF)

The RHF expresses the potential health hazard of consuming fish or water containing heavy metals (Gnandi et al. 2011).

$$RHF = \frac{\text{Heavy metal concentration in fish or water}}{\text{Maximum limit for heavy metal in fish or water}}$$

### Condition factor (CF) for fish

The CF expresses the fatness, wellbeing, and relative robustness of a fish. It is believed that a heavier fish of a given length is in better condition than a lighter fish of the same length. The Condition factor is expressed below (Baijot et al. 1997).

$$CF = 100 * \text{Weight of fish (g)} / \text{Length of fish (cm)}^3$$

#### Maximum acceptable risk index (MAR) for heavy metals

The MAR, is a simplified representation of biomagnifications in food webs (Romijn *et al.*, 1993; Reinhold *et al.*, 1999; Wangboje *et al.*, 2014).

MAR=

$$\frac{\text{Dietary no observed effect concentration of chemical element in man}}{\text{Bioaccumulation Quotient (BQ) for chemical element in fish}}$$

Where: MAR>1 = High MAR level and MAR<1= Low MAR level

#### Average daily intake (ADI) of heavy metals by man via fish

ADI (mg/person/day) = Heavy metal content in fish \* Per capita consumption/ Body weight

Where; Per capita consumption = 40 g/person/day; Body weight= 70 kg

#### Average annual intake (AAI) of heavy metals by man via fish

$$AAI \text{ (mg/person/year)} = ADI * 365 \text{ days}$$

#### Distribution co-efficient (DC) for heavy metals

The DC essentially expresses the relative solubility of heavy metals in water and is given below;

$$DC = \frac{\text{Concentration of heavy metal in water}}{\text{Concentration of heavy metal in sediment}}$$

#### Theoretical maximum daily intake (TMDI) for heavy metals

The TMDI is used for making a first estimate of heavy metal residue intake (WHO, 1997; Wangboje *et al.* 2017).

$$TMDI = \sum ML^1 * F^1$$

Where: ML = Maximum limit for a given food; F = Per capita/ regional food consumption.

#### Total toxicity of mixtures (TTM) index for heavy metals

Whether or not a mixture of metals in a particular medium exceeds the quality guideline value for that medium, was determined by applying the TTM index (ANZECC/ARMCANZ, 2000)

$$TTM = \sum (C^1 / GV^1)$$

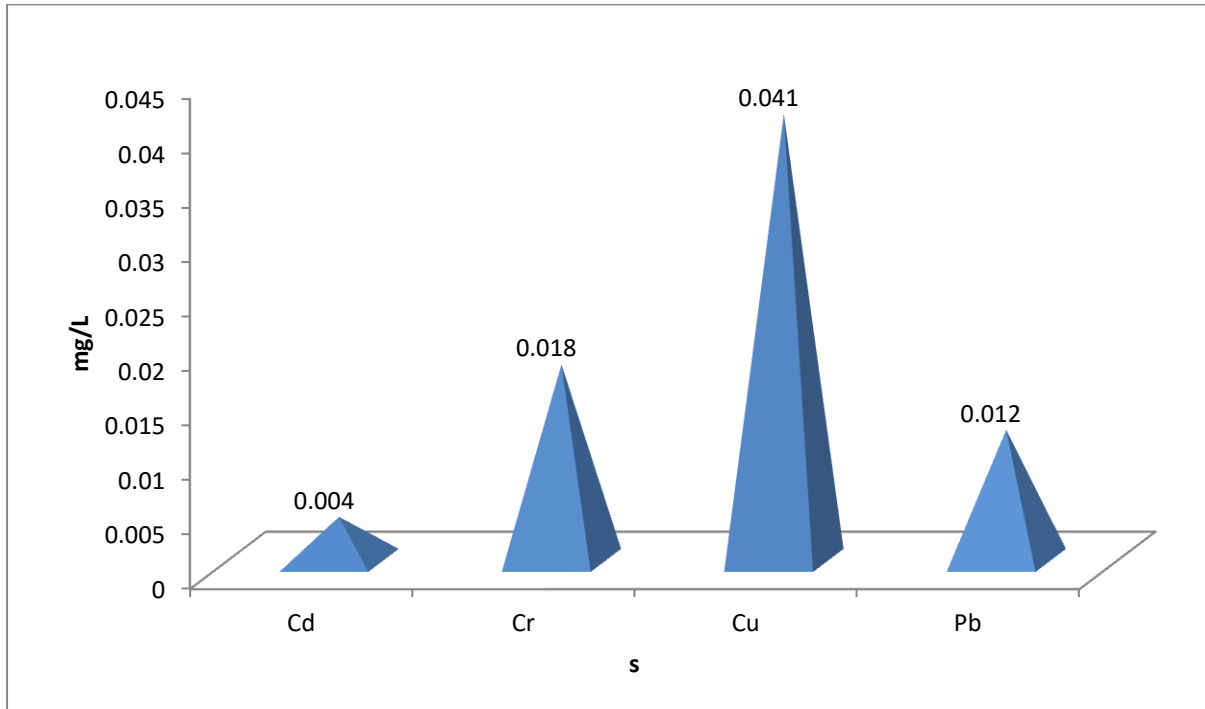
Where: C<sup>1</sup> = Concentration of the 'i<sup>th</sup>' component of mixture

GV<sup>1</sup> = Guideline value for the 'i<sup>th</sup>' component

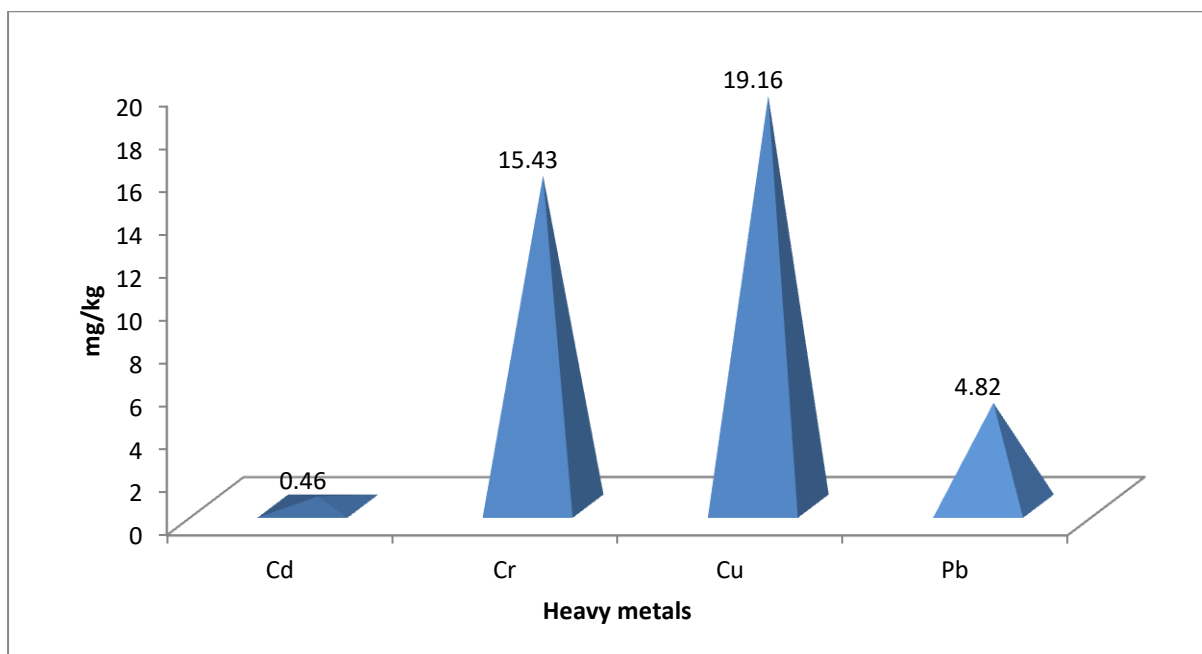
TTM >1 = The mixture has exceeded the Guideline value

### RESULTS

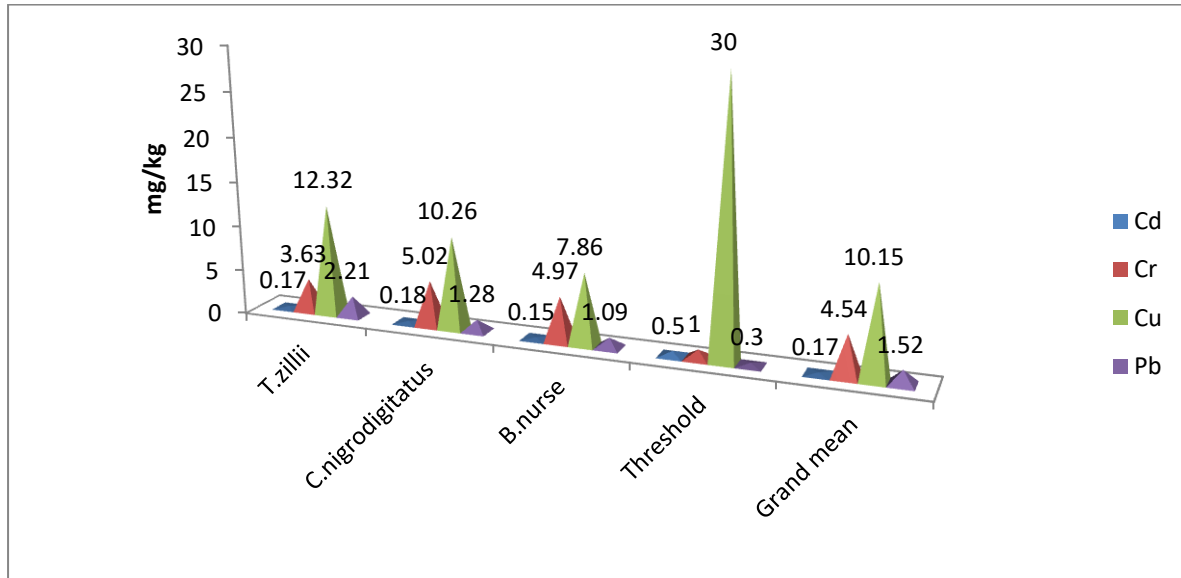
The mean concentrations of heavy metals in water ranged from 0.004 mg/L for Cd to 0.041 mg/L for Cu (Fig.2) while the mean concentrations of heavy metals in sediment ranged from 0.46 mg/kg for Cd to 19.16 mg/kg for Cu (Fig.3). The mean concentrations of heavy metals in experimental fish species ranged from 0.15 mg/kg for Cd in *B. nurse* to 12.32 mg/kg for Cu in *T. zillii* as shown in Figure 4. The mean concentrations of heavy metals in water monthly-wise, ranged from below detection limit (BDL) for Cd in October and November to 0.05 mg/L for Cu in August. There were significant differences ( $P < 0.05$ ) in the mean concentrations of Cr and Cu in water between months (Table 1).



**Fig 2: Mean concentrations (mg/L) of heavy metals in water**



**Fig 3: Mean concentrations (mg/kg) of heavy metals in sediment**



**Fig.4: Mean concentration (mg/kg) of heavy metals in fish species**

**Table 1: Mean concentrations of heavy metals (mg/L) in water by months**

| Heavy Metal | Aug.                     | Sept.                    | Oct.                     | Nov.                     | Dec.                     | Jan.                     | SE M  | WHO (2008) Threshold | USEPA (2012) Threshold |
|-------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------|----------------------|------------------------|
| Cd          | 0.007±0.00 <sup>a</sup>  | 0.003±0.00 <sup>a</sup>  | 0.00                     | 0.00                     | 0.007±0.012 <sup>a</sup> | 0.007±0.012 <sup>a</sup> | 0.006 | 0.003                | 0.005                  |
| Cr          | 0.020±0.01 <sup>b</sup>  | 0.23±0.006 <sup>a</sup>  | 0.003±0.006 <sup>b</sup> | 0.003±0.006 <sup>b</sup> | 0.027±0.012 <sup>b</sup> | 0.030±0.017 <sup>b</sup> | 0.008 | 0.05                 | 0.10                   |
| Cu          | 0.050±0.01 <sup>a</sup>  | 0.047±0.006 <sup>a</sup> | 0.043±0.005 <sup>a</sup> | 0.033±0.006 <sup>b</sup> | 0.04±0.01 <sup>a</sup>   | 0.033±0.006 <sup>b</sup> | 0.006 | 2.0                  | 1.30                   |
| Pb          | 0.017±0.006 <sup>a</sup> | 0.017±0.015 <sup>a</sup> | 0.007±0.006 <sup>a</sup> | 0.010±0.012 <sup>a</sup> | 0.013±0.012 <sup>a</sup> | 0.010±0.001 <sup>a</sup> | 0.009 | 0.01                 | 0.00                   |

Rows with similar superscripts are not significantly different ( $P>0.05$ ); SEM= Standard Error of Mean

**Table 2: Mean concentrations of heavy metals (mg/L) in water by stations**

| Heavy metal | Ale-Obite                | Egbemeji-Odo             | Odo                      | SEM   | WHO (2008) Threshold | USEPA (2012) Threshold |
|-------------|--------------------------|--------------------------|--------------------------|-------|----------------------|------------------------|
| Cd          | 0.005±0.008 <sup>a</sup> | 0.005±0.008 <sup>a</sup> | 0.002±0.004 <sup>a</sup> | 0.005 | 0.003                | 0.005                  |
| Cr          | 0.018±0.013 <sup>a</sup> | 0.020±0.019 <sup>a</sup> | 0.015±0.008 <sup>a</sup> | 0.006 | 0.05                 | 0.10                   |
| Cu          | 0.038±0.004 <sup>a</sup> | 0.045±0.011 <sup>a</sup> | 0.040±0.011 <sup>a</sup> | 0.004 | 2.0                  | 1.30                   |
| Pb          | 0.010±0.011 <sup>a</sup> | 0.010±0.011 <sup>a</sup> | 0.017±0.005 <sup>a</sup> | 0.006 | 0.01                 | 0.00                   |

Rows with similar superscripts are not significantly different ( $P > 0.05$ ); SEM= Standard Error of Mean

**Table 3: Mean concentrations of heavy metals (mg/kg) in sediment by months**

| Heavy metal | Aug.                    | Sept.                   | Oct.                    | Nov.                    | Dec.                    | Jan.                    | SE M | USDOE-ISQG* (1997) Threshold (PEC) | WDNR-CBSQG* (2003) Threshold (PEC) |
|-------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------|------------------------------------|------------------------------------|
| Cd          | 1.02±0.16 <sup>a</sup>  | 0.88±0.09 <sup>a</sup>  | 0.21±0.17 <sup>b</sup>  | 0.24±0.07 <sup>b</sup>  | 0.21±0.17 <sup>b</sup>  | 0.19±0.14 <sup>b</sup>  | 0.12 | 11.7                               | 5.0                                |
| Cr          | 18.08±9.42 <sup>a</sup> | 18.77±3.09 <sup>a</sup> | 13.39±2.95 <sup>b</sup> | 13.38±2.95 <sup>b</sup> | 16.22±1.94 <sup>a</sup> | 12.74±1.79 <sup>b</sup> | 4.21 | 159                                | 110                                |
| Cu          | 16.70±2.42 <sup>b</sup> | 17.77±2.83 <sup>b</sup> | 20.17±5.39 <sup>a</sup> | 17.81±3.72 <sup>b</sup> | 23.02±5.26 <sup>a</sup> | 20.48±5.45 <sup>a</sup> | 3.57 | 77.7                               | 150                                |
| Pb          | 3.31±0.51 <sup>b</sup>  | 4.09±0.78 <sup>b</sup>  | 3.21±0.55 <sup>b</sup>  | 3.32±0.55 <sup>b</sup>  | 6.82±1.33 <sup>a</sup>  | 8.12±1.22 <sup>a</sup>  | 0.62 | 396                                | 130                                |

Rows with similar superscripts are not significantly different ( $P > 0.05$ ); SEM= Standard Error of Mean \* Integrative Sediment Quality Guideline; \*\* Consensus Based Sediment Quality Guideline. PEC = Probable effect concentration.



**Table 4: Mean concentrations of heavy metals (mg/kg) in sediment by stations**

| Heavy metal | Ale-Obite               | Egbemeji-Odo            | Odo                     | SEM  | USDOE-ISQG (1997) Threshold(PEC) | WDNR-CBSQG (2003) Threshold(PEC) |
|-------------|-------------------------|-------------------------|-------------------------|------|----------------------------------|----------------------------------|
| Cd          | 0.49±0.42 <sup>a</sup>  | 0.43±0.33 <sup>a</sup>  | 0.46±0.37 <sup>a</sup>  | 0.08 | 11.7                             | 5.0                              |
| Cr          | 18.94±6.68 <sup>a</sup> | 12.58±4.02 <sup>b</sup> | 14.77±3.59 <sup>b</sup> | 2.93 | 159                              | 110                              |
| Cu          | 20.69±5.95 <sup>a</sup> | 17.34±1.53 <sup>a</sup> | 19.44±4.10 <sup>a</sup> | 2.53 | 77.7                             | 150                              |
| Pb          | 5.01±1.93 <sup>a</sup>  | 4.20±1.74 <sup>a</sup>  | 5.24±2.81 <sup>a</sup>  | 0.44 | 396                              | 130                              |

Rows with similar superscripts are not significantly different ( $P>0.05$ ); SEM= Standard Error of Mean

**Table 5: Comparison of mean heavy metal levels (mg/kg) in sediment to selected studies**

| Heavy metal | This study | Mediterranean Sea, Egypt (Khaled <i>et al.</i> , 2017) | Khoshk River, Iran (Moore <i>et al.</i> , 2011) | Ikpoba River, Nigeria (Oronsaye <i>et al.</i> , 2010) | River Ngada, Nigeria (Akan <i>et al.</i> , 2010) | Kubanni River, Nigeria (Butu and Iguisi, 2013) | Taylor Creek, Nigeria (Okafor and Opuene, 2007) |
|-------------|------------|--|---|---|--|--|---|
| Cd          | 0.46       | 0.76   | 0.26  | 0.53  | 12.56  | ND   | 3.03  |
| Cr          | 15.43      | ND   | 72.26   | 0.41  | 32.89  | 24.3   | 3.02  |
| Cu          | 19.16      | 5.36   | 68.25   | 7.96  | 34.13  | ND   | ND  |
| Pb          | 4.82       | 15.21  | 39.25   | 2.07  | 58.98  | ND   | 119.63  |

ND= Not determined

**Table 6: Comparison of mean heavy metal levels (mg/kg) in fish to selected studies**

| Heavy metal | This study | <i>Hydrocynus forskahlii</i> , Ogun Coastal water (Murtala <i>et al.</i> , 2012) | <i>Clarias gariepinus</i> , Wadi Hanefah, Saudi Arabia (Mahboob <i>et al.</i> , 2016) | <i>Tilapia zillii</i> , Cross river, Nigeria (Uwem <i>et al.</i> , 2013) | <i>Oreochromis niloticus</i> , Gaza strip, Palestine (Elnabris <i>et al.</i> , 2013) |
|-------------|------------|--|---|--|--|
| Cd          | 0.17       | 0.26   | 0.25  | 0.26   | ND   |
| Cr          | 4.54       | 1.36   | 0.40  | 0.19   | ND   |
| Cu          | 10.15      | 0.43   | 1.72  | 0.53   | 0.64   |
| Pb          | 1.52       | 0.05   | 0.20  | 0.33   | 0.12   |

ND= Not determined

**Table 7: Comparison of mean heavy metal levels (mg/L) in water to selected studies**

| Heavy metal | This Study | Mediterranean Sea, Egypt (Khaled <i>et al.</i> , 2017) | Golubo Creek, Nigeria (Wangboje <i>et al.</i> , 2014) | River Niger, Nigeria (Nsofor and Ikpeze, 2014) | River Niger, Nigeria (Wangboje and Ikhuabe, 2015) |
|-------------|------------|--|---|--|---|
| Cd          | 0.004      | 2.38   | ND  | ND   | 0.02  |
| Cr          | 0.018      | ND   | 0.86  | ND   | ND  |
| Cu          | 0.041      | 9.30   | 0.65  | 0.14   | 0.18  |
| Pb          | 0.012      | 16.71  | 1.50  | ND   | 0.06  |

ND= Not determined

The mean concentrations of heavy metals in water station-wise, ranged from 0.002 mg/L for Cd at Odo to 0.045 mg/L for Cu at Egbemeji-Odo. There were no significant differences ( $P > 0.05$ ) in the mean concentrations of heavy metals in water between stations (Table 2). The mean concentrations of heavy metals in sediment monthly-wise, ranged from 0.19 mg/kg for Cd in January to 18.77 mg/kg for Cr in September. There were significant differences ( $P < 0.05$ ) in the mean concentrations of heavy metals in sediment between months (Table 3). The mean concentrations of heavy metals in sediment station-wise, ranged from 0.43 mg/kg for Cd at Egbemeji-Odo to 20.69 mg/kg for Cu at Ale-Obite. There was a significant difference ( $P < 0.05$ ) in the mean concentrations of Cr in sediment between stations (Table 4). The DC values ranged from 0.0012 for Cr to 0.0087 for Cd as presented in Figure 5. The RHF values for water ranged from 0.02 for Cu to 1.33 for Cd (Fig. 6) while the RHF values

for fish ranged from 0.33 for Cu to 5.06 for Pb (Fig. 7). The Condition factor for fish species ranged from 1.18 in *T. zillii* to 1.65 in *B.nurse* as presented in Figure 8. The BQ values, using water as a component ranged from 37.5 for Cd in *B.nurse* to 300.48 for Cu in *T. zillii* (Fig.9) while the BQ values, using sediment as a component ranged from 0.23 for Pb in *B.nurse* to 0.64 for Cu in *T. zillii* (Fig. 10). The ADI values (in mg/person/day) ranged from 0.09 for Cd in *B.nurse* to 7.04 for Cu in *T. zillii* (Fig.11) while the AAI values (in mg/person/year) ranged from 32.85 for Cd in *B. nurse* to 2569.6 for Cu in *T. zillii* (Fig. 12). The MAR values peaked for Cu in all the experimental fishes and ranged from 0.04 in *T. zillii* to 0.16 in *B.nurse* as shown in Figure 13. The TTM value for the study was 39.08 (Fig. 14) while the TMDI value was 1220 (Fig.15).

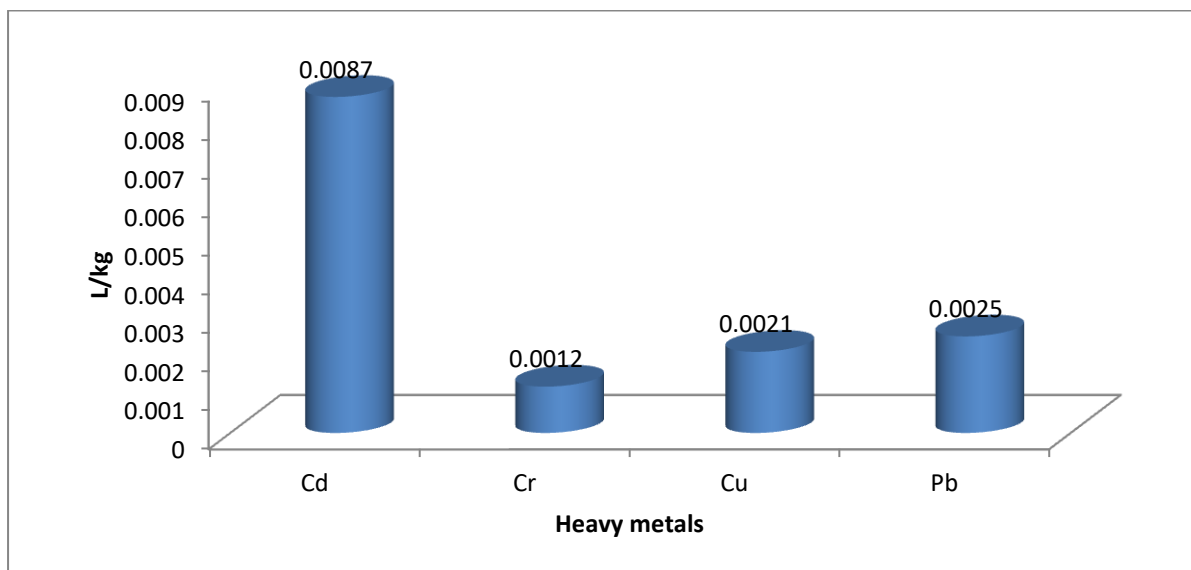


Fig. 5: Distribution co-efficient for heavy metals

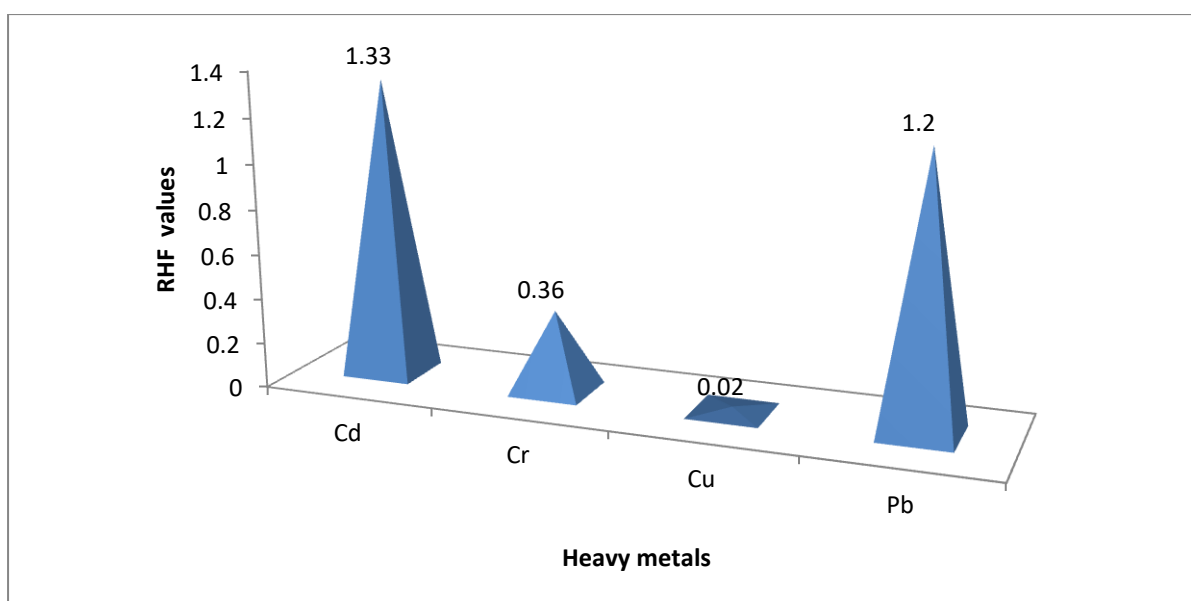


Fig. 6: Relative health factor values for heavy metals in water

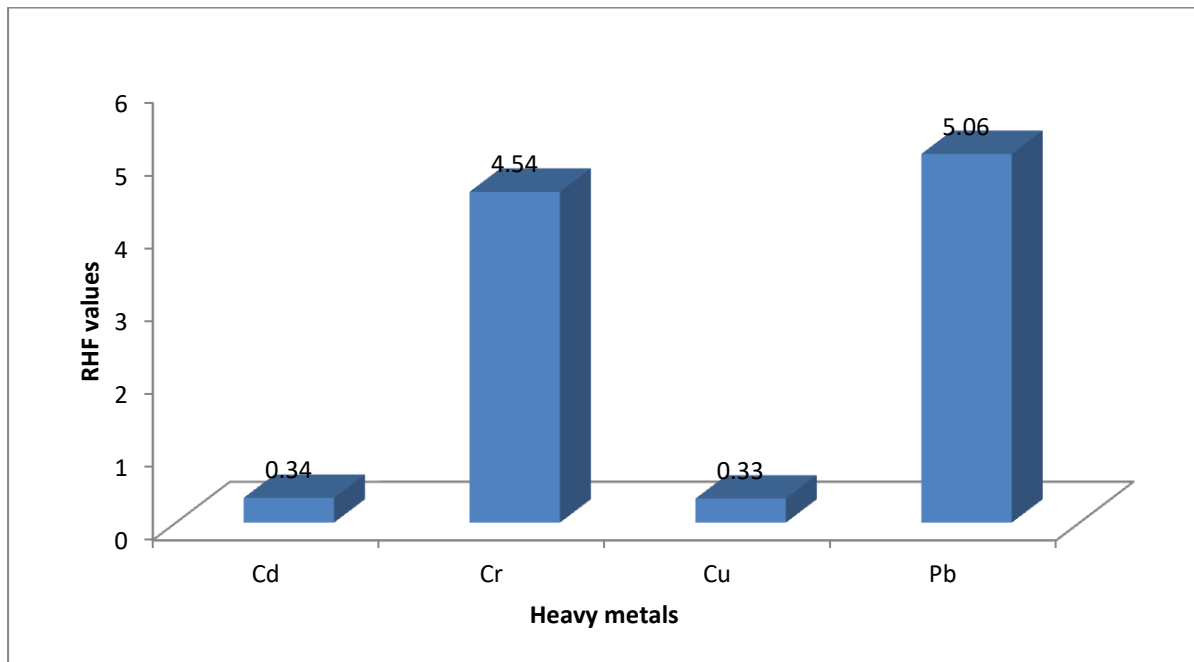


Fig. 7: Relative health factor values for heavy metals in fish

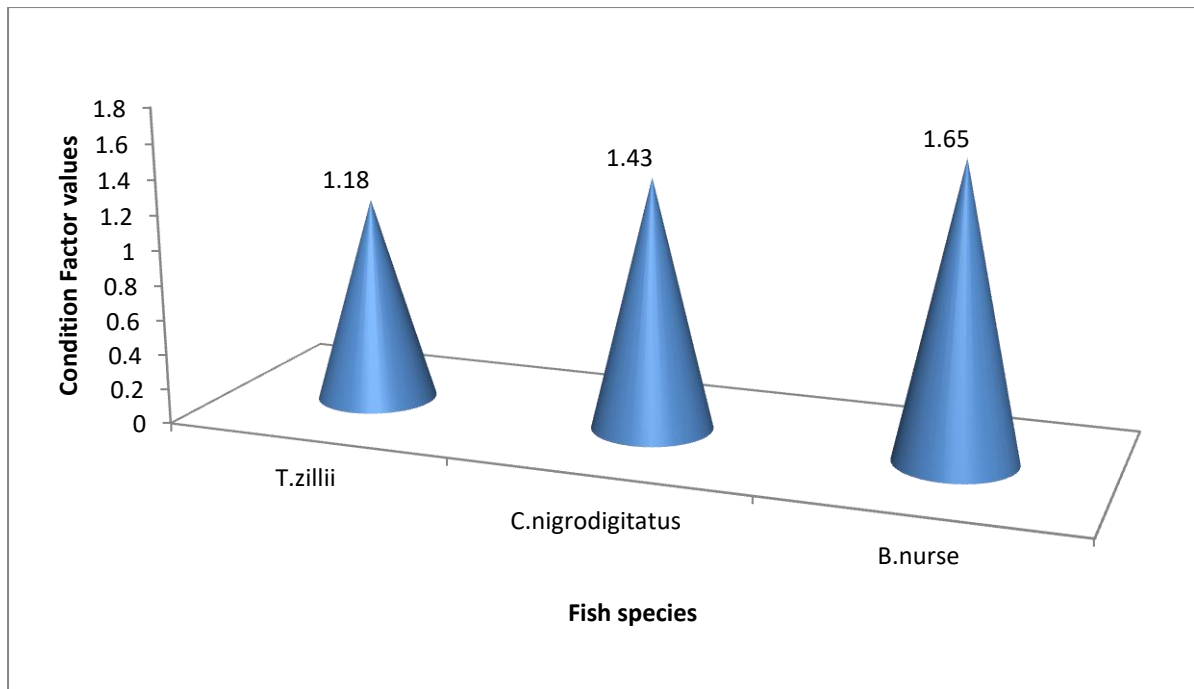


Fig. 8: Condition factor for fish species

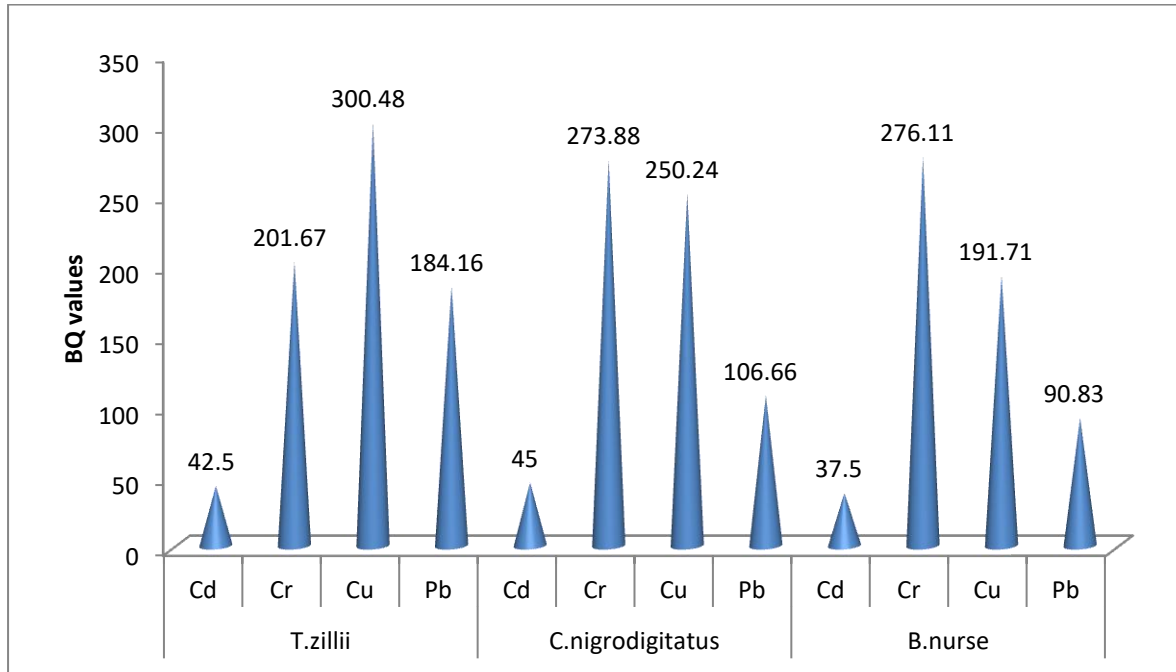


Fig. 9: Bioaccumulation Quotient ( $BQ^{Water}$ ) value for heavy metals in fish

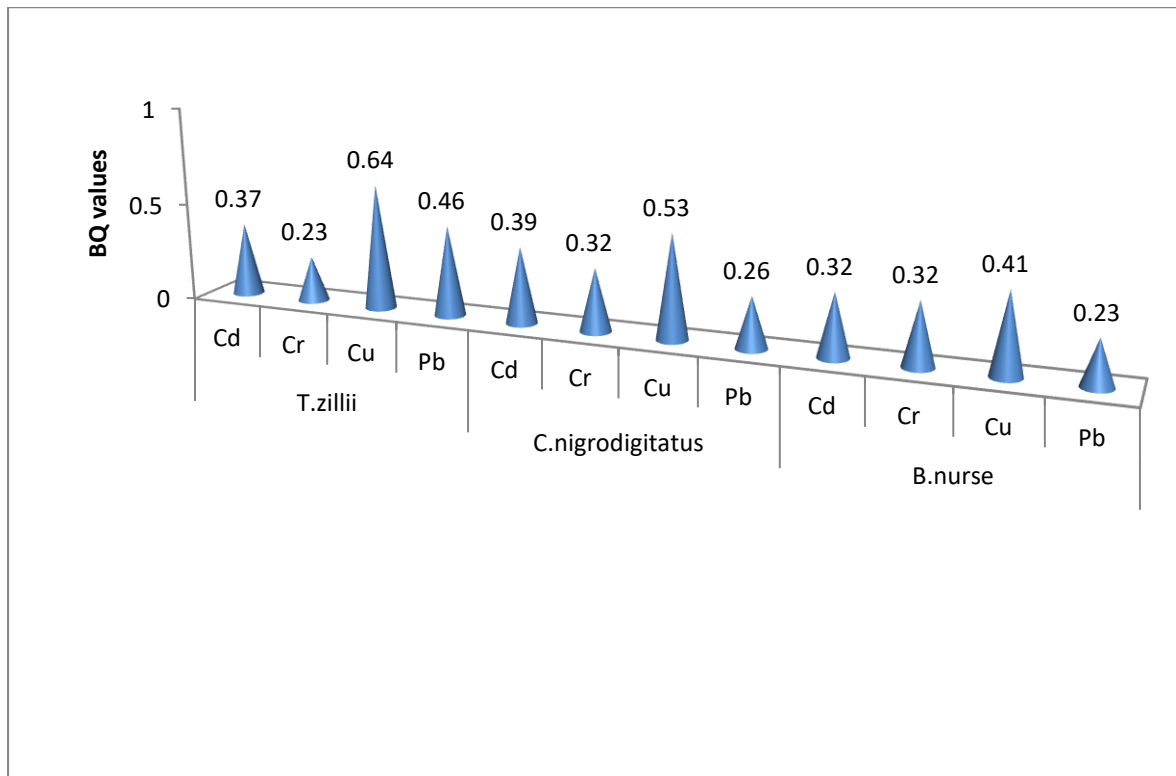


Fig. 10: Bioaccumulation Quotient ( $BQ^{Sediment}$ ) for heavy metals in fish

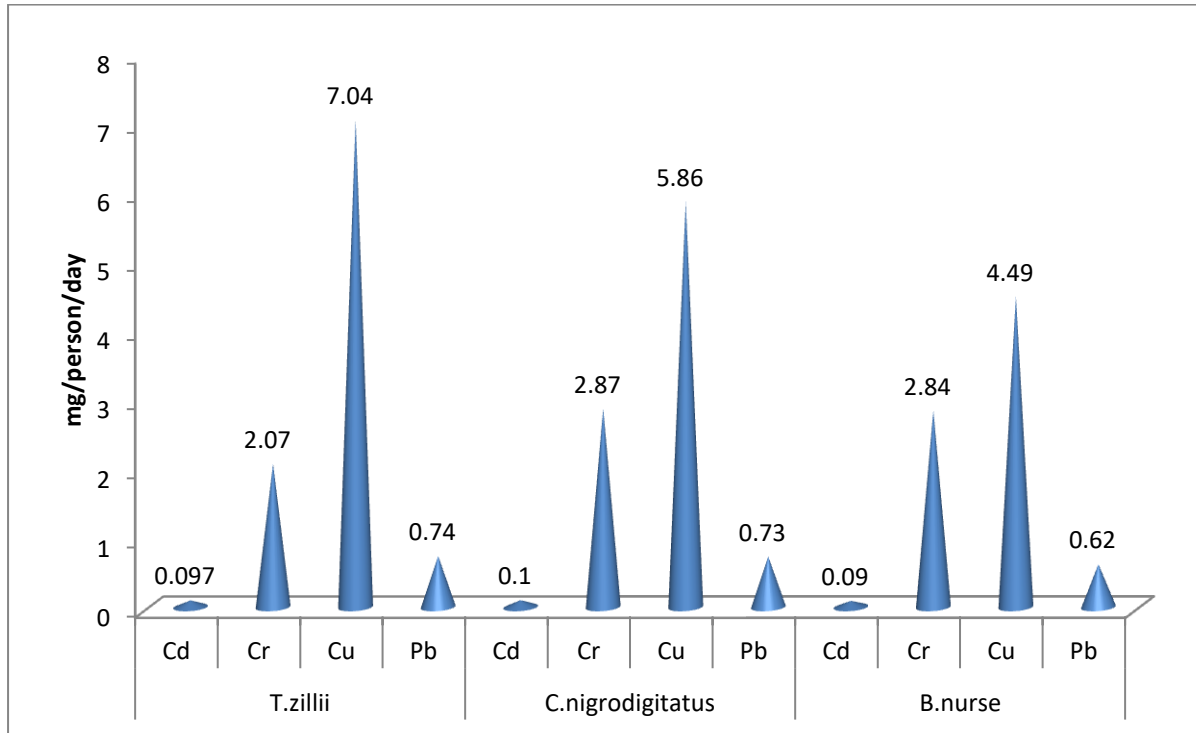


Fig.11: Average daily intake values for heavy metals

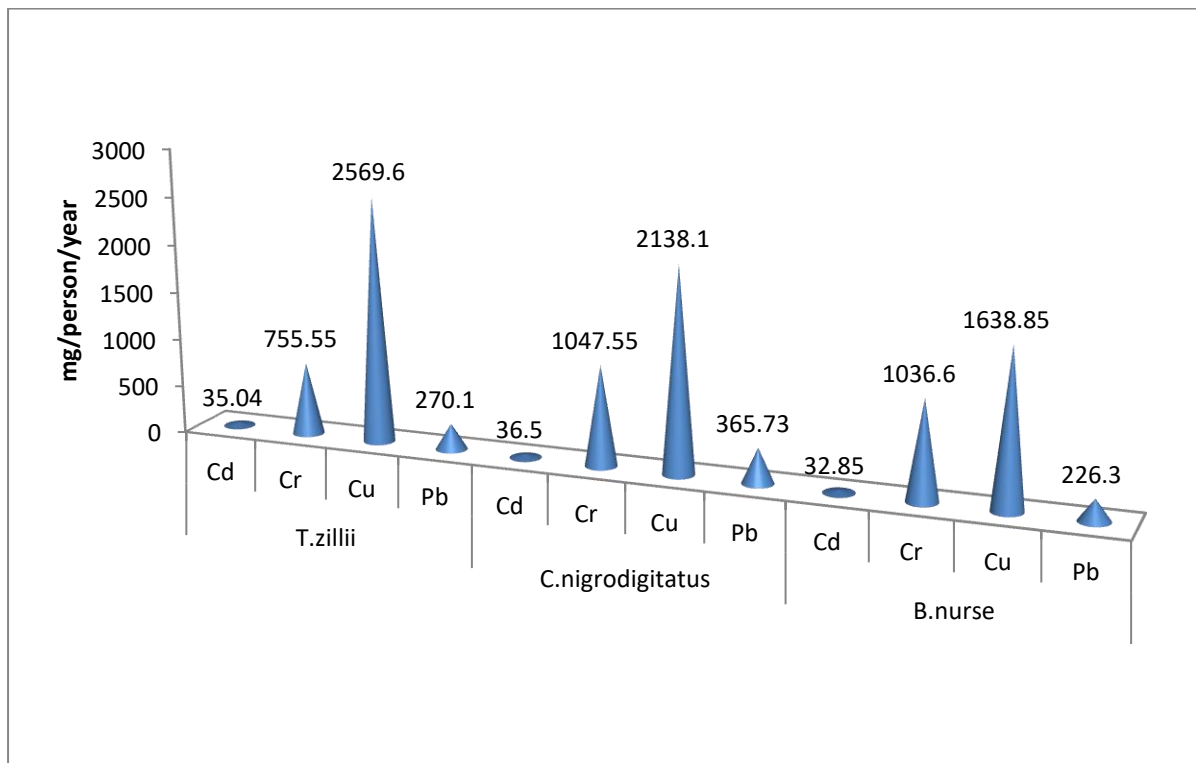
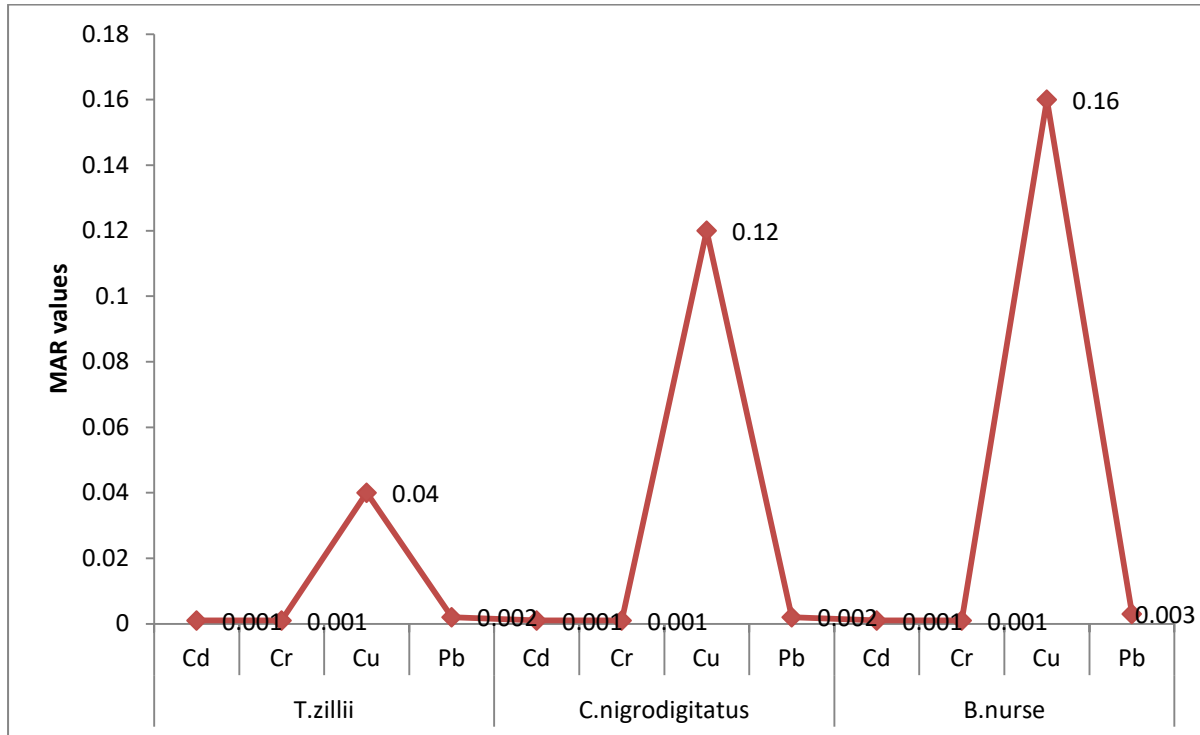
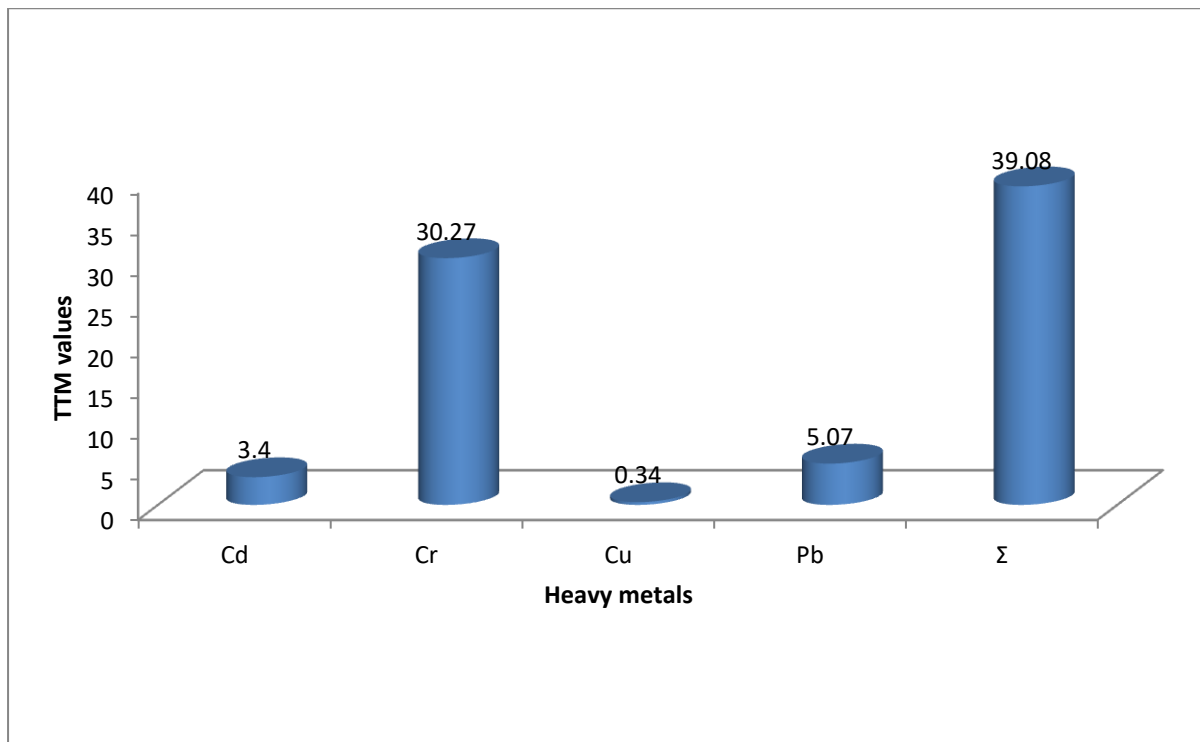


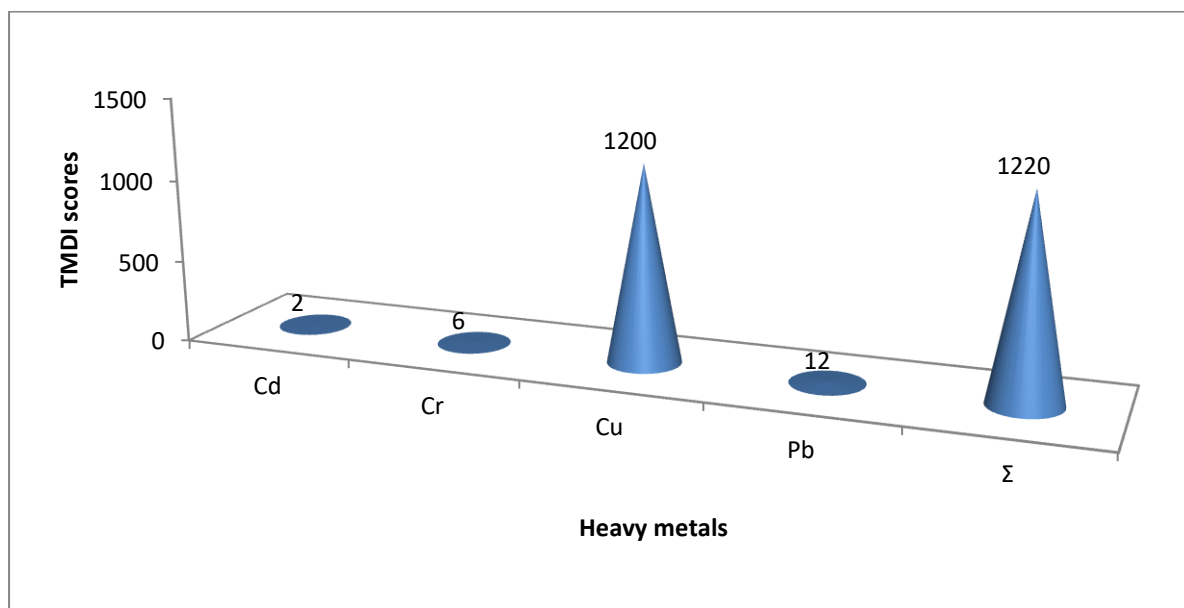
Fig.12: Average annual intake values for heavy metals



**Fig.13: Maximum acceptable risk values for heavy metals in fish species**



**Fig: 14: Total toxicity of mixtures index for heavy metals**



**Fig.15: Theoretical maximum daily intake values for heavy metals**

## DISCUSSION

Heavy metals may enter natural aquatic media from natural and anthropogenic sources including industrial and domestic sewage, storm runoff, leaching from landfills and atmospheric deposits (Dhinamala et al. 2017). The heavy metal rank profile in water was  $Cu > Cr > Pb > Cd$  while the same trend was observed for sediment, an indication that the heavy metal content in water was proportionally related to the corresponding heavy metal load in sediment. Clearly, there was an intimate link between the heavy metal profiles of both media. In addition, sediments are repositories for diverse pollutants and are thus capable of feeding the overlying water column with such domiciled pollutants especially under perturbed conditions (Wangboje and Oguzie, 2013). It was observed that the mean concentrations of Cd, Cr and Cu in water were highest at the Egbemeji-Odo station, which was probably influenced by the direct influx of effluents such as palm oil mill effluents. The mean concentrations of Pb in water and sediment were highest at the Odo station, probably due to the boating activities at this station which could introduce fossil fuel into the water. The DC values, which generally express the solubility of metals in water, took the order  $Cd > Pb >> Cu > Cr$ . Since Cu had the highest mean concentrations in water and consequently in sediment, the DC value for Cu, would have been dominant but obviously some other factors may have come into play which produced the variation. For example, heavy metals are known to be associated with different fractions in sediment which may have accounted for the variation. These operationally defined fractions include exchangeable metal fraction, carbonate-bound metal fraction, Fe- Mn oxide metal fraction, organic/ sulphide metal fraction and residual metal fraction (Tessier et al. 1979; Lin et al. 2003; Wangboje et al. 2014b). Significant differences ( $P < 0.05$ ) were observed in the mean concentrations of Cr and Cu in water between months, an indication of the effects of seasonal variation on the concentrations of metals in natural aquatic media. On the other hand, there were no significant differences ( $P > 0.05$ ) in the mean concentrations of metals in water between stations, an indication that there was a conceivably steady input of the metals and their associated compounds into the



aquatic medium at the stations. Significant differences ( $P < 0.05$ ) were also observed in the mean concentrations of metals in sediment between months while no significant difference ( $P < 0.05$ ) was observed in the mean concentrations of metals between stations, the only exception being Cr, an indication of the varied influx of the metal (Cr) into the sediment structure and chemistry during the study period. The heavy metal profile in fish had the rank order  $Cu > Cr > Pb > Cd$ . This was the same pattern observed for water and sediment. It would therefore imply that the heavy metal load in fish would logically be defined by the heavy metal levels in water and sediment as such bioindicators derive their heavy metal input from the aforesaid matrices. According to Jaffar et al. (1988), the heavy metal load in fish can be influenced by factors such as food habits, uptake, metabolism and habitat of fish. The RHF values for water revealed that Cd is the metal that presents a health risk to the consuming public as unity was surpassed. This observation is further buttressed by the fact that the mean concentration of Cd in water exceeded the WHO threshold for drinking water. The mean concentration of Pb in water also surpassed the WHO threshold, implying the unfitness of such water for human consumption. In a similar vein, the RHF values for fish showed that Cr and Cd present a health risk to potential consumers. The calculated CF values revealed that the fish species were well conditioned in their host aquatic medium. This observation could have been due to an abundance of fish prey and conducive water chemistry for their existence as corroborated by Wangboje et al. (2015) who studied the heavy metal levels in fish from River Niger, Nigeria. The  $BQ^{(water)}$  values showed that all the heavy metals were bioaccumulated by the fish species however the  $BQ^{(sediment)}$  values showed a non-bioaccumulation of metals by fish. The ecological habits of these fishes could be responsible for the non-bioaccumulation of heavy metals from sediment as they are principally pelagic species, which implies that direct contact with sediment would be limited. Bioaccumulation has been described as the net accumulation of a substance from water or sediment into an aquatic organism resulting from the simultaneous uptake and elimination of such a substance (Adaka et al. 2017). The ADI and AAI values were highest and lowest for Cu and Cd respectively for all the fish species. This observation is due to the fact that Cu and Cd had the highest and lowest mean concentrations respectively in fish, as corroborated by Wangboje et al. (2017), who reported that the direction of ADI and AAI values is defined by the concentrations of metals in fish. The MAR values revealed that Cu is the metal that has the greatest tendency to biomagnify in man assuming these fish species were to be consumed. The calculated TTM value of 39.08 clearly exceeded unity, indicating that guideline values were exceeded for heavy metals in fish and as such fish should be consumed with caution in order to avert heavy metal poisoning over time. To buttress this finding, the mean concentrations of Cd and Pb in fish exceeded the thresholds ( $Cd = 0.05$  mg/kg;  $Pb = 0.30$  mg/kg) established by CODEX Alimentarius (2015) while the mean concentrations of Cr in fish exceeded the threshold ( $Cr = 1.0$  mg/kg) established by Food and Agriculture Organization of the United Nations (FAO, 1983). The mean concentration of Cu in fish species were however below the 30 mg/kg maximum limit set by FAO. The Food Safety Authority of Ireland (FSAI), has documented the adverse effects of heavy metals, especially Cd, Pb, Sn, Hg and As in man (FSAI, 2009). The TMDI value for the study was 1220 mg/person/day, which was calculated based on the maximum limits for metals in fish and the per capita consumption of fish. The mean heavy metal levels in sediment fell below the probable effect concentrations (PEC) for heavy metals in sediment established by the USDOE and WDNR. The implication of this finding is that the environmental integrity and

health of sediment are satisfactory with regard to heavy metals and thus sediment dwelling organisms are presently not at risk, although chemical speciation of heavy metals in sediment may be required to further buttress this finding. It is pertinent to note at this point that the ISQG established by USDOE takes into consideration marine and estuarine ecosystems while the CBSQG established by WDNR takes into consideration freshwater ecosystems. Both thresholds were applied in this study in order to present a more holistic scenario. The heavy metal levels in sediment, fish and water observed in this study, compared well with the heavy metal levels reported for the same media in selected studies, as highlighted in Tables 5, 6 and 7. In conclusion, the mean concentrations of Cd, Cr and Pb in fish were above established thresholds implying that such fish should be consumed with caution in order to avert unwholesome health consequences over time. In a similar vein, water was considered unsuitable for drinking owing to possible Cd and Pb poisoning over time. Although the quality of sediment with regard to heavy metal content was satisfactory, there must be a sustained monitoring system in place in order to ensure that heavy metals in this river ecosystem do not attain hazardous and critical levels. It is suggested that future monitoring exercises should include heavy metals not covered in this study in order to attain a broader metal base.

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