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Research Paper

Risk Assessment and Bioconcentration of Heavy Metals in *Mugil Cephalus* (Mullet) obtained from Azuabie Creek in Port Harcourt, Nigeria.

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ABSTRACT: Fish samples (*Mugil cephalus*) were collected from Azuabie creek for heavy metal and health risk analysis. Samples were collected monthly (January to December 2015) and examined for heavy metals using Atomic Absorption Spectrophotometery. Temporal variations of heavy metal concentration was significant with mean metal concentrations as Cr 1.96 ± 0.81 mg/kg, Ni 1.82 ± 0.40 mg/kg, Cu 4.12 ± 1.07 mg/kg, Pb 2.96 ± 0.67 mg/kg, Ag 1.20 ± 0.33 mg/kg and Cd 0.33 ± 0.09 mg/kg. The values of Cr and Cu were below their recommended limits by FAO/WHO while Ni, Pb and Cd had mean concentrations above recommended limits. Health risk assessment indices show that Estimated Daily Intake (EDI-mg/kg body weight/day) values of metals were generally lower than their respective reference doses with Cu having the highest value (6.9×10^{-4}) while Cd had the least (5.5×10^{-5}). Target Hazard Quotient of the metals observed were <1 with highest observed for Pb (0.141) and the least (0.015) for Ni. The Hazard Index (HI) obtained in this study was <1 (0.454) while Target Cancer Risk (TR) calculated only for Ni was 1.01×10^{-3}. The study concluded that heavy metal concentration in fish samples examined indicated bioaccumulation over time with some metals above recommended limits. EDI, THQ and HI indices suggests minimal risk while TR for Ni indicated moderate risk for public health concern with regards to human exposures to the contaminants. It is therefore necessary for continuous monitoring to detect changes.

Keyword: Heavy metal pollution, Fish, Risk, Niger Delta,

I. INTRODUCTION

Municipal and industrial wastes are often discharged into aquatic environment. Such wastes contain different concentrations of heavy metals. The term 'heavy metals' refers to metals whose specific gravity is greater than 5 g/cm^3 in their standard state [1] and adversely affect the environment and living organisms [2]. Agricultural effluents and discharged industrial waste water that contain different chemical compounds, including heavy metals are key entry route of such metals into aquatic ecosystems [3]. Such heavy metals have the tendency to bioaccumulate in the food chain [4] stated that bioaccumulation is an increase in the degree of a chemical content in a living organism over time, compared with chemical's level in the environment and identified that pumping of sewage water into the sea causes a number of hazards to marine life; including phytoplankton, zooplankton, crustacean, macro-algae and fish species. Ingestion of particulate material suspended in water, through food, through the ion-exchange of dissolved metals across lipophilic membranes (e.g., the gills), and through adsorption onto tissue and membrane surfaces are ways via which fish accumulate heavy metals [5]. Monitoring programs and investigations on the existence of heavy metals in marine water environments have increased significantly due to alarms over the accumulation of contaminants and toxic effects in marine organisms and to humans over the food chain [6]. According to FAO statistics, fish accounted for about 16% of the global population's intake of animal protein and 6% of all protein consumed [7]. Consumption of contaminated fish (dietary intake) is the main route of exposure to contaminants by humans. [8, 9, 10] had all stated that dietary intake of toxic elements is the main route of exposure for most people while [11] stated that major interest is in edible commercial species of fish. The ultimate discharge of effluents by industries and other anthropogenic activities in and around creeks and rivers constitute a major environmental

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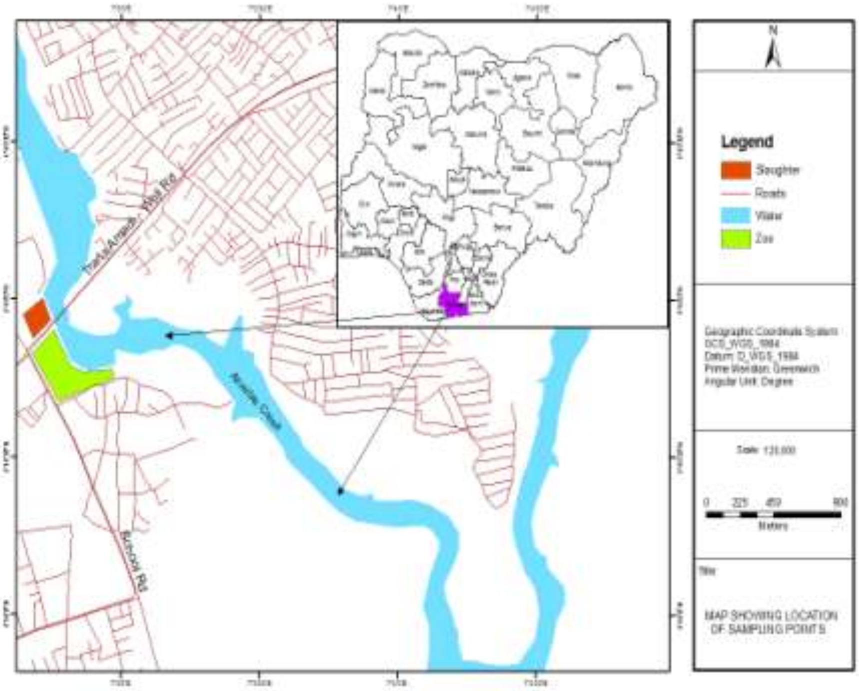
challenge particularly in developing areas such as the Niger Delta in Nigeria [12]. Azuabie creek is one of such estuarine creeks in the Niger Delta that receives sewage, domestic, municipal and industrial wastes discharged by coastline and urban dwellers as well as industries located around the Trans-Amadi industrial layout in Port Harcourt city, Nigeria. Works done [13, 14, 15, 16, 17] had shown elevated levels of heavy metals within the creek raising concerns of possible accumulation of contaminants but reports of health risk assessment vis-avis consumers of fish from Azuabie creek is rare. Since fish can bio-accumulate contaminants over time and has also been reported as bio-indicators of the aquatic environment [17, 18]. Mugil cephalus (Mullet) commonly caught and consumed fish from Azuabie creek was evaluated for heavy metal concentration and health risk assessment of humans who consume the fish.

II. MATERIALS AND METHOD

The study location is the Azuabie creek which is a tributary of the upper Bonny estuary. The creek is tidal and drains into the Okpoka River that empties into the Bonny River. The creek is located on the eastern part of Port Harcourt in the Niger Delta region of Nigeria (Fig. 1). Industrialization and urbanization had resulted in the clearing of the mangrove vegetation along the creek. Domestic waste are dumped at the bank of the creek, a city abattoir is also located along the bank in addition to the municipal and industrial wastes that are discharged into the creek. The creek serves as source of livelihood to a lot of persons as indicated by the enormous fishing activity observed on the creek during the 12 months sampling.



© IOSR 2017. **Fig. 1**: Location of Study site where fish samples were collected

1.1 Sample Collection and Analysis

Three fish (*Mugil cephalus*) samples were collected and composited on a monthly basis for a period of 12 months (January – December, 2015). Fish samples were obtained directly from fishermen using cast net methods. Samples were immediately preserved in ice packs and transported to the laboratory where they were frozen before analysis. The composited samples were dried and digested using HCl/HNO_3 following the method of the American Society for Testing and Materials [19]. The concentrations of heavy metals were determined using an Atomic Absorption Spectrophotometer (GB Avanta PM AAS, S/N A6600). The concentrations were blank-corrected and expressed as mg/kg dry weight of sample. Significant differences in metal concentrations between months were tested by Analysis of Variance (ANOVA) performed using MS Excel.

Estimated daily intake (EDI) The exposure pathway of heavy metals to humans via intake contaminated food had been worked [20, 21]. The estimated daily intake (EDI) of each heavy metal in this study was determined by the equation:

$$EDI = \frac{E_F \; x \; E_D \; x \; F_{IR} \quad x \quad C_F \quad x \quad C_M}{W_{AB} \;\; x \;\; T_A} \quad x \quad 10^{-3}$$

E_F = Exposure frequency 365 days/year
E_D = Exposure duration, equivalent to verge life time (65 years)
F_{IR} = Fresh food ingestion rate (g/person/day) was taken as 48/g/person/day [22]
C_F = Conversion factor = 0.208
C_M = Heavy metal concentration in food stuffs (mg/kg d-w)
W_{AB} = Average body weight (bw) was taken as 60kg
T_A = Average exposure of time for non-carcinogens (it is equal to (E_F x E_D) as used by in previous studies [23]. The public health risk evaluated by using the Estimated Daily Intake (EDI) [24] to determine the Target Hazard Quotient (THQ).

Target Hazard Quotient (THQ) is given by: THQ = $\frac{EDI}{RFDO}$

Where EDI = Estimated daily intake

RFDO = the reference oral dose of individual metal (mg/kg/day)
Reference oral doses (RfD) used for Cr, Cu, Zn, Fe, Ni, Pb, and Cd are 1.5x 10^{-3}, 4.0 x 10^{-2}, 2.0 x 10^{-2}, 3.5 x 10^{-3}, and 1.0 x 10^{-3} mg/kg/day respectively [25].

Hazard Index (HI) To estimate the risk to human health through more than one HM, the hazard index (HI) has been developed [26]. The hazard index is the sum of the hazard quotients for all HMs, which was calculated by the equation [27].
$HI = \sum HQ = HQ_{cr} + HQ_{Cu} + HQ_{Ni} + HQ_{pb} + HQ_{cd}$

Target Cancer Risk (TR)
The Target cancer risk (TR) was evaluated based on [28] using the formula

$$TR = \frac{Mc \times IR \times 10^{-3} \times CPSo \times EF \times ED}{BW \times ATc}$$

where MC = metal concentration, IR = ingestion rate, EF = exposure frequency, ED = Exposure duration, BW = Body weight, CPSo = carcinogenic potency slope, oral ($mgkg^{-1}$ bw-day^{-1} which is 1.7 for Ni - [28,29]. ATc is the averaging time for carcinogens (365 days/year × 67 years)

III. RESULTS

The monthly variation in heavy metal concentration is shown in Fig 2a - f while the mean values and recommended limits are provided in Table 1. The value of Cr ranged from <0.001 - 10.32 mg/kg with a mean of 1.96 ± 0.81 mg/kg while Ni varied between <0.001 - 4.55 mg/kg with mean of 1.82 ± 0.40 mg/kg and Cu differed between 0.42 - 11.78 mg/kg with a mean value of 4.12 ± 1.07 mg/kg. Other heavy metals examined had the following ranges and mean values respectively: Pb <0.001 - 5.67 (2.96 ± 0.67 mg/kg); Ag <0.001 - 3.2 mg/kg (1.20 ± 0.33 mg/kg) and Cd <0.001 - 0.92 mg/kg (0.33 ± 0.09). Analysis of variance generally showed significant difference (p<0.01) in heavy metals concentration across months of study.

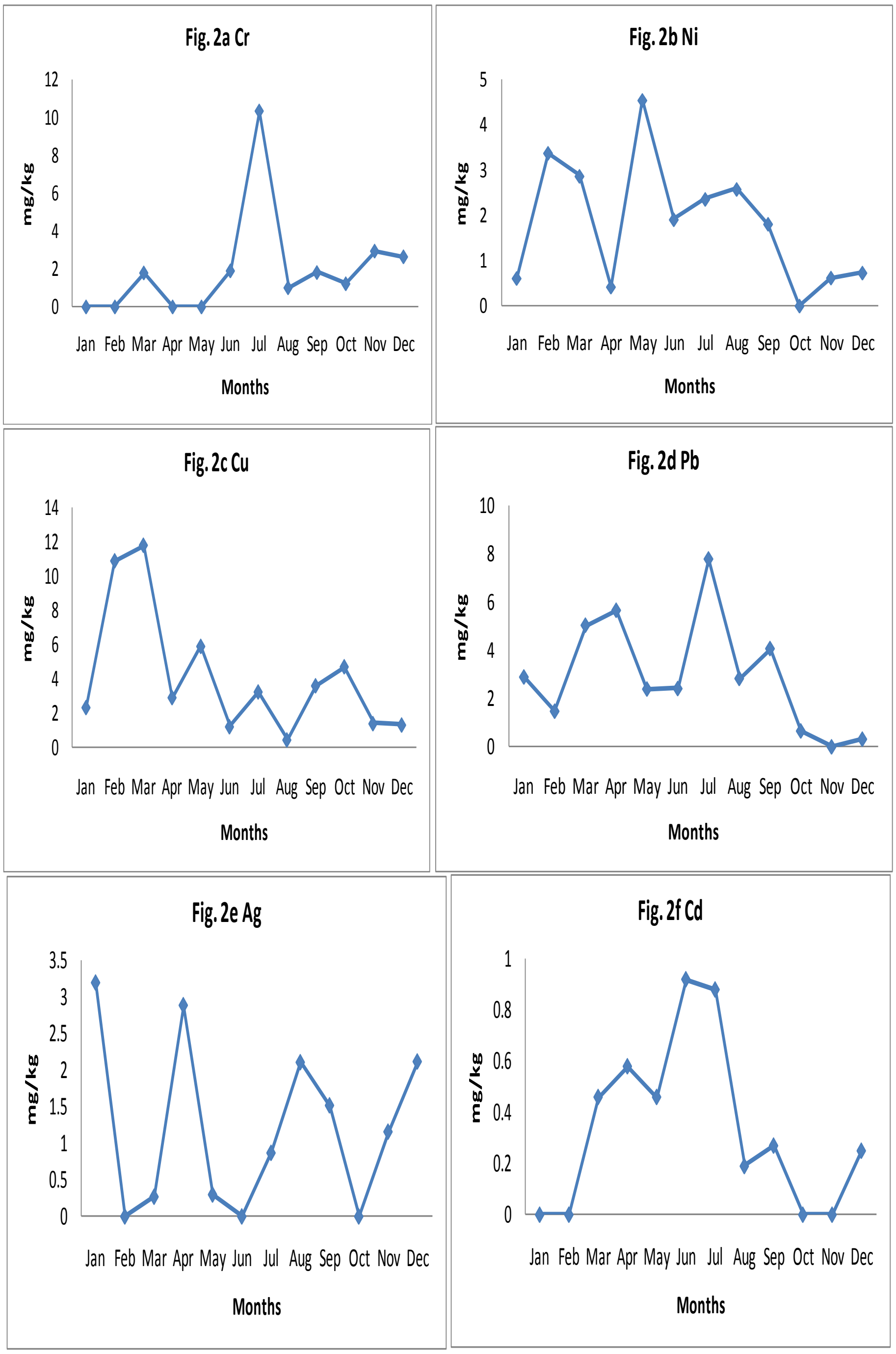


Fig. 2a - f: Monthly variation in the concentration of heavy metals in fish muscle

Table 1: Mean Concentration of heavy metals in fish tissue (Muscle) and Recommended limits

Heavy Metals	Mean Concentration in fish tissue (Muscle)	Recommended limits (ppm)
Cr (mg/kg)	1.96 ± 0.81	12 - 13 [30, 31]
Ni (mg/kg)	1.82 ± 0.40	0.2 [32]
Cu (mg/kg)	4.12 ± 1.07	30 [33]
Pb (mg/kg)	2.96 ± 0.67	0.5 [34]
Ag (mg/kg)	1.20 ± 0.33	No guideline
Cd (mg/kg)	0.33 ± 0.09	0.1 [35]

The EDI, THQ, HI and TR values are presented in Table 2. Cd had the lowest EDI value (5.5×10^{-5}) while Cu had the highest of (6.9×10^{-4}) and others were Ni (3.0×10^{-4}), Pb (4.5×10^{-4}) and Ag (1.9×10^{-4}). The TQH values of the heavy metals were Cr (0.22), Ni (0.015), Cu (0.017), Pb (0.141) and Cd (0.055). The HI value of all heavy metals was 0.454 and the TR value for Ni was to be $1.01 \times 10^{-3.}$

Table 2: Values of EDI, THQ, HI and TR of the heavy metals examined

Heavy Metals	EDI	THQ	HI	TR
Cr	3.3×10^{-4}	0.22	0.454	
Ni	3.0×10^{-4}	0.015		**0.001**
Cu	6.9×10^{-4}	0.017		
Pb	4.5×10^{-4}	0.141		
Ag	1.9×10^{-4}	-		
Cd	5.5×10^{-5}	0.055		

IV. Discussion

The concentrations of heavy metals obtained in this study varied across the months of study. Cu had the highest mean value of 4.12 ± 1.07 mg/kg but was less than the recommended limit of 30 ppm [33] followed by Pb with a concentration of 2.96 ± 0.67 mg/kg which rated above the recommended limit (0.5 ppm) by [34]. Mean Cr value (1.96 ± 0.81 mg/kg) was below the range 12 - 13 ppm [30, 31] while mean concentration of Ni (1.82 ± 0.40 mg/kg) and Cd (0.33 ± 0.09 mg/kg) were above the recommended limits by [32, 35] respectively. [15] had found mean Cd concentrations of 0.05 ± 0.007 mg/kg and Pb value of 0.104 ± 0.030 mg/kg in fish samples in the study area. These concentrations were lower compared to the findings of this study indicating bio-accumulation over time. However, concentrations of heavy metals obtained in this study favourably compared to values obtain in mudskipper fish samples from the study area [17]. [36] reported average values of Cu, Ni and Pb as 0.907± 0.17 l mg/kg, 0.978 ± 0.19 mg/kg, 0.172 ± 0.09 mg/kg respectively in Mugil cephalus tissue which were significantly less than values obtained in this study. However, studies have reported Mugil cephalus to accumulate higher level of metals compared to other species [37, 38, 39] which is related to their feeding habit. Mugil cephalus are always close to the sediment zone [39], feeding on detritus, diatoms, algae, microscopic invertebrates and fish parts [40]. The concentration of Ni and Cd found in fish tissue of this study also falls within the range of values (Ni 0.05 - 2.52 mg/kg, Cd 0.02 - 0.51mg/kg) reported in muscle tissues of Mugil cephalus elsewhere [4]. The parameters used for risk assessment give an estimation of the human risk evaluation of exposure to metal laden fish in the study area. [41] stated that these parameters depend not only on intake amount of contaminant but also deal with exposure frequency and duration, average body weight and oral reference dose (RfD).The EDI values of the heavy metals in this study were generally lower than the reference doses of the respective metals examined with Cu having the highest EDI and Cd had the least. This is apparently related to the amount of each metal observed in the tissue of the samples examined. The observed EDI values suggest minimal risk to consumers exposed to such contaminants in view of the fact that EDI to RFD ratio generally equal to or < RFD of the metal indicate minimal risk [42]. THQ of the metals observed were all below 1 with highest THQ observed for Pb (0.141) and the least (0.015) for Ni. The observed value of THQ suggest no risk of non carcinogenic effect to the consumers of the fish but studies have found that THQ >1 indicate potentials of non carcinogenic risk to human exposures [43, 44, 45]. [44, 46] in their findings stated that THQ does not assess risk but creates a level of alarm for caution regarding exposure to contaminants. To estimate the risk to human health through more than one heavy metal, the hazard index (HI) according to [26] was calculated. This is because tissue samples often contain more than one heavy metal that can have individual or synergistic effects. The HI is the summation of the THQ for all metals observed. The HI index obtained in this study was <1(0.454) indicating minimal concern for public health. [47,48] had in separate studies stated that HI values should not be > 1 in order to reduce public health concern. The target carcinogenic risk (TR) was estimated for Ni only due unavailability of carcinogenic potency slope factor for other metals examined. The TR value obtained in this study was 1.01×10^{-3} which could be described as moderate with respect to the ranges given by [42]. This is not certain but an upper limit of probability that an exposed person may have cancer once in life [42].

V. CONCLUSION

The study concludes that heavy metals in Mugil cephalus obtained from Azuabie creek showed fluctuations and significantly different over time. The health risk assessment indices generally indicated minimal risk concern with respect to human exposure and public health however, regular monitoring is advocated. The outcome of such research would guide policy makers and provide legislative framework targeted to protect the health of consumers of aquatic resources like fish.

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