Levels of heavy metals in fish obtained from two fishing sites in Akwa Ibom State, Nigeria

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Akwa Ibom State is located in the Niger Delta region of Nigeria and a substantial amount of the fishes consumed in the area are bought at Ifiayong and Ibaka beaches. This study was carried out to analyze heavy metals (Zn, Cu, Cd, Pb, Cr and As) in kidney, heart, gills and liver of silver catfish (*Chrysichthys nigrodigitatus*) from these locations. Analysis was performed using Atomic Absorption Spectrophotometry (AAS). The results show that the levels of Zn and Cu were significantly higher than maximum recommended levels (p<0.05) at both locations and were significantly higher in Ifiayong than Ibaka in all the organs (p<0.05). Concentrations of Pb, As, Cr and Cd were significantly higher (P <0.05) in Ibaka than Ifiayong in all the organs of fish analyzed. The order of accumulation of metals in the organs were as follows; Ibaka: heart/gills: Zn > Cu > Cr > Pb > As > Cd; kidney: Zn > Cu > Cr > Pb > Cd > As; liver: Zn> Cu > Cr > As > Pb > Cd. Ifiayong: gills/heart: Zn> Cu > Cr > Pb > Cd > As; kidney: Zn > Cu > Cr > As > Cd = Pb and Liver: Zn > Cu > Cr > Pb > Cd = As. In general, these results show that the levels of Zn, Cu, Pb, Cr and As in the fish bought at Ibaka were above recommended levels while those bought at Ifiayong (with the exception of Zn and Cu) were significantly lower (p<0.05) than standards set by WHO/FAO/UNEP. This study, therefore, suggests the need for regular monitoring and assessment of fishing sites in this region for heavy metal contamination to protect the health of consumers.

**Key words:** *Chrysichthys nigrodigitatus*, heavy metals, Ibaka, Ifiayong, Niger Delta region, silver catfish.

INTRODUCTION

Heavy metal contamination of aquatic ecosystem constitutes a major public health problem (Ashraf et al., 2006). Consequently, researchers and regulatory agencies carry out periodic assessment of the aquatic ecosystem to ascertain the quality of fish consumed by the populace. Heavy metals such as iron, copper, chromium, and zinc are essential for metabolic activities, but become toxic at higher concentrations, whereas lead and cadmium have no beneficial roles in living organisms but are toxic (Malik and Zeb, 2009). Nutritionally, fish consumption is widely encouraged due to its high content of omega-3 polyunsaturated fatty acids: eicosapentanoic

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acid (EPA), docosahexaenoic acid (DHA) and protein (Clarkson, 2002). However, the presence of toxic heavy metals can counteract the positive effects of omega-3 fatty acids present in fish. There is evidence that metals accumulate in tissues of fish; therefore, levels of heavy metals measured in tissues of fish can reflect previous exposure to these pollutants (Ashraf, 2005). Heavy metals cause damage by enhancing the production of free radicals in several organs (brain, liver, kidney, heart) and interfering with cellular mechanisms against oxidation, leading to oxidative stress which has been implicated in the aetiology of several diseases (Castro-Gonzalez and Mendez-Armenta, 2008). Exposure to crude oil and its derivatives can act as a mediator in free radical generation and can induce a variety of toxic symptoms in experimental animals (Achuba and Osakwe, 2003). Heavy metal toxicity, persistence and tendency to accumulate in water and sediment, render them severe poisons for all living organisms in high concentrations (Has-Schon et al., 2006).

Many authors have reported increased concentrations of toxic metals in fish caught in Nigerian waters. For example, Farombi et al. (2007) reported high concentration of metals (Zn, Cu, Cd, Pb, As) above WHO/FAO standards in Ogun river. Alinnor (2005) reported that Aba River is polluted due to the discharge of waste from six (6) industries located close to it. High concentrations of heavy metals have also been reported in Ollfant River, South Africa (Avenant-Oldewage and Marx, 2000). The present study assessed the quality of silver cat fish (Chrysichthys nigrodigitatus) obtained from Ibaka and Ifiayong beaches, Nigeria, by determining heavy metal concentrations in various organs (liver, heart, kidney and gills).

**MATERIALS AND METHODS**

**Study area**

The sampling areas for this study are indicated in Figure 1. Ibaka beach is located on the banks of Mbo river which is one of the major rivers in Akwa Ibom State, Nigeria. Mbo River lies within latitude 4° 39' North and longitude 8° 19' East on the southeastern Nigerian coastline. It empties into the Cross River Estuary at Ibaka in the Bight of Bonny and plays a major role in the fisheries resources of Akwa Ibom State (Essien-Ibok et al., 2010). Presently, the river is receiving serious developmental attention by both the state government (the proposed establishment of an international seaport at its banks) and the Mobil oil company that has discovered new oil deposits within the rivers catchment area (Essien Ibok et al., 2010). Conversely, Ifiayong beach is located at latitude 5° 03’ North and longitude 8° 01’ in Ifiayong, Uruan, Akwa Ibom State. To the best of our knowledge, Ifiayong river is devoid of oil exploration activities but may be susceptible to fertilizer run-offs from fertilizers applied to soils as well as waste discharges.

**Collection of fish samples**

Samples of *C. nigrodigitatus* were bought directly from fishermen at Ibaka and Ifiayong beaches. They were transported to the labora-

**Heavy metal analysis**

All fresh organs from the fish were dried in an oven at 105°C for 24 h to constant weight and milled with a mortar and pestle. The samples were transferred into dry labeled plastic containers and stored in a desiccator until required for digestion. A procedure similar to that described by Poldoski (1980) was used to digest the samples. This involved digesting 1 g portion of the ground samples with 10 ml HNO₃/2 ml HClO₃ and heating on a hot plate for one hour. After complete digestion, the residue was dissolved and diluted with 0.2 % v/v HNO₃ to 20 ml. The concentrations of metals (Zn, Cu, Cd, Pb, Cr and As) were determined in an Atomic Absorption Spectrophotometer (Bulk Scientific 205).

**Statistical analysis**

Data were expressed as mean ± standard deviation (SD) and analyzed with the SPSS 18.0 software. Independent T-test was used for the evaluation of data between Ibaka and Ifiayong beaches. P values <0.05 were regarded as statistically significant.

**RESULTS AND DISCUSSION**

Four different organs (gills, liver, kidney and heart) were analyzed for six metals (Cd, Pb, As, Cr, Zn and Cu) and the results obtained are presented in Table 1. The concentrations (ppm) of Zn and Cu were significantly higher (P< 0.05) in all the organs of fish obtained from Ifiayong than Ibaka with the exception of Zn concentrations in the gills which showed no significant difference at the two locations. The characteristic similarity in metal accumulation in liver, gills, kidney and heart in both locations were in the order Zn > Cu > Cr. There was slight variation in the pattern of bioaccumulation of the other metals (As, Cd and Pb) in the organs. This may be attributed to difference in the affinity of metals to fish tissue (Jezierska and Witeska, 2006), metabolic disposition of the organ (Karadede and Unlu, 2000), route of absorption (Ney and Vanhassel, 1983) and age of the fish (Khan et al., 2012).

The accumulation of Zn and Cu in the liver has been attributed to the role of this organ in the storage, metabolism and detoxification of heavy metals (Langston et al., 1998). Also metallothionine which is abundant in fish liver (Atli and Canli, 2007) has affinity for Cu and Zn and therefore may concentrate these metals (Sakulsak, 2012). Jezierska and Witeska (2001) reported that the levels of heavy metals in fish liver can be used to monitor the extent to which water is polluted by these elements. This is due to the fact that the concentration of metals in fish liver is proportional to those in the aquatic environ-
The high mean concentration of Cu and Zn obtained in this study correlates with the report of other authors (Farombi et al., 2007; Etesin and Benson, 2007; Avenant-Oldewage and Marx, 2000). Zn is neurotoxic at high concentrations and causes neuronal cell death in a dose dependent manner (Chen-Jung and Su-Lan, 2003).
The harmful toxicity of Copper is largely attributed to its cupric (Cu⁺) form which is commonly found in the species (Olaifa et al., 2004). The permissible limits of Zn and Cu in fish are 5.0 and 0.5 ppm respectively (UNEP, 1986).

The gills also accumulate high concentrations of Zn and Cu. Metal ions are first absorbed through the gills because they are directly in contact with the contaminated medium and also have thinnest epithelium when compared to other organs (Bebianno et al., 2004) Also, the kidney showed high concentration of Zn which according to Jaffer et al. (2011) could be based on specific metabolic process and co-enzyme catalyzed reactions involving Zn in the kidneys.

Zn and Cu concentrations were found to be higher than the WHO/UNEP/FAO permissible limits of 5.0 and 0.5 ppm respectively, (UNEP, 1986) in fish obtained from Ibaka and Ifiayong.

In the present study, the level of Cr was found to be significantly higher (P<0.05) in fish obtained from Ibaka than Ifiayong in all the tissues except liver. This observation might be due to activities such as oil exploration. The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium) is of low toxicity. The hexavalent form is toxic and is known to be carcinogenic and teratogenic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions (Velma et al., 2009). Low doses of Cr produce marked inhibition of glucose reabsorption as a result of damage to convoluted proximal tubules (Stine and Brown, 2006). The mean concentration of Cr in fish from Ibaka was within the range reported by Nyirenda et al. (2011) (0.13 ± 0.01 ppm—liver and 0.11 ± 0.03 ppm—kidney) in catfish caught at Modila Dam, South Africa. The mean concentration of Cr at the two locations was lower than the permissible limits of 0.05 ppm by International Program on Chemical Safety (WHO, 1992). The mean concentrations of Cr in the organs of fish at Ifiayong and Ibaka were similar to the values reported by Nyirenda et al. (2011). The Cd concentrations in Ibaka and Ifiayong were lower than that reported in the work of Farombi et al. (2007), Cogun et al. (2006) and Ashraf (2005). The results further showed that the mean concentration of As and Pb in fishes bought at Ibaka was significantly higher (p< 0.05) than that of Ifiayong in all the organs. The mean concentration of Pb and As in the gills and kidney

<table>
<thead>
<tr>
<th>Location</th>
<th>Organ</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
<th>As</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibaka</td>
<td>Gills</td>
<td>0.0178±0.0055*</td>
<td>0.1109±0.0222*</td>
<td>0.0193±0.0017*a</td>
<td>0.0180±0.0098</td>
<td>151.1853±0.4161*</td>
<td>56.664±8.4159*b</td>
</tr>
<tr>
<td>Ifiayong</td>
<td></td>
<td>0.0129±0.0016</td>
<td>0.0018±0.0006</td>
<td>0.0020±0.0005</td>
<td>0.0016±0.0007</td>
<td>151.3052±0.6325 *a</td>
<td>77.5724±2.7408*</td>
</tr>
<tr>
<td>Ibaka</td>
<td>Heart</td>
<td>0.0103±0.0057a</td>
<td>0.1360±0.0143*</td>
<td>0.0170±0.0034</td>
<td>0.0108±0.0048</td>
<td>152.3543±9.1324*</td>
<td>81.3210±3.0650a</td>
</tr>
<tr>
<td>Ifiayong</td>
<td></td>
<td>0.0138±0.0005</td>
<td>0.0013±0.0005</td>
<td>0.0013±0.0005</td>
<td>0.0013±0.0005</td>
<td>170.4480±4.3357*a</td>
<td>88.8493±3.5911</td>
</tr>
<tr>
<td>Ibaka</td>
<td>Kidney</td>
<td>0.0229±0.0089*</td>
<td>0.1334±0.0180*</td>
<td>0.0311±0.005*</td>
<td>0.0174±0.0082</td>
<td>145.5368±10.8170*</td>
<td>64.6692±9.6776*</td>
</tr>
<tr>
<td>Ifiayong</td>
<td></td>
<td>0.01156±0.0025</td>
<td>0.0021±0.0019</td>
<td>0.0021±0.0030</td>
<td>0.0021±0.0110*</td>
<td>208.6261±13.8601*</td>
<td>80.4076±10.8079*</td>
</tr>
<tr>
<td>Ibaka</td>
<td>Liver</td>
<td>0.0109±0.0044</td>
<td>0.0436±0.0510</td>
<td>0.0129±0.0032</td>
<td>0.0165±0.0215</td>
<td>223.0013±23.4667</td>
<td>81.3645±5.0634</td>
</tr>
<tr>
<td>Ifiayong</td>
<td></td>
<td>0.0178±0.0129</td>
<td>0.0010±0.0000</td>
<td>0.0058±0.0066</td>
<td>0.0010±0.0000</td>
<td>250.6429±16.7823</td>
<td>93.3513±6.7834</td>
</tr>
</tbody>
</table>

Values are expressed as mean ± S.D of 10 fishes. *Significantly different from liver at P<0.05; a = significantly different from kidney at P<0.05; b = significantly different from heart at P<0.05.
samples of fish in both locations ranged between 0.0174-0.0311 ppm. The two organs contained the highest concentration of these metals compared to other organs. The results showed that kidney possesses the ability to concentrate heavy metals; this may be due to the presence of metal binding proteins (Kargin and Cogun, 1999). Also the high concentrations of metals in the gills may be due to its direct contact with the contaminated medium (Bebianno et al., 2004). Has-Schon et al. (2006) also reported concentrations of As to be within the range (0.001-0.019 ppm) in fish obtained from river Neretva (Croatia). In contrast to the present study, high concentrations of As had been reported by some authors (Nyiresha et al., 2011; Farombi et al., 2007; Usero et al., 2003). Our findings on mean concentration of Pb was in line with the results of Falco et al. (2006) who reported lead concentrations in various edible marine species which varied from 0.002-0.21 μg/fw. The mean concentration of As and Pb in both locations were below the permissible limits of 0.01 and 0.29 ppm respectively (FAO/WHO, 2005; WHO, 1995). However, ATSDR (2007) states that there is no safe concentration of lead. Lead causes toxicity by replacing zinc in heme synthesis and inhibiting the function of heme-synthesizing enzymes (Goyer and Clarkson, 2001). National Academy of Science/National Research Council (1993) reported that substitution of calcium by lead resulted in toxicity of several vital enzyme systems in the central nervous system. This toxicity impaired the development and function of enzymes involved in the production and transport of neurotransmitters. Victims of Pb intoxication have been reported to manifest various forms of neurological syndrome such as lead palsy and encephalopathy, especially in children (Klaassen, 1995). Some of the clinical manifestations include muscular weakness and fatigue which are more pronounced in the fingers, wrist, toes and forearm; clumsiness, ataxia, headache, insomnia and irritability. Arsenic causes coagulation of proteins, forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration (Institute of Environmental Conservation and Research, 2000). It is possibly carcinogenic and high-level exposure can cause death (Ogwuegbu and Ijioma, 2003; USDOL, 2004).

Conclusion

This study shows that C. nigrodigitatus obtained from Ibaka and Ifiaoyong beaches were at various levels of contamination by heavy metals. The concentrations of these metals in the fish could endanger public health since this species of fish is most preferred by consumers in this environment. Metals with concentrations below the permissible limits may cause harm due to their synergistic effects. Therefore, regular monitoring of these rivers is desirable. Also, effective methods of waste disposal should be adopted to prevent agricultural runoff into these rivers, preserve healthy aquatic environment and ultimately protect the health of the humans who consume the fish.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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