Introduction

The Federal Government of Nigeria, in its drive to address the problem of the inability of millions of people in accessing quality food and nutrition, recently organized a stakeholder’s dialogue on the Reviewed National Policy on Food and Nutrition (RNPFN). The policy is expected to critically examine several issues taking into account food, nutrition and food safety (Elebeke, 2016). Food items being consumed by man must be wholesome both in quantity and quality. In this realm, the study examined the concentrations of some heavy metals in samples of smoke-dried Ethmalosa fimbriata (Mean length=26.52 ± 3.35 cm; mean weight=74.05 ± 4.56 g) from selected markets in Warri, Delta state, Nigeria, by Atomic Absorption Spectrometric technique, in order to ascertain their suitability for human consumption. The grand mean for heavy metals in fish ranged from 0.195 mg/kg (Cd) to 329 mg/kg (Fe) while the heavy metal profile in fish was Fe>Zn>Cu>Pb>Cd. The estimated daily intake (EDI) for heavy metals in mg/person/day ranged from 0.008 (Cd) to 3.52 (Fe) while the EDI profile for the metals followed the rank order Fe>Zn>Cu>Pb>Cd. The total toxicity of mixtures (TTM) index for heavy metals was 27.16 while the toxicity/hazard quotient (TQ) for heavy metals ranged from 0.63 (Cu) to 10.97(Fe). The theoretical maximum daily intake (TMDI) for heavy metals was 3614 mg/person/day while the margin of exposure (MOE) for heavy metals ranged from 0.09 (Fe) to 1.60 (Cu). The mean concentrations of the investigated metals exceeded the maximum limits established by Food and Agriculture Organization (FAO) and Commission Regulation (EC), indicating that such fish must be consumed with caution to avoid heavy metal poisoning and its related myriad of health problems.

Materials and Methods

Description of study area

Warri town is located in Delta state, Nigeria (Fig. 1). Its geographical co-ordinates are 5° 31’ N and 5° 45’ E. The town is a renowned oil hub in the Niger Delta region of the country and plays host to the Warri refinery. Atmospheric temperature is 27°C while humidity is 85%. The town plays host to an airport and the Federal University of Petroleum Resources (Wikipedia, 2016). Population of the area is over 311,970 according to the 2006 National census figures. Warri shares boundaries with Ughelli, Agbarho, Sapele, Okpe, Udu and Ukwie. The region is especially known for crude oil exploration activities. Four markets namely, Otuocha, Gbagbe-Ijoh, Sapele, and Udu were specifically chosen for the study based on the relative abundance of smoked-dried Bonga fish in these markets.
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Collection of fish samples
Samples of smoke-dried Bonga fish were purchased from the aforesaid markets fortnightly. Collection of samples spanned 6 months (November, 2015 to May, 2016). The samples were placed in polythene bags and sealed with selotape® after which the bags were taken to the laboratory within 24 h. A total of 50 fish samples were used for the research.

Laboratory procedures
Smoke-dried fish samples were weighed whole in grams using an ATOM A-110C® electronic compact scale while their total lengths were recorded using a stainless steel ruler. Fish samples were oven dried at a temperature of 50°C for 12 h in a Surgifield-Uniscope® (SM 9023 model) laboratory oven. Each dried sample was milled separately using a porcelain mortar and pestle and kept in foil paper prior to digestion. Two (2) g of the milled fish sample was weighed into 250 ml conical flask and 5 ml of 70 % HClO4 and 15 ml of 55 % HNO3 were added. The mixture was heated till the solution become clear. Five (5) ml of 20 % HCl was added. The mixture was filtered into a 100 ml volumetric flask using No. 42 Watman® filter paper and made up to mark with deionized water, which was prepared using a Labtech® ultra-pure water deionizer. The digest was stored in a 100 ml plastic reagent bottle ready for Atomic absorption spectrophotometer (AAS) analysis. Fish digests were analyzed for Pb, Cr, Cu and Cd by means of an Atomic Absorption Spectrophotometer (Unicam® 696 series) equipped with solar software using air acetylene flame. Concentrations of metals in fish were expressed in mg/kg. Blanks, spiked samples, reference material analyses (DORM 1, Institute of Environmental Chemistry, NRC, Canada), and duplicate analyses were performed for all analytes as part of the quality assurance procedures. All reagents used were of analytical grade (BDH, Poole, UK) and were made up using deionizer. The digest was stored in a 100 ml plastic reagent bottle ready for Atomic absorption spectrophotometer (AAS) analysis. Fish digests were analyzed for Pb, Cr, Cu and Cd by means of an Atomic Absorption Spectrophotometer (Unicam® 696 series) equipped with solar software using air acetylene flame. Concentrations of metals in fish were expressed in mg/kg.

Estimated daily intake (EDI) of heavy metals by man
The daily intake of metals was calculated in order to estimate the daily loading of metals into the body system of man via the consumption of fish (Anayakora et al., 2008).

\[
EDI = \frac{40 \text{ g/person/day} \times \text{HM (mg/kg)}}{1000 \text{g/kg}} 
\]

Where: 40 g/person/day = Estimated consumption of fishery products in Niger Delta
HM = Mean concentration of heavy metal in fish species.

Calculation of theoretical maximum daily intake (TMDI) for heavy metals

The TMDI is used for making a first estimate of heavy metal residue intake. It is calculated by multiplying the established maximum limit by the estimated average daily regional consumption for each food item and then summing the products (WHO, 1997).

\[
\text{TMDI} = \sum \left( \text{ML} \times \text{F} \right) 
\]

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

Evaluation of margin of exposure (MOE) for heavy metals

The MOE index is usually applied in cumulative risk assessments. It is essentially a margin between a reference dose for a heavy metal and the calculated or actual exposure for the same metal (Purchase, 2000).

\[
\text{MOE} = \frac{\text{Reference dose}}{\text{Calculated or actual exposure}} 
\]

Calculation of 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, can be determined by applying the TTM index (ANZECC/ARM/CANZ, 2000).

\[
\text{TTM} = \sum \left( \frac{C}{GV} \right) 
\]

Where: \( C \) = Concentration of the \( i^{th} \) component of mixture; \( GV \) = Guideline value for the \( i^{th} \) component; \( TTM > 1 \) = The mixture has exceeded the Guideline value.

Toxicity/hazard quotient (TQ) for heavy metals

The Toxicity/hazard quotient (TQ) for chemical elements is a comparison of the measured concentration of site-related elements in ecological matrices with specific health-based criteria (Newstead et al., 2002).

\[
\text{TQ} = \frac{\text{Concentration of heavy metal in fish sample}}{\text{Health based criteria}} 
\]

Statistical protocol

Statistical software (GENSTAT® version 13.3 for Windows) was used for analyzing data. One-way analysis of variance (ANOVA) was used to test for significant differences between mean values of heavy metals at 5% level of probability while Duncan Multiple Range Test was used to separate significant means. Microsoft Excel (for Windows 2010), was used for all graphical presentations.

Results and Discussion

As shown in Table 1, the mean concentration of Zn ranged from 68.27 mg/kg at Orhuwhorun market to 106.83 mg/kg at Ogbe-Ijoh market. There was no significant difference (\( P>0.05 \)) in the mean concentrations of Zn in fish between the various markets. In the case of Fe, the mean concentration of the metal in fish ranged from 231.1 mg/kg at Orhuwhorun market to 439.0 mg/kg at Jibele market. There was a significant difference (\( P<0.05 \)) in the mean concentrations of Cd in fish between the various markets. For Cu, the mean concentration of the metal in fish ranged from 15.14 mg/kg at Orhuwhorun market to 21.54 mg/kg at Jibele market. There was a significant difference (\( P<0.05 \)) in the mean concentrations of Fe in fish between the various markets. For Pb, the mean concentration of the metal in fish ranged from 1.877 mg/kg at Orhuwhorun market to 3.280 mg/kg at Jibele market. There was no significant difference (\( P>0.05 \)) in the mean concentrations of Pb in fish between the various markets.
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Table 1: Mean concentration (mg/kg) of heavy metals in *Ethmalosa fimbriata*

<table>
<thead>
<tr>
<th>Market</th>
<th>Zn</th>
<th>Fe</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orhuwhorun</td>
<td>68.27&lt;sup&gt;a&lt;/sup&gt;</td>
<td>231.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15.14&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.600&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.877&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Igbudu</td>
<td>85.49&lt;sup&gt;a&lt;/sup&gt;</td>
<td>311.40&lt;sup&gt;a&lt;/sup&gt;</td>
<td>18.80&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.132&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.812&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Jibele</td>
<td>91.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>439.90&lt;sup&gt;a&lt;/sup&gt;</td>
<td>21.54&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.398&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.280&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ogbe-Ijoh</td>
<td>106.83&lt;sup&gt;a&lt;/sup&gt;</td>
<td>332.90&lt;sup&gt;b&lt;/sup&gt;</td>
<td>19.61&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.188&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.527&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>S.E.M</td>
<td>17.61</td>
<td>74.30</td>
<td>5.39</td>
<td>0.118</td>
<td>0.840</td>
</tr>
</tbody>
</table>

Means with similar superscripts are not significantly different (P>0.05). Vertical comparisons only. S.E.M. = Standard error of mean.

Table 2: Mean concentration (mg/kg) of heavy metals in *Ethmalosa fimbriata* by months

<table>
<thead>
<tr>
<th>Months</th>
<th>Zn</th>
<th>Fe</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>November</td>
<td>47.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>243.20&lt;sup&gt;b&lt;/sup&gt;</td>
<td>28.17&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0850&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.663&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>December</td>
<td>81.71&lt;sup&gt;a&lt;/sup&gt;</td>
<td>336.30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.125&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>January</td>
<td>81.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>220.60&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.3500&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.000&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>February</td>
<td>80.98&lt;sup&gt;a&lt;/sup&gt;</td>
<td>279.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.69&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0950&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.185&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>March</td>
<td>96.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>347.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>18.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.2875&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.793&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>April</td>
<td>139.29&lt;sup&gt;a&lt;/sup&gt;</td>
<td>546.20&lt;sup&gt;a&lt;/sup&gt;</td>
<td>34.58&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.3000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.978&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>S.E.M</td>
<td>21.57</td>
<td>91.00</td>
<td>6.60</td>
<td>0.1442</td>
<td>1.029</td>
</tr>
</tbody>
</table>

Means with similar superscripts are not significantly different (P>0.05). Vertical comparisons only. S.E.M. = Standard error of mean.

As shown in Table 2, the mean concentration of Zn in fish ranged from 47.60 mg/kg in November to 139.29 mg/kg in April while there was a significant difference (P<0.05) in the mean concentration of the metal in fish between the months. In the case of Fe, the mean concentration of the metal in fish ranged from 220.6 mg/kg in January to 546.2 mg/kg in April while there was a significant difference (P<0.05) in the mean concentration of the metal in fish between the months. For Cu, the mean concentration of the metal in fish ranged from 47.60 mg/kg in November to 139.29 mg/kg in April while there was a significant difference (P<0.05) in the mean concentration of the metal in fish between the months. For Cd, the mean concentration of the metal in fish ranged from 0.00 mg/kg in December to 0.3500 mg/kg in January and April while there was a significant difference (P<0.05) in the mean concentration of the metal in fish between the months. For Pb, the mean concentration of the metal in fish ranged from 0.663 mg/kg in November to 5.125 mg/kg in December while there was a significant difference (P<0.05) in the mean concentration of the metal in fish between the months.

As shown in Fig. 2, the grand mean for heavy metals in the experimental fish ranged from 0.195 mg/kg for Cd to 329 mg/kg for Fe while the heavy metal profile in fish was Fe>Zn>Cu>Pb>Cd. The estimated daily intake (EDI) for heavy metals in mg/person/day for Zn, Fe, Cu, Cd and Pb were 3.52, 13.2, 0.75, 0.008 and 0.105 respectively while the EDI profile for the metals followed the order Fe>Zn>Cu>Pb>Cd (Fig. 3).

The theoretical maximum daily intake (TMDI) for heavy metals was 3614 mg/person/day (Fig. 4) while the margin of exposure (MOE) for heavy metals ranged from 0.09 for Fe to 1.60 for Cu, as presented in Fig. 5. The total toxicity of mixtures (TTM) index for heavy metals was 27.16 as shown in Table 3 while the toxicity/hazard quotient (TQ) for heavy metals ranged from 0.63 for Cu to 10.97 for Fe (Fig. 6). The heavy metal quota in fish ranged from 0% (Cd) to 75% (Fe) as shown in Fig. 7. The dominant status of heavy metals by market is presented in Fig. 8, in which levels of Fe, Cu and Pb were at their peak in fish at Jibele market.
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Location-wise, the mean concentrations of the investigated heavy metals in fish varied from one market to another. It was observed that the mean concentrations of Zn, Fe, Cu and Pb in fish were generally lower at Orhuwhorun market, with the exception of Cd while the highest mean concentrations of Fe, Cu and Pb were recorded for fish from Jibele market. However, the mean concentrations of Zn, Cu and Pb in fish were not significantly different (P>0.05) between the investigated markets but the contrary was the case for Fe and Cd. An indication that the smoke-dried Bonga fish may have been sourced from different places and prepared by different handlers. Time-wise, the highest mean concentrations of Zn, Fe, Cu and Cd in fish were observed to occur in the month of April, with the exception of Pb while the lower mean concentrations of all the investigated metals were recorded in the dry months of November, December and January. There were significant differences (P<0.05) in the mean concentrations of the heavy metals in fish between the months, an indication that seasonal variation may have accounted for such differences. This observation is in agreement with Adeyemo et al. (2008), who reported that seasonal changes can affect the physiochemical levels in environmental media. The fishes may have had a higher concentration of metals in the wet months owing to runoff and allochthonous input of land derived pollutants into the aquatic media from where the fishes were caught. Of all the investigated metals, Fe had the highest mean concentration (and invariably the highest metal quota) in Bonga fish while Cd had the least mean concentration. The variation in the metal levels in fish may be attributed to the degree of bioavailability and consequent bioaccumulation of these metals by fish in their aquatic media (Wangboje and Ekundayo, 2015). Meredith-Williams et al. (2012), recognized that bioaccumulation of contaminants by aquatic species depends largely on the relationship between uptake and depuration of such contaminants. Iron, dominated the metal profile in fish in this study. This observation may be due to the fact that both the ferrous and ferric forms of the metal are highly soluble in water hence promoting the bioavailability of the metal to fish. Furthermore, Fe is a vital component of fish blood in the form of haemoglobin; hence it is naturally present in such biological entities. It was observed that the mean concentrations of the non-essential metals (Pb and Cd), were lowest in fish, an indication that the fish conceivably bioaccumulated less of these metals compared to the essential elements (Fe, Zn and Cu).

In a study on heavy metals in smoke-dried Bonga fish from markets in Agbor, Delta State, Nigeria, Anigboro et al. (2011), recorded higher mean concentrations for Zn (104-126 mg/kg), Cd (1.0-3.4 mg/kg) and Pb (20-23 mg/kg) while the mean concentrations of Fe and Cu in fish in this study, were higher than those recorded in the study carried out at Agbor. The implication of this comparison is that potential consumers of smoke-dried Bonga fish in Warri will be exposed to higher levels of Fe and Cu than their counterparts in Agbor. Similarly, Ako and Salihu (2004) investigated the levels of heavy metals including Zn, Fe, Cu and Pb in smoke-dried cat fish (Clarias gariepinus) from markets in Minna town, Niger state, Nigeria and reported lower mean values for Zn (62 mg/kg), Cu (5.2 mg/kg) and Pb (0.56 mg/kg). However, the workers recorded higher mean values for Fe (804.5 mg/kg), compared to this study. Nduka et al. (2010), carried out a study on heavy metals in fresh Bonga fish netted from Aladja River in Warri and reported lower mean concentrations of Zn (1.85 mg/kg), Fe (6.2 mg/kg), Cd (0.10 mg/kg) and Pb (2.4 mg/kg), compared to this study. It is pertinent to note at this point that heavy metal levels in smoke-dried and fresh fish, even of the same species, will not be the same, owing to the peculiarities of the host environment, handling, transportation, processing, body size and weight of fish, amongst other factors. The estimated daily intake (EDI) values for heavy metals, by man was dominated by Fe, with a rank profile of Fe>Zn>Cu>Pb>Cd. This finding is not surprising as Fe had the highest mean concentration in Bonga fish while Cd had the least mean concentration. It would thus appear that man will be exposed to more of Fe compared to the other investigated elements through the consumption of smoke-dried Bonga fish from these markets. The theoretical maximum daily intake (TMDI) value for heavy metals was 3614 mg/person/day. This index, takes into consideration the maximum limits for heavy metals in fish along the per capita consumption of fish.

**Fig. 6:** Toxicity/hazard quotient (TQ) for heavy metals in smoke-dried Ethmalosa fimbriata

**Fig. 7:** Heavy metal quota in smoke-dried Ethmalosa fimbriata

**Fig. 8:** Dominant status of heavy metals in smoke-dried Ethmalosa fimbriata by market
Assessment of Human Health Risk in Relation to Concentrations of Some Heavy Metals

Table 3: Total toxicity of mixtures (TTM) index for heavy metals

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Grand mean value (mg/kg)</th>
<th>Guideline value (mg/kg)</th>
<th>Individual TTM scores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>87.95</td>
<td>30*</td>
<td>2.93</td>
</tr>
<tr>
<td>Fe</td>
<td>329</td>
<td>30*</td>
<td>10.97</td>
</tr>
<tr>
<td>Cu</td>
<td>18.8</td>
<td>30*</td>
<td>0.63</td>
</tr>
<tr>
<td>Cd</td>
<td>0.195</td>
<td>0.05**</td>
<td>3.90</td>
</tr>
<tr>
<td>Pb</td>
<td>2.62</td>
<td>0.30**</td>
<td>8.73</td>
</tr>
</tbody>
</table>

ΣTTM = 27.16

*FAO Guideline values, **Commission Regulation (EC) Guideline values

In the Niger Delta, the per capita figure is 40 mg/person/day (Anyakora et al., 2008). This same figure was adopted in this study for the calculation of the TMDI. Higher sub-TMDI values were calculated for Zn, Fe and Cu owing to the fact that these metals had higher maximum limits in fish compared to Cd and Pb. In this study, the Food and Agriculture Organization of the United Nations (FAO, 1983) and Commission Regulation (EC, 2006) maximum limits for metals in fish were employed. The margins of exposure (MOE) values were below unity for Zn, Fe, Cd and Pb while the highest MOE value of 1.60 was calculated for Cu. The implication of this finding is that Cu should be closely monitored as it may have the propensity of risk in future. The total toxicity of mixtures (TTM) value of 27.16 calculated in this study for heavy metals far exceeded unity, indicating that the Guideline values were surpassed (ANZECC/ARMCANZ, 2000). According to the TQ values Zn, Fe, Cd and Pb exceeded unity, indicating the presence of a hazard to man through the consumption of smoke-dried Bonga fish. This finding is further buttressed by the fact that the mean concentrations of the investigated metals exceeded the maximum limits/Guideline values established by FAO and EC, adding credence to the point that such fish must be consumed with caution to avoid heavy metal poisoning and its related myriad of health problems. For example according to the Nigerian Industrial Standard for drinking water quality (NIS, 2007), health impacts associated with Cu, Cd and Pb include gastrointestinal disorder, damage to the kidneys and cancer, respectively.

Conclusion

The study successfully ascertained the concentrations of Zn, Fe, Cu, Cd and Pb in smoke-dried Bonga fish (Ethmalosa fimbriata), from some markets in Warri, in the Niger Delta region of Nigeria. Essentially, the study revealed that the mean concentrations of the aforementioned heavy metals exceeded the maximum limits/Guideline values established by FAO and EC, indicating that such fish is unsuitable for consumption. Accordingly, smoke-dried Bonga fish from the investigated markets must be consumed with caution to avoid heavy metal poisoning. It is further advocated that Health Inspection Officers from the Ministry of Health and Environmental Monitoring Officers from the Ministry of Environment, be mandated to jointly monitor the activities of fish mongers and to carry out periodic spot checking of fishery products, in order to ensure and promote the fitness of such products for human consumption. Other heavy metals not covered in this study, especially the non-essential elements, should be investigated in future studies in order to obtain a more holistic profile of the metals found in fish.

Acknowledgement

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