ABSTRACT
Thirty-three samples belonging to five fish families were investigated for metal load with a view to determining the health implications on infants, children and adults in Yenegoa where the fish samples were collected. The metal analysis was done using X-ray Fluorescence Spectrometry (XRF); dietary intake and health impact were calculated for metals using the Estimated Dietary Intake (EDI) and Hazard Index (HI) respectively. The study revealed that the family Cichlidae had the highest metal load (513.20 mg/kg) followed by Synodontidae (303.97 mg/kg), Mormyridae (278.99 mg/kg), Mugilidae (278.33 mg/kg) and Cyprinidae (229.43 mg/kg). The difference between the metal load for each family was statistically significant at P<0.05. For metal species, the order from the highest to the lowest was Fe>Zn>Cr>Ni>Mn>Cu>Ba>V>Pb>Cd>As>Hg corresponding to mean values of 137.79, 60.59, 25.03, 18.86, 18.25, 18.12, 10.31, 8.71, 2.29, 2.12, 0.55 mg/kg respectively. The EDI showed that seven (7) metals for adults and six (6) metals for children out of the twelve (12) metals in the study were above the limits set by United States Environmental Protection Agency (USEPA) and FAO/WHO. The HI revealed that eight (8) out of the twelve (12) metals studied were >1 for both children and adults while infants had just three (3) metals >1. This calls for serious concern for consumers of fish in Yenegoa and may also be indicative of some high level of water and sediment pollution in the surrounding waters.

Key Words: Bayelsa, Hazard Index (HI), Estimated Dietary Intake (EDI), Health Impact, Infants, Adults, Children

1.0 INTRODUCTION
Fish plays an important role in global food supplies as a source of cheap healthy protein; its demand is expected to rise due to ever growing world population and increased awareness of its benefits (FAO/WHO, 2011; Sikoki, 2013; Uche et al., 2014). This relatively cheap source of protein is harvested from the aquatic environment where most industrial wastes are discharged, in some cases as partially or untreated effluents (Hamidalddin, and AlZahrani, 2016).

The Nigerian economy is a crude oil driven economy and has experienced the merits and demerits of this source of revenue and development (Osuji, 2002; Joel and Ovuru, 2009; Uche et al., 2015). The aquatic ecosystem has received the highest impact of this activity with
most cases of pollution unreported as the waters of aquatic ecosystem are readily self-
cleansing but not the sediment and aquatic organisms (Uche et al., 2015). Sediment has been
shown to store pollutants and release them over time, sometimes as more potent pollutants.
Fish has also been shown to take up pollutants from the water and through its diet (Li et al.,

The human body requires trace amounts of a few metals which can be obtained through food,
water and air. However, metal poisoning can occur as a result of the unhealthy accumulation
of specific metals in the body. This unhealthy accumulation occurs more commonly from the
food. Mercury, lead, cadmium, copper and aluminium are metals that can cause serious
problems in man. When they are introduced into the body at high levels, they can cause
damage at the cellular level by initiating oxidative stress. This damage can contribute to the
development of many diseases and health problems (Mathai and Bhanu, 2010).

Bayelsa is a state in Nigeria with problems of domestic sewage disposal because most
domestic wastes are channelled into surrounding water bodies or city drainages. This is
further compounded by the high water table which makes it easy for seepage to occur even
when sewage collection tanks are present, eventually finding its way back into the aquatic
environment (Uche et al., 2015). While industrial sewage is the primary source of high
concentrations of trace metals in inland water sediment, domestic waste (organic matter)
 hastens the accumulation of these trace metals (Li et al., 2013). High concentrations of metals
(chromium, nickel, copper, lead, zinc and cadmium) in water and sediment are associated
with urban activities (Devyatova, et al., 2011). The phenomenon of bioaccumulation of
metals in organisms is a well-studied case in developed and most developing countries and is
a health tool used to predict and curb the possible harmful effects of pollutants being ingested
by humans through their diet (Sandor, et al., 2001; Ennouri et al., 2010; Hamidalddin, and
AlZahrani, 2016).

Various fish types are consumed by humans based on different individual preferences such as
taste, texture, oil content, bone mass etc. In the light of this, there was no particular fish that
covers the wide range of fish species consumed by different people.

This study was therefore designed to determine the:

- Metal concentrations in various fish families;
- Fish families with the highest metal concentration
Dietary intake of these metals by man through fish consumption;

2.0 METHODOLOGY

2.1 Study Area

The Nun River is a direct continuation of Niger River, it flows through sparsely settled zones of freshwater and mangrove swamps and coastal sand ridges before completing its 160km course to the Gulf of Guinea (inlet of the Atlantic Ocean) (NEDECO, 1961). Petroleum was discovered in 1963 along the Nun River which lead to the completion of the Trans-Niger Pipeline to pipe oil from the Nun river fields (Bouvier et al., 1989; Kerr and White 1996). The River also houses the ever busy Swali market (Figure 1) which uniquely sits on the bank of the Nun River in the Bayelsa State capital – Yenegoa (4° 54′ 48.20″ N/6° 16′ 0.22″ E). The market is a place where residents can obtain fresh farm and aquatic produce for their domestic use.

Every Tuesday and Thursday, locals from the bordering islands bring their produce from Nembe, Brass, and Southern Ijaw local government areas for sale at the market. As early as 5:00am, trading activities commence.

Several local toilets can be seen constructed just above the water surface and as such, faecal matter is discharged directly into the river. Many floating gas stations can also be seen anchored on the river banks. Laundry, domestic waste disposal, meat washing, bathing, ferrying etc are some of the other activities in this area (Plate 1) (Uche et al., 2015).
Figure 1: Map of Bayelsa State showing the Study area
2.2 Fish Sample collection

Thirty three various fish specimens belonging to 5 families were collected randomly from the Swali market before 10am from different traders who sold dead fish (preserved in ice) (Table 1). The fish specimens were placed in an ice chest and transported to the laboratory where they were immediately processed.

Table 1: Sampled Fish families, Common names and number collected.

<table>
<thead>
<tr>
<th>Family Name</th>
<th>Common name</th>
<th>Number collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cichlidae</td>
<td>Tilapia</td>
<td>4</td>
</tr>
<tr>
<td>Cyprinidae</td>
<td>Carp</td>
<td>6</td>
</tr>
<tr>
<td>Mormyridae</td>
<td>Elephant fish</td>
<td>10</td>
</tr>
<tr>
<td>Mugilidae</td>
<td>Mullet</td>
<td>7</td>
</tr>
<tr>
<td>Synodontidae</td>
<td>Upside down catfish</td>
<td>6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>33</strong></td>
</tr>
</tbody>
</table>
2.3 Fish Processing and Analysis

The fish species (fillets) were placed in foil plates and covered before being placed in an oven at 50°C until dried. Each dried fish sample was properly homogenized, milled using a mixer (Mixer Mill MM400) and 4.5 g of the sample was weighed. An additional 0.45 g of a binder mix was added to the fish sample and compressed into pellets using a compressing apparatus (Spectro Hydraulic Press 360) before placing them in the XRF sample compartment for analysis of the twelve (12) metals of interest (ISO 18227 – 2014). The XRF device (SPECTRO XEPOS) was used to run elemental analysis by turning on the X-LabPro version 5.1 Software. A primary fine focus beam provided by the X-Ray tube with a molybdenum anode was automatically mono-chromatised and directed to the sample at a glancing angle less than the critical angle. The tube was operated at 50 kV and 30 mA and the fluorescent x-rays derived from the sample were detected with a solid state lithium-drifted silicon detector of 20 mm² front area, cooled with liquid helium. The energy resolution of the Si (Li) detector was 140 eV for Mn Kα and its beryllium window was 8 μm thick (Zarazúa et al., 2014; ISO 18227 – 2014). After 21 minutes the elemental analysis result was obtained and the value for the metals of interest recorded in mg/kg. The metals of interest are: Arsenic (As), Lead (Pb), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Barium (Ba), Mercury (Hg), Iron (Fe), Vanadium (V), Manganese (Mn), Copper (Cu)

2.4 Quality Control

Calibration verification was run on the equipment to ensure optimal performance and recovery. Blank sample of the binder mix was also analyzed alongside samples and used to correct for any form of contamination. A quality control sample was also analyzed just after the blank analysis and at the end of the analysis with recovery between 80-120%. All samples were run in triplicates and the average recorded. Duplicate analysis was also carried out for every 10 samples or a batch of sample and relative percentage difference (RPD) for each duplicate sample was less than ±10%.
2.5 Health Impact Calculations

The estimated daily intake (EDI) was determined using the following equation (Korkmaz 2012):

\[
\text{EDI (kg/day)} = C_{\text{metal}} \frac{W}{m}
\]

Where:
- \(C_{\text{metal}}\) is the metal concentration level of metals in fish;
- \(W\) represents the daily average consumption of fish is given as: 0.003, 0.025, and 0.068 kg/day for Infants, children and adults respectively (UNSCEAR, 2008);
- \(m\) is the bodyweight of 10 kg for Infants, 30 kg for children and 70 kg for adults.

Assessments of heavy metals hazard index (HI) in fish samples:

A hazard index (HI) may be used to describe the risk from metal intake through the oral route and was calculated by using the equation below (US EPA, 2013; Akoto, et al., 2014):

\[
\text{HI (mg/kg)} = \frac{\text{EDI}}{\text{RfD}}
\]

Where:
- \(\text{EDI}\) is the estimated daily intake of body weight per day; and
- \(\text{RfD}\) is the reference dose.

If HI > 1.0, then the EDI of a particular metal exceeds the RfD, pointing out that there is a potential non-carcinogenic risk associated with that metal (US EPA, 2013).

2.6 Statistical Analysis

The data was subjected to the Measures of central tendency. ANOVA was also run to determine the significance and variation of the data.

3.0 RESULTS AND DISCUSSION

3.1 Mean Metal Concentration in the various studied fish species

Table 2 shows the mean metal concentration in the various studied fish species. The metals in the order of highest to lowest concentration in most of the sampled fish species are:
Fe>Zn>Cr>Ni>Mn>Cu>Ba>V>Pb>Cd>As>Hg corresponding to 137.79, 60.59, 25.03, 18.86, 18.25, 18.12, 10.31, 8.71, 2.29, 2.12, 0.55, 0.15 mg/kg respectively. These values were above the FAO/WHO (1983) set limits for Fe, Mn, Cr, Pb and Zn (100, 2-9.00, 0.15, 0.30, 50.0 mg/kg respectively) only.

The result obtained did not agree with studies by Abrahão et al. (2012), Kamal et al. (2013), Vázquez-Luis et al. (2016) who studied other fishes and seafood. The disagreement of the various results was in the order of the metal concentration hierarchy. However, there was some level of agreement in the area of Iron (Fe) and Zinc (Zn) being above the set limit for metals in fish and seafood.

The total metal concentration among the fish families in the order of highest to least is as follows: Cichlidae>Synodontidae>Mormyridae>Mugilidae>Cyprinidae, with corresponding values of 5.13.00, 303.00, 278.99, 278.33 and 229.43 mg/kg respectively.
<table>
<thead>
<tr>
<th>Fish Families</th>
<th>As (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Hg (mg/kg)</th>
<th>Ba (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>V (mg/kg)</th>
<th>Mn (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Total Metal Load (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mormyridae</td>
<td>ND</td>
<td>0.02</td>
<td>2.33</td>
<td>7.77</td>
<td>75.08</td>
<td>ND</td>
<td>8.35</td>
<td>150.70</td>
<td>2.39</td>
<td>18.38</td>
<td>5.12</td>
<td>8.85</td>
<td>278.99</td>
</tr>
<tr>
<td>SD</td>
<td>ND</td>
<td>0.06</td>
<td>2.47</td>
<td>4.33</td>
<td>52.26</td>
<td>ND</td>
<td>15.53</td>
<td>71.27</td>
<td>1.71</td>
<td>7.01</td>
<td>3.05</td>
<td>7.59</td>
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</tr>
<tr>
<td>Cyprinidae</td>
<td>2.08</td>
<td>0.83</td>
<td>1.67</td>
<td>54.42</td>
<td>27.08</td>
<td>0.83</td>
<td>4.72</td>
<td>72.68</td>
<td>1.37</td>
<td>19.77</td>
<td>8.15</td>
<td>35.83</td>
<td>229.43</td>
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<tr>
<td>SD</td>
<td>4.13</td>
<td>0.41</td>
<td>0.82</td>
<td>24.75</td>
<td>18.10</td>
<td>0.41</td>
<td>5.05</td>
<td>26.38</td>
<td>0.44</td>
<td>3.57</td>
<td>4.03</td>
<td>15.89</td>
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<tr>
<td>Mugilidae</td>
<td>0.33</td>
<td>4.64</td>
<td>2.11</td>
<td>8.21</td>
<td>69.23</td>
<td>ND</td>
<td>11.17</td>
<td>154.74</td>
<td>1.60</td>
<td>13.84</td>
<td>4.74</td>
<td>7.72</td>
<td>278.33</td>
</tr>
<tr>
<td>SD</td>
<td>0.62</td>
<td>6.92</td>
<td>2.00</td>
<td>0.46</td>
<td>10.60</td>
<td>ND</td>
<td>5.16</td>
<td>59.74</td>
<td>1.23</td>
<td>8.53</td>
<td>1.54</td>
<td>6.36</td>
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</tr>
<tr>
<td>Synodontidae</td>
<td>0.30</td>
<td>3.52</td>
<td>1.60</td>
<td>8.23</td>
<td>64.32</td>
<td>ND</td>
<td>16.23</td>
<td>178.67</td>
<td>1.53</td>
<td>17.90</td>
<td>4.37</td>
<td>7.30</td>
<td>303.00</td>
</tr>
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<td>SD</td>
<td>0.71</td>
<td>8.82</td>
<td>3.37</td>
<td>12.11</td>
<td>103.85</td>
<td>0.04</td>
<td>16.75</td>
<td>233.16</td>
<td>2.51</td>
<td>21.21</td>
<td>7.12</td>
<td>11.91</td>
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</tr>
<tr>
<td>Cichlidae</td>
<td>0.40</td>
<td>4.20</td>
<td>3.03</td>
<td>27.83</td>
<td>53.93</td>
<td>ND</td>
<td>13.23</td>
<td>112.18</td>
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<td>109.60</td>
<td>106.15</td>
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<tr>
<td>SD</td>
<td>0.80</td>
<td>7.00</td>
<td>2.87</td>
<td>40.52</td>
<td>1.23</td>
<td>ND</td>
<td>3.43</td>
<td>20.84</td>
<td>114.17</td>
<td>8.00</td>
<td>211.61</td>
<td>200.57</td>
<td></td>
</tr>
<tr>
<td>Total Mean</td>
<td>0.55</td>
<td>2.29</td>
<td>2.12</td>
<td>18.86</td>
<td>60.59</td>
<td>0.15</td>
<td>10.31</td>
<td>137.79</td>
<td>8.71</td>
<td>18.25</td>
<td>18.12</td>
<td>25.03</td>
<td></td>
</tr>
<tr>
<td>Total SD</td>
<td>1.84</td>
<td>5.00</td>
<td>1.91</td>
<td>24.22</td>
<td>34.09</td>
<td>0.36</td>
<td>9.72</td>
<td>64.00</td>
<td>39.74</td>
<td>7.24</td>
<td>73.46</td>
<td>69.91</td>
<td></td>
</tr>
</tbody>
</table>

*ND = Not detectable

P value <0.05
3.2 Metal EDI and HI in Infants

Figure 2 shows the Estimated Daily Intake (EDI) for infants consuming fish. Based on the calculation, none of the metals were above the set limit by USEPA (2013) and WHO/FAO (2010). However, the Hazard Index (HI) was above the set value of 1 for Ni (1.8860), V (2.613), and Cr (2.503).

Figure 2: EDI and HI for metals in Infants

3.3 Metal EDI and HI in Children

Figure 3 shows the Estimated Daily Intake (EDI) for children consuming fish. Based on the calculation, Pb (0.0028), Cd (0.0021), Ni (0.0189), Hg (0.0002), V (0.0087) and Mn (0.0183) were above the set limit for USEPA (2013) and WHO/FAO (2010) at 0.001, 0.001, 0.003, 0.0001, 0.001, and 0.14mg/kg per day respectively.

The Hazard Index (HI) was above the set value of 1 for As (1.528), Pb (1.908), Cd (1.767), Ni (5.239), Hg (1.250), V (7.258), Mn (1.086) and Cr (2.503).

This agrees with studies by Iwegue (2015) and Orisakwe et al. (2015) who reported values above one for some metals in the seafood and fish species they studied.
3.4 Metal EDI and HI in Adults

Figure 4 shows the Estimated Daily Intake (EDI) for children consuming fish. Based on the calculation, As (0.0005), Pb (0.0022), Cd (0.0021), Ni (0.0183), V (0.0085), Mn (0.0177) and Cr (0.0243) were above the set limit for USEPA (2013) and WHO/FAO (2010) at 0.0003, 0.001, 0.001, 0.003, 0.001, 0.14, and 0.003 mg/kg per day respectively.

The Hazard Index (HI) was above the set value of 1 for As (1.780 mg), Pb (2.225 mg), Cd (2.059 mg), Ni (6.107), Hg (1.460), V (8.4610), Mn (1.266) and Cr (8.105).

This also agrees with studies by Iwegue (2015) and Orisakwe et al. (2015) who reported values above one for some metals in the seafood and fish species they studied.
4.0 CONCLUSION

The study revealed that while only a few metals (Cr, Mn, Pb, Zn and Fe) had values above the set limit by USEPA and WHO/FAO for the overall metal concentration across the five studied families, individual family metal concentration shows that the cichlids had the highest total metal load while cyprinids had the lowest. Furthermore, based on the EDI and HI values, adults and children are more at risk than infants from health impacts accruing from consumption of fish from the study area.

It is therefore advised that cichlids from this area should be consumed with caution to avoid possible metal poisoning.

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