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# Determination of Heavy Metal Concentration in Scomberscombrus and Clupeaharengus Ice Fish Sold At Mubi Market

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***Abstract:*** *Concentrations of six heavy metals (Iron (Fe), Lead (Pb), Nickel (Ni), Copper (Cu), Zinc (Zn) and Chromium (Cr)) in the flesh were investigated for two most consumed frozen fish species (Clupeaharengus and Scomberscombrus) in Mubi, metropolis. Samples were collected from Mubi market and taken to the Department of Fisheries and Aquaculture, Adamawa State University, Mubi for analysis.Length and Weight were measured using meter rule and weighing balance respectively.Wet digestion of the samples was doneand the concentrations of metals were evaluated using Atomic Absorption Spectrophotometer (AAS). Results revealed the highest concentrations of* $18.152\pm0.696^{b}$, $0.036\pm0.001^{a}$, $0.040\pm0.003^{a}$, $19.590\pm0.012^{a}$, $0.019\pm0.001^{b}$ *and* $0.082\pm0.018^{bc}$ *for Fe, Pb, Ni, Cu, Zn and Cr respectively in Clupeaharengus. In Scomberscombrus, the highest concentrations for Fe, Pb, Ni, Cu, Zn and Cr were* $17.980\pm o.201^{a}$, $0.031\pm0.035^{b}$, $0.041\pm0.002^{a}$, $20.285\pm0.998$, $0.012\pm0.011^{a}$ *and* $0.065\pm0.001^{a}$ *respectively. In Clupeaharengus, a positive correlation (r=0.504) and (r=0.905) were obtained between Fe and standard length and Pb and Standard length respectively. Positive correlation (r=0.510 and r=0.658) was obtained between Fe and Pb with Weight of Clupeaharengus. Negative correlation (r=-0.552 and r=-0.814) was also obtained between Ni and Zn with standard length and weight of Clupeaharengus respectively. In Scomberscombrus, only Ni had a negative correlation (r=-0.816) with standard length. The result is within the international standards safe for consumption of these fish except for Cu.*

***Key Words:*** *Contamination, Consumption, Bioaccumulation, Bio-magnifications and Danger.*

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## I. Introduction

Heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Heavy metals generally is a collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm$^3$, or 5 times or more, greater than water. Heavy metals include Lead (Pb), Cadmium (Cd), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), and Chromium (Cr), Copper (Cu), Iron (Fe), and the Platinum group elements. Heavy metals are natural trace components of the aquatic environment, whose level have been reported to be on the increase in recent times due to pollution from industrial wastes, changes in geochemical structure, agricultural and mining activities (Singh *et al.*, 2007; Sprocati*et al.*, 2006). Heavy metals unlike organic contaminants are not degraded with time, but concentration can only increase through bio- accumulation (Aksoy, 2008). Fish are often at the top of aquatic food chain and studies have shown that they assimilate these heavy metals through ingestion of suspended particulates, food materials and/or by constant ion exchange process of dissolved metals across some membranes like the gills or adsorption of dissolve metals on tissues and membrane surfaces (Melville and Burchett, 2002). On adsorption, the pollutant is carried in the blood stream to either a storage point (bone) or to the liver for transformation or storage (Obasohan, 2008). With fish constituting an important link in the food chain, its contamination by toxic metals causes a direct threat, not only to the entire aquatic environment, but also to humans that utilize it as food. This study therefore is aimed at investigating the concentration of some heavy metals in the flesh of *Scomberscombrus* (Atlantic herring) and *Clupeaharengus*(Atlantic mackerel) iced fish sold in Mubi market.

## II. Materials and Method

### 2.1 STUDY AREA

The study was carried out in Mubi for the periods of four months (March-June). Fish samples were bought from Mubi market, Mubi North Local Government Area of Adamawa State, Nigeria.

### 2.2 SAMPLE COLLECTION/LABORATORY MEASUREMENT/EXCISION OF FLESH

*Scomberscombrus*(Atlantic Mackerel) and *Clupeaharengus* (Atlantic Herring) were bought from Mubi Market. The fish samples were transported to the Department of Fisheries and Aquaculture Laboratory for measurement and excision. Laboratory measurement was determined as described by Olatunde (1983). Total length was measured from the tip most part of the mouth to the tip of the caudal fin. Standard length was measured from the tip most part of the mouth to the hypural bone using meter rule. Fresh weight was measured using an electronic weighing balance after removing water and other substance on the surface of the samples. The lengths were measured in centimetres while the weight in grams. The fish samples were prepared for excision by cleaning them with de-ionized water, freeing them of mechanical additives. Fish flesh (muscle tissues) was separated from the spinal column and ribs, and each species was kept in a labelled specimen bottle.

### 2.3 DIGESTION OF SAMPLES

Wet digestion technique was used as described by AOAC (2002). The procedure of wet digestion of fish was carried out by transferring 5g of the muscle tissue (flesh) of each fish sample into a kjeldahl flask and adding 25ml of digestion acids (Perchloric acid, 60% and Nitric acid, 71% in the ratio 1:4). The mixture was then swirled and heated gently at first until frothing stopped; then, it was heated more strongly until a clear light green solution resulted. The solution was allowed to cool and digest was transferred into a 100ml volumetric flask. The flask was made up to the mark with distilled water ready for metal analysis.

### 2.4 DETERMINATION OF HEAVY METALS IN FISH SAMPLE USING ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS)

Heavy metal concentration was determined using Atomic Absorption Spectrophotometer Buck 210 model as described by Ajayi and Osinbanjo (1981). A blank cell (containing distilled water) was inserted into the machine and run in other to zero it. The standard for the various metals was also run to see that the curve corresponds to the standard curve for the individual metals after which the digested samples were run using the same standard as the metal in question. The running was done by dipping a capillary tube into the digested sample in the bottle and little of the sample was taken up and the result was displayed on the screen, showing the corresponding concentration of the metals. This was done twice for a particular element and the mean was taken. This was done for the various metals under consideration and the results recorded.

### 2.5 DATA ANALYSIS

Data obtained in this study was subjected to descriptive statistics to established means. ANOVA (Analysis Of Variance) was used to evaluate the significant difference in heavy metals.Results were compared with International Standard FAO and WHO, (1989 and 1992) for maximum permissible limits in fish food for recommendation. Correlation coefficient (Pearson) was used to determine the relationship between heavy metal concentration and sizes (Length and weights) of the iced fish samples.

## III. Results

The monthly mean concentration of heavy metal in *Scomberscombrus* (Atlantic Mackerel) is shown in table 1. Concentration of Fe ranged from $17.042\pm1.175^{a}$ ppm in the month of June to $17.980\pm0.201^{a}$ ppm in the month of May. There was no significant difference observed in Fe concentration ($P<0.05$).Pb ranged in concentration from $0.013\pm0.018^{ab}$ ppm in the month of June to $0.031\pm0.035^{b}$ ppm in the month of March. There was significant difference ($P>0.05$) observed inPb. The concentration of Ni ranged from $0.021\pm0.023^{b}$ in May and $0.041\pm0.001^{a}$ in June. There was no significant difference ($P>0.05$) observed in Ni. Cu ranged in concentration from $10.712\pm12.369^{b}$ ppm in March to $20.285\pm0.998^{bc}$June. A significant difference ($P<0.05$) was observed in Cu. Zn ranged in concentration from $0.011\pm0.998^{a}$ in June to $0.012\pm0.014^{a}$ in March and April. Cr ranged from $0.032\pm0.001^{b}$ in April to $0.065\pm0.001^{a}$ in March. There was no significant difference ($P>0.05$) observed in both Zn and Cr in *Scomberscombrus.* Zn was not detected in *Scomberscombrus* in the month of May.

The monthly mean concentration of heavy metal in *Clupeaharengus* is shown in table 2. The concentration of Fe ranged from$17.022\pm0.021^{a}$ ppm June to $17.93\pm1.042^{a}$ ppm in April. There was no significant difference observed in Fe concentration of *Clupeaharengus* ($P>0.05$). The concentration of Pb ranged from $0.012\pm0.010^{ab}$ ppm in May to $0.036\pm0.006^{b}$ ppm in March. There was significant difference ($P>0.05$) observed in Pb. Ni ranged in concentration from $0.038\pm0.00^{a}$March to $0.040\pm0.003^{a}$ in June. There was no significant difference ($P>0.05$) observed in Ni. Cu ranged in concentration from $9.715\pm11.218^{b}$ ppm in April to $19.590\pm0.012^{a}$ ppm in March. A significant difference ($P<0.05$) was observed in Cu. Zn and Cr ranged in concentration from $0.009\pm0.011^{a}$ ppm in April to $0.019\pm0.001^{b}$ in June and $0.016\pm0.018^{ab}$ in May to $0.082\pm0.018^{bc}$ ppm in March respectively. There was no significant difference ($P>0.05$) observed in both Zn and Cr in *Clupeaharengus.* Zn was not detected in *Clupeaharengus*in March.

The means of the lengths (standard length and total length) and the weights of *Scomberscombrus* and *Clupeaharengus* are shown in table 3 below. The table revealed that *Scomberscombrus* and *Clupeaharengus* differ in their length and weight measurement. The total means of the total length, standard length and weight of *Scomberscombrus* were 37.65±6.73cm, 29.15±7.93cm and 245.12±148.26g respectively. While that of *Clupeaharengus* were 27.48±1.56cm, 22.83±2.29cm and 157.38±61.35g respectively.

The comparison of heavy metal concentrations and the sizes of *Scomberscombrus*and *Clupeaharengus* are shown in table 4 and table 5 respectively. Correlations were obtained at P=0.05. The results in Table 4 showed that a negative correlation was obtained between Ni and standard length (r = -0.816) in *Scomberscombrus*. The results in Table 5 also revealed that a significant positive correlation occurred between standard length (r=0.504) and weight(r=0.510) of Fein*Clupeaharengus*. A positive correlation in Standard length (r=0.905) and weight (r=0.658) of Pb in *Clupeaharengus*was also observed. On the other hand, a negative correlation was obtained between standard length (r=-0.761) in Ni. Zn correlated negatively (r=-0.814) with weight of *Clupeaharengus* and standard length (r=-0.552) of Clupea*harengus*.

**Table 1**:Monthly mean concentration of Heavy Metals in *Scomberscombrus.*

| Month | Heavy Metal Concentration | | | | | |
|---|---|---|---|---|---|---|
| | Fe (ppm) | Pb (ppm) | Ni (ppm) | Cu (ppm) | Zn (ppm) | Cr (ppm) |
| March | $17.352±0.794^{a}$ | $0.031±0.035^{b}$ | $0.038±0.002^{a}$ | $10.712±12.369^{b}$ | $0.012±0.014^{a}$ | $0.065±0.001^{a}$ |
| April | $17.932±1.042^{a}$ | $0.022±0.021^{a}$ | $0.041±0.002^{a}$ | $19.387±0.413^{a}$ | $0.012±0.014^{a}$ | $0.032±0.001^{b}$ |
| May | $17.980±0.201^{ab}$ | $0.021±0.022^{a}$ | $0.021±0.023^{b}$ | $19.507±0.044^{a}$ | ND | $0.045±0.052^{c}$ |
| June | $17.042±1.175^{a}$ | $0.013±0.018^{ab}$ | $0.041±0.001^{a}$ | $20.285±0.998^{bc}$ | $0.011±0.998^{a}$ | $0.059±0.009^{a}$ |
| Total | 17.576±0.891 | 0.021±0.023 | 0.035±0.013 | 17.532±6.887 | 0.009±0.012 | 0.050±0.027 |

Means with the same superscript on the same column for each sample are not significantly different (P<0.05).

**Table 2:** Monthly mean concentration of Heavy metals in *Clupeaharengus*

| MONTH | HEAVY METAL CONCENTRATION | | | | | |
|---|---|---|---|---|---|---|
| | Fe (ppm) | Pb (ppm) | Ni (ppm) | Cu (ppm) | Zn (ppm) | Cr (ppm) |
| MARCH | $17.900±0.021^{a}$ | $0.036±0.006^{b}$ | $0.039±0.001^{a}$ | $19.590±0.012^{a}$ | ND | $0.082±0.018^{bc}$ |
| APRIL | $18.152±0.696^{b}$ | 0.022±0.023a | $0.038±0.000^{a}$ | $9.715±11.218^{b}$ | $0.009±0.011^{a}$ | $0.033±0.038^{b}$ |
| MAY | $17.570±0.282^{a}$ | $0.012±0.010^{ab}$ | $0.038±0.001^{a}$ | $19.342±0.432^{a}$ | $0.011±0.013^{a}$ | $0.016±0.018^{ab}$ |
| JUNE | $17.022±0.021^{a}$ | $0.018±0.015^{a}$ | $0.040±0.003^{a}$ | $10.110±11.674^{b}$ | $0.019±0.001^{b}$ | $0.063±0.002^{a}$ |
| TOTAL | 17.661±0.551 | 0.022±0.016 | 0.038±0.002 | 14.689±8.766 | 0.099±0.010 | 0.048±0.033 |

Means with the same superscript on the same column for each sample are not significantly different (P<0.05).

Table 3: Means of total length (cm), standard length (cm) and weight of *Clupeaharengus* and *Scomberscombus.*

| Month | Sample | Total Length | STL | Weight (g) |
|---|---|---|---|---|
| MARCH | C. harengus | $28.05±3.46^{a}$ | $23.55±3.46^{a}$ | $210.55±73.50^{a}$ |
| | S. scombrus | $37.75±0.35^{b}$ | $32.00±0.71^{b}$ | $209.05±199.33^{a}$ |
| APRIL | C. harengus | $28.65±2.33^{a}$ | $28.65±2.33^{b}$ | $175.10±21.07^{b}$ |
| | S. scombrus | $38.90±1.55^{b}$ | $38.90±1.55^{c}$ | $438.95±9.26^{c}$ |
| MAY | C. harengus | $26.25±4.59^{a}$ | $22.00±4.24^{a}$ | $138.55±87.89^{b}$ |
| | S. scombrus | $27.55±7.70^{a}$ | $23.56±6.29^{a}$ | $209.05±199.33^{a}$ |
| JUNE | C. harengus | $26.95±1.34^{a}$ | $22.15±0.21^{a}$ | $105.30±9.76^{bc}$ |
| | S. scombrus | $28.35±6.15^{a}$ | $37.65±9.69^{c}$ | $228.15±186.46^{a}$ |
| TOTAL | C. harengus | 27.48±1.56 | 22.83±2.29 | 157.38±61.35 |
| | S. scombrus | 37.65±6.73 | 29.15±7.93 | 332.88±160.42 |
| | TOTAL | 30.31±5.73 | 25.99±6.52 | 245.12±148.26 |

STL=Standard Length

**Table 4:** Correlation between size and concentrations of heavy metals in *Scomberscombrus.*

| Size | Heavy Metal concentrations | | | | | |
|---|---|---|---|---|---|---|
| | Fe (ppm) | Pb (ppm) | Ni (ppm) | Cu (ppm) | Zn (ppm) | Cr (ppm) |
| | | | | | | |
| STL (cm) | 0.207 | -0.240 | -0.816* | -0.137 | -0.418 | -0.106 |
| Sig. (2-tailed) | 0.623 | 0.568 | 0.014 | 0.746 | 0.303 | 0.803 |
| Weight (g) | 0.325 | 0.080 | -0.331 | 0.097 | -0.123 | 0.173 |
| Sig. (2-tailed) | 0.432 | 0.851 | 0.423 | 0.820 | 0.771 | 0.682 |

* Correlation is significant at the 0.05 level (2-tailed).

**Table 5:** Correlation between size and concentrations of heavy metals in *Clupeaharengus*

| Size | Heavy Metal concentrations | | | | | |
|---|---|---|---|---|---|---|
| | Fe (ppm) | Pb (ppm) | Ni (ppm) | Cu (ppm) | Zn (ppm) | Cr (ppm) |
| STL (cm) | 0.504* | 0.905* | -0.761* | -0.552* | -0.141 | -0.176 |
| Sig. (2-tailed) | 0.203 | 0.02 | 0.028 | 0.156 | 0.740 | 0.676 |
| Weight (g) | 0.510* | 0.658* | -0.134 | -0.814* | 0.244 | 0.291 |
| Sig. (2-tailed) | 0.197 | 0.076 | 0.752 | 0.014 | 0.561 | 0.484 |

*Correlation is significant at the 0.05 level (2-tailed).STL=Standard Lengthppm=Parts per million

## IV. Discussion

In food, including fish, the allowed amounts of heavy metals (HMs) vary from country to country and based both on the WHO recommendations and local requirements (Beetseh and Abrahams, 2013). According to FAO/WHO, the permissible limit of Fe, Pb, Cu, Zn, Ni and Cr in fish is 34-107 ppm, 0.5 ppm, 10.0 ppm, 5.0 ppm, 0.5-1.0 ppm and 1.0 ppm respectively. Iron (Fe) is essential trace element required by all forms of life. It is required for synthesis of haemoglobin which functions in transport of oxygen and in many enzymes system (CAC, 2011). In this study, the total mean concentration of Fe was 17.661±0.551 and 17.576±0.891 ppm in *Clupeaharengus* and *Scomberscombrus* respectively. The concentration of Fe in both the fish species were within permissible level of 34-107 ppm recommended by FAO and WHO, (1992). This is in agreement with report by other authors (Alinnor and Obiji, 2011; Nwaedozie, 1998; and Igwemmar*et al*., 2013). No correlation (r< ±0.50) was observed between size (standard length and weight) and the concentration of Fe in both *Scomberscombrus* and *Clupeaharengus*.Exposure to lead (Pb) is widely recognized as a major risk factor for several human diseases, and the structure of industrial ecological systems have made exposure to Pb unavoidable for most people alive today (Needleman, 1999; Pruss-Ustun*et al*., 2004; WHO, 2000). The total mean concentration of Pb in *Clupeaharengus* and *Scomberscombrus* were 0.022±0.016 and 0.021 respectively. These values were within the permissible level of 5.0 ppm Pb concentration recommended in fish food by FAO and WHO (1992 and 1989). A significant positive correlation (r = 0.905) was obtained between Pb and standard length at a significant level of 0.05 in *Clupeaharengus* but no significant correlation at significant level of 0.05 in *Scomberscombrus*. Nickel (Ni) is essential for normal growth and reproduction in animals and humans, but shows carcinogenic effect when consumed in high amount. The total mean concentration of Ni in this study was 0.038±0.002 and 0.035±0.013 in *Clupeaharengus* and *scomnberscombrus* respectively. A significant negative correlation (r = -0.816) was obtained between Ni and standard length in*Scomberscombrus*. A negative correlation (r = -0.761) was also obtained between Ni concentration and size (standard length and weight) of *Clupeaharengus*. Ni concentration in both *Clupeaharengus* and *scomnberscombrus* were within the recommended level of 0.5-1.0 ppm set by FAO and WHO, (1989 and 1992).Zinc (Zn) is essential element for animals. Although humans can handle proportionally large amount of Zn, too much Zn can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia (Kumar and Mukherjeee, 2011). Very high level of Zn can damage pancreas and disturb the protein metabolism, and cause arteriosclerosis (Kumar and Mukherjee, 2011). In this study, highest Zn concentration (0.019±0.001b was observed in Herring in the month of June and lowest Zn concentration of 0.009±0.011a was observed in *Clupeaharengus* again in the month of April. Zn was not detected in *Clupeaharengus* and *Scomberscombrus* in the month of April and May respectively. Zn concentration found in this study in both the fish species were within the recommended levels of 1.0 ppm set by FAO and WHO (1989 and 1992). A significant negative correlation (r = -0.814 and r=-0.552) was observed between Zn and weight of *Clupeaharengus* and standard length of *Scomberscombrus* respectively. Copper (Cu) is an essential nutrient for both animals and humans. Although Cu is an essential trace element, high levels of intake can cause symptoms of acute toxicity. In this current study, the total mean concentration of Cu was 14.689±8.766 and 17.532±6.887 in Herring and Mackerel respectively. The concentration of Cu obtained in both fish species in this research were above the recommended level of 10.0 ppm set by FAO and WHO, (1989 and 1992). Cu was above recommended level of 10.0 ppm as reported by other authors (Alinnor and Obiji, 2011; Nwaedozie, 1998; and Igwemmar*et al*., 2013). There was no correlation between the size (standard length and weight) of the fish the Cu concentration level.Chromium recorded the total mean concentration of 0.048±0.033 and 0.050±0.027 in *Clupeaharengus* and *scomnberscombrus* respectively. These concentrations were within the recommended level of 1.0 ppm set by FAO and WHO, (1989 and 1992) in fish food. Cr concentration showed no correlation with the size of the two fish in this study. The pattern of metal concentration in Herring in this study is Fe>Cu>Zn>Cr>Ni>Pb while the pattern of metal concentration in Mackerel is Fe>Cu>Cr>Ni>Pb>Zn.

## V. Conclusion

In conclution therefore, all the heavy metal investigated were present in both *Scomberscombrus and Clupeaharengus.* However, all were within the recommended limits except Cu. Since approximately equal ratio of positive and negative correlation was observed between metal concentrations and sizes of the fish species, it can be said that Heavy metal concentration in fish is directly related to size of fish. However, it should be noted that the level of heavy metal contamination depends majorly on the rate of exposure of the fish to these heavy metals in its environment as reported by Kucuksegin*et al.* (2006).

### 5.2RECOMMENDATION

1) Biological monitoring ofice fish for consumption should be done regularly to ensure its safety for Consumption.
2) More research should be carried out on the other heavy metals not considered in this research in the iced fishSpecies studied to ensure their total dietary safety from heavy metal contamination.

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