## Dangers of Bioaccumulation of some heavy metals consumed in Sardine and Mackerel (ice fish) in Benue State Nigeria

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#### Abstract

Buck Scientific Atomic Absorption Spectrophotometer (AAS) VGP 2110 was used to investigate the presence of Lead(Pb), cadmium (Cd) and Iron (Fe) in Mackerel and Sardine fish species popularly referred to as ice fish consumed in Benue State and Nigeria. In Sardine the total concentration was 0.0105, 0.016, 15.1 mg/L for Lead(Pb), Cadmium (Cd), and Iron (Fe) ) respectively. Mackerel had the concentration of 0.013, 0.063, 16.06 mg/L of Lead(Pb), cadmium (Cd), and Iron (Fe) respectively. The result seem within the international standards safe for consumption of these fish. Continuous consumption can also lead to bioaccumulation and biomagnifications of these metals in the human body exposing it to danger. Key words: Accumulation, Consumption, Equilibrium, Metabolism, Supply.

#### 1. Introduction

According to <u>Berkeley Wellness</u> (2012) some 85 percent of the seafood Americans consume is imported and much of that is farm-raised in Asia and elsewhere in the developing world where fish farms are not inspected by U.S. officials and only a fraction of imported seafood is actually tested for drug residues when it enters the country. According to a report captioned 'Importing bad news' the Food and Drug Administration (FDA) checks just two percent of imports for contaminants (including drug residues, microbes, and heavy metals), compared to 20 to 50 percent in Europe, 18 percent in Japan and up to 15 percent in Canada. And when the FDA does inspect seafood imports, it looks for residues from only 13 drugs. In contrast, Europe tests for 34 drugs. That means overseas fish farms can be using a range of drugs for which the U.S. doesn't even screen The European (EU) is the dominant supplier of frozen seafood products with more than 70% of market share in Nigeria . Other supplying countries include China, Korea, Brazil, Paraguay, Uruguay, USA & Gambia, Mauritania, Namibia, Angola and Morocco.

Imported frozen seafood is usually shipped to Apapa-Lagos, Port Harcourt and Warri and are inspected, passed through custom clearance. After clearance the products are transported in refrigerated trucks to cold storage warehouses located within Lagos and other urban centers. Imported seafood products are shipped in branded boxed packages of 20kg, 25kg and 30kg and the number of fish per box varies with fish sizes- small, medium or large, which range from 80 to 120 pieces per carton. The threat of toxic and trace metals in the environment is more serious than those of other pollutants due to their non bio-degradable nature, accumulative properties and long biological half lives. It is difficult to remove them completely from the environment once they enter into it Aderinola et al., (2009). Heavy metal contamination may have devastating impacts on the ecological balance of natural water bodies including the loss of aquatic diversity (Vosyliene & Jankaite, (2006); Farombi et al., (2007;) Hayat & Javed, (2008). With increased use of a wide variety of metals in industries and in our daily life, there is now a greater awareness of toxic metal pollution of the environment. Many of these metals tends to remain in the ecosystem and eventually move from one compartment to the other within the food chain (Sadasivan & Tripathi, (2001).

#### 2 .Literature Review

Fish are always at the top of aquatic food chain and when pollutants build up in the food chain, fish are widely used to evaluate the health of aquatic ecosystems. Fish may concentrate large amounts of metals from the water and therefore are responsible for adverse effects and death in the aquatic systems Mansur & Sadly,( 2002); Farkas et al, (2002).

The Agency for Toxic Substances and Disease Registry (ATSDR) in Atlanta, Georgia, (a part of the U.S. Department of Health and Human Services) was established by congressional mandate to perform specific functions concerning adverse human health effects and diminished quality of life associated with exposure to hazardous substances. One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnifications causing heavier exposure for some organisms than is present in the environment alone. A typical food chain includes algae eaten by the water flea eaten by a minnow

eaten by a trout and finally consumed by a human being. If each step results in increased bioaccumulation, then an animal at the top of the food chain, through its regular diet, may accumulate a much greater concentration of chemical than was present in organisms lower in the food chain . Bioaccumulation of heavy metals in fish has been reported by many researchers. The uptake of heavy metals in fish was found to occur through absorption across the gills surface or through the gut wall trait. Diffusion facilitates the transportation in gills and surface mucus and mechanisms of uptake through the gut from food and the rate of excretion. Gills generally have the highest metal concentration due to their intimate contact with the environment and their importance as an effect or of ionic and osmotic regulation. Liver in its role as a storage and detoxification organ can also accumulate much less. The aspect of human health linked to the consumption of contaminated fish as a result of the presence of heavy metals is of great concern. (Khare & Singh, 2002; Hayat & Javed, 2008

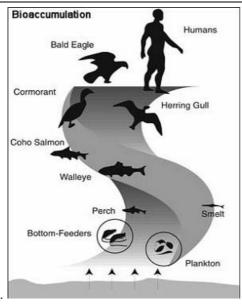


Figure 1, Food chain -the simplest possible representation of producer-consumer relationships in an ecosystem. Curtesy EXTOXNET primary files(1993)

Figure 2 . SARDINE and





According to Extension Toxicology Network EXTOXNET primary files(1993), bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Understanding the dynamic process of bioaccumulation is very important in protecting human beings and other organisms from the adverse effects of chemical exposure, and it has become a critical consideration in the regulation of chemicals Bioconcentration is the specific bioaccumulation process by which the concentration of a chemical in an organism becomes higher than its concentration in the air or water around the organism. Biomagnification describes a process that results in the accumulation of a chemical in an organism at higher levels than are found in its food. It occurs when a

chemical becomes more and more concentrated as it moves up through a food chain . Bioaccumulation begins when a chemical passes from the environment into an organism's cells. The chemical tend to move, or diffuse, passively from a place of high concentration to one of low concentration. The force or pressure for diffusion is called the chemical potential, and it works to move a chemical from outside to inside an organism. A number of factors may increase the chemical potential of certain substances. For example, some chemicals do not mix well with water. They are called lipophilic, meaning "fat loving," or hydrophobic, meaning "water hating." In either case, they tend to move out of water and enter the cells of an organism, where there are lipophilic microenvironments. One factor important in uptake and storage is water solubility; the ability of a chemical to dissolve in water. Usually, compounds that are highly water soluble have a low potential to bio accumulate and do not leave water readily to enter the cells of an organism. Once inside, they are easily removed unless the cells have a specific mechanism for retaining them. Another factor affecting bioaccumulation is whether an organism can break down and/or excrete a chemical. This ability varies among individual organisms and species and also depends on characteristics of the chemical itself. Chemicals that dissolve readily in fat but not in water tend to be more slowly eliminated by the body and thus have a greater potential to accumulate. Many metabolic reactions change a chemical into more water soluble forms called metabolites, that are readily excreted.

...Lead is number 2 on the ATSDR's "Top 20 List." and accounts for most of the cases of pediatric heavy metal poisoning Roberts (1999). It is a very soft metal and was used in pipes, drains, and soldering materials for many years. Millions of homes built before 1940 still contain lead (e.g., in painted surfaces), leading to chronic exposure from weathering, flaking, chalking, and dust. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries. The remainder is used for cable coverings, plumbing, ammunition, and fuel additives. Other uses are as paint pigments and in PVC plastics, x-ray shielding, crystal glass production, and pesticides. Target organs are the bones, brain, blood, kidneys, and thyroid gland (International Occupational Safety and Health Information Centre 1999; ATSDR ToxFAQs for Lead). Cadmium is a byproduct of the mining and smelting of lead and zinc and is number 7 on ATSDR's "Top 20 list." It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Cadmium may be found in reservoirs containing shellfish. Cigarettes also contain cadmium. Lesser-known sources of exposure are dental alloys, electroplating, motor oil, and exhaust. Inhalation accounts for 15-50% of absorption through the respiratory system; 2-7% of ingested cadmium is absorbed in the gastrointestinal system. Target organs are the liver, placenta, kidneys, lungs, brain, and bones (Roberts 1999; ATSDR ToxFAQs for Cadmium).

Iron ingestion accounts for most of its toxic effects because it is absorbed rapidly in the gastrointestinal tract, its corrosive nature seems to further increase the absorption and most overdoses appear to be the result of children mistaking red-coated ferrous sulfate tablets or adult multivitamin preparations for candy. (Fatalities from overdoses have decreased significantly with the introduction of child-proof packaging. In recent years, blister packaging and the requirement that containers with 250 mg or more of iron have child-proof bottle caps have helped reduce accidental ingestion and overdose of iron tablets by children.) Other sources of iron are drinking water, iron pipes, and cookware. Target organs are the liver, cardiovascular system, and kidneys

## 4.0 Materials and Methodology

#### 4.1 Apparatus/Reagents

All reagents

used for this study were of analytical grade. All glass wares were soaked in 10% HNO<sub>3</sub> for 2 hours and later rinsed with distilled de-ionized water prior to use for metal analysis. Distilled water was used for the preparation of all solutions.

#### 4.2 **Collection and Treatment of Samples**

The two fish species collected for investigation were: Atlantic Horse Mackerel (Tracburus traburus) simply called kote and fresh water Sardine (Sardinella tawilis) they were bought at Makurdi and Otukpo Markets which are the major cities of Benue State and pooled together. These species were chosen because they are the commonest species The fish were prepared for analysis by cleaning them with de-ionized water, freeing them of mechanical additives and were allowed to thaw at room temperature. Fish inner organs were removed. Fish flesh was separated from the spinal column and ribs, and each species was kept in a labelled polyethylene bag and dried in an oven at 250°C for two hours each day for two days before digestion. The dried fish samples were crushed into a fine powder by porcelain mortar and pestle and stored in amber colored bottles in vacuum desiccators.

### 4.3 Wet Digestion of Samples

A mixture of HCl and HNO<sub>3</sub> acid in the ratio of 3:1 was used. About 1.0g of each blended fish sample was weighed into a beaker, 10ml of 3:1 HCl/HNO<sub>3</sub> was added and the beaker covered by watch glass.

This was placed on thermostatically controlled hot plate maintained at  $90^{\circ}$ C,  $110^{\circ}$ C and  $120^{\circ}$ C respectively at different times for 20 minutes. The best digesting temperature was achieved at  $90^{\circ}$ C for 20 minutes The beaker and the watch glass were cooled and its content transferred into analytical bottles (sample bottles) and made up to 25mL with distilled water. The digested samples were analyzed for heavy metal concentration using the Buck Scientific Atomic Absorption Spectrophotometer (AAS) VGP 2110 .

### 4.4 Preparation of AAS Standards.

Iron: 5.0503g ferrous ammonium sulphate was dissolve in distilled water and made up to 1 litre mark [1mL = 1mg Fe]. The AAS was run at a wavelength of 248.3nm.

.Cadmium: 1.630g  $CdCl_2$  was dissolved in distilled water and made up to 1 litre mark [1mL = 1mgCd]. The AAS was run at wavelength of 228.8nm.

Lead: 1.5985g lead nitrate, Pb  $(NO_3)_2$ , was dissolved in distilled water and made up to 1 litre mark [1mL = 1mgPb]. The AAS was run at a wavelength of 283.3nm (Whiteside, 1979).

## 4.5 Determination of Heavy metals in Fish Sample using AAS

The Buck Scientific VGP 2110 AAS was switched on and the gas fed to supply the flame needed to heat the cathode lamps. A blank cell (containing distilled water) was inserted into the machine and run in other to zero it. The standard for the various metals were 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 metal. This was done three times for a particular element and the mean was taken. This was done for the various metals under consideration.

## 5.0 Results

The concentrations of the heavy metals in the fish organs (Gills and flesh) are given in table 5.1 and 5.2 respectively.

Source	Cd mg/L	Fe mg/L	Pb mg/L	Total
Sardine				
Gills	0.009	6.50	0.002	6.6922
Flesh	0.016	7.15	0.003	7.4093
Total	0.025	13.65	0.005	14.1015
Mackerel				
Gills	0.019	7.60	0.0025	7.8399
Flesh	0.027	7.94	0.0028	8.2672
Total	0.046	15.54	0.0053	16.1071

## Table 1 Metal concentration in mg/L in organs of Sardine and Mackerel ( Makurdi)

(Otukpo)						
Source	Cd mg/L	Fe mg/L	Pb mg/L	Total		
Sardine						
Gills	0.007	7.30	0.005	7.5762		
Flesh	0.009	7.80	0.0055	8.1047		
Total	0.016	15.1	0.0105	15.6809		
Mackerel						
Gills	0.028	7.62	0.006	8.0003		
Flesh	0.035	8.44	0.007	8.9025		
Total	0.063	16.06	0.013	16.9028		

# Table 2 Metal concentration in mg/L in organs of Sardine and Mackerel (Otukpo)

The concentration of Cadmium (Cd) concentration ranged between 0.009 mg/L to 0.007 mg/L in gills and 0.016 mg/L to 0.009 mg/L in flesh. Iron ranged between 0.50 mg/L to 7.30 mg/L in gills and 7.15 mg/L to 7.80 mg/L inn flesh. Lead concentration range between 0.002 mg/L to 0.005 mg/L in gills and 0.003 mg/L to 0.0055 mg/L in flesh.

For mackerel the concentration of Cadmium ranged between 0.019mg/L to 0.028mg/L in gills and 0.027mg/L to 0.038 mg/L in flesh. Iron ranged between 7.60 mg/L to 7.62 mg/L in gills and 7.94 mg/L to 8.440 mg/L in flesh Lead concentration ranged between 0.025 mg/L to 0.006mg/L in gills and 0.0028 mg/L to 0.007 mg/L in flesh.

In all the samples iron concentration was high in both gills and flesh and lead is the lowest in the two species of fish used. Comparative study of accumulation of these metals in the different organs of the fishes shows that the flesh of the two fish samples accumulates metals than other parts while mackerel ice fish has the highest accumulation of heavy metals compared to the sardine ice fish.

## 6. DISCUSSION

In food the allowed amounts of heavy metals (HMs) vary from country to country and based both on the WHO recommendations and local requirements. According to Lithuanian Standards of Hygiene (LSH, 2001) the Maximum Tolerable Limit (MTL) of lead in fish meat is 0.4mg/kg which is same as the value adopted by the European Commission for lead in marine fish muscle EC, 2000) while FAO set a limit of 0.5mg/kg (FAO, 1983). Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities, 2001). Lead is a neurotoxin that causes behavioral deficits in vertebrates, decreases in survival, growth rate, learning and metabolism (Weber et al., 1997; Burger and Gochfeld, 2000). FOA of the United Nations and WHO (1994) have established a provisional tolerable weekly intake (PTWI) of lead as 25mg/kg body weight for humans. In this study, the levels of lead are within the tolerable limits. Cadmium is highly toxic (Jarup, 2003). Cd is associated with nephrotoxic effects particularly long term exposure may cause bone damage. (Friberg et al., 1986). The threshold concentration of cadmium in fish muscles design for human consumption set by the European Commission is 0.1mg/gw.w, the guideline limit set for Cd by FAO, (1983) is 0.05mg/kg for fish. In the present study the concentration of cadmium is some marketed fishes were found to be lower (both in gills and flesh). However these heavy metals may be transferred to man on consumption and may be hazardous to health because of their cumulative effect in the body. According to Jakimska et al (2011) it is the diet of an animal that dictates its accumulation of metals in its tissue. The more we consume fish that shows the type of results above the more exposed we are to bioaccumulation and its consequences.

#### 7 Recommendation

(i) Biological monitoring of the water body and fish meant for consumption should be done regularly to ensure its safety for consumption.

- (ii) Laws should be established to protect the environment around the water body and more research centers should be established to aid closer and regular checks of these metals in the environment.
- (iii) Since heavy metals are product of environmental pollution resulting from human activities, the ultimate goals of reducing heavy metals exposure is to control metals emissions as well as well as stopping their pathways into the water body and marine food. This can be achieved via the following ways:
  - a. Discharge of untreated industrial sewage should be discouraged.
  - b. Appropriate regulatory measures on hazardous waste containing heavy metals.
  - c. Promotion of technical solutions such as the use of unleaded petrol .
  - d. The establishment of cleaner production programmes in industry
  - e. Establishment of information services on technology and ways to reduce or eliminate pollution by heavy metals.
  - f. Vary your seafood choices to minimize overexposing yourself to any particular contaminants they may contain.

## REFERENCES

<u>Berkeley Wellness</u> How Safe Is Your Imported Seafood? Environmental Science & Technology May 01, 2012 Clark, R.B (1986): Marine Pollution, Reinhold Publisher, United State of America

Duffus, J.H. (2002): 'Heavy Metals' a meaningless term? (IUPAC Technical Report), Pure and Applied Chemistry 2002, Vol. 74, page 793-807

FAO/WHO. (1976). List of Maximum levels recommended for contaminants by the Joint FAO/WHO Codex Alimentarius Commission. 2<sup>nd</sup> series CAC/FAL, rome, 3, 1-8

Bu-olayan and Thomas A. (2005): Chemistry and Ecology Vol. 21, (3) page 191-197.

Bill, D (2007): Trace Elements in Fish and Fish Oil supplement the application network.

Jekin, U.S. (1989). Environmental Protection Agency, Monitoring of Toxic Trace Metals, (Report: N0 EPA/600/3/089/Washington DC pg 2).

King, R.P., and Jonathan, G.E. (2003): Aquatic environmental perturbations and monitoring; African experience, USA.

Petro, A.R and Marisa, R.A. (2007). Matrix importance in animal material pre-treatment for metal determination. Whiteside, P. (1979). An Introduction to Atomic Adsorption Spectrophotometer. Published by Pye Unicam Ltd, 1<sup>st</sup> Edition, pye Unicam Ltd York Street Cambridge, UK. Pg 24-25.

Aderinola O.J,; Clarke E.A, Olarinmoye O.M, Kusemiju V and Anatekhai M.A,2009. Heavy Metals in Surface Water, Sediments, Fish and Perwinkles of Lagos Lagoon. American-Eurasian J. Agricultural and Environmental Scince., 5(5): 609-617.

Anderson, E.D and Parciorkowski, A.J. 1980: A review of the Northwest Atlantic Mackerel Fishery. Rapp.P.V. Reun. Cons. Int. Explor. Mer., 177-211.

EPA, 1994. National Guidance: Guidance for Assessing Chemical Contaminant data for use in Fish Advisories. Vol. II. Risk Assessment and Fish Consumption Limits. 3<sup>rd</sup> Edition, Office of Water, Philadelphia.

EC, 2000. Setting maximum levels for certain contaminant in foodstuffs. EC No 104/2000, Brussels, pg: 2-28.

FAO, 1983. Complication of legal limits for hazardous substances in fish and fishery products. Food and Agriculture Organization of the United Nations, Rome. Italy, pp: 5-100.

Long-range Transboundary Air Pollution (LRTAP) Convention of the United Nations Economic Commission for Europe- <u>http://www.unece.org/env.lrtap/wel-</u>Come.html

http://en.wikipedia.org/wiki/Heavy-metal\_(Chemistry)

http://en.wikipedia.org/wiki/sardine

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