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DISTRIBUTION OF TRACE METALS IN PARTS OF STOCK FISH MARKETED IN THREE MARKETS AROUND PORT HARCOURT, NIGERIA.

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ABSTRACT

This research was carried out to determine the distribution of trace metals in parts (head and tail) of stock fish marketed in three markets around Port Harcourt (Rumuokoro, Choba and Alakahia markets). Iron (Fe) concentration values was the highest in all the fish samples (ranging from 0.98-3.09 mg/kg) while Nickel was below the detection limit with exception of the fish head sample obtained from Alakahia market (0.003 mg/kg). The concentration of the heavy metals were below the recommended limit suggested by the Food and Agricultural Organization (FAO), World Health Organization (WHO), European Union Commission (EU/EC), United States Environmental Protection Agency (USEPA) and the Federal Protection Agency (FEPA) with the exception of cadmium (Cd) in the fish head samples (0.061 and 0.081 mg/kg) obtained from the Choba and Alakahia markets which were above the EU recommended limits (0.05 mg/kg).

INTRODUCTION

Fish is an important source of protein around the world. Stock fish is an unsalted fish usually air-dried, sun-dried or wind-dried on wooded racks called hjell (Kurlansky, 2014). Stock fish, locally known as *Okporoko* by the Igbos and to most marketers in the Niger-Delta markets, is popularly made from the Cod (*Gardusmorhua*), although other fishes like the Haddock (*Melanogrammus aeglefinus*), Ling (*Molvamolva*) and Tusk (*Brosmebrosme*) have been used for stock fish production but to a lesser extent (Koster *et al*., 2009). Stock fish consumption has been highly recommended because it is a rich source of omega-3 and omega-6 fatty acid and thus is known to have a lot of health benefits like anticancer properties, anti-inflammatory properties, helps in proper cognitive functioning, regulates cholesterol level because of its low-fat protein content, and contains several vitamins and minerals which are needed to nourish the human body (Brawn, 2011).

It is unfortunate that water pollution by human and industrial activities has greatly affected aquatic life, leading to bioaccumulation of pollutants and toxins in fishes and other aquatic life (flora and fauna). Heavy metal pollutants have been found in various levels in different water bodies in Nigeria (Obahiagbon and Okieimen, 2007; Oboh and Edema, 2007; Okoye, 1991). Heavy metals in low concentrations play certain metabolic roles in living organisms, these include zinc (Zn), copper (Cu), iron (Fe), chromium (Cr), cobalt (Co) and manganese (Mn). However, at higher concentrations, these metals are found to be toxic to living organisms causing various health complications as a result of heavy metal poisoning. In addition, certain heavy metals possess no biological function, for example, lead (Pb), mercury (Hg) and cadmium (Cd), even at low concentrations (Ugwu and Okoye, 2010; Odoemelam and Ibezim, 2010; Iwuoha *et al*., 2013).

The purpose of this research was to determine the concentration of certain heavy metals (Cr, Cu, Fe, Ni, Pb, Zn and Cd) in the head and tail of stock fish obtained from three different markets in Rivers State, Nigeria due to the high consumption of this particular type of fish in Nigeria.

MATERIALS AND METHOD

The heads and tails of the stock fishes were randomly sampled at various markets located at the heart of Port Harcourt city in the Niger delta. Three sampling locations were used namely; Rumuokoro, Alakahia and Choba axis of Port Harcourt. Figure 1 shows the position of Port Harcourt in Niger Delta, Nigeria. The geographical co-ordinate of the city is roughly latitude $4^0 88^1$N and longitude $6^0 96^1$ E. The head and tail of each of the stock fish samples were removed using a saw. The stock fish samples (head and tail) were homogenised and oven dried afterwards at oven temperature of 105^0 C. The dried samples were ground to fine powder. In a separate beaker 20ml of trioxonitrate V acid (HNO_3), 20ml of tetraoxosulphate VI (H_2SO_4) and 10ml of perchloric acid ($HClO_4$) were mixed together. Two grams each of the ground samples were separately weighed into conical flasks and 2mls each of the mixed acid prepared were added separately to the samples in the conical flasks. The mixtures were heated in fume chambers with hot plate until white dense fumes appeared. The conical flasks were allowed to cool and the contents each filtered into three separate 100mls volumetric flasks and were made up to mark with distilled water. The samples were later aspirated for the respective heavy metal's concentration determination using atomic absorption spectrometer AAS model 200. The average of the triplicate data for each heavy metal was taken.

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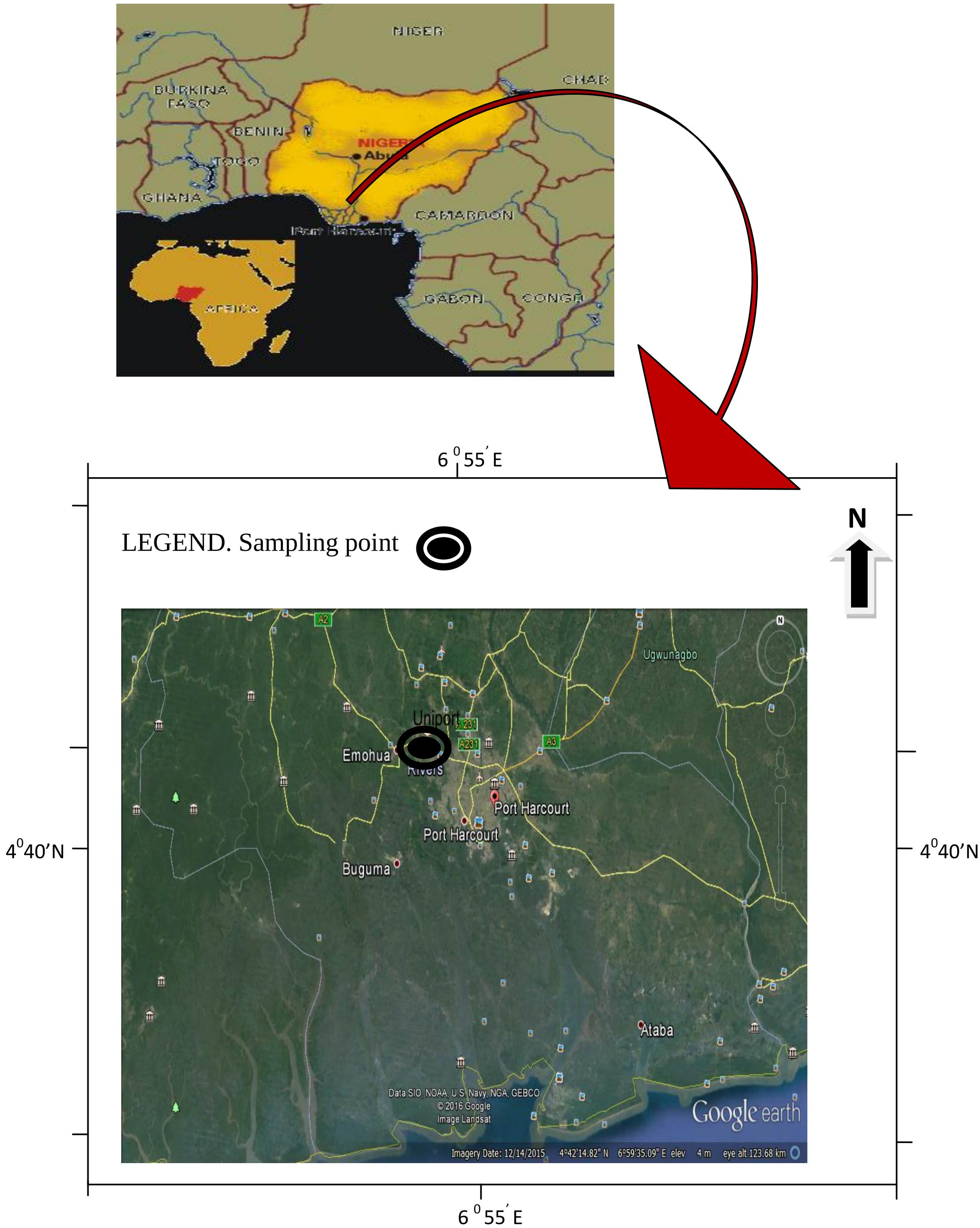

Figure 1. Map of Port Harcourt, Nigeria indicating sampling points Rumuokoro, Alakahia and Choba area of University of Port Harcourt.

RESULTS AND DISCUSSION

The concentration of seven heavy metals; chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), zinc (Zn) and cadmium (Cd) in stock fish parts (head and tail) obtained from three different markets in the Port Harcourt, Niger-Delta (Rumuokoro, Choba and Alakahia market) were determined. This is presented in Table 1.

Heavy metals (mg/kg)	Rumuokoro		Choba		Alakahia		Recommended regulatory standards(mg/kg)
	Head	Tail	Head	Tail	Head	Tail	
Cr	0.051	0.013	0.09	BDL	BDL	BDL	**0.15-1.0** ^{w}
Cu	0.093	0.091	0.071	0.064	0.19	0.12	**30** ^{w}
Fe	2.341	1.081	3.09	1.94	0.98	1.00	**100** ^{w}
Ni	BDL	BDL	BDL	BDL	0.003	BDL	**0.5-0.6** ^{w}
Pb	0.18	0.01	0.27	0.02	0.11	BDL	*0.2-0.5* ^{EU}
Zn	0.54	0.291	0.71	0.31	0.42	0.28	**100** ^{w}
Cd	0.0055	0.002	0.061	0.001	0.081	0.039	**0.2** ^{w}/*0.05* ^{EU}

NOTE: W = WORLD HEALTH ORGANIZATION (1985 OR 1989); EU = EUROPEAN UNION (2006)

BDL =Below Detection Limit (<0.001)

Iron plays an important role in the formation of haemoglobin by merging with protein and copper (Girina *et al*., 2015). Haemoglobin allows oxygen to be carried from the lungs to the tissues. It is essential to human beings as a nutrient but if above certain recommended values, it may cause hazard to the health when consumed (Girina *et al*., 2015). It is essential in human diet and fish contains relatively high amounts of readily absorbable haem iron (Girina *et al*., 2015). Iron occurs naturally in foods and water. Its deficiency is one of the most common nutritional deficiencies in children, pregnant women and in women of child bearing age (Nordberg *et al*., 2007). Iron deficiency is known to cause anaemia and acute anaemia if not properly treated may even lead in most cases to death (Nordberg *et al*., 2007). Toxic doses of iron in animals may result in depression, coma, convulsion, respiratory failure and cardiac arrest (Nordberg *et al*., 2007). Mammals are unfortunately not equipped with mechanisms for the excretion of excess iron and chronic iron overload is associated with failure of various organs including the liver, pancreas and heart which can bring about early death (Nordberg *et al*., 2007). From the results in Table 1, the concentration of Iron ranged from 0.98-3.09 mg/kg in both fish parts obtained from the three markets. These values were far below the acceptable level of Iron in fish (100 mg/kg) as recommended by WHO (1989).

Lead is known to be one of the most toxic metals (Moustafa and El-Sayed, 2014). It is an industrial pollutant which has strong detrimental effects on living organisms. Lead acts like a mimetic agent physiologically and biochemically, thus interfering or participating in certain biological and chemical processes (Moustafa and El-Sayed, 2014). It interferes with zinc and iron in the biosynthesis of heme, in the function of sulfhydryl group rich-protein enzymes and in protein synthesis (Moustafa and El-Sayed, 2014). It also binds to transport proteins like transferring metallothionein, etc (Moustafa and El-Sayed, 2014). Lead is a human

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carcinogen and can affect every organ and system in the body. Exposure to high levels of Pb can severely damage the brain and kidney and further cause death. It leads to miscarriages in pregnant women and can damage the organs responsible for sperm production in men (Martin and Grisworld, 2009). In addition, long-term exposure can result in decrease in the functioning of the nervous systems, increase in blood pressure, anaemia and weakness in joints (Martin and Grisworld, 2009). The values for the concentration of lead as presented in Table 1 were in the range of 0.01-0.27 mg/kg. The highest concentration of Lead was from the fish head sample obtained from Choba market which gave a value of 0.27 mg/kg. This was observed to fall in the range allowed for Pb in fish food (0.2-0.5 mg/kg) (EU, 2006; FAO, 1983).

Zinc is an essential element and it is found naturally in the earth crust and in living organisms. At high concentrations, it can be toxic to aquatic organisms causing mortality, growth retardation and reproductive impairment (Sorenson, 1991). At concentrations above 100 mg/kg, which is the recommended limit for zinc in fish food (WHO, 1985), anaemia, neurological degradation, change in iron function and reduced immunity may result in humans (Iwuoha *et al*., 2013). The values for the concentration of zinc as obtained in the analysis ranged from 0.42-0.71 mg/kg for stock fish head and 0.28-0.31 mg/kg for stock fish tail from the three markets. These values are far below the recommended limit of 100 mg/kg.

Chromium (III) is regarded as nutritionally essential to humans but in trace amounts, however chromium (VI) can penetrate cell membranes and cause genotoxic effects and cancer (Robert, 2004). This hexavalent chromium occurs naturally in the environment and is mainly generated by production industries like stainless steel, welding and painting. Thus Cr is now a major factory or industry run-off pollutant, and is carcinogenic, especially affecting the lungs via inhalation (Robert, 2004). The concentration of chromium in the stock fish samples obtained from Alakahia market as well as the tail from the Choba market where found to be below detection limit (BDL). However, the fish head sample from Choba market recorded a concentration of 0.09 mg/kg, and samples from Rumuokoro recorded concentrations of 0.051 and 0.013 mg/kg for head and tail respectively. These values were found to be below the maximum limit for chromium in fish food, i.e. 0.15-1.0 mg/kg (WHO, 1985; FEPA, 2003 and FAO, 1983).

Copper (Cu) is regarded as the third most common mineral in the human body (Robert G., 2004). It is an essential element in the body for growth, and bone development and is required for various functions. It is not considered to be mutagenic or carcinogenic, although teratogenicity is observed in some animals like rat. Toxic effects of copper include jaundice, emesis, nausea, diarrhea, haematuria, coma and death (Robert G., 2004). It is ubiquitously distributed in seafood (Robert G., 2004). The highest concentration for copper in the fish samples was obtained from Alakahia market with values of 0.19 and 0.12 mg/kg for the head and tail respectively. Both of which are lower than the recommended limit for copper in fish food, of 30 mg/kg (USEPA, 2000; WHO, 1989 and FAO, 1983).

Cadmium (Cd) has no beneficial effect in the human body and thus there is no known homeostatic mechanism for it (Vieira *et al*., 2011). It is a highly toxic heavy metal. Even at low concentration, cadmium is very harmful to living organisms. It accumulates in the human body via food and negatively affects organs such as liver, lung, bones, kidney, brain and the central nervous system. It is also known to affect the hepatic system, reproductive system as well as the immune system (Makimiyua and Afua, 2013). Cadmium is released to the environment through wastewater by contamination from fertilizers (Makimiyua and Afua, 2013). The accumulation of Cd in fish samples can be as a result of agricultural activities through the application of agro-chemicals. The values obtained from the analyses for the concentration of cadmium in the stock fish head were found to be higher ranging from 0.0055-0.081 mg/kg. The highest concentration of Cd was found in the fish parts obtained from Alakahia market with values of 0.081 mg/kg and 0.039 mg/kg for head and tail respectively while the lowest value was that from Rumuokoro market samples with concentrations of 0.0055 mg/kg and 0.002 mg/kg for head and tail respectively. The concentration of Cd in the fish samples were observed to be lower than that recommended for Cd in fish food (2.0 mg/kg) by FAO (1983) and that recommended by WHO (0.2 mg/kg). Although the values are low and may seem not to pose a problem, long-term exposure to lower levels of cadmium could lead up to a build-up in the kidneys and this may result to kidney disease and even death. It must be mentioned that the EU regulation (2006) recommends 0.05mg/kg as its limit for cadmium in fish food and from the results in Table 1, the fish head samples from Choba and Alakahia markets gave values above this limit (0.061 mg/kg and 0.081 mg/kg respectively) thus raising a question on health safety.

For humans, nickel (Ni) is mainly obtained from food or from natural sources as well as food processing (NAS-NRC, 1975). The use of agrochemicals such as pesticides, herbicides and fertilizers add to the nickel uptake by aquatic life, via the uptake by soil and leaches and run-offs into aquatic systems (Apori *et al*., 2012). Nickel exposure may lead to carcinogenic reactions in humans. Nickel has not been shown to be an essential nutrient to humans; however, it may act as a cofactor or structural component of specific metalloenzymes with a variety of physiological functions in lower animals (Robert G., 2004). It has been shown to facilitate ferric ion metabolism (Robert G., 2004). The concentration of nickel in the fish parts were below detection limit except for the stock fish head obtained from Alakahia market which gave a concentration of 0.003mg/kg that was far below the permissible limit for Ni in fish food, i.e. 0.5-0.6 mg/kg (WHO, 1985; FAO, 1983 and FEPA, 2003).

From Table 1, a general observation shows that the heavy metal concentration was found to be higher in the head of the stock fish samples obtained from the three markets than in the tails, thus indicating bioaccumulation of heavy metals in the head of the fish. The high concentration level can be attributed to the fact that water always passes through the mouth and gills during water filtration by the fishes, thus sticking to the tissues and muscles in the fish head before passing to the rest of the body (Olowu *et al.,* 2010).

The results so far show that the bioaccumulation of selected heavy metals

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(Cd, Zn, Pb, Fe, Cu, Ni and Cr) in fishes in general should be taken as a serious matter because fish is a major source of protein in the world today, so is industrialization and the pollution of the water bodies by agrochemicals and the release of heavy metal-packed effluents from industries. From this study, all the heavy metals except Pb and Cd as observed in some of the samples were below the permissible or recommended limits for heavy metals in fish foods as stated by the mentioned regulatory bodies. Pb and Cd are both toxic heavy metals and their ingestion even at low doses, over a period of time, may pose serious health hazards like kidney failure to the consumers of the stock fish.

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