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Full Length Research Paper

Effects of season, salting and drying on heavy metal contents of four fish species from three locations in Borno state of Nigeria

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Abstract

This study was designed to evaluate the effects of season and a fish preservation process — namely salting and sun-drying (using a solar-tent-dryer) on the levels of lead, cadmium, mercury and arsenic in the fresh and processed fish species: Tilapia nilotica (Tilapia), Synodontis guntheri (Kurungu), Heterotis niloticus (Bargi), and Clarias anguillaris (Catfish). The objective was to determine whether the preservation method may lead to an increase in the levels of the metals in the treated fresh fish samples harvested from three different locations during the dry and rainy seasons. Samples were wet-digested, and the heavy metals were quantified with an AAS (for lead and cadmium) and ICP-OES (for mercury and arsenic). Results indicated significant (P≤0.05) differences between the levels of the heavy metals in fresh fish harvested during the dry and rainy seasons on one hand and the concentrations of the metals in salted and sun-dried samples on the other hand. Cadmium and arsenic were the lowest recorded metals in both the fresh and treated fish samples during the two seasons and in all the locations. The sequence of the heavy metal concentrations in all the fish samples was Pb>Hg>Cd>As. The heavy metal concentrations in the fresh and salted sun-dried fish from all the locations were however lower than the internationally recommended threshold levels. It was concluded that many factors including season during growth of fish, handling and processing, could influence the levels of toxic heavy metal contamination in fresh fish and processed product; and that, although salt does have its limitations and disadvantages, its utilization conditions must be optimized to provide safe food for consumers, at the same time addressing their needs and concerns.

Key words: Heavy metals, fish, season, solar-tent- dryer, AAS, ICP-OES.

INTRODUCTION

Fish is a food of excellent nutritional value, providing high quality protein and a wide variety of vitamins and minerals, including vitamins A and D, phosphorus, magnesium, selenium, and iodine in marine fish. With the rising costs of meat and cheese protein foods, consumers have become increasingly interested in fish as an alternative source of dietary protein. Its protein, like that of meat, is easily digestible and favourably complements dietary protein provided by cereals and legumes that are typically consumed in many developing countries, including Nigeria. It is estimated that 60% of people in those countries obtain 40 – 100% of the animal

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protein in their diets from fish (Clucas and Ward, 1996; Toth *et al*., 2012; Igwegbe, 2014). Experts agree that, even in small quantities, fish can have a significant positive impact in improving the quality of dietary protein by complementing the essential amino acids that are often present in low proportions in vegetable-based diets. Nigeria has a compact landmass of 923,762km^2; 860kms of coastline on a major Gulf of Guinea, abundant water resources with major rivers of the Niger and the Benue traversing its territory, in addition to numerous smaller rivers and streams crisscrossing its vast terrains (Olaosebikan and Raji, 1998). It has vast but diminishing fishing grounds of lakes, swamps, lagoons, deltas and estuaries. Fish supplies in Nigeria come from three main activities, which include artisans, commercial trawlers and fish farming (Igwegbe, 2014). Water quality parameters are essential for the survival, growth and reproduction of fish and other aquatic animals. However, increasing human activities in the vicinity of our lakes and rivers, particularly due to urbanization, industrialization, technological development, growing human population, indiscriminate sewage and waste disposal, agricultural activities, oil exploration and exploitation may lead to an increase in man-made pollutants in our aquatic environment. This in turn will not only result in elevation of the levels of organic contaminants such as nitrite, nitrate, ammonia and phosphates which ultimately increase the level of suspended solids making the water increasingly turbid (Ahmed, 2007; Akan *et al*., 2009); but also contamination with toxic heavy metals such as lead, cadmium, mercury, arsenic and many others. Contaminated water run-offs, mining and industrial activities such as textile, paper mills, tanneries, sugar and petroleum refineries have also been reported to constitute sources of trace metal pollution to freshwater bodies in the developing countries including Nigeria (Igwegbe *et al*., 1993; Obasohan and Eguavoen, 2008; Eneji *et al*., 2011; Ambedkar and Muniyan, 2011; Ashraf *et al*., 2012). There are also many evidences of bioaccumulation of metal compounds to potentially toxic levels in fish (USGS, 2003; Hamed and Emara, 2006; Akan *et al*., 2009; Toth *et al*., 2012). The possible presence of pollutants in fish is a matter of concern. Therefore, investigation of levels of contaminants in fish is of considerable importance because of their potential effects on the fish on one hand, and on the top-level predators that consume them, including humans, on the other hand.

Fish are highly perishable, and they will spoil rapidly if they are not processed immediately after catch or properly handled. The term fish preservation or processing refers to the processes associated with fish and fish products between the time fish are caught or harvested, and the time the final product is delivered to the consumer. Methods that have long been used to preseve fish include freezing, canning, drying, smoking and the use of chemical preservative such as salt. The simplicity of the salting process, the low cost of production and the ease with which it combines with other preservation methods, such as drying or smoking, has led to its popularity and extensive use in fish preservation especially in the tropical countries of the world (Berhimpon *et al*. 1991). Because salt does have its limitations and disadvantages, its utilization conditions must be optimized to provide safe food for consumers, at the same time addressing their needs and concerns. Although, the possibility of contamination of lakes, ponds and rivers, and fisheries with potentially dangerous chemicals exists in Nigeria, the literature is still limited on the many possible factors, including processing method such as salting and drying, which may affect the level of the heavy metals on the processed fish in the country. This study was therefore designed to investigate the level of heavy metals — lead, cadmium, mercury and arsenic in salted and dried fish species harvested during the rainy and dry seasons, from three locations within the Lake Chad Basin in Borno State of Nigeria.

MATERIALS AND METHODS

The Study Area

The Lake Chad Basin was selected for this study. The Basin is located on longitude 14^0 North and latitude 13^0 East in Borno State and shared by four West African countries: Chad, Nigeria, Niger and Cameroon. It lies within the high tropical regions of extreme scorching heat, where temperatures in the shade can reach 45-49^{0}C in most parts of the year. There are about 200 permanent and semi-permanent fishing communities and / or islands and over 40,000 fishermen on the Nigerian sector of the Lake Chad basin. It is the second largest basin in Africa after Congo basin (Akande and Odogbo, 2005; World Atlas, 2005; Ahmed, 2007); and one of the important sources of freshwater fish in Nigeria (Raji, 1992, Akande and Odogbo, 2005). It is located in the Sahel vegetational belt, south of Sahara with less than 600mm of rain annually, and contributes significantly to the domestic fish production, with an estimated annual yield of 70,000mt/year from Lake Chad and 870mt/year from Alau Dam (Ahmed, 2007). The inland waters of Lake Chad basin, which include Dabamasara and Dorobaga (Figure 1), occupy vast marshy swamps on the flood plains during the wet season (July – September). The Basin is also endowed with shallow euthrophic water bodies, all produce approximately 13% of

Nigerian inland fish (Raji, 1992), the predominant fish species in the area include *Clarias, Tilapia, Gymnarchus, Heterotis, Lates niloticus, Protopterus, Alestes, Synodontis, Citharius*, etc (Ahmed, 2007). The area is also characterized by unstable and sporadic rain patterns, drought, overfishing, mining and other human activities capable of contributing to environmental

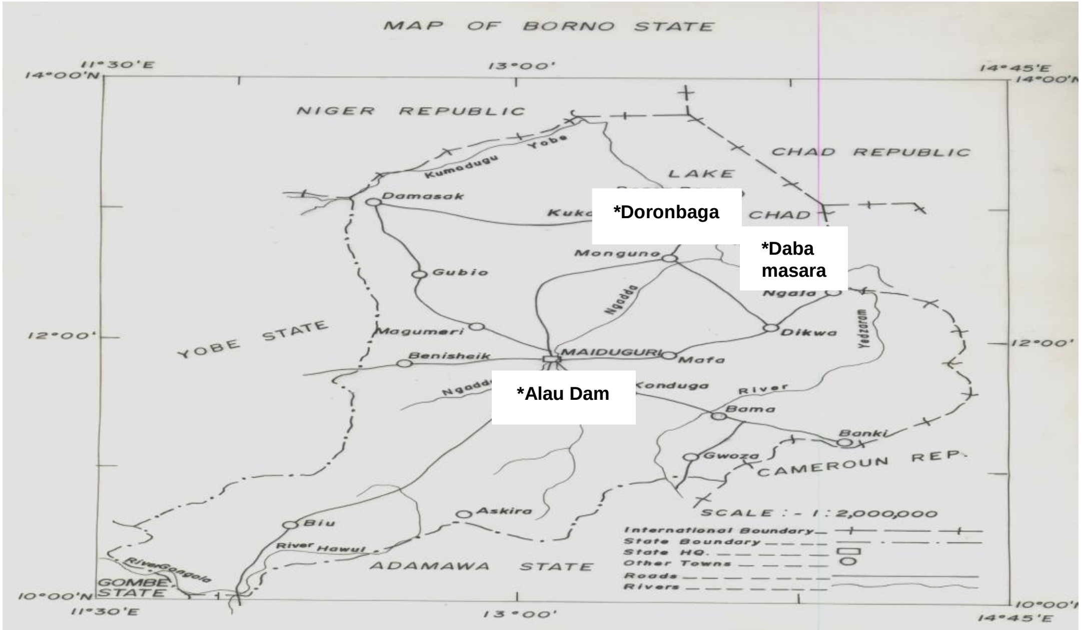

Figure 1: Base Map of Borno State showing the Sampling Locations from Lake Chad Basin
*Sampling Points: Alau Dam, Dabamasara and Doronbaga.

pollutions. Specifically, Lake Chad reportedly receives waste water from Komadugu Yobe River in Yobe State and the Ngadda and Yedzeram River Systems from Borno State (Figure 1). The Basin is also polluted by textile and tannery effluents in the upstream part of the lake on one hand, and from the waste water discharged from the settlements along Chari Lagoon and Kamadugu Yobe River course, from abattoirs, hotels, hospitals, mining wastes, agricultural wastes (used pesticides and agrochemicals through return flow of water, runoff and percolation from irrigated fields), on the other hand. The banks of these water bodies are dominated by intensive irrigational farming and fishing activities and serve as nesting ground for several species of birds as well as points for different types of livestock (cattle, camels, etc). Salt mining is also a common feature in Lake Chad basin. Alau Dam, on the other side, also receives waste water from agricultural activities as a result of water flow from River Yedzram and River Gombole which meet at a confluence at Skambisha from where they flow, with large quantities of waste, as River Ngala into Alau Dam. There is therefore need to periodically assess the burden of heavy metals in processed fish and water bodies in the area so as to determine their suitability as seafood and sources of fish to the inhabitants of the immediate environment and beyond. Thus, the three major fish harvesting sites — Alau Dam, Doronbaga and Dabamasara, were chosen for this investigation.

Apparatus

Solar tent dryer (Figure 2); a wooden mortar and pestle. Food grade blender with stainless steel blades. All glass and plastic wares were soaked over night in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid, and thoroughly rinsed with double distilled water (Khansari *et al*., 2005; Bureau of Chemical Safety (BCS), 2006; Igwegbe *et al*., 2013). A Buck 205 Atomic Absorption Spectrophotometer (AAS) and Inductively Coupled Plasma / Optical Emission Spectrophotometer (ICP-OES), Buck Scientific Inc., USA, were used in the quantification of the heavy metals: lead and cadmium, mercury and arsenic, respectively.

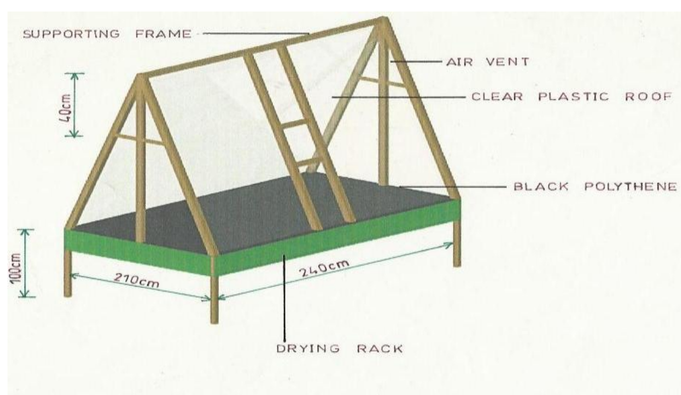

Figure 2: Solar Tent Dryer used in this study (Idakwo, 2014)

Sample Digestion (metal extraction)

Reagents

All reagents used were of analytical grades, and included concentrated nitric acid (sp. gr. 1.42 g/ 20^{0}C, 68-72% m/w; BHD Chemical Ltd., Poole, England), concentrated hydrochloric acid (sp. gr. 1.73 g/20^{0}C, 35 – 37.5%; May and Baker Ltd., Bagenmam, England), concentrated sulfuric acid (sp. gr. 1.84 g/20^{0}C, 98% m/w; Fison Scientific Equipment, Loughborough, England. Oxides of lead, cadmium, mercury and arsenic (98.5 - 99.5%) metals (Reidel-de Haem, Germany). The metallic oxides were used to spike selected samples with measured concentrations of the heavy metals for the recovery and repeatability test.

Sample Collection and Preparation

Four (4) species of fish namely: *Tilapia nilotica* (Tilapia), *Synodontis guntheri* (Kurungu), *Heterotis niloticus* (Bargi), and *Clarias anguillaris* (Catfish) were collected directly from the locations due to their availability in large quantities in all the three sites: Alau Dam, Doronbaga, and Daban Masara (Figure 1). For the purpose of comparison, care was taken to select only the similar species, both in quantity and size, from all the three locations under study, and in sufficient quantities A Buck 205 Atomic Absorption Spectrophotometer (AAS) and Inductively Coupled Plasma / Optical Emission Spectrophotometer (ICP-OES), Buck Scientific Inc., USA, were used in the quantification of the heavy metals: lead and cadmium, mercury and arsenic, respectively.

Fish salting and drying

A locally constructed solar tent dryer (Figure 2) was used for both salted and unsalted sun-drying of fish samples. The fish samples for this treatment were cleaned as indicated previously, and rinsed three times with double distilled water. The unsalted sun-dried samples were hung with nylon twines in the solar tent dryer to dry for two to three days during the dry season — when the ambient temperature ranged from 30 - 39^{0}C and the relative humidity was less than 75%; or to dry for five days during the rainy season — when the ambient temperature ranged from 25 - 29^{0}C and the relative humidity was more than 80%. While in the salted treatments, each sample batch was thoroughly rubbed into 300g of common table salt before hanging them with the twines inside the solar tent dryer. Measures were taken to ensure proper penetration of salt into the fish tissues, either by splitting the large fish or by stuffing the salt properly into the gutted fish, before sun-drying (Yankah *et* al., 1996; Essuman, 2005).

Fresh fish samples were first macerated and then homogenized thoroughly in the food blender, whereas the unsalted and salted dried samples were crushed properly in the wooden mortar with the pestle. Three (3) grams of homogenized oven-dried fresh samples or crushed dried samples were weighed, in triplicate, into the 50ml Teflon glass beakers and then passed through the digestion process. The salted, sun-dried samples were thoroughly cleaned of excess salt, before pulverizing them. In order to determine the possible effect of washing on the level of the heavy metals on unsalted and salted dried samples, the dried samples were first cleaned of dusts, excess salt, and then washed three times with double distilled water before pulverizing them. The sequence of the digestion process was as follows: 10ml of concentrated HNO_3 and 5ml of concentrated H_2SO_4 were slowly added to the previously weighed samples, covered with the watch glass, and allowed to digest overnight (Khansari *et al*., 2005; Voegborlo *et al*., 1999; Rahimi *et al*., 2010). The beakers containing the samples were then heated gently in a hot water bath at a boiling temperature for 2 to 3 hours, to complete the dissolution of the sample (appearance of clear solution). The beakers were then removed from the hot water bath, cooled and the solution transferred quantitatively into 50ml volumetric flasks and made up to the mark with double distilled water, then stored in the PFTE plastic containers until analyzed with the AAS and ICP-OES. Blanks were prepared exactly in the similar manner but without the fish samples.

Validation of the method

To determine and verify the repeatability of the analytical methodology, standard stock solutions of lead, cadmium, mercury and arsenic were prepared by dissolving 2±0.1g of each of the metal oxides separately in 5ml of the concentrated HCl, quantitatively transferring into one liter volumetric flasks and making up the marks with the double distilled water. Homogenized fresh fish sample, Bargi from Alau Dam was spiked in triplicate for each metal, with 2ml of the stock solutions to yield 2ppm of lead, cadmium, mercury, and arsenic from each spiked sample. The spiked samples and blanks were then subjected to the digestion procedures (Wiersma *et al*., 1986; Khansari *el al.,* 2005). The resulting solutions were analyzed for the metal concentrations.

Statistical Analysis

Data obtained from the experimental analysis were subjected to analyses of variance (ANOVA). The test for significant of differences between the factors investigated (otherwise known as mean separation), was conducted at 5% levels of significance, using the Duncan's Multiple Range Test (Montgomery, 1976; Gomez and Gomez, 1983).

RESULTS AND DISCUSSION

The mean recovery for the four metals from the fish samples examined is 100.20% for lead (ranging from 99.94 - 100.60%), cadmium 99.96% (ranging from 99.95 – 99.96%), mercury 99.41% (ranging from 99.40 – 99.41%), and arsenic 100.02% (ranging from 100.01 – 100.02%). The recovery of these heavy metals obtained

Table 1: Mean Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) Concentrations (ppm) in Fresh Fish Samples collected during the Dry Season

Fish Type	Location*											
	Alau Dam				Dabamasara				Doronbaga			
	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$
Bargi	1.27^{a}	0.47^{a}	0.93^{a}	0.30^{a}	1.67^{a}	0.37^{a}	1.63^{a}	0.43^{a}	2.53^{a}	0.53^{a}	0.67^{a}	0.20^{a}
Catfish	1.63^{b}	0.33^{a}	0.97^{a}	0.37^{a}	1.40^{a}	0.20^{a}	1.00^{b}	0.30^{a}	1.67^{b}	0.27^{a}	0.67^{a}	0.23^{a}
Kurungu	1.26^{a}	0.33^{a}	1.73^{b}	0.47^{a}	1.40^{a}	0.23^{a}	1.10^{b}	0.37^{a}	6.33^{c}	0.30^{a}	1.20^{c}	0.17^{a}
Tilapia	1.13^{a}	0.43^{a}	1.00^{a}	0.53^{a}	1.77^{a}	0.47^{a}	0.90^{b}	0.50^{a}	1.47^{b}	0.20^{a}	0.93^{b}	0.33^{a}
Mean	**1.32**	**0.39**	**1.16**	**0.42**	**1.43**	**0.32**	**1.16**	**0.40**	**1.58**	**0.33**	**0.86**	**0.23**
SE	0.09	0.06	0.18	0.08	0.11	0.09	0.15	0.08	0.16	0.11	0.06	0.07
LSD (5%)	0.31	0.21	0.61	0.29	0.38	0.32	0.52	0.28	0.59	0.38	0.22	0.26
CV (%)	11.80	26.60	26.30	35.10	13.40	50.50	22.40	35.10	18.10	58.0	13.0	54.9

SE = standard error; LSD = least significant difference; CV = coefficient of variation
Standard Deviation for all means (average of three determinations) ranged from ± **0.000** to ±**0.0002**
*****In any column, means bearing similar superscripts are not significantly different (**P≥0.05**).

Table 2: Mean Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) Concentrations (ppm) in fresh fish samples collected during the Rainy Season

Fish Type	Locations*											
	Alau Dam				Dabamasara				Doronbaga			
	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$
Bargi	2.23^{a}	0.50^{b}	0.87^{a}	0.30^{d}	1.27^{c}	0.30^{f}	$0.60^{a.}$	0.23^{b}	1.43^{a}	0.23^{b}	0.80^{b}	0.30^{b}
Catfish	1.83^{b}	0.43^{b}	1.03^{c}	0.37^{d}	1.43^{c}	0.23^{f}	0.50^{a}	0.20^{b}	2.10^{b}	0.67^{a}	1.90^{c}	0.60^{b}
Kurungu	1.80^{b}	0.43^{b}	1.00^{c}	0.43^{d}	1.06^{c}	0.23^{f}	0.67^{a}	0.27^{b}	2.36^{b}	0.73^{a}	2.00^{c}	0.60^{b}
Tilapia	1.60^{b}	0.37^{b}	0.83^{a}	0.30^{d}	1.70^{c}	0.40^{f}	1.00^{a}	0.37^{b}	2.53^{b}	0.73^{a}	1.00^{b}	0.40^{b}
Mean	**1.87**	**0.43**	**0.93**	**0.35**	**1.37**	**0.29**	**0.69**	**0.27**	**2.12**	**0.59**	**1.44**	**0.48**
SE	0.34	0.18	0.11	0.06	0.21	0.13	0.11	0.06	0.17	0.08	0.18	0.09
LSD(5%)	0.17	0.62	0.39	0.20	0.73	0.43	0.38	0.20	0.58	0.26	0.61	0.31
CV(%)	31.40	71.60	21.10	28.20	26.60	74.30	27.70	37.00	13.90	22.40	21.30	32.70

SE = standard error; LSD = least significant difference; CV = coefficient of variation
Standard Deviation for all means (average of three determinations) ranged from ± **0.000** to ±**0.0002**
*****In any column, means bearing similar superscripts are not significantly difference (**P≥0.05**).

in this study is highly comparable to those obtained through the similar techniques by other investigators including Ashraf (2006), Voegborlo *et al*. (1999), Khansari *et al*. (2005), Ekpo *et al*. (2008), Rahimi *et al*. (2010); Olusegun (2011). Voegborlo *et al*. (1999), recorded recoveries in spiked fish samples ranging from 90 – 110% for lead, 95 to 104% for cadmium, and 96 – 101% for mercury. Similarly, Rahimi *et al*. (2010), recorded recoveries of the heavy metals from spiked fish samples ranging from 96 – 103% for mercury; 99 – 107% for cadmium and 99-104% for lead. Whereas, the mean recoveries recorded by Ashraf (2006), for lead, cadmium and mercury were 98.8%, 99.2%, and 97.5%, respectively. Good recoveries of the metals from the spiked samples demonstrate accuracy of the analytical methods.

Concentration of the Heavy Metals in Fresh Fish Samples

The mean heavy metal concentrations recorded in the fresh fish samples from the three locations during the two seasons are presented in Tables 1 and 2 together with their statistical parameters (i.e., standard error, least significant difference and coefficient of variation). The overall mean lead concentrations observed in the fresh fish samples collected during the dry season ranged from 0.0013ppm in Alau Dam to 0.0016ppm in Doronbaga, while 0.0014ppm was recorded for lead in Dabamasara (Table 1). There were significant variations (P≤0.05) among fish species and between locations with regards to the concentration of lead in the fresh fish samples collected during the dry season. The highest concentration of lead, 0.0063ppm was recorded in Kurungu fish from Doronbaga. The lowest concentration of lead, 0.0013ppm, was observed in Tilapia fish from Alau Dam, whereas Tilapia from Dabamasara and Doronbaga contained 0.0018ppm and 0.0015ppm of lead, respectively. The concentration of lead, 0.0025ppm, was also higher in Bargi sampled from Doronbaga when compared with the concentrations in the similar fish from Alau Dam and Daba- masara which are 0.0013 and 0.0017ppm, respectively (Table 1). The catfish collected from Daba- masara had lower concentrations of lead than those from Alua dam and Doronbaga, which contained 0.0016ppm and 0.0017ppm, respectively.

The overall mean lead concentrations recorded in fresh fish samples collected during the rainy season, ranged from 0.0013ppm to 0.0017ppm in Alau Dam and Doronbaga, respectively, while that of Dabamasara was 0.0014ppm (Table 2). Significantly different variations (P≤0.05) were also observed among fish types and between locations in the concentrations of lead in Alau Dam and Dabamasara; the highest concentrations of lead were recorded in all the fish types from Alua Dam during the rainy season than was observed during the dry season in the similar fish types from the same Alau Dam (Tables 1 and 2**)**. Doronbaga had the lowest lead concentrations and no significant variations (P≥0.05) were observed among the fish types from this location during the rainy season (Table 2).

With respect to other metals, the fresh fish samples recorded overall mean levels of cadmium as 0.0004, 0.0003, and 0.0003ppm in Alau Dam, Dabamasara, and Doronbaga, respectively. The highest concentrations of cadmium, 0.0005ppm, were recorded in fresh Bargi fish from Doronbaga and Tilapia from Dabamasara; and there were no significant variations (P≥0.05) among the fish types and between the locations in cadmium concentrations during the dry season (Table 1). Also, in the fresh fish samples collected during the rainy season, the lowest overall mean concentrations of cadmium, 0.0004ppm, was recorded in Doronbaga, whereas the overall mean for both the Alau Dam and Dabamasara is 0.001ppm (Table 2). Significant variations (P≤0.05) were observed among the fish types and between the locations in cadmium concentrations as recorded in Alau Dam and Dabamasara, whereas those of Doronbaga did not vary significantly (P≥0.05).

The fresh fish samples recorded overall mean mercury concentrations of 0.0012, 0.0012 and 0.0010ppm; and 0.0010, 0.0011 and 0.0010ppm in Alau Dam, Dabamasara, and Doronbaga, during the dry and rainy seasons, respectively (Tables 1 and 2). Significant variations (P≤0.05) were however observed among fish types and between locations, in mercury concentrations in the fresh fish samples, during the dry and rainy seasons. The mean concentrations of mercury recorded in the fresh samples were insignificant during the two seasons (Tables 1 and 2), and the lowest concentrations of this heavy metal, 0.0001ppm, was observed in fresh sample of Tilapia from Dabamasara, collected during the rainy season (Table 2).

The overall mean concentration of arsenic was again lowest, 0.0002ppm in fresh fish samples from Doronbaga, whereas the concentrations in fresh samples from Alau Dam and Dabamasara were 0.00042 and 0.00040ppm recorded during the dry season (Table 1**)**. No significant variations (P≥0.05) were observed both among the types of fish and between locations in fresh fish samples collected during this season. The overall mean concentrations of arsenic recorded during the rainy season were 0.0005, 0.0004, and 0.0005ppm in fresh fish samples from Alau Dam, Dabamasara, and Doronbaga, respectively (Table 2**)**. Significant variations were recorded (P≤0.05), among types of fish only in Dabamasara during this season. The variations in the metal contents of the fresh fish samples investigated during the two seasons could be attributed to the different pollution levels at these locations. Lake Chad is reported to receive its water from various rivers in Nigeria, Chad, Cameroon and Niger Republic (Bdliya and Tagi, 2011). The rivers, whose peak flows are usually recorded during the rainy season, are suspected to carry materials ranging from elements washed from the earth to effluents from domestic and farming activities and industries located along the banks of these rivers to different water bodies in the basin including Alau Dam, Dabamasara and Doronbaga. Also, differences in water chemistry and in the numbers and types of organisms present in a lake can also produce significant lake-to-lake variations in the amount of metals that moves from the water through the food chain and finally to fish. Thus, fish in different water bodies may frequently carry different metal burdens even when the water bodies are located within the same geographic region (Chen *et al*., 2000; Igwegbe, 2013). In addition, Obasohan and Eguavoen (2008) attributed low rainy season metal levels in fish muscles to low bio-availability of the metals due to reduced metal concentrations in rivers arising from dilution associated with heavy rains during the rainy season, whereas increased heavy metal concentrations in fresh fish samples observed during the dry season was attributable to changes associated with increased water temperatures and subsequent evaporation during the season.

Concentration of the Heavy Metals in Salted Sun-dried Fish Samples

Drying is one of the traditional methods of fish preservation in which the actions of the sun and wind are used to effect evaporative drying. Salting is often used in combination with drying and/or smoking in traditional fish processing in many countries of the world. Salting and subsequent sun-drying of the fish samples investigated in this study, resulted in higher concentrations of the four heavy metals than in the corresponding fresh samples collected during the dry season Table 3 (and also Tables 1). Significant variations (P≤0.05) were observed among the types of fish and between locations in all the heavy metal concentrations except in arsenic content in sun-dried fish samples from Doronbaga; and in cadmium concentrations in samples from Dabamasara (Table 3).

This result is also in agreement with the findings of Essuman (2005), who observed that combination of

Table 3: Mean Concentrations (ppm) of Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) in Salted and Sun-dried fish samples collected from the Locations during the Dry Season

	Locations*											
	Alau Dam				Dabamasara				Doronbaga			
Fish Type	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$
Bargi	3.97^{a}	1.87^{b}	2.40^{a}	1.20^{bc}	2.57^{a}	1.47^{a}	2.00^{b}	1.17^{b}	3.77^{a}	1.80^{d}	2.23^{c}	1.20^{a}
Catfish	3.80^{a}	2.10^{a}	2.43^{a}	1.40^{b}	3.43^{b}	1.60^{b}	2.57^{a}	1.37^{b}	3.00^{b}	1.27^{a}	2.33^{c}	1.17^{a}
Kurungu	2.83^{b}	1.83^{b}	2.20^{b}	1.10^{c}	2.90^{c}	1.73^{b}	2.47^{a}	1.10^{a}	3.17^{c}	1.50^{c}	2.10^{c}	1.10^{a}
Tilapia	2.73^{b}	1.57^{c}	1.63^{c}	1.30^{bc}	2.73^{d}	1.83^{b}	1.93^{b}	1.37^{b}	2.50^{d}	0.50^{c}	1.00^{c}	1.27^{a}
Mean	**3.33**	**1.84**	**2.17**	**1.25**	**2.91**	**1.66**	**2.24**	**1.25**	**3.11**	**1.27**	**1.92**	**1.18**
SE	0.08	0.07	0.03	0.09	0.07	0.09	0.05	0.08	0.04	0.07	0.11	0.08
LSD(5%)	0.27	0.24	0.09	0.31	0.24	0.32	0.16	0.26	0.15	0.25	0.37	0.27
CV (%)	4.10	6.60	2.00	12.40	4.20	9.60	3.60	10.30	2.30	9.90	9.70	11.50

SE = standard error; LSD = least significant difference; CV = coefficient of variation

Standard Deviation for all means (average of three determinations) ranged from ± **0.000** to ±**0.0002**

***** In any column, means bearing similar superscripts are not significantly difference (**P≥0.05**).

Table 4: Mean Concentrations (ppm) of Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) in Salted, Sun-dried and washed fish samples collected from the Locations during the Dry Season

	Locations*											
	Alau Dam				Dabamasara				Doronbaga			
Fish Type	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$	Pb $x10^{-3}$	Cd $x10^{-3}$	Hg $x10^{-3}$	As $x10^{-3}$
Bargi	1.97^{a}	0.97^{b}	0.87^{a}	0.43^{a}	1.13^{b}	0.33^{c}	1.13^{a}	0.27^{d}	1.40^{a}	0.57^{a}	0.97^{b}	0.53^{a}
Catfish	170^{b}	0.87^{b}	0.97^{ab}	0.53^{a}	1.53^{b}	0.67^{a}	1.37^{b}	0.47^{a}	1.13^{b}	0.37^{b}	0.57^{a}	0.30^{a}
Kurungu	1.53^{c}	0.83^{b}	1.03^{b}	0.43^{a}	1.50^{b}	0.80^{a}	1.03^{c}	0.40^{a}	1.23^{b}	0.47^{b}	0.93^{b}	0.50^{a}
Tilapia	1.50^{c}	0.60^{a}	0.90^{b}	0.43^{a}	1.36^{b}	0.83^{a}	9.67^{d}	0.53^{a}	1.33^{ab}	0.33^{b}	0.50^{a}	0.47^{a}
Mean	**1.67**	**0.82**	**0.94**	**0.46**	**1.40**	**0.66**	**1.13**	**0.42**	**1.28**	**0.43**	**0.74**	**0.45**
SE	0.07	0.06	0.05	0.10	0.08	0.05	0.06	0.05	0.06	0.06	0.04	0.09
LSD(5%)	0.23	0.22	0.16	0.34	0.28	0.16	0.21	0.18	0.20	0.19	0.14	0.30
CV (%)	6.80	13.50	8.50	37.30	10.20	12.10	9.40	21.50	7.80	25.80	16.40	21.90

SE = standard error; LSD = least significant difference; CV = coefficient of variation

Standard Deviation for all means (average of three determinations) ranged from ± **0.000** to ±**0.0002**

***** In any column, means bearing similar superscripts are not significantly difference (**P≥0.05**).

salting and sun-drying treatments resulted in significantly high concentrations of a number of heavy metals including lead, mercury, cadmium and arsenic in processed Tilapia and *Chrysichthys* when compared with the metal concentrations in the fresh samples. In the present study, however, washing the samples three times with double distilled water resulted in more than 50% reduction in the concentrations of the four heavy metals from the salted sundried fish samples (Table 4). Significant variations were also observed among the fish types and between locations in the heavy metal concentrations in salted and sun-dried fish samples from all the three locations except in arsenic concentrations in treated fish samples from Alau dam and Doronbaga (Table 4). The comparison of the effects of the combination of salting, and sun-drying treatments of the fish samples from the three locations is presented in Table 5. Slight, but insignificant variations ($P \geq 0.05$), were observed between sun-dried and fresh fish samples from all the locations. Salting was therefore observed to increase the level of the metals in the sun-dried fish samples as compared with their fresh counterparts (Tables 1 and 2). This may be as a result of presence metal contaminants in the table salt used in the salting process; in addition to the concentration effects of the drying process (reduction of moisture) on the fish constituents. Because moisture is lost during the drying process, the concentrations of the heavy metals were actually higher than they were in the fresh un-dried fish. Salt has been used for centuries as a seasoning and flavor enhancer as well as a preservative or curing agent. Salt has played a major role in many aspects of human life: nutritional, economic, political, and military. However, use of crude NaCl which contains impurities such as

Table 5: Comparison of Mean Heavy Metal Concentrations in Fresh and Salted sun- dried Fish Sampled from the Locations during the Dry Season (ppm)*

LOCATION:		**Alau Dam**		**Daban Masara**		**Doronbaga**	
Treatment:		**Fresh**	**sundried**	**Fresh**	**sundried**	**Fresh**	**Sundried**
Type of Fish	**Metal**	**x10^{-3} ppm**					
Bargi	Pb	1.27^{a}	3.97^{b}	1.67^{c}	2.57^{d}	2.54^{e}	3.77^{f}
	Cd	0.47^{c}	1.87^{b}	0.37^{d}	1.47^{e}	0.53^{f}	1.80^{a}
	Hg	0.93^{g}	2.40^{f}	1.63^{e}	2.00^{a}	0.67^{c}	2.23^{b}
	As	0.30^{d}	1.20^{c}	0.43^{d}	1.17^{e}	0.20^{f}	1.20^{a}
Catfish	Pb	1.63^{d}	3.80^{a}	1.40^{f}	3.43^{c}	1.67^{g}	3.00^{b}
	Cd	0.33^{a}	2.10^{b}	0.20^{d}	1.60^{c}	0.27^{h}	1.27^{g}
	Hg	0.97^{b}	2.43^{a}	1.00^{f}	2.57^{i}	0.67^{j}	2.33^{d}
	As	0.37^{a}	1.40^{b}	0.30^{c}	1.37^{d}	0.23	1.17^{e}
Kurungu	Pb	1.26^{g}	2.83^{b}	1.40^{f}	2.90^{c}	6.33^{k}	3.17^{d}
	Cd	0.33^{b}	1.83^{a}	0.23^{c}	1.73^{e}	0.30^{f}	1.50^{d}
	Hg	1.73^{c}	2.20^{d}	1.10^{e}	2.47^{a}	1.20^{g}	2.10^{b}
	As	0.47^{e}	1.10^{a}	0.37^{b}	1.10^{c}	0.17^{f}	1.10^{g}
Tilapia	Pb	1.13^{f}	2.73^{e}	1.77^{g}	2.73^{a}	1.47^{b}	2.50^{c}
	Cd	0.43^{a}	1.57^{b}	0.47^{d}	1.83^{c}	0.20^{e}	0.50^{f}
	Hg	1.00^{a}	1.63^{c}	0.90^{d}	1.93^{f}	0.93^{b}	1.00^{b}
	As	0.53^{c}	1.30^{a}	0.50^{d}	1.37^{b}	0.33^{e}	1.27^{f}

***** In any row, and under each location, means bearing different superscripts are significantly different ($P \leq 0.05$)

chlorides, sulfates, calcium, and heavy metals during fish drying may adversely affect the overall quality of the finished product.

Heavy metals are highly toxic substances, exposure to which can trigger both acute and chronic symptoms of poisoning. Acute intoxications only occur through the consumption of relatively large single doses of soluble salts of the metals (Carpenter, 2001; Ferner, 2001; Dodd, 2003;). Chronic intoxication can arise through the regular consumption of foodstuffs that are slightly contaminated with these metals over a long period of time (Falco *et al.,* 2006). Lead, cadmium, mercury and arsenic are typical cumulative poisons. The danger of chronic intoxication should therefore be the greater concern of all the regulatory agencies.

In general, the concentrations of lead, cadmium, mercury and arsenic recorded in this study are within the ranges, and below the values obtained in some similar studies in Nigeria and around the world (Luczynskan and Bruck-Jastrzebska, 2006; Obasohan and Eguaveon, 2008; Abdel-Baki *et al*., 2011; Ambedkar and Muniyan, 2011). Many previous literatures have shown that the occurrence of toxic elements in fish is related to length of time in water, weight, age, sex of fish, their feeding habits and bio-availability of the specific metal (Khansari *et al.,* 2005; Ashraf, 2006; Ekpo *et* al., 2008; Akan *et al*., 2009 and 2012; Rahimi *et al*., 2010; Voegborlo *et al*., 1999). Season and location are also important in the levels of toxic elements accumulation in various species of fish (Moore, 2000; Rahimi *et al*., 2010). The difference in ability of some fish to accumulate more metals than other fish species have been attributed to differences in physiological role of fish organs, including their regulatory ability, behaviour and feeding habits of the fish (Eneji *et al*., 2011).

CONCLUSION

Salting and sun-drying of the various fish species investigated in this study were observed to increase the levels of the four toxic heavy metals, lead, cadmium, mercury and arsenic. Although the levels of the four heavy metals recorded in this study from both the fresh and salted sun-dried fish samples were lower than the maximum permissible limits and guidelines set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO), and adopted by many countries, for fish and fish products (FSAI, 2009) it is important to note, however, that consumption of trace amounts of the toxic heavy metals over a long period of time may result to serious health problems ranging from neuro- nephro-, carcino-, terato-, to immunological disorders; and that toxic heavy metal contamination can be influenced by many factors including environmental conditions during growth, processing, handling, and storage of food products. Because salt does have its limitations and disadvantages, its utilization conditions must be optimized to provide safe food for consumers, at the same time addressing their needs and concerns.

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