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Full Length Research Paper

Effects of season and location on heavy metal contents of fish species and corresponding water samples from Borno State of Nigeria

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This study was designed to investigate the level of toxic heavy metals: lead, cadmium, mercury and arsenic in edible muscles of four fish species namely Tilapia nilotica (Tilapia), Synodontis guntheri (Kurungu), Heterotis niloticus (Bargi), and Clarias anguillaris (Catfish), harvested from three locations — Alua Dam, Doron Baga and Daban Masara within the Lake Chad Basin of Borno State, Nigeria. The main objective was to investigate the possible effects of the locations and season, as well as species of fish, on the concentration of the metals in the fish following wet digestion. The toxic heavy metals, expressed in parts per million (ppm), were detected in all the fish species from the three (3) inland waters investigated. The overall mean concentrations of the heavy metals were significantly higher ($P \leq 0.05$) in fresh fish samples harvested during the rainy season than the dry season. Significantly different variations were also observed within fish types and between locations in the concentrations of the four heavy metals. Cadmium and arsenic were the lowest recorded metals in fresh fish during the two seasons and in all the locations. The sequence of the heavy metals concentrations in all the fish samples was Pb>Hg>Cd>As. The concentrations of the metals in both the fresh fish and the corresponding water samples from all the locations during the two seasons were however lower than the internationally recommended threshold levels. Follow up studies were recommended while it was concluded that fish from inland waters within the Lake Chad basin are still safe for human consumption in terms of their heavy metal contents.

Key words: heavy metals, fish, season, smoking, AAS, ICP-OES.

INTRODUCTION

Globally, consumer demand for fish continues to climb (Doe, 2002; Akende and Odogbo, 2005), both amongst the affluent as well as the not so well to do sections of any population. Nearly one billion people, most of them in developing countries, currently depend on fish for their primary source of protein (Toth *et al.*, 2012; Igwegbe, 2013). There are many health advantages from seafood consumption; these include cardio-vascular benefits which reduce the risk of heart attack, the anti-inflammatory properties of *omega-3* products in the body, childhood brain and sight development, and likely anti-cancer benefits (Garthwaite, 1999; Igwegbe, 2013). Also,

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medical research has proved that children born to mothers who consume higher quantities of *omega-3*-rich fish are healthier at birth, exhibit higher IQs, and have better health later in life (Garthwaite, 1999).

International trade in fish and other aquatic products was put at US$10 billion annually (Doe, 2002). Fish and fish products constitute up to 60% of total protein intake in adults of rural habitats in Nigeria, and are used as medications (fish oils), in recreations and vital inclusions of livestock feeds (Ahmed, 2007; Igwegbe, 2013). Fish serve as a good source of animal protein for man and his live stock (Doe, 2002). The role of fish in nutrition is recognized, as it supplies a good balance of protein, vitamins and minerals, and of relatively low caloric content (Clucas and Ward, 1996). Fish and other seafood now constitute an important and popular part of the diet of many Nigerians and as the main supply of animal protein for low and middle income groups (Igwegbe, 2013). The use of fish meal in poultry and fish oil in cosmetics and pharmaceutical industries are only a few of its potentials that are yet to be harnessed in the developing countries. Fish importation has been observed to be a source of serious foreign exchange drain on Nigerian economy (Akande and Odogbo, 2005). Nigeria is reported to spend over a billion naira annually on importation of fisheries products (Ahmed, 2007).

Nigeria has a compact landmass of 923,762km^2; 860kms of coastline on a major gulf of the South Atlantic, 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 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, 2013). The gap between fish demand and supply is unfortunately widening due to increasing population, drop in meat and fish supply, thus prompting the search for methods of improving fish quantity and quality. Consequently, many methods have been used, including the application of herbicides for the control of Hyacinth, observed to have a profound effect on fish production attributed to the upsurge of available food for fish and increased nymphal proliferation at the post-application period (Ahmed, 2007). The application of chemical poison in fishing and during handling of fish may contribute to contamination of both the aquatic environment and fish and fish products with heavy metals among other contaminants (Mrosso and Werimo, 2005). 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 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; Igwegbe, 2013). Contaminated water run-offs, mining and industrial activities such as textile, paper mills, tanneries, sugar and petroleum refineries have been reported to constitute sources of trace metal pollution to freshwater bodies in the developing countries including Nigeria (Obasohan and Eguavoen, 2008; Eneji *et al.*, 2011; Ambedkar and Muniyan, 2011; Ashraf *et al.*, 2012). Both terrestrial and aquatic food chains are capable of accumulating certain environmental contaminants up to toxic concentrations. In general, many of the thousands of chemicals produced by human industry may eventually end up in aquatic environment. Some of these chemicals are basically considered as part of seafood's natural environment (Akan *et* al., 2012), while others have anthropogenic sources (Igwegbe, *et al.*, 1990). Chemical contaminants can also come from industrial, municipal, or agricultural sources. In terms of organic chemicals, the best known examples of bioaccumulation in aquatic food chains are the polychlorinated biphenyls (PCBs), dioxins, and organo-chlorine pesticides such as dichlorodiphenyl trichloroethane (DDT). 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 knowledge of the levels of contaminants in fish is of considerable importance because of its potential effects on the fish on one hand, and on the top-level predators that consume them, including humans, on the other hand. Although, the possibility of heavy metal contamination of lakes, ponds and rivers, and fisheries exists in Nigeria, the literature is still limited on the many possible factors, including location, season and species of fish, which may affect the level of the heavy metals on fresh and processed fish in the country. This study was therefore designed to investigate seasonal variations in the level of heavy metals — lead, cadmium, mercury and arsenic in fish and the corresponding water from selected locations within the Lake Chad Basin in Borno State of Nigeria.

MATERIALS AND METHODS

Description of 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 Daban Masara 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 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 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 Daban Masara, were chosen for this study.

Apparatus

Insulated plastic coolers (100 liters capacity), stainless steel cutting utensils (knives and spoons), a food grade grinder with stainless steel cutting blades, Teflon glass beakers, volumetric flasks (50, 100, 1000mL capacity), graduated cylinders, watch glass, plastic funnels, polyethylene sheets, Whatman ashless filter papers 125mm, hot water bath, polyfloro-tetratheylene (PFTE) plastic containers with screw caps (100ml). 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 (Wiersma *et al*., 1986; Khansari *et al*., 2005; BCS, 2006; Igwegbe, 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.

Reagents

All reagents used were of analytical grades, and included concentrated nitric acid (sp. gr. 1.42 g/ 20^0C, 68-72% m/w; BHD Chemical Ltd., Poole, England), concentrated hydrochloric acid (sp. gr. 1.73 g/20^0C, 35 – 37.5%; May and Baker Ltd., Bagenmam, England), concentrated sulfuric acid (sp. gr. 1.84 g/20^0C, 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* (locally known as *Kurungu*), *Heterotis niloticus* (locally known as *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 investigation, and in sufficient quantities to guarantee representative sample of each species from each location. Sampling for the dry season commenced from

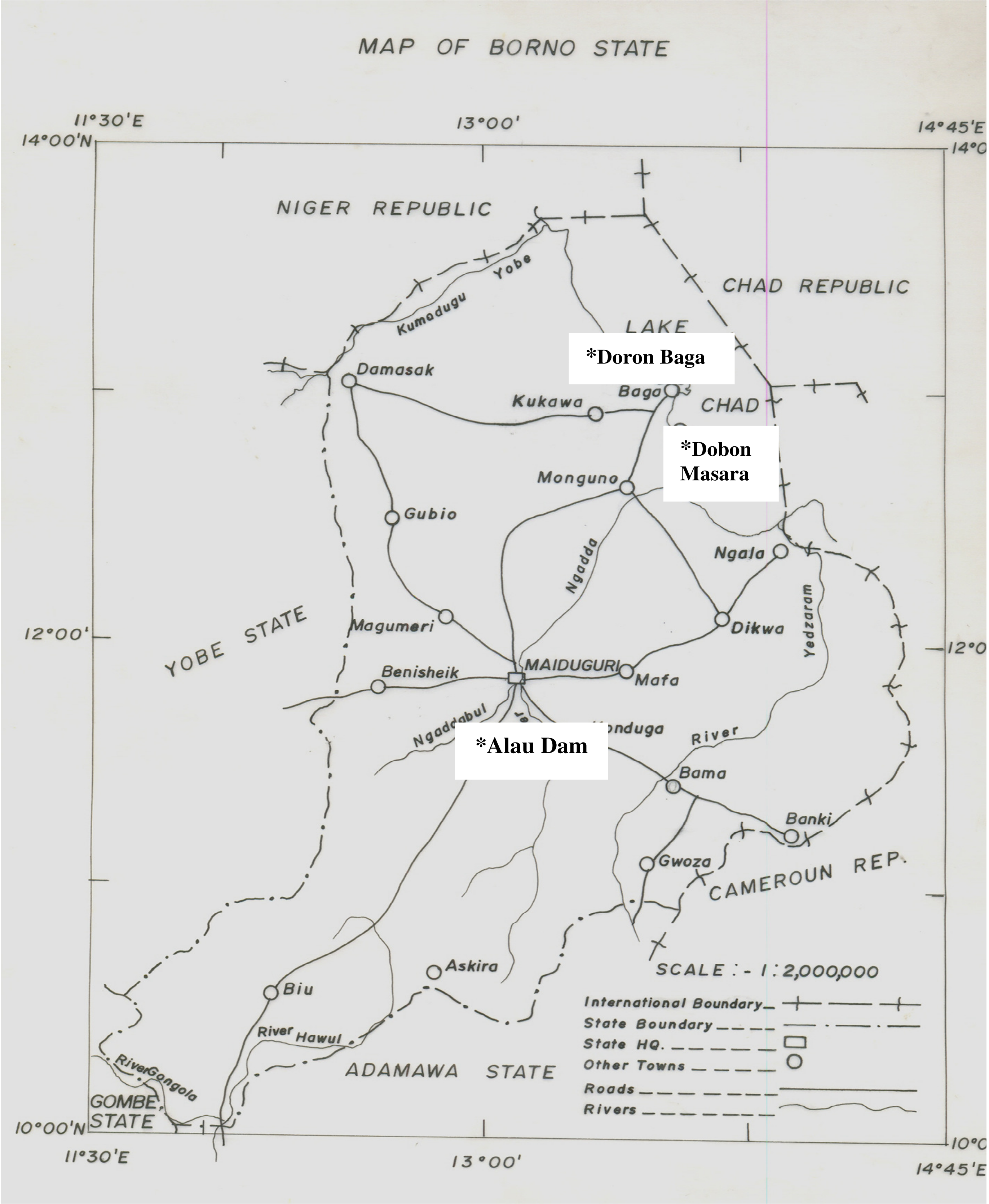

Figure 1. Base Map of Borno State showing the Sampling Locations from Lake Chad Basin (Igwegbe, 2013)

***Sampling Points:** Alau Dam, Doban Masara and Doron Baga.

September to March; , while the sampling for the rainy season started from May to August, within the sample period. Samples were transported from sites to Food Science laboratory, University of Maiduguri, inside the previously cleaned insulated plastic coolers (100 liters capacity) containing ice blocks, where they were identified (with the help of Olaosebikan and Raji, 1998), sorted by location, species, and size. Fish packed in the insulated containers with ice blocks maintained its fresh quality for at least 72 hours. Sample for each treatment consisted of 3 to 5 individual fish from each location. Fish were trimmed, eviscerated, scaled, washed and rinsed three times with double distilled water and stored in ice blocks until wet-digested with the concentrated acids. A sample preparation technique was developed to prevent cross-contamination between samples as metals are found in slimes, blood and scales of fish. Only stainless steel cutting utensils were used during the trimming, evisceration and cleaning of the fish, and the preparation surfaces were covered with polyethylene sheets, with the sheets replaced between the preparations of each sample. Only the edible parts (the muscles) of the fish species were used and samples were treated and / or prepared as though they were for human consumption.

Water Sampling

Water samples were collected from five (5) different points and at depths of at least two (2) meters, from each of the three locations under investigation. The water samples were collected with plastic bottles, pooled, before taking one (1) liter into the previously cleaned plastic bottles. The samples were acidified with 10% HNO_3 to keep the metals in solution and minimize their adsorption on the plastic bottles (Igwegbe, 2013). Precautions were taken to minimize risks of contamination. Fifty (50) mL of water from each location was measured and filtered into the PFTE plastic bottles using the ashless filter papers and then stored until analyzed by the AAS and ICP-OES.

Sample Digestion (metal extraction)

The previously cleaned fresh fish samples were first macerated and then homogenized thoroughly in the food blender with stainless steel cutters. Three (3) grams of the homogenized oven-dried fresh samples were weighed, in triplicate, into the 50ml Teflon glass beakers and then passed through the digestion process. 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 the hot water bath to complete dissolution for 2 to 3 hours (appearance of clear solution). The beakers containing the samples were then cooled and the solution transferred quantitatively into 50ml volumetric flasks and made up to the mark with double distilled water; and then stored in the PFTE plastic containers until analyzed with the AAS. 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 in this study 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). Correlation analysis was also conducted at 5%.

RESULTS AND DISCUSSION

Recovery Test

The results of analysis of the heavy metals for the spiked samples are given in **Tables 1 – 4**. The mean recovery for each of 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 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) and Olusegun (2011). Good recoveries of the metals from the spiked samples demonstrate accuracy of the

Table 1. Recovery of Lead (Pb) from spiked fresh Bargi from Alau Dam

Concentration of Pb added (ppm)	Concentration of Pb recovered (ppm)	% Recovery
2.000	2.0012	100.60
2.000	1.9988	99.94
2.000	1.9989	99.95
Blank	*ND	-

*ND = not detected in triplicate determinations

Table 2. Recovery of cadmium (Cd) from spiked fresh Bargi from Alau Dam

Concentration of Cd added (ppm)	Concentration of Cd recovered (ppm)	% Recovery
2.000	1.9992	99.96
2.000	1.9989	99.95
2.000	1.9989	99.95
Blank	*ND	-

*ND = not detected in triplicate determinations

Table 3. Recovery of Mercury (Hg) from spiked fresh Bargi from Alau Dam

Concentration of Hg added (ppm)	Concentration of Hg recovered (ppm)	% Recovery
2.000	1.9882	99.41
2.000	1.9880	99.40
2.000	1.9881	99.41
Blank	*ND	-

*ND = not detected in triplicate determinations

Table 4. Recovery of Arsenic (As) from spiked fresh Bargi from Alau Dam

Concentration of As added (ppm)	Concentration of As recovered (ppm)	% Recovery
2.000	2.0003	100.02
2.000	2.0002	100.01
2.000	2.0003	100.02
Blank	*ND	-

*ND = not detected in triplicate determinations

analytical methods.

The levels of the heavy metals recorded from the water samples during the dry and rainy seasons are presented in **Table 5**, together with their statistical parameters. The result revealed the presence, but at low concentrations, of the four toxic heavy metals in the water samples collected from the three locations during the two seasons. On a seasonal scale, significant variations ($P \leq 0.05$) were observed in the concentrations of lead between the three locations, and in mercury concentrations between Alau Dam and Daban Masara and Doronbaga, during the dry season (**Table 5**). A significant variation was also observed in mercury concentrations between Alau Dam and Daban Masara and Doronbaga during the rainy season. The highest mean lead values, 0.00277 and 0.00220 ppm, were recorded in water samples from Doronbaga and Daban Masara, during the dry and rainy seasons, respectively (**Table 5**). The highest concentrations of cadmium, 0.00280 and 0.00283ppm were recorded in water samples from Alau Dam and Doronbaga, respectively, during the dry season. Arsenic was observed to be the lowest among the heavy metal concentrations (0.00026 and 0.00027 ppm) in Doronbaga and Alau Dam, respectively, in both seasons. Although

Table 5. Effects of Season on the concentration of Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) in water Samples from the three Locations (ppm)

	Heavy Metal							
	Dry Season				Rainy Season			
Location	Pb $(x10^{-3})$	Cd $(x10^{-3})$	Hg $(x10^{-3})$	As $(x10^{-3})$	Pb $(x10^{-3})$	Cd $(x10^{-3})$	Hg $(x10^{-3})$	As $(x10^{-3})$
Alau Dam	1.27^{a}	2.80^{b}	1.37^{a}	0.40^{b}	2.13^{a}	0.73^{c}	0.70^{a}	0.27^{c}
Dabamasara	2.47^{b}	0.67^{a}	0.77^{b}	0.33^{b}	2.20^{a}	1.23^{b}	2.13^{b}	0.77^{b}
Doronbaga	2.77^{b}	2.83^{b}	0.50^{b}	0.26^{b}	1.93^{a}	0.93^{b}	1.93^{b}	0.60^{b}
Mean	**2.17**	**2.10**	**0.87**	**0.33**	**2.09**	**0.97**	**1.59**	**0.54**
SE	0.07	1.66	0.13	0.08	0.15	0.28	0.13	0.07
LSD (5%)	0.26	6.53	0.51	0.31	0.60	1.10	0.51	0.29
CV (%)	5.30	37.40	75.80	40.60	12.60	50.50	14.20	23.30

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

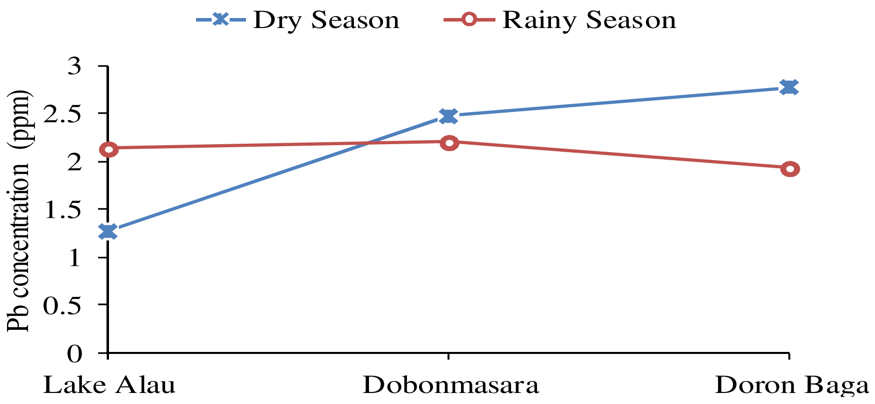

Figure 2. Seasonal variation on the concentration of Pb (ppm) in water samples from the three locations

there was no uniformity in the distribution of the metals in water samples from the three locations, higher levels of the heavy metals, particularly lead and cadmium, were generally observed in water samples collected during the dry season than that of the rainy season (**Figures 2** to **5**). The possible reasons for this could be (a) concentration of the metals due to reduced volume of the water bodies associated with higher evaporation rate induced by the higher water temperatures during the dry season, and (b) seasonal variations in the nature of anthropogenic sources of pollutants, such as application of fertilizers by dry season

farmers, farming along the banks of these water bodies, in addition to the burning of bushes and waste incinerations which are very common around the areas during the dry seasons. Ahmed (2007) recorded high levels of ammonia and dissolved oxygen as well as high pH in Alua Adam, associated with extensive application of fertilizers by dry season farmers, particularly along the banks of Alua Dam. It has also been reported (Akan et al., 2009 and 2012) that River Nagada, which receives copious amounts of wastes from both residential houses and abattoirs sited along its course, empties into Alau Dam. The authors also observed that treated water from the Municipal waste and the abattoir located near the river contained large amounts of heavy metals, which when in super abundance, may cause disruption to the ecological balance of the river. The general trend in the concentrations of the heavy metals in the water samples during the dry and rainy seasons were, respectively, as follows: Cd > Pb > Hg > As and Pb > Hg > Cd > As (**Table 5** and **Figures 2** to **5**).

On the hand, The comparison between the dry and rainy season heavy metal mean concentrations in the fresh fish samples from the three locations are presented in **Table 6**. Significant variations (P≤0.05) were mainly observed in mean lead concentrations among the fish types and between the locations. The seasonal mean concentrations of lead in fresh Bargi from Alau Dam were 0.00127ppm (dry season) and 0.00223ppm (rainy season). The corresponding values for the similar fish from Daban Masara and Doronbaga were 0.00167ppm

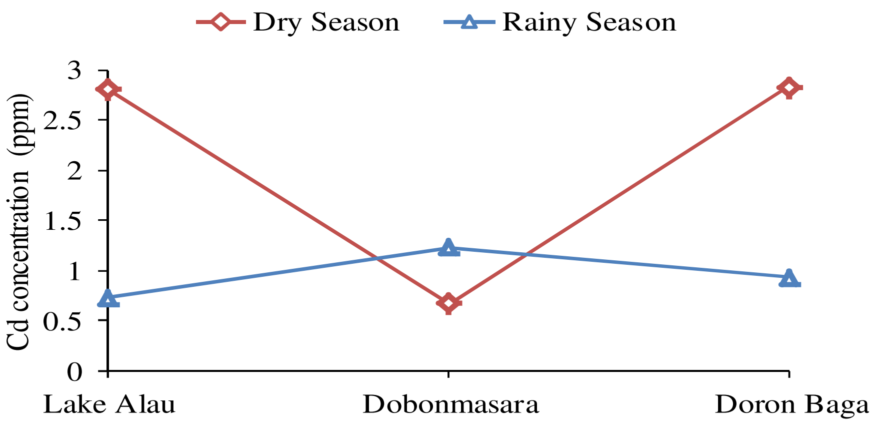

Figure 3. Seasonal variation on the concentration of Cd (ppm) in water samples from the three locations

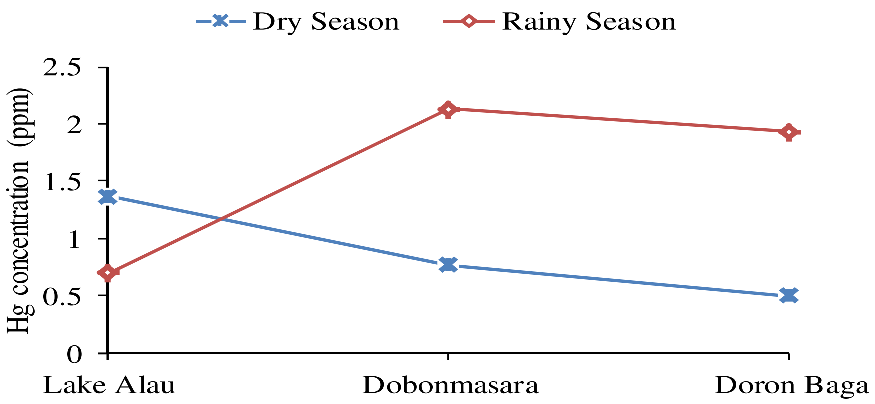

Figure 4. Seasonal variation on the concentration of Hg (ppm) in water samples from the three locations

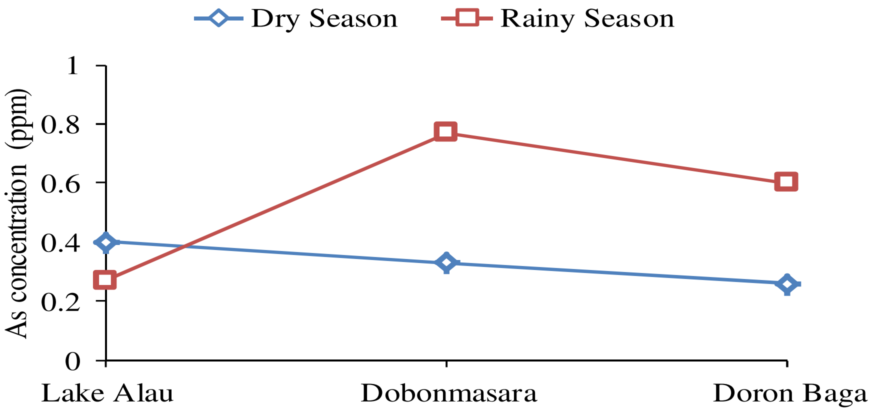

Figure 5. Seasonal variation on the concentration of As (ppm) in water samples from the three locations

(dry season) and 0.00127ppm (rainy season) and, 0.00253ppm (dry season) and 0.00143ppm (rainy season). Similarly, the mean lead concentrations recorded in catfish from Alau Dam, Daban Masara and Doronbaga were 0.00163 and 0.00183ppm; 0.00163 and 0.00143ppm and, 0.00167 and 0.00210ppm in dry and rainy seasons, respectively. The highest mean concentration of lead, 0.00633ppm, was recorded in fresh

Table 6. Comparison of Dry and Rainy Season Mean Heavy Metal Concentrations (ppm) in Fresh Fish Samples from the Three Locations

LOCATION:		**Alau Dam**		**Daban Masara**		**Doronbaga**	
Season:		**Dry**	**Rainy**	**Dry**	**Rainy**	**Dry**	**Rainy**
Type of Fish	**Metal**	**$x10^{-3}$ ppm**					
Bargi	Pb	1.27^{a}	2.23^{b}	1.67^{c}	1.27^{a}	2.53^{d}	1.43^{a}
	Cd	0.47^{a}	0.50^{a}	0.37^{ab}	0.30^{ab}	0.53^{a}	0.23^{b}
	Hg	0.93^{b}	0.87^{b}	1.63^{c}	0.60^{ab}	0.67^{ab}	0.80^{ab}
	As	0.30^{a}	0.30^{a}	0.43^{a}	0.23^{a}	0.20^{a}	0.30^{a}
Catfish	Pb	1.63^{a}	1.83^{a}	1.63^{ac}	1.43^{ac}	1.67^{ac}	2.10^{b}
	Cd	0.33^{a}	0.43^{ac}	0.33^{a}	0.23^{a}	0.27^{a}	0.67^{c}
	Hg	0.97^{a}	1.03^{a}	0.97^{a}	0.50^{c}	0.67^{c}	1.90^{b}
	As	0.37^{ac}	0.37^{ac}	0.37^{ac}	0.20^{a}	0.23^{a}	0.60^{c}
Kurungu	Pb	1.26^{a}	1.80^{d}	1.26^{a}	1.06^{a}	6.33^{b}	2.36^{c}
	Cd	0.33^{a}	0.43^{a}	0.33^{a}	0.23^{a}	0.30^{a}	0.73^{c}
	Hg	1.73^{a}	1.00^{b}	1.73^{a}	0.67^{c}	1.20^{b}	2.00^{d}
	As	0.47^{a}	0.43^{a}	0.47^{a}	1.00^{b}	0.12^{c}	0.60^{a}
Tilapia	Pb	1.13^{a}	1.60^{b}	1.13^{a}	1.70^{b}	1.47^{b}	2.53^{c}
	Cd	0.43^{a}	0.37^{a}	0.43^{a}	0.40^{a}	0.20^{a}	0.73^{b}
	Hg	1.00^{a}	0.83^{a}	1.00^{a}	1.00^{a}	0.93^{a}	1.00^{a}
	As	0.53^{a}	0.30^{a}	0.53^{a}	0.37^{a}	0.33^{a}	0.40^{a}

Standard Deviation for all means ranged from ± **0.000** to **±0.0002**

*In any row, means bearing different superscripts are significantly different (**P≤0.05**)

Kurungu fish sampled from Doronbaga during the dry season; and the corresponding value obtained during the rainy season was 0.00236ppm (**Table 6**). Cadmium, mercury and arsenic seasonal mean concentrations among the fish types and between the locations were not significantly different (P≥0.5), though higher concentrations of the heavy metals were recorded in fresh fish samples collected during the rainy season than the dry season. These variations in the metal contents of the fish samples can 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 recorded during the rainy season are suspected to carry materials ranging from elements washed from the earth to effluents from domestic and farming activities as well as industries located along the banks of these rivers to different water bodies in the basin including Alau Dam, Daban Masara and Doronbaga. Obasohan and Eguavoen (2008) attributed slight seasonal variations in mean concentration of some heavy metals including lead and cadmium, to lack of uniformity in the distribution and possible bio-availability of the metals in different sample stations. They also suggested that low rainy season metal levels in fish muscles could be as result of low bio-availability 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 during the season.

Toxic heavy metals may influence the role of essential metals as cofactors for enzymes or metabolic processes. For instance, lead has been observed to interfere with the calcium-dependent release of neuro-transmitters (Annua and Cuomo, 1988; Bellinger *et al*., 1992). Also, lead, cadmium and vitamin D have been shown to have a complex relationship affecting mineralization of bone, and there exists a more direct influence involving impairment of 1-25-dihydroxy vitamin D synthesis in the kidney (Lutz *et* al., 1996; Needleman *et al*., 1979)**.**

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).

Table 7. Comparison of Dry and Rainy Season Mean Heavy Metal Concentrations in Fresh Fish and Water samples from the Three Locations (ppm)

LOCATION:		Alau Dam		Daban Masara		Doronbaga	
Season:		**Dry**	**Rainy**	**Dry**	**Rainy**	**Dry**	**Rainy**
Type of Fish	**Metal**	**x10^{-3} ppm**					
Bargi	Pb	1.27^{w}	2.13^{w}	2.47^{w}	2.20^{w}	2.77^{w}	1.93^{w}
		1.27^{f}	2.23^{f}	1.67^{f}	1.27^{f}	2.53^{f}	1.27^{f}
	Cd	2.80^{w}	0.73^{w}	0.67^{w}	1.23^{w}	2.83^{w}	0.93^{w}
		0.47^{f}	0.50^{f}	0.37^{f}	0.30^{f}	0.53^{f}	0.23^{f}
	Hg	1.37^{w}	0.70^{w}	0.77^{w}	2.13^{w}	0.50^{w}	1.93^{w}
		0.93^{f}	0.87^{f}	1.63^{f}	0.60^{f}	0.67^{f}	0.80^{f}
	As	0.40^{w}	0.27^{w}	0.33^{w}	0.77^{w}	0.26^{w}	0.60^{w}
		0.30^{f}	0.30^{f}	0.43^{f}	0.23^{f}	0.20^{f}	0.30^{f}
Catfish	Pb	1.27^{w}	2.13^{w}	2.47^{w}	2.20^{w}	2.77^{w}	1.93^{w}
		1.63^{f}	1.83^{f}	1.63^{f}	1.43^{f}	1.67^{f}	2.10^{f}
	Cd	2.80^{w}	0.73^{w}	0.67^{w}	1.23^{w}	2.83^{w}	0.93^{w}
		0.33^{f}	0.43^{f}	0.33^{f}	0.23^{f}	0.27^{f}	0.67^{f}
	Hg	1.37^{w}	0.70^{w}	0.77^{w}	2.13^{w}	0.50^{w}	1.93^{w}
		0.97^{f}	1.03^{f}	0.97^{f}	0.50^{f}	0.67^{f}	1.90^{f}
	As	0.40^{w}	0.27^{w}	0.33^{w}	0.77^{w}	0.26^{w}	0.60^{w}
		0.37^{f}	0.37^{f}	0.37^{f}	0.20^{f}	0.23^{f}	0.60^{f}
Kurungu	Pb	1.27^{w}	2.13^{w}	2.47^{w}	2.20^{w}	2.77^{w}	1.93^{w}
		1.26^{f}	1.80^{f}	1.26^{f}	1.06^{f}	6.33^{f}	2.36^{f}
	Cd	2.80^{w}	0.73^{w}	0.67^{w}	1.23^{w}	2.83^{w}	0.93^{w}
		0.33^{f}	0.43^{f}	0.23^{f}	0.23^{f}	0.30^{f}	0.73^{f}
	Hg	1.37^{w}	0.70^{w}	0.77^{w}	2.13^{w}	0.50^{w}	1.93^{w}
		1.73^{f}	1.00^{f}	1.10^{f}	0.67^{f}	1.20^{f}	2.00^{f}
	As	0.40^{w}	0.27^{w}	0.33^{w}	0.77^{w}	0.26^{w}	0.60^{w}
		0.47^{f}	0.43^{f}	0.37^{f}	0.37^{f}	0.17^{f}	0.60^{f}
Tilapia	Pb	1.27^{w}	2.13^{w}	2.47^{w}	2.20^{w}	2.77^{w}	1.93^{w}
		1.13^{f}	1.60^{f}	1.77^{f}	1.70^{f}	1.47^{f}	2.53^{f}
	Cd	2.80^{w}	0.73^{w}	0.67^{w}	1.23^{w}	2.83^{w}	0.93^{w}
		0.43^{f}	0.37^{f}	0.43^{f}	0.40^{f}	0.20^{f}	0.73^{f}
	Hg	1.37^{w}	0.70^{w}	0.77^{w}	2.13^{w}	0.50^{w}	1.93^{w}
		1.00^{f}	0.83^{f}	1.10^{f}	1.00^{f}	0.93^{f}	1.00^{f}
	As	0.40^{w}	0.27^{w}	0.33^{w}	0.77^{w}	0.26^{w}	0.60^{w}
		0.53^{f}	0.30^{f}	0.50^{f}	0.37^{f}	0.33^{f}	0.40^{f}

w = mean concentration of the heavy metal in water sample (three determinations)
f = mean concentration of the heavy metal in fish sample (three determinations)

Season and location are also important in the levels of toxic elements accumulation in various species of fish (Moore, 2000; Rahimi *et al.*, 2010). This can be clearly observed in the comparison of dry and rainy seasons mean heavy metal concentrations in fresh fish samples with the metals concentration in the corresponding water sample from each of the locations investigated (**Table 7**). Higher values of some of the metals were recorded in water, while lower values of other metals are recorded in corresponding fish samples during the two seasons and the values varied among the fish species and from one location to another. Some fish species investigated in this study were observed to have the ability to concentrate some of the metals even when the concentrations in the surrounding water were very low and vice versa (**Table 7**) 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). The result of this study is also

Table 8. Coefficient of Correlation between Heavy Metal Concentrations in Three Locations based on Season

	Pb (D)	Pb (R)	Cd (D)	Cd (R)	Hg (D)	Hg (R)	As (D)	As (R)
Pb (D)	1.00							
Pb (R)	-0.45	1.00						
Cd (D)	-0.32	-0.71	1.00					
Cd (R)	0.68	0.36	-0.91	1.00				
Hg (D)	-0.99	0.55	0.20	-0.58	1.00			
Hg (R)	0.95**	-0.14	-0.60	0.870	-0.91	1.00		
As (D)	-0.94	0.71	-0.01	-0.40	0.98**	-0.79	1.00	
As (R)	0.86	0.07	-0.75	0.96**	-0.80	0.98**	-0.65	1.00

D = Dry season; R = Rainy season; R = 0.878 at 5%.
** = significant at 5%

in line with the notion that the rains may wash down intercontinental contaminants including heavy metals into rivers, lakes and ponds, leading to gradual build up of these toxicants in the aquatic systems. Higher concentrations of the heavy metals in water samples, where it occurs, may also be as a consequence of the channeling of flood water from all corners of the fishing communities, with its attendant contaminants from waste dumps and flowing through farm areas where pesticides, fungicides, and other agrochemicals, may have been applied, to these bodies of water, during the rainy season; in addition to the atmospheric deposits of the heavy metals from both the natural and anthropogenic sources — as indicated earlier, at the beginning of every rainy season. However, good agreements were observed when the results of this study were compared with those reported by other investigators (CIFA, 1992; FSAI, 2009; Bdliya and Tagi, 2011). High lead and copper on roadside soil of Maiduguri had earlier been observed by Bababe *et al* (2003) to constitute possible health risk through the washing away of the metals into the surrounding water bodies. Many investigations on bio-accumulation of heavy metals by various fish species have also indicated that some fish species have the capability to concentrate some heavy metals in their organs and muscles many folds than that of their surrounding water bodies, through diffusion via skin and gills as well as oral consumption or drinking of the water (Ashraf *et* al., 2012; Ambedkar and Muniyan, 2011; Ekpo *et* al., 2008; Eneji *et* al., 2011; Obasohan and Eguavoen, 2008; Vinodhini and Narayanan, 2008; Ozuturk *et al*., 2009).

Metal to metal correlation studies between the locations during the two seasons (**Table 8**) showed that only three of the heavy metals were significantly correlated ($R \leq 0.05$). The significant correlation coefficient was found between Pb and Hg, As and Cd, and As and Hg (**Table 8**).

CONCLUSION

The four toxic heavy metals lead, cadmium, mercury and arsenic investigated in this study were detected in all the fish species sampled from the three locations — Alau Dam, Daban Masara and Doronbaga in the Lake Chad Basin of Borno State. This has confirmed the observations of other similar studies across the country, concerning the gradual build up of toxic pollutants in our aquatic environment. The levels of the four toxic heavy metals observed in the fish species investigated in this study are much lower than the maximum permissible limits and guidelines set by WHO and FAO, and adopted by many countries, for fish and fish products. This study reveals that eating fish obtained from rivers and lakes in the Lake Chad Basin is safe, and does not pose any immediate threat to the health of the fish-consuming public for now. However, it is important to note that the presence of trace heavy metal pollutants in diets could create serious health problems ranging from neuro-, nephro-, carcino- to immunological disorders, if ingested over a long period of time.

It is therefore recommended that assessment of heavy metal content in fresh and processed fish harvested from inland waters of Lake Chad Basin should be continued. This should be done at least twice annually and the analysis should be limited to lead, cadmium, mercury and arsenic. Samples of water from the various inland waters within the Lake Chad Basin should also be analyzed regularly to determine their heavy metal contents.

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