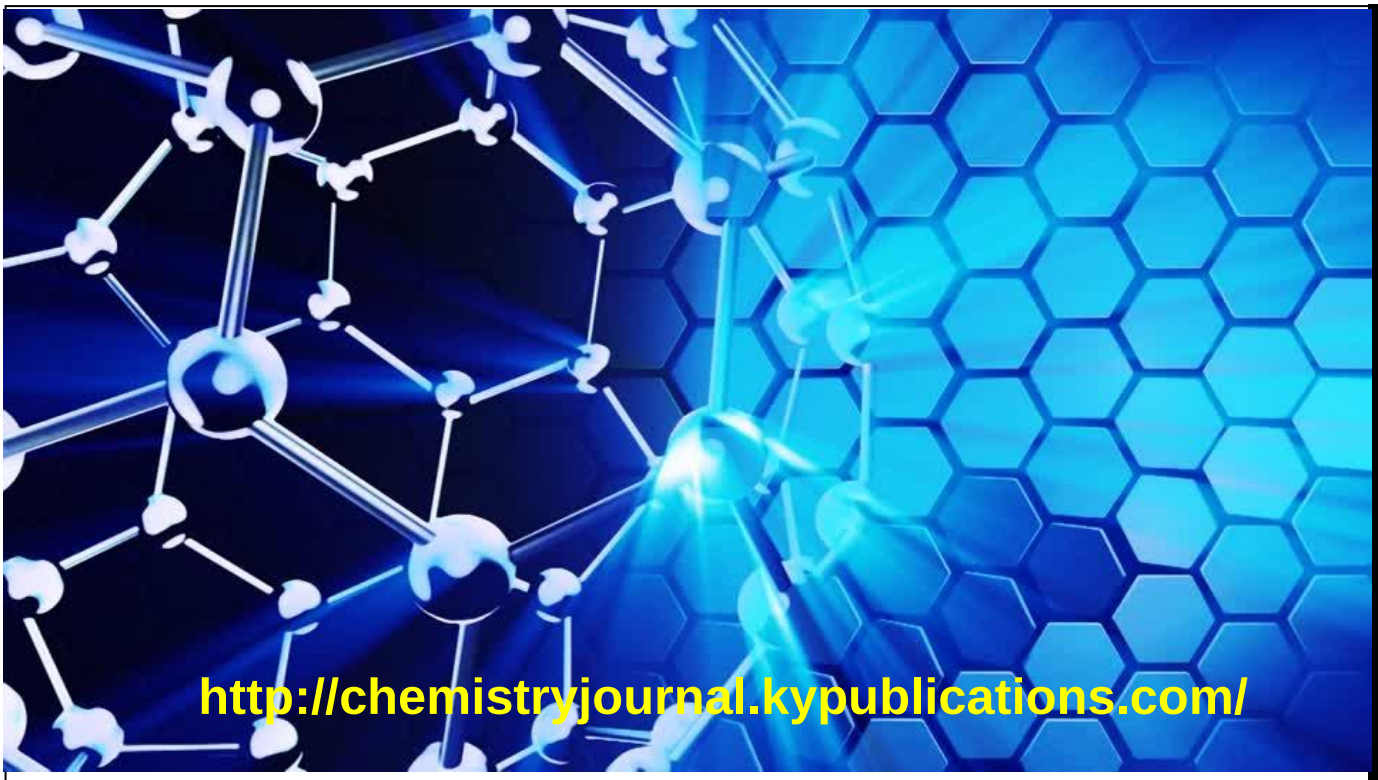

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Distribution of Heavy Metals in Tissues of Freshwater Fish from River Kalong and River Shendam in Shendam Local Government Area of Plateau State, Nigeria.

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RESEARCH ARTICLE

Ogah

ABSTRACT

The present study was carried out to investigate the accumulation profile of heavy metals in three fish species namely; Albula vulpe, Clarias gariepinus and Tilapia zilli. Concentrations of Cd, Cr, Mn, Ni and Pb were measured in all the samples analysed. Ni, Co and Cr however, recorded 80, 60 and 20% incidence respectively in the fish samples. The highest mean concentration, 53.95 mg/kg was recorded for Mn in the liver Cd, Cr and Pb, measured relatively lower concentrations from as low as 0.0 mg/kg, <0.001 mg/kg. The least detectable concentration, 0.0 mg/kg was measured for Cd in gills Ni in liver and Pb in liver all of Albula vulpe gariepinus. Most of the heavy metals exceeded the recommended maximum guidelines. Similarly, the concentration of Mn measured in all the fish samples exceeded the WHO limit of 0.5 mg/L in drinking water. All the concentrations measured for Pb, were above the FAO limit of 0.5 mg/kg except at a few locations where the concentrations were 0.0, 0.3 mg/kg, measured in gills of Albula vulpe and liver of Clarias gariepinus repectively. The mean of the total concentration of each metal in all the samples indicate that the concentrations of the heavy metals in the samples are generally well above the respective recommended guidelines. Thus fish species from the Kalong and Shendam Rivers, may not be safe for human consumption.

Key words: Albula vulpe, Clarias gariepinus, Tilapia zilli, Concentration, species

INTRODUCTION

Aquatic pollution is still a problem in many freshwater and marine environments as it causes negative effects for the health of the various organisms (Fent, 2007). Trace amounts of heavy metals are always present in fresh waters due to the weathering of rocks and soils (Muwanga, 1997; Babel and Opiso, 2007; Samarghandi *et al.,* 2007; Igwe *et al.,* 2008; Al-Juboury, 2009). Some heavy metals have no useful functions to the body and can be highly toxic. If they penetrate into the body through inhalation, ingestion and skin absorption they accumulate in the body tissue faster than the body can detoxify and dispose of them (Ekpo *et al*., 2008).

In recent times, water quality monitoring has become a matter of concern in stream and river water systems affected by careless disposal of urban effluents. Runoff, atmospheric deposition, domestic and industrial effluent discharges are the main sources of aquatic pollution (Wasswa, 1997; Linnik and Zubenko, 2000; Campbell, 2001; Lwanga *et al*., 2003 and Lomniczi *et al*., 2007) and physicochemical characteristics such as dissolved oxygen and the pH of aquatic ecosystems are helpful in determining stream water ecosystem integrity. Monitoring of physicochemical properties and heavy metal concentration of stream water is necessary to establish the levels of contamination in wastewater. Increasing urbanisation and industrialization has given rise to rapid increase in industrial effluent discharge into stream water, leading to increased pollution load. In aquatic ecosystems, trace elements may be immobilized within the stream water and may involve complex formation and co-precipitation of oxides and hydroxides of Mn, Fe or may occur in particulate form (Awofolu *et al*., 2005; Mwiganga and Kansiime, 2005; Nyangababo *et al*, 2005; Srivastava *et al*., 2008).

The contamination of freshwater with a variety of pollutants has become a matter of great concern in the last few decades, not just because of the threats posed to public water supplies but also due to the damage they cause to the aquatic life (Canli. *et al*., 1998). The natural aquatic systems may be contaminated extensively with heavy metals generated from domestic and industrial wastes, agricultural activities, physical and chemical weathering of rocks, soil erosions, as well as sewage disposal and atmospheric deposition (Alloway and Ayres, 1993).

The increasing importance of fish as a source of protein and the interest in understanding the accumulation of heavy metals at the trophic levels of food chain, increase the focus towards fish (Deb and Santra; 1997). Heavy metals in fish, increases with the increments of the metal levels in water, sediment and fish food organism (Arvind; 2002).

Heavy metals like Cu, Co, Zn, Fe and Mn at low concentrations are essential metals for enzymatic activity and many biological processes. On the other hand, metals such as Cd, Pb, and Hg have no known essential role in the body of living organisms, and are toxic even at low concentrations. The essential metals also become toxic at high concentration (Alloway and Ayres; 1993).

Demirak and other workers (Demirak *et al.,* 2006.) investigated the concentrations of heavy metals in water, bottom sediment and tissues (muscle and gills) of *Leuciscus cephalus* from the Dipsiz stream in the Yatagan basin (southwestern Turkey), at a thermal power plant. They found that there was less metal accumulation in the muscle compared to the gills. Concentrations of Cd, Pb, Zn and Cr in the muscle were lower than that in the gills; however, Cu levels were lower in the gills than in the muscle. Whereas many studies (Calta and Canpolat, 2006, deMora *et al.,* 2004, Pyle, *et al.,* 2005). have linked industrial or human activities as possible source of pollution of the water body and biota. The work of Karadede and Unlu (Karadede, H., E. Unlu, 2000) on the concentrations of some heavy metals in the water, sediment and fish species (*Acanthobrama marmid, Chalcalburnus mossulensis, Chondrostoma regium, Carasobarbus luteus, Capoetta trutta and Cyprinus carpio*) from the Ataturk Dam Lake Turkey indicated general absence of serious pollution. Nigeria's crude is known to contain heavy metals in sizeable quantity (Nwadinigwe and Nworgu, 1999). Previous studies have shown that fish species from water bodies in non oil producing regions of Nigeria such as Sokoto (Abdulrahman, and Tsafe, 2004.) and Lagos (Odukoya and Ajayi, 1987b, Odukoya and Ajayi, 1987a) show minimal heavy metal accumulation.

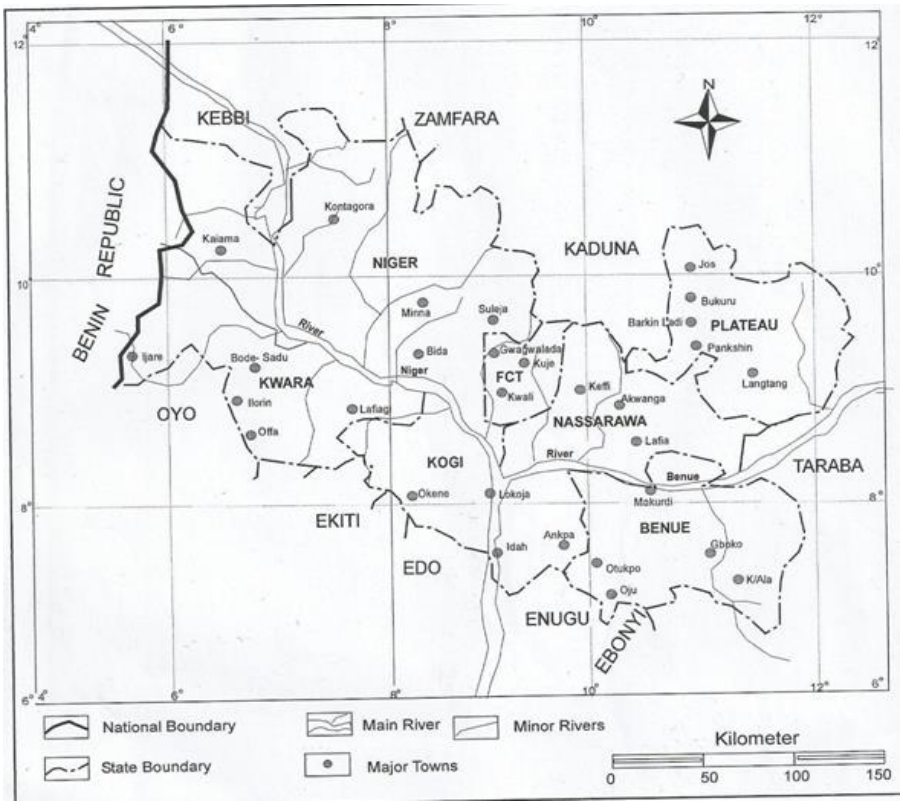

Fig.1: Map of North Central Nigeria Showing the Major and Minor Rivers.
Source: Longman School Atlas, 2003.

3.4 Sample Collection

Samples (water and fish) were collected at the peak of both the dry (February-March) and wet season (August-September). Dugout canoes with paddles were used for sampling from the stations. Water samples were collected in plastic bottles previously cleaned with detergent and soaked overnight in 5% nitric acid. Fish samples were collected using gill nets, baited hook and lines and traps. The fish samples were placed in plastic bags and stored in ice box and taken to the laboratory after cleaning with distilled water to remove any adhering dirt.

3.5 Sample Treatment

The fish samples after defrosting were dissected into gills, liver and muscle, using stainless steel dissection instruments, while wearing surgical gloves. After dissection, all tissue samples were separately oven-dried at 105 oC to constant weight and were each ground to powder. 1 gram of each powdered sample was digested using a mixture of 1.5.1, 70% perchloric, conc. nitric and conc. sulphuric acid at 80 ± 5 oC in a fume chamber, until colorless liquid was obtained.

3.3 Stock Solutions

3.3.1 Cadmium: 1.000 g of cadmium metal was dissolved in 20 ml of 1+1 HCl and then diluted to 1000 mL to make 1000 mgL-1 Cd stock solution. An intermediate stock solution of 100 mgL-1 Cd was made from the stock solution and a series of working standards of the following concentrations were prepared: 0.0, 0.5, 1.0, 2.0, 3.0, 5.0 mgL-1 Cd. The absorbance was determined on AAS and wavelength set at 228.9 nm.

3.3.2 Chromium :2.828 g of anhydrous potassium dichromate (K2Cr2O7) was dissolved in 200 mL distilled water and 1.5 mL concentrated HNO3 was added and then diluted to 1000 mL with distilled water to make 1000 mgL-1 Cr. An intermediate stock solution of 100 mgL-1 Cr was made from the stock solution and a series of working standards of the following concentrations were prepared: 0.0, 0.5, 1.0, 2.0, 3.0, 5.0 mg L-1 Cr. The absorbance was determined on AAS and wavelength set at 357.9 nm.

3.3.3 Manganese: 1.000 g of manganese metal is dissolved in 50 mL of conc. HCl. The solution was then made up to 1L in a volumetric flask with distilled deionized water

3.3.4 Nickel: 1.000 g of nickel is dissolved in 20 mL of conc. HNO3. The solution was diluted to 1L in a volumetric flask with distilled deionized water.

3.3.5 Lead : 1.598 g of lead nitrate (Pb(NO3)2) was dissolved in 200 ml distilled water and 1.5 ml concentrated HNO3 was added and then diluted to 1000 mL to make 1 000 mgL-1 Pb. An intermediate stock solution of 100 mgL-1 Pb was made from the stock solution and a series of working standards of the following concentrations were prepared: 0.0, 0.5, 1.0, 2.0, 3.0, 5.0, mgL-1 Pb. The absorbance was determined on AAS and wavelength set at 283.7 nm (APHA, 1985).

3.6 Instrumentation

The measurements were performed using the Perkin Elmer® Analyst 400 atomic absorption spectrophotometer (PerkinElmer, Inc. Shelton, CT, USA) equipped with WinLab32™ for AA version software, which features all the tools needed to analyze samples, report and archive data and ensure regulatory compliance. PerkinElmer high efficiency double beam optical system and solid–state Deuterium background correction eliminates most interference. A PerkinElmer corrosion – resistant nebulizer, which can be used for solutions containing HF, was used for all the flame absorption measurements. A single slot air-acetylene 10cm burner head was used for all air acetylene experiments.

Table 1: Elemental concentrations in organs of Albula vulpe (Concentration mg/kg)

	Gill					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
K	10.2	0.1	6.7	1	1.1	4	25.9	45.4	13.3	8	2.1	32.4	42.2	24.9	12.8
L	2.4	18.2	178.4	10.7	12.4	2.9	12.6	27.2	4.6	19.9	1.9	26.3	33.3	10.1	0.3
W	0.7	4.2	4.9	1.4	12.8	0.8	12.6	120.3	6.8	7.4	1.7	18	26.6	1.2	12
X	0.4	8.3	49.3	3.7	0	0	2.8	22.9	0	17	0.6	8	79.9	4.5	2.7

Table 2: Elemental concentrations in organs of *Clarias gariepinus* (Concentration mg/kg)

Sample code	Gill					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
K	1.9	11	54.1	10	25	2.9	20	44.7	23.1	1	0.7	1.2	4.3	1	7.8
L	3.2	29	43.1	7.1	2.5	3	18.9	60.5	86.5	17.5	2.7	19.1	35.4	4.7	21.9
W	3.6	41.7	67.3	6.1	0. 001	3.6	21.7	42	22.1	11.1	0.7	7.5	117.8	1.5	34.2
X	2.7	27.8	30.9	16.9	0.3	0.8	18.5	12.8	1.2	2.8	0.3	3.5	1.9	0.6	13

Table 3: Elemental concentrations in organs of *Tilapia zilli* (Concentration mg/L)

Sample code	Gill					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
K	4.7	21.6	80	5.7	9.8	3.4	24	35.6	15.7	11.2	0.9	16	9.2	0.8	0.9
L	0.6	24.8	40	8.4	13.1	2.5	16.9	40.4	9.7	2.7	0.3	6	36	1.5	0.5
W	11	7.3	104.9	1.9	10.6	2.4	15.8	39.2	7.2	3.9	2.3	8.9	10	0.8	7.4
X	0.6	26	134	1.5	7	1.6	29.1	33.6	12	1	2.6	20.8	59.7	25.1	45.6

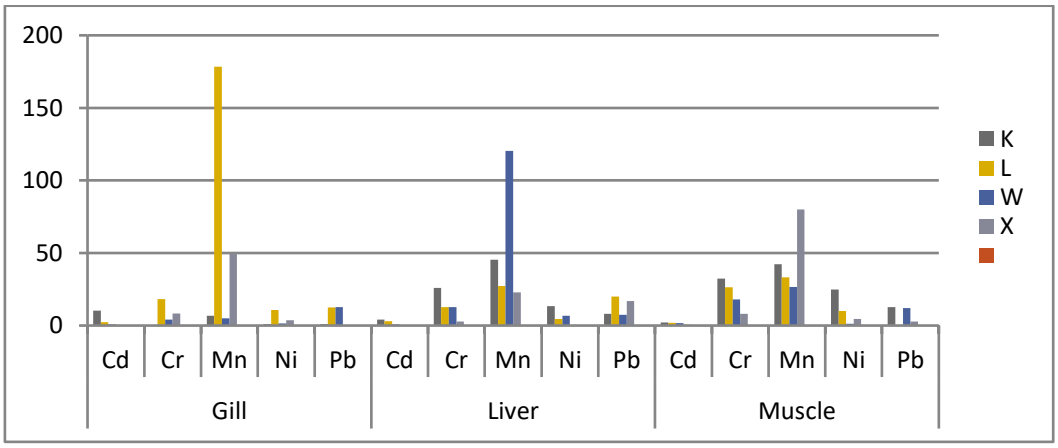

Figure 2: Concentration of heavy metals in the various organs of *Albula vulpe*

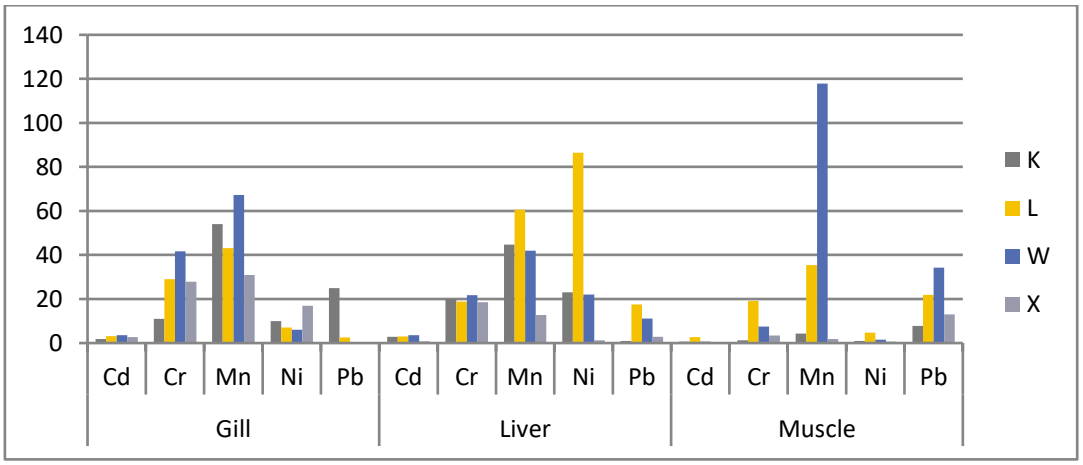

Figure 3: Concentration of heavy metals in the various organs of *Clarias gariepinus*

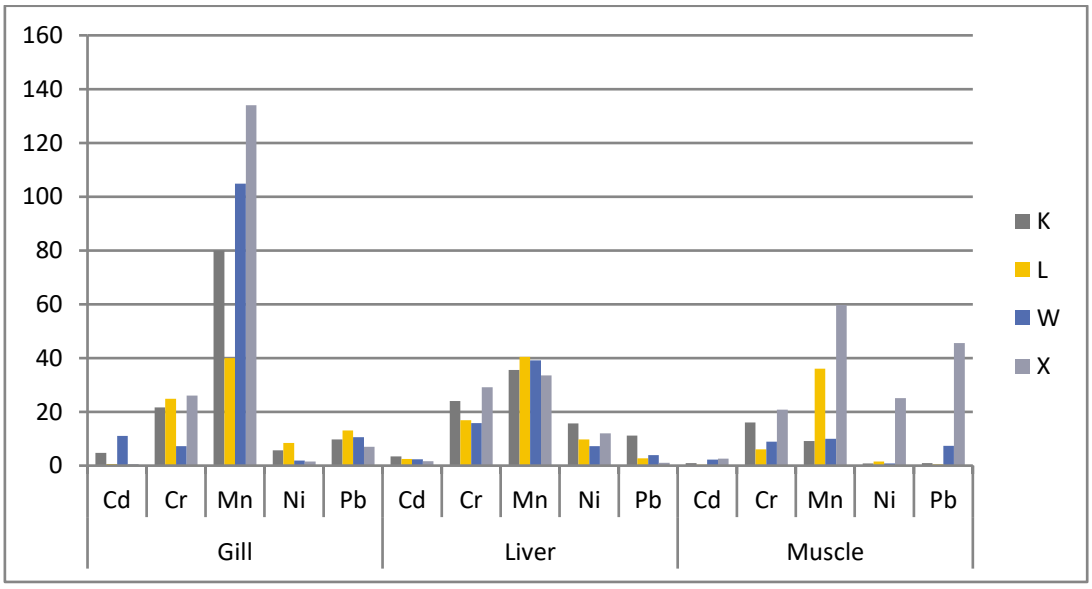

Figure 3: Concentration of heavy metals in the various organs of *Tilapia zilli*

The concentrations of cadmium in the different organs of the three fishes are as presented in Table 1 to 3. The maximum concentration of cadmium (11.0 mg kg^{-1}) was detected in the gill of *Tilapia zilli* (Table 1), while the lowest detection limit of 0.0 mg/kg was observed in the liver *Albula vulpe* Table 1. The mean concentration of Cd in the fish species follow the order *Tilapia zilli>Albula>Clarias gariepinus* while with respect to the organs it follows gills>liver>muscle.

The concentrations of chromium in the different organs of the three fish species varied from 0.1 to 41.7 mg/kg (Table 1 to 3). It was found that the concentrations of chromium in the different organs of three the fish species from Shendam varied from one organ to another. The maximium concentration of chromium (41.7mg/kg) was detected in the gill tissue of *Clarias gariepinus* Table 1, while the minimium (0.1 mg/kg) was observed in the gill of *Albula vulpe* (Table 1).

Their least mean concentration was found in the gill tissues of *Albula vulpe*. On the other hand, the highest mean concentrations of Cr were found in gills of *Clarias gariepinus out of* the three species studied. Chromium is an essential trace element in humans and some laboratory animals (Lee, and Schultz, 1994), but in excess, it could have lethal and sublethal effects on fish and wildlife (Robertson, *et al*., 1991.). No guideline documents were available for chromium in the edible part of fish; neither was it assessed by NCBP or FEPA. In view of other sanctions, the present chromium concentrations in the gill of *Clarias gariepinus* which were the highest are well below the levels validated by USEPA (53.8 ppm) for fish tissue (Pastorok, 1987). However, surveys of contaminants in edible shellfish conducted by FDA and National Marine Fisheries Service reported chromium levels from 0.1 µg to 0.9 mg/g, which is in line with the above regulatory limit. The present chromium tissues concentrations for this study were below 4.0 mg/g levels suggested as indicative of Cr contamination.

Mn tends to reside in the liver in all the fish samples studied, while the muscle is the least accumulated organ. The maximum concentration of Manganese (178.4 mg/kg) was detected in the gills of *Albula vulpe* (Table 1), while the minimum (1.9 mg/kg) level was detected in the muscle of *Clarias gariepinus*. From the result of this analysis, the mean concentrations of nickel in the fish organs were in the order of gills>liver> muscle while the order of concentration with respect to species was *Albula vulpe>Clarias gariepinus>Tilapia*.

The maximum concentration of nickel (86.5 mg/kg) was detected in the liver of *Clarias gariepinus* (Table 1), while the minimum level (0.6 mg/kg) was detected in the muscle of *Clarias gariepinus*. From the result of this analysis, the mean concentrations of nickel in the fish organs are in the order of liver> muscle>gill. Nickel level of 0.7mg/g is viewed as potentially lethal to fish and aquatic birds that consume them (Lemly, 1993). Nickel concentrations of 2.3 mg/g or greater, could cause reproductive impairment and lack of recruitment in fishes (Baumann and May, 1984). None of the samples in this study approached these levels of concern. Hence, nickel concentrations in the entire species of fish do not constitute any threat immediate upon its consumption.

The highest levels of lead (45.6 mg/kg) was detected muscle tissue of *T. zilli* Table 3, while the lowest level (0.0 mg/kg) was detected in the gills of *Albula vulpe* Table 1. The average concentrations of lead in tissues of were higher in the following order Muscle>liver>gills while the order with respect to species were *Tilapia zilli>Clarias gariepinus>Albula vulpe.*

Lead is highly toxic to aquatic organisms, especially fish. The biological effects of sublethal concentrations of lead include delayed embryonic development, suppressed reproduction, and growth inhibition, elevated mucous formation, neurological problems, enzyme inhalation and kidney dysfunction (Rompala, *et al.,*1984, Leland, and Kuwabara. 1985).

CONCLUSION

Fish absorb metals through ingestion of water or contaminated food. Heavy metals have been demonstrated to undergo bioaccumulation in the tissue of aquatic organisms. On consumption of fish and other aquatic organisms these metals are relocated to man. It can be seen that the fishes in the Rivers Kalong and Shendam have been severely affected by heavy metals based on the results obtained from this study (Cd, Mn and Pb) and pose serious health implications for human consumption. The study also reveals that the heavy metals concentrations in the fish species are not sensitive to the seasonal changes as heavy metals are lost slowly or never once bioaccumulated.

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Key to sample codes: K: Kalong wet season, L: Shendam wet season, W: Kalong dry season, X: Shendam dry season