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Distribution of Heavy Metals in Organs of Freshwater Fishes from Kalong and Shendam Rivers, Shendam Local Government Area of Plateau State, Nigeria.

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ABSTRACT
This work was carried out to investigate the accumulation profile of heavy metals in three fish species namely; Albula vulpe, Clarias gariepinus and Tilapia zilli. The maximum 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 of Albula vulpe. 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.

Keywords: Albula vulpe, Clarias gariepinus, Heavy metals, Plateau State, Tilapia zilli

INTRODUCTION

Aquatic pollution remains a problem in many freshwater and marine environments as it causes negative effects on the health of various organisms. Trace amounts of heavy metals are always present in fresh waters due to the weathering processes on rocks and soils (Babel and Opiso, 2007; Igwe *et al.,* 2008; Al-Juboury, 2009). Several heavy metals such as Cd, Pb, and Hg have no known useful functions to the body and can be quite toxic even at low concentrations. When they gain entry into the body either via inhalation or ingestion they accumulate in the body tissue more rapidly than the body can detoxify and dispose them (Ekpo *et al*., 2008).

Monitoring of physicochemical characteristics and heavy metal concentration of stream water is essential to establish the levels of contamination in wastewater. The rising trend of urbanisation and industrialization has given rise to rapid increase in industrial effluent discharge into stream water, leading to increase in 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).

Demirak and other workers (2006) studying 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 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 several investigations (Calta and Canpolat, 2006, deMora *et al.,* 2004, Pyle, *et al.,* 2005) have linked industrial or human activities as source of pollution of the water body and biota. The work of Karadede and 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 revealed a general absence of serious pollution. Nigeria's crude is known to contain heavy metals in sizeable quantity (Nwadinigwe and Nworgu, 1999). Similarly, studies have shown that fish species from water bodies in non oil producing areas of Nigeria such as Lagos (Odukoya and Ajayi, 1987b, Odukoya and Ajayi, 1987a) showed minimal heavy metal accumulation. The aim of this study was to determine the level of heavy metals in

Albula vulpe, *Clarias gariepinus* and *Tilapia zilli* in Shendam Local Government Area of Plateau State.

Materials and Methods

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.

Sample Treatment

The fish samples after defrosting were dissected into gills, liver and muscle, using stainless steel dissecting instruments, while wearing surgical gloves. After dissection, all tissue samples were separately oven-dried at 105 ^{o}C 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 ^{o}C in a fume chamber, until colorless liquid was obtained.

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

Stock Solutions

Cadmium

1.000 g of cadmium metal was dissolved in 20 mL of 1M 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: 1.0, 2.0, 3.0, 4.0, 5.0 mgL^{-1} Cd. The absorbance was determined on Perkin Elmer® Analyst 400 atomic absorption spectrophotometer and wavelength set at 228.9 nm.

Chromium

2.828 g of anhydrous potassium dichromate ($K_2Cr_2O_7$) was dissolved in 200 mL deionized water and 1.5 mL concentrated HNO_3 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: 1.0, 2.0, 3.0, 4.0, 5.0 mg L^{-1} Cr. The absorbance was determined on AAS and wavelength set at 357.9 nm.

Manganese

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

Nickel

1.000 g of nickel metal was dissolved in 20 mL of conc. HNO_3. The solution was diluted to 1L in a volumetric flask with distilled deionized water.

Lead

1.598 g of lead nitrate ($Pb(NO_3)_2$) was dissolved in 200 ml distilled water and 1.5 ml concentrated HNO_3 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: 1.0, 2.0, 3.0, 4.0, 5.0, mgL^{-1} Pb. The absorbance was determined on AAS and wavelength set at 283.7 nm (APHA, 1985).

Instrumentation

The measurements were carried out using the Perkin Elmer® Analyst 400 atomic absorption spectrophotometer equipped with WinLab32™ for AA version software.

Result

The result of the analysis of heavy metals in the three fish samples namely *Albula vulpe, Clarias gariepinus and Tilapia zilli* are presented in Tables 1-3.

Table 1: Concentrations in organs of *Albula vulpe* (mg/kg)

Sample code	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	1.0	1.1	4.0	25.9	45.4	13.3	8.0	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	18.0	26.6	1.2	12.0
X	0.4	8.3	49.3	3.7	0.0	0.0	2.8	22.9	0.0	17.0	0.6	8.0	79.9	4.5	2.7

Table 2: Concentrations in organs of *Clarias gariepinus* (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	11.0	54.1	10.0	25.0	2.9	20.0	44.7	23.1	1.0	0.7	1.2	4.3	1.0	7.8
L	3.2	29.0	43.1	7.1	2.5	3.0	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	42.0	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	13.0

Table 3: Concentrations in organs of *Tilapia zilli* (mg/L)

Sample code	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**
K	4.7	21.6	80.0	5.7	9.8	3.4	24.0	35.6	15.7	11.2	0.9	16.0	9.2	0.8	0.9
L	0.6	24.8	40.0	8.4	13.1	2.5	16.9	40.4	9.7	2.7	0.3	6.0	36.0	1.5	0.5
W	11.0	7.3	104.9	1.9	10.6	2.4	15.8	39.2	7.2	3.9	2.3	8.9	10.0	0.8	7.4
X	0.6	26.0	134.0	1.5	7.0	1.6	29.1	33.6	12.0	1.0	2.6	20.8	59.7	25.1	45.6

DISCUSSION

The concentrations of cadmium in the different organs of the three fishes are as presented in Tables 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 concentration (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). No guideline documents were available for chromium in the edible part of fish; neither was it assessed by Federal Environmental Protection Agency, 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 Food and Drug Administration 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 level of lead (45.6 mg/kg) was detected in the muscle 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 the fish organs were 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 (Leland and Kuwabara. 1985).

CONCLUSION

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 were not dependent on the seasonal changes in heavy metal concentrations. This is so as heavy metals once they are bioaccumulated become difficult to excrete from animal tissues.

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