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## TRACE METAL DISTRIBUTION IN SURFACE WATER, SEDIMENT, AND TISSUES OF FRESHWATER CATFISH (*CLARIAS. GARIEPINUS*), FROM OKE- AFA CANAL, LAGOS NIGERIA

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#### ABSTRACT

This paper discusses concentrations of 7 essential trace metals (chromium, cadmium, copper, lead, nickel, manganese and zinc) in water, sediment and freshwater fish (Clarias. gariepinus) tissues from Oke-Afa Canal, Lagos Nigeria The sampling and analysis of the samples from Oke Afa canal were carried out between the month of June-October, 2011 and experimental procedures used followed the description of American Public Health Association (APHA) The results showed that Liver concentrated highest level of zinc, copper and lead ( $6.851\pm0.005 \text{ mg/Kg}$ ,  $1.876\pm0.001 \text{ mg/Kg}$  and  $0.143\pm0.001 \text{ mg/Kg}$  respectively). This was followed by sediments with mean values of (nickel =  $0.400\pm0.001 \text{ mg/Kg}$ , chromium= $0.127\pm0.003 \text{ mg/Kg}$ ,  $m = 0.092\pm0.001 \text{ mg/Kg}$  and cadmium=  $0.076\pm0.003 \text{ mg/Kg}$ ). Surface water equally concentrated some metals such as Manganese, cadmium and lead with mean values of  $0.069\pm0.101 \text{ Mg/L}$ ,  $0.043\pm0.011 \text{ Mg/L}$ ,  $0.039\pm0.016 \text{ Mg/L}$  respectively.

The order of bioaccumulation in sediment are Zn > Cu > Ni > Cr > Pb > Mn > Cd while the order of bioaccumulation in liver was Zn > Cu > Ni > Pb > Cd > Mn > Cr Also the order of concentration in surface water was Mn > Zn > Cd > Pb > Ni > Cu > Cr

Metal concentration in the fish tissues (flesh, bones gills and guts) was low in concentration, but the values were still significant at 95 percent confidence limit (P < 0.05) with the exception of Manganese. This suggest that the water quality of Oke Afa canal system is adversely affected and impaired by the discharge of domestic, agricultural and industrial wastes.

Comparison of these values with FAO/WHO limits in fish tissue showed that it is safe to consume the fish species from Oke -Afa canal for now but may be unsafe due to possible bioaccumulation of the metals in the organs of man since humans are at the top of food chain.

**Key Words:** Heavy metal pollution, Bioaccumulation, Clarias gariepinus, Oke-Afa Canal, Chromium, Copper, Manganese, Zinc. Lead, Cadmium, Nickel

## INTRODUCTION

Rivers all over the world have supported the growth of human civilization since the first towns appeared some 7000 years ago (Meybeck, 1996) but as a result of this growth and the diversification of activities, most of the world's rivers have been negatively affected. Human activity has profoundly affected rivers and streams in all parts of the world to such an extent that it is now extremely difficult to find any stream which has not been in some way altered and probably quite impossible to find any such river'. Historically, canal does not only serve sanitary purposes, the structure assisted in irrigating fields for farmers and gardeners and greatly boosted the growth of gardening in the community.

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In Lagos Nigeria, the notable amongst the canals are located in Oke-Afa-Isolo, Mile 2, Alaka, Orile, Oyingbo, Apapa areas. To date, there has been no systematic monitoring of canal water quality in Lagos State to evaluate what type of remedial actions may be necessary for the canals. There are many different types of contaminants present in the environment. These range from synthetic chemicals to trace metals that are required for life. Concerns about these contaminants range from possible harmful effects on the ecosystem to possible harm to humans consuming contaminated organisms (Melancon, 1995). According to Adams (1990) organisms like fish are continuously challenged or stressed by the normal demands of the aquatic environment and may be exposed to sub-lethal levels of contaminants and to unfavorable environmental variables like temperatures, water velocities, sediment loads, dissolved oxygen concentrations, food availability and other variables. These factors can impose stress on physiological systems.

However, in recent years, there has been a remarkable population growth, accompanied by intense urbanization, an increase of industrial activities and a higher exploitation of cultivable land. These transformations have brought about a huge increase in the quantity of discharges and a wide diversification in the types of pollutants, including heavy metals that reach Oke Afa Canal waters and have undesirable effects on its environment. Surveying literatures showed that data on heavy metals in Oke Afa Canal waters are scanty (Olowo *et. al*, 2009)

Heavy metals are one of the serious pollutants in natural environment due to their toxicity, persistence and bioaccumulation problems (Pekey, 2006; Nouri et al., 2006). The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to urban areas (Nouri et al., 2008). Heavy metals from incoming tidal water and fresh water sources are rapidly removed from the water body and deposited onto the sediments (Tam and Wong, 2000; Samarghandi et al., 2007). Over the last decades, the study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. (Vinodhini and Narayanan, 2008; Nadia, 2009).because sediment analysis offers certain advantages over water analysis for the control and detection of metal pollution in estuaries (Forstner and Wittman, 1983; Luamo, 1990), although its metal concentrations can also fluctuate over time (Araujo et al., 1988). In the same vein, it was observed that the rate of change is well below that of the water (Boyden et al., 1979). On the other hand, surface sediment often exchanges with suspended materials, thereby affecting the release of metals to the overlying water (Zvinowanda et al., 2009). Therefore, the top few centimetres of the sediments reflect the continuously changing present-day degree of contamination, whereas the bottom sediments record its history.

Among animal species, fishes are the inhabitants that cannot escape from the detrimental effects of these pollutants (Olaifa *et al.*, 2004; Clarkson, 1998; Dickman and Leung, 1998). Fish are widely used to evaluate the health of aquatic ecosystems because pollutants build up in the food chain and are responsible for adverse effects and death in the aquatic systems (Farkas *et al.*, 2002; Yousuf and El-Shahawi, 1999). The studies carried out on various fishes have shown that heavy metals may alter the physiological activities and biochemical parameters both in tissues and in blood (Canli, 1995; Tort and Torres, 1988; Basa and Rani, 2003). The organisms developed a protective defense against the deleterious effects of essential and inessential heavy metals and other xenobiotics that produce degenerative changes like oxidative stress in the body (Abou EL-Naga *et al.*, 2005; Filipovic and Raspor, 2003). *Clarias gariespinus* was selected due to its adoption in polluted aquatic environment. The purpose of this research is to quantify the concentration of heavy metals in Oke-Afa canal surface water, sediment and in organs to the amount accumulated in different organs of organs of *Clarias gariepinus*.

#### MATERIALS AND METHODS

#### Description of Sampling Site

Oke Afa canal is a 13.3 km stretch water body in Lagos Nigeria. It is on latitude of 6.45°N and longitude 3.47°E. Along the stretch of the canal are located the Isolo open dumpsite, Oke Afa Plank market, mechanic workshop and sand mining sites. This same canal also receives industrial

waste water from industrial areas of Fatai Atere, Ilupeju, Ogba and Ladipo industrial estate and also domestic waste from these areas , alongside the domestic area of Oshodi, Apakun, Shasha , Airport Road then liked to Mile 2 canals and finally to the Lagos harbour. SAMPLING OF WATER, SOIL, AND FISH

#### Water

Samples were collected in 250ml glass bottle for chemical parameters. The bottles were precleaned by washing with non-ionic detergents, rinsed in distilled water. Before sampling, the bottles were rinsed three times with sample water before being filled with the sample. The samplings were done midstream by dipping each sample bottle at approximately 20-30 cm below the water surface, projecting the mouth of the container against the flow direction. The samples were then transported in cooler boxes to the laboratory. In the laboratory, water samples were acidified with concentrated HCl and preserved in a refrigerator till analysis for Zn, Mn, Cu, Cd, Cr Ni and Pb.

## Sediment

The bottom sediments at the sampling sites collected using ekman grab.

In the laboratory, the sediment samples were dried at 105 °C, grinding, sieving and about (10 gm) of the most fine dried grains were digested with a mixture of conc.  $H_2O_2$ , HCl and HNO<sub>3</sub> as the

method described in Page et al. (1982) and preserved in a refrigerator till analysis.

**FISH SAMPLES:** Adult *Clarias gariepinus* were purchased from the Oke Afa from the fishermen fishing there using set nets. It was then preserved in a cooler with ice and then transported to the laboratory for further analysis.

**Digestion of samples**: The samples were digested in open 50ml beakers on a hot plate.10 grams of each organ (wet weight) were weighed out in an open beaker and 10 ml of freshly prepared 1:1 nitric acid – hydrogen peroxide added. The beaker was covered with a watch glass till initial reaction subsided in about 1 hour. The beaker was placed in a water bath on a hot plate and the temperature gradually allowed rising to 160°C and the content boiled gently for about 2 hours to reduce the volume to between 2 - 5 ml. The digests were allowed to cool and transferred to 25 ml volumetric flasks and made up to mark with de-ionized water (FAO/SIDA, 1993). The digests were kept in plastic bottles and later the heavy metal concentrations were determined using an atomic absorption spectrophotometer (AAS).

## **Statistical Analysis**

The obtained data were subjected to descriptive statistical analysis (95 % confidence limit). The computation were achieved with the use of statistical package for social sciences (SPSS 17) to determine the mean, standard deviation, and standard error of mean values of metal concentration in the surface water, sediments and tissues of *Clarias gariepinus* 

## RESULTS

The results obtained for the analysis were as represented below. The result showed wide variability in the sediment, surface water and the different organs of *Clarias gariepinus* analysed

#### Lead

The results showed that the concentration of lead in the liver has the highest mean value compared to all other organs of *Clarias gariepinus* with the mean value of  $0.143\pm0.001$  mg/kg. Other organs such as gills, guts, bone and muscle have lower concentration of lead with mean values of  $0.048\pm0.001$  mg/kg,  $0.037\pm0.001$  mg/kg,  $0.012\pm0.001$  mg/kg, and  $0.006\pm0.001$  mg/kg respectively

In the sediment however, the concentration of lead was equally high with mean values of  $0.095\pm0.001 \rm mg/Kg$ 

In the surface water, the value recorded was  $0.039\pm0.016$  mg/L. This are represented in Table 1, Fig.1.The concentration values of this element in the fish has exceeded the allowable concentration of 0.0002 mg/kg (USEPA, 1987). Similarly, this concentration is significant at (P<0.05) confidence limit.

### Chromium

Figure 2 showed that the sediment has the highest concentration of chromium with mean value of  $0.0127\pm0.003$  mg/kg; the surface water has the mean value  $0.012\pm0.006$  mg/l. The liver, gill and the gut has relatively low result with the following mean value  $0.009\pm0.001$  mg/kg,  $0.004\pm0.001$  mg/kg, and  $0.03\pm0.001$  mg/kg respectively. For the bone and muscle, they both have the same mean value of  $0.001\pm0.000$  respectively. However, the concentration was found to be significant at (P<0.05) confidence limit.

## Cadmium

The level of cadmium analyzed in sediment has a high mean value of  $0.076\pm0.003$  mg/kg and surface water with mean value $0.043\pm0.011$  mg/l. However the mean value of liver is  $0.061\pm0.001$  mg/kg which is also high. The gut and the gill have the following mean value  $0.014\pm0.001$  mg/kg and  $0.010\pm0.000$  mg/kg. The bone has the lowest mean value which is  $0.002\pm0.001$  mg/kg. The ANOVA result showed that the concentration was significant at (P<0.05) confidence limit.

## Manganese

In fig 4, the level of manganese in the sediment had the highest mean manganese value compared with water and fish. The mean values of  $0.092\pm0.001$  mg/kg next to the surface water with value of  $0.069\pm0.101$  mg/l. The liver has  $0.024\pm0.001$  mg/kg,  $0.009\pm0$ 

.001 mg/kg in the gut, 0.007 $\pm$ 0.001 mg/kg in the gill, the bone has the mean value of 0.005 $\pm$ 0.000 mg/kg. The muscle has the lowest mean value of 0.004 $\pm$ 0.001 mg/kg.

Analysis of variance indicated that, values were not significant at (P>0.05) confidence limit.

## Nickel

Fig 5 showed that nickel was more concentrated in the sediment compared with water and tissue . The concentration of nickel in the sediment has the mean value of  $0.400\pm0.001$  mg/kg. However the surface water has the mean value of 0.033±0.013 mg/l.In the organs of the fish, liver, gut, gill, bone flesh had the following mean values of and  $0.157 \pm 0.001$ mg/kg,0.020±0.001mg/kg,0.016±0.001 mg/kg, 0.008±0.001 mg/kg and 0.006±0.001 mg/kg respectively. However, the concentration were found to be significant at (P<0.05) confidence limit.

## Copper

The mean concentration of copper was established in fig.6. The highest values were found in the liver with  $1.876\pm0.001$  mg/kg, the gut has  $0.792\pm0.021$  mg/kg, bone, flesh are relatively low with mean value of  $0.184\pm0.115$  mg/kg and  $0.107\pm0.000$  mg/kg. The level of copper in the sediment is high with mean value of  $1.573\pm0.003$  mg/kg, the concentration of copper in the surface water  $0.029\pm0.010$  mg/L. The concentration was found to be significant at (P<0.05) confidence limit.

#### Zinc

Fig 7 showed that the level of zinc in the liver was of very high with the mean value of  $6.851\pm0.005$  mg/kg. However the gut, gill, bone and flesh mean valueswere  $2.884\pm0.001$  mg/kg,  $0.568\pm0.288$  mg/kg,  $0.515\pm0.001$  mg/kg and  $0.387\pm0.001$  mg/kg respectively. The concentration of zinc in the sediment has the mean value of  $4.415\pm0.013$  mg/kg which is also high. The water has the lowest mean value of  $0.068\pm0.020$  mg/l.

However, the concentration were found to be significant at (P<0.05) confidence limit.

## CHAPTER FIVE DISCUSSION

The concentration of the trace metals determined in the sediments surface water and organs of *Clarias gariespinus* from Oke Afa canal were as indicated in Tables 1 and Fig. 1-7. zinc, nickel, lead, manganese, cadmium, chromium and copper were detected in the samples analyzed with sediments having the highest concentrations. The high content of nickel, chromium, manganese and cadmium were found in the sediment (Nickel =  $0.400\pm0.001$ Mg/Kg, Chromium =  $0.127\pm0.003$ Mg/Kg, Mn = $0.092\pm0.001$ Mg/Kg and Cadmium=  $0.076\pm0.003$ Mg/Kg) respectively may be because of the nature of the bottom sediment which was found to be clayey or muddy material that forms the canal bed in the area sampled. This may explain the high concentration recorded in the fish liver. The fish, being carnivores may have taken the lead from polluted bed material along with food which is in an agreement with previous report(Adeniyi *et al* 2007).

Not only that, the disposal of industrial liquid waste, dischargingof agricultural drainage as well as sewage effluent from industries around the area could be responsible for the high levels of heavy metals in Oke Afa canal. This opinion was equally shared by Abdel Sabour, (1998), Adefemi*et. al*2008. In view of this, sedimentation has long been recognized as the principal process in the removal of heavy metals from the water not only in natural wetlands, but also in constructed ones (Walker and Hurl, 2002).

Furthermore, the value of lead in sediment  $(0.095\pm0.009$  mg/kg (Fig 1) was higher than the value obtained in water; the value is still within the acceptable limitof CEQG, 2003 standard of 350 mg/kg. The reason for high concentration of lead in sediment could be adduced to the fact that many of these are rapidly removed from waters into the underlying sediments. Sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants. The highest pb concentrations in sediment samples obtained from this study is an indication of leakage of oil, grease and anti-fouling paints which are serious pollution sources for Pb, Also the printing byproduct wastes contain high levels of Pb which appeared at the sites. This is corroborated by the findings of Mourad, (1996); ETPS, (1995). Consequently, in the event of pollution in an aquatic ecosystem, sediments are known to habour more of the contaminants (Aderinola, *et.al*, 2009, Adeniyi *et al.*, 2008; Yusuf and Osibanjo, 2006; Monteiro and Roychoudhury, 2005; Awofolu et al., 2005; Ikem *et al.*, 2003).

The heavy metals such as chromium (Cr), cadmium (Cd) Copper (Cu) lead (Pb) nickel (Ni), manganese (Mn) were analyzed in different organs like gills, liver, bone and flesh of *Clarias gariepinus*. The liver accumulates relatively higher amounts of zinc, copper and lead $0.851\pm0.005$  Mg/Kg,  $1.876\pm0.001$ Mg/Kg and  $0.143\pm0.001$ Mg/Kg respectively. The liver has the concentration of lead with mean value  $0.143\pm0.001$ Mg/Kg which is very high compared to other organs such as gills, gut, bone and flesh. The concentration of lead in the environment was found to be significant at (P<0.05) confidence limit. The high concentration of zinc, copper and lead found in the fish could Suggest that their uptake was probably through food which agrees with the opinion of Enk and Mathis (1977) and Fortner and Wittmann (1981) that the bio-availability and nature of food items, affect metals bioaccumulation in fish. *Clarias gariepinus is* a known carnivorous predator, which feeds on small fish such as *Tilapia zillii*, and other smaller fishes(Reed *et al*, 1967) and mollusks (Idodo-Umeh, 2000) and therefore forms an important link in the food web of aquatic ecosystems in the locality. Fish has been reported to accumulate metals from water by diffusion via skin and gills as well as oral consumption (Nussey et al, 2000; Oguzie, 2003).

The gills concentrated high values of  $0.048\pm0.001$  mg/Kg,  $0.010\pm0.000$  mg/Kg and  $0.392\pm0.035$  mg/Kg for Pb, Cd and Cu respectively. The concentration of this metal element were found to be significant at (P<0.05) confidence limit .The allowable limit of cadmium in fish is 2.000 according to WHO, (1985).

Jennings, et. al., (1996) reported in his findings that death or permanent damage to the central nervous system, the brain, and kidneys could occur with increase in concentration of lead in the

environment. Gbem, *et. al*, 2001 reported that liver and kidney are also known to accumulate high amounts of metals The higher accumulation in liver may alter the levels of various biochemical parameters in liver. This may alsocause severe liver damage (Ferguson, 1989; Mayersand Hendricks, 1984) Surface water concentrated high values for some metals such as Manganese, cadmium and lead with mean values of  $0.069\pm0.101$  Mg/L,  $0.043\pm0.011$  Mg/L,  $0.039\pm0.016$  Mg/L respectively. The result obtained showed that, the trace metal concentrations in water exceeded the WHO standard (World. Health Organisation, 1992). The concentration of metal in lead and cadmium were found to be significant at (P<0.05) confidence limit, but manganese was not significant.

These findings imply that consumption of the polluted water by animals or human beings could be hazardous to their health. The resultant increased in metal concentrations can be toxic to fish and render the water unsuitable for other uses. Monitoring and reducing human actions will help keep Oke Afa canal safe.

#### CONCLUSSION

Metals (copper, lead, cadmium, zinc,chromium,nickel and zinc determined in the Oke Afa canal water, sediment and fish samples were found at elevated levels. This gives cause for concern. The socio- economic activities around the canal catchment are the probable sources of these contaminants. Elevated levels of metals in water have been implicated as risk to human health and the "health" of the aquatic system. The continuous monitoring of metal pollution of the canal system is essential. Activities that predict point source and diffuse contamination should be discouraged by the appropriate governmental agencies.

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 Table-1: Mean values of heavy concentration in surface water, sediments and organs of Clarias
 gariepinus from Oke Afa Canal

	Lead (pb) (mg/kg)	Chromiu m (mg/kg)	Cadmium (mg/kg)	Manganes e (mg/kg)	Nickel (mg/kg)	Copper (mg/kg)	Zinc (mg/kg)
Liver	0.143±0 .001	0.009±0.0 01	0.061±0.001	0.024±0.0 01	0.151±0.00 1	1.876±0.00 1	6.851±0.005
Gut	0.037±0 .001	0.003±0.0 01	0.014±0.001	0.009±0.0 01	0.020±0.00 1	0.792±0.02 1	2.884±0.001
Gill	0.048±0 .001	0.004±0.0 01	0.010±0.000	0.007±0.0 01	0.016±0.00 1	0.392±0.03 5	$0.568 {\pm} 0.288$
Bone	0.012±0 .001	0.001±0.0 00	0.002±0.001	$0.005 \pm 0.0$ 00	0.006±0.00 1	0.184±0.11 5	0.515±0.001
Flesh	0.006±0 .001	0.001±0.0 00	0.007±0.001	0.004±0.0 01	0.008±0.00 1	0.107±0.00 0	0.387±0.001
Sedime nt	0.095±0 .001	0.127±0.0 03	0.076±0.003	0.092±0.0 01	0.400±0.00 1	1.573±0.00 3	4.475±0.013
Water	0.039±0 .016	0.012±0.0 06	0.043±0.011	0.069±0.1 01	0.033±0.01 3	0.029±0.01 0	$0.068 \pm 0.020$
Total	0.054±0 .046	0.022±0.0 43	0.031±0.028	0.032±0.0 51	0.088±0.13 6	0.677±0.70 4	$2.157 \pm 2.454$

Fig-1. Mean values of lead concentration in surface water, sediments and organs of Clarias

gariepinus from Oke Afa Canal



Fig-2. Mean values of Chromium concentration in surface water, sediments and organs of *Clarias gariepinus* from Oke Afa Canal



Fig-3. Mean values of Cadmium concentration in surface water, sediments and organs of *Clarias* gariepinus from Oke Afa Canal







Specimens

Fig-5. Mean values of Nickel concentration in surface water, sediments and organs of *Clarias gariepinus* from Oke Afa Canal



Fig-6. Mean values of Copper concentration in surface water, sediments and organs of *Clarias gariepinus* from Oke Afa Canal



Fig-7. Mean values of Zinc concentration in surface water, sediments and organs of *Clarias gariepinus* from Oke Afa Canal metals and organochlorines in fish . FAO fisheries Technical Paper, 212. Federal Environmental



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