



## Assessment of heavy metal residues in water, fish tissue and human blood from Ubeji, Warri, Delta State, Nigeria

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**ABSTRACT:** Residual levels of lead, chromium, cadmium and zinc in water and fish tissue from Ubeji River, Warri and blood samples from residents of Ubeji were analysed. Control water and fish samples were obtained from Eleyele River and blood from residents of Ibadan. All the samples collected were digested using a modified procedure from the Association of Official Analytical Chemists (AOAC) and were subsequently analyzed using Atomic Absorption Spectroscopy. Levels of lead and cadmium in Ubeji river were significantly higher than levels in Eleyele River. Fifty fish samples from five species (*Citharinus citharus*, *Liza falcipinis*, *Brycinus macrolepidotus*, *Polydactylus quadrifilis* and *Tilapia zilli*) were analysed. Lead concentration (ppm) was highest in *C. citharus* (76.07±161.48) and least in *T. zilli* (23.16±26.30). Chromium was not detected in *B. macrolepidotus*, *P. quadrifilis* and *T. zilli*. Concentrations of all heavy metals detected, except zinc, in the fish species were higher than WHO permissible limit. Lead, Cadmium and Zinc concentrations in the tissues of the control fish were significantly lower ( $p>0.05$ ) than those recorded in fish from Ubeji River. There were no statistically significant differences in heavy metal concentration in fish gills and muscle ( $p>0.05$ ). Lead and cadmium levels in Ubeji river significantly exceeded ( $p=0.0$  and  $p=0.012$ ) the permissible limits for aquaculture and drinking. Levels of Chromium (1737.17±2996.01), Zinc and Lead (149.35±188.28 and 123.49±350.85 respectively) were significantly high ( $p<0.05$ ) in the 101 human blood samples screened, while concentrations of Cadmium was comparatively low (10.11±10.71). Lower levels of cadmium, zinc and lead (8.54± 7.49, 79.89±62.65 and 53.46±57.17, respectively) were recorded for the control samples from Ibadan. This study highlights the high levels of heavy metals in the Ubeji River and suggests the need for interventions to stem the tide of pollution in the river. It would also be important to assess health problems that may arise as a result of contact and continuous use of the water. @ JASEM

DOI: <http://dx.doi.org/10.4314/jasem.v17i2.12>

**Key Words :** Heavy metal residues , Fish tissue, Human blood, Ubeji River.

The unselective dumping of refuse, discharge of industrial effluents, petroleum wastes and crude oil spills replete with heavy metals give rise to consequences which are of paramount importance to the health of the environment. These discharged wastes contain heavy metals which, although considered essential macro- and micro-elements especially at non-adverse effect levels (Dimari *et al.*, 2008), may have adverse effects on the population in the concentrations encountered in polluted environments. Metals such as copper and zinc are generally regarded as essential trace metals (Nduka *et*

*al.*, 2010) because of their valuable role in the metabolic activities of organisms. However, heavy metals like Cadmium, Lead, Nickel and Mercury exhibit extreme toxicity even at trace levels. Most essential metals have been found to be toxic when supplied in concentrations in excess of the optimal levels.

Heavy metal contamination of aquatic environments is of critical concern because of their toxicity and accumulation in aquatic organisms. Many dissolved metals entering rivers are adsorbed onto colloid

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particulates; at high alkalinity and pH, the metals particularly lead and cadmium, precipitate by forming complexes, further influencing the metal toxicity (Dimari *et al.*, 2008). Aquatic organisms such as phytoplankton, zooplankton, fishes and other higher organisms, during feeding may incorporate these heavy metals into their bodies where they may remain for a very long time in sea foods. The metals that accumulate in the tissue of the sea food, concentrate to high amount and are passed on in the food chain.

Accumulation of heavy metals in an aquatic environment has direct consequences for man and the ecosystem. The most significant problem associated with heavy metals in the environment apart from accumulation through the food chain and persistence in nature is their toxicity (King and Jonathan, 2003; Dimari *et al.*, 2008). Fishes, being major components of most aquatic habitats have also been recognized as good bio-accumulators of organic and inorganic pollutants (King and Jonathan, 2003). They also act as bio-indicators of heavy metal levels in such environments, and can be used to evaluate the health of such aquatic ecosystems. (Farkas *et al.*, 2002; Yousuf and El-Shahawi, 1999).

The degree to which a system, organ, tissue or cell is affected by a heavy metal depends on the toxin itself and the individuals' degree of exposure to the toxin. Thus, metals contribute to a variety of adverse effects that can impact human health and each will produce different behavioral, physiological and cognitive changes in an exposed individual.

Studies on the Ubeji Creek have mainly been focused on the effect of petrochemical effluents on the water quality (Uzoekwe and Oghosanine, 2011; Asagbra Unpublished dissertation, 2010; Achudume, 2009). It is known that the process of bioaccumulation concentrates metals in some food species which may be hazardous to human health, therefore knowledge of the concentration of metals existing in any aquatic ecosystem is necessary. Since the Warri Refinery and Petrochemical Company (WRPC) discharges wastes into the Ubeji Creek, this study aimed at assessing the levels of metal residues in fish and water from the Ubeji River and in the people living in the environment of Ubeji River.

## MATERIALS AND METHODS

*Study Area:* Ubeji community is located beside the Warri Refinery and Petrochemical Company

(WRPC) Warri, Delta State, Nigeria. The Ubeji River which runs through the community receives untreated or minimally treated industrial wastes directly from the Warri refinery through the Ubeji Creek. The average atmospheric temperature in Ubeji is 25.5°C in the rainy season and 30.1°C in the dry season. The daily relative humidity values ranged from 55.5% in the dry season to 96% in the rainy season. The occupation of the human population in Ubeji is mainly fishing and they depend on the creek as a major outlet to the larger water body.

*Sample Collection :* Water samples for this study were collected at two different locations, up and downstream of the Ubeji River. Water was collected in a litre container at a distance of 200m between sampling stations (Fig.1). Samples of five fin-fish species (*Citharinus citharus*, *Liza falcipinis*, *Brycinus macrolepidotus*, *Polydactylus quadrifilis* and *Tilapia zilli*) collected from both up and downstream on the Ubeji River, were transported frozen to the laboratory for heavy metal analysis.

A total of 101 volunteers were recruited into the study after obtaining their informed consent. The volunteers live and work in Ubeji and are reported to have contact with Ubeji river. Blood (0.5ml) was collected on labeled filter paper from each person, filter papers were air dried and transported to the University of Ibadan for analysis. The study protocol followed approved ethical procedures for this study as obtained from the UI/UCH research ethics committee. Control (water, fish and human) samples were collected in and around Eleyele River in Ibadan, Nigeria.

*Laboratory analysis: Digestion of water samples,* 10ml of nitric acid was added to 50ml of each water sample and heated at 150°C for 30mins. 5ml of nitric acid was then added to each tube and heated for 30 minutes at 200°C, to the mixture was added 2ml of hydrogen peroxide before further heating at 200°C for 30minutes. The resulting solutions were allowed to cool at room temperature and then the volume made up to 25ml with distilled water (AOAC, 1995).

*Digestion of fish samples:* Fish samples were analysed by a modified procedure from the Association of Official Analytical Chemists (AOAC, 1995). One gram wet weight each of gill and muscle for each of the fin-fish sample was dried for 8hrs at 180°C. 0.3g of each dried sample was placed separately in labeled test-tubes and 5ml of a mixture of chloroform-

methanol-water (2:1:0.5) was added to each tube and allowed to stand overnight at room temperature for lipid extraction. The samples were subsequently

Thereafter, 20ml of de-ionized water was added to each tube to give a final Nitric acid concentration of Lead Cadmium, Zinc and Chromium using Atomic Absorption Spectroscopy, (model-analyst 200, PerkinElmer).

*Digestion of blood samples:* Blood samples were digested according to the method of Mei *et al.*, (2001). Four punches were made from each of the blood spotted air dried filter papers and transferred into labeled digesting test-tubes. Ten (10) ml of nitric acid was added to each tube and heated at 150°C for 30mins then another 5ml of nitric acid was added to each tube and further heated at 200°C for 30mins. 2ml of hydrogen peroxide was subsequently added to each sample and heated at 200°C for 30mins. The solution was allowed to cool and the volume was made up to 25ml with distilled water to compensate for evaporation.

## RESULTS AND DISCUSSION

The levels of Chromium(Cr), Cadmium(Cd), Lead (Pb) and Zinc(Zn) in water, fish and human blood samples from Ubeji were determined.

*Water Analysis:* Lead and Cadmium levels in water samples from Ubeji River were significantly higher than levels recorded in Eleyele River, which served as the control (Table 1). Chromium was not detected in Ubeji River. Lead and cadmium levels were significantly higher in water samples from Ubeji river than in the Eleyele control samples. This is probably as a result of heavy metals from crude oil sources, which are main pollutants in Ubeji river. (Achudume 2009) The heavy metal concentrations recorded in Ubeji river were higher than standard limits for portable water and aquaculture (WHO, 1996). Even though there was no indication that inhabitants of Ubeji drink from the river, aquatic life abound in the waters and can bioaccumulate these metals and subsequently transfer it to consumers. This is suggested by the high concentration of these metals recorded both in the fish species collected from the Ubeji river and the blood from the inhabitants of Ubeji who eat the fish from the river.

*Heavy metals in fish gills and muscle:* The concentrations of Cd, Zn and Pb in the muscle of the five fish species analysed were not significantly

washed in de-ionized water before the addition of 5ml of nitric acid to each tube for sample digestion.

20%. Digested samples were analyzed for levels of

different ( $p > 0.05$ ). The mean values for Pb (mg/g) were 76.07; 35.27; 37.80 42.15; 23.16 and 22.72 for *Citharinus citharus*, *Liza falcipinis*, *Brycinus macrolepidotus*, *Polydactylus quadrifilis*, *Tilapia zilli* and control samples respectively. Chromium was not detected in *B. macrolepidotus*, *P. quadrifilis* and *T. zilli* while mean values recorded in *C. citharus* and *L. falcipinis* were 0.48mg/g and 1.60mg/g respectively (Figures 1-4).

The pattern of heavy metal accumulation in the gills of the fish species was slightly different from the muscles. There was a highly significant difference in the concentrations of cadmium, zinc and lead recorded in the gill of the five species. Highest concentration of lead and cadmium was recorded in *B. macrolepidotus* ( $47.80 \pm 3.72$  and  $5.35 \pm 5.24$ ) and the lowest levels ( $29.92 \pm 15.01$  and  $2.38 \pm 2.25$ ) were in *Liza falcipinis* (Figures 1,4). The highest concentration of zinc ( $140.76 \pm 105.58$ ) was recorded in the gills of *C. Citharus* and the lowest in *L. falcipinis*, ( $61.23 \pm 38.72$ ). There was a significant difference between the values of chromium recorded in *B. macrolepidotus* ( $7.80 \pm 9.81$ ) when compared to concentration in the other species (Figure 3).

When comparing the pattern observed in the gills and muscle, the concentrations of zinc was highest in both gills and muscle of all five fish species, followed by levels of lead (Figures 2). The levels of chromium and cadmium were comparatively lower in the fish samples (Figure 1, 3). There was no appreciable significance in lead concentrations in the muscle of the five fish species used in this study; *Citharinus citharus* had lead levels almost twice the concentration recorded in some of the other fish species in this study. This concentration was also about 50 times higher than the permissible limit of 1.5 ppm, being the FAO/WHO (1984) recommended standard. Moreover, there were differences in the ability of the various fish species to accumulate lead. *Tilapia* had the least concentration of lead though the value was 15.3 times higher than the permissible limit. This report is similar to that of Obasohan (2007) in which high levels of heavy metals were detected in mudfish from Ogba River, Benin city, Nigeria. The high concentration of lead recorded in

this study may be due to recurrent oil-based pollutants which are the main sources of pollution to Ubeji River.

All the five fish species examined in this study had heavy metal concentrations higher than the permissible limit by FAO/WHO (1984). This suggests that these fish species may not be suitable for consumption. The variation in the level of heavy metal accumulation in the gills and muscle of the different fish species may support the view that there is a variation in ability of different fish organs to accumulate heavy metals. Vinodhini and Narayanan (2008) found that lead and cadmium accumulation in gills was relatively higher than other metals.

The gill has also been reported as an important site for the entry of heavy metals which provokes lesions and gill damage (Lock and Overbeeke, 1981; Bols *et al.*, 2001). Although Moore and Ramamurthy, (1984) reported that Cadmium is accumulated primarily in major organ tissues of fish rather than in muscles, in this study higher Cadmium concentration was found in the muscle than gills of most of the fish species examined.

**Heavy metal concentration in human blood:** Analysis of the blood samples collected showed lead levels in 61.39% of the study participants, cadmium in 75.25%, chromium in 98.01% and zinc in 99.01%. Chromium levels were significantly higher ( $1737.17 \pm 2996.01$ ) than the levels of any the other heavy metals ( $p < 0.05$ ), levels of cadmium ( $10.11 \pm 10.71$ ) were the lowest in the study group (Figure 5). The values of the heavy metals in the human blood in this study were higher than the stipulated permissible levels (WHO 1996).

There were gender-related differences in the concentrations of the metals in the participants. Cadmium ( $10.50 \pm 10.68$  mg/g) and Lead ( $129.73 \pm 440.93$  mg/g) levels in males were higher than in female participants ( $9.69 \pm 10.84$  mg/g and  $116.87 \pm 223.10$  mg/g respectively). Chromium and

Zinc levels were however higher in the females ( $1908.50 \pm 105.67$  mg/g and  $154.96 \pm 151.14$  mg/g respectively) than in the males ( $1575.71 \pm 909.9$  mg/g and  $144.06 \pm 218.97$ ). These differences were however not significantly different ( $p > 0.05$ ) for Cd, Pb, Cr and Zn respectively. The heavy metals except zinc were present in high amounts in the human blood samples, the levels of zinc recorded were below the permissible limit (WHO 1996). The source of the heavy metals detected in human blood in this study location may be linked to bioaccumulation from consumption of fishes from the Ubeji river.

Cadmium levels showed a weak negative, but significant ( $p < 0.05$ ) correlation with age of participants ( $r = -0.241$ ). Cadmium accumulation in human blood may likely reduce with age.

The high levels of the heavy metals from this study further underscore the high level of environmental pollution prevalent in Nigeria as a result of effluents and spillages from the oil and gas industry. Various other studies have reported high levels of environmental pollution in the Nigerian environment (Adekola and Saidu, 2005; Egbereonu and Ozuzu, 2005).

**Conclusion:** This study reports high level of heavy metal pollution in Ubeji River. The pollution occurs at levels that can constitute serious health problems for the inhabitants of this area. Efforts should be directed towards remediating the water body and stopping the discharge of pollutants from the refinery into the Ubeji river. It may not be out of place for the government to provide alternate source of protein to the inhabitants of Ubeji to reduce their consumption of polluted fish from the river until the water has been cleaned up.

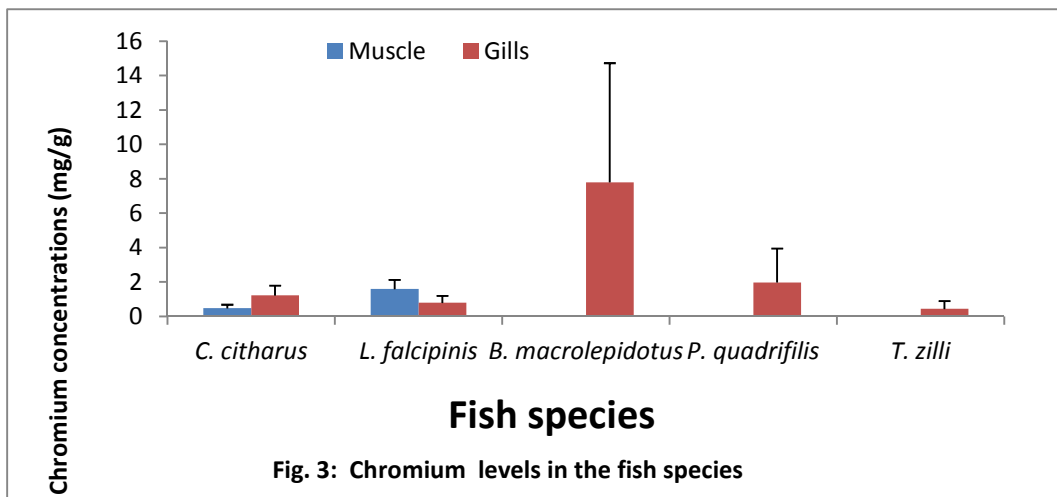
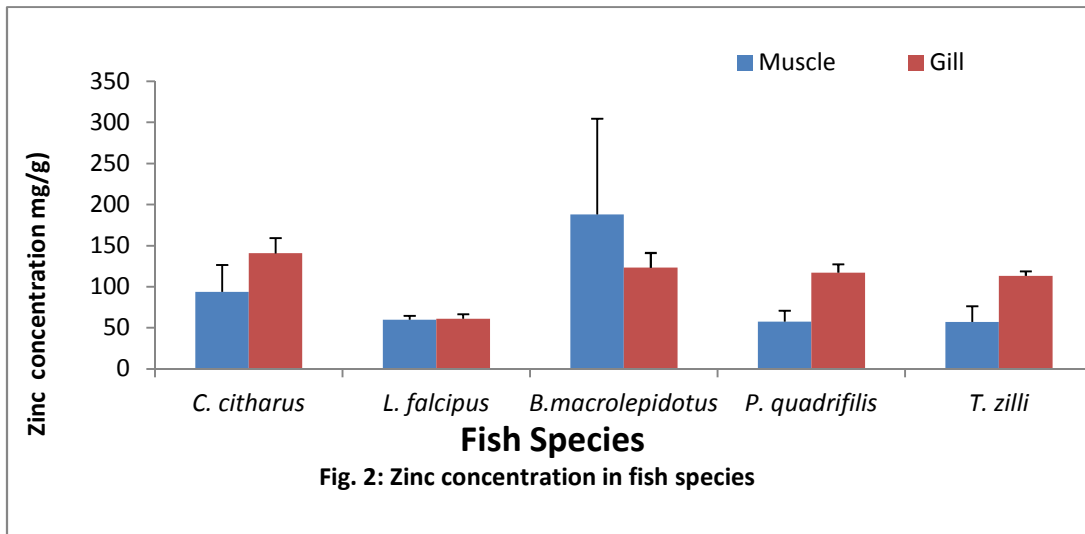
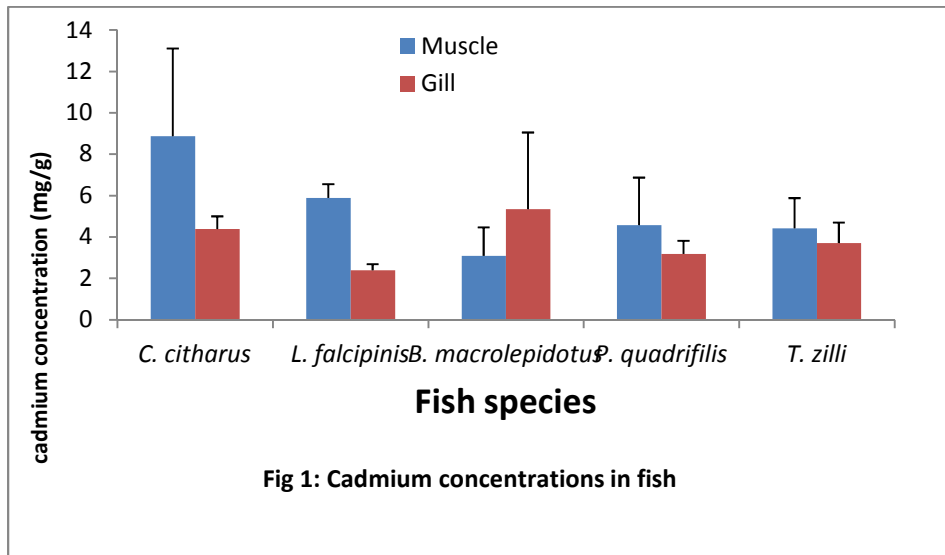
**Conflict Of Interest:** Authors declare no conflict of interest. **Acknowledgement:** The authors acknowledge Ubeji community and the study participants for their cooperation.

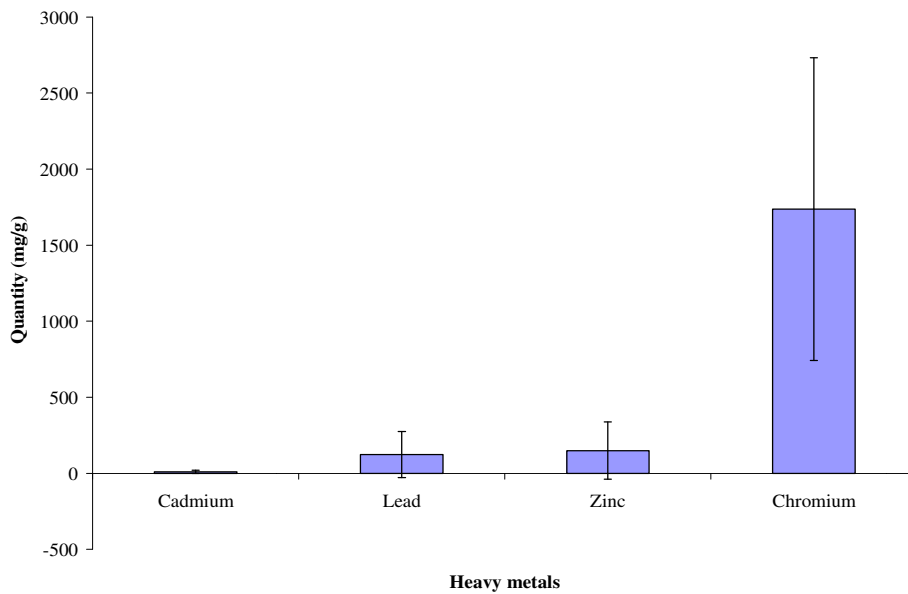
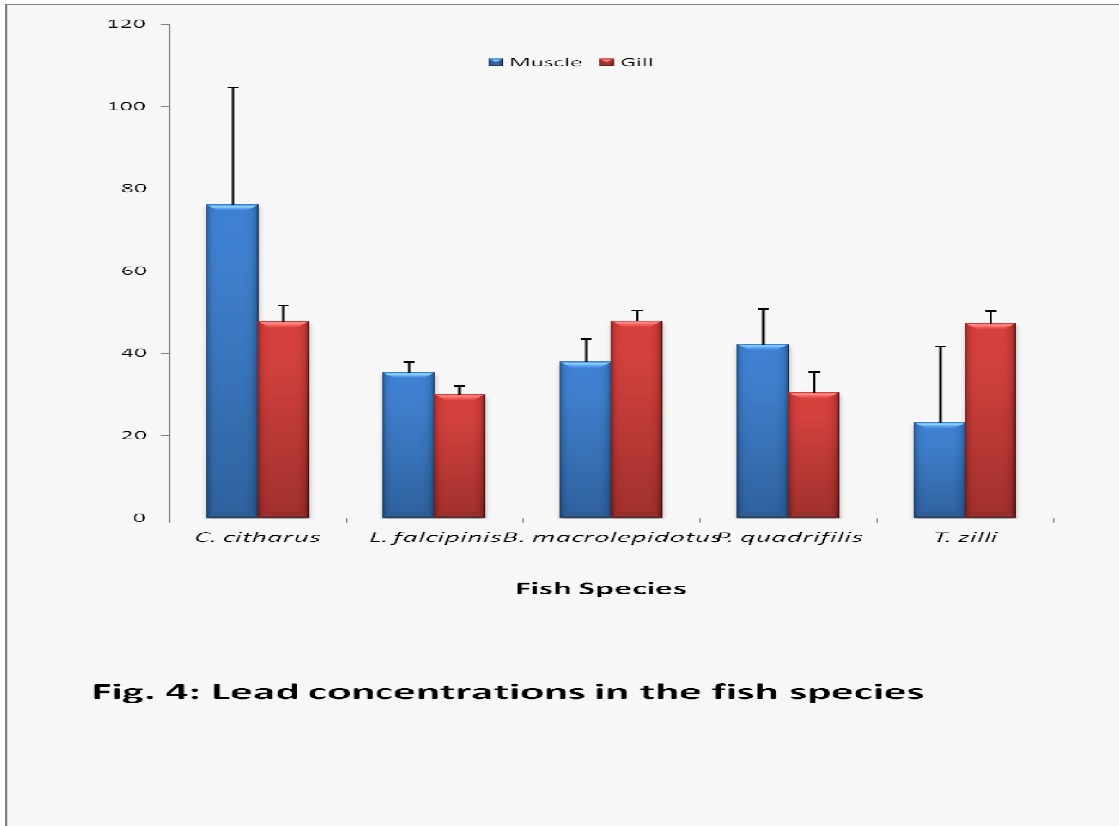
**Table 1:** Concentrations of heavy metals in water samples from Ubeji river

Heavy metal	Test sample (mg/L)	Control (mg/L)	t value	P value
Lead	0.051	0.036	8.660	0.037*
Cadmium	0.045	0.036	4.191	0.012*
Chromium	ND	0.037	-0.611	0.325
Zinc	0.253	0.276	-0.543	0.313

ND – Not detected

\*Differences in mean values of test samples and control are significantly different ( $p < 0.05$ )





**Fig 4: Heavy metal concentration in human blood from Ubeji**

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