

## Trace Metals Distribution in Fish Tissues, Bottom Sediments and Water from Okumeshi River in Delta State, Nigeria

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**Abstract:** Water samples, bottom sediments, Tilapia and Cat Fish from Okumeshi River in Delta state of Nigeria were analysed quantitatively for the presence of lead, nickel, chromium, manganese and cadmium using Atomic Absorption Spectrophotometer. The fishes contained higher concentration of manganese with a value of 7.77 mg kg<sup>-1</sup> against 2.76 mg kg<sup>-1</sup> in sediment and 0.13 mg L<sup>-1</sup> in water. Studies on the different parts of the fish revealed higher concentrations of 1.97 mg kg<sup>-1</sup> manganese in the muscle of tilapia fish while the lowest concentration of 0.13 mg kg<sup>-1</sup> was detected on the gill of catfish. The highest concentration of 0.62 mg kg<sup>-1</sup> cadmium was detected on the muscle of tilapia while the lowest concentration with a value of 0.04 mg kg<sup>-1</sup> was recorded in tilapia bone. In most of the fish samples, cadmium concentration was found to be above the maximum tolerable values provided by international institutions.

**Key words:** Trace metals, fish tissues, water, bottom sediments, Okumeshi river, institutions

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### INTRODUCTION

The pollution of the aquatic environment with heavy metals has become a world wide problem during recent years because they are indestructible and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000). Among environmental pollutants, metals are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi *et al.*, 2006). The presence of heavy metals in aquatic ecosystems is the result of two main sources of contamination; natural processes or natural occurring deposits and anthropogenic activities. The main sources of heavy metal pollution to life forms are invariably the result of anthropogenic activities (Kennish, 1992; Francis, 1994). In the fresh water environment, toxic metals are potentially accumulated in sediments and marine organisms and subsequently transferred to man through the food chain. Heavy metal concentration in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota (Camusso *et al.*, 1995) which generally exist in low levels in water and attain considerable concentration in sediments and biota (Namminga and Wilhm, 1976). Heavy metals including both essential and non essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms (Storelli *et al.*, 2005).

Studies on heavy metals in rivers, lakes, fish and sediments (Ozmen *et al.*, 2004; Begum *et al.*, 2005; Fernandes *et al.*, 2008; Ozturk *et al.*, 2008; Pote *et al.*, 2008; Praveena *et al.*, 2008) have been a major environmental focus especially during the last decade. Sediments have been reported to form the major repository of heavy metal in aquatic system while both allochthonous and autochthonous influences could make a concentration of heavy metals in the water high enough to be of ecological significance (Oyewo and Don-Pedro, 2003).

Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish even when the exposure is low. The presence of metal pollutant in fresh water is known to disturb the delicate balance of the aquatic systems.

Fishes are notorious for their ability to concentrate heavy metals in their muscles and since they play important role in human nutrition, they need to be carefully screened to ensure that unnecessary high level of some toxic trace metals are not being transferred to man through fish consumption (Adeniyi and Yusuf, 2007). This study is geared towards determining the distribution of heavy metal in the fish part, water and bottom sediments of Okumeshi River located in the Ukwuani Local Government Area of Delta State, Nigeria with the view to establishing

a baseline data on the current pollution status of the river. The results obtained from this study would also provide information for background levels of metals in the water, sediments and fish species of the River contributing to the effective monitoring of both environmental quality and health of the organisms inhabiting the river.

## MATERIALS AND METHODS

**Sample collection and preparation:** Two fish samples Cat fish (*Chrysichthys nigrodidatus*) and Tilapia (*Tilapia nilotica*) were collected from Okumeshi River. Fish specimens weighing 269.7 g were collected and dissected for gills, liver, muscles and bones.

Bottom sediments and water was also collected from the River. All samples were prepared following standard protocols (Welz and Sperling, 1999). Fish samples were dissected to collect different organs like gills, liver, bones and muscles. About 10-15 g of the native organs were taken into crucibles and dried inside a muffle furnace at 1500°C for 3 h. These were then cooled to room temperature and the dried weight taken. These were then transferred inside the cooled muffle furnace and slowly the temperature was raised to a range 500±50°C for 11 h. The samples were removed and cooled inside the desiccators to room temperature. A volume, 2.0 mL of concentrated HNO<sub>3</sub> was added into the crucible and swirled, then acidified as was gently warmed on a hot plate till evaporation of NO<sub>2</sub> ceased and then heating continued to evaporate the acid completely. The mass thus formed was transferred into the cool furnace once again. The furnace was gradually heated to a range of 450-500°C for 2 h and then the mass was cooled to room temperature. The process was repeated once again until white coloured ash was obtained. About 1.0 mL of 1.0N HCl was added and the mixture was gently warmed until a clear solution was obtained. These were then cooled and transferred into 25 mL volumetric flasks. Distilled water was added up to the mark and stored inside an incubator at 20°C.

**Water samples:** About 200 mL of water sample collected from the river was filtered through whatman 0.45 µm glass fibre filter and transferred to acid cleaned 250 mL polypropylene bottles and then acidified with concentrated Nitric acid to pH not exceeding 2.0.

**Bottom sediment samples:** Bottom sediment sample collected from the River was dried (80±10°C for 10 h in a hot air oven) homogenised and sieved for extraction of

lead, nickel, chromium, manganese and cadmium from dry ashes. About 1.0±0.05 g dried and grounded sediment samples were placed inside a crucible and ignited in a muffle furnace at 500°C for 3 h.

The ignited mass was cooled inside desiccators and transferred into a 100 mL borosil beaker. Inside the beaker was added 10 mL concentrated HCl and the suspension was swirled. The suspension was kept inside a thermostat controlled water bath in a temperature range of 70-80°C for 1 h.

The supernatant was decanted and kept inside a 100 mL volumetric flask. This contains mostly alkaline earth metals. To the residue in the beaker, 10 mL each of HCl (concentrated) and HClO<sub>4</sub> (concentrated, 70% pure) and few porous beads were added and was evaporated to dryness over a hot plate.

The process was repeated when necessary. The dried residue was dissolved completely by using minimum amount of concentrated HCl. This solution was then transferred to the same volumetric flask where previous extract containing alkaline earth metal extract was stored. The flask were then made up to the mark by distilled water and stored inside a refrigerator. These extracts were analysed for trace metals.

**Analysis of samples:** Atomic absorption Spectrophotometry (Buck Scientific Model-210) using element specific hollow cathode lamps in default condition by flame absorption mode was used to approximate the metal concentration within samples.

**Statistical analysis:** Data were presented as mean of duplicate determinations.

## RESULTS AND DISCUSSION

Table 1 shows the total extractable metals from Okumeshi River water sediments and other sediment quality guidelines. The heavy metal concentrations in sediment samples decreased in the sequence Mn>Cd>Ni>Cr>Pb.

Table 1: The trace metal concentration in the Okumeshi river sediment and comparison with sediment quality guidelines (mg kg<sup>-1</sup> dry weight)

Locality	Cd	Cr	Mn	Ni	Pb	References
LEL (Lowest Element Level)	0.60	26.00	-	16.000	31.00	NOAA, 2009
TEL (Threshold Element Level)	0.99	43.40	-	22.700	35.80	NOAA, 2009
PEC (Probable Effect Concentration)	4.90	111.00	-	48.600	128.00	NOAA, 2009
SEC (Severe Effect level)	10.00	110.00	-	75.000	250.00	NOAA, 2009
Okumeshi river	1.32	0.87	2.76	1.210	0.45	This Study

Table 2: The trace metal concentration in Okumeshi river water and comparison with water quality guidelines (mg L<sup>-1</sup>)

Guidelines	Cd	Cr	Mn	Ni	Pb	References
SON	0.005	0.05	0.20	0.02	0.01	SON, 2007
WPCL	0.003	0.02	-	0.02	0.01	WPCL, 2004
CIW	0.010	0.10	-	0.20	5.00	Anonymous, 1997
WHO	0.010	0.05	0.50	0.02	0.05	WHO, 2003
EPA	0.010	0.05	0.02	-	0.05	EPA, 2002
EC	5.000	50.00	0.05	20.00	10.00	EC, 1998
Okumeshi river	0.030	0.09	0.13	0.27	0.01	This study

Table 3: Trace metals concentration (mg kg<sup>-1</sup> dry weight) in fish tissues from Okumeshi river samples

Samples	Elements				
	Pb	Ni	Cr	Mn	Cd
<b>Tilapia</b>					
Gill	<0.01	0.11	0.06	0.17	0.21
Liver	0.01	0.14	0.17	0.49	0.31
Muscle	<0.01	0.17	0.06	1.97	0.62
Bone	<0.01	0.07	0.04	1.48	0.04
<b>Catfish</b>					
Gill	<0.01	0.05	0.04	0.13	0.14
Liver	0.01	0.09	0.14	0.43	0.28
Muscle	<0.01	0.13	0.04	1.89	0.45
Bone	<0.01	0.06	0.05	1.21	0.09

Table 2 shows the water quality constituent of Okumeshi river and reference freshwater values. Trace metals concentration in the river were decreased in the sequence of Ni>Mn>Cr>Cd>Pb. Table 3 shows the trace metals concentration in fish tissues from Okumeshi river samples.

The result obtained for tilapia showed that the trace metals concentration were decreased in the sequence Cd>Mn>Ni>Cr>Pb in gills, Mn>Cd>Cr>Ni>Pb in liver, Mn>Cd>Ni>Cr>Pb in muscle and Mn>Ni>Cr and Cd>Pb in bones. The result obtained for catfish showed that the trace metals concentration decreased in the sequence Cd>Mn>Ni>Cr>Pb in gills, Mn>Cd>Cr>Ni>Pb in liver, Mn>Cd>Ni>Cr>Pb in muscle and Mn>Cd>Ni>Cr>Pb in bones.

The higher elemental concentration bottom sediments of Okumeshi river was in agreement with the concept that bottom sediment contains higher concentrations of metals than that of overlying water (Depinto and Martin, 1980). In the bottom sediments, manganese was found to be of higher concentration with value 2.76 mg kg<sup>-1</sup> followed by cadmium with value 1.32 mg kg<sup>-1</sup> and the least was lead with values 0.45 mg kg<sup>-1</sup>. The metal concentrations obtained from the sediment samples were compared with sediment quality guidelines which showed that these concentrations did not exceed the Probable Effect Concentration (PEC) levels.

The lead, nickel, chromium, manganese and cadmium concentration in the river water was compared with national and international standards. The result obtained showed that with the exception of manganese and lead, the trace metal concentrations in water exceeded the

Table 4: The tolerable values of some trace metals (mg kg<sup>-1</sup> dry weight)

Source	Cd	Cr	Mn	Ni	Pb	References
UNEP	0.30	-	-	-	0.30	UNEP, 1985
IAEA-407	0.18	0.73	11.0	0.60	0.12	Wyse <i>et al.</i> , 2003
FEPA	0.05	<0.10	5.0	-	0.20	FEPA, 1991
Directive 2005/78/EC	0.05	-	-	-	0.20	EC, 2005

(WHO, 2003), EPA (Environmental Protection Agency), WPCL (Water Pollution Control Legislation, 2004), CIW (Anonymous, Criteria for Irrigation Water) and Standards Organisation of Nigeria (SON, 2007) guidelines (Table 2).

Concentrations of trace metals in fish tissues were always higher than that of water (Chale, 2002). Entry of metals occurs either through gill membrane or through ingestion. A difference in concentration of trace metals in fish organs as indicated by the study was reported by Mathis and Cumming (1973), Kalay and Canli (2000), Bury *et al.* (2003) and Chatterjee *et al.* (2006). Accumulation of bioactive metals like lead, nickel, chromium, manganese and cadmium was actively controlled by fish through different metabolic processes and the level of accumulations usually dependent of ambient concentrations. On the other hand, environmental concentrations affect the accumulation of non-essential toxic elements like lead (Pattee and Pain, 2003) (Table 4).

Some bioactive metals play important role in metabolism, thus in physiology and pathology of fish. Metals like manganese function as a cofactor in several enzyme systems (Bury *et al.*, 2003). However, when in excessively high concentration, these bioactive metals may pose serious threats to normal metabolic processes.

## CONCLUSION

In fish, gills are considered to be the dominant site for contaminant uptake because of their anatomical and/or physiological properties that maximise absorption efficiency from water (Hayton and Baron, 1990). However, it was evident from the study that, in general muscle and liver were the sites of maximum accumulation for the elements while gill was the overall site of least metal accumulation in both species.

Fishes are known to be notorious for their ability to concentrate trace metals in their muscles (Adeniyi and Yusuf, 2007). Cadmium level in liver and muscle of Tilapia and Catfish were above the tolerable values of trace metals in fish. Although, the levels of other trace metals were found to be within permissible limits, bioaccumulation and magnification is capable of leading to toxic level of these metals in fish even when the exposure is low. There is need for constant monitoring of

the trace metals concentration in Okumeshi river since the river serves as source of drinking water, irrigation and fish for the local inhabitants in the study area.

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#### REFERENCES

- Adeniyi, A.A. and K.A. Yusuf, 2007. Determination of heavy metals in fish tissues, water and bottom sediments from Epe and Badagry Lagoons, Lagos, Nigeria. *Environ. Monitor. Assess.*, 37: 451-458.
- Begum, A., M.N. Amin, S. Kaneco and K. Ohta, 2005. Selected elemental composition of fish, *Tilapia nilotica*, *Cirrhina mrigala* and *Clarius batrachus* from the fresh water Dhanmondi Lake in Bangladesh. *Food Chem.*, 93: 439-443.
- Bury, N.R., P.A. Walker and C.N. Glover, 2003. Nutritive metal uptake in teleost fish. *J. Exp. Biol.*, 206: 11-23.
- Camusso, M., L. Vigano and R. Baistrini, 1995. Bioaccumulation of trace metals in rainbow trout. *Ecotoxicol. Environ. Safety*, 31: 133-141.
- Censi, P., S.E. Spoto, F. Saiano, M. Sprovieri and S. Mazzola *et al.*, 2006. Heavy metals in coastal water system. A case study from the North Western Gulf of Thailand. *Chemosphere*, 64: 1167-1176.
- Chale, F.M.M., 2002. Trace metal concentration in water, sediments and fish tissues from lake Tanganyika. *Sci. Total Environ.*, 299: 155-161.
- Chatterjee, S., B. Chattopadhyay and S.K. Muckhopadhyay, 2006. Trace metal distribution in tissues of Cichlids (*Oreochromis niloticus* and *O. mossambicus*) collected from waste water fed fish ponds in East Calcutta wetlands, A Ramsar site. *Acta Ichthyol. Piscatoria*, 36: 119-125.
- Depinto, J.V. and S.C. Martin, 1980. Aquatic sediments. *J. Water Pollut. Control Federat.*, 52: 1656-1670.
- EC, 1998. Council directive 98/83/EC of November 1998 on the quality of water intended for human consumption. L330/32, European Commission. <http://vlex.com/vid/quality-water-intended-human-consumption-24517862>
- EC, 2005. Commission regulation (EC) No. 78/2005 of 19 January 2005 amending regulation (EC) No. 466/2001 as regards heavy metals. *Official J. Eur. Union*, L16: 43-45.
- FEPA, 1991. Guidelines and standard for environment pollution control in Nigeria. Federal Environment Protection Agency, Lagos.
- Fernandes, C., A. Fontainhas-Fernandes, D. Cabral and M.A. Salgado, 2008. Heavy metals in water, sediment and tissues of *Liza saliens* from *Esmoriz-paramos* Lagoon, Portugal. *Environ. Monitor. Assess.*, 136: 267-275.
- Francis, B.M., 1994. Toxic Substances in the Environment. 2nd Edn., John Wiley and Sons Inc., New York, pp: 360.
- Hayton, W.L. and M.G. Baron, 1990. Rate limiting barriers to xenobiotic uptake by the gill. *Environ. Toxicol. Chem.*, 9: 151-157.
- Kalay, M. and M. Canli, 2000. Elimination of essential (Cu, Zn) and non-essential (Cd, Pb) metals from tissues of a fresh water fish, *Tillapia zilli*. *Turk. J. Zool.*, 24: 429-436.
- Kemish, M.J., 1992. Ecology of Estuaries: Anthropogenic Effects. CRC, Press, Boca Raton, FL pp: 494.
- MacFarlane, G.R. and M.D. Burchett, 2000. Cellular distribution of copper, lead and zinc in the grey mangrove, *Avicennia marina* (Forsk.) Vierh. *Aquat. Bot.*, 68: 45-59.
- Mathis, B.J. and T.F. Cumming, 1973. Selected metals in sediments, water and biota in the Illinois River. *J. Water Pollut. Control Federat.*, 45: 1573-1583.
- Namminga, H.N. and J. Wilhm, 1976. Effect of high discharge and an oil refinery clean up operation on heavy metals in water and sediments in skeleton creek. *Proc. Oklahoma Acad. Sci.*, 56: 133-138.
- Oyewo, E.O. and K.N. Don-Pedro, 2003. Lethal and sub lethal effects of copper to the African Catfish (*Clarias gariepinus*). *West Afr. J. Appl. Ecol.*, 4: 115-123.
- Ozmen, H., F. Kulahci, A. Cukurovali and M. Dogru, 2004. Concentrations of heavy metals and radioactivity in surface water and sediment of Hazar Lake (Elazig, Turkey). *Chemosphere*, 55: 401-408.
- Ozturk, M., G. Ozozen, O. Minareci and E. Minareci, 2008. Determination of heavy metals in tissues of fishes, water and sediment from the Demirkopru Dam Lake (Turkey). *J. Appl. Biol. Sci.*, 2: 99-104.
- Pattee, O.H. and D.J. Pain, 2003. Lead in the Environment. In: Handbook of Ecotoxicology, Hoffman, D.J., B.A. Rattner, G.A. Jr. Burton and J. Jr. Cairn (Eds.). 2nd Edn., Lewis Publishers, Boca Raton, FL USA., pp: 1290.
- Pote, J., L. Haller, J.L. Loizeau, A.G. Bravo, V. Satre and W. Wildi, 2008. Effects of sewage treatment plant outlet pipe extension on the distribution of contaminants in the sediments of the Bay of Vidy, lake Geneva, Switzerland. *Bioresour. Technol.*, 99: 7122-7131.

- Praveena, S.M., M. Radojevic, M.H. Abdullah and A.Z. Aris, 2008. Application of sediment quality guidelines in the assessment of mangrove surface sediment in mengkabong Lagoon, Sabah, Malaysia. *Iranian J. Environ. Health Sci. Eng.*, 5: 35-42.
- SON, 2007. Nigerian standards for drinking water quality. Nigerian Industrial Standards NIS: 554. [http://www.unicef.org/nigeria/ng\\_publications\\_Nigerian\\_Standard\\_for\\_Drinking\\_Water\\_Quality.pdf](http://www.unicef.org/nigeria/ng_publications_Nigerian_Standard_for_Drinking_Water_Quality.pdf).
- Storelli, M.M., A. Storelli, R. D'ddaabbo, C. Morano, R. Bruno and G.O. Marcotrigiano, 2005. Trace Elements in loggerhead turtles (*Caretta caretta*) from the Eastern Mediterranean: Overview and Evaluation. *Environ. Pollut.*, 135: 163-170.
- UNEP, 1985. Reference methods for marine pollution studies. Determination of Total Hg in Marine Sediments and Suspended Solids by Cold Vapour AAS, Vol. 26.
- WHO, 2003. Malathion in drinking water. Background Document for Preparation of WHO Guidelines for Drinking Water Quality. World Health Organistaion (WHO/SDE/WSH/03.04/103). Geneva.
- WPCL, 2004. Land based water quality classification. Official Journal, 25687, Water Pollution Control Legislation, Turkey.
- Welz, B. and M. Sperling, 1999. Atomic Absorption Spectrophotometry. 3rd Edn., Wiley-VCH., Weinheim, Germany.
- Wyse, E.J., S. Azemard and S.J. Mora, 2003. Report on the world wide inter-comparison exercise for the determination of trace elements and methyl mercury in fish Homogenate IAEA-407. IAEA/AL/144 (IAEA/MEL/72), IAEA, Monaco.