KMITL Sci. Tech. J. Vol. 7 No. 1 Jan. - Jun. 2007

# DETERMINATION AND ASSESSMENT OF HEAVY METAL CONTENT IN FISH AND SHELLFISH IN ABA RIVER, ABIA STATE, NIGERIA

A.O. Ubalua[1*], U. C. Chijioke[2] and O.U. Ezeronye[3]

[1]Cassava Research Programme
National Root Crops Research Institute (NRCRI), Umudike,
P. M. B 7006, Umuahia, Abia State, Nigeria

[2] College of Medicine
Abia State University (ABSU),
Abia State, Nigeria

[3]Department of Microbiology,
Michael Okpara University of Agriculture, Umudike,
P.M.B. 7267 Umuahia, Abia State, Nigeria.

## ABSTRACT

Levels of lead (0.064μg/l), iron (0.81μg/l), zinc (4.82μg/l), copper (0.19μg/l), arsenic (0.05μg/l), manganese (0.03μg/l), chromium (0.005μg/l) and mercury (0.01μg/l) were determined in the water and in some fish and shellfish from Aba river, Nigeria. They were found to be below the maximum allowable levels set by the United States Environmental Protection Agency (USEPA), except for lead, iron and mercury. This implies that the waste assimilation capacity of the river is high, a phenomenon that could be ascribed to dilution, sedimentation and continuous water exchange. Emperical evidence shows that the metals were at low levels in these organisms. However, when compared with levels determined in fish from a rural river, relative enrichment, ranging from 0.01 for lead to1.5 for zinc, were observed in the Aba river fish. This is an indication that urban and industrial wastes discharged into the Aba river has had a significant effect on the ecological balance of the river.

**KEYWORDS**: Heavy metals, pollution, waste assimilation, lead, fish and shellfish

*Corresponding author: Tel: 0803-545-7833 E-mail: alfreduba@yahoo.com

## 1. INTRODUCTION

Aba river is a deep freshwater river in southern Nigeria. The river is of economic importance in Abia State, Nigeria, hence it's use for various human activities including car washing and fishing. People living within the uptsream vicinity draw water from the river for drinking and other domestic purposes. The river originates from the hinterland of Aba and stretches down to Cross Rivers State where it empties with its creeks into the Atlantic ocean. The river receives copious amounts of wastes from industries and abattoirs sited along its course. Aba ranks as about the second highest industrialized city in Nigeria and is thickly populated. Urban waste management in the city is very poor and garbage disposal practices here is, at present, in a least to be desired state

The enrichment of heavy metals in Aba river has been reported in previous research papers [7]. Process water from the cosmetic, detergent and textile industries located near the river contains large amounts of heavy metals, which when in super abundance may cause disruption to the ecological balance of the river [13]. Allochthonous and authochthonous influences could make concentrations of heavy metals in the water high enough to be of ecological significance. Moreover, bioconcentration and biomagnification could lead to toxic levels of these metals in organisms, even when the exposure level is low [11]. The proven toxicity of high concentrations of heavy metals in water to fish and other aquatic life poses the problem of an ultimate dis-equilibrium in the natural ecological balance [4], [2]. Under such conditions, the toxicity of a moderately toxic metal could be enhanced by synergism [12] and, as a result, fish populations may decline [7]. Apart from destabilising the ecosystem, the accumulation of these toxic metals in aquatic food is a potential threat to public health. The Minamata Bay epidemic in Japan remains a classic example of this phenomenon [ 8].

Dumping wastes into rivers contribute to the larger problem of river pollution, which can seriously damage the marine environment and cause health hazards to people in some areas. Botkin and Keller [3] reported that shellfish have been found to contain organisms that cause diseases, such as polio and hepatitis. Recent work suggest that toxic materials threaten the ocean bottom as well as the entire marine ecosystem. The base of the marine food chain consists of planktonic life abundant in the upper 3mm of ocean water. The young of certain fish and shellfish also reside in the upper few millimeters of water in the early stages of their life [3]. Unfortunately, the upper few millimeters of the ocean also tend to concentrate pollutants, such as toxic chemicals and heavy metals. One study reported that the concentrations of heavy metals including zinc, lead, and copper in the upper 3mm (or microlayer) are from 10 to 1000 times higher than in the deeper waters. There is a fear that disproportionate pollution of this microlayer will have especially serious effects on marine organisms [9].

Marine pollution can also have major impacts on people and society. Contaminated marine organisms may transmit toxic elements or diseases to people who consume them. When solid waste, oil and other materials pollute beaches and harbours, there is a loss to the visual amenity of the river. The economic loss, as a result, is considerable. Not only does loss of shellfish from pollution in the United States amount to many millions of dollars per year but a great deal of money is spent cleaning up solid and liquid waste and other pollutants in coastal areas [5]. Poor management of solid municipal waste poses great discomfort and danger to the human environment. Concerns over potential health related issues make it imperative that all the sewage that is discharged to the river should undergo secondary treatment before discharge.

There are two main seasons in Nigeria-the dry and rainy seasons. The rains commence in the Aba area from March, reaching it's the peak between July/August and receding in November. The average annual variation of rainfall is about 20% of the mean total [10]. During these rains, immense volumes of urban run-off water enters the river from its vast watershed. This influx of run-off characteristically delivers into the river high fluxes of suspended solids, nutrients and other pollutants washed from the land and refuse dumps which have remained common features in the urban centres. This research paper assesses the levels of heavy metals in fish and shellfish as well as the assimilative capacity of the water body. Data obtained could be helpful in defining future waste management practices in the area.

## 2. MATERIALS AND METHODS

### 2.1 Sampling

Five different water samples were each collected with 1 litre sterile polyvinyl chloride (PVC) plastic water bottles from the five designated sampling points in Aba river. At each point, three water samples were drawn at random from three points and pooled. This was carried out by dipping the bottles below the water surface to minimize contamination by surface film. Dry season (November/December to March) samples were collected in January while rainy season (March/April to November) samples were collected in July. The samples were subsequently placed on ice in a cooler and transported to the laboratory for analysis.

Fish and shellfish were harvested from the Aba and Imo rivers for analysis. Fish and shellfish were collected from the Imo river for comparative studies. The fish included Mugil cephalus and Tilapia guineensis while Tympanotonus fuscatus, Clibanarius africana and Crassestrea gasar represented typical shellfish. The Imo river is a rural river that is located away from direct waste discharge and as such represents average general conditions in terms of pollutant levels in a rural river. The fish species used in the analysis were selected based on their abundance in the river and their popularity in Nigerian local diets.

### 2.2 Analysis

Recovery experiments conducted with 1% oxine solution in chloroform (3g in 200ml) showed optimum recoveries ranging from 61% for copper (cu) to 76% for iron (fe) at pH7 in a one step recovery of all the metals. The pH of each unfiltered water sample was adjusted to 7 using drops of dilute HCl and the metals were recovered from 500ml aliquots by shaking with 25ml of 1% oxine in chloroform for 2mins. The bottom layer was decanted into a 100ml beaker and the remaining chloroform in solution evaporated at low temperature in a water bath. The residue was dissolved with 5ml of 1:1HCl, filtered into a 25ml standard flask using Whatman no.1 filter paper and the solution made up to the mark with distilled water [12].

Metal free water for preparing blank and standard solutions were obtained by shaking each aqueous layer with 25ml of 1% oxine solution. The chloroform layer was discarded, leaving the condensate. A 500ml aliquot of the 'metal free' water was shaken with 25ml of the oxine solution and the extract subjected to the same procedures as the sample extracts. The resulting solution was set aside as a blank. Three 500ml serially diluted standard solutions containing all the metals in parts per million (ppm) ranges were prepared using the 'metal free' water as a diluent. These were also extracted with 25ml of the oxine solution and the extracts subjected to the same procedures as sample and blank extracts.

The fish samples were de-scaled, washed with distilled water and left to thaw enough for skinning and cutting of muscle fillets to be completed before the onset of drainage of body fluid. Muscle samples of M.cephalus and T.guineensis were obtained from 8 and 5 fish respectively, while the whole of the meat from 8 shellfish were used for shellfish analysis. The samples were homogenised separately in a mortar and weighed accurately in a porcelain crucible. Before ashing, 1ml of conc. HNO3 was added to the samples and allowed to pre-digest overnight in order to reduce losses of volatile metals. The samples were charred on a electric hot plate before ashing in a muffle furnace at 550oc for 4hrs. The white ash was dissolved in 5ml of 1:1 HCl, and a solution made in a 25ml standard flask [12].

Metal concentrations of the samples were read against appropriate blank and standard solutions using a Perkin-Elmer model 306 Atomic Absorption spectrophotometer (AAS) with an oxy-acetylene flame. A blank solution for the biotic samples was made by diluting 1ml conc.

HNO3 with 5ml 1:1 HCl and a 25ml solution made up with distilled water. The emperical data generated were analyzed statistically.

## 3. RESULTS AND DISCUSSION

The average levels of zinc, copper, manganese, chromium, mercury and arsenic were below the United States Environmental Protection Agency (EPA) maxima, except for lead and iron. They were not comparable to those obtained in the Niger Delta Waters (Table 1). Though, levels of lead and iron were high, they were not significant. Analysis of the variance (ANOVA) did not reveal significant spatial variations in any of the metals, neither did the least significant digit (LSD) reveal any significant seasonal variations ($P<0.05$). The low levels of metals determined could be as a result of dilution, sedimentation and continuous water exchange. Though the water flow in Aba river is mainly slow with little or no upwelling during the rainy season, immense volumes of fresh water passes through the river and out to the sea. The Aba river forms the major outlet for water draining a vast watershed, hence the influx has a lot of force and only a short residence time in the river. During the rainy season, there is more than twice the dilution of river water as normal. The short residence time of the influx means that most of the input materials are discharged into the sea, leaving a comparatively small quantity in the river. Slow-flow conditions enhance sedimentation, thus sedimentation would likely become the more important mechanism for removing heavy metals and other pollutants from the water at low tide and during the dry season when the influx of fresh water is very minimal. Thus the accumulative impact of all the processes described above is that heavy metal levels are kept low in spite of high fluxes from industrial and urban wastes including the immense urban run-off [7].

Data obtained by analysis of fish and the shellfish are presented in Table 2, and were used for comparative studies of heavy metal accumulation in biotic components having different ecological characteristics. Emperical data obtained revealed that feeding modes influenced accumulation patterns, as exemplified by *C.gasar*. *C.gasar*, being a filter feeder among all three shellfish, recorded the lowest levels of all the metals except zinc. The metal levels are comparable to those determined in fish which feed by picking food near the water surface. The levels in T. guineensis and M.cephalus, which are deposit feeders are high ($P<0.05$). The variation in the occurrence of high levels of zinc in *C. gasar*, higher ($P<0.05$) levels of zinc and copper in T. guineensis's muscle than in M. caphalus's muscle could be explained by their intrinsic physiological characteristics.

Fish head, a favourite delicacy in this part of the world was analysed to ascertain the content of heavy metal in consumed fish. The student t-test revealed that T. guineensis head contained high ($p<0.05$) manganese, and zinc than the fish muscle. M. cephalus head was found to contain higher ($p<0.05$) manganese, lead and zinc levels than the fish muscle. These findings suggest that fish head, often eaten together with the gills by the unsuspecting consumers, could contribute significantly to total lead content in consumed fish which when in excess may cause mental retardation, un-coordination and bizarre behavior in humans [3].

The empirical figures in Table 3 are at variance with that of [13], as a result of rapid urbanization and industrialization that is associated with Lagos State, Nigeria. These have brought with it alarming unmanageable, inevitable and persistent problems associated with environmental degradation.

The impact of waste disposal in the rivers were assessed by comparing the metal levels in the Aba river fish with those determined in fish from the Imo river, a rural water, and with some literature values in Table 3. Comparative studies of "metal enrichment" in the rivers show relative presence of the heavy metals in Aba river fish while the metal levels in Imo river fish were below detection. This confirms the earlier report concerning a significant impact which urban and industrial waste disposal has had on heavy metal baseline levels in the Aba river.

The current national specification for lead in petrol sold in Nigeria is 0.7g Pb/l, which, based on national daily petrol consumption of about 20 million litres per day emits via the motor exhaust pipe an estimated 15,000kg of lead per day [1]. On the basis of available records and surveys, no practical attempts have been initiated to minimise the environmental impact of this source of lead [1].

## 4. CONCLUSIONS

Research conducted by this paper found that high levels of lead in Aba river fish could be traced to urban and industrial wastes, leaded-petrol and expired motor batteries commonly dumped by battery chargers around their workshops located near the river. Waste management in urban and industrial centres in Nigeria, especially around the city of Aba, have remained very unsatisfactory to-date and it can be concluded that this poses a health hazard to both aquatic life and humans alike.

**Table 1** Seasonal mean value of heavy metal levels in the surface sediments of the Aba river, Abia state, Nigeria

| VARIABLES | UP STREAM1 | UP STREAM2 | ABATTOIR | DOWN STREAM1 | DOWN STREAM 2 | MEAN | EPA MAXIMAa | NIGER DELTA |
|---|---|---|---|---|---|---|---|---|
| Pb | | | | | | | | |
| Dry season | 0.04 | 0.12 | 0.08 | 0.08 | 0.06 | 0.08±0.03 | | |
| Rainy season | 0.04 | 0.08 | 0.04 | 0.04 | 0.06 | 0.05±0.02 | | |
| MEAN | 0.04 | 0.1 | 0.06 | 0.06 | 0.06 | 0.064 | 0.05 | Nd-22.45 |
| Fe | | | | | | | | |
| Dry season | 0.82 | 0.96 | 0.88 | 0.84 | 0.84 | 0.89±0.06 | | |
| Rainy season | 0.84 | 0.68 | 0.68 | 0.88 | 0.64 | 0.74±0.12 | | |
| MEAN | 0.83 | 0.82 | 0.78 | 0.86 | 0.74 | 0.81 | 0.1 | 94.35-901.00 |
| Zn | | | | | | | | |
| Dry season | 3.80 | 6.80 | 6.40 | 4.20 | 4.20 | 5.08±1.04 | | |
| Rainy season | 3.64 | 4.62 | 6.48 | 3.80 | 4.20 | 4.55±1.44 | | |
| MEAN | 3.72 | 5.71 | 6.44 | 4.0 | 4.20 | 4.82 | 5.0 | 4.50-42.86 |
| Cu | | | | | | | | |
| Dry season | 0.18 | 0.24 | 0.24 | 0.20 | 0.18 | 0.24±0.03 | | |
| Rainy season | 0.08 | 0.20 | 0.12 | 0.18 | 0.12 | 0.14±0.05 | | |
| MEAN | 1.13 | 0.22 | 0.18 | 0.19 | 0.15 | 0.19 | 1.0 | 3.1-34.03 |
| As | | | | | | | | |
| Dry season | 0 | 0.12 | 0.06 | 0.06 | 0.04 | 0.06±0.04 | | |
| Rainy season | 0 | 0.04 | 0.02 | 0.04 | 0.04 | 0.03±0.02 | | |
| MEAN | 0 | 0.08 | 0.04 | 0.05 | 0.04 | 0.05 | 0.05 | - |
| Mn | | | | | | | | |
| Dry season | 0 | 0 | 0.04 | 0.04 | 0 | 0.02±0.02 | | |
| Rainy season | 0 | 0.02 | 0.04 | 0.06 | 0.02 | 0.03±0.02 | | |
| MEAN | 0 | 0.01 | 0.04 | 0.05 | 0.01 | 0.03 | 0.05 | - |
| Cr | | | | | | | | |
| Dry season | Nd | 0.04 | Nd | Nd | Nd | 0.01±0.02 | | |
| Rainy season | Nd | 0.02 | Nd | Nd | Nd | 0.00±0 | | |
| MEAN | Nd | 0.03 | Nd | Nd | Nd | 0.005 | 0.05 | - |
| Hg | | | | | | | | |
| Dry season | 0.01 | Nd | Nd | 0.02 | 0.02 | 0.01±0.02 | | |
| Rainy season | 0 | Nd | Nd | 0.02 | 0.02 | 0.1±0.02 | | |
| MEAN | 0.01 | Nd | Nd | 0.02 | 0.02 | 0.01 | 0.002 | - |

All values are in µg/l; A: source; EPA (1976); B: source; Kakulu (1985), nd :not detectable

**Table 2** Heavy metals levels in shellfish and fish in Aba river, Abia State, Nigeria

| Shellfish | Pb | Fe | Zn | Cu | As | Mn | Cr | Hg |
|---|---|---|---|---|---|---|---|---|
| T.fuscatus | 0.02±0.02 | 0.3±0.02 | 1.0±0.06 | 0.03±0.02 | 0.01±0.02 | 0.01±0.02 | 0.0±0 | 0.0±0 |
| C.africana | 0.03±0.02 | 0.5±1.40 | 2.0±1.21 | 0.04±0.02 | 0.02±0.02 | 0.02±0.02 | 0.01±0.02 | 0.01±0.02 |
| C.gasar | 0.01±0.02 | 0.02±0.02 | 3.02±0.05 | 0.02±0.02 | 0.01±0.02 | 0.0±0 | 0.0±0 | 0.01±0.02 |
| FISH | | | | | | | | |
| M.cephalus | 0.01±0.02 | 0.3±0.02 | 1.5±0.8 | 0.14±0.61 | 0.2±0.12 | 0.01±0.04 | 0.0±0 | 0.01±0.04 |
| T.guineensis | 0.02±0.02 | 0.35±0.02 | 2.5±0.02 | 0.03±0.03 | 0.01±0.04 | 0.2±0.02 | 0.0±0 | 0.01±0.04 |

Data are mean ± std. dev.

**Table 3** Comparison of literature standards with metal levels found in Imo and Aba river fish

| | **Pb** | **Fe** | **Zn** | **Cu** | **As** | **Mn** | **Cr** | **Hg** |
|---|---|---|---|---|---|---|---|---|
| Lit. std. | 2.0 b,c | - | 40 b,50 c | 20b30c | - | - | - | - |
| Imo River fish M.cephalus | Nd | 0.02 | 0.05 | Nd | nd | nd | nd | nd |
| Aba River Fish M.cephalus | 0.01 | 0.30 | 1.5 | 0.14 | 0.2 | 0.01 | nd | 0.01 |

All values are in µg/g, wet wt.
A:source:Nauen (1983)
b : New Zealand
c : United Kingdom
Lit. std.: Literature standard.

## 5. ACKNOWLEDGEMENTS

We are grateful to the Executive Director of NRCRI, Umudike, Umuahia, Abia State, Nigeria for allowing this work to be conducted in their Central Services Laboratory and to Professor O.U. Ezeronye of the Dept. of Microbiology, Michael Okpara University of Agriculture, Umudike, Umuahia Abia State, Nigeria for his professional advice.

## REFERENCES

[1] Arah, R.O. **1985**. Lead-free gasoline in Nigeria by the year 2000, *Proceedings of Seminar on the Petroleum Industry and the Nigerian Environment.* 339-346.

[2] Babich, H. and Stoczky, G. **1985**. Heavy metals toxicity to microbemediated ecologic processes: a review and potential application to regulatory policies. *Journal of Environmental Resources* 36,111-115.

[3] Botkin,D.B. and Keller, E.A. **1998**. *Environmental Science; Earth as a Living Planet*, 2nd Edition. Canada, John Wiley and Sons, Inc.

[4] Cain, J.R, Paschal, D.C.and Hayden, C.M. **1980**. Toxicity and bioaccumulation of cadmium in the colonial green algae (Scenedesmus obliquus). *Archieves of Environmental Contamination Toxicology*, 9, 9-16.

[5] Council on Environmental Quality. **1970**. Ocean dumping: a national policy; report to the President. Washington D.C., Government printing office.

[6] Environmental Protection Agency (EPA). **1976**. Quality criteria for water, USEPA, 440(9), 76-123. Washington, D.C.

[7] Ezeronye, O.U. and Ubalua, A.O. **2004**. Studies on the effect of Abattoir and Industrial effluents on the heavy metals and microbial quality of Aba river in Nigeria. *African Journal of Biotechnology*. 4(3), 266-272.

[8] Laws, E.A.**1981**. *Aquatic Pollution*. New York, John Wiley and Sons.

[9] Lenssen, N. **1989**. The ocean blues. World watch, July/Aug., pp. 26-35.

[10] Nauen, C.E. **1983**. Compilation of legal limits for hazardous substances in fish and fishery products, *FAO Fish Circulation*, 764, 5-91.

[11] Oguntoyinbo, J.S **1982**. Climate11: Precipitation 1 In: *Nigeria in maps* Barbour K.M.,eds, London, Hodder and Stoughton,16-19.

[12] Okoye, B.C.O. **1991**. Heavy metals and organisms in the Lagos Lagoon. *International Journal of Environmental Studies*, 37, 285-292.

[13] Pickering, Q.H. **1980**. Chronic toxicity of hexavalent chromium to fathead Minnow (Pipephales promelas). *Archieves of Environmental Contamination Toxicology*, 9, 405-413.