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Determination and Assessment of Heavy Metal Content in Fish and Shellfish in Aba River, Abia State, Nigeria

[1]A.O. Ubalua, [2]U.C. Chijioke and [3]O.U. Ezeronye
[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 (0.064 μg L^{-1}), iron (0.81 μg L^{-1}), zinc (4.82 μg L^{-1}), copper (0.19 μg L^{-1}), arsenic (0.05 μg L^{-1}), manganese (0.03 μg L^{-1}), chromium (0.005 μg L^{-1}) and mercury (0.01 μg L^{-1}) were determined in the water and in some fish and shellfish from Aba river. 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 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 the organisms. However, when compared with levels determined in fish from a rural river, relative enrichment in the Aba river fish, ranging from 0.01 for lead to1.5 for zinc were observed. This is an indication that urban and industrial wastes discharged into the Aba river had significant effect on the ecological balance of the river.

Key words: Heavy metals, pollution, waste assimilation and lead fish

INTRODUCTION

Aba river is a deep fresh water in southern Nigeria. The river is of economic importance in Abia State of Nigeria, hence it is used for various human activities including car washing and fishing. People living within the uptsream vicinity draw water from the river for drinking and for other domestic uses. 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 about the second highly industrialized city in Nigeria and is thickly populated. Urban waste management in this city is very poor and garbage disposal practices here is least to be desired.

The enrichment of heavy metals in Aba river has been reported by Ezeronye and Ubalua[1]. Process water from cosmetic, detergent and textile industries located near the rivers contain a lot of heavy metals, which when in super abundance may cause disruption in the ecological balance[2]. However, allochthonous and authochthonous influences could make concentrations of heavy metals in the water high enough to be of ecological significance. Moreover, bioconcentration and magnification could lead to toxic levels of these metals in organisms, even when the exposure level is low[3]. The proven toxicity of high concentrations of heavy metals in water to fisheries and other aquatic lifes poses the problem of an ultimate dis-equilbrium in the natural ecological balance[4,5]. Under such conditions, the toxicity of a moderately toxic metal could be enhanced by synergism[6] and fish populations may decline[1]. Apart from destabilising the ecosystem, the accumulation of these toxic metals in the aquatic food is a potent threat to public health. The Minamata Bay epidemics in Japan remains a classic example Laws[7].

Dumping of wastes in rivers contributes to the larger problem of river pollution, which has serious damaged the marine environment and caused a health hazard to people in some areas. Botkin and keller[8] reported that shellfish have been found to contain organisms that causes diseases, such as polio and hepatitis. Recent works 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 3 mm of ocean water. The young of certain fish and shellfish also reside in the upper few millimeters of

Corresponding Author: A.O. Ubalua, Cassava Research programme National Root Crops Research Institute (NRCRI), Umudike, P. M. B 7006, Umuahia, Abia State, Nigeria

water in the early stages of their life r[8]. 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 3 mm (or microlayer) are from 10 to 1000 times higher than in the deeper waters. There is fear that disproportionate pollution of the microlayer will have especially serious effect 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 eat them. When solid waste, oil and other materials pollute beaches and harbours, there is a loss of visual appeal and other amenties from the river. Economic loss 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 waste, liquid waste and other pollutants in coastal areas[10]. Poor management of solid municipal wastes poses great discomfort and danger in the human environment. Concerns over potential health-related issues makes imperative that all the sewage should under go secondary treatment before discharge.

There are two main seasons in Nigeria-the dry and the rainy seasons. The rains starts in Aba area from March, reaching the peak between July/August and ending in November. The average annual variation is about 20% of the mean total[11]. During the rains, immense volumes of urban run-off water enters the river from its vast watershed. This run-off influx characteristically delivers into the water high fluxes of suspended solids, nutrients and other pollutants washed from the land and refuse dumps which have remained common features in the urban centers. The present study asseses 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.

MATERIALS AND METHODS

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 done 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.

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

Analysis: Recovery experiments done with 1% oxine solution in chloroform (3g in 200 mL) 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 500 mL aliquots by shaking with 25 mL of 1% oxine in chloroform for 2 min. The bottom layer was decanted into a 100 mL beaker and the remaining chloroform in solution evaporated at low temperature in water bath. The residue was dissolved with 5 mL 1:1HCL, filtered into 25 mL standard flask using Whatman no.1 fitter study and the solution made up to the mark with distilled water Okoye[6].

Metal free water for preparing blank and standard solutions were obtained by shaken each aqueous layer with 25 mL of 1% oxine solution. The chloroform layer was discarded, leaving the condensate. A 500 mL aliquot of the “metal free’ water was shaken with 25 mL of the oxine solution and the extract subjected through the same procedures as the sample extracts. The resulting solution was set aside as a blank. Three 500 mL serially diluted standard solutions containing all the metals in parts per million (ppm) ranges were prepared using the “metal free” water as diluent. These were also extracted with 25 mL of the oxine solution and the extrtacts subjected through the same procedures as sample and blank extracts[6].

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 meat of 8 shellfish were used for shellfish analysis. The samples were homogenised

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

Variables	Upstream1	Upstr-eam2	Abattoir	down Stream1	down Stream 2	Mean	Epa Maxima[a]	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	0.10	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	5.00	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	1.00	3.1-34.03
As								
Dry season	0.00	0.12	0.06	0.06	0.04	0.06±0.04		
Rainy season	0.00	0.04	0.02	0.04	0.04	0.03±0.02		
Mean	0.00	0.08	0.04	0.05	0.04	0.05	0.05	-
Mn								
Dry season	0.00	0.00	0.04	0.04	0.00	0.02±0.02		
Rainy season	0.00	0.02	0.04	0.06	0.02	0.03±0.02		
Mean	0.00	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	0.00	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^{-1} A :source; EPA[12] B :Source; Kakulu (1985) nd :not detectable

separately in a mortar and weighed accurately in a porcelain crucible. Before ashing, 1 mL conc.HNO_3 was added to the samples and allowed to predigest overnight in order to reduce losses of volatile metals. The samples were charred on electric hot plate before ashing in a muffle furnace at 550°C for 4 h. The white ash was dissolved in 5 mL 1:1HCl and solution made in 25 mL standard flask[6]

The 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 air-acetylene flame. Blank solution for the biotic samples was made by diluting 1 mL conc. HNO_3 + 5 mL 1:1 HCL to 25 mL with distilled water. Emperical data generated were analyzed statistically.

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 either 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 variance (ANOVA) did not reveal significant spatial variations in the levels of 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 the Aba river is mainly slow with little or no upwelling during the rainy season, immense volumes of fresh water pass 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 short residence time in the river. During this season, there is more than twice the dilution of the river water. The short residence time 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 is that heavy metal levels are kept low in spite of high fluxes from industrial and urban wastes including the immense urban run-off[1].

The obtained data on the analysis of the fish and the shellfish are presented in Table 2 and were used for

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±0.00
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±0.00	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 means ± std. dev.

Table 3: Some literature standards[a] and metal levels in Imo river fish compared with the levels in Aba river fish

	Pb	Fe	Zn	Cu	As	Mn	Cr	Hg
Lit. std.	2.0[b,c]	-	40[b],50[c]	20[b]30[c]	-	-	-	-
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^{-1}, wet wt. A:source:Nauen[17] b : New Zealand c : United Kingdom Lit. std.: Literature standard

comparative studies on heavy metals accumulation in biotic components having different ecological characteristics. Emperical data obtained revealed that feeding modes influenced accumulation pattern, as exemplified by *C.gasar*. *C.gasar*, being a filter feeder among all the three shellfish recorded the lowest level of all the metals except zinc. The metal level is 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 level of zinc in *C. gasar*, higher ($p<0.05$) levels of zinc and copper in *T. guineensis* muscle than in *M. caphalus* 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 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 anemia, mental retardation, uncoordination and bizarre behavior in humans[8].

The empirical figures in Table 3 are at variance with that of Okoye[6], as a result of rapid urbanization and industrialization that is associated with Lagos State. These has brought with it an alarming unmanageable, inevitable and persistent problems associated with environmental degradation.

The impact of waste disposal on the rivers were assessed by comparing the metal levels in the Aba river fish with those determined in fish from Imo river, a rural water and with some literature values in Table 3. Comparative studies of "metal enrichment" in the rivers shows relative presence of the heavy metal in the Aba river fish while that ofImo river 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 Aba river. The occurrence of lead levels in the Aba river fish could be traced to urban and industrial wastes, high-petrol lead and expired motor batteries commonly dumped by battery chargers around their workshops.

The current national specification for lead in petrol sold in Nigeria is 0.7g Pb L^{-1}, which , based on national daily petrol consumption of about 20 million litres per day, emits via motor exhaust pipe an estimated 15,000 kg of lead per day[13]. On the bases of available records and surveys, no practical attempts have been initiated to minimise the impacts of this source of environmental lead[13]. High lead levels in Aba river fish could be traced to urban and industrial wastes and high-petrol lead. Waste management in urban and industrial centers in the country, especially around Aba has remained very unsatisfactory.

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