Biological Sciences

Pak. J. Sci. Ind. Res. 2003 **46**(6) 439 - 442

Variation of Heavy Metal Concentrations in Water and Freshwater Fish in Niger Delta Waters - A Case Study of Benin River

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(Received January 3, 2002; accepted February 25, 2003)

Levels of Cd, Cr, Fe, Pb and Zn were determined in water and fish samples from three different locations in the Benin river. The sampling points were chosen such that Gbokoda, a village between Koko and Ogheye where a flow station (Olague flow station or crude oil well) is situated serves as a pollution point source and Koko as a baseline concentration point. Three species of fish each, that are top feeder, *Tilapia mariae* (which is herbivorous and feeds mainly on floating phytoplankton), middle feeder, *Pseudotolithus elongatus* (that is ominivorous) and bottom feeder, *Chrysichthys nigrodigitatus* (also ominivorous) were used for the study. The mean wet weight of the species sampled at the different locations ranged between 385.17 - 417.44g. The maximum concentration levels observed in water samples for Cd, Cr, Fe, Pb and Zn were 3.50 x 10^{-4} g/l, 1.24 x 10^{-3} g/l, 3.10 x 10^{-3} g/l and 1.50 x 10^{-3} g/l, respectively. The mean concentration levels determined for the various species of fish are: for Cd, *Tilapia mariae* 7.30 x 10^{-5}, *Pseudotolitus elongatus* 8.67 x 10^{-4} and *Chrysichthys nigrodigitatus* 1.581 x 10^{-4}, for Fe, *Tilapia mariae* 5.500 x 10^{-3}, *Pseudotolithus elongatus* 4.700 x 10^{-3} and *Chrysichthys nigrodigitatus* 3.9133 x 10^{-3}, for Pb, *Tilapia mariae* 4.4240 x 10^{-3}, *Pseudotolithus elongatus* 3.4100 x 10^{-3} and *Chrysichthys nigrodigitatus* 9.6730 x 10^{-3} for Zn, *Tilapia mariae* 5.467 x 10^{-3}, *Pseudotolithus elongatus* 5.067 x 10^{-3} and *Chrysichthys nigrodigitatus* 8.833 x 10^{-3}. (All values are g/g of fish)

Key words: Heavy metal, Fresh water fish, Benin river, Herbivorous, Omnivorous.

Introduction

Heavy metals have water bodies in both natural and anthropogenic origin and they will cause long-term damage to the aquatic environment.

The levels of heavy metals on freshwater fish and aquatic organisms reported by (Comparetto and Jester 1981; Hart 1982; Luoma 1983; Ndiokwere 1983). The concentration of these heavy metals in an organism's environment and its rate of ingestion and excretion. The concentration of harmful substances especially hydrophobic compounds are higher in sediments and biological tissues than in water itself (Florence and Batley 1980). It is likely that some of these hydrophobic compounds can form chelates with heavy metals.

Many aquatic organisms are able to concentrate these metals to a high level which become hazardous to health. Preston *et al* (1972), suggested that some aquatic organism may provide a useful means of monitoring elemental concentration in surface waters and their impact on the aquatic environment. One objective of this study is to determine the concentration of some heavy metal Cd, Cr, Fe, Pb and Zn in water and fish samples from the Benin river. A second objective is to determine the concentration of these heavy metals at different depths using three species that are top, middle and bottom feeders.

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The Benin river runs through an area of dense oil activities including exploration and drilling of crude oil by Chevron, Shell companies, Nigeria Limited. These heavy metals are known to be associated with oil-drilling operations and several oil spills resulting from these activities have been reported in this area of study. Effluent from these activities is discharged either directly into the river on into creeks which drain into the river. The Benin river finally runs into the Atlantic Ocean at Ogheye a distance of 42km from Koko, one of the sampling station.

Through the liver of fish is known to concentrate more metals than any other part (De Goeji *et al* 1974). We chose to focus on muscle tissue which is highly consumed by man. Heavy metals are known to be deleterious to humans, therefore, man is exposed to a health hazard when large quantities of contaminated fishes are consumed.

Method. Sample collection and preparation: The fish and water samples were collected from three sampling locations on Benin river *viz* Ogheye, Gbokoda and Koko. The water sampling was done twice a month for a period of 6 months (Fig 1).

The water samples were collected using 'grab sampling method' (APHA 1985). The samples were stored in 2.5 litre plastic containers which were previously washed with 2% v/v HNO_3 and rinsed thoroughly with distilled water. A two litre sample was collected at each point and immediately preserved with conc. HNO_3 at about 1.5ml/l. The fish species were identified by their scientific names with the help of Zoology Department, University of Benin, Benin City (Table 1). The fish tissues were neatly cut out using a clean dissecting stainless steel knife and forceps and sealed in small polyethylene bags, which had been previously rinsed with 1M HNO_3 and distilled water. Care was taken to prevent contamination by cleaning the dissecting tools thoroughly after each use. The tissues were then placed in a watch glass and dried at 105˚C to constant weight. About 5g (dry weight) each of the fish samples were accurately weighed into a digestion flask. A mixture of concentrated HNO_3 and $HClO_4$ (2:1) was added and heated to dryness. The resultant residue was dissolved in 10ml (1:1) H_2SO_4 and diluted to 100ml with distilled water. The solution was used for heavy metal analyses using a Hitachi 180 - 170 Zeeman Atomic Absorption Spectrophotometer. All the chemicals and reagents used were of analytical grade.

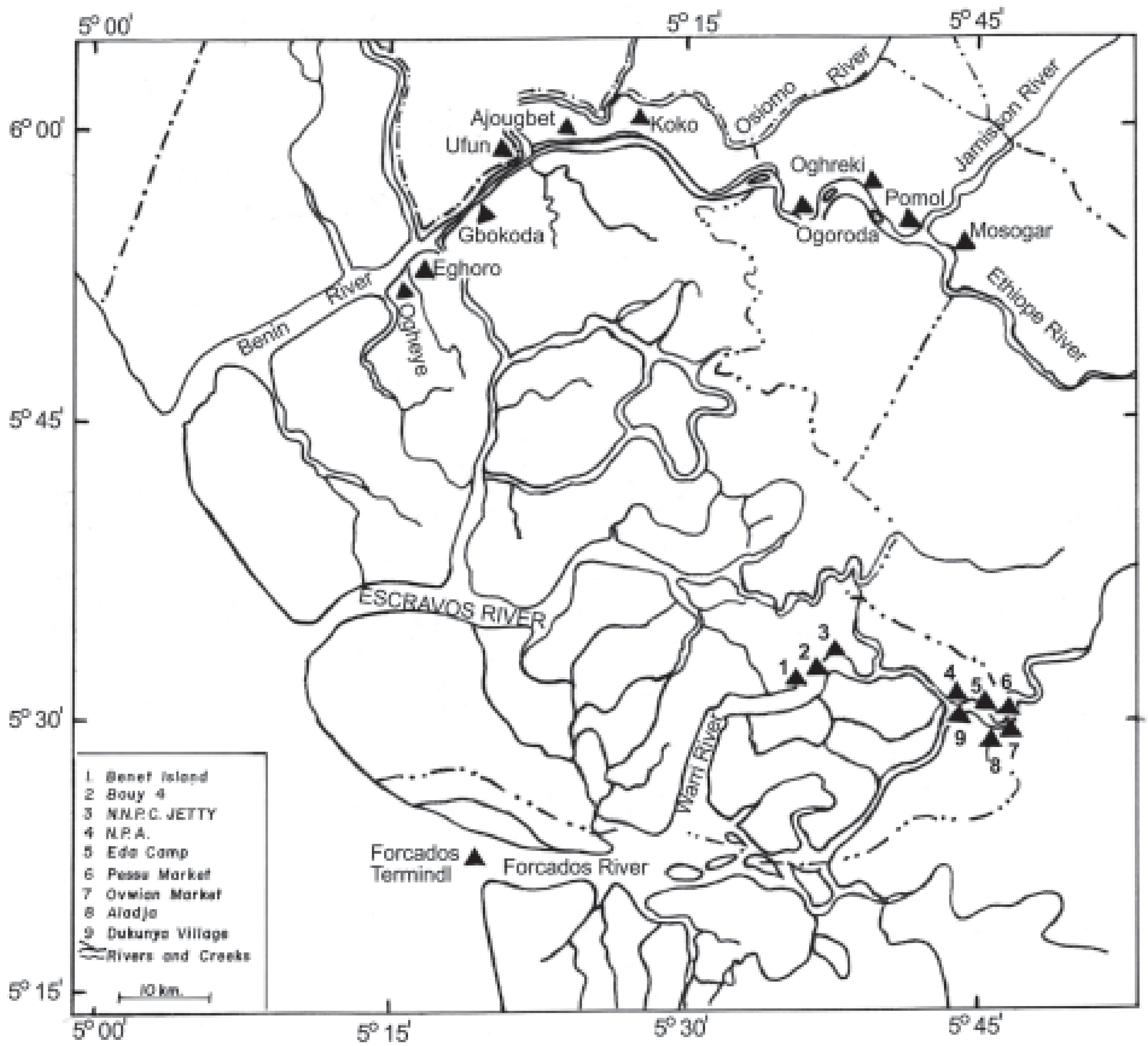
Table 1

Fish samples collected for analysis.

Sampling point	Scientific name	Number of samples
Koko	*Tilpia mariae* (Top feeder)	12 samples
Gbokoda	*Pseudotolithus elongatus* (middle feeder)	for each
Ogheye	*Chrysichthys nigrodigitatus* (bottom feeder)	species

Results and Discussion

The concentration levels of heavy metals in water samples at different locations is presented in Table 2, while the mean



A map showing Benin river and the sampling locations

Table 2
Mean levels of heavy metal concentration in water samples at different locations

Location	Number of samples (n)	Parameters g/l				
		Cd	Cr	Fe	Pb	Zn
Koko	12	$2.00 \times 10^{-5} \pm 5.00 \times 10^{-6}$	BDL	BDL	$1.00 \times 10^{-4} \pm 2.00 \times 10^{-5}$	BDL
Gbokoda	12	$3.50 \times 10^{-4} \pm 1.10 \times 10^{-4}$	$5.00 \times 10^{-4} \pm 3.00 \times 10^{-5}$	$3.10 \times 10^{-5} \pm 6.00 \times 10^{-4}$	$6.30 \times 10^{-4} \pm 2.40 \times 10^{-5}$	$1.51 \times 10^{-4} \pm 7.00 \times 10^{-5}$
Ogheye	12	$1.20 \times 10^{-4} \pm 2.00 \times 10^{-5}$	$1.24 \times 10^{-4} \pm 1.10 \times 10^{-5}$	$7.40 \times 10^{-4} \pm 2.00 \times 10^{-6}$	$6.20 \times 10^{-4} \pm 5.50 \times 10^{-5}$	$6.90 \times 10^{-4} \pm 4.10 \times 10^{-5}$

BDL, Below detection limit of instrument

Table 3
Mean levels of heavy metals in the three species of fish at different sampling location.

Location	Species of fish	Parameters x 10^{-4} g/g of fish				
		Cd	Cr	Fe	Pb	Zn
Koko	*Tilapia mariae*	BDL	BDL	2.920	0.032	
	Pseudotolithus elongatus	0.140	BDL	2.220	0.023	BDL
	Chrysichthys nigrodigitatus	0.040	BDL	BDL	0.320	
Gbokoda	*Tilapia mariae*	0.040		4.420	0.880	0.500
	Pseudotolithus elongatus	0.140	BDL	3.620	0.640	0.630
	Chrysichthys nigrodigitatus	0.160		2.840	0.880	0.630
Ogheye	*Tilapia mariae*	0.180		9.160	0.360	1.140
	Pseudotolithus elongatus	0.120	BDL	8.770	0.360	0.890
	Chrysichthys nigrodigitatus	0.310		8.900	0.390	2.020

Table 4
Mean values of heavy metals in the three species of fish.

Species	Parameters x 10^{-3} g/g fish			
	Cd	Fe	Pb	Zn
Tilapia mariae	0.0733 ± 0.0950	5.5000 ± 2.3690	0.4240 ± 0.4276	0.5467 ± 0.5714
Pseudotolighus elongatus	0.0867 ± 0.0757	4.8700 ± 4.3820	0.3410 ± 0.4904	0.5067 ± 0.4577
Chrysichthys nigrodigitatus	0.1581 ± 0.1528	3.9130 ± 4.5461	0.3673 ± 0.4340	0.8833 ± 4.1891

values of the heavy metals in the three species of fish at each location and the entire body of the river are presented in Tables 3 and 4.

The range of concentrations found in water samples are: $2.00 \times 10^{-5} - 3.50 \times 10^{-4}$ g/l, Cd, $5.00 \times 10^{-5} - 1.24 \times 10^{-3}$ g/l, Cr, $7.40 \times 10^{-4} - 3.10 \times 10^{-3}$ g/l, Fe, $1.00 \times 10^{-4} - 6.00 \times 10^{-4}$ g/l, Zn. This showed that heavy metals were present in considerable amounts. This is so because of the discharge of heavy metals in the environment from industry which has been increased by human activities and urban storm water discharge. Effluents from a petroleum refinery sited on the surrounding ecosystem of the river are known to contain among other heavy metals, lead, cadmium and chromium (Ndiokwere 1983). Also, plywood and timber (saw mill industry) is sited along the course of the river. Copper-chromium arsenate is used as a timber preservative by timber and saw mill industries to prevent fungal attack (Hunton and Symon 1986). All these might contribute to the level of Cd, Cr, and Pb found in the water samples.

The concentration of all the heavy metals determined were highest at Gbokoda (Table 2), a Sampling location where Olague crude oil well is situated and this provides an indication of the difference between baseline point and pollution source. This probably suggest Gbokoda as the pollution point and pollution source. This probably suggest Gbokoda as the pollution point of the river.

There are differences in the bio-concentration of these metals by the different species of fish. The *Chrysichthys* *nigrodigitatus* specie, the bottom feeder tends to bio-accumulate more of Cd and Zn with concentrations of 1.58 x 10^{-4} g and 8.83 x 10^{-4} g/g of fish, respectively. The highest concentration of 5.50 x 10^{-3} g/g and 4.240 x 10^{-5} g/g of fish for Fe and Pb, respectively were determined for *Tilapia mariae*, the top feeder. The high concentrations may be as a result of exposure to, and feeding in contaminated fresh water sediments. Other human activities such as the washing of clothes and motor vehicles at various sites on the bank of this river, can possibly contribute to its pollution by heavy metals. Cr was not detected in any of the fish samples. The concentration of Cr in the fish samples might be below the detection limits of 0.005 μg of the Hitachi 180 - 170 Zeeman Atomic Absorption Spectrophotometer.

The average size of the fish samples from the different locations were approximately the same. The degree to which the differences in the fish sizes influence the bio-accumulative behaviour of the fish species cannot be correlated with the difference in the heavy metal concentration levels, though not investigated. The high levels of heavy metals determined in all the fish samples might be due to local contamination of the river.

Conclusion

Conclusively, the bio-concentration of heavy metals in biota such as fish is an indicator of the pollution of water bodies by heavy metals. This is apparent in the elevated levels of metals observed in the fish samples than that obtained for the water samples. The heavy metals pollutant levels in the fish samples were in the decreasing order Fe > Zn > Pb and Cd.

Acknowledgement

The authors are grateful to the Department of Chemistry, University of Benin, Benin City, for funding this research work. We also acknowledge Mrs Ukwade, P.O., for putting this work in print.

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