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COMPARATIVE STUDIES OF METALS IN FISH ORGANS, SEDIMENT AND WATER FROM NIGERIAN FRESH WATER FISH PONDS

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Fish samples (*Illisha africana*) were collected from six man-made fish pond in Edo and Ondo States, Nigeria. Some organs of the fish, sediment and water from the fish habitat were analysed for Cd, Pb, Hg, Ca, Fe, Zn, Cu and Cr. Physico-chemical properties of water samples from the ponds were also re-corded. The concentration of the metals varied in the sediment water as well as in different organs of the fish. However, chromium was absent in all the samples. The descending order of metal concentration in fish organs was: gills, intestine, head and muscle. To avoid harmful accumulation of these metals in the human system, the gills and the intestine should preferably be discarded while processing fish for consumption. The head with a relatively high concentration of calcium might be useful in feed formulation.

Key words: Metals, Fish organs, Fish ponds.

Introduction

One of the side effects of disafforestation in Nigeria is the dramatic reduction in the population of wild animals which for a long time have been the major source of animal protein in southern Nigeria. Hunting used to be a popular profession for which many families were famous while "bush meat", the processed carcass of a wild animal, has remained a delicacy in many Nigerian homes. In order to compensate this dwindling source of animal protein, the hitherto less popular fish farming has come to the lime light. Fish, like meat is valuable in the diet because apart from supplying good quality protein and vitamin A and D, it also contains several metals such as Ca, Fe etc. which are beneficial to man [1,2]. However, toxic metals such as Pb, Cd etc. may also be present especially if the environment of the fish is polluted. A few years ago the establishment of River Basin Development Authorities in many parts of Nigeria encouraged fish farming and construction of fish ponds.

Pollution has remained a major problem in fish farming. Water soluble toxicants from industrial and municipal wastes, leached soils and the atmosphere have rapidly transferred to natural bodies of water [3,4]. While some of the pollutants decompose or volatilise, others form insoluble salts which precipitate and get incorporated into the sediment [1]. Uptake of such toxicants by aquatic organisms like fish may be followed by metabolism of the toxicants into more toxic derivatives [5,6]. For example mercury from industrial effluents may be converted by microbial action into the highly toxic methyl mercury which can then be taken up by fish. Many aquatic organisms have been known to concentrate toxic solutes from their habitat without any obvious damage to themselves [7,8]. They thus act as toxiciant amplifiers, making the toxicants available to predators at dangerously high levels.

Several cases of the adverse effects of environmental pollution on fish and fish consumers have been reported [1,9]. The annual yield of fish has been observed to be a function of water quality [10]. Few studies have been published on the level of metals in the tissue of fish from Nigerian waters, [11,12a,b] which have been restricted to the fish alone or sometimes extended to the associated waters. However, the aquatic ecosystem consists of the community of living organisms along with the surrounding water and soil sediment, all functioning as a dynamic integrated system where nutrient exchange occur freely [13]. It therefore, becomes necessary to carry out chemical analysis not only of fish and the associated water but also of the sediment.

A case study involving some man-made fish ponds located within Edo and Ondo states of Nigeria is hereby reported.

Experimental

Sampling. Six man-made fish ponds comprising four from Edo State and two from Ondo State were used for the study carried out in 1994. The ponds in Edo included two from Okada and one each from Ogba C.R.A. and Ogbenede fish farm, Benin. The ponds in Ondo State are at Ondo State College of Education (OSCE), Ikere and at Alagbaka G.H.A.,

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Akure. All the ponds are fed by surface waters except one pond at Odaka which receives its water supply from a borehole.

Grab samples were taken at six different locations in the fish ponds using 1L acid-leached polythene bottles and stored at -18°C. An auger was used to take soil sediment samples from the surface down to a depth of about 15 cm at locations from where water samples were taken. The samples were collected in polythene bags and kept in a deep freezer pending analysis. Four speciman of the fish *Illisha africana* caught by local fishermen from each pond were carefully scaled, washed and stored in the deep freezer.

Sample treatment. Five ml concentrated HCL was added to 250ml of water sample and evaporated to 25ml. The concentrate was transferred to 50ml standard flask and diluted to mark with distilled water [14]. Air dried soil samples were sieved using 200mm mesh. Five g of the soil was weighed into a 150ml conical flask to which 50ml of 0.1m HC1 was added and the flask was agitated on an orbital shaker for 30 mins at 250 rmp. The content was then filtered into a 50ml standard flask and made to the mark with 0.1m HCl[15].

Different organs of the fish samples were dried at 105°C, blended and weighed accurately ranging between 0.18 and 0.20g for digestion. Two ml of concentrated HNO_3 was added to each sample in a beaker, covered with a watch glass and allowed to stay overnight in a fume cupboard. The beaker was then heated gently on a hot plate until frothing stopped and no visible solid material was observed. The temperature was increased to 60°C unitl borwn fumes ceased to come out. Heating to near dryness was done at a temperature between 78°C and 80°C. The digest was then removed, and 2ml of 5% lanthanium chloride solution added before re-heating to near dryness. The final solution was washed into a 25ml standard flask with 0.1m HNO_3 and made up to the mark [15].

Analysis. For analysis BDH grade reagents were used. Temperature, pH, conductivity, alkalinity and chloride of the water samples were determined immediately after sampling. pH was measured with a KENT EIL 7020 pH-meter and conductivity measured with JSI model 33 conductivity meter after standardising with KC1 and NaC1 solutions. Various standard analytical methods [16] were used for the determination of other parameters. Total alkalinity was determined by titration using bromocresol green/methyl red mixed indicator; chloride by mohr's method; total hardness by EDTA titration using Erichrome Black T indicator. The metals were determinded with atomic absorption spectrophotometer (Perkin Elmer, model 306).

The physico-chemical parameters for water are shown in Table 1. A pH range of 6.5 to 7.2 was observed for fish ponds filled by surface waters but the highest pH of 8.4 was recorded for the fish pond filled by a borehole. All the pH values were within the acceptable range for optimum fish culture [17].

The total alkalinity range of 30.5 - 122.0 ppm would provide adequate quantity of carbon dioxide to encourage plankton production which is the base of the food web. There is a close relationship between plankton abundance and fish production [10]. The degree of hardness of the waters was rather low and this might encourage the dissolution of heavy metals [18]. This may explain the presence of most of the metals in the water samples and the high level of conductivity. With respect to chloride, all the fish ponds were polluted

TABLE 1. PHYSICO-CHEMICAL DATA FOR WATER ANALYSIS.

Parameter	Benin Ogba GRA	Ogbenede Farm	Okada Borehole	Surface Water	Akure Alagbaka GRA	Ikere OSCE
Temperature (°C)	24.9 ±0.8	26.0 ± 0.6	25.5 ± 0.9	26.0 ±0.8	25.0 ± 1.0	25.0 ±0.7
pH	7.2 ± 0.5	7.6 ±0.5	8.4 ±0.7	7.4 ±0.6	6.8 ±0.8	7.2 ±0.4
Conductivity (mhos/cm)	460.5 ±50.8	470.0 ±80.2	540.2 ±60.8	520.8 ±40.8	600.7 ±58.3	462.3 ±30.5
Total alkalinity (ppm)	30.5 ±5.2	30.5 ±3.8	122.0 ±10.5	20.6 ±3.6	71.1 ±10.2	55.0 ±8.5
Chloride (ppm)	8.9 ±1.2	10.8 ±1.6	57.3 ±5.2	62.1 ±6.1	173.7 ±10.2	41.0 ±5.2
Total hardness as $CaCO_3$ (ppm)	30.0 ±2.8	31.1 ±5.2	90.0 ±6.2	40.1 ±2.5	88.4 ±8.5	60.8 ±10.3

+ OSCE = Ondo State College of Education.

TABLE 2. CONCENTRATION (PPM) OF METALS IN WATER SAMPLES.

Metals	Ogba GRA	Ogbenede farm	Bore Hole	Water surface	Alagbaka GRA	OSCE+
Co	0.28 ±0.5	0.48 ±0.09	0.28 ±0.2	0.28 ±0.4	0.27 ±0.8	0.03 ±0.01
Pb	0.99 ±0.08	0.88 ±0.10	1.60 ±0.01	- nd	1.00 ±0.08	- nd
Cd	0.16 ±0.02	0.01 ±0.01	0.01 ±0.01	nd	0.001 ±0.001	0.002 ±0.001
Fe	0.001 ±0.001	nd	0.04 ±0.01	0.002 ±0.001	0.001 ±0.001	0.002 ±0.001
Ca	6.01 ±1.02	12.02 ±1.10	28.10 ±2.31	14.03 ±2.01	18.53 ±2.50	21.75 ±1.98
Mg	3.65 ±0.80	0.24 ±0.06	4.86 ±1.00	1.23 ±0.61	6.41 ±1.05	7.39 ±0.99
Cu	nd	nd	nd	nd	0.13	0.06
Hg	nd	nd	0.01± 0.01	nd	nd	0.002 ±0.001

nd= not detected.

but the effects have not been observed in the fish. Chlorides are relatively harmless to organisms except when converted to Cl_2, ClO^- and ClO_3^- which are toxic [1].

The water sample from the borehole had relatively concentration of Pb, Fe, Ca and Zn (Table 2). Chromium was not detected in any of the samples but lead and cadmium were detected in some water samples having concentrations above the recommended values for warm water fisheries. The toxicity of metals is, however, affected by many factors such as pH, temperature, calcium concentration of the water and the presence of complexing agents of biological origin [1]. Consequently metal toxicity to man through fish consumption also depends on the capacity of the fish to concentrate these metals from the habitat, a factor that is affected by the fish species [1]. Fish ponds, like lakes in river systems, function as sink traps for heavy meals that are leached by streams. However, it is known [1] that in large lakes the biological effects of metal pollution appear slowly. Since fish cropping can be carried out within a period of 6 months of stocking the pond under favourable weather conditions, it means that the breeding period of fish may not be long enough to encourage serious metal accumulation in their body tissues especially in newly constructed ponds.

The generally high concentration ranges of metals indicate a lack of uniform distribution of metals within the water samples, however large variations of these magnitude have also been reported by other workers [19, 20]. The static nature of the ponds might be a major factor for the large variations in metal concentration within the ponds while those among ponds could be attributed to the geographical locations of the fish ponds as the nature of the mineral deposits in the neighbourhood of the ponds would influence their concentrations.

The concentration of metals in the sediment was generally higher than the corresponding values for water (Tables 2 and 3). The relatively high pH values of the water samples could be one of the factors as metal hydrolysis is more favourable at high pH[21]. The metals in the fish organs were several fold higher than their corresponding values in water and sediments (Tables 4 - 9). The metal contents also showed large variation among fish samples from different fish ponds and also among the organs of the fish. Similar large variations have been reported elsewhere [12]. For example, Zn concentration which ranged between 7.48 and 19.50 µg/g of the fish taken from Ikere was between 2.5 and 84.3µg/g of the fish taken from Haifa Bay sea and between 3.17 and 40.0 µg/g of the fish taken from gulf of Mexico [22].

Comparing the levels of metals in the fish organs, the general trend appeared to be gill > intestine > head > muscle. The head and gill accumulated large quantity of calcium which is useful in feed formulation. Protein parvolbumin which contains strongly bound calcium has been reported tobe present infish [23]. Gills have affinity for many metals and this might be attributed to the primary function of the gills. Fish can absorb ions through gills, since they have special salt-secreting cells [1]. Since virtually all metals become toxic if the tolerance level is exceeded, [24,25] the

TABLE 3. CONCENTRATION (µg/g) OF METALS IN SEDIMENTS.

Metals	Benin Ogba GRA	Benin Ogbendde Form	Okada Borchole	Okada Surface Water	Akure Alagbaka GHA	Ikere OSCE
Ce	nd	30.1 ±2.9	29.9 ±1.2	79.9 ±5.4	76.7 ±4.8	90.1 ±10.5
Fb	10.5 ±1.8	nd	10.1 ±2.5	nd	nd	1.0 ±0.3
Cd	nd	40.0 ±6.1	39.4 ±5.4	nd	nd	nd
Fe	90.1 ±10.3	30.2 ±3.5	37.0 ±3.3	190.1 ±12.5	190.0 ±20.0	80.2 ±8.9
Ca	31.4 ±6.5	28.9 ±4.6	35.6 ±11.8	50.2 ±9.4	42.4 ±4.8	60.5 ±12.5
Mg	370.1 ±20.6	880.4 ±120.2	180.0 ±90.1	178.0 ±80.0	240.0 ±80.2	180.1 ±60.5
Cu	20.0 ±1.5	nd	80.0 ±6.8	160.3 ±50.8	10.1 ±1.0	20.1 ±3.2
Zu	38.0 ±7.2	50.0 ±6.4	84.3 ±11.6	88.0 ±10.9	20.2 ±2.1	10.4 ±0.9
Hg	nd	nd	1.1	0.8	nd	0.9

TABLE 4: CONCENTRATION (MG/G) OF METALS IN THE ORGANS OF FISH SAMPLES FROM OGBA, BENIN.

	Concentration (µg/g) infish organs			
Metals	Gill	Head	Intestine	Muscle
Ce	nd	nd	nd	nd
Pb	nd	20.0 ± 2.5	nd	nd
Cd	nd	nd	3.1 ± 0.9	nd
Fe	40.8 ± 5.3	87.7 ± 9.2	75.6 ± 17.2	42.5 ± 6.8
Ce	535.4 ± 120.5	645.5 ±100.4	283.7 ± 60.8	290.5 ± 80.8
Mg	38.1 ± 4.5	19.1 ± 3.0	70.8 ± 8.9	91.20 ± 7.7
Cu	nd	nd	nd	nd
Zu	53.1 ± 4.8	24.0 ± 2.2	110.8±9.6	72.1±12.4
Hg	0.5 ± 0.2	nd	1.2 ± 0.6	nd

TABLE 5. CONCENTRATION (µG/G) OF METALS IN THE ORGANS OF FISH SAMPLES FROM OGBENEDE FARM, BENIN.

	Concentration (µg/g) in fish organs			
Metals	Gill	Head	Intestine	Muscle
Co	36.7 ± 5.8	3.7 ± 0.9	34.0 ± 8.2	11.0 ± 1.5
Pb	200.4 ± 50.2	92.6 ± 15.5	30.4 ± 3.2	100.1 ± 8.8
Cd	0.01 ± 0.01	nd	5.0 ± 0.8	nd
Fe	65.8 ± 8.4	14.4 ± 2.1	44.0 ± 7.3	240.1 ± 60.5
Ca	874.1 ± 130.0	1056.9 ± 200.0	391.8 ± 110.2	182.3 ± 70.5
Mg	40.4 ± 6.6	23.4 ± 1.8	76.5 ± 12.2	67.7 ± 10.9
Cu	nd	nd	nd	nd
Zn	59.2 ± 8.1	26.8 ± 3.5	94.1 ± 10.7	136.2 ± 11.9
Hg	nd	nd	1.0 ± 0.3	nd

TABLE 6. CONCENTRATION (μg/g) OF METALS IN THE ORGANS OF FISH SAMPLES FROM OKADA .

Metals	Concentration (μg/g) in fish organs			
	Gill	Head	Intestine	Muscle
Co	nd	nd	nd	nd
Pb	138.0 ± 10.4	61.6 ± 4.5	200.2 ± 40.3	nd
Cd	4.6 ± 0.8	6.9 ± 1.0	4.1 ± 0.7	4.0 ± 0.9
Fe	174.7 ± 11.0	781.3 ± 110.0	172.0 ± 50.1	128.5 ± 18.2
Ca	945.1	1202.3 ± 250.0	1021.9 ± 158.2	122.0 ± 25.6
Mg	62.0 ± 8.0	35.9 ± 4.3	41.2 ± 6.5	72.8 ± 9.2
Cu	nd	1.9 ± 0.7	2.1 ± 0.6	nd
Zn	80.6 ± 12.2	36.5 ± 4.6	91.8 ± 10.6	85.1 ± 8.2
Hg	0.5 ± 0.1	nd	5.6 ± 1.0	1.4 ± 0.3

TABLE 7. CONCENTRATION (μg/g) OF METALS IN THE ORGANS OF FISH SAMPLES FROM OKADA (SURFACE WATERS).

Metals	Concentration (μg/g) in fish organs			
	Gill	Head	Intestine	Muscle
Co	nd	nd	2.0 ± 0.5	nd
Pb	179.8 ± 13.4	80.3 ± 8.8	300.1 ± 50.6	200.0 ± 39.4
Cd	nd	nd	0.01 ± 0.01	nd
Fe	58.4 ± 4.9	58.5 ± 6.2	74.6 ± 9.5	29.0 ± 3.4
Ca	167.9 ± 15.8	201.7 ± 40.9	150.9 ± 21.1	182.3 ± 30.2
Mg	38.5 ± 3.6	22.3 ± 2.1	22.48 ± 1.9	66.2 ± 14.7
Cu	2.1 ± 0.4	nd	0.2 ± 01.	nd
Zn	43.9 ± 5.1	19.8 ± 2.7	87.0 ± 14.3	19.4 ± 3.2
Hg	1.2 ± 0.5	nd	nd	nd

TABLE 8. CONCENTRATION (μg/g) OF METALS IN THE ORGANS OF FISH SAMPLES FROM ALAGBAKA, AKURE.

Metals	Concentration (μg/g) in fish organs			
	Gill	Head	Intestine	Muscle
Co	1.32 ± 0.6	nd	1.0 ± 0.4	nd
Pb	69.2 ± 7.6	30.9 ± 5.8	nd	nd
Cd	nd	nd	0.9 ± 0.2	nd
FE	130.1 ± 15.3	50.2± 8.1	230.0 ± 40.2	160.2 ± 48.0
Ca	1127.3 ± 220.2	1357.2 ± 300.0	716.3 ± 140.5	704.3 ± 120.9
Mg	44.7 ± 4.9	25.8 ± 3.3	26.3 ± 2.8	98.0 ± 12.5
Cu	nd	0.5 ± 0.2	0.8 ± 0.2	nd
Mg	nd	nd	nd	nd

TABLE 9. CONCENTRATION (μg/g) OF METALS IN THE ORGANS OF FISH SAMPLES FROM O.S.C.E. IKERE.

Metals	Concentration (μg/g) in fish organs			
	Gill	Head	Intestine	Muscle
Co	28.9 ± 4.5	nd	nd	7.5 ± 1.8
Pb	250.8 ± 12.8	112.0 ± 9.3	97.8 ± 9.5	27.9 ± 2.1
Cd	10.0 ± 1.9	12.9 ± 4.1	10.5 ± 2.1	5.0 ± 0.9
Fe	162.3 ± 20.0	166.4 ± 18.6	399.3 ± 70.1	116.1 ± 26.1
Ca	1234.5 ± 300.0	1580.4 ± 250.5	227.6 ± 34.9	668.8 ± 140.7
Mg	104.5 ± 11.3	60.5 ± 7.8	90.4 ± 11.2	68.8 ± 8.1
Cu	3.8 ± 1.0	2.5 ± 1.1	2.3 ± 0.8	nd
Zn	19.9 ± 2.6	9.0 ± 1.8	17.0 ± 3.4	7.5 ± 2.0
Hg	0.6 ± 0.2	1.2 ± 0.7	2.5 ± 0.8	0.9 ± 0.2

removal of the head, gill and intestine of the fish would be a judicious step while processing gfish for consumption as this step would drestically reduce the metal in-take.

Some metals such as Pb, Cd and Hg could be detected in the fish body even when they appeared to be absent from the associated water and sediments. Since the fingerlings were brod indifferent environments from the fish ponds, there was the possibility of the metals having been acquired at this stage or from the fish meal. For the purpose of fish farming then, there might be the need to monitor fish pollution right from the fingerling production stage.

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