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Heavy metals in water and fish (*Synodontis membranaceus*) from Ora and Ebe rivers in the vicinity of Nigerian cement factory, Nkalagu

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ABSTRACT

Water and Synodontis membranaceus samples collected from Ora and Ebe Rivers were analysed for heavy metal concentrations. Using atomic absorption spetrophotometry (Spectra AA-10 varian and Emmission/absoption –200A). The metals concentrations obtained in water and Synodontis membranaceus in this study showed that there were no significant mean difference between water samples from Ora Rive and Ebe Rivers. There were metal variations due to seasonal changes. Metals analysed in Synodontis membranaceus revealed that lead, cadmium, nickel and cobalt were below detection limits in the intestine sample from Ebe River. Relationships between Synodontis membraneceus tissue from Ora River and Ebe River were presented in Tables 5 and 6 respectively. Also the relationships between metals Synodoutis membranaceus tissues were presented in Table 7. These relationships showed variations of metals in head, muscle and intestine of Synodontis membranaceus from the two rivers. The concentration of metals such as lead, copper, manganese, iron, nickel, cadmium and chromium in Synodontis membrananceus from Ora River exceeded those of Ebe River. Arsenic levels in Synodontis membranaceus in this study was found to have exceeded those levels (0.07-0.43 µg/g obtained from River Niger and Niger Delta areas of Nigeria. Concentrations Cr, Cu, Fe and Zn in Synodonti membranceus in this study were lower than those obtained from the Kuwait Coast (Cr 6.2-8.8, Cu 4.2-96.2, Fe 18.8-126.4 and Zn 7.6-81.3µg/g dry weight). Metals such as tin, cadmium, mercury and aluminium were found to be positively carrelated between river water and fish tissue from Ora River whereas inverse relationships were found for copper, chromium and zinc. Considering Ebe River, only chromium showed ($p<0.01$) relationship whereas lead manganese, iron, cadmium, chromium and cobalt were positively correlatated ($p<0.01$).

Key words : Water; Synodontis Membranaceus; Ora and Ebe Rivers Cement factory; metal concentrations.

INTRODUCTION

Environmental problems in Nigerian are numerous. They include: inefficient wastes disposal, poor sewage system, oil spills, poor urban planning and over population, all these lead to air and water pollution. These anthropegenic activities are largely caused by living habits of Nigerians and illegal practices of companies factories and other corporate bodies.

Contamination of terrestrial ecosystem with metals may upset normal ecological processes by altering the relative abundance and diversity of specie of microorganisms, plants and animals. (Voisanan and Melivaara, 1988). The cumulative effects of cadmium on aquatic organisms, particularly in freshwater can affect the functioning of the ecosystem (Eisler, 1995). Fish and large crustaceans may accumulate anthropogenic contaminants from contaminated sediments and elicit biological response (Beyer et al, 1996). The major sources of pollution in streams and rivers are the effluents from industries and untreated wastes. This continuous contamination of our water resources affects the fauna and flora which explains the presence of toxic heavy metals in crabs (Okoye et al, 2002). Several studies of fish and aquatic invertebrates have revealed a high degree of variability in the uptake and accumulation of heavy metals both within and between populations (Wong and Rainbow, 1986; Moore and Rainbow, 1987; Bjerregaard, 1988, 1990; Rainbow and white 1989, 1990; Donker and Bogert, 1991; Bjerregaard and Deplede, 1994).

Major causes of aquatic pollution include the discharge of sewage, industrial and agricultural wastes, both organic and inorganic; mining, cement production; dredging and china clay wastes; fertilizers and pesticides washed off the land by rain; spills of oil; chemical and other toxic substances from ships, waterside installations and road tankers; heat from power station cooling outlets; radioactivity; atmospheric fall-out, acid rain and irrigation (Linda et al, 1997). One method to qualify observed chemical concentration levels is compare them with background standards, obtained by analyzing samples from remote and largely uncontaminated areas. (Fostner, and Wittmann, 1979).

Bioaccumation of nickel and vanadium in catfish (Clarius batrachus) was investigated (Ray 1990). The bioaccumulation of zinc and copper in several different tissues of African sharptooth casfish was studied and compared. Marked differences between the different types of tissue were observed (Bezuidehout, 1990). The concentrations of several heavy metals were determined in 42 Tilapia nilotica fish samples taken from the Nile River at Aswan. The results were found to be within the human safety baseline levels (Mohamed, 1990). Concentration of seven heavy metals were measured and studied in Northern pike, white suckers, and the sediment near a metal smelter. Metal concentrations in muscle tissue were poor indicator of metal concentrations in the sediment (Harrise and Klaverkamp, 1990). The intense lead release due to human activities during the last two centuries has led scientists to investigate possible perturbations induced by anthropogenic emissions on atmospheric geochemical cycling. Industrial lead has been introduce in the atmosphere from several sources (mainly fossil fuel combustion and smelting so that such an industrial lead flux has largely altered natural concentrations in oceans and rivers (Ritson et al, 1994). The increase in concentration of Fe, Ni, As, Ba and Co in water samples of the Betim River, is coursed by several industries and the discharge of the domestic sewage from Betim, a town with 100,000 inhabitants (Maria-Adelaide et al, 2002). Studies of freshwater ecosystem in Minas Gerais are just beginning and ecological problems have been identified in rivers, lakes and reservoirs (Coelho and Giani, 1994, Jordao et al, 1999). This study is an attempt to estimate the present levels of heavy metals in water and fishes from Ora and Ebe Rivers; to compare metal concentrations in fishes from Ebe and Ora Rivers and to identity the major sources of metal pollution from both rivers.

Study area

Geographically, the study area comprises Enugu and Ebonyi states. Ebe River which rises from the hills of umosigide village of Obollow-Eke flows by the Nigerian cement factory at Nkalagu and before emptying into the Cross River as Ebonyi River is joined by Ora River which rises from Ezimo Hills and also flows by the Nigerian cement factory. This cement factory discharges its industrial emissions and effluents into the rivers.

MATERIAL AND METHODS

Two sample points were located at the Ora River in Ebunyi State. Sample 01 was located by the bridge along Eha-Amufu road and the second one (02) was located just after water pumping station of Nigercem. At that same point the fish was collected. The distance between sample points 01 and 02 was about two kiliometres.

Also at Ebe River, two sample points were located. Sample point 01 was located by the bridge at Eha-Amufu town. The second sample point (02) was located about a kilometer apart from 01 along the direction of flow (down stream) of the river. The fish was collected at sample point 02.

River water samples for the study were collected between June 1996 to May 1997. The samples were collected at a depth of about 15cm in clean white polyethylene stoppered bottles which have been washed with soap solution, rinsed three times with pure water and then raised another three times with 1% HNO_3. The river water to be collected was used to rinsed the bottles and stoppers for three times. The final samples were taken at a depth of several centimetres. The water samples were stoppered and labeled. The samples were filtered by passing water through a 0.45mm Millipore membrane filter placed in an all glass Millipore filtering system. The membrane filters had been washed with 1% HNO_3 followed by rinsing in high purity water prior to filtration (Meranger et al 1979). The samples were taken to laboratory and stored in cold at 4°C prior to digestion. 100cm^3 of each water sample was transferred into a beaker and 5.00cm^3 of concentrated HNO_3 was added. The beaker containing the solution was placed on a hot plate and evapourated to near dryness making sure that the ample does not boil. The beaker containing the residue was cooled. Then 5.00cm^3 of concentrated HNO_3 was further added (Ahn et al 1996). This was retuned to the hot plate until digestion was completed. Them 2.00cm^3 of concentrated HNO_3 was added and the beaker was warned slightly to dissolve the residue. The digested sample was filtered. The filtrate was made up to 50cm^3 mark with deionized water. The solutions were returned to the laboratory and kept in the refrigerator before they were analysed the blanks were also prepared using the same procedure of digestion as in samples.

Fishes were obtained from Ebe and Ora Rivers. The fishes were brought life in a plastic bucket containing the river water to the laboratory. The Synodontis membranaceus (Cat fish) were caught into three parts, with stainless steel, namely the head, muscle and intestine. These parts were separately dried at 60°C (Ney et al 1983). They were crushed with mortar and were kept in the refrigerator prior to digestion. Each component of the dried synodontis membranaceus (5g) was weighed out and digested in a conical flask with mixed acid (4ml) prepared from 2ml $HCLO_4$ and 20ml HNO_3 (Prosi et al, 1983 and Ney et al, 1983). The resultant solutions in the conical flask were placed on hot plate with constant stirring before they were transferred into the fume cupboard and allowed to stand overnight. On cooling, the mixture was filtered and the filtrate was made up to 100ml in a volumetric flask with deionised water. The solutions were stored in the refrigerator, prior to metal analysis.

RESULTS AND DISCUSSION

Mean concentrations of metals analysed in water samples from Ora and Ebe Rivers are given in Tables 1 and 2 while those for the fishes are also given in Tables 3,4,5,6,7 and 8.

Table - 1: Mean concentrations (ppm) of water samples from Ora River

	SAMPLING SITE 01		SAMPLINGS SITE 02	
Element	Mean	Range	Mean	Range
Ca	25.60	0.30 – 61.11	26.46	0.33 – 61.11
Mg	3.22	0.53 – 7.20	3.09	1.02 – 6.00
Na	1.90	0.833 – 3.65	1.75	0.799 – 3.46
K	4.97	0.60 – 6.55	5.14	0.56 – 6.58
Fe	1.58	0.578 – 2.48	1.61	0.401 – 2.48
Cu	0.102	0.00 – 0.313	0.106	0.00 – 0.314
Zn	0.195	0.028 – 0.42	0.222	0.100 – 0.400
Pb	0.32	0.00 – 0.645	0.261	0.00 – 0.76
As	0.486	0.052 – 1.464	0.610	0.251 – 1.481
Hg	0.221	0.01 – 0.60	0.262	0.01 – 0.66
Cd	0.047	0.00 – 0.10	0.063	0.00 – 0.106
Mn	0.44	0.01 – 1.46	0.67	0.01 – 2.25
Ni	0.125	0.00 – 0.391	0.132	0.00 – 0.386
Cr	0.036	0.00 – 0.087	0.034	0.00 – 0.093
Al	0.03	0.005 – 0.080	0.04	0.004 – 0.083

Table - 2: Mean concentrations (ppm) of water samples from Ebe River

	SAMPLING SITE 01		SAMPLINGS SITE 02	
Element	**Mean**	**Range**	**Mean**	**Range**
Ca	26.62	0.49 – 75.00	26.77	0.38 – 72.00
Mg	1.997	1.19 – 4.60	2.02	1.19 – 4.92
Na	2.00	0.87 – 2.73	2.01	0.87 – 2.60
K	6.34	0.69 – 8.87	5.61	0.66 – 7.97
Fe	1.84	0.699 – 4.13	1.84	0.10 – 4.13
Cu	0.12	0.00 – 0.33	0.13	0.00 – 0.39
Zn	0.174	0.075 – 0.390	0.176	0.075 – 0.384
Pb	0.384	0.012 – 1.00	0.448	0.018 – 1.63
As	0.405	0.165 – 0.873	0.410	0.157 – 0.615
Hg	0.115	0.006 – 0.245	0.105	0.006 – 0.24
Cd	0.062	0.028 – 0.106	0.06	0.024 – 0.10
Mn	0.327	0.10 – 1.425	0.279	0.005 – 1.031
Ni	0.139	0.002 – 0.447	0.146	0.005 – 0.443
Cr	0.054	0.015 – 0.10	0.052	0.01 – 0.10
Al	0.023	0.005 – 0.073	0.025	0.012 – 0.075

Table - 3: Metal Concentrations in Synodontis membranaceus (catfish) (mg/kg dry weight) parts (Head, muscle and intestine from Ora River

Metal	Head	Muscle	Intestine	Whole-body
As	1.49	1.544	1.55	1.528
Pb	3.80	2.042	2.575	2.806
Cu	0.572	0.552	0.574	0.566
Mn	3.309	4.312	4.524	4.048
Sn	0.100	0.090	0.080	0.09
Fe	4.919	5.00	3.355	4.425
Mg	10.558	9.196	10.683	10.146
Ni	4.78	6.28	4.30	5.123
Zn	1.777	1.217	2.679	1.891
Cd	0.309	0.197	0.274	0.26
Hg	0.018	0.040	0.042	0.033
Cr	4.843	2.954	4.89	4.229
Al	0.346	0.326	0.361	0.344

Table - 4: Metal Concentrations in Synodontis membranaceus (catfish) (mg/kg dry weight) parts (Head, muscle and intestine from Ebe River

Metal	Head	Muscle	Intestine	Whole body
Na	400.00	320.00	198.00	306.00
K	490.00	718.00	464.00	557.33
Mg	2219.00	1067.00	1029.00	1438.33
Ca	4689.00	1738.00	93.00	2173.33
Fe	1.70	1.90	0.20	1.29
Zn	3.22	1.70	2.58	2.50
Cu	0.70	0.40	0.60	0.57
Pb	2.90	0.90	ND	1.27
Cd	0.20	0.10	ND	0.10
Ni	1.30	0.60	ND	0.63
Mn	0.20	0.70	0.50	0.47
Cr	6.20	0.30	0.10	2.20
Co	0.50	0.20	ND	0.23

Table - 5: Relationship between Synodontis memberanaceus Tissues from Ora River.

Metal	Tissues
As	Intestine > Muscle > Head
Pb	Head > Intestine > Muscle
Cu	Head = Muscle = Intestine
Mn	Intestine > Muscle > Head
Sn	Head > Muscle > Intestine
Fe	Muscle > Head > Intestine
Mg	Intestine > Head > Muscle
Ni	Muscle > Head > Intestine
Zn	Intestine > Head > Muscle
Cd	Head > Intestine > Muscle
Hg	Intestine > Muscle > Head
Cr	Intestine > Head > Muscle
Al	Intestine > Head > Muscle

Table - 6: Relationship between Synodontis memberanaceus Tissues from Ebe River.

Metal	Tissues
Pb	Head > Muscle > Intestine
Cu	Head > Intestine > Muscle
Mn	Muscle > Intestine > Head
Fe	Muscle > Head > Intestine
Ni	Head > Muscle > Intestine
Zn	Head > Intestine > Muscle
Cd	Head > Muscle > Intestine
Cr	Head > Muscle > Intestine
Co	Head > Muscle > Intestine
Mg	Head > Muscle > Intestine
Ca	Head > Muscle > Intestine
K	Head > Muscle > Intestine
Na	Head > Muscle > Intestine

Table -7: Relationship between Metals in Synodontis memberanaceus Tissues from Ora and Ebe River respectively.

Tissues	Metals
Head*	Mg>Cr>Fe>Ni>Pb>Mn>Zn>As>Cu>Al>Cd>Sn>Hg
Muscle*	Mg>Ni>Fe>Mn>Cr>Pb>As>Zn>Cu>Al>Cd>Sn>Hg
Intestine*	Mg>Cr>Mn>Ni>Fe>Zn>Pb>As>Cu>Al>Cd>Sn>hg
Head$^+$	Ca>Mg>K>Na>Cr>Zn>Pb>Fe>Ni>Cu>Co>Mn=Cd
Muscle$^+$	Ca>Mg>K>Na>Fe>Zn>Pb>Mn>Ni>Cu>Cr>Co>Cd
Intestine$^+$	Mg>K>Na>Ca>Zn>Ca>Zn>Cu>Mn>Fe>Cr

*Ora River + Ebe River

A close look at water samples from Ora and Ebe Rivers showed that there were metal variations interms of their concentrations. Also all the metals analysed were detected. There were no significant mean difference between metal concentration obtained from sampling site o1 and o2 for each river. Analysis of variance also revealed that there were no significant mean difference in metal concentrations between water samples from Ora and Ebe River. This implies that environmental changes did not influence metal values from both rivers. It is possible that sources of metal contamination in water samples from both river are the same. Calcium is the most abundant element found in both rivers. This is due to presence of the cement factory at Nkalagu. The availability of metals such as iron, calcium and aluminium in water samples are traced to cement factory (Nsi and Shallsuku 2002).

Metals analysed in Synodontis membranaceus revealed that metals such as lead, cadmium, nickel and cobalt were below detection limits in intestine of the fishes from Ebe River. Other metals were detected in the head, muscle and intestine of fishes from Ora and Ebe Rivers. The relationship between metals and fish tissue are present in Table 7 for both rivers. A further look at

Table 5 and 6 on the relaionship between Synodontis membranaceus tissues showed that there were variations of metals in head, muscle and intestine of fishes from the two rivers. The concentrations of metals such as lead, copper, manganese, iron, nickel, cadmium and chromium in fish from Ora River exceeded those for Ebe River. This implies that the uptake of metals by fish is a function of the size. High concentration of metals (non-critical metal) such as sodium, magnesium, potassium and calcium were recorded in fish from Ebe River. Magnesium and calcium being the most abundant metals in the earth crust were found to have the highest concentrations in the whole body of the fish.

The concentrations of metals such as chromium, copper, iron, and zinc in fish from both rivers were lower than those obtained by Buu-olayan and Subrahmanyan (1996) from the Kuwait coast (Cr 6.2 – 8.8, Cu 4.2 –96.2, Fe 18.8 – 126.4 and Zn 7.6 – 81.3µg/g dry weight) whereas lead and nickel concentration in this study were within those values from Kuwait Coast (lead 0.2 – 14.6 and Ni 0.05 – 20.4µg/g dry weight) Mercury concentrations in fish from Ora River were lower than those values (0.4 – 1.33µg/g) reported by Ndiokwere (1983) from River Niger and Delta Areas of Nigeria and those values 90.14 and 0.32 ppm) from River Kaduna as reported by Nwaedozie (1998). Arsenic concentrations in fish samples from Ora River exceeded those values (0.07 - -0.42µg/g) reported by Ndiokwere (1983).

Correlation between river water and fish tissues from Ora River showed that inverse relationship were observed ($p<0.01$) for copper, chromium and zinc. Whereas positive relationships were observed (p,0.01) for tin, cadmium, mercury and aluminium. Metals such as arsenic, lead, manganese, iron and nickel were not found to be significant between river water and fish tissue. From Ebe River only chromium showed an inverse relationship ($p<0.01$) whereas lead, manganese, iron, cadmium, chromium, and cobalt were positively correlated ($P<0.01$). Copper, zinc and nickel were not correlated. The inverse correlations, according to Bordin et al (1992)can occur if the metal uptake by fish is more rapid than the uptake by river water. The positive relationship is an indication that metal accumulations in fish is from the river water. The discharge of agricultural leaching and wastes mining, cement production, soil leaching and wastes, fertilizes and other toxic substances helped to account for the levels of metals in Ora and Ebe Rivers.

CONCLUSION

Metals analysed in water samples from Ora and Ebe River revealed that there were no significant mean difference between the two rivers. A close look at the mean concentrations showed that there were metal variations from sampling sites 01 and 02. This is as a result of seasonal changes.

A further look at Tables 5 and 6 showed there were variations of metal concentrations in the three parts (head, muscl and intestine) of Synodondis membrnaceus from both rivers. Cd, Cu, Pb and Hg found in this study were lower than the maximum permissible concentrations (Cd:1mg/kg; Cu;20 mgIkg; Pb:5 mgIKg and Hg:1 mgIkg) reported by BOE, (1991). Arsenic concentrations in Synodontis membranaceus can be considered dangerous in this study because it exceeded the maximum permissible concentration of 1.0mgIkg. Other metals (C u, Mu, Sn, Fe, Mg, Ni, Zn, Cr, Al, Ca, K, Na and Co) analysed in Synodondis membranaceus may not be dangerous to consumers of fishes from both rivers. The positive correlation found for some metal concentrations is an indication that, metal accumulations in fishes is from river water. Therefore the sources of metal contaminations in water and fishes are traced to soil leaching and runoff occasioned by rainfall, effluents and emission from the Nigerian Cement Factory at Nkalagu.

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