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Biomagnification of Some Heavy and Essential Metals in Sediments, Fishes and Crayfish from Ondo State Coastal Region, Nigeria

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Abstract. The biomagnification levels of some essential (Fe, Zn, Cu) and toxic metals (Pb, Ni, Cd, Cr, Co, Mn) were determined in sediments, three kinds of fish (*Oreochromis niloticus*, *Synodonthis* sp., and *Clarias gariepinus*), and crayfish from the Ondo State coastal region. The metal biomagnification in the fish and crayfish was several times greater than in water, while that in the sediments was several thousand-folds greater than in both the organisms and water. Among the metals examined in water, Fe was the most abundant with average values of 146.7 and 74.3 mg/l, respectively, for wet and dry seasons, while Co was the least with average values of 2.4 and 1.6 mg/l. In the sediments, concentrations of Pb, Ni, Fe, Cr, Co and Mn in the wet season were relatively higher than those obtained for the dry season. Fe with an average of 50.9 mg/kg in *C. gariepinus* was the most abundant metal in the fish samples, while Cu with an average value of 0.3 mg/kg in *O. niloticus* was the least. The metal biomagnification for most of the metals for both seasons was found to vary widely from one location to the other. This was confirmed by the coefficient of variation that ranged from 31% to 144% and 29% to 130% in the wet and dry seasons, respectively. The present study has shown that fish, crayfish and sediments can be used to monitor the pollution level of metals in the Nigerian coastal water.

Keywords: metal biomagnification, heavy metals, sediments, crayfish, metal pollution, metal accumulation in fish

Introduction

The occurrence of metals in excess of natural loads is a problem of serious concern (Adeyeye, 2000). This is attributed to the rapid population increase, industrial development, urbanization, and agricultural practices (Calamari and Naeve, 1994). Some of these metals are extremely dangerous to human health, such as Cd accumulation is associated with hypertension, osteomalacia and itai-itai disease (Ipinmoroti *et al.*, 1997; Oloyede *et al.*, 1990). Lead poisoning has been associated with permanent brain damage, behavioural disorders and impaired hearing (Ipinmoroti *et al.*, 1997; Mirian *et al.*, 1994). Toxic and essential metals enter the aquatic environment through natural and artificial processes that involve weathering of rocks and soil, dissolution of aerosol particles in the atmosphere, oil spillage, sewage effluents, auto-emissions, dredging activities, and industrial effluents (Asaolu *et al.*, 1997; Ipinmoroti and Oshodi, 1993). With increased diversification in industrialization and extensive use of metal based fertilizers, such as phosphate and ammonia fertilizers in Nigeria, the concentration of metal pollutants in the freshwater reservoirs is expected to rise through natural run-offs (Finerty *et al.*, 1990). High percentage of acid leachable metals, such as Fe, Mn, Zn, Pb, Cu and Ni, have been reported for some lakes in and around Ibadan, Nigeria (Ajayi and Mombeshora, 1989). After entering the water, metals may precipitate, get adsorbed on solid surface, remain soluble or suspended in water, or are taken-up by fauna and flora, eventually accumulating in marine organisms that are consumed by human beings (Asaolu *et al.*, 1997; Mohammed *et al.*, 1982; Gutheric *et al.*, 1979). The presence of metal pollutants in fresh and marine waters has been found to disturb the delicate balance of the aquatic ecosystem, including concentration of some metals in the body tissues of fish (Asaolu *et al.*, 1997; Munshi and Singh, 1989; Kakulu and Osibanjo, 1986).

In the natural aquatic ecosystems, metals occur normally in nanogram to microgram levels. However, some of these metals occuring at low concentrations in surface waters are found in high concentrations in the corresponding sediments and fishes in the aquatic environments (Asaolu *et al.*, 1997; Calamari and Naeve, 1994; Kakulu and Osibanjo, 1986). It is, therefore, necessary to understand the biomagnification levels of some of these metals in the sediments and biota in the aquatic ecosystems. This work was designed to examine the biomagnification levels of some metals in the sediments, fishes and crayfish from the coastal regions of Ondo State, Nigeria with a view to creating baseline documentation and environmental awareness.

Materials and Methods

Surface water samples were collected from fourteen different locations between Igbokoda and Jirinwo where the sea incursion takes place (Fig. 1). The water samples were collected in 2.5 litre polythene bottles, previously washed and leached with

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10% NHO_3 for 48 h. The water samples were chemically preserved by the addition of 5 ml conc HNO_3 per litre, kept in refrigerator prior to analysis.

Sediment samples were collected by divers from each location from where the surface water samples were collected. The sediment samples were collected in polythene bags that were previously soaked in 10% HNO_3 for 48 h, followed by rinsing with distilled water and then allowed to drain to dryness.

Three different types of fish (*Oreochromis niloticus*, *Synodontis* sp., and *Clarias gariepinus*) and crayfish were bought randomly from fishermen fishing along the coastal area of study. The samples were carefully washed with distilled deionised water to remove any adhering contaminants and then dried in filter paper folds. The samples were then wrapped in aluminium foils and kept in the deep freezer at -18 °C prior to analysis.

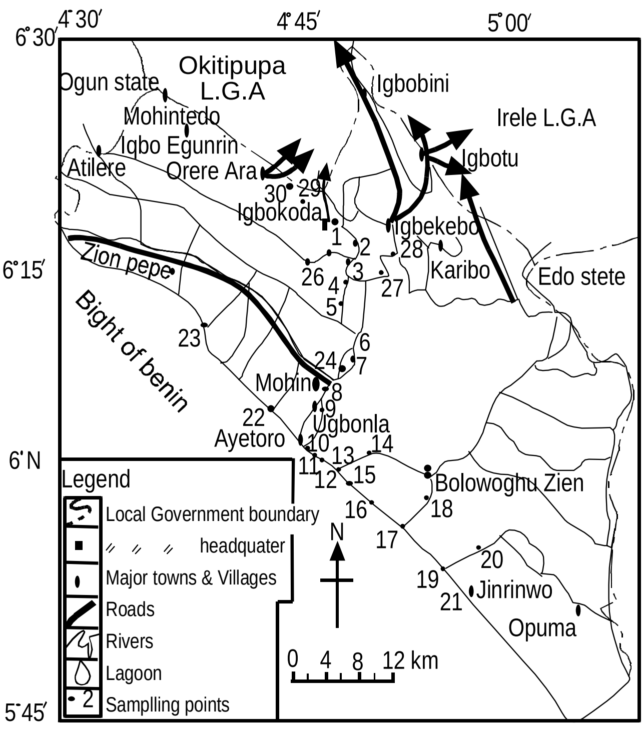

Fig. 1. Map of Ilaje/Ese Odo Local Government of Ondo State showing water and sediment sampling points.

Sample treatment and metal determination. Metals were extracted from the water samples, using a mixture of ammonium pyrolidinedithiocarbamate (APDC) and sodium diethyldithiocarbamate (NaDDC) solution as reported by Lo *et al.* (1982) and Ipinmoroti *et al.* (1997). The method has been reported to extract nearly all the metals from solution at pH 4.0-4.5, with an extraction efficiency of about 95%, 94%, 100%, 88%, 96% and 92% for Cd, Co, Fe, Ni, Pb and Zn, respectively. Metal concentrations in the extract were determined by atomic absorption spectrophotometer (Varian Model Spectral AA-10).

The sediment samples were air dried, ground and sieved through a nylon sieve of 200 mesh size. 0.5 g of the sieved sample was digested in a teflon beaker with a mixture of HNO_3, HCl_4 and HF in the ratio 7:2:8 ml, respectively (Asaolu *et al.*, 1997). The resultant solutions from the digest were filtered, in each case, into a 100 ml volumetric flask and made up to the mark with distilled deionised water. The metals were determined in the resultant solutions by atomic absorption spectrophotometer.

About 4 g of the homogenized samples of the fishes and crayfish were digested with a mixture of conc HNO_3 and 72% HCl_4 in the ratio 100:3 in an air tight nelgene bottle in a temperature controlled waterbath at about 85 °C for 3 h (Asaolu *et al.*, 1997). Resultant solutions from the digest were filtered into 100 ml volumetric flasks and then made up to the mark with 0.5% HNO_3. The metals from the solutions were determined by atomic absorption spectrophotometer.

Results and Discussion

The map of the coastal region showing the sampling locations is given in Fig. 1. Tables 1 and 2 present the mean metal levels (mg/l) of some toxic and essential metals in water samples for both the wet and dry seasons, respectively. Except for Cu, Zn and Cd, metal concentrations in the water during the wet season were relatively higher than the dry season. This may be attributed to the natural run-offs during the raining period from various sources, including the mineralised areas which eventually end up in the aquatic system (Ipinmoroti *et al.*, 1997). Iron was the most abundant metal during the wet and dry seasons with average values of 146.7 and 74.3 mg/l, respectively, while Co was the least with average values of 2.4 and 1.6 mg/l for the wet and dry seasons.

Metal concentrations in water from this area (Tables 1 and 2) have been discussed exhaustively (Asaolu, 1998; Ipinmoroti *et al.*, 1997). Tables 3 and 4 present mean metal levels (mg/kg) in sediments of the coastal region for both the wet and dry seasons. Concentrations of Pb, Ni, Fe, Cr, Co and Mn in the wet season were relatively higher than those obtained in the dry season. This is similar to the trends observed for the surface water in the present study. This is probably due to the high flushing rate during the rains in the wet season (Asaolu *et al.*, 1997).

The higher concentration of Fe, as compared to other metals, in the sediments from the locations of sampling has been

Table 1. Metal levels (mg/l x 10^{-3}) in the Ondo coastal waters during the wet season

Location of sampling/ statistical analysis	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Igbokoda	2.5	9.2	197.5	6.9	7.4	7.5	3.1	2.1	13.4
Kajola	1.3	9.9	135.8	5.6	10.1	3.3	2.1	2.4	12.6
Ibila	2.0	10.35	121.1	5.2	7.8	4.1	2.4	0.7	10.6
Elegboro	4.7	15.5	141.3	6.1	8.9	5.5	14.4	1.0	14.1
Legha	5.0	7.8	145.4	4.4	7.7	2.7	1.4	3.7	10.0
Mahin	4.7	14.4	122.6	5.8	8.0	5.1	14.4	2.3	13.4
Ugbonla	3.4	9.2	161.8	5.8	7.4	3.8	4.5	0.6	12.3
Ayetoro	3.8	11.1	159.3	5.8	6.5	3.6	4.9	5.3	12.3
Alagbo	4.4	20.3	161.3	4.4	6.3	2.4	0.7	1.4	8.4
Asumaga	4.0	19.8	153.0	4.3	5.4	5.3	14.0	3.8	12.8
Ilepete	0.8	12.1	188.2	4.8	6.0	2.8	0.8	4.1	8.6
Obenle	0.4	6.7	69.5	2.3	3.9	1.7	0.4	0.3	8.2
Ojumole	0.9	7.8	141.5	2.5	6.2	2.2	1.5	1.1	11.9
Jirinwo	1.5	18.4	156.4	6.3	8.1	3.9	2.3	3.5	12.6
Mean values	2.8	12.3	146.7	5.0	7.1	3.9	4.8	2.4	11.5
sd	1.7	4.6	30.9	1.3	1.5	1.6	5.3	1.5	2.0
cv	0.59	0.37	0.21	0.27	0.22	0.40	1.10	0.6	0.17

sd: standard deviation; cv: coefficient of variation

Table 2. Metal levels (mg/l x 10^{-3}) in the Ondo coastal waters during the dry season

Location of sampling/ statistical analysis	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Igbokoda	2.2	6.8	23.2	6.4	11.1	4.1	1.2	2.0	9.3
Kajola	1.1	5.5	45.7	7.0	9.7	4.0	1.6	1.1	10.4
Ibila	1.6	6.6	31.9	6.5	10.9	5.2	1.6	0.9	11.5
Elegboro	4.1	5.4	44.4	7.5	11.8	4.9	10.2	5.0	12.7
Legha	1.2	4.4	29.0	5.7	9.5	3.1	0.7	0.5	9.0
Mahin	4.2	8.0	26.6	8.3	11.3	4.4	6.9	1.0	12.1
Ugbonla	2.9	7.4	31.0	7.5	10.4	3.7	6.9	1.0	12.1
Ayetoro	3.3	7.8	51.6	6.7	10.3	3.9	3.5	2.0	12.3
Alagbo	7.0	3.4	38.3	7.5	10.4	2.7	0.4	0.8	11.6
Asumaga	3.5	7.7	52.9	7.8	9.6	6.3	10.0	5.0	11.9
Ilepete	0.6	6.1	29.6	5.4	7.6	2.7	0.2	0.4	8.4
Obenle	0.4	3.1	76.8	3.5	5.3	2.4	0.4	0.6	8.0
Ojumole	0.6	4.4	316.5	7.4	8.5	3.1	0.6	1.1	11.0
Jirinwo	1.4	5.7	242.4	7.0	5.7	3.6	1.5	2.0	12.1
Mean values	2.4	5.9	74.3	6.7	9.7	3.9	3.3	1.6	10.9
sd	1.9	1.6	89.2	1.2	1.7	1.1	3.6	1.6	1.6
cv	0.77	0.27	1.2	0.18	0.17	0.27	1.1	0.97	0.15

sd: standard deviation; cv: coefficient of variation

attributed to the high iron concentrations in the Nigerian soils (Asaolu *et al.*, 1997; Okoye, 1991). Table 5 presents the mean metal concentrations (mg/kg) for the three different types of fishes and crayfish from the coastal region. Among the fish samples, *Synodontis* sp., tended to accumulate more metals, such as Pb, Ni, Cu, Zn, Cr and Co, than *C. gariepinus* and *O. niloticus*. Iron with an average of 50.9 mg/kg in *C. gariepinus* was the most abundant metal in the fish samples, while Cu with an average value of 0.3 mg/kg in *O. niloticus* was the least. Similar observations have been reported earlier (Okoye, 1991). Concentrations of Pb, Fe, Cu and Zn in crayfish were higher than in the fishes. Present study suggests that higher concentrations of such metals in the crayfish were due to the bottom feeding habit, since the concentrations of these metals were higher in the sediments. It is quite possible that the crayfish ingest more metals during feeding on benthos and hence concentrated the metals more than the fishes (Asaolu, 1998).

The high concentration of the metals in fish and crayfish samples, as compared with the water samples, could be an advantage particularly in respect of some of the essential minerals. For example, Fe has been found to play a vital role in the formation of haemoglobin, Co as a component of vitamin B (cyanocobalamin) is essential for the prevention of anaemia, and Cu and Zn have been found to play important role in enzymatic activities (Cater and Fernando, 1979). However, high concentrations of the toxic metals in this respect would be dangerous as some of these metals, such as Cd and Pb have been reported to be extremely toxic even at very low concentrations (Adeyeye, 2000; Ipinmoroti *et al.*, 1997).

Table 3. Metal levels (mg/kg) in sediments collected from the Ondo coastal waters during the wet season

Location of sampling/ statistical analysis	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Igbokoda	7.4	16.8	214.1	7.5	7.0	10.4	16.9	5.7	62.5
Kajola	9.5	18.1	120.7	7.1	8.2	9.6	18.0	6.1	57.9
Ibila	6.8	16.7	198.9	6.7	7.7	8.5	15.3	9.2	49.0
Elegboro	9.5	22.5	233.9	6.3	7.8	9.9	19.3	6.4	55.0
Legha	10.1	25.8	515.0	8.1	9.5	10.0	20.9	6.5	203.5
Mahin	7.0	18.6	216.7	5.5	9.3	8.9	16.1	8.3	61.1
Ugbonla	7.4	20.8	214.3	7.6	8.3	9.2	17.5	9.8	47.8
Ayetoro	9.8	22.6	328.4	8.3	8.4	9.8	19.1	6.6	97.2
Alagbo	8.7	20.8	196.2	7.4	8.3	9.0	18.4	6.0	72.5
Asumaga	9.1	22.6	235.5	8.8	8.5	9.3	18.8	6.5	177.8
Ilepete	4.3	17.5	193.2	4.8	6.3	8.0	11.9	9.6	58.1
Obenle	8.5	20.1	240.0	7.8	8.7	9.3	17.6	13.0	78.5
Ojumole	9.8	26.1	348.9	7.9	9.4	10.2	19.4	12.7	149.3
Jirinwo	5.8	22.2	194.2	5.7	7.0	0.1	15.1	12.1	65.3
Mean values	8.1	20.8	246.4	7.1	8.2	9.3	17.5	8.5	88.3
sd	1.7	3.0	95.6	1.2	0.94	0.75	2.3	2.6	50.8
cv	0.21	0.15	0.39	0.16	0.11	0.08	0.13	0.31	0.58

sd: standard deviation; cv: coefficient of variation

Table 4. Metal levels (mg/kg) in sediments collected from the Ondo coastal waters during the dry season

Location of sampling/ statistical analysis	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Igbokoda	7.0	10.9	134.7	7.7	7.9	8.5	12.9	1.4	56.2
Kajola	8.9	15.5	124.6	10.0	9.3	10.5	15.4	1.6	51.8
Ibila	6.6	8.3	100.5	7.6	7.2	8.3	11.2	1.0	45.0
Elegboro	8.9	12.2	155.2	9.4	10.0	10.1	15.2	1.7	52.0
Legha	9.7	18.9	338.2	10.7	11.7	12.0	17.2	2.3	190.0
Mahin	6.6	9.4	122.2	8.4	7.5	8.5	11.6	1.2	55.6
Ugbonla	6.6	10.0	112.5	7.3	8.9	8.6	12.9	1.3	41.6
Ayetoro	9.0	16.1	256.4	9.4	10.2	10.5	15.5	1.8	91.5
Alagbo	8.0	10.3	199.2	8.5	9.9	9.0	14.3	1.5	72.1
Asumaga	9.3	18.3	172.7	10.0	11.2	9.3	13.8	1.9	170.0
Ilepete	5.6	8.6	85.1	7.0	7.0	8.3	10.7	1.4	52.1
Obenle	8.5	11.7	155.9	9.5	9.3	9.8	16.9	1.5	71.1
Ojumole	9.8	16.9	312.6	10.6	10.6	11.7	18.8	2.0	146.0
Jirinwo	6.5	10.2	124.2	7.9	7.9	8.6	13.1	1.6	58.3
Mean values	7.8	12.0	167.5	8.9	9.2	9.6	14.3	1.6	82.4
sd	1.3	4.8	78.4	1.2	1.5	1.2	2.4	0.34	49.2
cv	0.18	0.40	0.47	0.14	0.17	0.13	0.17	0.31	0.60

sd: standard deviation; cv: coefficient of variation

Table 5. Metal levels (mg/kg) in the three fish species and crayfish

Fish species/ crayfish samples	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Oreochromis niloticus	1.2	4.8	13.8	0.3	1.5	2.2	2.7	1.6	41.3
Synodontis sp.	1.5	5.8	42.6	0.6	1.9	14.0	6.1	3.8	30.0
Clarias gariepinus	1.4	5.3	50.9	0.4	1.7	21.3	3.6	3.6	22.5
Crayfish	4.5	1.9	78.4	12.8	19.1	0.8	nd	2.9	nd

nd: not detected

Tables 6 and 7 present the level of metal biomagnification in sediments for wet and dry seasons, respectively, while Table 8 presents the level of metal biomagnification in fishes and crayfish. From Tables 6 and 7 it may be observed that the biomagnification of Ni, Cu, Zn, Cd, Co and Mn in the wet season was higher than that obtained in the dry season. Except for Co and Ni, the concentrations of these metals in the sediments in the wet season were lower than those of the dry season. The direct relationship between the concentration and biomagnification of Co and Ni in the wet season suggests that the coastal environment might be naturally rich in Co and Ni, and these could be so leached into the aquatic system during rains. The levels of metal biomagnification determined in the sediments reveal that the metals were present in greater amount (several thousand-folds) than in the corresponding surrounding water (Tables 1-7). Similar observations have been made by Ipinmoroti and Oshodi (1993) in their study of some metals present in fish, water and sediment samples from a pond. The present study suggests that the pollution level of all the metals can be better monitored in the sediments of an aquatic environment. Also, the presence of some metals that may seem to be absent or present at relatively low concentrations, for example Pb and Co, in the surface water can be greater and detectable in the sediment samples. The biomagnification of most of the metals for both seasons varied widely from one location to the other.

This is indicated by the coefficient of variation that ranged from 31% to 144% and 29% to 130% in the wet and dry seasons, respectively (Tables 6 and 7). This indicates that some of the locations were heavily loaded with some of the metals as compared with their values in the corresponding surface water. Such locations, as Igbokoda, Legha, Alagbo, Ilepete, Obenla and Ojumole can be used to monitor the accumulation of metals like Pb, Cr, Co, Mn and Cd (Tables 1-7).

Table 6. The levels of metal biomagnification in sediment samples collected during the wet season

Location of sampling/ statistical analysis	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Igbokoda	2960	1826	1054	1087	946	1387	5452	2714	4664
Kajola	7308	1828	889	1268	812	2909	8571	2542	4595
Ibila	3400	1606	1642	1288	987	2073	6375	13142	4623
Elegboro	2021	1452	1655	1033	876	1800	1340	6400	3900
Legha	2020	3308	3542	1841	1234	3703	1492	81667	20350
Mahin	1489	1292	1768	948	1163	1961	1118	3609	4560
Ugbonla	2176	2261	1324	1310	1122	2421	3889	16333	3886
Ayetoro	2579	2036	2062	1431	1292	1722	3898	1245	7902
Alagbo	1977	10246	1216	1681	1317	3750	26286	4286	8631
Asumaga	2275	1141	1539	2047	1574	1755	1343	1712	13891
Ilepete	5375	1446	1027	1000	1050	2857	23875	2341	6756
Obenle	21250	3000	3453	3391	2231	5471	4400	43333	9573
Ojumole	10888	3346	3466	3160	3116	4636	1293	6045	12521
Jirinwo	3867	1207	1242	905	864	2077	6565	3457	5159
Mean values	4970	2571	1850	1599	1213	2823	7167	7773	7929
sd	5354	2332	941	758	375	1184	7121	11159	4802
cv	1.08	0.91	0.51	0.49	0.31	0.42	0.99	1.44	0.61

sd: standard deviation; cv: coefficient of variation

Table 7. The levels of metal biomagnification in sediment samples collected during the dry season

Location of sampling/ statistical analysis	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Igbokoda	3182	1588	5806	1203	712	2073	10750	700	6043
Kajola	8091	2818	2726	1429	959	2625	9625	1455	4981
Ibila	4125	1258	3150	1169	667	1596	7000	1111	3913
Elegboro	2170	2259	3495	1253	847	2061	1490	340	4094
Legha	8083	4295	11662	1877	1232	3871	24571	4600	21111
Mahin	1571	1175	4594	1012	664	1932	1681	12000	4595
Ugbonla	2276	1351	3629	973	856	2324	1869	1300	3438
Ayetoro	2727	264	4969	1403	990	2692	4429	900	7439
Alagbo	1143	3029	3896	1133	952	3444	35750	1875	16207
Asumaga	2657	2377	3265	1282	1167	1476	1380	380	14285
Ilepete	9333	1410	2875	1296	921	3037	53500	3500	6190
Obenle	21250	3774	2030	2714	1755	8083	42250	2500	8887
Ojumole	16333	3841	988	1432	1282	3774	31333	1818	13272
Jirinwo	4642	1789	512	1129	814	2389	8667	800	4858
Mean values	6256	2231	3828	1379	987	2670	16735	2377	7808
sd	5982	1184	2668	444	294	852	17436	3021	5065
cv	0.96	0.53	0.70	0.322	0.29	0.32	1.04	1.30	0.65

sd: standard deviation; cv: coefficient of variation

Table 8. Biomagnification factor of metals in fish

Fish type	Pb	Ni	Fe	Cu	Zn	Cd	Cr	Co	Mn
Oreochromis niloticus	429	390	94	60	211	564	563	667	3591
Synodontis sp.	536	471	290	120	268	3590	1271	1583	2609
Clarias gariepinus	500	431	347	80	239	5462	750	1500	1975
Crayfish	2885	209	710	2188	2262	231	nd	1500	nd

nd: not detected

The biomagnifications of the metals in fishes and crayfish samples were lower than those obtained for the sediment samples (Tables 6-8). However, metal concentrations in the fish and crayfish samples were greater than their corresponding values in water. Similar trends are usual in the aquatic ecosystems (Adeyeye, 2000; Ipinmoroti and Oshodi, 1993). The higher value of the biomagnification of metals in the fishes, and particularly in the crayfish, indicates that the organisms have greater tendency to concentrate the metals in their body tissues. These organisms, therefore, can be considered as pollution indicators of metals in the aquatic environments. The levels of biomagnification of the metals in fishes and crayfish indicate some degree of consistency for which *Synodontis* sp. was noted to concentrate nearly all the metals. It was further observed that *O. niloticus* can be useful for Mn monitoring, *C. gariepinus* for Cd and few other metals, and crayfish for Pb, Cu, Zn and possibly Co.

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