

Original Research Article**TRACE METAL DISTRIBUTION IN FISH, SEDIMENT AND
WATER SAMPLES FROM NKISA RIVER, NIGERIA.****Abstract**

The toxic metals in fish, sediment and water samples from Nkisa river were studied. The elements studied were Cr, Pb, Zn, Cd, Cu, Co, Fe and Mn. Three water, sediment and fish samples of different species were collected from different stations in the river. The water, sediment and fish samples were analyzed for toxic metals using Atomic Absorption Spectrophotometer (AAS). The heavy metals Zn, Fe and Mn were identified in appreciable amounts in fish species *Protoplerus annactus*, *Claries gariepinus* and *Gymnarchus niloticus* of mean values 221.33, 346.00 and 34.88 mg/kg, respectively. The concentration of Pb and Cd were of mean values 0.98 and 0.79 mg/kg in *Protoplerus annactus*. Iron was identified in appreciable amount in the sediment of different stations 1, 2, 3, 4, and 5 of mean values 6457, 24169.66, 23360, 23971.33 and 23264.33 mg/kg, respectively. Pb and Zn were identified in appreciable amount in the sediments of the river. The level of heavy metals Pb, Zn and Cd in water samples from stations 1, 3 and 5 were of mean values 0.207, 0.048 and 0.015 mg/L, respectively. This study is aimed at determining the level of heavy metal toxicants in water, sediment and fish samples from Nkisa river. The effect of these elemental contaminants and the associated health hazards were examined.

25 **Keywords:** Heavy metals, water samples, sediment samples, fish
26 samples, health hazards.

27

28 **Introduction**

29 The contamination of surface water and sediments by heavy metals
30 have been a problem of developing countries of the world especially
31 Nigeria. In Nigeria, the growing rate of industrialization is gradually
32 leading to contamination and deterioration of the environment.
33 Therefore, industrialization and heavy metal pollution of river and
34 water bodies are positively correlated (Wash, 2000, Olaifa and
35 Ayodele, 2004; Oboh and Edema, 2007; Alinnor, 2005a). The danger
36 of accumulation of trace metals in various aspect of the environment
37 has in recent times gained prominence and therefore draw the
38 attention of many researchers (Usman et al; 2004; Alinnor and Ukiwe,
39 2010; Akporhonor et al, 2007). These researchers attributed the
40 incidence of trace metals to indiscriminate disposal of domestic,
41 industrial and mining waste waters. The fate of trace metals in the
42 aquatic environment is of great concern owing to their impact on the
43 entire ecosystem. This is true of slow running streams which receive
44 non – point municipal and industrials discharge from industries, cities
45 or towns. Heavy metals in aquatic environment are accumulated in
46 water and sediment reservoir. Therefore, stream and river sediments
47 act as sink or traps for heavy metals carried into them by feeder
48 tributaries (Lyons and Fitzgeraled, 1980).

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50 Nkisa river flows in Egbema, Imo state of Nigeria. Agip (Nig) Plc is an
51 oil exploration and exploitation company. The crude oil pipe lines of
52 the company runs beside the river. There have been cases of oil pipe
53 line leakages and vandalization of oil pipe lines by crude oil thieves, all
54 these occur regularly in the vicinity. These oil spills or leakages always
55 enter the river. The communities living near the river carry out fishing
56 and other domestic activities in the river. In view of the crude oil and
57 metal works activities that goes on near the river, it is important to
58 ascertain the level of contamination of water, sediment and fish
59 samples by heavy metals. Associated health hazards of the heavy
60 metals were examined.

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62 Studies have shown that many rivers in Nigeria contains various levels
63 of heavy metal pollutants (Shabanda et al, 2012; Usman, 2011;
64 Aiyesanmi, 2006; Alinnor, 2005a). These metals find their way into
65 the aquatic environment either by natural process of weathering or
66 through man's activities such as agricultural and industrial waste
67 water disposal. Iwegbue et al (2011) working on Orogodo river in
68 Delta State of Nigeria reported heavy metal contamination of fish
69 samples such as Cd, Cu, Cr, Ni, Zn, Pb and Mn. These heavy metals
70 may be ingested directly by eating the fish contaminated with
71 elemental toxicants. Obodo (2004) working on Anambra river, has
72 reported bioaccumulation of heavy metals in fish samples obtained

from the river. Luinnik and Zubenko (2000) have reported trace metal pollution of aquatic ecosystems in sediment, water and fish samples. They reported that trace metal concentrations were high in sediment and fish samples than water samples. Burger et al; (2002) reported heavy metal contamination of fish samples from Savannah river and potential health hazards of fish samples from the river.

2.0 Materials and method.

2.1 Collection of Water Samples

Polyethylene containers of 2.5 dm^3 were washed with soap solution and rinsed with distilled water, and finally rinsed with deionized water. Water samples were collected using sterile 2.5 dm^3 polyethylene containers along the reaches of Nkisa river at various stations 1, 2, 3, 4 and 5 as shown in Fig .1. The water samples were preserved with concentrated hydrochloric acid ($2 \text{ cm}^3 \text{ acid/dm}^3 \text{ water}$) and stored at 4°C until use.

2.2 Collection for Sediment Samples

A grab sampler was used to collect benthic sediments at various stations 1, 2, 3, 4 and 5 along the reaches of the river. The sediments were packed in cellophane bags, labeled and stored below 4°C in a refrigerator until use.

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98 **2.3 Collection of Fish Samples**

99 The fresh fish samples collected from Nkisa river were *Protoplerus*
100 *annactus*, *Gymnarchus niloticus* and *Claries gariepinus*. These fish
101 samples were collected from different stations of the river during the
102 dry season of the year precisely between months of November and
103 December. The fresh fish were collected with locally made wire net of
104 2.5 mm diameter. The samples were stored below 4 °C in a
105 refrigerator until use.

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107 **2.4 Analysis of Water Samples**

108 Water samples were pre-treated by repeated evaporation with analar
109 grade nitric acid (HNO₃) as outlined in the standard methods for the
110 Examination of water and wastewater (APHA – AWWA – WPCF,
111 2005). Heavy metal contaminants in the water samples were
112 determined using Unicam 919 Atomic Absorption Spectrophotometer
113 (AAS).

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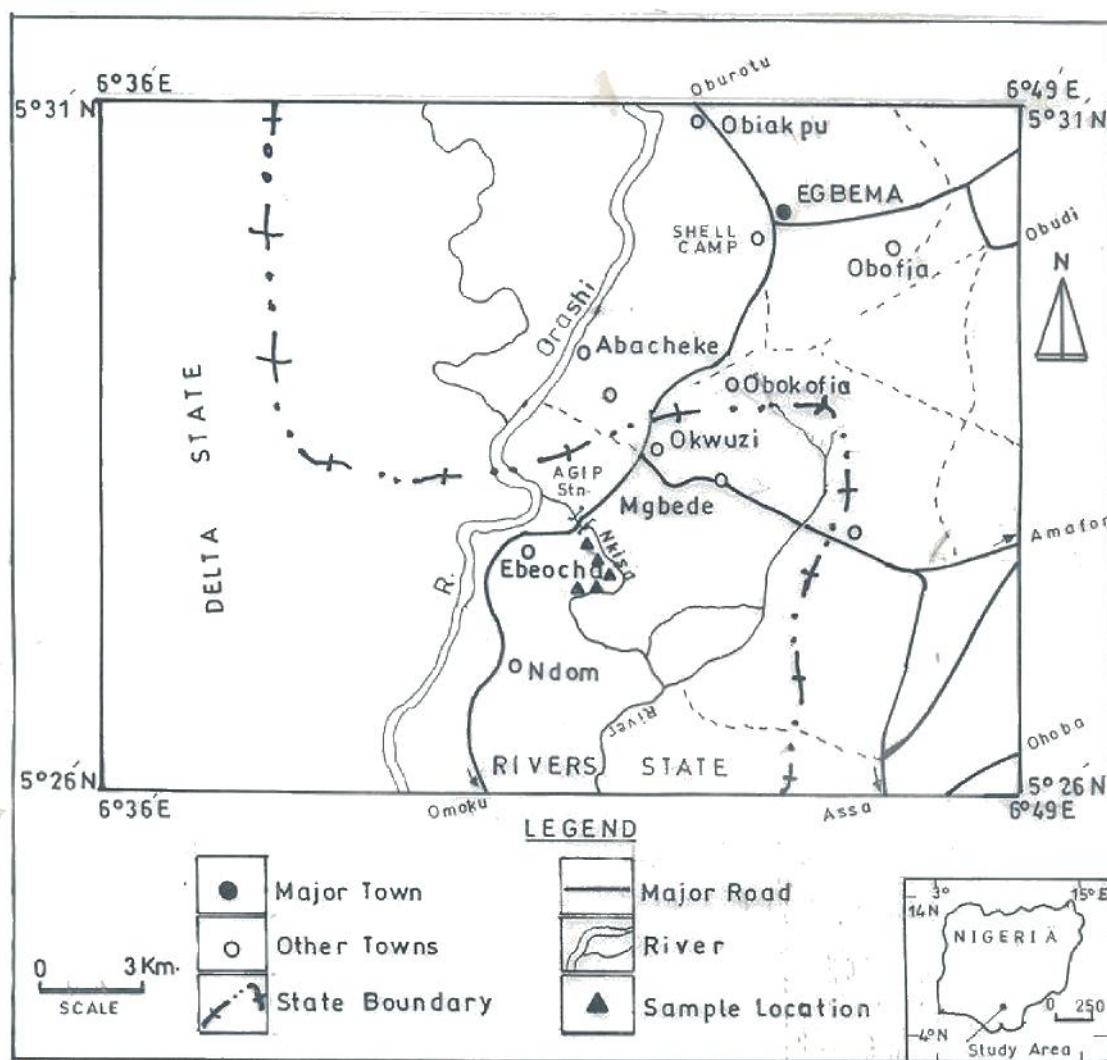


Fig: 1 Location Map of the study area

2.5 Analysis of Sediment Samples

The wet sediment samples were ash at 555 °C, it was pulverized and sieved through a 63 µm mesh prior to digestion. The vial containing the sediment was shaken for homogenization. After homogenization 5 g of dried sediment was weighed into a Teflon crucible and 1 cm³ of (HNO₃ /HCl, 1:3 v/v) and 6 cm³ of hydrofluoric acid were added into

the crucible for complete decomposition of organic material. The crucible was closed to allow the sample pre-digest at room temperature for 1 hr. Then the crucible was placed on a hot plate at 120 °C for 6 hr until organic material was completely destroyed. The digestion unit was cooled to room temperature. The resulting solution after digestion was collected in a 50 cm³ glass volumetric flask containing 2.7 g of boric acid in 20 cm³ of doubly distilled water (Akan and Abiola, 2008). It was diluted to the mark. The boric acid neutralizes the hydrofluoric acid in the digest. The digested samples were analyzed using Unicam 919 AAS.

2.6 Analysis of fish samples.

The whole fish were dried in an electric oven at 70-80 °C for 3 days. A homogenized 2 g of the ground fish was weighed in an analytical balance and ash in a furnace at 550 °C. The samples were put in flasks, and 10 ml each of concentrated HNO₃ and HCl were added. The samples were digested for 2-3 hr until brown fumes ceased to evolve (Cappon, 1987; Alinnor, 2005a).

Filtration was done through a Whatman GFK glass filter and solution made up to 100 ml mark with deionized water and kept ready for AAS analysis. The digested samples were analyzed using Unicam 919 AAS according to the technique as described by Frank et al; (1992). All chemicals used were of analytical reagent grade.

3.0 Results and Discussion

The data presented in Tables 1 and 2 shows that water and sediment samples obtained from Nkisa river were contaminated with heavy metals. This study revealed that the river is contaminated with chromium along the reaches of the river at stations 1, 2, 3, 4 and 5 of mean values 0.103, 0.084, 0.089, 0.079 and 0.053 mg/L, respectively. The World Health Organization (WHO,1993) acceptable value for Cr in drinking water is 0.05 mg/L. The result indicates that Cr concentration at station 5 is within the acceptable recommended limit of WHO. Aiyesanmi (2006) working on Ominla and Oluwa rivers in Okitipupa, Ondo State of Nigeria reported Cr concentration of mean values 0.013 and 0.006 mg/L, respectively. These values were within the WHO recommended limit and below the values obtained in this study. Shabanda et al (2012) working on River Jega in Kebbi state of Nigeria reported high Cr concentration of mean value 0.193 mg/L. Chromium is carcinogenic when inhaled. The chief health problems associated with chromium compound are related to chromium (VI). The breathing of dust or mists containing chromium (VI) compounds leads to ulceration and eventual perforation of cartilaginous portions of the nasal septum. Table 2 shows that sediments of Nkisa river were contaminated with chromium along the reaches of the river at stations 1,2,3 4 and 5. The Cr concentration in the sediment were of mean values 1.70, 32.29, 31.24, 33.13 and 31.1 mg/kg at stations 1,2, 3, 4 and 5, respectively. Shabanda et al; (2012) working on River Jega

193 reported Cr concentration in sediment of the river of mean value
 194 0.591 mg/kg. The high concentration of Cr in Sediments of Nkisa river
 195 may be attributed to crude oil and metal works activities that goes on
 196 near the river.

197
 198 Table 1: Concentration (mg/L) of some heavy metals in water samples
 199 form Nkisa river

Station	Water sample	Cr	Pb	Zn	Cd	Cu	Co	Fe	Mn
1	A	0.103	0.214	0.058	0.028	0.051	0.123	0.631	0.113
	B	0.105	0.202	0.051	0.025	0.058	0.110	0.627	0.108
	C	0.101	0.204	0.054	0.023	0.049	0.120	0.625	0.107
2	E	0.091	0.193	0.041	0.012	0.032	0.103	0.291	0.100
	F	0.084	0.184	0.032	0.021	0.043	0.100	0.272	0.102
	G	0.076	0.171	0.024	0.020	0.041	0.107	0.274	0.090
3	H	0.090	0.198	0.053	0.024	0.048	0.111	0.563	0.110
	J	0.094	0.192	0.048	0.021	0.050	0.121	0.552	0.106
	K	0.082	0.203	0.042	0.023	0.042	0.109	0.514	0.098
4	M	0.083	0.196	0.047	0.015	0.045	0.105	0.381	0.103
	N	0.072	0.188	0.038	0.022	0.046	0.104	0.363	0.105
	P	0.079	0.183	0.043	0.016	0.038	0.108	0.375	0.096
5	S	0.061	0.164	0.031	0.011	0.041	0.091	0.345	0.102
	T	0.054	0.176	0.027	0.021	0.032	0.101	0.326	0.093
	R	0.043	0.157	0.033	0.013	0.030	0.086	0.316	0.106

Lead is identified in appreciable amount in water samples in different stations 1, 2,3,4 and 5 of mean values 0.207, 0.183, 0.198, 0.189 and 0.166 mg/L, respectively. Aiyesanmi (2006) working on Ominla and Oluwa rivers reported Pb concentration of means values 0.009 and 0.005 mg/L, respectively. Alinnor (2005b) working on Aba river in Nigeria reported high Pb concentration of mean values 0.90, 0.80 and 0.710 ppm at point of discharge of waste from Nigeria Breweries Plc, International Glass Industry Plc and Paterson Zochonis Plc, respectively. It has been reported that high concentration of Pb found in Aba river might be attributed to these industries that discharge waste into the river. The WHO acceptable concentration for Pb in drinking water is 0.01 mg/L. The result of this study indicates that Nkisa river is contaminated when compared to WHO recommended limit. Pb is a well – known toxicant that has several deleterious effects on human being even at low concentration because it is cumulative. Pb reduces neuro – psychological function leading to inattention and intelligence quotient (IQ) deficiency (Waldboh, 1978). The result of this study as shown in Table 2 indicates that sediments in Nkisa river have high Pb concentration 17.46, 16.09, 16.80 and 17.36 mg/kg at stations 2,3,4 and 5, respectively. Usman (2011) working on Asa river in Ilorin Metropolis of Kwara state of Nigeria reported high concentration of Pb in sediment of the river of mean value 370.40 µg/g. The high level of Pb in sediment of Asa river was attributed to slow movement of the river water and high absorption ability of the metal by the sediment. This study shows that sediment of Nkisa river is contaminated with Pb. The high level

of Pb in the sediments of the river may be attributed to crude oil and metal works activities that goes on near the river.

Table 1 shows that water samples from the river were contaminated with Zn at stations 1, 2, 3, 4 and 5 of mean values 0.054, 0.032, 0.048, 0.043 and 0.030 mg/L, respectively. Obodo (2001) working on River Niger in Nigeria reported Zn concentration of mean value 0.22 mg/L in water sample. Alinnor (2005a) working on Aba river in Nigeria reported high concentration of Zn of mean values 6.902, 11.28, 7.57 and 10.54 mg/L from discharge point of the following industries Paterson Zochonis Plc, International Glass Industry Plc, International Equitable Association Plc and Nigeria Breweries Plc, respectively. These values shows that Aba river has high concentration of Zn as compared to values obtained from Nkisa river. The high level of Zn in Aba river might be attributed to number of industries that discharge their waste into the river. The WHO maximum acceptable concentration for Zn in drinking water is 3.0 mg/L. The values obtained for zinc in water samples from various stations of Nkisa river when compared to WHO standard shows that Nkisa river is not contaminated with zinc. This study as shown in Table 2 indicates that sediments of Nkisa river were contaminated with Zn of high mean values 64.12, 68.33, 59.06 and 68.52 mg/kg at stations 2,3,4 and 5, respectively. Mayerson et al (1981) have reported that river sediments act as a reservoir which may either concentrate metals from the water or release metals to the water. Mayerson et al (1981) report might be attributed to high Zn concentration in sediments than water samples from this study. Whitton

249 and Harding (1978) have reported high enrichment of sediment with Zn as
250 a result of urban and industrial pollution in Southern Lake Michigan.

251
252 Table 2: Concentration (mg/kg) of some heavy metals in sediment samples
253 from Nkisa river

Station	Sediment sample	Cr	Pb	Zn	Cd	Cu	C _o	Fe	Mn
1	A	1.70	1.00	0.50	0.43	1.30	3.00	6474	77.32
	B	1.64	1.21	0.47	0.40	1.20	2.96	6556	75.14
	C	1.76	1.46	0.49	0.41	1.46	3.26	6341	79.21
2	D	33.20	17.81	64.41	0.101	13.30	7.80	24150	108.21
	E	31.41	16.89	63.22	0.112	12.94	6.97	25143	106.45
	F	32.26	17.67	64.73	0.104	13.56	8.67	23216	109.76
3	G	31.10	16.33	68.73	0.196	12.10	9.40	23760	96.21
	H	32.13	16.03	67.12	0.187	12.67	8.24	24106	94.35
	I	30.50	15.92	69.13	0.194	11.48	10.61	22214	97.62
4	J	33.62	16.93	59.70	0.193	11.24	10.40	23860	93.93
	K	34.25	17.01	57.43	0.171	11.30	10.00	23640	94.12
	L	31.51	16.45	60.13	0.182	10.96	9.67	24414	92.71
5	M	31.71	17.63	68.94	0.141	13.30	10.70	23260	103.02
	N	33.10	17.01	67.17	0.153	12.71	10.50	23431	101.23
	P	30.01	17.45	69.45	0.157	12.46	10.98	23102	105.63

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This study revealed that the river is contaminated with Cd along the reaches of the river. The Cd concentration of the river were similar at stations 2,3,4 and 5 of mean values 0.018, 0.023, 0.018 and 0.015 mg/L, respectively. Alinnor (2005b) working on Aba river reported high Cd concentration in water sample of mean value 0.212 mg/L at discharge point of waste into the river from Paterson Zochonis Plc. The WHO acceptable concentration for Cd in drinking water is 0.003 mg/L. The result of the analysis indicates that Nkisa river is contaminated with Cd when compared to WHO standard. Cadmium is not an essential element in biological process, instead it is toxic and poisoning occurs through inhalation and ingestion. On inhalation cadmium causes acute bronchitis and pneumonitis and inflammation of the liver. Cadmium causes slight anaemia possibly due to competition between iron and cadmium in the body resulting to iron deficiency Lauwerys (1979) . The result of this study indicates that Cd concentration in sediments of Nkisa river were of mean values 0.41, 0.106, 0.192, 0.182 and 0.150 mg/kg at stations 1, 2, 3, 4 and 5, respectively. Shabanda et al (2012) reported low concentration of Cd in sediment of Jega river of mean value 0.005 mg/kg. The Cd value in Jega river was lower than the values obtained in this study because of metal works and crude oil activities that goes on near Nkisa river.

Table 1 shows copper concentration in water samples of this study of mean values 0.053, 0.039, 0.047, 0.043 and 0.034 mg/L at stations 1,2,3,4 and 5, respectively. The WHO recommended acceptable level for Cu in drinking water is 2.0 mg/L. Aiyesanmi (2006) reported copper concentration of

mean value 0.303 mg/L in water sample from Ominla river. Both Nkisa and Ominla rivers have copper concentrations below the recommended WHO limit. Table 2 shows that sediments of Nkisa river have high copper concentration at stations, 2,3, 4 and 5 of mean values 13.27, 12.08, 11.24 and 12. 82 mg/kg, respectively . High Cu concentration in the sediments of the river may be attributed to crude oil exploitation going on near the river and other metal works activities by the communities living near the river.

The result of the analysis indicates that the river is contaminated with cobalt of mean values 0.118, 0.103, 0.114, 0.106 and 0.093 mg/L at stations 1,2,3,4 and 5, respectively. Alinnor (2005a) working on Aba river reported cobalt concentration of mean value 1.022 mg/L at discharge point of waste from International Equitable Association Plc that produces soaps, detergents and beverages. The result indicates that Aba river is contaminated with cobalt when compared to values obtained from Nkisa river. High concentration of cobalt in the body poses health hazards. The sediments of Nkisa river as shown in Table 2 indicates that the river sediments were contaminated with cobalt at stations 1,2,3,4, and 5 of mean values 3.07, 7.81, 9. 42, 10.02 and 10.70 mg/kg, respectively. The result shows that cobalt concentration increases along the reaches of the river.

Table 1 shows that Fe concentration in water samples were of mean values 0.628, 0.279, 0.543, 0.373 and 0.329 mg/L at stations 1,2,3,4 and 5, respectively. Obodo (2001) working on River Niger reported high

concentration of iron of mean value 18.67 mg/L. The high level of iron in River Niger was attributed to metal and blacksmith works that goes on near the river. The WHO acceptable concentration for Fe in drinking water is 0.30 mg/L. Iron concentration above the acceptable level may affect the taste of water. Table 2 shows that iron is in appreciable amount in sediments of Nkisa river. All the stations have high Fe concentration of mean values 6457, 24169.66, 23360, 23971.33 and 23264.33 mg/kg at stations 1,2,3 4 and 5, respectively. Akan and Abiola (2008) reported Fe in sediment of Lagos Lagoon in Nigeria of mean value 12.23 mg/kg. The High concentration of Fe in sediments of Nkisa may be attributed to activities that goes on near the river especially welding and metal works by artisans and Agip (Nig) Plc activities.

Table 1 shows the level of manganese in water samples from stations 1,2,3, 4 and 5 of mean values 0.108, 0.097, 0.105, 0.101 and 0.100 mg/L, respectively. Obodo (2001) working on River Niger reported Mn concentration of mean value 0.31 mg/L from water sample collected from the river. The WHO acceptable level for Mn in drinking water is 0.10 mg/L. The result of the analysis indicates that water samples from Nkisa river were within WHO recommended limit. Table 2 shows that sediments of Nkisa river were contaminated with manganese at various stations 1,2,3,4 and 5 of means values 77.22, 108.14, 96.06, 93.59 and 103.29 mg/kg, respectively. The high level of Mn in sediments of Nkisa river were in agreement with the concept that sediment contains higher concentrations of metals than that of overlying water (Depinto and Martin, 1980).

Shabanda et al (2012) reported Mn concentration of mean value 0.407 mg/kg in sediment of Jega River. The high level of manganese in sediment of Nkisa river may be attributed to metal works activities going on near the river.

Table 3: Concentration (mg/kg) of some heavy metals in fish samples from Nkisa river.

Name of Fish	Fish samples	Cr	Pb	Zn	Cd	Cu	C _o	Fe	Mn
Protoplerus	A	1.09	0.91	221	0.84	4.90	3.00	175	11.80
Annecteus	B	1.03	0.98	236	0.63	4.94	2.96	177	11.91
	C	0.97	1.04	207	0.90	4.92	2.41	172	11.72
Gymnarchus	D	1.01	0.84	82.40	0.10	0.51	6.60	194.33	34.88
niloticus	E	0.93	0.77	83.50	0.09	0.46	7.10	194.00	34.80
	F	0.86	0.68	81.70	0.06	0.49	6.12	197.00	32.13
Claries	G	0.73	1.00	82.40	0.08	1.40	6.40	346	24.50
gariepinus	H	0.67	0.90	83.53	0.05	1.23	6.66	320	26.10
	J	0.51	0.72	76.10	0.03	1.56	6.32	372	22.80

Table 3 shows the level of heavy metal contamination of different species of fresh fish samples obtained from Nkisa river. Chromium concentration in *Protopleus annectues*, *Gymnarchus niloticus* and *Claries gariepinus* were of mean values 1.03, 0.93 and 0. 64 mg/kg, respectively. Shabanda et al (2012) working on Jega River reported Cr concentration of mean values

0.381, 0.243 and 0.466 mg/kg in fresh fish samples *Tilapia*, *miligi* and *synodontis sorex*, respectively. Odoemelam (2005) working on Oguta lake in Nigeria reported Cr concentration of mean values 1.86, 0.84 and 2.86 mg/L in fish samples *Alestes nurse*, *Sarotherodon niloticus* and *Auchenoglanis occidentalis*, respectively. The high concentration of Cr in fish samples from Nkisa river when compared to water samples indicates that fish species are benthic feeder and hence acquire much of the heavy metal from the sediment that is saturated with chromium.

The level of Pb in fish species *Protoplerus annecteus*, *Gymnarchus niloticus* and *Claries gariepinus* were of mean values 0.98, 0.76 and 0.87 mg/kg, respectively. Alinnor (2005b) working on Aba river reported Pb concentration of mean value 1.60 mg/L in fish specie *Scrombrus scrombrus*. Akan and Abiola (2008) working on Lagos Lagoon in Nigeria reported high concentration of Pb in fish species *Tilapia guineensis*, *Liza grandisquamis*, *Chrysichthys nigrodigitatus* and *Psettias sebae* of mean values 17.98, 12.81, 15.75 and 11.66 mg/kg, respectively. The high level of Pb found in Lagos Lagoon as compared to Nkisa river may be attributed to dumping of industrial and domestic solid waste into the Lagoon. The Pb in the fish sample may be transferred to human on consumption of fish that is contaminated with Pb which poses health hazards.

Table 3 shows the level of zinc in different fish species found in Nkisa river. The result of the analysis indicates that *Protoplerus annecteus* has high concentration of Zn of mean value 211.33 mg/kg, whereas *Gymnarchus*

niloticus and *Claries gariepinus* have zinc concentration of mean values 82.53 and 80.68 mg/kg, respectively. The high level of zinc in fish samples poses health hazard to individual that feed on the fish. The high concentration of zinc may be attributed to crude oil activities going on near the river. Obodo (2002) working on lower reaches of River Niger reported Zn concentration of mean values 72.33 and 65.33 mg/kg in *Synodontis membranaceus* and *Tilapia zilli*, respectively. It has been reported that zinc concentration has effect on the hepatic distribution of other trace metals in fish. Toxic metals such as Zn, Cu and Mn are essential elements that exhibit similar atomic structure and could therefore compete for the same site (Underwood, 1977).

The concentration of Cd in *Protoplerus annecteus* was high of mean value 0.79 mg/kg when compared to mean values 0.08 and 0.05 mg/kg for *Gymnarchus niloticus* and *Claries gariepinus*, respectively. Alinnor (2005b) working on Aba river reported Cd concentration of mean value 0.033 mg/L in fish sample *Scombrus Scombrus*. Okoye et al (2002) working on Warri river in Nigeria reported high concentration of Cd in aquatic organism of mean value 1.50 mg/L. The high level of Cd in aquatic organism from Warri river when compared to Nkisa river was attributed to Warri refinery that discharge waste into Warri river and other industries located near the river. Shimizu (1972) has reported detrimental effects attributed to cadmium poisoning in the Jintsu river in Japan.

Table 3 shows that fish species *Protoplerus annecteus*, *Gymnarchus niloticus* and *Claries gariepinus* were contaminated with copper of mean values 4.92, 0.49 and 1.39 mg/kg, respectively. Obodo (2002) working on lower reaches of River Niger reported Cu concentration of mean value 8.33 mg/kg in *Synodontis membranaceus*. High concentration of Cu in River Niger may be attributed to human activities such as urbanization and industrial effluents that were being discharged into River Niger. Copper is an essential element that promotes the activity of certain enzyme systems in the body. It is toxic to man and animals when ingested in large amount (Pearson, 1976).

The concentration of cobalt in fish species *Protoplerus annecteus*, *Gymnarchus niloticus* and *Claries gariepinus* were of mean values 2.79, 6.61 and 6.46 mg/kg, respectively. Alinnor (2005a) working on Aba river identified cobalt in fish species of mean values 0.05 and 0.04 mg/L in *Sadillina* and *Hetretis niloticus*, respectively. Cobalt poses health hazards on consumption of fish contaminated with cobalt.

The result of the analysis as shown in Table 3 indicates that *Protoplerus annecteus*, *Gymnarchus niloticus* and *Claries gariepinus* have Fe concentration of mean values 174.66, 194.33 and 346.00 mg/kg, respectively. Abdulraham and Tsafe (2004) working on Sokoto Rima river in Nigeria reported Fe concentratin of mean values 1.22 and 2.284 µg/g in fish species *Tilapia zilli* and *Bagrus bayad*, respectively. The result indicates that fish samples from Nkisa river accumulate more Fe than fish species

obtained from Sokoto Rima river. This may be attributed to metal and welding works that goes on near Nkisa river. Odoemelum (2005) working on Oguta lake in Nigeria reported iron concentration of mean value 156.00 mg/L in fish sample *Auchenoglanis occidentalis*. Iron is an essential constituent of haemoglobin which is indicated in the transport of oxygen in the blood of human. Studies show that fish generally concentrate metallic ions in their body organism directly or indirectly through ingested food (Vinikour and Goldstein, 1987) and Kakulu et al (1980).

Manganese concentration in fish samples from Nkisa river were in appreciable amount when compared to values obtained from water samples. *Gymnarchus niloticus* has high concentration of Mn of mean value 34.88 mg/kg when compared to mean values 11.81 and 24.47 mg/kg for *Protoplerus annecteus* and *Claries gariepinus*, respectively. Alinnor and Ukiwe (2010) working on Mbaa river, Imo State of Nigeria reported Mn concentration of mean values 8.60 and 10.30 mg/L in fish species *Tilapia guineensis* and *Synodontis membrabaceus*, respectively. Manganese in trace amount is an essential element. Eating fish contaminated with Mn can result in manganese poisoning. Mn poisoning result in chronic manganism, which is the disease of the central nervous system and this can be transferred to man on consumption of fish contaminated with Mn. One of the first toxic effects of Mn is its interference with iron metabolism, specifically haemoglobin formation.

Conclusion

This study revealed that Nkisa river is contaminated with heavy metals from crude oil pipe line leakages and vandalization. These crude oil are being discharged into the river. The contamination of the river is also being attributed to domestic activities as well as metal works that goes on near the river. This study indicates that the river sediment is contaminated with heavy metals in appreciable amount. These heavy metals are transferred to fish that feed on the sediment and the heavy metals are transferred to man on consumption of fish. This report is significant because it gives an idea to the mechanism of depletion and possible extinction of fish species in Nkisa river. The study revealed that water samples from the river are generally high in heavy metals exceeding permissible limit by WHO standard. This study revealed the order of accumulation of heavy metals by different fish species as follows:- $Zn > Fe > Mn > Cu > Co > Cr > Pb > Cd$ for *Protoplerus annactus*. Whereas *Gymnarchus niloticus* has the order $Fe > Zn > Mn > Co > Cr > Pb > Cu > Cd$. The order of accumulation of heavy metals in *Claries gariepinus* is $Fe > Zn > Mn > Co > Cu > Pb > Cr > Cd$. The result shows that fish samples studied have similar trend in accumulation of Mn and Cd.

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