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Trace Metal Distribution in Fish, Sediment and Water Samples from Nkisa River, Nigeria

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Authors' contributions

This work was carried out in collaboration between the authors. Author IJA designed the study, performed the graphics, wrote the first protocol, wrote the first manuscript. Author AFA managed the analysis of this study and literature research. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Aims: Contamination of surface water, sediment and fish samples by heavy metals have been a problem of developing countries as a result of growing rate of industrialization. This study was 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.
Study Design: Unicam 919 Atomic Absorption Spectrophotometer (AAS) was used for the determination of heavy metals in water, sediment and fish samples.
Place and Duration of Study: Department of Chemistry, Federal University of Technology, Owerri, Nigeria, between October and December, 2012.
Methodology: Water samples were pre-treated by repeated evaporation with analar grade nitric acid (HNO_3) and heavy metal contaminant in the water samples were determined using Unicam 919 AAS. The wet sediment samples were ashed at 555ºC. 5 g of dried sediment was weighed into a Teflon crucible and 1 cm^3 of (HNO_3/HCl 1:3 v/v) and 6 cm^3 hydrofluoric acid were added into the crucible. The resulting solution after digestion was collected in volumetric flask containing 2.7 g of boric acid. The digested sample was analyzed using Unicam 919 AAS. The whole fish were dried in an electric oven at 70-80ºC. A homogenized 2 g of the ground fish samples were put in flasks and 10 ml each of concentrated HNO_3 and HCl were added. After digestion the samples were analyzed using Unicam 919 AAS.

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Results: The result of this study revealed that water, sediment and fish samples were contaminated with heavy metals such as Cr, Pb, Cd, Fe, Mn. The study indicates that heavy metal contaminant were observed more in the sediment of the river. The associated health hazards of the metals were examined.
Conclusion: This study revealed that Nkisa River is contaminated with heavy metals from crude oil pipeline leakages and vandalization. This study gives an idea to the mechanisms of depletion and possible extinction of fish species in Nkisa River.

Keywords: Heavy metals; water samples; sediment samples; fish samples; health hazards.

1. INTRODUCTION

The contamination of surface water and sediments by heavy metals have been a problem of developing countries of the world especially Nigeria as result of the growing rate of industrialization which is gradually leading to contamination and deterioration of the environment. Therefore, industrialization and heavy metal pollution of river and water bodies are positively correlated [1-4]. The danger of accumulation of trace metals in various aspects of the environment has in recent times gained prominence and therefore, draws the attention of many researchers [5-7]. These researchers have attributed the incidence of trace metals to indiscriminate disposal of domestic, industrial and mining waste waters. The fate of trace metals in the aquatic environment is of great concern owing to their impact on the entire ecosystem. This is true of slow running streams which receive non – point municipal and industrial discharge from industries, cities or towns. Heavy metals in aquatic environment are accumulated in water and sediment reservoir. Therefore, stream and river sediments act as sink or traps for heavy metals carried into them by feeder tributaries [8].

Nkisa River flows in Egbema, Imo state of Nigeria. Agip (Nig) Plc is both, an oil exploration and exploitation company. The crude oil pipelines of the company run beside the river. There have been cases of oil pipeline leakages and vandalization of pipelines by crude oil thieves, regularly in the vicinity. These oil spills or leakages always enter the river. The communities living near the river carry out fishing and other domestic activities in the river. In view of the crude oil and metal works activities that go on near the river, it is important to ascertain the level of contamination of water, sediment and fish samples by heavy metals. Also, the associated health hazards of the heavy metals were examined.

Studies have shown that many rivers in Nigeria contain various levels of heavy metal pollutants [9-11,4]. These metals find their ways into the aquatic environment either by natural process of weathering or through man's activities such as agricultural and industrial wastes water disposal. Iwegbue et al. [12] working on Orogodo River in Delta State of Nigeria reported heavy metal contamination of fish samples with metals such as Cd, Cu, Cr, Ni, Zn, Pb and Mn. These heavy metals may be ingested directly by eating the fish contaminated with elemental toxicants. Obodo [13] working on Anambra River, has reported bioaccumulation of heavy metals in fish samples obtained from the river. Luinnik and Zubenko [14] have reported trace metal pollution of aquatic ecosystems in sediment, water and fish samples. They reported that trace metal concentrations were higher in sediments and fish samples than water samples. Burger et al. [15] reported heavy metal contamination of fish samples from Savannah River and potential health hazards of fish samples from the river. Atici et al. [16] studied the accumulation of heavy metals Cd, Pb, Hg and Cr in water samples, phytoplanktonic algae and zooplanktonic organisms in Beysehirlake and

Moganlake in Turkey. Also Atici et al. [17] working on Sariyar Dam reservoir in Turkey reported pollution of phytoplanktonic algae and zooplanktonic organisms by heavy metals.

2. MATERIALS AND METHODS

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 NkisaRiver at various stations 1, 2, 3, 4 and 5 as shown in Fig. 1. The water samples were preserved with concentrated hydrochloric acid (2 cm^3 acid/dm^3 water) and stored at 4ºC until use.

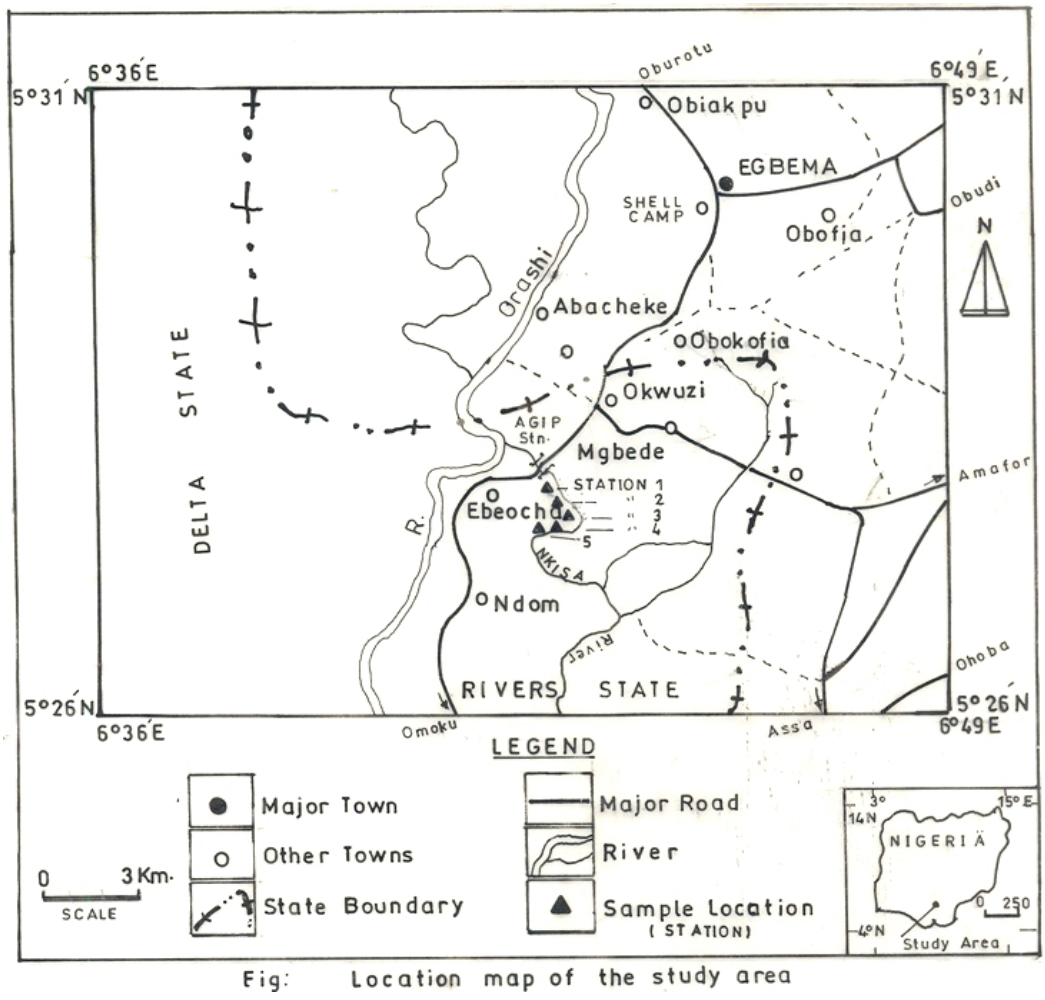

Fig: Location map of the study area

Fig. 1. Location map of the study area

2.2 Collection of 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 4ºC in a refrigerator until use.

2.3 Collection of Fish Samples

The fresh fish samples collected from Nkisa River were *Protopterus annectes, Gymnarchus niloticus* and *Clarias gariepinus*. These fish samples were collected from different stations of the river during the dry season of the year 2012 precisely between the months of November and December with locally made wire net of 2.5 mm in diameter. The fish samples collected from Nkisa River were sold at the nearby markets in Imo and Rivers States of Nigeria. The fish species feed on the bottom sediments of the river. The samples were stored below 4ºC in a refrigerator until use.

2.4 Analysis of Water Samples

Water samples were pre-treated by repeated evaporation with analar grade nitric acid (HNO_3) as outlined in the standard methods for the Examination of water and wastewater [18]. Heavy metal contaminants in the water samples were determined using Unicam 919 Atomic Absorption Spectrophotometer (AAS).

2.5 Analysis of Sediment Samples

The wet sediment samples were ash at 555ºC. 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 cm^3 of (HNO_3 /HCl, 1:3 v/v) and 6 cm^3 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 120ºC for 6 hrs until organic material was completely destroyed. The digestion unit was cooled to room temperature. The resulting solution after digestion was collected in a 50 cm^3 glass volumetric flask containing 2.7 g of boric acid in 20 cm^3 of doubly distilled water [19]. It was diluted to the mark. The boric acid neutralized the hydrofluoric acid in the digest. The digested samples were analyzed using Unicam 919 AAS.

2.6 Analysis of Fish Samples

Fishes collected from all stations were pooled together. The whole fish were dried in an electric oven at 70-80ºC for 3 days. A homogenized 2 g of the ground fish was weighed in an analytical balance and ash in a furnace at 550ºC. The samples were put in flasks, and 10 ml each of concentrated HNO_3 and HCl were added. The samples were digested for 2-3 hrs until brown fumes ceased to evolve [20,4].

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 [21]. All chemicals used were of analytical reagent grade.

3. RESULTS AND DISCUSSION

The data presented in Tables 1 and 2 show 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. World Health Organization [22] 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 [11] 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. [9] 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 NkisaRiver 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. [9] working on River Jega reported Cr concentration in sediment of the river of mean value 0.591 mg/kg. The high concentration of Cr in Sediments of Nkisa River may be attributed to crude oil and metal works activities that go on near the river.

Table 1. Concentration (mg/L) of some heavy metals in water samples from 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
Mean		0.103	0.207	0.054	0.025	0.053	0.118	0.628	0.109
SD		0.002	0.0064	0.0035	0.0025	0.0058	0.0068	0.0031	0.0032
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
Mean		0.084	0.183	0.032	0.018	0.039	0.103	0.279	0.097
SD		0.0053	0.011	0.0085	0.0025	0.0059	0.0035	0.010	0.0064
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
Mean		0.089	0.198	0.048	0.023	0.047	0.114	0.543	0.105
SD		0.0061	0.0055	0.0055	0.0016	0.0042	0.0064	0.026	0.0061
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
Mean		0.078	0.189	0.043	0.018	0.043	0.106	0.373	0.101
SD		0.0056	0.0066	0.0045	0.0038	0.0044	0.0021	0.0092	0.0047
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
Mean	R	0.043	0.157	0.033	0.013	0.030	0.086	0.316	0.106
SD		0.053	0.166	0.030	0.015	0.034	0.093	0.329	0.100
		0.0091	0.0096	0.0031	0.0053	0.0059	0.0076	1.225	0.0067

SD = Standard Deviation

Lead is identified in appreciable amount in water samples at 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 [11] working on Ominla and Oluwa Rivers reported Pb concentration of mean values 0.009 and 0.005 mg/L, respectively. Alinnor [23] 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 the high concentration of Pb found in Aba River might be attributed to these industries that discharge wastes 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 concentrations because it is cumulative. Pb reduces neuro – psychological functions leading to inattention and intelligence quotient (IQ) deficiency [24]. The result of this study as shown in Table 2 indicates that sediments in Nkisa River have high Pb concentrations 17.46, 16.09, 16.80 and 17.36 mg/kg at stations 2, 3, 4 and 5, respectively. Usman [10] 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 go on near the river.

Table 1 shows that water samples from the river were contaminated with Zn at stations I, 2, 3, 4 and 5 of mean values 0.054, 0.032, 0.048, 0.043 and 0.030 mg/L, respectively. Obodo [25] working on River Niger in Nigeria reported Zn concentration of mean value 0.22 mg/L in water sample. Alinnor [4] 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 the discharge point of the following industries: Paterson Zochonis Plc, International Glass Industry Plc, International Equitable Association Plc and Nigeria Breweries Plc, respectively. These values show that Aba River has a high concentration of Zn as compared to values obtained from Nkisa River. The high level of Zn in Aba River might be attributed to the number of industries that discharge their wastes 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 show 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. [26] have reported that river sediments act as a reservoir which may either concentrate metals from the water or release them into the water. Mayerson et al. [26] report might be attributed to high Zn concentration in sediments than water samples from this study. Whitton and Harding [27] have reported high enrichment of sediment with Zn as a result of urban and industrial pollutions in Southern Lake Michigan.

This study revealed that the river is contaminated with Cd along the reaches. The Cd concentrations 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 [23] working on Aba River reported high Cd concentration in water sample of mean value 0.212 mg/L at the discharge point of wastes 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 processes. Instead it is toxic and poisoning occurs through inhalation and ingestion. On inhalation cadmium causes acute bronchitis and pneumonities and

inflammation of the liver. Cadmium causes slight anaemia possibly due to competition between iron and cadmium in the body resulting to iron deficiency [28]. The result of this study indicates that Cd concentrations in the 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. [9] 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 go on near Nkisa River.

Table 2. Concentration (mg/kg) of some heavy metals in sediment samples from Nkisa River

Station	Sediment sample	Cr	Pb	Zn	Cd	Cu	Co	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
Mean		1.70	1.22	0.487	0.413	1.32	3.07	6457	77.22
SD		0.06	0.2303	0.0153	0.0153	0.1311	0.1627	108.50	2.037
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
Mean		32.29	17.48	64.12	0.106	13.27	7.81	24169.7	108.14
SD		0.802	0.495	0.796	0.006	0.311	0.850	963.65	1.656
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
Mean		31.24	16.09	68.33	0.192	12.08	9.42	23360	96.06
SD		0.824	0.212	1.064	0.005	0.602	1.185	599.11	1.185
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
Mean		33.13	16.80	59.06	0.182	11.17	10.02	23971	93.59
SD		1.435	0.303	1.489	0.075	0.181	0.366	398.83	0.765
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
Mean	P	30.01	17.45	69.45	0.157	12.46	10.98	23102	105.63
SD		31.61	17.36	68.52	0.150	12.82	10.73	23264	103.29
		1.548	0.319	1.197	0.0083	0.4313	0.2411	164.54	2.213

SD = Standard Deviation

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 [11] 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 [4]

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 concentrations of cobalt in the body poses health hazards. The sediments of Nkisa River as shown in Table 2 indicate 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 [25] 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 go 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 [19] 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 go 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 [25] 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 indicate 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 [29]. Shabanda et al. [9] 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 shows the level of heavy metal contamination of different species of fresh fish samples obtained from Nkisa River. Chromium concentration in *Protopterus annectes, Gymnarchus niloticus* and *Clarias gariepinus* were of mean values 1.03, 0.93 and 0. 64 mg/kg, respectively. Shabanda et al. [9] working on Jega River reported Cr concentration of mean values 0.381, 0243 and 0.466 mg/kg in fresh fish samples *Tilapia miligi* and *synodontis sorex*, respectively. Odoemelam [30] 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 indicate that fish species are benthic feeder and hence acquire much of the heavy metal from the sediment that is saturated with chromium.

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	Co	Fe	Mn
Protopterus annectes	A	1.09	0.91	221	0.84	4.90	3.00	175	11.80
	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
Mean		1.03	0.98	221.3	0.79	4.92	2.79	174.7	11.81
SD		0.06	0.07	14.50	0.142	0.02	0.33	2.52	0.095
Gymnarchus niloticus	D	1.01	0.84	82.40	0.10	0.51	6.60	194.33	34.88
	E	0.93	0.77	83.50	0.09	0.46	7.10	194.00	34.80
Mean	F	0.86	0.68	81.70	0.06	0.49	6.12	197.00	32.13
		0.93	0.76	82.53	0.08	0.49	6.61	195.11	33.94
SD		0.075	0.08	0.907	0.021	0.025	0.49	I.645	1.565
Clarias gariepinus	G	0.73	1.00	82.40	0.08	1.40	6.40	346	24.50
	H	0.67	0.90	83.53	0.05	1.23	6.66	320	26.10
Mean	J	0.51	0.72	76.10	0.03	1.56	6.32	372	22.80
		0.64	0.87	80.68	0.05	1.40	6.46	346	24.47
SD		0.114	0.142	4.003	0.025	0.165	0.178	26	1.650

SD = Standard Deviation

The level of Pb in fish species *Protopterus annectes, Gymnarchus niloticus* and *Clarias gariepinu*s were of mean values 0.98, 0.76 and 0.87 mg/kg, respectively. Alinnor [23] working on Aba River reported Pb concentration of mean value 1.60 mg/L in fish specie *Scrombrus scrombrus.* Akan and Abiola [19] working on Lagos Lagoon in Nigeria reported high concentration of Pb in fish species *Tilapia guineenis, 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 beings 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 *Protopterus annectes* has high concentration of Zn of mean value 211.33 mg/kg, whereas *Gymnarchus niloticus* and *Clarias 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 [31] 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 [32].

The concentration of Cd in *Protopterus annectes* 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 *Clarias gariepinus*, respectively. Alinnor [23] working on Aba River reported Cd concentration of mean value 0.033 mg/L in fish sample *Scombrus scombrus*. Okoye et al. [33] working on Warri River in Nigeria reported high concentration of Cd in aquatic organisms of mean value 1.50 mg/L. The high level of Cd in aquatic organisms from Warri River when compared to Nkisa River was attributed to Warri refinery that discharges wastes into Warri River and other

industries located near the river. Shimizu [34] has reported detrimental effects attributed to cadmium poisoning in the Jintsu River in Japan.

Table 3 shows that fish species *Protopterus annectes, Gymnarchus niloticus* and *Claria sgariepinus* were contaminated with copper of mean values 4.92, 0.49 and 1.39 mg/kg, respectively. Obodo [31] 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 amounts [35].

The concentration of cobalt in fish species *Protopterus annectes, Gymnarchus niloticus* and *Clarias gariepinus* were of mean values 2.79, 6.61 and 6.46 mg/kg, respectively. Alinnor [4] 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 it.

The result of the analysis as shown in Table 3 indicates that *Protopterus annectes, Gymnarchus niloticus* and *Clarias gariepinus* have Fe concentration of mean values 174.66, 194.33 and 346.00 mg/kg, respectively. Abdulraham and Tsafe [36] working on Sokoto Rima River in Nigeria reported Fe concentration of mean values 1.22 and 2.284 µg/g in fish species *Tilapia zilli* and *Bagrusbayad*, 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 go on near Nkisa River. Odoemelam [30] 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 functions 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 [37,38].

Manganese concentration in fish samples from Nkisa River were in appreciable ratio 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 *Protopterus annectes* and *Clarias gariepinus,* respectively. Alinnor and Ukiwe [6] 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. But 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. One of the first toxic effects of Mn is its interference with iron metabolism, specifically hemoglobin formation.

4. CONCLUSION

This study revealed that Nkisa River is contaminated with heavy metals from crude oil pipeline leakages and vandalization. This crude oil is being discharged into the river. The contamination of the river is also attributed to domestic activities as well as metal works that go on near the river. The study indicated that the river sediment was contaminated with heavy metals in appreciable amount. These heavy metals are transferred to fish that feed on the sediments and the metals are transferred to man on consumption of the fish. This report is significant because it gives an idea to the mechanisms 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 standards. This study revealed the order of accumulation of heavy metals by different fish species as follows:- Zn>Fe>Mn>Cu>C_o>Cr>Pb>Cd for *Protopterus* annectes. Whereas *Gymnarchus niloticus* has the order Fe>Zn>Mn>C_o>Cr>Pb>Cu>Cd. The order of accumulation of heavy metals in *Clarias gariepinus* was Fe>Zn>Mn>C_o>Cu>Pb>Cr>Cd. The result showed that fish samples studied had similar trend in accumulation of Mn and Cd.

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COMPETING INTERESTS

Authors have declared that no competing interest exist.

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