

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 (quantity) 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 (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.

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

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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 as a result of In Nigeria, the growing rate of industrialization
which 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 aspects of the
environment

37 has in recent times gained prominence and therefore, draws the
38 attention of many researchers (Usman et al; 2004; Alinnor and
Ukiwe,

39 2010; Akporhonor et al, 2007). These researchers have 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 industrial 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 Fitzgerald, 1980).

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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 runs beside the river. There have been cases of oil pipe line leakages and vandalization of oil pipelines by crude oil thieves, all these occur 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 goes 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 contains various levels of heavy metal pollutants (Shabanda et al, 2012; Usman, 2011; Aiyesanmi, 2006; Alinnor, 2005a). These metals find their way 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 (2011) 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 (2004) working on Anambra river, has reported bioaccumulation of heavy metals in fish samples obtained

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from the river. Luinnik and Zubenko (2000) have reported trace
meta⁷³ l

⁷⁴ pollution of aquatic ecosystems in sediment, water and fish samples.

⁷⁵ They reported that trace metal concentrations were higher in
sediment^s

⁷⁶ and fish samples than water samples. Burger et al; (2002) reported
⁷⁷ heavy metal contamination of fish samples from Savannah river and
⁷⁸ potential health hazards of fish samples from the river.

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⁸⁰ **2.0 Materials and method.**

⁸¹ **2.1 Collection of Water Samples**

⁸² Polyethylene containers of 2.5 dm³ were washed with soap solution
⁸³ and rinsed with distilled water, and finally rinsed with deionized
water.

⁸⁴ Water samples were collected using sterile 2.5 dm³ polyethylene
⁸⁵ containers along the reaches of Nkisa river at various stations 1, 2,
³,

⁸⁶ 4 and 5 as shown in Fig .1. The water samples were preserved with
⁸⁷ concentrated hydrochloric acid (2 cm³ acid/dm³ water) and stored at
⁴

⁸⁸ °C until use.

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⁹² **2.2 Collection for^(of) Sediment Samples**

⁹³ A grab sampler was used to collect benthic sediments at various
⁹⁴ stations 1, 2, 3, 4 and 5 along the reaches of the river. The
sediments

⁹⁵ were packed in cellophane bags, labeled and stored below 4 °C in a
⁹⁶ refrigerator until use.

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⁹⁸ **2.3 Collection of Fish Sample^s**

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 the months of November
and
103 December. The fresh fish were collected with locally made wire net
of
104 2.5 mm in diameter. The samples were stored below 4 °C in a
105 refrigerator until use.

106 107 **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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2.5 Analysis of Sediment Samples

140 The wet sediment samples were ash at 555 °C. It was pulverized and

141 sieved through a 63 µm mesh prior to digestion. The vial containing

142 the sediment was shaken for homogenization. After homogenization 5

143 g of dried sediment was weighed into a Teflon crucible and 1 cm³ of
144 (HNO₃/HCl, 1:3 v/v) and 6 cm³ of hydrofluoric acid were added into

Fig: 1 Location Map of the study area

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the crucible for complete decomposition of organic material. The
145 e
146 crucible was closed to allow the sample pre- digest at room
147 temperature for 1 hr. Then the crucible was placed on a hot plate at

148 120 °C for 6 hrs until organic material was completely destroyed. The

149 digestion unit was cooled to room temperature. The resulting solution

150 after digestion was collected in a 50 cm³ glass volumetric flask
151 containing 2.7 g of boric acid in 20 cm³ of doubly distilled water (Akan

152 and Abiola, 2008). It was diluted to the mark. The boric acid
153 neutralized the hydrofluoric acid in the digest. The digested samples

154 were analyzed using Unicam 919 AAS.

155

2.6 Analysis of fish samples.

157 The whole fish were dried in an electric oven at 70-80 °C for 3 days. A

158 homogenized 2 g of the ground fish was weighed in an analytical
159 balance and ash in a furnace at 550 °C. The samples were put in
160 flasks, and 10 ml each of concentrated HNO₃ and HCl were added.
161 The samples were digested for 2-3 hrs until brown fumes ceased to
162 evolve (Cappon, 1987; Alinnor, 2005a).

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164 Filtration was done through a Whatman GFK glass filter and
solution

165 made up to 100 ml mark with deionized water and kept ready for
AAS

166 analysis. The digested samples were analyzed using Unicam 919
AAS

167 according to the technique as described by Frank et al; (1992). All
168 chemicals used were of analytical reagent grade.

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3.0 Results and Discussion

170 The data presented in Tables 1 and 2 shows that water and
sediment

171 samples obtained from Nkisa river were contaminated with heavy
172 metals. This study revealed that the river is contaminated with
173 chromium along the reaches of the river at stations 1, 2, 3, 4 and 5
of

174 mean values 0.103, 0.084, 0.089, 0.079 and 0.053 mg/L,
175 respectively. The World Health Organization (WHO,1993)
acceptable

176 value for Cr in drinking water is 0.05 mg/L. The result indicates
that

177 Cr concentration at station 5 is within the acceptable recommended
178 limit of WHO. Aiyesanmi (2006) working on Ominla and Oluwa
rivers

179 in Okitipupa, Ondo State of Nigeria reported Cr concentration of
mean

180 values 0.013 and 0.006 mg/L, respectively. These values were
within

181 the WHO recommended limit and below the values obtained in this
182 study. Shabanda et al (2012) working on River Jega in Kebbi state
of

183 Nigeria reported high Cr concentration of mean value 0.193 mg/L.
184 Chromium is carcinogenic when inhaled. The chief health problems
185 associated with chromium compound are related to chromium (VI).
186 The breathing of dust or mists containing chromium (VI)
compounds

187 leads to ulceration and eventual perforation of cartilaginous
portions

188 of the nasal septum. Table 2 shows that sediments of Nkisa river
were

189 contaminated with chromium along the reaches of the river at
stations

190 1,2,3 4 and 5. The Cr concentration in the sediment were of mean
191 values 1.70, 32.29, 31.24, 33.13 and 31.1 mg/kg at stations 1,2, 3,
4

192 and 5, respectively. Shabanda et al; (2012) working on River Jega

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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 the 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

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Lead is identified in appreciable amount in water samples in(at) differen200 t
 201 stations 1, 2,3,4 and 5 of mean values 0.207, 0.183, 0.198, 0.189 and
 202 0.166 mg/L, respectively. Aiyesanmi (2006) working on Ominla and
 Oluwa

203 rivers reported Pb concentration of means values 0.009 and 0.005
 mg/L,

204 respectively. Alinnor (2005b) working on Aba river in Nigeria reported
 high

205 Pb concentration of mean values 0.90, 0.80 and 0.710 ppm at point of
 206 discharge of waste from Nigeria Breweries Plc, International Glass
 Industry

207 Plc and Paterson Zochonis Plc, respectively. It has been reported that
 thehigh

208 concentration of Pb found in Aba river might be attributed to these
 209 industries that discharge wastes into the river. The WHO acceptable
 210 concentration for Pb in drinking water is 0.01 mg/L. The result of this
 study

211 indicates that Nkisa river is contaminated when compared to WHO
 212 recommended limit. Pb is a well – known toxicant that has several
 213 deleterious effects on human being even at low concentrationsbecause
 it is

214 cumulative. Pb reduces neuro – psychological functions leading to
 215 inattention and intelligence quotient (IQ) deficiency (Waldboh, 1978).
 The

216 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

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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 I, 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 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 shows 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

240 obtained for zinc in water samples from various stations of Nkisa river
 241 when compared to WHO standard shows that Nkisa river is not
 242 contaminated with zinc. This study as shown in Table 2 indicates that
 243 sediments of Nkisa river were contaminated with Zn of high mean
 values
 244 64.12, 68.33, 59.06 and 68.52 mg/kg at stations 2,3,4 and 5,
 respectively.
 245 Mayerson et al (1981) have reported that river sediments act as a
 reservoir
 246 which may either concentrate metals from the water or release
 metals(them) into
 247 the water. Mayerson et al (1981) report might be attributed to high Zn
 248 concentration in sediments than water samples from this study. Whitton

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 and Harding (1978) have reported high enrichment of sediment with Zn 249
 as

250 a result of urban and industrial pollution in Southern Lake Michigan.

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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 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

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 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 (2005b) 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 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 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 (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 go on near Nkisa river.

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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

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mean value 0.303 mg/L in water sample from Ominla river. Both Nkisa 280 and

281 Ominla rivers have copper concentrations below the recommended WHO

282 limit. Table 2 shows that sediments of Nkisa river have high copper
283 concentration at stations, 2,3, 4 and 5 of mean values 13.27, 12.08,
11.24

284 and 12. 82 mg/kg, respectively . High Cu concentration in the sediments
of

285 the river may be attributed to crude oil exploitation going on near the
river

286 and other metal works activities by the communities living near the
river.

287

288 The result of the analysis indicates that the river is contaminated with
289 cobalt of mean values 0.118, 0.103, 0.114, 0.106 and 0.093 mg/L at
290 stations 1,2,3,4 and 5, respectively. Alinnor (2005a) working on Aba
river

291 reported cobalt concentration of mean value 1.022 mg/L at discharge
point

292 of waste from International Equitable Association Plc that produces
soaps,

293 detergents and beverages. The result indicates that Aba river is
294 contaminated with cobalt when compared to values obtained from Nkisa
295 river. High concentrations of cobalt in the body poses health hazards.

The

296 sediments of Nkisa river as shown in Table 2 indicates that the river
297 sediments were contaminated with cobalt at stations 1,2,3,4, and 5 of
298 mean values 3.07, 7.81, 9. 42, 10.02 and 10.70 mg/kg, respectively.

The

299 result shows that cobalt concentration increases along the reaches of
the

300 river.

301

302 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

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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.

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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 results 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

328 agreement with the concept that sediment contains higher
concentrations
329 of metals than that of overlying water (Depinto and Martin, 1980).

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Shabanda et al (2012) reported Mn concentration of mean value 0.40³³⁰⁷
331 mg/kg in sediment of Jega River. The high level of manganese in
sediment
332 of Nkisa river may be attributed to metal works activities going on near
the
333 river.

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

336 Nkisa river.

337

Name of

Fish

Fish

samples

Cr Pb Zn Cd Cu Co 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

338 Table 3 shows the level of heavy metal contamination of different
species

339 of fresh fish samples obtained from Nkisa river. Chromium concentration
340 in *Protopleus annectues*, *Gymnarchus niloticus* and *Claries gariepinus*
were

341 of mean values 1.03, 0.93 and 0. 64 mg/kg, respectively. Shabanda et
al

342 (2012) working on Jega River reported Cr concentration of mean values

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0.381, 0.243 and 0.466 mg/kg in fresh fish samples *Tilapia*, *miligi* and *synodontis*, 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 species *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 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 *Protoplerus annecteus* has a high

concentration of Zn of mean value 211.33 mg/kg, whereas *Gymnarchus*

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niloticus and *Claries gariepinus* have zinc concentration of mean value

369 82.53 and 80.68 mg/kg, respectively. The high level of zinc in fish
 samples
 370 poses health hazard to individual that feed on the fish. The high
 371 concentration of zinc may be attributed to crude oil activities going on
 near
 372 the river. Obodo (2002) working on lower reaches of River Niger
 reported
 373 Zn concentration of mean values 72.33 and 65.33 mg/kg in *Synodontis*
 374 *membranaceus* and *Tilapia zilli*, respectively. It has been reported that
 375 zinc concentration has effect on the hepatic distribution of other trace
 376 metals in fish. Toxic metals such as Zn, Cu and Mn are essential
 elements
 377 that exhibit similar atomic structure and could therefore compete for the
 378 same site (Underwood, 1977).
 379
 380 The concentration of Cd in *Protoplerus annecteus* was high of in mean
 value
 381 0.79 mg/kg when compared to mean values 0.08 and 0.05 mg/kg for
 382 *Gymnarchus niloticus* and *Claries gariepinus*, respectively. Alinnor
 (2005b)
 383 working on Aba river reported Cd concentration of mean value 0.033
 mg/L
 384 in fish sample *Scombrus Scombrus*. Okoye et al (2002) working on Warri
 385 river in Nigeria reported high concentration of Cd in aquatic organisms
 of
 386 mean value 1.50 mg/L. The high level of Cd in aquatic organisms from
 Warri
 387 river when compared to Nkisa river was attributed to Warri refinery that
 388 discharges wastes into Warri river and other industries located near the
 river.
 389 Shimizu (1972) has reported detrimental effects attributed to cadmium
 390 poisoning in the Jintsu river in Japan.
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Table 3 shows that fish species *Protoplerus annecteus*, *Gymnarchu*^{392 s}
 393 *niloticus* and *Claries gariepinus* were contaminated with copper of mean

394 values 4.92, 0.49 and 1.39 mg/kg, respectively. Obodo (2002) working
on

395 lower reaches of River Niger reported Cu concentration of mean value
8.33

396 mg/kg in *Synodontis membranaceus*. High concentration of Cu in River
397 Niger may be attributed to human activities such as urbanization and
398 industrial effluents that were being discharged into River Niger. Copper
is

399 an essential element that promotes the activity of certain enzyme
systems

400 in the body. It is toxic to man and animals when ingested in large
amounts

401 (Pearson, 1976).

402

403 The concentration of cobalt in fish species *Protoplerus annecteus*,
404 *Gymnarchus niloticus* and *Claries gariepinus* were of mean values 2.79,
405 6.61 and 6.46 mg/kg, respectively. Alinnor (2005a) working on Aba river
406 identified cobalt in fish species of mean values 0.05 and 0.04 mg/L in
407 *Sadillina* and *Hetretis niloticus*, respectively. Cobalt poses health
hazards

408 on consumption of fish contaminated with itcobalt.

409

410 The result of the analysis as shown in Table 3 indicates that *Protoplerus*
411 *annecteus*, *Gymnarchus niloticus* and *Claries gariepinus* have Fe
412 concentration of mean values 174.66, 194.33 and 346.00 mg/kg,
413 respectively. Abdulraham and Tsafe (2004) working on Sokoto Rima
river

414 in Nigeria reported Fe concentratin of mean values 1.22 and 2.284 µg/g
in

415 fish species *Tilapia zilli* and *Bagrus bayad*, respectively. The result
indicates

416 that fish samples from Nkisa river accumulate more Fe than fish species

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obtained from Sokoto Rima river. This may be attributed to metal an417 d
418 welding works that goes on near Nkisa river. Odoemelam (2005)
working

419 on Oguta lake in Nigeria reported iron concentration of mean value
156.00
420 mg/L in fish sample *Auchenoglanis occidentalis*. Iron is an essential
421 constituent of haemoglobin which functions is indicated in the transport
of oxygen in
422 the blood of human. Studies show that fish generally concentrate
metallic
423 ions in their body organism directly or indirectly through ingested food
424 (Vinikour and Goldstein, 1987) and Kakulu et al (1980).
425
426 Manganese concentration in fish samples from Nkisa river were in
427 appreciable ratio amount when compared to values obtained from water
428 samples. *Gymnarchus niloticus* has high concentration of Mn of mean
429 value 34.88 mg/kg when compared to mean values 11.81 and 24.47
mg/kg
430 for *Protoplerus annecteus* and *Claries gariepinus*, respectively. Alinnor
and
431 Ukiwe (2010) working on Mbaa river, Imo State of Nigeria reported Mn
432 concentration of mean values 8.60 and 10.30 mg/L in fish species
Tilapia
433 *guineensis* and *Synodontis membrabaceus*, respectively. Manganese in
434 trace amount is an essential element. But eating fish contaminated with
Mn
435 can result in manganese poisoning. Mn poisoning result in chronic
436 manganism, which is the disease of the central nervous system. and this
437 can be transferred to man on consumption of fish contaminated with
Mn.
438 One of the first toxic effects of Mn is its interference with iron
metabolism,
439 specifically haemoglobin formation.
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Conclusi442 **on**

443 This study revealed that Nkisa river is contaminated with heavy metals
444 from crude oil pipeline leakages and vandalization. This crude oil is are

445 being discharged into the river. The contamination of the river is also
being
446 attributed to domestic activities as well as metal works that goes on
near
447 the river. The study indicated that the river sediment was is contaminated
with
448 heavy metals in appreciable amount. These heavy metals are
transferred to
449 fish that feed on the sediments and the heavy metals are transferred to
450 man on consumption of the fish. This report is significant because it
gives an
451 idea to the mechanism of depletion and possible extinction of fish
species
452 in Nkisa river. The study revealed that water samples from the river are
453 generally high in heavy metals exceeding permissible limit by WHO
454 standards. This study revealed the order of accumulation of heavy
metals
455 by different fish species as follows:- Zn>Fe>Mn>Cu>Co>Cr>Pb>Cd for
456 *Protoplerus annactus*. Whereas *Gymnarchus niloticus* has the order
457 Fe>Zn>Mn>Co>Cr>Pb>Cu>Cd. The order of accumulation of heavy
458 metals in *Claries gariepinus* was Fe>Zn> Mn>Co>Cu>Pb>Cr>Cd. The
result
459 showed that fish samples studied had a similar trend in accumulation of
Mn
460 and Cd.

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