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# Some Heavy metals content in fish of River Benue

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**Abstract** Five fish species comprising forty-eight samples were collected from River Benue and analysed for heavy metals. The heavy metal levels in the fish were found to be in the order: Zn > Cu > Pb > Co > Cd. The mean Zn concentrations in µg/g ranged from 4664 ± 446.35 in *Clarias lazera* to 5013.37 ± 638.38 in *Chrysichthys nigrodigitatus*. Mean Cu concentrations ranged from 14.63 ± 2.45 in *Chrysichtys nigrodigitatus* to 30.90 ± 12.95 in *Oreochromis niloticus* while the least metal contents in fish were those of Cd which ranged from 1.38 ± 0.69 in *Chrysichthys nigrodigitatus* to 2.80 ± 2.09 in *Eutropius niloticus*. The concentration of Pb in *Clarias lazera* and *Eutropius niloticus* were significantly higher ($P > 0.05$) than the concentrations obtained in other fish species. Similarly, the one-way ANOVA showed a significant difference ($P > 0.05$) between the concentrations of Co in *Clarias lazera* and *Eutropius niloticus*. It was recommended that the research be extended to cover fish from other water bodies to enable a comparison between heavy metal concentrations in fish of River Benue and those of such water bodies.

**Keywords** Heavy metals, fish, River Benue

## Introduction

Benue state is predominantly an agricultural state with a very low level of industrialization. However, in addition to the agricultural activities, a few industries have been established by the state government and some individuals. Two of these industries, the Benue Brewery Ltd and Pepsi-Cola factory have been sited by the bank of River Benue, on km 5 and km 6 along Makurdi-Gboko road respectively. River Benue therefore receives agricultural waste drains and runoffs, including agro-pesticides from the farms along its course, and in the valleys. Wastewater effluents from these factories also flow into it. Solid municipal wastes from the neighbouring Abinsi town and Makurdi, the state capital are discharged directly into the river.

Heavy metals may be defined as a group of metals and metalloids with an atomic density of about 6 g $cm^{-3}$ [1]. The metals occur in very small quantities of less than 1000 ppm in the earth's crust [2] hence are often called *trace metals*. Heavy metals fall under the category of toxic and accessible metals that are commonly associated with pollution and toxicity problems. The metalloids, arsenic (As) and selenium (Se) are also classified as toxic [3]. These group of pollutants are of public interest because of their potential health hazards [4], even though some trace metals are essential nutrients for both plants and animals.

At elevated concentrations, heavy metals are not only toxic to organisms, but accumulate and magnify along the food chain [5 – 10].

Fish are often used as indicators of heavy metals contamination in the aquatic ecosystem in consideration of their high trophic levels and as important food sources [11, 12] Exceptionally high levels of lead and mercury were reported in the study on tissues of African catfish, *Clarias gariepinus* from River Niger [13]. Similarly, the levels of lead, copper and zinc reported in the study on Nile tilapia, *Oreochromis niloticus* caught from River Delimi, Jos were too high for frequent human consumption [14].
The objectives of this study were to determine the concentrations of Cu, Zn, Pb, Cd and Co in five fish species obtained from River Benue and as well establish a significant relationship (if any) between concentrations of these heavy metals in the fish samples.

## Materials and Methods

### Sampling for fish

The five fish samples used in the study were caught from five sampling stations, by means of a local trap with a net mesh. All the fish species could not be obtained from some sampling stations on the first day of sampling. However, the required number of fifty (50) samples, spreading over the five species were obtained within three days of sampling. The fish samples were identified by appearance and physical features as described by Holden and Reed [15] and further confirmed by an expert from Federal University of Agriculture, Makurdi – Benue State.
Efforts were made to ensure that only fish samples of fairly uniform size and length were selected for analysis.

### Treatment of fish samples

The fish samples were oven-dried at 105 °C to constant weight. Whole fish samples were then ground in a porcelain mortar to powder and mixed until homogeneous. 3 g of the homogeneous mixture were weighed using a Metler analytical balance and ashed in a NEY M – 525 furnace at 550 °C for 2 h until white ash was obtained.
The ashed samples were then digested based on the method of Greenberg *et al* [16] using concentrated nitric acid. Here, the ashed samples were dissolved in 100 mL of distilled water in a beaker and digested with 10 mL of concentrated $HNO_3$ on a hot plate with boiling. At the completion of digestion which was marked by a light coloured clear solution, the mixture had evaporated to about 20 mL volume. The mixtures were then filtered using Whatman No. 1 filter papers into standard 100 mL volumetric flasks. After cooling, the filtrates were transferred into clean 100 mL plastic containers from which the respective metals were analysed for, using the Pye–Unicam SP 192 model of atomic absorption spectrophotometer (AAS).

## Results

The results of the findings are as presented in the tables below:

**Table 1:** Mean concentrations (±SD) in µg/g of copper in fish species by sampling station

| Station | Fish Species | | | | |
|---|---|---|---|---|---|
| | *Clarias lazera* | *Oreochromis niloticus* | *Synodontis filamentosus* | *Eutropius niloticus* | *Chrysichthys nigrodigitatus* |
| **A** | 12.5 ± 0.5 | 34.5 ± 6.5 | 13.5 ± 1.5 | 12.5 ± 6.5 | 15 ± 1.0 |
| **B** | 24 ± 3.0 | 15.5 ± 1.5 | 15.5 ± 3.5 | 22.5 ± 1.5 | 13 ± 1.0 |
| **C** | 19 ± 2.0 | 22.5 ± 3.5 | 17 ± 4.0 | 17 ± 5.0 | 12.5 ± 1.5 |
| **D** | 23.5 ± 1.5 | 39 ± 5.0* | 22.5 ± 3.5 | 18.5 ± 5.5 | 18 ± 1.0 |
| **E** | 28.5 ± 4.5 | 43 ± 15.0 | 24 ± 2.0 | 30.5 ± 2.5 | -nd- |

Key for all tables where applicable:
A = Pepsi-Cocacola factory (Control) * = Significant
B = Benue Brewery Limited ** = Highly significant
C = New Bridge
D = St. Joseph's Technical College nd = Not detetectable
E = Wadata Market (Recovery) n = Number of samples

**Table 2:** Mean concentrations (±SD) in µg/g of zinc in fish species by sampling station

| Station | Fish Species | | | | |
|---|---|---|---|---|---|
| | *Clarias lazera* | *Oreochromis niloticus* | *Synodontis filamentosus* | *Eutropius niloticus* | *Chrysichthys nigrodigitatus* |
| **A** | 4497.5 ± 206.5 | 4970 ± 335.5 | 4509.5 ± 103.5 | 5010 ± 57.0 | 5012 ± 121.5 |
| **B** | 5168 ± 439.0 | 5017 ± 123.0 | 4446 ± 119.0 | 5059 ± 536.0 | 4564.5 ± 209.5 |
| **C** | 4539.5 ± 94.5 | 5184 ± 713.0 | 4996 ± 359.0 | 4964.5 ± 304.5 | 5268.5 ± 208.5 |
| **D** | 4582 ± 20.0 | 4681.5 ± 89.5 | 4745 ± 506.0 | 4285 ± 293.0 | 4708 ± 790.0 |
| **E** | 4533 ± 656.0 | 5205 ± 291.0 | 4695 ± 15.0 | 5600 ± 291.5 | -nd- |

**Table 3:** Mean concentrations (±SD) in µg/g of lead in fish species by sampling station

| Station | Fish Species | | | | |
|---|---|---|---|---|---|
| | *Clarias lazera* | *Oreochromis niloticus* | *Synodontis filamentosus* | *Eutropius niloticus* | *Chrysichthys nigrodigitatus* |
| **A** | 2.0 ± 1.0 | 7.5 ± 1.5 | 2.0 ± 1.0 | 2.5 ± 1.5 | 1.0 ± 0.0 |
| **B** | 2.0 ± 1.0 | 7.0 ± 1.0 | 3.0 ± 1.0 | 5.0 ± 4.0 | 5.0 ± 3.0 |
| **C** | 6.0 ± 3.0** | 2.5 ± 1.5 | 1.5 ± 0.5 | 7.0 ± 1.0** | 3.5 ± 0.5 |
| **D** | 4.5 ± 2.5 | 6.0 ± 1.0 | 1.5 ± 0.5 | 11.0 ± 2.0 | 5.5 ± 0.5 |
| **E** | 15.5 ± 2.5 | 10 ± 6.0 | 6.5 ± 1.5 | 4.0 ± 3.0 | -nd- |

**Table 4:** Mean concentrations (±SD) in µg/g of cadmium in fish species by sampling station

| Station | Fish Species | | | | |
|---|---|---|---|---|---|
| | *Clarias lazera* | *Oreochromis niloticus* | *Synodontis filamentosus* | *Eutropius niloticus* | *Chrysichthys nigrodigitatus* |
| **A** | 1.0 ± 0.0 | 1.0 ± 0.0 | 1.0 ± 0.0 | 2.5 ± 0.5 | 2.0 ± 1.0 |
| **B** | 1.0 ± 0.0 | 2.5 ± 1.5 | 2.0 ± 1.0 | 3.0 ± 2.0 | 1.5 ± 0.5 |
| **C** | 3.5 ± 2.5* | 1.5 ± 0.5 | 1.0 ± 0.0 | 2.5 ± 0.5* | 1.0 ± 0.0 |
| **D** | 1.5 ± 0.5 | 2.5 ± 1.5 | 2.0 ± 1.0 | 5.0 ± 3.0 | 1.0 ± 0.0 |
| **E** | 5.0 ± 2.0 | 5.0 ± 4.0 | 4.0 ± 2.0 | 1.0 ± 0.0 | -nd- |

**Table 5:** Mean concentrations (±SD) in µg/g of cobalt in fish species by sampling station

| Station | Fish Species | | | | |
|---|---|---|---|---|---|
| | *Clarias lazera* | *Oreochromis niloticus* | *Synodontis filamentosus* | *Eutropius niloticus* | *Chrysichthys nigrodigitatus* |
| **A** | 4.0 ± 2.0 | 1.5 ± 0.5 | 7.0 ± 4.0 | 3.5 ± 1.5 | 2.0 ± 1.0 |
| **B** | 3.0 ± 2.0 | 2.0 ± 1.0 | 3.5 ± 1.5 | 4.0 ± 3.0 | 2.0 ± 1.0 |
| **C** | 3.5 ± 1.5* | 1.0 ± 0.0 | 1.5 ± 0.5 | 7.0 ± 2.0* | 3.0 ± 1.0 |
| **D** | 1.5 ± 0.5 | 2.5 ± 1.5 | 1.0 ± 0.0 | 5.0 ± 1.0 | 2.0 ± 1.0 |
| **E** | 3.0 ± 1.0 | 6.0 ± 5.0 | 7.5 ± 5.5 | 4.5 ± 2.5 | -nd- |

Table 6: Mean concentrations (±SD) in µg/g of Heavy metals in fish species

| **Fish Species** | **Heavy Metal** | | | | |
|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cd | Co |
| *C. lazera*<br>n = 10 | 21.5 ± 6.0 | 4664 ± 446.4 | 5.8 ± 5.1** | 2.4 ± 2.2* | 3.0 ± 1.7* |
| *O. niloticus*<br>n = 10 | 30.9 ± 12.9 | 5011.6 ± 425.8 | 6.6 ± 3.8 | 2.5 ± 2.5 | 2.6 ± 3.0 |
| *S. filamentosus*<br>n = 10 | 18.5 ± 5.1 | 4678.3 ± 345.9 | 2.9 ± 2.1 | 2.0 ± 1.6 | 4.1 ± 4.1 |
| *E. niloticus*<br>n = 10 | 20.2 ± 7.6 | 4983.8 ± 534.7 | 5.9 ± 3.9** | 2.8 ± 2.1* | 4.8 ± 2.4* |
| *Chrys. nigrogititatus*<br>n = 10 | 14.6 ± 2.5 | 5013.4 ± 638.9 | 3.8 ± 2.3 | 1.4 ± 0.7 | 2.3 ± 1.1 |

**Table 7:** Comparison in metal concentrations between fish species by student's t-test

| **Fish pairs** | **Heavy metal/tcal** | | | | |
|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cd | Co |
| *C. lazera/O. niloticus* | -1.750 | -1.483 | -0.384 | -0.167 | 0.375 |
| *S. filamentosus/E. niloticus* | -0.785 | -0.625 | -1.447 | -0.794 | -0.387 |
| *S. filamentosus/Chrys. nigrogititatus* | 1.768 | -1.862 | -1.698 | 0.293 | 0.673 |
| *O. niloticus/S. filamentosus* | 3.027* | 2.029 | 4.922* | 3.162* | -1.316 |
| *C. lazera/S. filamentosus* | 1.834 | 0.090 | 1.795 | 0.645 | -0.935 |
| *O. niloticus/E. niloticus* | 2.009 | 1.249 | 0.302 | -0.267 | -1.849 |
| *C. lazera/E. niloticus* | 1.123 | -0.669 | -0.035 | -0.304 | -2.343 |
| *O. niloticus/Chrys. Nigrogititatus* | 3.058 | 0.593 | 1.234 | 0.926 | -0.926 |
| *E. niloticus/Chrys. Nigrogititatus* | 1.155 | -0.287 | 2.193 | 2.512 | 4.735* |
| *C. lazera/Chrys. nigrogititatus* | - | -0.654 | -0.104 | 0.485 | 0.245 |

**Table 8:** Correlation of mean heavy metal concentration between fish species

| **Fish pairs** | **Heavy metal/r** | | | | |
|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cd | Co |
| *C. lazera/O. niloticus* | 0.183 | 0.109 | 0.438 | 0.683 | -0.236 |
| *S. filamentosus/E. niloticus* | 0.700 | 0.283 | -0.454 | -0.425 | -0.651 |
| *S. filamentosus/Chrys. nigrogititatus* | 0.681 | 0.690 | 0.117 | -0.302 | -0.428 |
| *O. niloticus/S. filamentosus* | 0.667 | 0.240 | 0.787 | 0.993 | 0.550 |
| *C. lazera/S. filamentosus* | 0.798 | -0.563 | 0.828 | 0.630 | 0.551 |
| *O. niloticus/E. niloticus* | 0.238 | 0.860 | -0.487 | -0.422 | -0.248 |
| *C. lazera/E. niloticus* | 0.925 | 0.328 | -0.097 | -0.667 | -0.099 |
| *O. niloticus/Chrys. Nigrogititatus* | 0.885 | 0.559 | -0.146 | -0.522 | -0.775 |
| *E. niloticus/Chrys. nigrogititatus* | -0.180 | -0.282 | 0.775 | -0.512 | 0.915 |
| *C. lazera/Chrys. nigrogititatus* | - | -0.725 | 0.282 | -0.658 | 0.309 |

**Discussion**

The mean concentrations of Cu, Zn, Pb, Cd and Co in five fish species according to sampling station have been presented in tables 1, 2, 3, 4 and 5 respectively. As expected, station A (Pepsi-Cola Factory) had the least concentration while station E (Wadata Market) had the highest concentration of all the heavy metals studied. Station

A was the control, while Wadata Market is the biggest market in Markurdi located along the river bank, and enjoys high human activities and traffic. Because station E is the recovery point as the river flows downwards, it's expected to receive the highest amount of industrial pollutants and effluents.

Unusually high concentrations of copper and zinc were observed in all the fish species sampled in station B, which could due to the fact that it's directly below the effluent discharge point of Benue Brewery Limited. The same observation could be made of lead, cadmium and cobalt for station C (New Bridge). It's a place of varied human activities which include all year farming, with increase in the dry season irrigation farming owing to the higher value addition of the produce at this time. There is also a motor park as well as rice mill close to the New Bridge station, and the sum total of all the anthropogenic activities give rise to the high concentration of the metals.

Similarly, mean concentrations of these heavy metals in all the fish species by sample population (n = 10) have been presented in table 6. It is obvious from the tables that the concentration of zinc is highest in all the fish species compared to the other heavy metals. This finding is in agreement with that of [6]. It is also interesting to note that the contents of cadmium, copper and lead in the whole fish samples, when their concentrations in the organs of flesh, liver, gills and bones are added together, in fish species from El – Mex Bay, Alexandria – Egypt [17] are similar even though the fish species are completely different from those of this study. Ironically, findings from a relatively recent study [18] also indicate similar concentration levels of Cd and Pb in the two whole fish species of *Barbus sharpeyi* and *Barbus xanthopterus* investigated. It can therefore be said that the fishes have the same pattern of heavy metals intake, even as fishes are known to travel very long distances across different water bodies.

The heavy metal contents of all the fish species were found to be in the order of Zn > Cu > Pb > Co > Cd. This is at variance with the findings of Gbem *et al* [5] which showed the distribution of four metals in fish exposed to a tannery effluent to be of the order Pb > Cr > Cu > Zn. This variation suggests that the water of River Benue is not as heavily polluted as the tannery effluent.

A one-way analysis of variance (ANOVA) was used to detect significant differences in mean metal concentrations between fish species. The result showed a significant difference ($p > 0.05$) between concentrations of cobalt in *Clarias lazera* and *Eutropius niloticus.* A similar level of significance was observed for Cd ($p > 0.05$) in respect of the two fish species while the mean difference in Pb concentrations between *Clarias lazera* and *Oreochromis niloticus* was highly significant, with a calculated F-value of 78.878, being greater than the three values of F for the three levels of probability; 0.1, 0.05 and 0.01.

Paired sample student's t-test was used to detect differences in mean metal concentrations in fish species and sampling station. The result showed among others, the difference in copper concentrations between *Oreochromis niloticus* and *Synodontis filamentosus* to be significant, $t_{cal(3.027} > t_{table(2.776)}$ at 95% confidence level (table 7). In the same vein, the concentrations of cobalt in *Eutropius niloticus* and *Chrysichtys nigrodigitatus* were found to differ significantly at 95% confidence level, $t_{cal(4.735)} > t_{table(3.182).}$ The lead and cadmium values in *Oreochromis niloticus* and *Synodontis filamentosus* were also observed to differ significantly (tables 3 and 4 respectively). These results are summarized in table 7 in which $t_{cal(4.922)} > t_{table(2.766)}$ for lead and $t_{cal(3.162} > t_{table(2.776)}$ for cadmium.

The mean concentration levels of heavy metals in fish of river Benue are inadmissible, when compared to WHO [19] and FAO [20] standards. The highest value of copper obtained in this study was 30.9 µg/g in *Oreochromis niloticus*, with the lowest value of 21.5 µg/g in *Clarias lazera*.

The recommended value for zinc in fish by FAO/WHO [21] was 4000 µg/g, while the values obtained in this study range from 4664 µg/g for *Clarias lazera* to 5013.37 µg/g for *Chryssicthys nigrodigitatus*. These Zn values are considered admissible because zinc is an essential element in the human body and not all of it will likely be transferred to man after consumption of the fish, owing to losses during processing. Excessively high levels of zinc may however cause fever, depression, vomiting, salivation and headache.

The lead concentration values of fishes in River Benue under study ranged from 2.9 µg/g in *Synodontis filamentosus* to 6.6 µg/g in *Oreochromis niloticus*. These values are at variance with the findings of another researcher [22] in which Pb levels of as high as 32.14 mg/g (32140 µg/g) for some fish samples in Qua Iboe river estuary were recorded. This trend is not surprising, given that Akwa Ibom state is heavily industrialized as compared to Benue state.

Cadmium values in fish sampled from River Benue ranged from 1.38 to 2.80 µg/g and these could be considered to be relatively low when compared with the FAO/WHO [20] dietary requirement in fish. As low as they may appear, these values are frightening, going by the report [2] that the cadmium concentration of rice that killed over 100 Japanese due to itai-itai was in the range of 0.6 to 1.0 µg/g.

In consideration of its essential roles in the synthesis of vitamin B12 and of its salts in the treatment of anaemia as well as cyanide poisoning, the concentration range of cobalt from 2.25 µg/g in *Chrysicthys nigrodigitatus* to 4.8 µg/g in *Eutropius niloticus* is admissible.

Paired sample correlations (table 8) indicated that apart from the concentrations of copper in *Eutropius niloticus* and *Chrysicthys nigrodigitatus* that were negatively correlated, heavy metal concentrations in 80% of paired fish species showed positive perfect correlation ($-1 < r < +1$). The concentrations of cadmium showed positive correlation for *Clarias lazera* and *Oreochromis niloticus*, *Clarias lazera* and *Synodontis filamentosus* as well as between *Oreochromis niloticus* and *Synodontis filamentosus*. The cadmium intake of 70% of the fish pairs indicated negative correlation.

Four fish species showed a positive correlation in cobalt concentration in contrast to Pb concentration in which 60% of fish pairs showed positive correlation while the Zn concentration in seven fish pairs, representing 70% showed positive correlation.

From these findings, it is safe to deduce that at least 40% of fish from river Benue have a similar trend in their consumption pattern and intake of the heavy metals under study.

## Conclusions

From the findings of the study, it is safe to state that fish of river Benue suffer relatively high pollution due to heavy metals, hence are not safe for excessive consumption. The lead contents of fish from River Benue particularly need to be watched, considering an expected rise in industrialization and domestic activities of solid waste disposal in view of corresponding upsurge in human population.

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