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Comparative Analysis of Metal Levels in *Clarias gariepinus* and Water from River Benue and Commercial Fish Ponds in Makurdi

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Authors' contributions

This work was carried out in collaboration between all authors. Author ISE designed the study, wrote the protocol and corrected the drafts of the manuscript. Author ST performed the laboratory work, did the statistical analysis and wrote the first draft of the manuscript. Author RSA managed the literature searches and analysis of the study. All authors read and approved the final manuscript.

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ABSTRACT

Aims: The present study assessed toxic metals content in the water, feeds and fish organs (liver, gills, and kidney) of *Clarias gariepinus* from River Benue and selected fish ponds within Makurdi metropolis of Benue State.
Place and Duration of Study: Sample: A total of eighteen (18) *Clarias gariepinus* fish samples were purchased within Makurdi metropolitan area of Benue State, Nigeria.
Methodology: Toxic heavy metals in fish samples were digested using standard procedures and determined using HG-AAS.
Results: The mean concentration (mg/kg) of heavy metals in fish organs from fish ponds and River Benue are respectively as follows –As: 0.90 and 0.77; Hg: 0.91 and 1.75; Pb: 1.42 and 1.67. The mean concentration (mg/kg) of As, Hg and Pb in feeds were (0.13, ND, and 0.13 respectively), water (mg/L) 0.10, 0.30 and 1.57, respectively. Hg and Pb had higher concentrations in river Benue compared to the fish ponds. However, As was higher in the fish ponds compared to river Benue.

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With the exception of As that falls within the EU set limit of fish, Hg and Pb are above the WHO and EU set limits of fish.
Conclusion: It is thus evident that adequate environmental policies are necessary to reduce the risk of heavy metal contamination of fish in Makurdi.

Keywords: River Benue; fish ponds; toxic metals; Clarias gariepinus; water quality; HG-AAS.

1. INTRODUCTION

The environmental and health risk associated with accumulation of toxic metals from anthropogenic sources has attracted significant scrutiny of their levels in the aquatic environment [1]. Toxic metals occur naturally in the environment but chaotic human activities have crucially changed their geochemical cycles and biochemical balance, which has resulted in their accumulation in living organisms [2]. The adverse effects of toxic metals, by the pollution of natural water has influenced the ecosystem and caused environmental risks and threat to humans [3,4]. The health risk associated with toxic metal poisoning in man and the ecosystem are of great concern to environmentalist. Therefore, the demand for incessant monitoring to alleviate the issues faced by environmental contamination by toxic metals is crucial.

Fish is one common source of animal protein and is usually consumed by all social categories in a population. The River Benue is a major source of fish to the population that resides along the river banks and beyond. Owing to increasing demand, fish farming has become an alternative source of fish. The risk of exposure of toxic metals in fish from River Benue is tied to inflows of untreated, urban and industrial effluents as well as run-offs from agricultural farmlands into the River. Whereas, heavy metals found in fishes from fish farms may result from the type of water and feeds given to these fishes in the pond and the soil environment. In this work, we assessed the levels of some critical toxic metals in *Clarias gariepinus* fish samples from River Benue and commercial fish ponds, as well as the fish feeds in Makurdi Metropolis. Furthermore, some associated physicochemical parameters of the water from River Benue and the fish ponds were also investigated accordingly.

2. MATERIALS AND METHODS

All solvents and reagents used in this study were of analytical grade (≥ 98% purity). These includes: HCl, H_2SO_4, $HClO_4$, and HNO_3.

2.1 Sampling

A total of eighteen (18) *Clarias gariepinus* fish samples were purchased within Makurdi metropolitan area of Benue State, Nigeria (Fig. 1). Three of the fishes were purchased from fishermen around River Benue, whereas, the remaining 15 were purchased from five selected commercial fish ponds (farms) in Makurdi metropolis of Nigeria. The fish collected were immediately stored in a cooler packed with icebox and transported to the laboratory for analysis. At each sampling station, 2.5 L of water samples were collected, as well as 20.0 g of the fish feeds from the various commercial fish farms. For the water samples, a total number of 6 water samples were collected; the samples were taken 5 cm below the water surface with the sample containers.

2.2 Sample Preparation

The obtained fish samples were washed with running tap water to remove dirt and to maintain freshness. The fish were dissected using sharp stainless knife to separate organs into gills, kidney and liver. The fish organs were dried in a food dehydrator at 68ºC for 48 hours to constant weight. The organs were grounded using a porcelain mortar and pestle. The samples were labeled and stored in plastic containers until digestion.

2.3 Sample Digestion

Three (3.0) grams of the grounded fish organs (gills, kidney and liver) and fish feeds were weighed carefully using a digital chemical balance. Exactly 20 mL of concentrated HNO_3, 4 mL $HClO_4$ and 2 mL H_2SO_4 acids were added into the grounded samples, which was heated on a hot plate for one hour till digestion was complete. The digest was stored in pre-clean polyethylene bottles for further analysis. Accordingly, the water samples meant for metal analyses were treated with 3 mL of concentrated HNO_3 for each liter and digested following the afore-described digestion procedure.

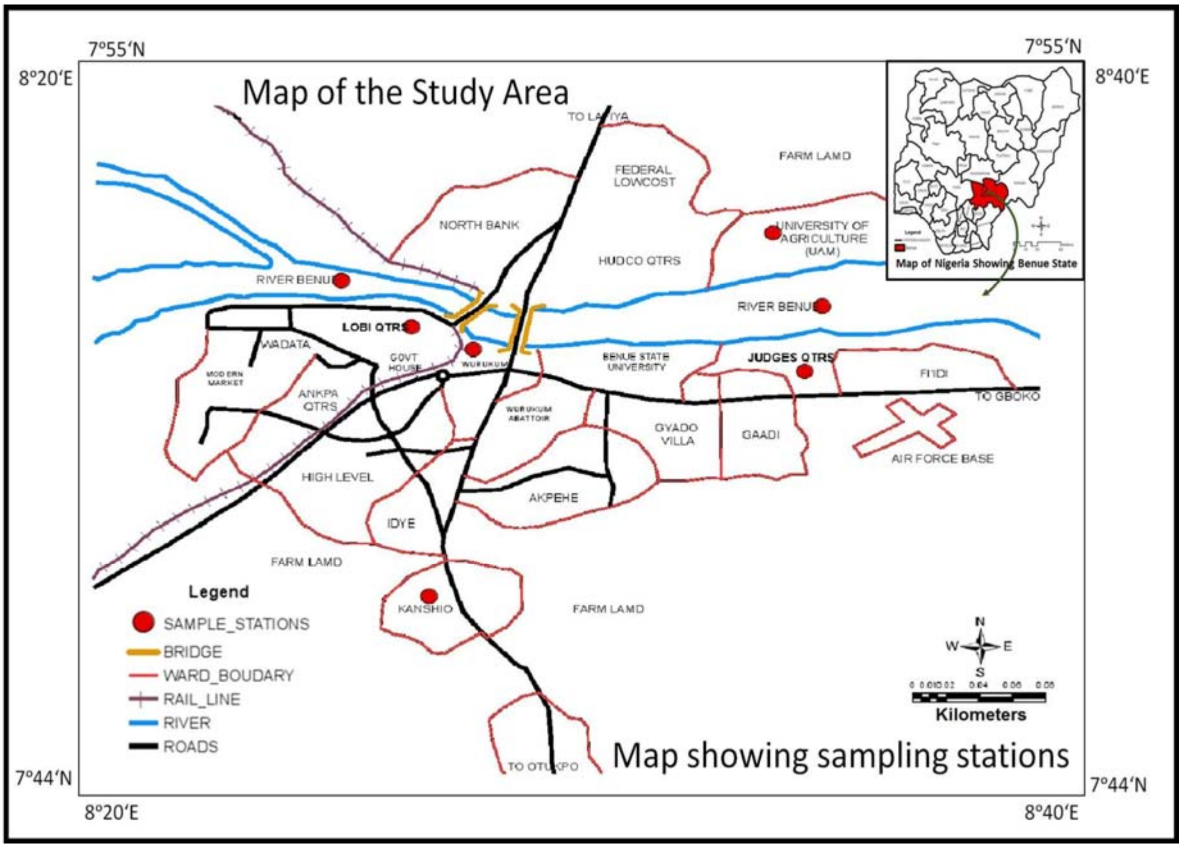

Fig. 1. Map of Nigeria showing Benue State and the study area with sampling stations in Makurdi metropolis

3. RESULTS AND DISCUSSION

3.1 Physicochemical Analysis of Water Samples

The results of the physicochemical parameters of the water samples obtained at the different sampling stations are shown in Table 1. The mean temperature value obtained was 29.08 ± 0.24°C from fish ponds and 29.20°C in River Benue. The temperature of water from River Benue and water from the fish ponds sampled were not statistically different ($p>0.05$), which indicates that all sampled locations were within the same geoclimatic zone. A similar observation was made by Akaahan et al. [5] and Eneji et al. [6] who reported temperature values of 27.96 ± 0.45°C and 28.20 ± 0.06 °C for water obtained from River Benue. There are no set regulations on water temperature for aquatic species by the WHO or the EU due to climatic variations. However, water temperatures above 30°C leads to all benthic organism suppression [7]. Further analysis of the pH of water samples from fish ponds gave a mean value of 7.62 ± 0.23, whereas, water from River Benue had a pH of 7.42. This observation is in agreement with Danba et al. [8] who reported that the best water for fish cultivation is that whose pH is neutral or slightly alkaline ranging from 7 - 8 and the result of this study falls within this range. Our results hereby indicate that the pH obtained from River Benue and the fish pond shows that the water is not polluted and it is suitable for the growth of fish. It is within the recommended ranged of 6.6 - 8.5 set by WHO [9].

The results of chloride ion obtained ranged from 28.6 - 48.1 mg/L from water obtained from fish ponds and 31.5 mg/Lin water from River Benue. Elsewhere, similar observations were made where chloride ion value of 36.8 mg/L was reported in Himalayan River, Twawi [10]. Chlorine, a major element and precursor for chloride is frequently used in treating the water in fish ponds. Bhatnagar and Devi [11] observed that concentration of chloride above 100.0 mg/L in the water may burn the edges of fish gills which could have long-term implications, as such; such levels are not suitable for aquaculture.

Table 1. Physico-chemical properties of water from River Benue and fish ponds obtained from Makurdi metropolis

Parameter	Pond 1	Pond 2	Pond 3	Pond 4	Pond 5	Mean ± Std	River Benue
Temperature (ºC)	28.9	29.1	29.4	29.2	28.8	29.1± 0.24	29.2
Turbidity (NTU)	4.5	5.0	4.0	3.0	2.5	3.80±1.0	3.5
Ph	7.76	7.89	7.67	7.48	7.30	7.62±0.23	7.42
DO (mg/L)	4.72	4.51	4.00	3.25	2.30	3.76±0.99	3.51
TDS(mg/L)	314	357	289	285	262	301±36	280
TH (mg/L)	255	267	127	118	93	172±82	109
TA (mg/L)	169	200	140	126	107	148±37	121
EC (μS/cm)	8.49	9.77	7.80	7.25	6.42	7.95±1.27	6.89
Chloride (mg/L)	36.6	48.1	33.7	30.0	28.6	35.4±7.8	31.5
Sulphate (mg/L)	10.9	15.7	8.10	7.48	6.40	9.72±3.7	7.10
Nitrate (mg/L)	3.60	4.48	3.05	2.95	2.11	3.24±0.88	2.77
Bicarbonate (mg/L)	44.1	55.2	42.7	36.1	30.6	41.7±9.23	34.3
Calcium (mg/L)	80.3	92.1	74.7	70.1	49.2	73.3±15.8	55.8
Magnesium (mg/L)	47.6	63.5	40.3	33.2	30.5	43.0±13.2	31.9
Phosphorus (mg/L)	23.2	37.2	20.5	19.8	16.3	23.4±8.10	18.2
BOD (mg/L)	2.80	3.30	2.40	2.40	2.30	2.64±0.42	3.00
COD (mg/L)	2.40	2.70	2.20	2.30	2.15	2.35±0.22	2.50

Key: TDS - Total dissolved solids, TH - Total hardness, TA - Total alkalinity, EC - Electrical conductivity, DO- Dissolve oxygen, BOD –Biochemical Oxygen Demand, COD- Chemical Oxygen Demand

From our study, the sulphate level in water from River Benue was 7.10 mg/L, whereas, the mean sulphate level in water from fish ponds was 9.72 ± 3.7 mg/L. These values are well below the WHO recommended value of 250.0 mg/L [9]. Akaahan et al. [5] also reported similar findings of 5.58 mg/L for sulphate concentration in River Benue. Alkalinity mean value for water from obtained from fish ponds was 148 ± 36.7 mg/Land 121 mg/L for River Benue water. High alkalinity (> 500 mg/L) usually correlates with high pH values, hardness and dissolved solids [12].

A mean value of 3.76 ± 0.99 mg/L was obtained for dissolved oxygen (DO) in fish pond water and 3.53 mg/L in water from River Benue. In a study by Okayi et al. [13], DO values within the range of 3.6 - 4.9 mg/L were reported in River Benue. DO values reported herein falls within the WHO recommended standard of >6 mg/L [9]. Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. BOD increases as a result of decrease in DO. The value of BOD rises when there is more organic matter such as leaves, wood and waste water in the water body. Researchers have reported that BOD greater than 5.00 mg/L usually indicates water pollution. In the present study, the BOD values obtained ranged from 2.30 - 4.72 mg/L in water from fish ponds and 3.00 mg/L from River Benue water. Indabawa [14] reported a BOD value of 12.47 mg/L which does not corroborate with the values obtained in the present study. However, our results agree with the findings of Keremah et al. [15] who reported BOD values in the range of 2.90 - 4.52 mg/L.

3.2 Heavy Metal Contamination

The presence of heavy metals in aquatic animals intended for human consumption is of much concern to food safety, environmental and human health. In the present study, we investigated the presence of some heavy metals in fish organs from River Benue and fish ponds as well as the water obtained from the same sources consumed in Benue State, and the results are presented in Table 2. Table 3 shows the mean concentration (mg/kg) of each metal in all the organs from each ponds and River Benue.

As: The mean concentrations of As in fish organs and fish feed from fish ponds, as well as fish organs from fish obtained from River Benue are presented in Table 3. Fishes obtained from River Benue had mean As concentration in the organs (liver, kidney and gills) as 0.37 ± 0.33 mg/kg, 0.23 ± 0.03 mg/kg and 0.17 ± 0.07 mg/kg, whereas, the mean concentration of As in the organs of fishes obtained from fish pond are 0.61 ± 0.08 mg/kg, 1.91 ± 0.11 mg/kg and 0.17 ± 0.03 mg/kg. In feed, the concentration obtained was 0.13 ± 0.03 mg/kg. The concentration of As in the water samples from the fish ponds were below detection limit while that of River Benue was 0.10 ± 0.03 mg/L. The highest concentration of As was recorded in fish liver from the pond.

Essentially, heavy metal contamination of fish organs is largely due to contamination of the water in which the fish is cultivated by heavy metals or via indirect uptake through the fish feed or both. Larissa et al. [16] worked on heavy metal contamination of edible fish species from Awassa and Koka Rift valley lake water and reported concentration of As within the range of

Table 2. Mean concentration (mg/L) of toxic metals in water samples

Sample	As	Hg	Pb
Pond 1	ND	ND	0.50±0.13
Pond 2	ND	ND	0.50±0.13
Pond 3	ND	ND	0.50±0.13
Pond 4	ND	ND	1.02±0.05
Pond 5	ND	ND	1.20±0.03
River Benue	0.10±0.003	0.30±0.03	1.57±0.07
WHO	0.01	0.001	0.01

Key: ND- not detected

Table 3. Mean concentration of toxic metals from fish organs and feeds obtained from ponds and River Benue in Makurdi metropolis

Sample	As(mg/kg)×10^{-3}	Hg(mg/kg) ×10^{-3}	Pb(mg/kg) ×10^{-3}
Liver			
Pond 1	0.77±0.03	1.73±0.07	0.68±0.05
Pond 2	0.63±0.09	2.23±0.03	3.90±0.03
Pond 3	0.70±0.03	2.51±0.05	1.57±0.07
Pond 4	0.50±0.13	1.97±0.03	1.20±0.03
Pond 5	0.44±0.12	2.20±0.03	1.02±0.05
Mean	0.61±0.08	2.13±0.42	1.67±0.05
R. B	0.37±0.33	2.92±0.05	2.22±0.08
Kidney			
Pond 1	0.37±0.33	0.40±0.07	0.50±0.13
Pond 2	0.31±0.05	0.60±0.03	0.27±0.07
Pond 3	0.63±0.13	0.60±0.07	0.50±0.13
Pond 4	0.37±0.03	0.30±0.07	1.02±0.05
Pond 5	0.23±0.03	0.60±0.03	0.20±0.07
Mean	1.91±0.11	0.50±0.05	0.50±0.09
R.B	0.23±0.03	1.73±0.07	1.57±0.07
Gills			
Pond 1	0.30±0.03	0.17±0.03	0.37±0.03
Pond 2	0.17±0.03	0.07±0.03	0.20±0.07
Pond 3	0.17±0.03	0.03±0.03	0.50±0.01
Pond 4	0.10±0.03	0.23±0.09	0.77±0.03
Pond 5	0.10±0.03	0.07±0.03	ND
Mean	0.17±0.03	0.11± 0.04	0.46± 0.04
R.B	0.17±0.07	0.60±0.07	1.21±0.05
TopFeed	0.10±0.03	ND	0.13±0.09
VitaFeed	0.17±0.03	ND	0.13±0.09
Mean	0.13±0.03	ND	0.13±0.09

Key: ND- not detected; R.B- River Benue

0.21 - 3.0 mg/L, and concentrations ranging from 76.8 – 263 mg/kg in the fish organs. The potential adverse effect of arsenic to animals is determined by the amount of inorganic arsenic present in the fish feed which is predominantly in the organic form of arsenobetaine and arsenochlorine in the fish. In this study, As concentration of fish from the ponds was higher than As concentration in fish from River Benue. The levels of As recorded were less than the WHO maximum limits for seafood and drinking water.

Hg: The mean concentration of Hg in fish organs from River Benue was 2.92 ± 0.05 mg/kg in liver, 1.73 ± 0.07 mg/kg in kidney and 0.60 ± 0.07 mg/kg in gills, whereas, the mean concentration of Hg in fish organs from fish ponds are 2.13 ± 0.42 mg/kg, 0.50 ± 0.05 mg/kg and 0.11 ± 0.04 mg/kg for liver, kidney and gills respectively. The concentration of Hg in feed and water from the ponds were below detection limit whereas Hg concentration in River Benue water was recorded as 0.30 ± 0.03 mg/L. Fishes from River Benue had higher Hg concentrations compared to fishes from ponds. The highest concentration of Hg (2.92 ± 0.05 mg/kg) was recorded in fish liver from River Benue, which can be attributed to activities from industries around the river and other open solid waste dumpsites around the river [17]. Amongst fish organs, the liver is a good indicator of environmental pollution and it accumulates large quantities of pollutants from the external environment and also plays an important role in storage, redistribution, detoxification and transformation of pollutants. Ijeoma et al. [18] reported Hg in fish liver to be 0.767 mg/kg and 0.392 mg/kg in gills. Mercury is a global pollutant that ultimately makes its way into the aquatic ecosystem through the hydrologic cycle and it is also as a result of natural and anthropogenic releases in the water [19]. Mercury gets into the body through the gastrointestinal and the respiratory tract and is distributed into the liver, kidney and gills.

The observed high As and Hg levels in the river water as compared to water from fish ponds which was apparently below the limit of detection was due to sewage and industrial disposal into the river, leading to high levels of pollution. For example, large market such as Wadata market and heavy industries along the bank of the river Benue such as Benue Breweries, which produce tonnes of industrial wastes daily, which ultimately end up in the river untreated. Moreover, these metals (As and Hg) occur naturally in the earth crust as pure crystals (for Asernic), or in other natural minerals usually in combination with other elements such as sulfur, e.t.c., as such, since river Benue stretches approximately 1400 km beginning from the Adamawa plateau in the Northern Cameroun, a possible reason for the high levels of these metals in the river water could be their gradual accumulation along the river path. On the other hand, water used in many of the fish ponds are treated and drinkable, or at least filtered, as such, the lower/absence of these metals is justifiable.

Pb: The Pb concentration in fish organs from River Benue was 2.22 ± 0.08 mg/kg in liver, 1.57 ± 0.07 mg/kg in kidney and 1.21 ± 0.05 mg/kg in gills, whereas the mean concentration of Pb in the fish ponds were 1.67 ± 0.05 mg/kg in liver, 0.50 ± 0.09 mg/kg in kidney and 0.46 ± 0.04 mg/kg in gills. In feed, the concentration was 0.13 ± 0.09 mg/kg. In water, River Benue had the highest Pb concentration of 1.57 ± 0.07 mg/L compared to water from fish ponds which is due to the amount of anthropogenic activities discharged into the river. The highest concentration of Pb was recorded in the liver of fish from River Benue which is due to accumulation of this metal from the river water.

Generally, toxic metal levels were higher in liver compared to the other fish organs, which is an indication that the liver accumulates more toxic metals than the other organs of fish. *C. gariepinus* is a known voracious bottom feeder and could thus have bio-accumulated high metal levels from the pond sediment and possibly metal uptake from the fish feed. El- Moselhy et al. [20] reported the concentration of Pb in some organs of fish species collected from Hurghada with results ranging from 0.3 ± 0.1 - 2.3 ± 0.5 mg/kg which is in line with the results obtained in this study. Similarly, Eneji et al. [21] reported 2.78 mg/kg of Pb concentration in *C. gariepinus* and 3.58 mg/kg in *T. zilli* from River Benue. In overall, Pb levels recorded in the organs of *C. gariepinus*, water and feed were above the WHO and EU maximum limits of 0.5 mg/kg in seafood and drinking water. Pb intake causes damages to memory deterioration and also to central and peripheral nervous system [22].

4. CONCLUSION

Physicochemical analysis of fish pond water was performed and the results indicated acceptable conditions for aquatic life. A comparison of heavy metal concentrations between fish samples from ponds and River Benue samples revealed that Hg occurred in higher concentrations in River Benue compared to the fish ponds. The levels of all the metals analyzed in this study were above the WHO and EU recommended limits with the exception of As. It is thus evident that fish consumers within Makurdi metropolis are at high risk of uncontrolled exposure to these heavy metals, which consequently have long-term effects on health.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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