academicJournals

Vol. 9(3), pp. 210-217, March 2015
DOI: 10.5897/AJEST2014.1849
Article Number: 8A20EE850847
ISSN 1996-0786

http://www.academicjournals.org/AJEST

African Journal of Environmental Science and Technology

Full Length Research Paper

Heavy metal content in fish and water from River Niger at Agenebode, Edo State, Nigeria

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Received 17 December, 2014; Accepted 21 January, 2015

The concentrations of Lead (Pb), Copper (Cu), Cadmium (Cd) and Zinc (Zn) in fish and water from River Niger at Agenebode, Nigeria were determined by atomic absorption spectrometric technique. The mean concentrations of heavy metals in water ranged from 0.00742 mg/L for Pb to 0.239 mg/L for Zn. The summary statistics for heavy metals in fish showed that the mean concentrations of metals ranged from 0.0291 mg/kg for Pb to 69.14 mg/kg for Zn, while the mean concentrations of metals in individual fish species ranged from below detection/quantification limit (BQL) for Pb in *Barbus occidentalis* and *Chrysichthys nigrodigitatus* to 128.87 mg/kg for Zn in *Hemichromis fasciatus*. The bioaccumulation quotient (BQ) values for metals in fish ranged from BQL for Pb in *B. occidentalis* and *C. nigrodigitatus* to 539.21 for Zn in *H. fasciatus,* while the condition factor for the fish species ranged from 0.32 in *Clarias gariepinus* to 2.07 in *Oreochromis niloticus*. The maximum acceptable risk (MAR) values for heavy metals in fish ranged from BQL for Pb in *B. occidentalis* and *C. nigrodigitatus* to 6.38 for Cu in *H. fasciatus*; while the Hazard Quotient (HQ) values for heavy metals in water ranged from 0.05 for Zn to 0.43 for Cd. In fish, the HQ values ranged from BQL for Pb in *B. occidentalis* and *C. nigrodigitatus* to 10.74 for Zn in *H. fasciatus*. The National Environmental Standard and Regulation Enforcement Agency (NESREA) were enjoined to ensure that the environmental safety of our inland water bodies is sustained in order to mitigate negative impacts on human health.

Key words: Heavy metals, fish, River Niger, maximum acceptable risk, hazard quotient.

INTRODUCTION

In today's environment, the potential for risks to humans and wildlife due to exposure to ever increasing levels of toxic chemical agents of both natural and synthetic origin is on the increase in scientific and regulatory interest (United States Environmental Protection Agency, US-EPA, 1998). Furthermore, environmental pollution is a worldwide problem with heavy metals belonging to the most important category of pollutants (Tabari et al., 2010). Heavy metals are classified as metallic elements which have relatively high atomic weight and are toxic at

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low concentrations (Butu and Igiusi, 2013).These metals are naturally found in the environment but can also be produced anthropogenically to levels high enough to cause disruptions amongst aquatic species such as, impaired metabolic functions, changes in distribution and abundance of populations (Elder, 1988).

All heavy metals are potentially harmful to most organisms at some levels of exposure and absorption (Adedeji and Okocha, 2011). The ingestion of heavy metals by fish via food and water may affect not only the productivity and reproductive capabilities of such fish, but ultimately affect the health of man that depends on these organisms as a major source of protein (Fonge et al*.,* 2011). Many ecotoxicological studies in Nigeria have focused on aquatic bodies within or around major cities with little emphasis on aquatic media in rural areas, which may also be impacted by heavy metals. The River Niger is one of the major rivers in Nigeria that is rich in fisheries resources that are widely exploited as human food. The river at the Agenebode axis of Edo State, Nigeria was selected for the study as the area is densely populated and plays host to numerous cottage industries with expected varied levels of anthropogenic impacts on the river. The study specifically ascertained the concentrations of Cadmium (Cd), Copper (Cu), Lead (Pb) and Zinc (Zn) in water and fish from the River Niger at Agenebode in order to determine potentially hazardous levels of these heavy metals especially with regard to human health.

MATERIALS AND METHODS

The study area

The River Niger at Agenebode lies within Latitude 7.106° N and Longitude 6.696° E. Agenebode is the Administrative Headquarters of Etsako East Local Government Area of Edo State, Nigeria. According to the 2006 National Census, the population of the Local Government Area was put at 145, 996. The area has a size of 1,132.82 km^2 with a population density of 86 people per km^2 (Stephen and Lanihan, 2007). The people are actively engaged in commerce, fishing, farming and mining. The major agricultural products are groundnut, rice, cassava, yam, maize, fish, tomatoes and melon. The substratum of River Niger consists mainly of fine sand mixed with mud and pebbles. Decaying macrophytes and debris also form part of the substratum. Other settlements along the River Niger within the same Local Government Area include Emokweme, Ofugbo, Obadolo, Udochi and Udaba. Directly opposite Agenebode, on the other side of River Niger is the Idah Community in Kogi State. The climate of Agenebode is tropical with the dry season running from November to March, while the wet season runs from April to October. Annual temperature ranges from 23 to 35°C while annual humidity ranges from 67 to 94%. Two stations namely, Abattoir and Boat House stations were established for the study based on the level of human activities, nature of effluents and accessisibility. Activities around the Abattoir station include abattoir activities, cattle grazing, bathing of animals in the river, operation of pig pens and fishing; while at the boat house station fishing, farming, laundry, and boat maintenance work can be observed. Both dug-out canoes and boats fitted with petrol powered outboard engines can be found at the boat station. The sampling stations are located approximately 4 km apart.

Collection of water and fish samples

Water samples were collected at 30 cm depth below the water surface using pretreated polypropylene bottles of 500 ml capacity. Five (5) ml of concentrated nitric acid was applied *in-situ* to each bottled sample in order to keep the metals in solution. Water samples were transported to the laboratory and stored at -5°C in a freezer. The fish samples were netted using cast nets with the assistance of fishermen. Fish samples were washed in River water to remove adhering debris and were thereafter placed in labeled polythene bags and transported to the laboratory within 24 h in a Thermolineo® ice box in order to preserve their integrity.

Laboratory procedures

In the laboratory, fish samples were identified with taxonomic keys as published by Olaosebikan and Raji (1998) and Adesulu and Sydenham (2007). The identified fish species were *Clarias gariepinus* (Burchell, 1822), n=4, *Hemichromis fasciatus* (Peters, 1857), n=6, *Barbus occidentalis* (Boulenger, 1911), n=2, *Synodontis sorex* (Gunther, 1864), n=2, *Alestes baremose* (Joannis, 1835), n=8, *Chrysichthys nigrodigitatus* (Lacepede, 1803), n=4 and *Oreochromis niloticus* (Linnaeus, 1758), n=6. They were weighed whole in grams using an ATOM A-110C® electronic compact scale while their total lengths were recorded using a stainless steel ruler. Fish samples were oven dried at a temperature of 70°C for 48 h. Each sample was milled separately using a porcelain mortar and pestle and kept in foil paper prior to digestion. The following steps were applied in digesting water samples. The water was pretreated with 5 ml of diluted nitric acid. Two (2) ml of water sample was pipetted into a 250 ml conical flask after which 5 ml of 70% $HClO_4$ and 15 ml of 55% HNO_3 were added. The mixture was heated till the solution became clear. Five (5) ml of 20% HCl was added and content was poured into a 100 ml volumetric flask and made-up to mark with distilled water. The digest was stored in 100 ml plastic reagent bottles prior to atomic absorption spectrophotometer analysis (Galyean, 2010).

The following steps were applied in digesting fish samples. Fresh fish was dried to constant weight in a Gallenkamp® hotbox oven. Two (2) g of the dried fish sample was weighed into 250 ml conical flask, 5 ml of $HClO_4$ and 15 ml HNO_3 were added. The mixture was heated till the solution became clear. Five (5) ml of 20% HCl was added. The mixture was filtered into a 100 ml volumetric flask using No.42 Watman filter paper and made up to mark with distilled water. The digest was stored in a 100 ml plastic reagent bottle ready for Atomic absorption spectrophotometer (AAS) analysis (Galyean, 2010). Fish and water digests were analyzed for Pb, Cr, Cu and Cd by means of an Atomic Absorption Spectrophotometer (Unicam® 696 series) equipped with solar software using air acetylene flame. Concentrations of metals in water and fish were expressed in mg/L and mg/kg, respectively. Blanks, spiked samples, reference material analyses and duplicate analyses were performed for all analytes as part of the quality assurance procedures. All reagents used were of analytical grade (BDH). All glassware were washed with detergent and rinsed with distilled water before they were soaked in potassium permanganate solution overnight. They were then rinsed with distilled water before use to ensure the acquisition of high precision results.

Bioaccumulation quotient (BQ) for heavy metals in fish

The Bioaccumulation Quotient (BQ) for heavy metals in fish is

Table 1. Summary statistics for heavy metals (mg/l) in water.

Metals	Mean	Minimum	Maximum	SD (±)
Cd	0.0219	0.00	0.14	0.0376
Cu	0.182	0.08	0.30	0.0664
Pb	0.00742	0.00	0.017	0.0047
Zn	0.239	0.15	0.35	0.0571

Table 2. Mean heavy metal concentrations (mg/l) in water by month.

Months	Pb	Cu	Cd	Zn
March	0.00475 ± 0.001^{b}	0.1650 ± 0.002^{a}	0.0452 ± 0.01^{a}	0.2175 ± 0.015^{a}
April	0.00875 ± 0.02^{a}	0.1975 ± 0.03^{a}	0.00950 ± 0.01^{b}	0.2775 ± 0.05^{a}
May	0.0875 ± 0.03^{a}	0.1825 ± 0.001^{a}	0.0110 ± 0.03^{b}	0.225 ± 0.04^{a}

Means with the same letters are not significantly different (P>0.05)

Table 3. Mean heavy metal concentrations (mg/l) in water by station.

Station	Pb	Cu	Cd	Zn
Abattoir	0.06	0.18	0.01	70.02
Boat House	0.06	0.18	0.02	68.25

expressed below (Latif et al., 1982):

$$BQ = \frac{\text{Heavy metal concentration in fish}}{\text{Heavy metal concentration in water}}$$

Condition Factor for fish

This expresses the fatness, wellbeing and relative robustness of a fish. It is believed that a heavier fish of a given length is in better condition than a lighter fish of the same length (Baijot et al., 1997). The condition factor is expressed below:

$$CF = \frac{100 * \text{Weight of fish (g)}}{\text{Length of fish (cm)}^3}$$

Maximum Acceptable Risk index (MAR) for heavy metals

The Maximum Acceptable Risk index (MAR), is a simplified representation of biomagnifications in food webs (Romijn et al., 1993). It is expressed by the following equation:

$$MAR = \frac{\text{Bioaccumulation Quotient (BQ) for chemical element in fish}}{\text{Dietary no observed effect concentration of chemical element in man}}$$

Where: MAR>1 = High MAR level and MAR<1= Low MAR level

Toxicity/Hazard Quotient (TQ) for heavy metals

The Toxicity/Hazard Quotient (TQ) for chemical elements is a comparison of the measured concentration of site-related elements in ecological matrices with specific health-based criteria (Newstead et al., 2002).

$$TQ = \frac{\text{Measured concentration of chemical element in ecological matrix}}{\text{Health based criteria}}$$

Where: TQ>1 = Toxicity/Hazard indicated.

Statistical method

Statistical software (GENSTAT® version 13.3 for Windows) was used for analyzing data. One-way Analysis of variance (ANOVA) was used to test for significant differences between mean values of heavy metals at 5% probability level. Duncan Multiple Range Test was used to separate significant means.

RESULTS

The mean concentrations of heavy metals in water ranged from 0.00742 mg/L for Pb to 0.239 mg/L for Zn (Table 1), while the mean concentrations of the heavy metals in water on a monthly basis ranged from 0.00475 mg/L for Pb in March to 0.2775 mg/L for Zn in April (Table 2). Station wise, the mean concentrations of heavy metals in water ranged from 0.01mg/L for Cd to 70.02 mg/L for Zn at the Abattoir station (Table 3). The summary statistics for heavy metals in fish showed that the mean concentrations of metals ranged from 0.0291 mg/kg for Pb to 69.14 mg/kg for Zn (Table 4); while on a monthly basis, the mean concentrations of metals ranged from 0.01850 mg/kg for Pb in May to 77.92 mg/kg for Zn in April (Table 5). Station wise, the mean concentrations

Table 4. Summary statistics for heavy metals (mg/kg) in fish.

Metals	Mean	Minimum	Maximum	SD(±)
Cd	0.0917	0.00	0.411	0.13
Cu	1.00	0.57	1.37	0.232
Pb	0.0291	0.00	0.09	0.0278
Zn	69.14	50.6	85.60	10.70

Table 5. Mean comparison of heavy metal concentrations (mg/kg) in fish by month.

Months	Pb	Cu	Cd	Zn
March	$0.02600±0.01^b$	$1.70±0.22^a$	$0.05625±0.02^a$	$57.76±1.23^b$
April	$0.04275±0.01^a$	$0.868±0.05^a$	$0.17225±0.02^a$	$77.92±0.89^a$
May	$0.01850±0.02^b$	$1.063±0.34^a$	$0.04650±0.01^a$	$71.78±0.77^a$

Means with the same letters are not significantly different (P>0.05).

Table 6. Mean heavy metal concentrations (mg/kg) in fish by station.

Station	Pb	Cu	Cd	Zn
Abattoir	0.03	0.96	0.13	70.03
Boat House	0.03	1.05	0.06	68.25

Table 7. Mean heavy metal concentrations (mg/kg) in specific fish species.

Fish species	Pb	Cu	Cd	Zn
H. fasciatus	0.04467	0.855	0.24847	128.87
O.niloticus	0.01500	0.967	0.04667	77.47
B. occidentalis	0.00*	0.957	0.08567	75.23
C. gariepinus	0.03667	0.967	0.07667	70.97
C. nigrodigitatus	0.00*	1.367	0.09167	65.70
S. sorex	0.04667	1.227	0.04667	62.37
A.baremose	0.05667	0.917	0.00*	52.23

*****Below detection/quantification limit

Table 8. Bioaccumulation Quotient (BQ) values for heavy metals in fish species.

Fish species	Pb	Cu	Cd	Zn
H. fasciatus	6.02	4.69	11.34	539.21
O.niloticus	2.02	5.37	2.13	324.14
B. occidentalis	0.00*	5.25	3.91	314.77
C. gariepinus	4.94	5.31	3.50	298.94
C. nigrodigitatus	0.00*	7.51	4.18	274.89
S. sorex	6.29	6.74	2.13	260.96
A.baremose	7.64	5.03	0.00*	218.53

*****Below detection/quantification limit

Table 9. Maximum Acceptable Risk (MAR) values for heavy metals in fish species **.**

Fish species	Pb	Cu	Cd	Zn
H. fasciatus	0.33	6.38	0.18	0.02
O.niloticus	0.99	5.59	0.94	0.04
B. occidentalis	0.00	5.71	0.51	3.50
C. gariepinus	0.41	5.64	0.57	0.04
C. nigrodigitatus	0.00	3.99	0.47	0.04
S. sorex	0.32	4.45	0.94	0.05
A.baremose	0.26	5.95	0.00	0.05

of heavy metals in fish ranged from 0.03 mg/kg for Pb at both stations to 70.03 mg/kg for Zn at the Abattoir station (Table 6).

The mean concentrations of metals in individual fish species ranged from below detection/quantification limit (BQL) for Pb in *B. occidentalis* and *C. nigrodigitatus* to 128.87 mg/kg for Zn in *H. fascistus* (Table 7); while the BQ values for metals in fish ranged from below detection/quantification limit for Pb in B*. occidentalis* and *C. nigrodigitatus* to 539.21 for Zn in *H. fasciatus* (Table 8). The Condition Factor for the fish species ranged from 0.32 in *C. gariepinus* to 2.07 in *O. niloticus* (Figure 1). The MAR values for heavy metals in fish ranged from below detection/quantification limit for Pb in *B. occidentalis* and *C. nigrodigitatus* to 6.38 for Cu in *H. fasciatus* (Table 9), while the HQ values for heavy metals in water ranged from 0.05 for Zn to 0.43 for Cd (Figure 2); while in the case of fish, the HQ values ranged from below detection/quantification limit for Pb in *B. occidentalis* and *C. nigrodigitatus* to 10.74 for Zn in *H. fasciatus* (Figure 3).

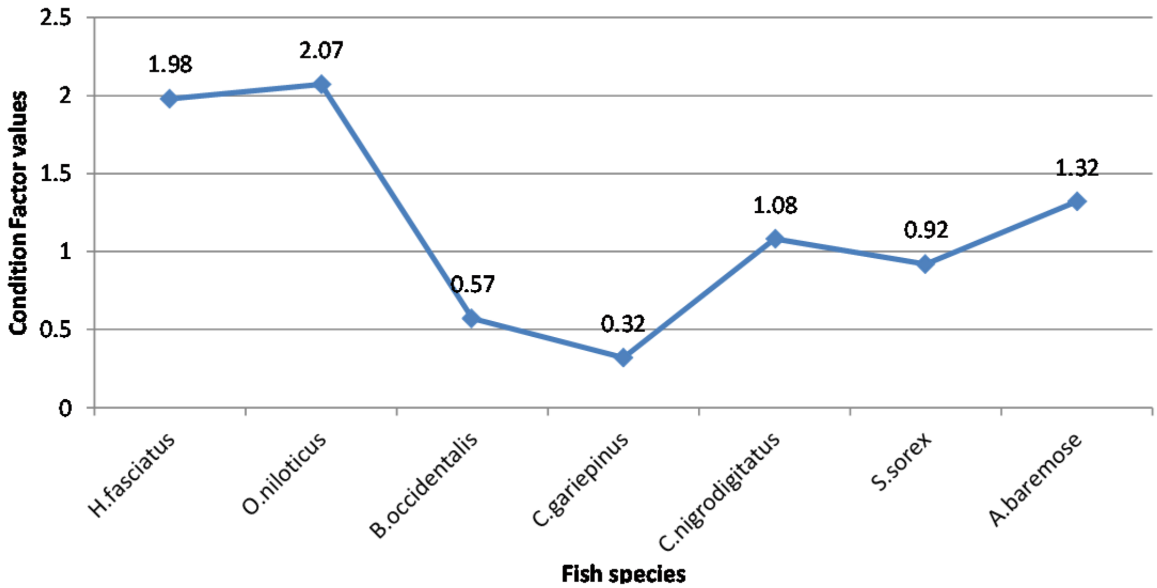

Figure 1. Condition Factor values for fish species.

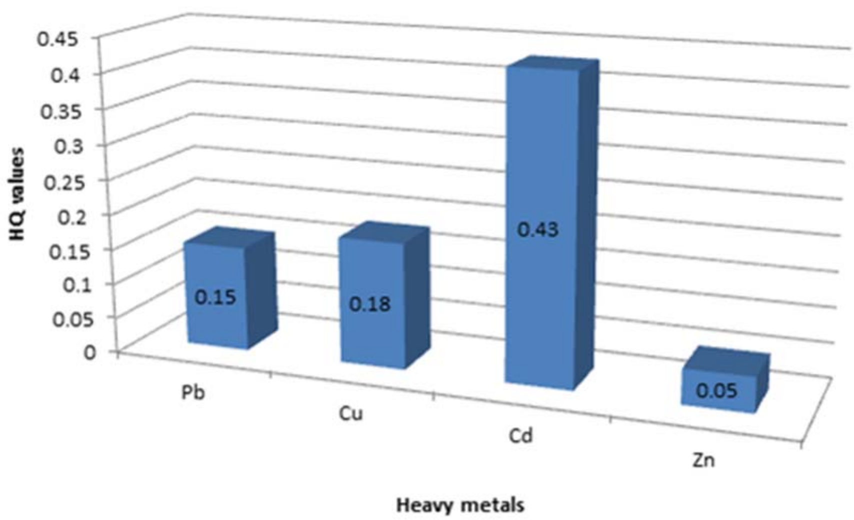

Figure 2. Hazard Quotient (HQ) values for heavy metals in water.

DISCUSSION

In this study, the mean concentrations of Zn in water were the highest across the sampled months, peaking in the month of April compared to the other metals. This finding may have been influenced by differences in precipitation patterns between the sampled months. The same metal had the highest concentrations at both stations, an indication that the water was more impacted with Zn and its associated compounds especially at the Abattoir station. The high Zn load recorded in water at the Abattoir station may be as a result of effluents and solid wastes emanating from the abattoirs which are completely void of proper waste disposal systems. Typical abattoir waste products include blood, stomach contents, bones, hoofs, hair, faecal material, urine and other unwanted parts of slaughtered cattle. Such waste products can impair water quality especially when their discharge into aquatic media continues unabated. Abattoir effluents are usually organically rich and may contribute to the eutrophication of the river.

The introduction of organic matter into natural aquatic media via eutrophication can provide additional binding sites for heavy metals. It has been recognized that under

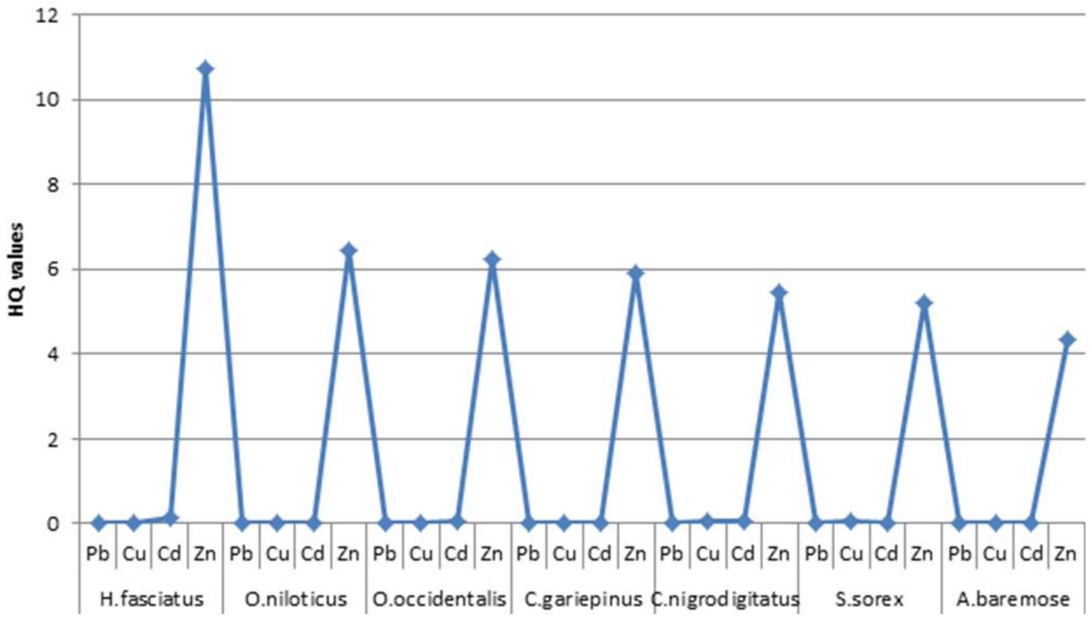

Figure 3. Hazard Quotient (HQ) values for heavy metals in fish species.

oxidizing conditions in natural waters, such organic matter can be degraded leading to the release of soluble metals into the aquatic medium (Tessier et al., 1979). Adekunle and Eniola (2008) observed that organic pollution of aquatic bodies can result from the discharge of raw effluents including sewage into such water bodies. Sangodoyin (1991) reported that effluents from domestic, agricultural and industrial sources can pollute receiving water bodies by altering their physical, chemical and biological properties.

The mean concentrations of heavy metals in water in this study compared well with the mean concentrations of metals recorded for water in some other studies on the African continent (Table 10). Not surprisingly, very high values of Zn were found in the captured fish species with fish at the Abattoir station generally recording higher values of Zn compared to the Boat House station. This finding may be attributed to a high bioavailability of the metal to fish in water especially at the Abattoir station. The highest mean value of Zn in fish was recorded for *H. fasciatus* an indication that this particular fish species was more impacted by Zn compared to the other fish species encountered in the study. The mean concentrations of Cd, Cu, Pb and Zn in *O. niloticus* from the Northern Delta Lakes in Egypt as reported by Saeed and Shaker (2008) were 0.014, 0.128, 0.019 and 0.450 mg/l respectively. These values were far exceeded by the mean concentrations of the aforementioned metals in the same fish species in this study, suggesting a higher impact by these metals on the Piscean community of River Niger.

The bioaccumulation pattern of heavy metals in fish varied with the highest BQ value recorded for Zn in *H. fasciatus* while Pb was not bioaccumulated by *B. occidentalis* and *C. nigrodigitatus.* The non-bioaccumulation of Pb by the aforesaid species may be attributed to the low levels of Pb in water compared to the levels of the other metals in the same medium. Bioaccumulation of metals can also be influenced by factors such as species size, species gender and seasons (Nussey et al*.,* 2000). Bioaccumulation of metals in fish can occur especially when the rate of uptake far outweighs the rate of expulsion. Normally, fish have the ability to regulate the metal burden in their bodies but only up to a limit beyond which bioaccumulation comes into play. Heavy metals can be obtained by fish from the surrounding water, food and sediment. Nussey et al*.* (2000) reported that when heavy metals are absorbed by fish, they are transported by the blood to either a storage point such as bones or to the liver for transformation and storage.

The Condition Factor revealed that *C. gariepinus* was the least conditioned fish in the study while on the other hand *O. niloticus* was the best conditioned fish. Factors that may be responsible for this variation may include the availability of suitable fish food and water quality conditions as corroborated by Baijot et al*.* (1997). The application of the Condition Factor in this study was warranted in order to assess the general well-being of the investigated fish species especially in the light of anthropogenic contamination by heavy metals which may alter the chemistry of the aquatic medium in which fish thrives. High MAR values were recorded for Cu in all the fish species in this study with the highest MAR value occurring in *H. fasciatus.*

Table 10. Comparison of heavy metal concentrations (mg/l) in water with selected studies on the African continent.

Heavy metal	River Niger at Agenebode	Kpong Headpond, Ghana (Biney, 1991).	Northern Delta Lakes, Egypt (Saeed and Shaker, 2008).	Ikpoba River Dam, Nigeria (Oronsaye et al., 2010).	Witbank Dam, South Africa (Nussey et al., 2000).	Doula Estuary, Cameroon (Fonge et al., 2011)
Cd	0.0219	< 0.010	0.019	0.035	ND	ND
Cu	0.182	< 0.02	0.186	0.025	ND	0.01-0.03
Pb	0.00742	< 0.02	0.064	0.060	0.08-0.25	0.01-0.03
Zn	0.239	< 0.02	0.177	0.490	ND	0.01-0.03

ND= Not Determined

The implication of this finding is that Cu has the greatest tendency to bio-magnify in man assuming these fish species were to be consumed especially *H. fasciatus*. In a study by Wangboje et al. (2014), high MAR values were recorded for Zn, Ni and Pb in the mangrove oyster (*Crossostrea gasar*) from Golubo Creek in the Niger Delta and the workers concluded that these metals conceivably had the greatest tendency to bio-magnify in man when the oysters are consumed. The HQ values calculated for heavy metals in water were all below unity, indicating that presently there are no toxicity/hazard risks associated with the metals in water as corroborated by Brooks et al. (2003). The HQ values for Zn in all fish species were above unity indicating a toxicity/hazard risk by the metal.

Similarly, Giri and Singh (2013) reported HQ values in shrimps that exceeded unity for Arsenic, Copper and Chromium. On the other hand, Bandowe et al. (2014) whom worked on Polycyclic Aromatic Hydrocarbons (PAHs) and trace metals in fish in Ghana, reported HQ values that were less than unity for Cd, Cu, Fe, Mn and Zn and observed that there was no danger to the fish consuming local population. In this study, the health based criteria employed in the evaluation of the risk indices were based on the World Health Organisation (WHO) maximum permissible limits for heavy metals in water and food (WHO, 2004). This is because when such stipulated limits are exceeded, unpleasant health impacts are expected to occur in man. Similarly, Gnandi et al. (2011) applied the WHO limit in calculating the Relative Health Factor (RHF), which is comparable to the HQ index applied in this study. In this study, with regard to human health risk, the mean concentration of Cd in water exceeded the WHO maximum permissible limit of 0.003 mg/l for Cd in drinking water. In the case of fish, the WHO maximum permissible limit of 75 mg/kg for Zn in fish food was exceeded by the mean concentrations of Zn in *H. fasciatus, O. niloticus* and *B. occidentalis.*

From the above findings, the heavy metals of ecological significance in this study are Zn, Cd, and Cu. Zinc is an essential element for both flora and fauna however, exposure to either deficient or high levels can have deleterious effects on an organism's health (Okafor and Opuene, 2007). Excessive intake of Zn by man can lead to vomiting, dehydration, abdominal pain, nausea, lethargy and dizziness (Agency for Toxic Substances and Disease Registry, 1994). Sources of this metal include batteries, refuse, pesticides, alloys, dyes and fossil fuels. Cadmium is a non-essential element that is of no use in the human body. It can be sourced from batteries, fossil fuel, fertilizers, plastics, alloys and paints. It has been reported that Cd can be assimilated from anoxic sediments with high organic matter content which generates the potential for bioaccumulation via dietary uptake (Muniz et al., 2004). According to the Erah et al. (2002), chronic exposure to Cd in humans results in kidney dysfunction, hypertension, anemia and liver damage. Copper is an essential element in the human body. The metal is present in pesticides, wood preservatives, alloys, fossil fuel, cooking utensils, piping and wiring. According to the Nigerian Industrial Standard for Drinking Water Quality (NIS, 2007), excess intake of copper can lead to gastrointestinal disorder. Other health problems associated with excess Cu uptake are anaemia, liver and kidney damage (Turnland, 1988).

Conclusion

The study successfully ascertained the concentrations of Cd, Cu, Pb and Zn in fish and water from River Niger at Agenebode, Edo State, Nigeria. The heavy metals of ecological significance in this study were essentially Zn, Cd, and Cu. The potential health hazards of these metals were also highlighted. Since heavy metals are non-biodegradable and toxic both to wildlife and man even at low concentrations, there is thus the need to ensure that fish and water from the river are safe for human consumption via a sustained monitoring programme that would take into consideration other chemical pollutants not covered in this study. The National Environmental Standard and Regulation Enforcement Agency (NESREA) are thus enjoined in this regard to ensure that the environmental safety of our inland water bodies is sustained in order to mitigate unwholesome health impacts on man.

Conflict of interest

The authors did not declare any conflict of interest.

ACKNOWLEDGEMENT

Special thanks to Martlet Environmental Laboratory, Benin City, for the use of their Atomic Absorption Spectrometric facility.

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