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Assessment of Heavy Metals in Water, Fish, and Sediment of River Benue, Benue State, Nigeria

***[1]Egesi, O.C., [1]Alum-Udensi, O., [2]Ogbonna, P.C. and [2]Ugor, N.N.**

[1]Department of Fisheries and Aquatic Resources Management;
[2]Department of Environmental Management and Toxicology,
Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria
*[1]Corresponding Author's email: chiomaegesi@yahoo.com

Abstract
Good Quality Rivers is a key source of drinking water and healthy aquatic organisms for human consumption. Water, fish, and sediment samples were each collected separately at four sampling stations viz: Wurukun abattoir, major storm drain, Wadata market, and 150 m upstream. Each of the samples was processed separately in the laboratory and analyzed to determine the concentrations of Mn, Cd, Pb, Zn, and Cu using an atomic absorption spectrometer. Results show that highest values of Cd (4.01± 0.01 mg/L and 6.01±0.01 mg/kg), Pb (13.01±5.77 mg/L and 10.01±0.01 mg/kg), Zn (4.44±2.79 mg/L and 12.02±0.02 mg/kg), Cu (19.31±0.01 mg/L and 0.51±0.01 mg/kg) and Mn (43.78±10.08 mg/L and 19.01±0.01 mg/kg) were recorded in water and catfish gills, respectively from the major drain station while the highest values of Cd (13.01±4.10 mg/kg), Pb (19.01±5.20 mg/kg), Zn (9.75±2.38 mg/kg), Cu (0.75±0.07 mg/kg) and Mn (22.02±5.02 mg/kg) were obtained in sediments from the abattoir station. The concentration of heavy metals in samples tested in this study was above the permissible limit recommended by WHO and FMEnvi except for Cu in catfish gills. Consequently, Sustained ingestion and consumption of Cd, Pb, Zn, and Mn-laced water and fish collected from River Benue may be a major source of this heavy metal toxicity in humans. Therefore, an assessment of other types of heavy metals not tested in this study should be carried out in River Benue.

Keywords: Heavy metals, water, fish, sediment, River Benue

Introduction

Good Quality River is a key source of healthy aquatic organisms and drinking water for human consumption, *inter alia*, conservation of aquatic resources for scientific research, ecotourism, and sustainable livelihood for people in developing countries such as Nigeria. Safe drinking water is essential for the sustenance of good health since water carries nutrients to all cells in our body, flushes out toxins and waste as well as regulates body temperature (Ogbonna *et al*., 2020). Thus, it is a basic human need for daily living and can be sourced from surface water (river, stream), rainwater, and groundwater. Available water supply sources are diminishing owing to pollution, climate change, and population rise, causing a globally acknowledged situation of water scarcity, especially in developing countries (Wheida and Verhoeven, 2007; Fang *et al*., 2007). It is estimated that about sixty (60) million Nigerians lack access to portable drinking water (Majuru *et al*., 2011) while global records showed that about 780 million people do not have access to clean and safe water (Rahmanian *et al*., 2015). Human settlements and industries have long been concentrated along rivers, estuaries, and coastal zones owing to the predominance of water-borne trade (Mustapha *et al*., 2013). For instance, a large number of communities in Benue State are living in proximity and or along the bank of River Benue and the inhabitants of these communities rely heavily on the aquatic body and its resources as a source of water, fish, and crabs for livelihood. The aquatic organisms are typically processed in commercial quantities for sale and consumption. According to FAO statistics, fish accounted for about 16% of the global population's intake of animal protein and 6% of all protein consumed (FAO, 2010).

Upstream use of water must be undertaken in such a way that it does not affect water quality or quantity for downstream users. The use of river water is the subject of major political negotiations at all levels (Meybeck, 1996). A river's water quality is the composite of several interrelated compounds, which are subjected to local and temporal variations and also affected by the volume of water flow (Mandal *et al*. 2010). The concern about the effects of anthropogenic pollution on the ecosystems is growing and heavy metals from man-made pollution sources are continually released into the aquatic and terrestrial ecosystems (Alturiqi and Albedair, 2012; Ogbonna *et al*., 2020). In aquatic ecosystems especially in the freshwater systems (lakes and rivers), heavy metals are considered predominant pollutants due to their persistence, toxicity, accumulation, and bio-magnification ability in the food webs (Saher and Siddiqui, 2019; Wang *et al*., 2019). Thus, heavy metals entered through surface runoff, fluvial transport, and atmospheric deposition; and accumulate and sink in sediment through the process of adsorption, co-precipitation and hydrolysis (Saeedi *et al*., 2011; Guo *et al*., 2018; Uddin *et al*., 2021).

River Benue has great social, economic, and ecological importance as it provides water for hundreds of thousands of people in the State, and a habitat for a variety of aquatic animals. Some activities that generate the most significant pollution in the River Benue include the Wurukun abattoir and Wadata market which covered hectares of land. Thus, the river receives wastewater that might be having a high load of heavy metals and organic chemical components from human activities. The River also receives high pollutant loads from the domestic discharges of communities living along the River banks or in proximity to the River Benue. Since fish constitute an important part of the human diet, it is not surprising that the quality and safety aspects of fish are of particular interest. Additionally, sediment assessment is vital since it is a basic component of the aquatic environment where it plays a vital role in elemental cycling and is responsible for transporting a large quantity of contaminants and nutrients. Literature showed that several kinds of research have been carried out on River Benue. These studies include a survey of ectoparasites associated with 3 species of fish *Auchenoglanis ocidentalis, Oreochromis niloticus* and *Bagrus bayad* in River Benue, Makurdi, Benue State, Nigeria (Nyaku *et al*., 2007), ecto and intestinal parasites of *Malapterurus electricus* from upper River Benue (Omeji *et al*., 2014), the prevalence of endoparasites of *Synodontis shcall* and *Synodontis ocellifer* (upside-down cat fish) from lower River Benue, Nigeria (Omeji *et al*., 2015), and seasonal prevalence of parasites of Clariids fishes from the lower Benue River, Nigeria (Uruku and Adikwu, 2017). Presently, there is a dearth of information on the heavy metal status of fish in River Benue. Hence, knowledge about the potential accumulation of heavy metals in fish is very important for the health of consumers. The study, therefore, determined the levels of heavy metals (cadmium (Cd), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) in water, fish, and sediment collected in River Benue. The levels were compared with the maximum permissible limits recommended by the World Health Organization and the Federal Ministry of Environment (Nigeria). It is expected that the results of this study shall serve the purpose of awareness to people on possible health risks associated with consuming fish harvested from River Benue as well as guide policymakers in making the best policies that will improve the water quality of River Benue, Nigeria.

Methodology

Study area

The study was carried out in River Benue which traverses via Makurdi, Benue State of Nigeria. Makurdi is the capital of Benue State and it is located on latitude 7°41′N and longitude 8°28′E. River Benue flows through Jimeta, Ibi, and Makurdi into Lokoja where it meets the river Niger. The size of the River Benue within Makurdi and the major settlements it runs through is approximately 671 meters (Akaahan *et al.,* 2015). The rainy season in Makurdi lasts for seven months (April to October) and has a mean annual rainfall ranging from 1200-2000 mm. Harmattan winds are accompanied by cooling effects mostly during the nights of December and January (Nyagba, 1995). The soil consists of basement complex rocks, cretaceous sandstones, and Albian limestone sediments. (Umeji, 2013). The main economic activity in Benue State is agriculture which is facilitated by the rich alluvial soil of the Benue Valley. However, large-scale fishing activity is carried out on the River. Four sampling stations were selected randomly for this study via paper balloting. Station 1 was behind Wurukun abattoir, station 2 was behind Wadata market, and Station 3 was upstream at Angbaaye on the outskirts of Makurdi town (i.e. the control) where there was very minimal human activity while Station 4 was a major storm drain in the north bank of the River. These human activities have a significant impact on the natural environment, primarily the water environment.

Fish collection and analysis

A field survey was carried out prior to the collection of samples. This was done in collaboration with two fishermen to determine the fish species that is common in the river. The possible effluents and rainwater runoff path, upstream locations as well as other human-ecological interactions were taken into consideration in choosing the targeted sampling positions (Simpson *et al*., 2005; Ogbonna *et al*., 2020). While in boat in River Benue, the fishermen cast their nets three to five times at each sampling station and sixteen similar sizes of catfish (*Clarias garipienus*) were selected from the fishes caught at each sampling station, put in small coolers containing river water collected at each point where the fish was harvested. The coolers were labeled well and placed in a bigger cooler to avoid contamination from external sources. The fish samples were taken to the laboratory for dissecting and digestion for analysis. The fish from each sampling station were dissected separately and the gills were extracted. Heavy metal detection in all the soft tissues was determined using the procedure of Siraj *et al*. (2016). The tissues were rinsed with double-deionized water and kept on blotting paper. Fifty grams of each tissue was placed in a separate 100 ml volumetric flask. Tissues were digested in a 5 ml mixed solution of perchloric and nitric acid. The next day, a fresh mixture of the two acids was added to each tissue. The tissues containing flasks were placed on a hot plate and allowed to digest at 200 to 250°C until a transparent and clear solution was obtained. 100 ml double distilled water was added to digested tissues and heavy metals were analyzed using an atomic absorption spectrometer (model Spectra-AA-700).

Water collection and analysis

Water sampling was done twice (6 am and 4 pm) from five different points at each sampling station where fish were harvested from River Benue. Each sampling bottle of 1 L by volume was pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de-ionized water. At each sampling station, the sampling bottles were rinsed with sampled water three times before sampling was done. The pre-cleaned sampling bottles were filled to the brim at a depth of 20 cm below the surface and covered tightly. The five representative water samples from each sampling station and control were acidified with 10% HNO^3 analytical grade, covered air-tight, labeled well, placed in an ice-chest container, and transferred to the laboratory for pre-treatment and analysis. Samples from each station were mixed separately to form one homogenous representative sample for the station (e.g. all water samples from five different points behind Wadata market were mixed thoroughly). The portion of the water sample for heavy metal analysis was treated with 1 ml of Hydrochloric acid (HCl) in a 500 ml sample to arrest microbial activities. While in the laboratory; the homogenous water samples were stored in the refrigerator at about 4°C prior to the analysis (APHA, 1998). Adequate precautions were exercised to avoid contamination of water during sampling, transport, and handling. Twenty (20) water samples each were collected morning and evening every ten (10) days in June 2019 from the three (3) sampling stations and control sites. A total of 480 water samples were collected in all. About 100 ml of acidified water samples were evaporated in a volumetric flask on a hot plate and reduced to about 20 ml within a fume cupboard and then a mixture of 5 ml of HNO_3 (55 %) and 10 ml of perchloric acid (70 %) was added. The mixture was evaporated on a hot plate until the brown fumes converted into dense white fumes of perchloric acid. The samples were cooled and diluted to 100 ml with double distilled water. The solutions were then analyzed through atomic absorption spectrophotometer (Spectra-AA-700) by using an air acetylene flame for the determination of these metals.

Sediment collection and analysis

The procedure of Siepak *et al*. (2020) with slight modification was adopted for the collection of bottom sediment samples around the points where fish and water samples were collected at different stations of River Benue. Bottom sediment samples of 10 cm depth were collected using a Czapla-1 core sampler (Mera-Błonie, Gdańsk, Poland) into self-sealing plastic bags. Figure 1 shows the locations of the sampling stations. Twenty (20) sediment samples were collected in the morning every ten (10) days in June 2019 from the three (3) sampling stations and control sites. A total of sixty (60) sediment samples were collected in all. The samples were well-sealed, carefully labeled, and taken to the laboratory in a cooler packed with ice blocks for pre-treatment and analysis. The procedure of Defew *et al*. (2005) with slight modification was adopted in the analyses of sediment samples. The sediments were sieved to remove any stones, pebbles, organic matter, and benthic fauna and air-dried at room temperature for approximately 17 days to eliminate water completely. The sediments were then ground to powder using acid-washed pestle and mortar and sieved with a 0.5 mm sieve. One gram (1 g) of the sieved sediment from each sampling position was transferred separately to an acid-washed 100 cm^3 beaker, and 10 ml of aqua regia was added and covered. Aqua regia solution is prepared by the combination of hydrochloric acid and nitric acid in a ratio of 3:1. The samples were left overnight to digest completely at room temperature. Twenty (20 ml) of distilled water was added to the sample and the mixture was filtered through a funnel containing Whatman filter paper no. 125 mm and finally made-up to 20 cm^3 with distilled water. Heavy metals were determined using Atomic Absorption Spectrometer (Spectra-AA-700).

Quality assurance and quality control

Quality assurance and quality control were carried out with parallel experiments, blank tests, and recovery tests. The recovery rates were between 90% and 110%, and the relative deviations of parallel tests were within 10%. All used acids and reagents were of analytical grade. The reagents used were ultrapure, and the water was de-ionized to a resistivity of 18.2 MΩ·cm in a Direct-Q UV3 Ultrapure Water System apparatus (Millipore, France).

Statistical analysis and Data presentation

The data from Laboratory analysis was subjected to one-way analysis of variance (ANOVA) with statistical package for social sciences (SPSS) v. 18 and means were separated by Duncan New Multiple Range Test (DNMRT) according to Steel and Torrie (1980). Results are presented as mean ± SD.

Results and Discussion

Concentration of heavy metals in water

The statistical summary of the selected heavy metals tested in water samples from the various stations in River Benue is presented in Table 1. The results indicated significant differences amongst the stations. It also indicated that the highest and lowest concentrations of heavy metals were observed in water samples collected from different land uses where human influence was high and in control sites, respectively. The highest values of Cd (4.01±0.01 mg/l), Pb (13.01±5.77 mg/l), Zn (4.44±2.79 mg/l), Cu (17.31±0.01 mg/l), and Mn (43.78±10.08 mg/l) were obtained in water samples collected around the major storm drain station, and the values are significantly ($p<0.05$) higher than their (Cd, Pb, Zn, Cu, and Mn) values at Wurukun abattoir station (3.01±0.01, 11.51±7.51, 1.37±0.13, 16.81±3.46, and 34.93±4.71 mg/l), Wadata market station (2.51±0.58, 8.02±0.03, 0.84±0.02, 10.55±6.70, and 27.25±0.07 mg/l), and control site (1.53±0.60, 4.51±1.73, 0.63±0.01, 1.75±0.21, and 16.43±6.95 mg/l) (Table 1). The high concentration of metals (Cd, Pb, Zn, Cu, and Mn) in water samples collected around the major storm drain station may be attributed to agricultural activities around the area. Benue State is the food basket of Nigeria, and contamination from large-scale agricultural production that uses agrochemicals (pesticides, chemical fertilizer, and other farm inputs) may have contributed to high values of metals in River Benue via surface runoff. For instance, surface runoff from urban and agricultural areas deteriorates the water quality of water bodies and this diffuse pollution is difficult to control (Kotti *et al*., 2005).

The values of Cd, Pb, Zn, Cu, and Mn in water samples collected around the major storm drain station were 1.3, 1.1, 3.2, 1.1, and 1.2 folds higher than its concentrations at Wurukun abattoir station, but 1.6, 1.6, 5.2, 1.8, and 1.6 folds higher than Wadata market station, and 2.6, 2.8, 7, 11, and 2.6 folds higher than control site (Table 1). The values of Cd increased from 1.53±0.58 to 4.01±0.01 mg/l, which is higher than 0.216 to 0.277 mg/l of Cd reported for Elelenwo River in Port Harcourt, Rivers State, Nigeria (Edori *et al*., 2019), 0.010 to 0.100 mg/l of Cd recorded for River Ijana in Ekpan-Warri, Delta State of Nigeria (Emoyan *et al*., 2006), 0.021 to 0.022 mg/l of Cd observed in Rivers in southwest Nigeria (Adesiyan *et al*., 2018), and 0.001 to 0.090 mg/l of Cd in Elele-Alimini stream Port Harcourt, Rivers State of Nigeria (Otene and Iorchor, 2019). The difference in concentrations of heavy metals in River Benue and these studies may be attributed to locational differences in terms of landscape and lithological mineral composition of the surrounding territory of the study sites.

The values of Cd (2.51-4.01 mg/l) in water from River Benue are well above 0.03 mg/L (Cd) recommended by both the World Health Organization (WHO, 2011) the and National Drinking Water Quality Standard of Malaysia (NDWQS, 2004). The use of water from River Benue for domestic purposes could pose cadmium-related hazards to consumers. The values of Pb increased from 4.51±1.73 to 13.01±5.77 mg/l, which is higher than 0.40 to 3.1 mg/l in Calabar, Cross River State of Nigeria (Ewa *et al*., 2013), 0.414 to 0.457 mg/l reported for Elelenwo River (Edori *et al*., 2019), 0.025 to 0.058 mg/l recorded for River Ijana (Emoyan *et al*., 2006), 0.016 to 0.018 mg/l observed in Rivers in southwest Nigeria (Adesiyan *et al*., 2018), 0.008 to 0.05 mg/l for Eme River Umuahia north, Abia State of Nigeria (Anyanwu and Umeham, 2020), and 0.008 to 0.077 mg/l in Escravos River (Membere and Abdulwasiu, 2020). The values of Pb in this study (4.51±1.73 to 13.01±5.77 mg/l) are well above 0.01 mg/L (Pb) recommended by both the World Health Organization (WHO, 2011) and National Drinking Water Quality Standard of Malaysia (NDWQS, 2004). The use of water from River Benue for domestic purposes could pose lead (Pb) related hazards to consumers.

The value of Zn increased from 0.63±0.01 to 4.44 mg/l, which is higher than 1.11 to 2.74 mg/l reported for Elelenwo River (Edori *et al*., 2019), 0.03 to 0.08 mg/l recorded for Calabar River (Ewa et al., 2013), 0.40 to 0.99 mg/l for Eme River (Anyanwu and Umeham, 2020), 0.088 to 0.122 mg/l for River Ijana (Emoyan *et al*., 2006), and 0.059 to 0.122 mg/l for Escravos River (Membere and Abdulwasiu, 2020). The values of Zn (0.63 to 4.44 mg/l) in this study are relatively higher than the 3.0 mg/L recommended by WHO (2004). Thus, the use of water from River Benue for domestic purposes could pose zinc-related hazards to consumers.

The values of Cu increased from 1.75±0.21 to 19.31±0.01 mg/l, which is higher than 0.17 to 0.26 mg/l reported for Calabar River (Ewa *et al*., 2013), 0.013 to 0.094 mg/l recoded for Escravos River (Membere and Abdulwasiu *et al*., 2020), 0.02 to 0.12 mg/l obtained in Eme River (Anyanwu and Umeham, 2020), 0.020 to 0.050 mg/l for River Ijana (Emoyan *et al*., 2006), and 0.674 to 0.844 mg/l for Elelenwo River (Edori *et al*., 2019). The values of Cu (1.75 to 19.31 mg/l) in this study is well above 1.5 to 2.0 mg/L recommended by WHO (2004). Consequently, the use of water from River Benue for domestic purposes could pose copper-related hazards to consumers. The values of Mn increased from 16.43±6.95 to 43.78±10.08 mg/l, which is higher than 0.07 to 0.65 mg/l reported for Calabar River (Ewa *et al*., 2013), 0.049 to 0.07 mg/l recorded for Escravos River (Membere and Abdulwasiu, 2020), 0.05 to 0.19 mg/l for Eme River (Anyanwu and Umeham, 2020), and 0.172 to 0.190 mg/l for Rivers in southwest Nigeria (Adesiyan *et al*., 2018). The values of Mn (16.43 to 43.78 mg/l) in this study is well above 0.2 mg/L recommended by WHO (2004). Hence, the use of water from River Benue for domestic purposes could pose manganese-related hazards to consumers. Generally, the concentration of heavy metals in water samples from River Benue ranked in the following order: Mn>Cu>Pb>Zn>Cd.

Concentration of heavy metals in fish gills

The results of the selected heavy metals tested in fish gills of *Clarias gariepillis* harvested from the various stations in River Benue is presented in Table 2. The results indicate the highest and lowest concentration of heavy metals in the gills of fish samples tested in this study were recorded in catfish harvested at stations where land use for various human activities were high (i.e. Wurukun abattoir, Wadata market, and major storm drain) and control area, respectively. The highest concentration of Mn (19.01±0.01 mg/kg), Cu (0.51±0.01 mg/kg), Zn (12.02±0.02 mg/kg), Pb (10.01±0.01 mg/kg), and Cd (6.01±0.01 mg/kg) was obtained in catfish gills harvested at the major storm drain station and the values were significantly ($p<0.05$) higher than their (Mn, Cu, Zn, Pb, and Cd) values in catfish gills harvested at the Wurukun abattoir station (17.01±0.01, 0.43±0.01, 7.85±0.07, 6.10±0.01, and 3.12±0.01 mg/kg), Wadata market station (12.01±0.01, 0.06±0.01, 4.02±0.01, 2.81±0.01, and 0.94±0.01 mg/kg), and the control area (9.01±0.01, 0.03±0.01, 2.10±0.01, 0.73±0.01, and 0.08±0.00 mg/kg) (Table 2). The high concentration of Mn, Cu, Zn, Pb, and Cd in catfish gills harvested at the major storm drain may be attributed to a high concentration of these heavy metals

(Mn, Cu, Zn, Pb, and Cd) in sediments in River Benue (Table 4). Research has shown that sediments form the major repository of heavy metals in the aquatic body (Atta *et al*., 1997; Adeniyi and Yusuf, 2007) and fish scavenges for food in sediments with the mouth and this might have increased the level of intake of heavy metals in their body (Ogbonna *et al*., 2020). Thus, Saeed (2000) and Ogbonna *et al*. (2018b) noted that catfish are mainly carnivorous, feeding on insect larvae, fish, molluscs, plankton organisms, seeds, worms, and detritus that accumulate large amounts of heavy metals. Additionally, dermal contact and ingestion of metal-contaminated water in River Benue might have contributed to the level of concentration of metals in catfish gills tested in this study.

The concentration of Mn in cat fish gills increased from 9.01 to 19.01 mg/kg, which is higher than 0.57 to 5.35 mg/kg in fish gills (Nwani *et al*., 2009) and 4.20 to 7.23 mg/kg in fish gills (Membere and Abdulwasiu, 2020). In this study, the concentration of Mn (9.01 to 19.01 mg/kg) in catfish gills is higher than maximum permissible limit of 0.02 mg/kg (Mn) recommended by the World Health Organization (WHO, 2011) (Table 3). Consumption of such manganese-contaminated fish by people can trigger some serious health challenges since manganese is a trace element required at a trace level in the human body. According to The National Research Council of Canada (NRC), the recommended safe and adequate daily intake levels for manganese range from 0.3 to 1 mg per day for children up to 1 year, 1–2 mg per day for children up to age 10, and 2–5 mg per day for children 10 and older (Institute of Medicine, 2003). Manganese plays a vital role in redox processes, as an activator of a large range of enzymes, and as a cofactor of a small number of enzymes, including proteins required for light-induced water oxidation in photosystem II (Stout and Arnon, 1939; Broadley *et al*., 2012).

The values of Cu in catfish gills increased from 0.03 to 0.51 mg/kg and the values are relatively higher than 0.08 to 0.43 mg/kg in *Clarias garipienus* harvested from Kpata River in Lokoja, Kogi State (Egbeja *et al*., 2019) but lower than 5.76 to 10.20 mg/kg reported in fish gills harvested in Anambra River (Nwani *et al*., 2009) and 3.10 to 5.3 mg/kg in fish gills obtained in Escravos River (Membere and Abdulwasiu, 2020). In this study, the values of Cu (0.03 to 0.51 mg/kg) in fish gills is lower than permitted level of 1 to 3 mg/kg (Cu) recommended by the Federal Environmental Protection Agency (FEPA) of Nigeria and 3 mg/kg (Cu) set by World Health Organization (WHO, 1994). Copper (Cu) is an essential element for living organisms at a trace level. For instance, it is a key constituent of blood pigment and haemoglobin in aquatic animals but its deficiency leads to severe disorders like anaemia and neutropenia (Oliver, 1997), while its excessive level leads to liver damage (Markmanuel *et al*., 2017), Alzheimer disorders, and may also cause nervous breakdown (Uriu-Adams and Keen, 2005) and other detrimental effects (Kumar *et al*., 2021). Consequently, the level of Cu in fish gills may pose serious health issues for the fish as well as man that depend on fish from River Benue as a source of food and protein. The prescribed dose-response curve of Cu in humans is U-shaped (Stern *et al*., 2007).

The values of Zn in cat fish gills increased from 2.10 to 12.02 mg/kg, which is lower than 8.10 to 21.30 mg/kg recorded for fish gills (Nwani *et al*., 2009) but higher than 3.85 to 7.15 mg/kg in fish gills (Membere and Abdulwasiu, 2020). The value of Zn (2.10 to 12.02 mg/kg) in this study is higher than the permitted level of 5.0 mg/kg (Zn) recommended by WHO (2011) (Table 3). Zinc is one of the most essential trace elements required by living organisms but Zn level in fish harvested from River Benue may pose serious health risk to consumers. For instance, Zn may produce adverse nutrient interaction with Cu (Johnson and Lamy, 2009), and a high level of Zn reduces immune function and the levels of high-density lipo-proteins (Spear, 2000). However, Zn is important in the synthesis of DNA, growth hormone, gene expression, gene regulation, cell division, immunity, and has catalytic, structural as well as regulatory actions (Vidyavati *et al*., 2016) and enhances the reproductive potential of men (Ogbonna *et al*., 2020).

The values of Pb increased from 0.73 to 10.01 mg/kg, which is higher than 1.03 to 2.11 mg/kg in *Clarias garipienus* (Egbeja *et al*., 2019), 0.50 – 2.50 in fish harvested from Ubeyi River, Ebonyi State (Ogbonna *et al*., 2018), 0.11 to 0.58 mg/kg recorded for Pb in fish gills (Nwani *et al*., 2009) and 0.15 to 0.31 mg/kg obtained in fish gills (Membere and Abdulwasiu, 2020). The value of Pb (0.73 to 10.01 mg/kg) in fish gills harvested in River Benue is well above the permitted level of 0.05 mg/kg (Pb) recommended by WHO (2008) (Table 3). The level of Pb recorded in fish gills tested in this study can be detrimental to the health and survival of both carnivorous animals and man that rely on fish harvested from River Benue as a source of food and protein. For instance, low-level chronic exposure to Pb cause adverse health effects such as neurological and reproductive effects (Ogbonna *et al*., 2018b). Exposure to Pb could lead to loss of memory, nausea, insomnia, anorexia, and weakness of the joints, irritation and producing tumour (Adelekan and Abegunde, 2011; Al Hagibi, 2018). The values of Cd increased from 0.08 to 6.01 mg/kg, which is higher than 0.23 to 0.41 mg/kg in *Clarias garipienus* harvested from Kpata River, Lokoja (Egbeja *et al*., 2019) and the maximum permissible limit <0.01 (WHO, 2008) (Table 3). Cadmium is toxic even at low concentrations (Jain *et al*., 2007) causing high blood pressure, adverse changes in the arteries of human kidney, kidney damage, replaces zinc biochemically (Feng *et al*., 2011), interferes with enzymes and causes Itai-itai (Sperotto *et al*., 2014). Sequel to a high level of Cd beyond the accepted limits by the World Health Organization, the consumption of catfish from River Benue will constitute a serious health risks to man and carnivorous animals such as Pel's fishing owl (*Scotopelia peli*), Lanner falcon (*Falco biarmicus*) and

Black kite (*Milvus migrans*) within the area (Ogbonna *et al*., 2020). The accumulation of heavy metals (Mn, Zn, Pb, and Cd) in fish that might be available in the Wadata market to such a degree that may constitute a potential threat to human health when ingested is of great concern. Generally, the concentration of heavy metals in cat fish gills harvested from River Benue ranked in the following order: Mn>Zn>Pb>Cd>Cu.

Concentration of heavy metals in sediments

The results of the selected heavy metals tested in sediment samples collected from the various stations in River Benue is presented in Table 4. The results indicate that the highest and lowest concentration of heavy metals in sediment samples tested in this study were recorded in sediments collected at stations where land use for various human activities were high (i.e. Wurukun abattoir, Wadata market, and major storm drain) and control area, respectively. The highest concentration of Cd (13.01±4.10 mg/kg), Pb (19.01±5.20 mg/kg), Zn (9.75±2.38 mg/kg), and Cu (0.75±0.07 mg/kg) was recorded in sediments collected from the Wurukun abattoir station and these values are significantly ($p<0.05$) higher than their corresponding values in sediments collected from the Wadata market station (5.01±0.01, 4.01±0.01, 1.81±0.01, and 0.21±0.01 mg/kg), major storm drain (10.01±2.10, 13.03±4.10, 2.01±0.01, and 0.34±0.01 mg/kg), and control (2.02±0.03, 0.11±0.02, 1.45±0.07, and 0.11±0.01 mg/kg), respectively for Cd, Pb, Zn, and Cu (Table 4). The high concentration of heavy metals (Cd, Pb, Zn and Cu) in sediments collected from Wurukun abattoir station may be attributed to the deposition of abattoir wastes (e.g., blood, small pieces of bones, and feces from animal intestines) at the abattoir station of the River Benue. Similarly, the displacement of heavy metal-contaminated organic materials from upstream during the pulling of casted fishing nets by fishermen and deposits downstream may be a contributing factor to a high content of heavy metals (Cd, Pb, Zn, and Cu) at the Wurukun abattoir station. According to Zhou (2019), the contents of heavy metals vary considerably in surface sediments from disparate sections of Rivers. The concentration of Cd in sediment increased from 2.02±0.03 to 13.01±4.10 mg/kg, which is higher than 4.4±±2.6 to 7.1±1.8 mg/kg in sediment collected from River Kabul, Pakistan (Khan *et al*., 2018), 4.4 to 7.1 mg/kg in sediment (Ibrahim *et al*. 2018), 0.04±0.02 to 0.16±0.02 mg/kg in sediment collected from Onu Asu River, Abia State of Nigeria (Ogbonna *et al*., 2020), and 0.105 to 8.35 mg/kg in sediment collected from Mashavera River, Republic of Georgia (Withanachchi *et al*., 2018). The concentration of Cd (2.02±0.03 to 13.01±4.10 mg/kg) in this study is well above the standard limit of 0.03 – 0.3 mg/kg (Cd) set by the Federal Ministry of Environment, Nigeria (FMEnv, 2011) and Department of Petroleum Resources (DPR, 2002). The level of Cd observed in sediment may pose serious challenges to the health, growth, and survival of benthic organisms in River Benue. The accumulation of heavy metals in surface sediments negatively affects the ecological environmental safety of a catchment area and threatens animals and plants (Chang *et al*., 2014).

The concentration of Pb in sediment increased from 0.11±0.01 to 19.01±5.20 mg/kg, which is lower than 0.00 to 698.34 mg/kg in the sediment of a tropical man-made lake southwestern, Nigeria (Ayoade and Nathaniel, 2018) and 41.22±3.33 to 56.88±4.89 ppm in sediment collected in Rosetta branch of the River Nile, Egypt (Yehia and Sebaee, 2012) but higher than 0.992±0.0008 mg/kg (Pb) in the sediment of Kpata River Lokoja, Kogi State, Nigeria (Funtua *et al*., 2016) and 0.22±0.09 to 2.05±0.13 mg/kg reported in sediment collected from Onu Asu River in Abia State of Nigeria (Ogbonna *et al*., 2020) (Table 5). The concentration of Pb (0.11±0.01 to 19.01±5.20 mg/kg) in this study is well above the standard limit of 0.5 mg/kg (Pb) set by the Federal Ministry of Environment, Nigeria (FMEnv, 2011) and the Department of Petroleum Resources (DPR, 2002). The concentration of Pb in the sediment of River Benue may affect the life and activities of smaller aquatic organisms such as phytoplankton and zooplankton. Lead (Pb) is a non-essential element and can be toxic even at low concentrations (Awofolu *et al*., 2005; Ogbonna *et al*., 2013; Ogbonna *et al*., 2020). However, the concentration of heavy metals in surface sediments and their potential ecological hazards differ according to geological conditions and human activities in various catchment areas (Zhou, 2019).

The concentration of Mn in sediment increased from 17.05±2.07 to 22.02±5.02 mg/kg, which is well above the permissible limit of 0.05 (Mn) recommended by World Health Organization (WHO, 2008). Manganese is required by aquatic organisms for healthy growth and development but the level of Mn in sediment of River Benue can be detrimental to benthic animals. Generally, the heavy metal contents in surface sediments in this study ranked in decreasing order are as follows: Mn>Pb>Cd>Zn>Cu.

Conclusion

The concentration of heavy metals (Cd, Pb, Zn, Cu, and Mn) in water was above the maximum permissible limit recommended by World Health Organization (WHO) which makes the water unfit for human consumption. Furthermore, the level of heavy metals (Cd, Pb, Zn, and Mn) in catfish gills was higher than the recommended level set by World Health Organization (WHO) for food fish. Thus, these heavy metals (Cd, Pb, Zn, and Mn) may pose a serious health threat to the consumers of fish and fish products from River Benue. Prolonged consumption of the catfish from River Benue will likely have adverse effects on the people of Benue State as well as commuters and passengers (travelers) that buy fish as they traverse via Benue State to other parts of the country. Therefore, it is recommended that heavy metals not tested in this study should be carried out to determine the status of heavy metal pollution in River Benue since the river serves as a source of drinking water and fish for millions of people in Nigeria.

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Conflict of interest
There is no conflict of interest associated with this work.

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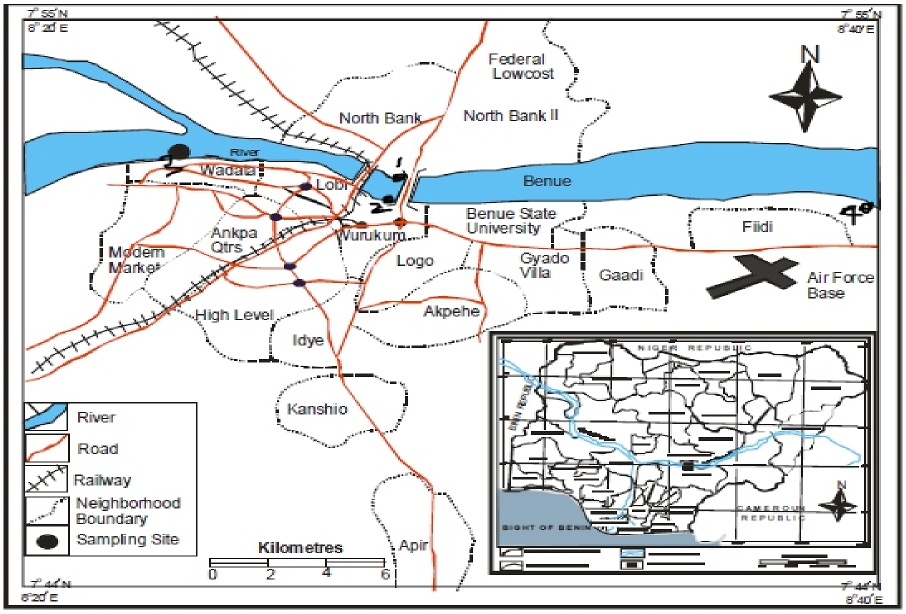

Fig. 1: Map of Makurdi showing the sampling stations (Uruku and Adikwu, 2017)

Table 1: Concentration of heavy metals (mg/L) in water

Sampling stations	Cd	Pb	Zn	Cu	Mn
Behind Wurukun abattoir	$3.01^{b}\pm0.01$	$11.51^{b}\pm7.51$	$1.37^{b}\pm0.13$	$16.81^{b}\pm3.46$	$34.93^{b}\pm4.71$
Behind Wadata market	$2.51^{c}\pm0.58$	$8.02^{c}\pm0.03$	$0.84^{c}\pm0.02$	$10.55^{c}\pm6.70$	$27.25^{c}\pm0.07$
Major storm drain	$4.01^{a}\pm0.01$	$13.01^{a}\pm5.77$	$4.44^{a}\pm2.79$	$19.31^{a}\pm0.01$	$43.78^{a}\pm10.08$
Control area	$1.53^{d}\pm0.60$	$4.51^{d}\pm1.73$	$0.63^{c}\pm0.01$	$1.75^{d}\pm0.21$	$16.43^{d}\pm6.95$

Values were expressed as mean ± standard deviation of 3 replicates; abcd Means in a column with different superscripts are significantly different (P<0.05)

Table 2: Concentration of heavy metals (mg/kg) in cat fish gills

Sampling stations	Cd	Pb	Zn	Cu	Mn
Behind Wurukun abattoir	$3.12^{b}\pm0.01$	$6.10^{b}\pm0.01$	$7.85^{b}\pm0.07$	$0.43^{b}\pm0.01$	$17.01^{b}\pm0.71$
Behind Wadata market	$0.94^{c}\pm0.02$	$2.81^{c}\pm0.08$	$4.02^{c}\pm0.20$	$0.06^{c}\pm0.00$	$12.01^{c}\pm0.17$
Major storm drain	$6.01^{a}\pm0.01$	$10.01^{a}\pm0.01$	$12.02^{a}\pm0.02$	$0.51^{a}\pm0.01$	$19.01^{a}\pm0.01$
Control area	$0.08^{d}\pm0.03$	$0.73^{d}\pm0.13$	$2.10^{d}\pm0.41$	$0.03^{d}\pm0.01$	$9.01^{d}\pm1.50$

Values were expressed as mean ± standard deviation of 3 replicates; abcd Means in a column with different superscripts are significantly different (P<0.05)

Table 3: Comparison with international standards and similar studies

Source	Cd	Mn	Pb	Zn	Cu
This study	0.08 – 6.01	9.01 – 19.01	0.73 – 10.01	2.10 – 12.02	0.03 – 0.51
Ogbonna *et al*. (2020)	0.00±0.00 – 0.01±0.00	NA	0.00±0.00 – 0.023±0.015	NA	NA
Egbeja *et al* (2019)	0.23–0.41	NA	1.03–2.11	NA	0.08–0.43
Baker *et al*. (2019)	0.860±0.566 – 5.101±1.455	NA	0.020±0.012 – 0.117±0.048	NA	NA
Khan *et al*. (2018)	0.9–1.2	35.1–45.3	10.1–31.9	41.7–50.4	2.7–3.6
Ibrahim *et al*. (2018)	0.020 – 0.10	NA	0.50 – 2.50	NA	0.30–0.68
Ogbonna *et al*. (2018b)	0.00±0,00 – 0.00015±0.00	1.99–2.15	0.00±0.00 - 0.00015±0.00	12.00–12.18	NA
Funtua *et al*. (2016)	NA	NA	1.099±0.0019 – 1.832±0.0004	NA	NA
FEPA 1999	>1.0	NA	0.05	<1.0	<1.0
WHO 2011		0.02		5.0	
WHO 2008	<0.01		0.05	NA	NA
EC 2005	0.05	NA	0.2		
EU 2001	0.1	NA	0.1	NA	10
England (MAFF 2000)	0.2	NA	2.0	50	20
Turkish Guidelines (Dural *et al*., 2007)	0.1	20	1.0	50	20
SASO 1997 (Saudi Arabia)	0.5	NA	2.0	NA	NA
FAO 1989	NA	NA	0.5	NA	NA

Table 4: Concentration of heavy metals (mg/kg) in sediments

Sampling stations	Cd	Pb	Zn	Cu	Mn
Behind Wurukun abattoir	13.01±4.10	19.01^{b}±5.20	9.75^{b}±2.38	0.75^{b}±0.07	22.02^{b}±5.02
Behind Wadata market	5.01±0.01.	4.01^{c}±0.01	1.81^{c}±0.01	0.21^{c}±0.01	21.02^{c}±4.01
Major storm drain	10.01±2.10	13.03^{a}±4.10	2.01^{a}±0.01	0.34^{a}±0.01	21.02^{a}±4.01
Control area	2.02^{d}±0.03	0.11^{d}±0.01	1.45^{d}±0.07	0.11^{d}±0.01	17.05^{d}±2.07

Values were expressed as mean ± standard deviation of 3 replicates ; *abcd Means in a column with different superscripts are significantly different (P<0.05).*

Table 5: Comparison with similar studies of sediments from rivers

Location	Cd	Mn	Pb	Zn	Cu	Reference
River Benue in Benue State, Nigeria	2.02 to 13.01	17.05 to 22.02	0.11 to 19.01	1.45-9.75	0.11-0.75	This study
Onu Asu River in Abia State, Nigeria	0.04-0.16	NA	0.22-2.05	NA	NA	Ogbonna *et al*. (2020)
Red Sea Coast of Yemen Al-Hodeidah	0.53	NA	14.25	NA	NA	Al Hagibi *et al*. (2018)
Sanglades Sundarbans	0.09	NA	25.61	NA	NA	Kumar *et al*. (2016)
Rosetta branch of the River Nile, Egypt Egypt Safaga Island United Arab Emirates	NA 0.40 4.5-5.1	NA NA NA	41.22-56.88 28.40 20.4-37.3	NA NA NA	NA NA NA	Yehia and Sebaee (2012) Dar and El-Saharty (2006) Shriadah (1999)
Thailand Pattani Bay	0.20	NA	47.30	NA	NA	Kaewtubtim *et al*. (2016)
Saudi Arabia Farasan Island	ND-1.04	NA	ND	NA	NA	Usman *et al*. (2013)
Panama Punta Mala Bay	<10	NA	78.20	NA	NA	Defew *et al*. (2005)
India Kannur	2.00	NA	28.00	NA	NA	Badarudeen *et al*. (2014)
China Futian	0.98	NA	133.30	NA	NA	Li *et al*. (2008)
Brazil Jequia	1.32	NA	160.80	NA	NA	Kehrig *et al*. (2003)
Iran Sirik Azini creek	18.93	NA	32.31	NA	NA	Parvaresh *et al*. (2011)
Australia Queensland	0.60	NA	36.00	NA	NA	Preda and Cox (2002)
Ubeyi River in Ebonyi State, Nigeria	0.00015	15.92-16.84	0.00015	2.31-2.68	NA	Ogbonna *et al*. (2018)
Nigeria Niger Delta	0.01-4.18	NA	0.06-8.75	NA	NA	Ugbomeh *et al*. (2019)
Nigeria Southwest Nigeria	0.00-9.00	NA	0.00-698.34	NA	NA	Ayoade and Nathaniel(2018)
Nigeria Lokoja, Kogi State	0.050	NA	0.992	NA	NA	Funtua *et al*. (2016)