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Heavy Metal Concentrations in Selected Fishes, and Water from Orogodo River, Agbor, Delta State in Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Authors OMW and PCE designed the study. Author PCE performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author UIE managed the analyses of the study. Authors OMW and PCE managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This study determined heavy metal:- (lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) and iron (Fe) concentrations in selected fish species including: (*Brycinus intermidus*, *Clarias gariepinus, Parachanna obscura, Ctenopoma kingsleyae, Hemichromis bimaculatus* and *Phractolaemus ansorgeii)* and water from Orogodo River situated in Agbor, Delta State, Nigeria. Furthermore, the health risk exposure to humans who consume the fish and utilized the water in Orogodo River was assessed. The mean (±SD) concentration of the heavy metal in water ranged from 0±0 mg/l for Cd to 0.35±0.29 mg/l for Fe. The mean (±SD) concentration of metals in fish species ranged from 0.06±0.02 mg/kg for Cd in *Brycinus intermidus* to 187.90±89.59 mg/kg for Fe in *Parachanna obscura.* The Bioaccumulation Quotient (BQ) values ranged from 4.51 mg/kg for Pb in *Hemichromis bimaculatus* to 1297.13 mg/kg for Fe in *Phractolemus ansorgei.* These results imply that continuous intake of fish and water obtained from this river would have cumulative deleterious effect on aquatic organisms and man.

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Keywords: Heavy metals; fish; water; bioaccumulation quotient; health risks; Orogodo River; Nigeria.

1. INTRODUCTION

Threats from pollutants in water supplies are under the spotlight owing to the associated adverse effects of the pollutants on hydrobionts and aquatic habitat integrity [1]. Heavy metals are toxic as they are persistent, non-biodegradable and readily accumulate in water, soil, bottom sediments and living organisms. Currently, there is an increasing ecological and global public health concern associated with environmental contamination by heavy metals. Heavy metals are ubiquitous and chemically stable, so they can be expected to be present in all parts of the biotic and abiotic matter. Heavy metals may be directly absorbed by organisms but are also transferred from lower to higher trophic levels of the food chain. The high accumulation of heavy metals in these components can result in serious ecological changes.

Also, human exposure to heavy metals has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications [2].

Heavy metal pollution affects aquatic ecosystem integrity as metals tend to be accumulative in the trophic food webs with apex predators like crocodiles [3] and human beings at health risk [4] Severity of the exposure risks derives from the persistent and accumulative nature of the metal species in the water phase [5,6]. As well, the contributions of the point and non-point sources of metal pollution determines their concentrations in a water body [7]. For the Agbor State in Nigeria, major anthropogenic sources of heavy metal pollution are mining and smelting activities, atmospheric deposition, disposal of untreated/ partially treated urban and industrial effluents, metal chelates from different industries, and haphazard use of heavy metal-containing fertilizers and pesticides during agricultural activities [8,9].

Regardless, heavy metals are some of the major contaminating agents in our food supply [8,10,4]. Fish absorb heavy metals from the surrounding water through a number of pathways though (not exclusive) for most species the gills are the primary route for the uptake of water borne pollutants [11,12,13,14]. The communities through which the Orogodo River transverses are predominantly engaged in agricultural activities which are heavily reliant on inorganic fertilisers, thus the river is subject to dumping of deleterious agricultural wastes. The Orogodo River also serves as the drainage point for all run off wastewater produced industrially or domestically within the Agbor metropolis and beyond. Because a majority of the drainage channels constructed by the State and Local Government within the Agbor metropolis and surrounding villages, aimed at controlling flooding and checking erosion are channelled directly into the river at various points along the river length.

Despite that most Agbor State community members diversify into fishing in the Orogodo River as an alternative livelihood, and to sustain and supplement their nutritional requirements especially in the off agricultural season. Fish forms part of their meal intake, however, humans may be at risk due to metal contamination in fish tissues and water derived from catchment pollution. Thus, it is imperative to assess metal pollution in the water phase and the different fish species utilised by the communities along the Orogodo River. It is prudent as well to estimate the health risks posed by exposure to river water and consumption of fish therein. This study aimed to determine the concentrations of heavy metal (Pb, Cd, Cu, Fe and Zn) in water and selected fish species in the Orogodo River in Agbor located in the Delta state in Nigeria. The underlying objective was to estimate the health risks posed by exposure water and consumption of fish from the river.

2. MATERIALS AND METHODS

2.1 Study Area

The study was conducted along Orogodo River which is located within Latitude 5°43'N and 5°30'N and Longitude 6°20'E and 6°12'E (Fig. 1). The geology of the area is mainly of the recent tertiary sedimentary sand stone. The climate of the study area exhibits the characteristics of a sub equatorial climate with an annual mean air temperature of 27°C [9]. The rainfall pattern is that of double peaks or maximal with mean annual rainfall of 2,225 mm; while the mean relative humidity is 81%, and the soil type is red-yellow ferrasols [15]. The rainy season is brought about by the South-West Trade Wind blowing across the Atlantic Ocean, while the dry, dusty, and often cold North-East Trade Wind blowing across the Sahara desert dominates the dry season with a short spell of Harmattan [16]. The River has its source at Mbiri village at an elevation of 150 m above sea level. It meanders and flows through Agbor and Abavo communities, both in Ika South Local Government Area to Obazagbon-Nugu and Evboesi both in Orhionmwon Local Government Area, Edo State and finally empties into a swamp near Abraka in Delta state [17]. Three sampling stations were established along the stretch of the river at Mbiri (6.30° N, 6.27°E) , Agbor (6.25° N, 6.20° E) and Obazagbon (6.20°N, 6.40°E) with the most upstream study site at station one (Mbiri) and the most downstream at station three (Obazagbon). The three sites were chosen so as to adequately reflect and capture the pollution across the different land use patterns available in the study area.

2.2 Sample Collection

Fish species were caught by the local fishermen using gill nets. The fish samples were then ice-packed and transported to the laboratory where they were identified using literature (key) as provided by Idodo Umeh (2003) and photographed using a digital camera (8.0 Megapixels). Water samples were collected once monthly using 1 L capacity plastic bottle with screw cap at a depth of 0-0.5 m at each sampling station. The study was carried out from November 2015 - April 2016.

2.3 Digestion and Analysis

The acid digestion process used for both the water and fish is a strong digestion method and was chosen so that the total metal content could be estimated. The water sample was aspirated into a flame and atomised. Metals in the sediments were also analysed using FAAS, after acid digestion to extract the metals from the sediments. This procedure consisted of two parts. (1) Digestion: the sediments were oven-dried at 75°C in an analytical oven (DHG-9023A) until constant weight was attained. Then 5 ml nitric acid and 2 ml perchloric acid were added to 1 g of the oven-dried sample. The mixture was heated on a hot plate until fumes were produced and allowed to cool to room temperature. (2) Acidification: 5 ml of 50% hydrochloric acid was added to the mixture from the first digestion. The acidified mixture was heated until boiling and then was cooled to room temperature. The acidified mixture was filtered and distilled water was added to the filtrate in a volumetric flask up to the 100 ml mark. Fish digest and water samples were analyzed for Cu, Zn, Fe, Cd and Pb by means of an Atomic Absorption Spectrophotometer AAS (PG Instruments AA-500F series, Leicestershire,United Kingdom) equipped with solar software using air acetylene flame and also with lamp with Ultraviolet wavelength changed at intervals for the analysis of each metal [18].

2.4 Quality Control

Quality control was assured by the use of procedural blanks and standards. In each case a known concentration of the standard solution was assayed after every 10 samples to verify the analytical quality of the result because there was no standard reference material available. In all the cases for water and fish, a preparation/reagent blank was prepared for every 20 samples and all the concentrations were below the detection limits. Each sample was analysed in triplicate for repeatability with a relative SD < 5% for all metals analysed. Concentrations of Cu, Zn, Fe, Cd and Pb were then determined using AAS (Cu, Pb, Zn, Cd, Fe, Ni and Cr in liver, gills, kidney and muscle were then determined using FAAS [18]. The concentration of heavy metals in water was expressed in mg/l, while concentration values in digested fish samples were expressed in mg/kg.

2.5 Calculation of Bioaccumulation Quotient (BQ) for Heavy Metals

This expresses the ability of fish to accumulate heavy metals above environmental concentrations [19].

$$BQ = \frac{Heavy\ metal\ concentration\ in\ fish\ (mg/kg)}{Heavy\ metal\ concentration\ in\ water\ (mg/l)}$$

A BQ value >1 indicates bioaccumulation of a heavy metal by fish.

2.6 Statistical Analysis

Data generated from the study were analyzed using GENSTAT computer software (Version 12.1 for Windows). One-way analysis of variance (ANOVA) was used to test for significant differences between mean values of metals at 5% level of probability. New Duncan multiple range test was used to separate significant means.

3. RESULTS

3.1 Heavy Metals in Water

Mean concentration of Pb in water ranged from Non-Detectable, 0 mg/l in November to 0.03 mg/l in January while a mean Pb concentration of 0.013 mg/l was recorded for the study period. Station one recorded the highest concentration of Pb in water (0.20 mg/l) while the least Pb concentration was observed in station three (0.008 mg/l). Cadmium concentration in water during the study ranged from ND, 0 mg/l in November, December, and February to 0.07 mg/l in January while station three recorded the highest Pb concentration in water (0.008 mg/l). Mean concentration of Cu recorded during the study ranked highest in November, March and April (0.04 mg/l) while the least concentration was recorded in January (0.01 mg/l). The mean concentration of Zn in water ranged from 0.04 mg/l in January to 0.17 mg/l in December while a mean concentration of 0.08 mg/l was recorded during the study. Station three recorded the highest mean concentration of Zn (0.095 mg/l) while the least concentration was observed in station two (0.077 mg/l). The mean concentration of Fe in the sampled stations varied between 0.122 mg/l for station two to 0.195 mg/l in station three while the mean concentration of 0.15 mg/l was observed during the study. There were no significant differences ($p>0.05$) in the mean concentration of Pb, Cd, Cu, Zn and Fe in water between the sampled stations. Significant differences ($p<0.05$) were observed in the mean concentration of Cd, Cu and Fe in water between the sampled months while no significant differences were observed in the mean concentration of Pb and Zn between sampled months. Overall, the concentrations of Pb and Cd surpassed the WHO and most probably the local effluent standards (Table 2).

3.2 Heavy Metals in Fish

The mean concentration of Pb in fish during the study ranged from 0.60 mg/kg in November to 2.68mg/kg in March (Table 3), while a mean concentration of 1.82 mg/kg was observed during the study. Mean concentration of Pb in fish species ranged from 0.06 mg/kg in *H. fasciatus* to 2.76 mg/kg in *P. ansorgei*. The mean concentration of Cd in fish during the study ranged from 0.03 mg/kg in December to 0.47 mg/kg in January while mean concentration of Cd in fish species ranged from 0.06 mg/kg in *B. intermidus* to 0.615 mg/kg in *P. obscura*. The mean concentration of Cu in fish during the study ranged from 1.97 mg/kg in November to 10.57 mg/kg in April while mean concentration of 6.71 mg/kg was recorded during the study. Mean concentration of Cu in fish species ranged from 1.34 mg/kg in *C. kingsleyea* to 10.07 mg/kg in *P. ansorgei*. The mean concentration of Fe in fish during the study ranged from 3.5 mg/kg in November to 286.1 mg/kg in December while a mean concentration of 129.72 mg/kg was observed during the study (Table 3). Mean concentration of Fe in fish species ranged from 5.70 mg/kg in *C. kingsleyea* to 274.15 mg/kg in *P. ansorgei*. The mean concentration of Zn in fish during the study ranged from 22.96 mg/kg in February to 82.30 mg/kg in January while mean concentration of 61.62 mg/kg was recorded for the study. Mean concentration of Zn in fish species ranged from 14.08 mg/kg in *H. bimaculatus* to 91.62 mg/kg in *P. obscura*. No significant difference was observed in the mean concentration of Cd in all fish species sampled between months. Significant differences were observed in the mean concentration of Pb, Cu, Zn and Fe in all fish species caught during the study except *Ctenopoma kingsleyea* between months. Significant differences were observed in mean concentration of Cd, Cu, Zn and Fe between months while no significant difference was recorded in the mean concentration of Pb between months.

Pb, Zn and Fe surpassed the FAO tissue level thresholds and most probably the local thresholds, and this is more significant for human health.

3.3 Bioaccumulation Quotient (BQ) Values for Chemical Elements

The BQ values ranged from 4.51 for Pb in *H. bimaculatus* to 1297.13 for Fe in *P. ansorgei*.

4. DISCUSSION

4.1 Heavy Metals in Water

Mean concentration of Pb ranked highest in Mbiri as compared to other stations; however, the mean concentration observed in this station was no significantly higher than what was observed in other two stations. The higher concentration of Pb at Mbiri (site one), which is located in the upstream reaches of the Orogodo River may have been due to the numerous anthropogenic activities occurring at this water front (washing of cars and motor bikes). Washbay effluent is toxic and impacts downstream sites [20], though it has scarcely received attention in pollution studies in Nigeria. We observed relatively higher concentrations of Cd, Zn and Fe in water sampled at site 3, Obazagbon. This site is the lowest downstream point in this study, thus, it tends to collect sewage effluent released from upstream activities. Moreso, there is an immediate open sewage channel which discharge close to the site hence this could explain the high concentrations of Cd, Fe and Zn recorded. Open dumping of market waste is rife at this site such that metal laden leachate could be enriching the concentrations of Cd, Zn and Pb. There was a significant temporal variation in the concentrations of Cd, Cu, Fe, Pb and Zn, with markedly higher concentrations observed in the dry months of November, December, January, February and March. This may have been due to reduced water volume owing to higher temperatures and increased evaporation during the dry season [21]. There were significant spatial differences in metal concentrations in water regardless of the season. This is attributable to different spatial anthropogenic activities, and geogenic backgrounds of the three sites. Such that any metal pollution redress and habitat rehabilitation program should consider site specific hydrodynamics, morphometrics and hydraulics [22].

In this study, it was observed that the concentration of Zn, Cu and Fe in water were lower than the maximum recommended limit while the level of Pb and Cd was higher than the values recommended by [23] and [24]. The elements Pb and Cd are more toxic and persistent, and thus our finding points to the need for urgent redress to minimize their effects and risks on human health in the Orogodo River. Though, the concentrations of trace elements Zn, Cu and Fe are lower than the WHO thresholds, it is prudent to institute long term monitoring action as they are toxic at elevated levels [4].

4.2 Heavy Metals in Fish

Aquatic animals (including fish) bioaccumulate trace metals in considerable amounts metals and store it over a long period of time in the bone, liver and gills as a result of their different physiological roles [14]. The high accumulation of heavy metals in these components can result in serious ecological changes. One of the most serious results of the persistence of these metals is their biological amplification in the food chain. In this study, the mean levels of Cd, Fe, Pb and Zn in fish ranked higher during the dry season months (November, December, January, February and March) as compared to the rainy season month (April). Similar trend was also observed by [25] in *Erpetoichthys calabaricus* obtained from Ogba River, Edo State. They attributed the trend to increased evaporation during the dry season. The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to metabolize the metals and the concentration of such metal in the river. The bioaccumulation of heavy metals varied between species, ages, sex and organs. In general, the target tissues of heavy metals are metabolic active ones which accumulate high levels of metal in fish such as liver and gills, whereas in muscles where the metabolic activity is relatively low accumulates less level of heavy metals [13]. In this study, higher level of Pb and Cu were recorded in *P. ansorgei* as compared to other fish species while *P. obscura* had higher concentration of Cd, Zn and Fe as compared to other fish species. It was observed that the concentration of Pb, Cd, Zn and Fe in fish obtained during the study were higher than the values recommended by [26] and [24] while the concentration of Cu was lower than the recommended values by the aforementioned bodies (FAO and WHO).

4.3 Bioaccumulation Quotient (BQ)

The Bioaccumulation Quotient of the metals in all the species investigated was greater than 1 thus indicating that there was bioaccumulation of all the metals in this study, however, the highest BQ value was observed for Fe in *P. ansorgei*. The high BQ observed in Fe may have been due to the high concentration observed in water. [27] asserted that heavy metal concentration in aquatic fauna is often proportional to the levels in the aquatic environment in which the fauna resides. The variations in the BQ value observed in the fish species may have resulted from variations in feeding habits or age of the fish species. [28] observed a lower concentration of heavy metals in pelagic fishes than those of benthic fishes. However, the BQ for Cu, Zn and Pb recorded in this study were higher than values observed by [29] for Cu (1.06), Zn (50.13) and Pb (1.55) in *Crossostrea gasar*.

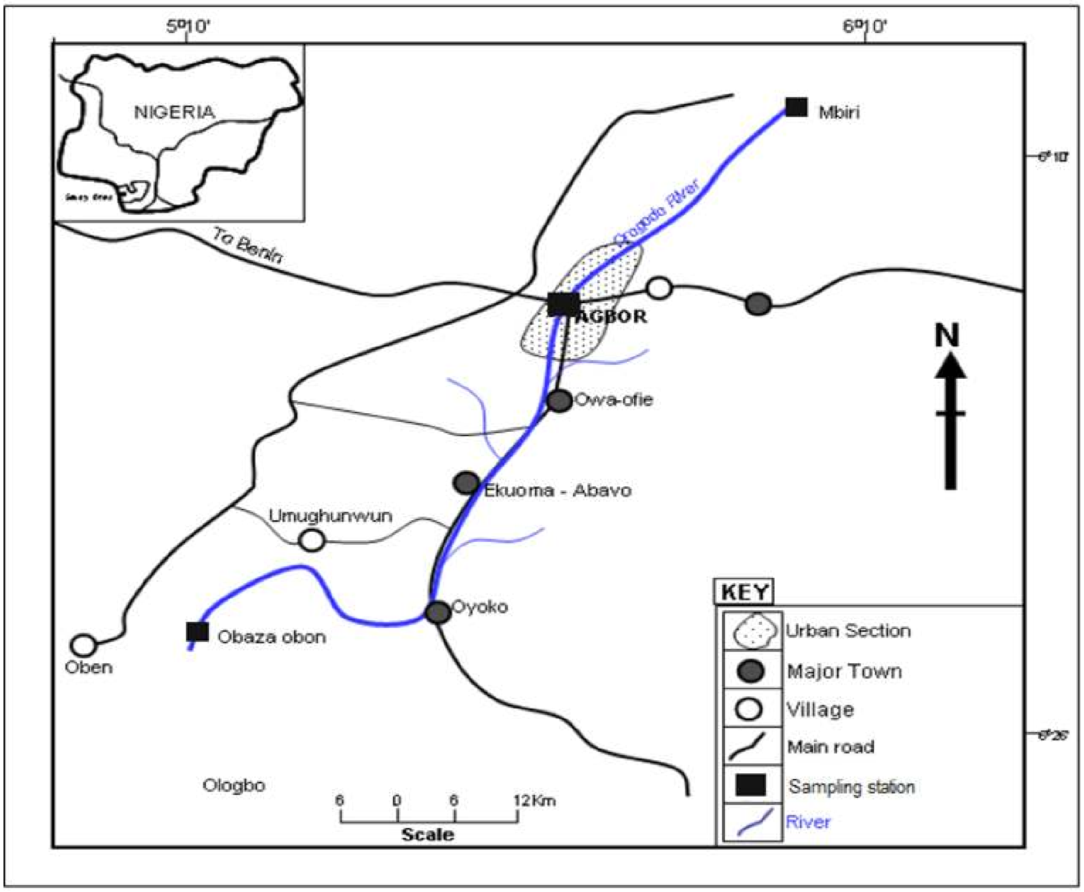

Fig. 1. Map of study area showing sampling stations
Source: [30]

Table 1. Mean (± SD) concentration of heavy metals (mg/l) in water obtained from the sampling stations

Stations	Pb	Cd	Cu	Zn	Fe
Mbiri	0.020^{a}±0.008	0.003^{a}±0.001	0.025^{a}±0.018	0.079^{a}±0.052	0.133^{a}±0.062
Agbor	0.012^{a}±0.009	0.005^{a}±0.002	0.035^{a}±0.021	0.077^{a}±0.054	0.122^{a}±0.014
Obazagbon	0.008^{a}±0.004	0.008^{a}±0.003	0.030^{a}±0.025	0.095^{a}±0.045	0.195^{a}±0.101

Table 2. Mean (± SD) concentration of heavy metals (mg/l) in water during the study period

Months	Pb	Cd	Cu	Zn	Fe
November	0^{a}±0	0^{a}±0	0.04^{bcd}±0.02	0.08^{a}±0.05	0.04^{a}±0.02
December	0.02^{a}±0.01	0^{a}±0	0.03^{bc}±0.02	0.17^{b}±0.12	0.35^{b}±0.29
January	0.03^{a}±0.02	0.07^{ab}±0.02	0.01^{a}±0.01	0.04^{a}±0.03	0.16^{a}±0.09
February	0.01^{a}±0.01	0^{a}±0	0.02^{ab}±0.02	0.07^{a}±0.04	0.10^{a}±0.06
March	0.01^{a}±0.01	0.01^{b}±0.01	0.04^{d}±0.02	0.06^{a}±0.04	0.11^{a}±0.08
April	0.01^{a}±0.01	0.01^{b}±0.01	0.04^{cd}±0.01	0.08^{a}±0.03	0.14^{a}±0.08
WHO threshold	0.01	0.01	2.00	3.0	0.3
SON threshold	0.01	0.01	1	3	0.3

Table 3. Mean (±SD) concentration of heavy metals (mg/kg) in fish during the study period

Months	Pb	Cd	Cu	Zn	Fe
November	0.60^{a}±0.47	0.18^{a}±0.10	1.97^{a}±1.33	48.97^{ab}±22.12	3.5^{a}±1.2
December	2.31^{a}±1.98	0.03^{a}±0.01	3.73^{ab}±2.98	70.34^{b}±35.21	286.1^{d}±123.2
January	2.40^{ab}±2.13	0.47^{a}±0.38	6.56^{abc}±4.32	82.30^{b}±54.32	100.3^{abc}±89.1
February	0.71^{a}±0.58	0.12^{a}±0.15	6.86^{bc}±3.25	22.96^{a}±15.41	22.0^{ab}±12.8
March	2.68^{b}±1.97	0.26^{a}±0.22	10.56^{c}±4.67	73.06^{b}±34.67	179.6^{bcd}±119.3
April	2.21^{ab}±2.01	0.25^{a}±0.19	10.57^{c}±3.27	72.06^{b}±43.21	186.8^{cd}±101.8
FAO threshold	0.5	0.5	30	30	100

Table 4. Heavy metals (Mean ± SD) in fish species obtained for the period November-April

Fish species	Pb	Cd	Cu	Zn	Fe
Clarias gariepinus	1.87^{ab}±0.54	0.195^{a}±0.071	7.97^{de}±3.42	52.61^{b}±32.13	125.03^{ab}±78.92
Brycinus intermidus	0.57^{a}±0.23	0.060^{a}±0.010	4.00^{b}±1.85	77.08^{c}±34.10	60.20^{a}±26.51
Parachanna obscura	2.60^{b}±1.23	0.615^{b}±0.235	6.97^{cd} ±2.34	91.62^{c}±54.21	187.90^{bc}±89.59
Phractolemus ansorgei	2.76^{b}±1.76	0.100^{a}±0.081	10.07^{e}±6.78	71.09^{bc}±44.32	274.15^{c}±67.87
Ctenopoma kingsleyae	0.29^{a}±0.11	0.230^{a}±0.120	1.34^{a}±0.89	28.30^{a}±12.35	5.70^{a}±2.31
Hemichromis bimaculatus	0.06^{a}±0.02	0.150^{a}±0.090	5.11^{bc}±3.21	14.08^{a}±6.87	11.0^{a}±4.53
FAO threshold	0.5	0.5	30	30	100

Table 5. Bioaccumulation quotient (BQ) in fish species obtained for the period November-April

Fish species	*C. gariepinus*	*B. intermidus*	*P. obscura*	*P. ansorgei*	*C. kingsleyea*	*H. bimaculatus*
Pb	140.60	42.57	195.49	207.52	21.80	4.51
Cd	34.82	10.71	109.82	17.86	47.06	26.79
Cu	265.67	133.33	232.33	334.67	44.67	170.33
Zn	630.82	924.22	1098.56	852.40	339.33	168.82
Fe	833.33	401.33	1252.67	1297.13	38.00	73.33

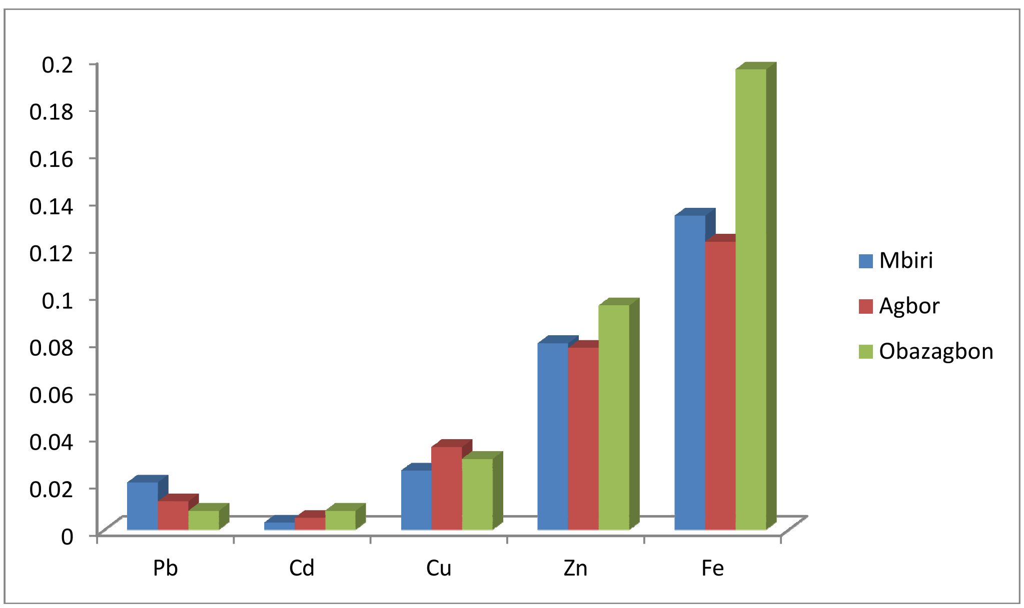

Fig. 2. Heavy metal in water obtained from the sampling stations

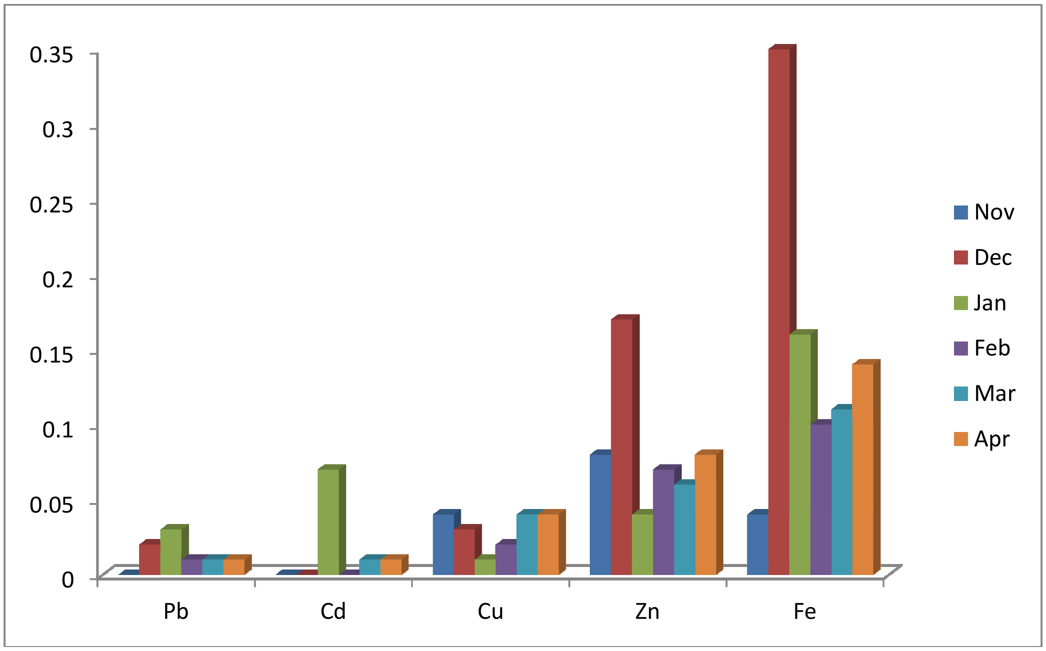

Fig. 3. Heavy metals in water during the study

5. CONCLUSION

The study show that the concentration of Zn, Cu and Fe in water were lower than the maximum recommended limit while the concentration of Pb and Cd was higher than the values recommended by [23] and [24]. Also, the concentration of Pb, Cd, Zn and Fe were higher than the values recommended by [26] and [24] while the concentration of Cu was lower than the recommended values by the aforementioned bodies. The concentration of these heavy metals in the fish and water thus indicate that it will have cumulative deleterious effect on any aquatic organism and man who feeds on the fish and use the water. Thus it is recommended for proper waste water treatment and possibly it may be channeled from drainages into farmlands for irrigation purposes. At a local scale there is need for carrying out massive awareness campaign on the environmental hazards of improper refuse disposal through the various forms of media. This will help in enlightening the public on their individual roles as regarding wastewater generation and constituents.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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