



## Heavy Metals Concentration in Sediment and Fish Samples from Owena Multi-Purpose Dam, Ondo State, Southern Nigeria

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### Authors' contributions

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

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### ABSTRACT

Sediment samples taken from eight locations within the Owena Multi-purpose Dam in six sampling campaigns, covering the wet and dry seasons were analyzed for Pb, Cd, Cu, Cr, Ni, Fe, Mn and Zn using the atomic absorption spectroscopic method. Samples of three fish species: *Clarias gariepinus*, *Clarias anguillaris* and *Oreochromis niloticus* collected from the dam were also analysed for the above metals concentration. Results of heavy metals determination revealed significant seasonal variation ( $P = .05$ ) in most measured parameters, while spatial variation was not significant. Generally, the results indicate that the measured parameters of the dam sediment were far lower than the Probable Effect Concentrations (PEC). Also, all metals monitored were detected in all the fish samples except cadmium that was not detected in the trunk of *Oreochromis niloticus*. They, however, showed values that were within the acceptable International Standards in fish for human consumption and so, could not presently cause any health hazard. The present study has produced vital information about the current status of the dam, which would also serve as a baseline for future monitoring of the dam.

**Keywords:** Sediment; heavy metals; Owena multi-purpose dam; fish; coefficient of variation.

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## 1. INTRODUCTION

The existing Owena Water Supply Scheme, completed as far back as 1960 has a design capacity to supply 10 million litres of water to Akure and other towns and villages in the present Ondo States.

The dam site is located along the Owena River at Igbaraoke (Fig. 1), about 14Km upstream from the Ondo-Akure Road. It was designed to create an impoundment of 120 million cubic metres gross capacity; to cover an area of approximately 16 sq Km at the normal water level. The design was reviewed to include usage for irrigation of 3,000 ha, as well as generation of hydro-electric power of 10MW capacity. In addition, fishing activity is currently going on there [1].

The degradation of dam water may depend on a combination of natural landscape features, such as geology, topography, sediment/ soils, climate and atmospheric contributions and human activities related to different land uses and land management practices [2].

The availability and quality of water are key factors in determining the state of public health, food production and other important aspects of the quality of life.

Contamination of water supplies by inorganic substances including metals present in water in excess of their limits can cause some cosmetic effect or even make the dam water unsafe for drinking[3,4] and the fishes unsafe for consumption.

These metals are washed into water bodies and may be persistent in the environment, accumulate in aquatic biomass; they are concentrated and passed up in food chain to human consumers. This explains the reason humans at the top of food chain, are particularly vulnerable to the effects of non-degradable pollutants [5]. Research also revealed that many chemical pollutants (trace metals) mimic sex hormones and interfere with human body's reproductive and developmental functions [6].

The data obtained were statistical tested for significance in seasonal variation and to establish the interplay of common contaminants in the various matrices. One level of significance ( $P=0.05$ ) was considered in the results interpretation. Bar charts were also used in comparing analyte concentrations and their interplay in the various matrices. The analytical results were also compared with local and international standards where applicable. Since comprehensive data on the various sources, characters and amount of wastes entering the Owena dam is not available, knowledge of the heavy metal concentration in the sediments and fish could give vital information regarding their sources, distribution, and degree of pollution, hence the result obtained in this study will serve as a base line data for future monitoring of the pollution status of the dam.

## 2. MATERIALS AND METHODS

### 2.1 Study Area

The study area is the Owena Multipurpose Dam located at Km10, off Akure-Ilesha Road, Igbara-Oke in Ifedore Local Government Area of Ondo State, Nigeria (Fig. 1). The dam is supplied with water from the Owena River and it covers an appropriate surface area of 7.8Km<sup>2</sup>. Currently, the water from the dam is to feed the 60,000 m<sup>3</sup>/day capacity Water

Treatment Plant built beside the dam, Moreover, fishing activities by registered local fishermen are also taking place within the dam.

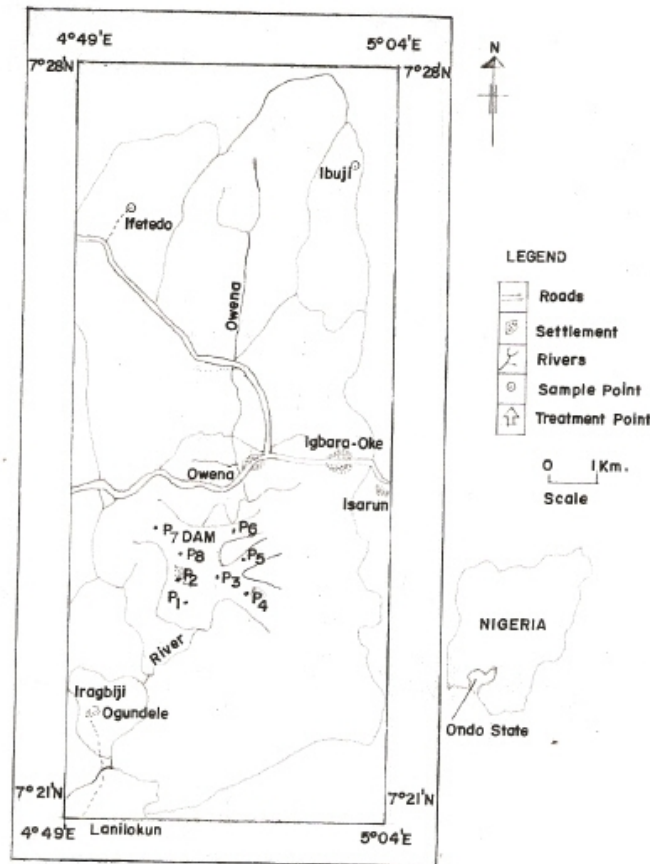


FIG. 1-0: MAP SHOWING OWENA RIVER, MULTIPURPOSE DAM AND THE SAMPLING POINTS.

## 2.2 Sampling and Sample Analysis

Grab sediment samples from the dam lake were collected with the aid of depth samplers from eight randomly selected locations (Fig. 1) in six sampling campaigns between December 2009 and October 2010, covering both the dry and wet seasons. Collected samples were allowed to drain and put in pre-cleaned polythene bags for heavy metals analyses. The samples were air dried ground and sieved in the laboratory before analysis. Live samples of three species of fish, *Clarias gariepinus* (Cattfish), *Clarias anguillaris* (Mudfish) and *Oreochromis niloticus* (*Tilapia* spp), were obtained from the sampling site of the dam with the assistance of local fishermen. The samples were transported live to the laboratory, where they were killed by asphyxiation, weighed and scales removed from *Oreochromis niloticus* and they were washed with distilled water. Their intestines were later removed, and each fish separated into two parts, the head and the trunk and these were further washed with distilled water and the water allowed drying between two pieces of filter paper [7,8]. The samples were kept in the freezer prior analysis.

Extraction of metals from the sediment samples was by mixed acid digestion [9,10]. The digestion was carried out with 20 ml of a mixture of conc.  $\text{HClO}_4$  and  $\text{HNO}_3$  at a 2:1 ratio (v/v) on a hot plate and the mixture heated to almost dryness. 20 ml of 0.5 M  $\text{HNO}_3$  were added and the solution filtered into 50 ml volumetric flask through Whatman No 42 filter paper. The filtrate obtained was made up to 50 ml mark with distilled water and used for heavy metals determination against those of the blank and calibration standards using Atomic absorption spectrophotometer, Buck Scientific model. Heavy metal concentrations in fish samples were determined having digested the samples in accordance with the standard procedure established by USEPA [4]. Homogenized fish trunk and head were separately prepared by first of all chopping with a stainless steel knife on a wooden board and blended in a food blender. 5 g of each homogenized samples were weighed into a 200 ml Kjeldahl digestion flask and digested with 20 ml of mixed concentrated nitric acid and 62% perchloric acid (ratio 2:1 v/v) on a heater. This was continued for 20 minutes after the disappearance of brown fumes of  $\text{NO}_2$ . Small quantity of distilled water was added and the solution was left to cool down after which it was filtered into a 50 ml volumetric flask and solution made to the mark. A blank made of distilled water was carried through the same treatment as the samples. The concentrations of metals in each sample were determined against those of the blank and standard solutions using Buck scientific AAS.

### 3. RESULTS AND DISCUSSION

#### 3.1 Heavy Metal Levels in the Dam Sediment

The mean results of heavy metals analyzed in sediment samples taken from eight sampling locations are presented in Tables 1(a) and 1(b) for the dry and wet seasons respectively. Some specific physico-chemical characteristics, such as sediment particle size, pH and organic carbon content, which are known to influence the interactions and dynamics of metals within the sediment matrix, were also presented.

**Table 1(a). Mean\* physico-chemical parameters and heavy metal concentrations (mg/kg) in dam sediment (Dry season)**

Parameter	DS-1	DS-2	DS-3	DS-4	DS-5	DS-6	DS-7	DS-8
pH	5.11	4.85	4.89	5.06	4.95	4.77	4.87	5.13
TOC (%)	0.60	0.59	0.62	0.64	0.61	0.64	0.54	0.57
Sand (%)	66.35	63.68	58.35	63.01	52.68	62.35	64.01	64.35
Clay (%)	25.65	23.65	27.65	28.32	27.65	23.65	21.65	21.65
Silt (%)	8.00	12.67	14.00	8.67	19.67	14.00	13.00	14.00
Cd	0.22	0.25	0.23	0.18	0.26	0.26	0.19	0.21
Cu	3.91	4.76	3.98	4.28	3.57	3.64	3.18	4.29
Cr	0.37	0.41	0.34	0.31	0.37	0.49	0.29	0.36
Ni	2.46	1.96	2.06	2.00	2.06	2.01	2.01	2.02
Fe	73.34	76.81	72.67	75.17	75.3	75.3	75.99	72.63
Mn	9.45	9.17	8.92	9.14	8.54	9.39	8.71	8.93
Pb	0.18	0.18	0.14	0.15	0.18	0.18	0.17	0.19
Zn	2.10	2.12	2.13	2.03	2.22	1.84	2.19	2.17

Data are replicate of 3; ND = Not detected; \*Values in mg/kg dry weight.

**Table 1(b). Mean\* physico-chemical parameters and heavy metal concentrations (mg/kg) in river sediment (Wet season)**

Parameter	DS-1	DS-2	DS-3	DS-4	DS-5	DS-6	DS-7	DS-8
pH	4.83	4.57	4.63	4.95	4.97	4.62	4.39	5.00
TOC (%)	0.87	0.83	1.00	0.88	0.79	0.94	0.96	0.81
Sand (%)	65.35	62.01	56.68	63.07	53.35	60.01	63.01	62.68
Clay (%)	24.32	24.32	28.65	24.65	27.65	24.32	22.99	20.32
Silt (%)	10.33	13.67	15.00	12.33	19.00	15.67	14.00	17.00
Cd	0.25	0.24	0.18	0.18	0.26	0.24	0.18	0.18
Cu	2.97	4.05	3.19	2.51	2.65	3.09	2.76	3.50
Cr	0.36	0.34	0.29	0.30	0.40	0.32	0.36	0.37
Ni	2.07	1.92	1.99	1.89	1.74	2.02	1.92	1.95
Fe	65.07	67.36	65.97	61.84	65.5	62.78	67.74	59.32
Mn	8.39	8.64	8.21	8.29	7.90	8.97	9.41	9.04
Pb	0.18	0.15	0.19	0.16	0.18	0.19	0.19	0.19
Zn	1.80	1.84	2.05	2.00	1.87	1.87	1.48	1.36

Data are replicate of 3; ND = Not detected; \*Values in mg/kg dry weight.

Table 2 shows the statistical data on the measured parameters, while Table 3 compares the heavy metal levels (mg/kg, dry weight) in dam sediment in the present study (Owena dam), with past studies on Ureje and Kainji dams. Comparative study of the results for dry and wet seasons revealed high significant difference ( $P = .05$ ) in sand, silt, pH, TOC, Cu, Ni, Fe, Mn, and Zn levels, while significant variation among sampling periods was recorded in Pb and Cd as revealed by the high coefficient of variation. Higher values for sand content were measured during the dry season over the wet season, while reverse was the case for silt content. The clay content maintained a more or less similar concentration for both seasons. The trend in the sand and silt content is attributable to the effects of run-off on the water body upstream in which more silts are eroded into water bodies compared to sand. The Owena river that feeds the dam, transverses through Owena town, hence exposing the river to more influx of run-off. Also observed from the calculated co-efficient of variation, was the different levels of variability in metal concentrations among the sampling locations which ranged between 10.48% in Ni and 35.00% in Cr. Except Pb, the variation in each of the metals in the sediment from one sampling point to the other are not as critical as their corresponding water samples.

The pH was within the acidic range of 4.39 - 5.13, which is peculiar to Nigerian soil/sediment [10,11]. The low pH condition affects metal speciation and may enhance metals' solubility and possible leaching into the water column. High soil or sediment acidity has been attributed to combination of possible oxidation of pyrite ( $\text{FeS}_2$ ) to produce sulphuric acid, depleted calcium level or increased aluminum concentration in soil/sediment [12,13]. The total organic carbon determined in the sediment samples ranged from 0.54 - 1.00%, while the sand, clay and silt levels were between 52.68 - 66.35%, 20.32 - 28.65% and 8.00 - 19.67 respectively. Clay and organic carbon/matter directly influence the other physical and chemical soil/sediment characteristics including reserve of exchange bases and the interaction and dynamics of trace metals, hence, maximum soil/sediment capacity for heavy metals are adjusted according to these macro-nutrients [9]. Concentrations of most metals investigated in Owena dam were higher than those reported for Ureje dam but were generally lower when compared to Kainji dam (Table 8) [14,15]. However, similar trend in some heavy metal loads was observed. Iron and Manganese were consistently found to be

most abundant in the sediment of the Owena dam. Similar observation was recorded for iron and manganese in Ureje dam [14], while these parameters were not determined in Kainji dam [15]. The high loads of iron and manganese in the sediment have no identifiable point source discharge rather than lithological or crustal origin. Manganese is one of the most abundant metals in the Earth's crust, usually occurring with iron [3]. Iron and manganese have been known to be commonly high in Nigerian soils. The pattern of distribution of these metals might suggest that the levels of heavy metals in the sediments are mainly lithological with possibly mild contribution from anthropogenic influences. Although comprehensive data on the various sources, characters and amount of wastes entering the Owena dam are not available, knowledge of the heavy metal concentration in the sediments could give vital information regarding their sources, distribution, and degree of pollution, since sedimentation is one of the most important fluxes in aquatic system [14]. The pattern of distribution of the heavy metals in the dam sediments suggests major contribution from natural source.

**Table 2. Statistical analysis of physico-chemical parameters and heavy metal concentrations in dam sediment (dry and wet seasons' means)**

Parameter	Range	O. Mean	Std. dev	CV (%)	T cal
pH	4.39 - 5.13	4.68	0.29	6.20	3.56*
TOC (%)	0.54 - 1.00	0.79	0.24	13.38	-5.78*
Sand (%)	52.68 - 66.35	59.43	1.89	3.18	2.81*
Clay (%)	20.32 - 28.65	24.49	2.97	12.13	0.55
Silt (%)	8.00 - 19.67	14.02	2.10	14.98	-3.79*
Cd	0.18 - 0.26	0.23	0.06	18.70	0.89
Cu	2.51 - 4.76	3.67	0.97	26.43	4.99*
Cr	0.29 - 0.49	0.40	0.14	35.00	0.60
Ni	1.74 - 2.46	2.10	0.22	10.48	2.97*
Fe	58.32 - 76.81	68.57	8.34	12.16	5.11*
Mn	7.90 - 9.45	8.68	0.93	10.71	2.23*
Pb	0.14 - 0.19	0.17	0.03	17.65	-1.43
Zn	1.36 - 2.22	1.96	0.41	20.92	3.78*

O. Mean = Overall mean; CV = Coefficient of variation; SD = Standard deviation  
T cal = t values calculated for test of sig. difference between dry and wet season  
\*Significant at  $p = .05$

**Table 3. Comparison of heavy metal levels (mg/kg, dry weight) in sediment of the Owena dam, Ureje dam in Ado-Ekiti and Kainji dam**

Metal	Present study	Ureje dam <sup>a</sup>	Kainji dam <sup>b</sup>
Zn	1.36-2.22	5.23	42.00
Mn	7.90-9.45	1.20	—
Cu	2.51-4.76	1.70	24.00
Fe	58.32-76.81	7.64	—
Ni	1.74-2.46	ND	—
Cd	0.18-0.26	2.02	—
Co	—	0.01	0.05
Cr	0.29-0.49	ND	15.00
Pb	0.14-0.19	1.02	16.00

Sources: <sup>a</sup>Adefemi et al. (2004); <sup>b</sup>Lateef (2005)

**Table 4. Heavy metal levels in *Clarias gariepinus* (mg/kg wet weight)**

Weight (g)		Pb	Cd	Cu	Cr	Ni	Fe	Mn	Zn
55.35	Head	2.34	0.32	1.40	3.58	1.35	39.16	6.17	3.88
	Trunk	1.41	0.14	1.00	1.71	1.41	21.00	4.83	1.93
	Mean*	1.88	0.23	1.20	2.65	1.38	30.00	5.50	2.91
52.89	Head	1.89	0.27	1.30	3.37	2.35	40.01	6.14	3.24
	Trunk	1.06	0.11	0.72	1.94	0.84	28.97	3.70	1.96
	Mean*	1.48	0.19	1.01	2.67	1.60	34.49	4.92	2.60
	Range	1.48-	0.19-	1.01-	2.65-	1.38-	30.00-	4.92-	2.60-
		1.88	0.23	1.20	2.67	1.60	34.49	5.50	2.91
	Overall. mean*	1.68	0.21	1.11	2.66	1.49	32.25	5.21	2.76

**Table 5. Heavy metal levels in *Clarias anguillaris* (mg/kg wet weight)**

Weight (g)		Pb	Cd	Cu	Cr	Ni	Fe	Mn	Zn
51.73	Head	2.45	0.23	1.93	2.07	0.70	43.00	7.01	3.00
	Trunk	2.02	0.19	1.35	2.00	0.22	20.05	4.23	2.20
	Mean*	2.24	0.21	1.64	2.04	0.46	31.53	5.62	2.60
52.33	Head	2.63	0.31	1.58	3.15	0.83	45.65	6.89	3.69
	Trunk	2.45	0.17	1.41	1.77	0.19	30.33	4.15	1.84
	Mean*	2.54	0.24	1.50	2.46	0.51	37.99	5.52	2.77
	Range	2.24-	0.21-	1.50-	2.04-	0.46-	31.53-	5.52-	2.60-
		2.54	0.24	1.64	2.46	0.51	37.99	5.62	2.77
	Overall. Mean*	2.39	0.23	1.57	2.25	0.49	34.76	5.57	2.69

**Table 6. Heavy metal levels in *Oreochromis niloticus* (mg/kg wet weight)**

Weight (g)		Pb	Cd	Cu	Cr	Ni	Fe	Mn	Zn
70.21	Head	0.74	0.10	0.90	1.23	1.50	32.10	4.05	3.12
	Trunk	0.63	ND	0.43	0.18	0.98	21.00	2.02	1.30
	Mean*	0.69	0.05	0.67	0.71	1.24	26.55	3.04	2.21
83.33	Head	1.19	0.15	1.67	0.90	1.88	27.50	4.94	2.70
	Trunk	0.50	0.07	1.08	0.81	0.90	12.72	2.98	1.05
	Mean*	0.85	0.11	1.38	0.86	1.39	20.11	3.96	1.88
	Range	0.69-	0.05-	0.67-	0.71-	1.24-	20.11-	3.04-	1.88-
		0.85	0.11	1.38	0.86	1.39	26.55	3.96	2.21
	Overall. Mean*	0.77	0.88	1.03	0.79	1.32	23.33	3.50	2.05

In addition, higher concentrations of the analysed metals were recorded in the dry season's study than in wet season. Similar observation was reported on the study of heavy metals in Ureje dam sediments in Ado-Ekiti by Adefemi et al. [14], Lateef [15] in Kanji dam sediments and other studies on heavy metals in sediments of surface water [5,10]. This observation could be attributed to a combination of water dilution, precipitation and adsorption of some metals in soil sediment during the wet season; and most importantly local concentration of metals via water evaporation from water body during the dry season [16,17].

Probable Effect Concentrations (PEC) of sediment metal levels (Pb 128, Cd 5, Cr 111, Cu 149, Zn 459 mg/kg) has been proposed by McDonald et al. [18]. The results of the present study show that the levels of Cd, Cu, Cr, Pb and Zn were much below the proposed effect

concentration of sediment levels. Above this level, metals may have adverse effects on sediment dwelling organisms [19].

### 3.2 Heavy Metal Concentrations in Fish

It was generally observed that these metals concentrated more in the head than the trunk of the fish. This observation might be associated with the fact that during feeding and breathing processes, the water entering the fish mouth passes through the gills in the head, thus making the gills exposed to the metals [20]. Similar observation was reported by Adefemi et al. [14] on two species of fish, *O. niloticus* and *C. gariepinus* sampled from Ureje dam in Ado-Ekiti.

Based on the different fish species, it could be seen that *O. niloticus* in spite of their larger weight compared to *C. gariepinus* and *C. anguillaris* recorded lower levels of most of the metals analysed. The high concentration of these metals in *C. gariepinus* and *C. anguillaris* could be attributed to the fact that both of them are typical bottom dwellers while *O. niloticus* is mostly found in the shores. Bottom feeders are known to pick up particulate matter more than the surface feeders [16,21]. Moreover, *O. niloticus* might have the least tendency to bioaccumulate these metals and/or even eliminate (excrete) them from its body.

With respect to body weight among fish species, it could be observed that higher concentrations of most metals were recorded in bigger fish than the smaller fish. Positive correlations between metal levels in fish tissue and body size (body weight and total length) had been reported by some other researchers [22,23].

Accumulation of metals in different fish species depends on the bioavailable metal concentration in the abiotic components of their habitats, their feeding habits, ecological needs, metabolism, age and size of the fish [24,25]. Observed wide ranges of specific metal levels detected in the fish collected from the dam may indicate that these fish had been exposed to a mixture of metals with different bioavailabilities within the dam through water, sediment and food items.

Figs. 2 and 3 show the comparison of the ratio of investigated metal levels in fish/water and fish/sediment respectively. It was observed that higher concentrations of the metals in the organism than in the water were recorded except for nickel in *C. angularis*, thus suggesting bioaccumulation of these metals in the fish body. Similar observations have been reported by many workers in Nigeria [7,14,15,16,21,26] and all over the world [22,23,27,28,29].

On the other hand, concentrations of some of these metals (Cu, Ni, Fe and Mn) in the sediment were higher than the values obtained in fish, while Pb, Cd, Cr and Zn recorded greater concentration in organism than in sediment, possibly due to low deposition of these metals on sediment; or they are more in their exchangeable or labile form in the sediment matrix, thus having low resident time in the sediment; or they are more bioaccumulated in the fish [10]. However, higher concentrations of some heavy metals in the sediment compared to fish has been reported by Okoye [21] and Asaolu et al. [16] for Lagos lagoon and Ondo State coastal waters respectively; just as Mohammed et al. [20] in their study of heavy metal concentration in fish and sediment samples from AD-Danna sewage outfall area in Saudi Arabia and Boran and Altınok and Boran [30] of heavy metals in water, sediment and living organisms in the Black Sea.



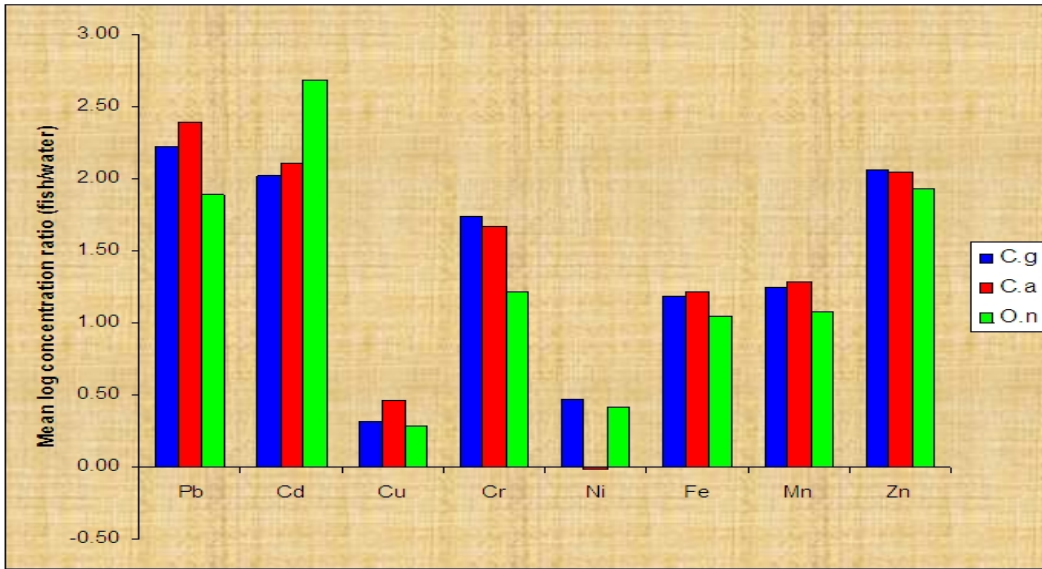


Fig. 2. A plot of the ratio of mean concentrations of metals in fish and water column  
 C.g=*Clarias gariepinus*; C.a = *Clarias anguillaris*; O.n = *Oreochromis niloticus*

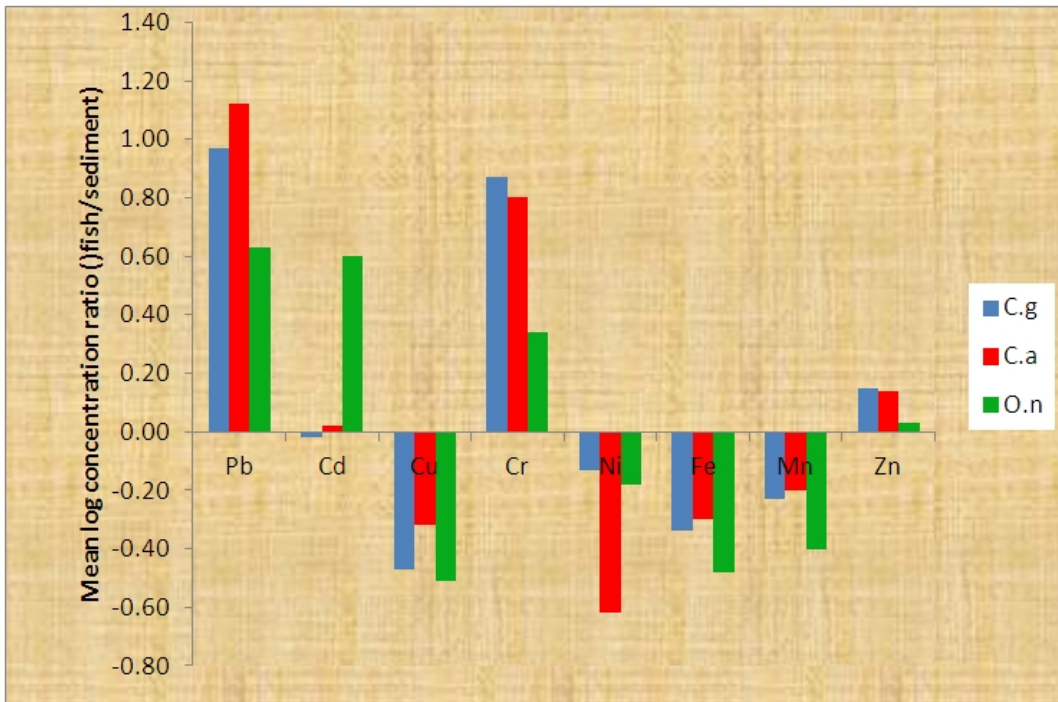


Fig. 3. A plot of the ratio of mean concentrations of metals in fish and sediment  
 C.g=*Clarias gariepinus*; C.a = *Clarias anguillaris*; O.n = *Oreochromis niloticus*

#### 4. CONCLUSION

The heavy metal levels in the dam sediment suggests more of lithological or crustal origin with little contribution from anthropogenic influences through run-off into the water body (Owena river) feeding the dam. Suspicion for more lithological influence on the presence of the metals in the dam water stemmed from the significant direct correlation ( $P = .05$ ) between the concentrations of some of the measured metals. The distribution of the heavy metals in sediment and fish samples revealed that Fe recorded the highest concentrations while Cd was least. The elevated level of Fe is not surprising, since it has been established that iron occurs at high levels in Nigeria soil/sediment. With respect to fish species, *Clarias anguillaris*, followed by *Clarias gariepinus* produced the highest concentrations of the studied metals, despite their smaller body weights. This may be attributed to the fact that they are typical bottom dwellers, which are more exposed to organic matter (sediment) harboring the metals. The present study has provided vital information about the current status of the dam, which would also serve as a baseline for future monitoring of the dam.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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