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Full Length Research Paper

Contamination profile of major rivers along the highways in Ondo State, Nigeria

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The quality of major rivers (Oluwa, Owena, Ogbese and Ose) along the highways in Ondo state, Nigeria were investigated using water, surface sediment and African catfish, *Clarias gariepinus*, as environmental indicators. Results from the study revealed that some of the water quality constituents exceeded the World Health Organization (WHO) standards for drinking water and water meant for other recreational uses. Of the four metals (Cd, Cu, Pb and Zn) determined, only Cd was recorded at toxic level in both water and sediment based on WHO and sediment quality guidelines respectively. Elevated concentrations of some pollutants detected in surface sediments and water are attributable to run-off from agricultural site and commercial activities. The pH, EC, TDS and PO_4^{3-} of the water displayed significant positive correlation with Pb (p = 0.05) and Zn (p = 0.01) while Cl^- equally showed correlation with all the metals. The index of geoaccumulation (I_{geo}) seems to be a more objective tool for assessing contamination. Highest and least microbial load were (439 × 10^6 cfu/100 ml) and least (259 × 10^6 cfu/100 ml) respectively. In the fish, the highest and least bioaccumulation factors (BAF) were recorded for Pb and Cu respectively. The bioaccumulated heavy metals in the tissues of *C. gariepinus* were above the acceptable limits stipulated by international codes of practice, implying critical pollution in the biota.

Key words: Anthropogenic input, heavy metals, seasonal changes, sediment, pollution.

INTRODUCTION

There are several exposure pathways contributable to contaminated water causing potential human health problems. These include exposure to water contaminants during swimming and recreational activities, drinking water supplies and the consumption of fish and shellfish that have been contaminated by water pollutants. In Nigeria, agencies such like the Federal Environmental Protection Agency (FEPA) and Natural Environment Management Authority (NEMA) are involved in environmental control and management. The FEPA, issued in 1998; a specific decree to protect, to restore and to preserve the Nigerian environment. The decree also empowered the agency to set up water quality standard. Through the decree, an Interim National Water Quality Guidelines and Standards in Nigeria was set up to address drinking water, recreational water use, fresh water aquatic life, agriculture (irrigation and livestock watering) and industrial water uses (FEPA, 1991; NEMA, 2003). Humans, livestock and aquatic organisms may be affected by poor quality water causing death, sickness or impaired growth. Thus, understanding water quality parameters are essential due to the daily demand for water by the entire ecosystem.

Pollution of the rivers examined in this study is mainly through run-off activities from agricultural practices and commercial activities. Many studies have shown that very large quantities of heavy metals are found in run-off associated with the operation of motor vehicles, atmospheric fallout and road surface materials (Harper, 1985). To the environmental scientists, the ultimate concern of trace metal contaminants in receiving water is their toxic impact on aquatic organisms and fish species (Sutherland and Tolosa, 2000; De Carlo et al., 2004).

Fish, form an important part of human food and it is therefore not surprising that numerous studies have been carried out on metal pollution in different species of edible fish (Roesijadi, 1996; Lewis et al., 2002).

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The analysis of sediment for trace metal concentrations is one aspect of the integrated assessment of water quality. Several reviews have shown that sediments serve as a metal pool that can release metals to the overlying water via natural or anthropogenic processes, causing potential adverse health effects to the ecosystems (Fatoki and Mathabatha, 2001; McCready et al., 2006; Ololade et al., 2007a). Moreover, marine organisms or biota can take up metals, which in turn enhances the potential of some metals entering into food chain. Therefore, a study of the distribution, enrichment, accumulation and seasonal variation of heavy metals in water and sediments along the major highways in Ondo State is important to the assessment of the possible influence of anthropogenic activities on Ondo River waters (Morillo et al., 2004; Adamo et al., 2005; Alagarsamy, 2006). In this study, assessment of sediment contamination was based on (1) sediment quality guidelines (SQGs) used by US EPA (2) degree of contamination using the geo-accumulation index (Igeo) and (3) applications of two sets of guidelines: ERL/ERM and TEL/PEL and mean toxic units (MacDonald et al., 2000; Woitke et al., 2003; Reddy et al., 2004).

On microbial level, several studies have shown increased health risk from exposure to recreational waters containing high levels of indicator bacteria (Pruss, 1998). Coliforms are found in human and animal feces; however, not all of them are of human faecal origin. Animal sources can contribute to high levels of indicator bacteria in receiving waters, but these waters may or may not contain pathogens that pose a significant health risk to humans. *Escherichia coli* have been found in pristine sites in a tropical rainforest, suggesting that they too may not be a reliable indicator of human faecal contamination (Bermudez and Hazen, 1988).

Assessing pollutants in different components of the ecosystem is an important task in preventing risk to natural life and public health. The purpose of this research was to acquire baseline chemical data, necessary to provide an evaluation of the ecological health and to establish a detailed quantitative assessment of the nature, pattern and trend of pollutants that contribute to the dissolved loads in the four major rivers along the major highway in Ondo State. Pollutants entering these receiving waters by way of run-off conveyance systems, indiscriminate dumping of wastes e.t.c, may adversely impact many of the desired uses. The data obtained will help to provide an evaluation of the ecological health of these rivers. Particularly, this study was designed to evaluate physico-chemical parameters of water including those of toxic metals in water, sediment and also fish tissues under the structure of a biomonitoring programme. This approach is built on calculations from sampling during a complete hydrological year that span from 2007 to 2008.

Study area

The study was carried out on four major rivers along the highway in Ondo State. Two of the rivers (Ogbese and Ose) are located in the Northern district of the State while the remaining two, Oluwa and Owena are located within the Ondo central and southern district, respectively. The map shown in Figure 1, illustrates the location of the sampling sites and the potential source of pollutants, which include sewage, agricultural wastes, animal wastes, market wastes, etc. It was observed during the dry season period that two of rivers (Ose and Ogbese) have a rocky basement. No record was available on the chemical composition of the basement before this study was carried out. Apart from the Ogbese River which lies entirely within the community, the other three rivers are located at some distances away from their respective communities. The Ogbese River is particularly unique for several reasons. The Ogbese community has undergone great economic development in recent years. In fact, it is notably one of the fastest growing, economically important communities in Ondo State and handles a considerable number of micro- industries. The very popular market (Ogbese market) and the timber business coupled with unequalled agricultural practices have drawn people from several cultural backgrounds in the country to make the settlement inter-tribal. This increase in anthropogenic activities surrounding the area has lead to an increase in environmental degradation. These multiple sources make it especially difficult to identify and isolate the risks associated with this contaminated water. Unfortunately, records of water quality parameters are non-existing and no known monitoring programmes on the water quality have been initiated within the state.

Generally, major material sources can easily be identified at each station. In each upper course, population is non-existing and the river chemistry is exclusively controlled by natural processes (thus, serves as control). In the middle part; the road environment, from where samples were collected, each of the rivers displays variability in possible pollutant sources while agriculture leaves its fingerprints in the water chemistry across the various river.

MATERIALS AND METHODS

Sampling

Sampling was conducted in June, 2007 and January, 2008, representing the peak periods of wet and dry seasons in Nigeria. Each of the rivers has associated bridge through which vehicles pass. Surface sediment samples were collected using a Shipek Grab sampler (0.1 m^2). Sediments collected were stored in clean plastic bottles in a cold container until analysis was carried out. Triplicate samples were obtained at each river at a distance of 15 m from the bridge (Popek, 2003). Sediment samples from the various sampling points in each river were pooled together and composite samples from the four rivers were air dried and 2 mm sieved prior to analysis. Grab samples of water were collected at same points of sediment across all the rivers under baseflow (n = 3) following standard procedure (American Public Health Association, APHA, 1998). In the field, the following water quality parameters were measured: temperature, pH and conductivity. One representative

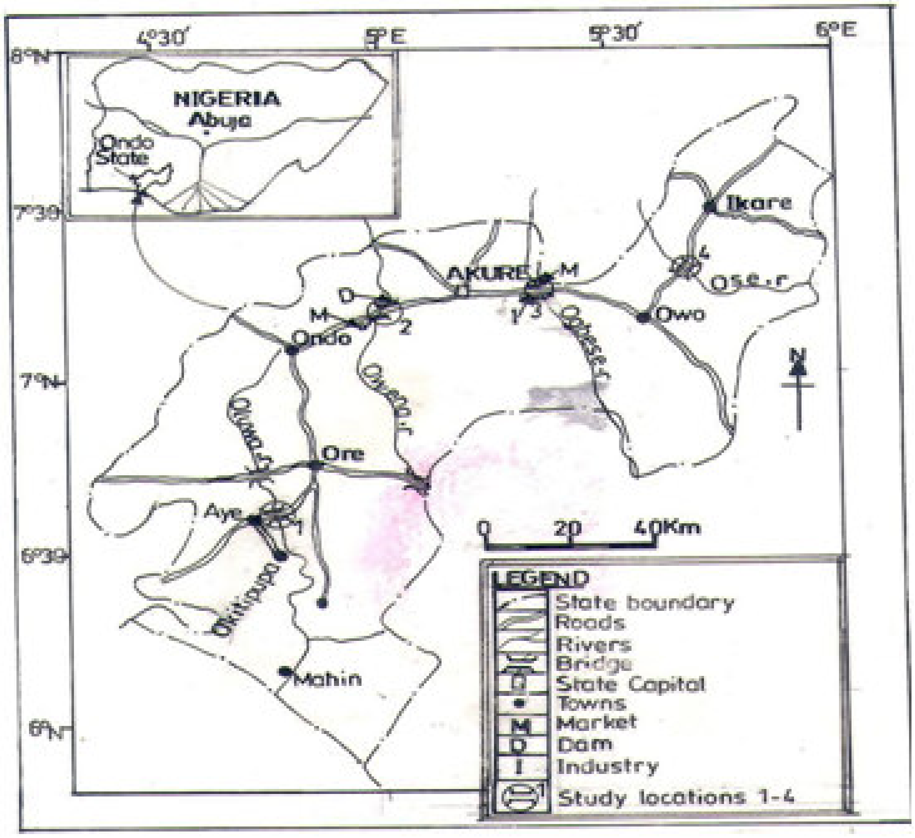


Figure 1. Map of Study Area (Inserted is the area map of Nigeria showing the geographical location of Ondo State).

sample of sediment and water (from four uncontaminated site) was collected from the upstream of each river, where both anthropogenic and industrial activities were not found to serve as control. Thus, the background levels for heavy metals in water and sediment in each river was defined as the average concentrations of eight samples collected from the control locations.

Considering the nature of fish species mostly found across the rivers, the species African catfish, *Clarias gariepinus* is dominant and consequently was selected as possible biomonitor in the various rivers along the highway. *C. gariepinus*, an omnivore freshwater fish is a popular delicacy throughout tropical Africa. It is a prominent culture species because of its hardiness and fast growth rate. Being a migratory species, samples of fish which were of averagely similar size were collected at each location ($7 \leq n \leq 10$). Some of the fish physical properties are presented in Table 1. Samples of fish at each location were pooled for chemical analysis. All the samples were immediately transported to the laboratory with ice and placed in a deep-freezer until chemical analysis. Due to the moderate size of the rivers (approximately, 15 m width), it was possible to sample all within one day.

Chemical analysis

In the laboratory, water samples were analysed for turbidity, settle-lable solids, total dissolved solids, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD) and alkalinity by using standard methods (APHA, 1998). Chloride and sulphate were determined using the Morhs and turbidimetric standard methods respectively while the Cadmium reduction and ascorbic acid methods were respectively employed for nitrate and phosphate determination. Sediment samples were passed through a 2 mm sieve. Sediment moisture content (sediment dry method) was analyzed in the laboratory. Mechanical analysis of sediments was done by Bouyoucos hydrometer method (Bouyoucos, 1927). The mud fraction of the sediment, consisting of the silt plus clay sizes (< 63 µn) were used for metal analysis based on literature guidance (Naidu et al., 2001). The pH (1:2.5 sediment: water) and electrical conductivity (EC) were measured using Hanna pH 211 microprocessor pH meter and EC meter respectively. Organic carbon was determined following modified Walkley and Blacks method as described by Nelson and Sommers (1982). Samples of water, sediment and fish were digested based on standard methods and literature guidance (APHA, 1998; Naidu et al., 2001; Leung and Furness, 1999). The concentrations of heavy metals (Cd, Cu, Pb and Zn) in waters, sediment extracts and fish extracts were analyzed by using atomic absorption spectrophotometer (Alpha 4AAS, Chemical Tech. Analytical Euro) as per the procedure described by APHA (1998). Detection limits (µg/l) were; Cd (0.002); Cu (0.001); Pb (0.004) and Zn (0.006).

Quality assurance and control (QA/QC) protocol prescribed by the U. S Environmental Protection Agency (EPA) for metal analysis was used. In this study, analytical precision through replicate runs and the use of certified standard reference material PACS-2 (heavily contaminated marine sediment available from the Natural Research Council, Canada) was employed. The percent recoveries are quite reasonable. Details are presented under results and discussion.

The index of geoaccumulation (I_{geo}) was used to quantify the extent of heavy metal contamination associating with the sediments

Table 1. Water Quality Parameters#.

Parameters	WHO*	This study	Control
pH	6.5 - 9, 8.0(p)	5.09 - 6.87	6.7 - 7.2
Alkalinity(as $CaCO_3$, mg/L)	30 - 500	67 - 112	36 - 55
EC(μScm^{-1})	20	50 - 220	19 - 24
Hardness (as $CaCO_3$, mg/L)	100 - 200	24.2 - 106.2	18.6 - 33
Turbidity (NTU)	5	8.3 - 17.3	2.1 - 2.2
TDS (mg/L)	500	325 - 1410	307 - 347
TOC (mg/L)	NI	0.35 - 2.04	0.03 - 0.07
Cl^{-1} (mg/L)	250	52.7 - 88.3	35.4 - 47.3
NO_3^- (mg/L)	50	40.4 - 90.3	35 - 42
SO_4^{2-} (mg/L)	250	3.0 - 18.0	22.1 - 33.4
PO_4^{3-} (mg/L)	0.5	40.3 - 120.0	18.1 - 22.3
DO (mg/L)	5.0 - 9.5	1.9 - 5.4	4.3 - 7.5
BOD (mgO_2/L)	2.0 - 4.0	14.1 - 29.1	2.4 - 2.9
COD (mg/L)	NI	22.4 - 45.6	3.6 - 4.7
Cd (mg/L)	0.003	nd - 2.67	nd
Cu (mg/L)	2.0 (p)	0.14 - 2.01	0.01 - 0.02
Pb (mg/L)	0.01	0.11 - 2.01	nd
Zn (mg/L)	3.0	nd - 2.95	nd

p = health based provisional value. #Concentrations are mean of triplicate analysis. NI: not indicated. Sources: WHO (1993); NEMA (2003).

of the four rivers. The I_{geo} was calculated using the following equation as presented by previous authors (Muller, 1969; Forstner et al., 1993; Reddy et al., 2004):

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n}$$

Where C_n represents the measured total concentrations of metals in the fine-grained sediment fraction (clay or silt) (mg/kg) and B_n represents the geochemical background values of metals (mg/kg). The interpretation of the obtained results is as follows: *Igeo* ≤ 0 practically uncontaminated, 0 ≤*Igeo* < 1 uncontaminated to moderately contaminated, 1 ≤ *Igeo* ≤ 2 moderately contaminated, 2 ≤ *Igeo* ≤ 3 moderately to heavily contaminated, 3 ≤ *Igeo* ≤ 4 heavily contaminated, 4 < *Igeo* ≤ 5 heavily to very heavily contaminated and *Igeo* ≥ 5 very heavily contaminated. The background levels for sediment heavy metals in each river samples were defined as the average concentrations of three samples collected from uncontaminated surface sediment within each geographical location.

Microbiological study

100 ml of the water samples were serially diluted using sterile distilled water. 1ml of the appropriate diluents was aseptically inoculated into sterile Petri-dishes. The total bacterial and coliform counts were estimated from a pour plate technique used to culture this water sample sources. The microbial colonies from these sources were isolated and subcultured on nutrient agar plates. The isolates were preserved on slants in McCartney bottles stored at 4℃ to be used when needed and for identification purposes.

Biochemical test

The microorganisms were studied for their cultural and morphological characteristics. The microbial colonies isolated were Gram stained identified by standard microbiological techniques.

Statistical analysis

We performed statistical analysis by combining data from the two seasons. Statistical differences in seasonal metals level were determined by one-way ANOVA. Relationships between metals and other controlling factors are determined by bivariate correlation using the Pearson coefficient in a two-tailed test (α = 0.01 and 0.05). All analysis was performed using SPSS software (version 13.0).

RESULTS AND DISCUSSION

Physicochemical properties of waters

The ranges and distribution pattern of water physicochemical parameters determined in the study are presented in Table 1 and Figures 2a – 2c respectively. The pH of the water ranges from 5.01 (at Ogbese) to 6.87 (at Ose) between the two seasons (Figure 2a). The pH value at Oluwa and Ose are generally between the WHO permissible limit (WHO, 1993; NEMA, 2003). Those of the other two rivers are lower than the acceptable limits. Numerous studies have confirmed that a pH range of 6.5 to 9.0 is appropriate for the maintenance of fish communities and drinking water (WHO, 1993; NEMA,

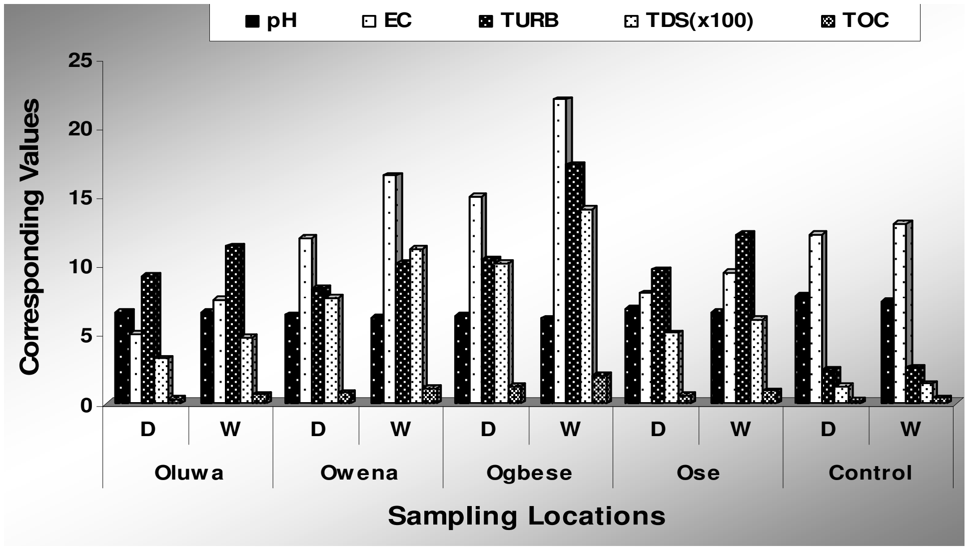


Figure 2a. Seasonal variation in PH, EC, Turbidity, TDS and TOC across all locations.

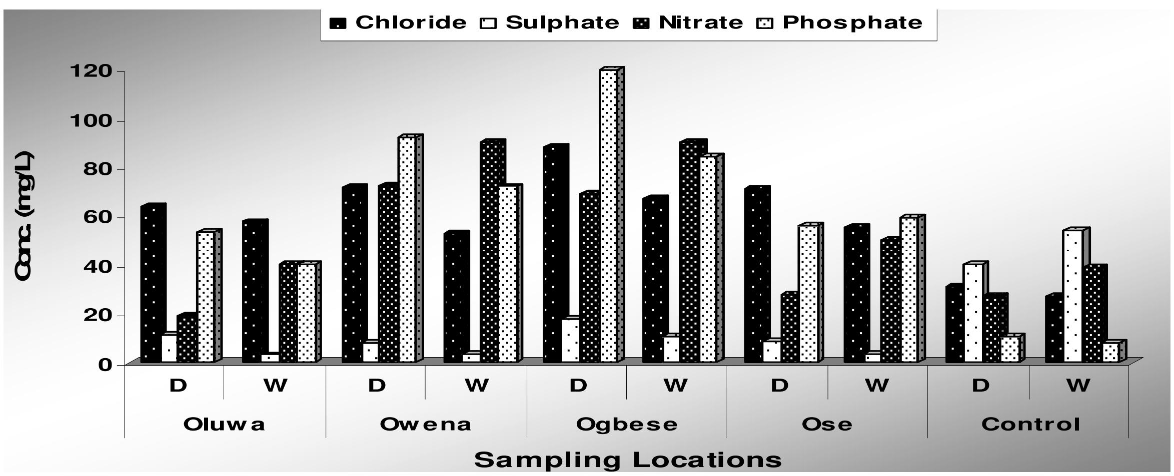


Figure 2b. Seasonal variation in nutrients ions across all locations.

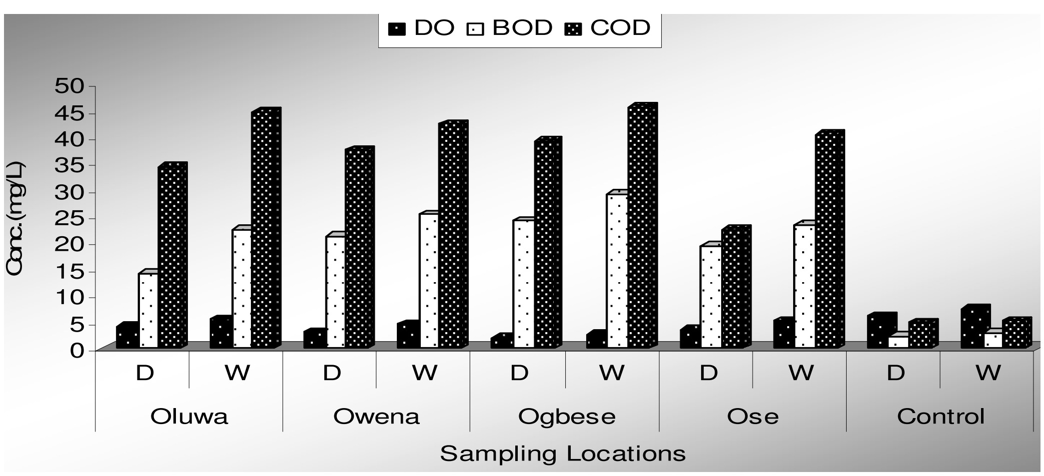


Figure 2c. Seasonal Variation in DO, BOD and COD across all locations.

Table 2. Correlation matrix between water physico-chemical properties and heavy metals[a] (n = 12).

	Cd	Cu	Pb	Zn
pH	0.176	0.183	-0.328	-0.590
EC	0.555	0.531	0.883**	0.807*
Turbidity	-0.108	0.021	-0.199	0.336
TDS	0.517	0.495	0.867**	0.799*
TOC	0.097	0.178	0.238	0.640
Cl	0.812*	0.775*	0.893**	0.740*
SO_4^{2-}	0.712*	0.686	0.902**	0.812*
NO_3^-	-0.070	-0.057	0.267	0.471
PO_4^{3-}	0.528	0.510	0.885**	0.805*
DO	-0.631	-0.620	-0.847**	-0.815*
BOD	0.039	0.108	0.030	0.425
COD	-0.457	-0.430	-0.055	0.320

*Significant at p= 0.05; **Significant at p = 0.01 [a]means from both seasons at each site were used.

2003). Low pH enhances the solubility of substances like metals in water, majority of which are toxic to human. Total alkalinities, measured in mg/l $CaCO_3$ ranged from 67 to 112 and were found to fall within the 30 – 500 mg/l $CaCO_3$ WHO limits. The total hardness, which is mostly due to the dissolved calcium and magnesium salts, ranged between 24.2 (Ose river) to 106.2 (Ogbese river) mg/l $CaCO_3$ between the two seasons across the various rivers. The levels of hardness which fall far below the WHO limit of 100 - 200 mg/l $CaCO_3$ except during the dry season of the river at Ogbese (106.2 mg/l $CaCO_3$), can be associated with the rocky nature of the river basement. This also implicates the possibility of the mineral salts of Ca and Mg being leached into the aqueous phase.

Turbidity is a measure of the cloudiness of water. No doubt, all the rivers are visibly coloured especially during the wet season. This may be attributed to run-off activities. The turbidity as obtained in this study ranged from 8.3 to 17.3 NTU with the highest level at Ogbese (Figure 2a).The values obtained are generally greater than the WHO recommended value of 5 NTU for drinking water (WHO, 1993). The relatively high level particularly at Ogbese could be attributed to the presence of decaying organic matter. These increased levels are often associated with higher level of disease causing micro-organisms such as viruses, parasites and some bacteria (United State Environmental Protection Agency, US EPA, 2004).

The levels of chloride (52.7 - 88.3 mg/l) and sulphate (3.0 - 18.0 mg/l) were greatly lower compared with the 250 mg/l WHO limits for each of the anions (Table 1).

The levels of chloride (both seasons) equally fell below the maximum allowable concentrations of Cl^- (< 700 mg/l) in water for agricultural purposes (e.g. irrigation) in Nigeria (WHO, 1993; NEMA, 2003). However, nitrates concentrations are higher at Owena and Ogbese (Figure 2b) than the WHO limits of 50 mg/l. Similarly, phosphates were recorded at much higher concentration across all the rivers at both seasons than the recommended WHO limits of 0.5 mg/l. The very high nitrate level at both Owena (90.1 mg/l) and Ogbese (90.3 mg/l) can be attributed to the high level of agricultural and economic activities around the area. This can pose serious health hazard due to its possible conversion to highly toxic nitrite by certain bacteria in the intestinal tract of infants. In fact, infants below the age of six months who drink water containing nitrate in excess of maximum contaminant level (MCL) of 10 mg/l could become seriously ill and if untreated, may die (US EPA, 2004). Additionally, the levels of NO_3^- and PO_4^{3-} obtained in this report are exceedingly too high for both aquatic life and irrigation purposes with guideline values of < 0.5 mg/l for NO_3^- and < 0.05 mg/l for PO_4^{3-} respectively (FEPA, 1991). The water is not equally suitable for livestock watering and recreational activities with guideline of < 10 mg/l for NO_3^- and < 0.05 mg/l for PO_4^{3-} respectively (FEPA, 1991; US EPA, 2004). Generally, comparing the mean TDS and nutrients (NO_3^- and PO_4^{3-}), it was observed that agricultural activities such as the use of fertilizers, particularly around Ogbese and to some extent at Ose rivers greatly influence the quality of the rivers.

There is a strong line of relationship between DO and many toxic existences. The range of DO (1.9 - 5.4 mg/l) and distribution pattern (Figure 2c) between the two seasons and across the various rivers is very low. Depending on the water temperature requirement for a particular aquatic species at various stages, the DO criteria values range from 5 to 9.5 mg/l for warm-water biota and 6.5 - 9.5 mg/l for cold-water biota (NEMA, 2003). Low concentration of DO as obtained from Owena and Ogbese Rivers when combined with the presence of toxic substances may lead to stress response in aquatic ecosystems because the toxicity of certain elements, such as Zn, Pb and Cu, is measured by low concentration of DO. Dissolved oxygen in water is usually depleted, if organic matters undergoing biological degradation are present The BOD and COD ranged from 14.1 to 29.1 mg O_2/l and 22.4 to 45.6 mg O_2/l respectively across the rivers between the two seasons. These values are very high. In Nigeria, the interim water quality criterion for BOD for the protection of aquatic life is 4 mg O_2/l (water temperature 20 - 33°C), for irrigation water it is 2mg O_2/l (water temperature 20 - 25°C) and for recreational water it is 2 mg O_2/l (Water temperature 20 - 33°C), (FEPA, 1991). The very high level particularly at Ogbese and Owena Rivers are indicative of contaminated waters resulting from the presence of decaying organic matter. These values are comparable with those reported from some rivers in Nigeria (Oguntimehin and Babatola, 2007). Comparatively, apart from pH and DO, all the other physico-chemical parameters are recorded at much lower concentration in the control sites than the study areas. It

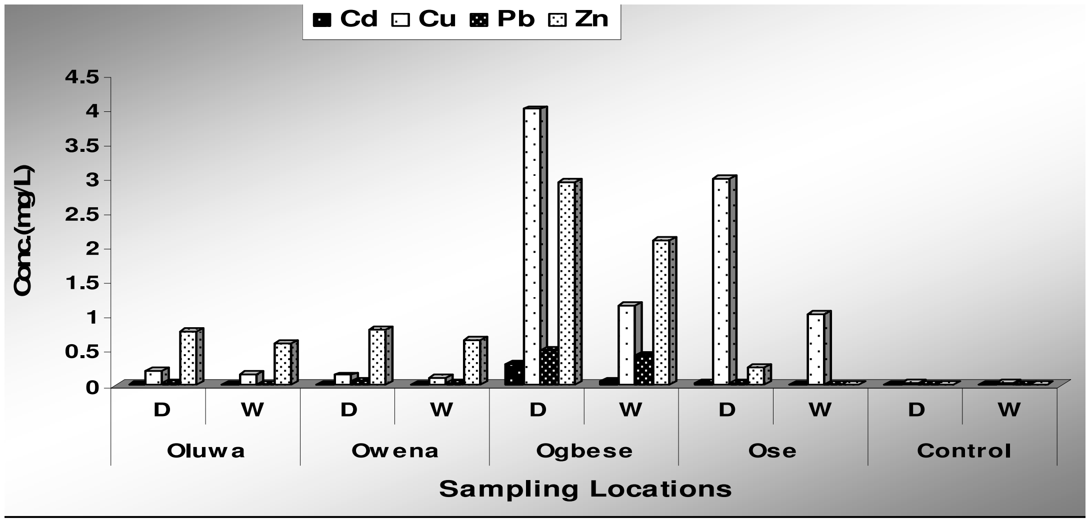


Figure 3. Distribution pattern of Cd, Cu, Pb and Zn in water during the dry and wet seasons.

was also observed that concentrations at the control sites generally falls within the recommended WHO limits. Anthropogenic stress into the water as observed in this report may adversely affect many species of aquatic flora and fauna that are dependent on both abiotic and biotic conditions. This is due merely to the fact that within aquatic ecosystem, a complex interaction of physical and biochemical cycles exists.

Statistically (Table 2), the pH, EC, TDS and PO_4^{3-} displayed significant positive correlation with Pb (p = 0.05) and Zinc (p = 0.01). Chloride and SO_4^{2-} equally showed correlation with all the metals except between SO_4^{2-} and Cu concentrations. The DO was equally noted to be negatively correlated with Pb (p = 0.05, r = -0.847) and Zn (p = 0.01, r= -0.815).

Seasonal variation in properties of water

Seasonal variations were noted in the physico-chemical properties of waters (Figures 2a - 2c). Different properties like pH, EC, Cl^-, SO_4^{2-}, PO_4^{3-}, BOD and COD showed maximum values during dry season while minimum values were recorded during wet season. The observed trend could be attributed to the evaporation of water from rivers during dry and subsequent dilution due to precipitation and run-off from the catchment area during wet season (Radhika and Gangaderr, 2004). The generally higher pH of waters during the dry season could be ascribed to increased photosynthetic assimilation of dissolved inorganic carbon by planktons. A similar effect could also be produced by water evaporation through the loss of half bound CO_2 and precipitation of mono-carbonate.

Higher alkalinity during the wet season indicated the potential susceptibility of these water bodies for eutrophication. Water body with alkalinity values above 100 mg/l is considered nutritionally rich (Farrel et al., 1979) and on the basis of this observation, Ogbese river could be considered prone to eutrophication problem. These were quite visible within the river at the time of sampling. In fact, the run-off resulting from a rice plantation plots and from cow dung which are indiscriminately distributed across the area may be contributing to the level of eutrophication observed at the site.

Lower DO during dry season across the various rivers might also be due to anticipated higher microbial activities. Decomposition of organic matter might be an important factor in consumption of DO, as more vigorous deposition could be likely during dry weather. Oxygen depletion observed can equally result from the oxidation of nitrogen and phosphorus (which are chemically combined in organic compounds) to nitrates and phosphates (values are very high during the dry season).The reoxygenation of waters during raining season might be occurring due to circulation and mixing by inflow after wet season rains.

Heavy metal concentrations in waters

The ranges and distribution pattern of metal concentrations in water are included in Table 1 and Figure 3 respectively. The ranges (in mg/l) during the wet season (dry season in brackets) are; Cd, nd - 0.16 (nd - 1.13); Cu, 0.11 - 2.02 (0.21 - 4.01); Pb, 0.41 - 1.73 (1.25 - 4.50) and Zn, nd - 2.09 (0.26 - 2.95). The data showed that Cd recorded the minimum range across the rivers while highest range was recorded for Pb. Except at Ogbese and Ose, Cd was not detected in water samples from the other two locations which might be linked to the very low level of cadmium-containing wastes into these rivers. The distribution pattern across the various rivers (Figure 3) as compared with those of the control site displayed

Table 3. Total microbial load/Microbial isolates encountered during the study.

	Oluwa	Owena	Ogbese	Ose	∑Organisms
Total bacterial count (cfu x 10^6)	231	261	439	259	1190
Isolates					
Bacillus subfilis	2	2	2	1	7
Bacillus circulans	1	1	2	1	5
Micrococcus sp	2	3	3	2	10
Staphylococcus sp	-	1	2	–	3
Bacillus sp	2	3	5	2	12
Klebsiella sp	-	-	2	1	3
Escherichia coli	2	2	3	2	9
Streptococci sp	-	-	1	–	1
Pseudomonas sp	-	1	–	–	1
Total	9	14	19	9	51

considerable variation with values of most of metals in non-detectable form at the control site. The concentrations of heavy metals in water of the control sites remained well below the toxic limits (WHO, 1993; US EPA, 2004) while a remarkably high concentration of Cd and Cu above the WHO recommended limit of 0.003 mg/l and 2.0 mg/l respectively were recorded in rivers Ogbese and Ose. For Pb, the levels recorded across all the rivers and between the seasons were generally higher than the WHO recommended limit of 0.01 mg/l.

The levels of Cd and Pb are higher than the maximum contaminant level (MCL) for livestock drinking (0.02 and 0.01 mg/l); agricultural purposes such as aqua culture (0.01 and 0.2 mg/l) and irrigation (0.2 - 1.8 and 1.7 µg/l) respectively (US EPA, 2004). This showed that water from the river is generally unsuitable for these activities with regards to the values obtained in this study, which could have chronic health effects on various users. Cadmium remains a metal without any known biological significance. Toxicity in water is expected based on the levels obtained in this study. Chronic exposure to Pb has been linked to growth retardation in children (Schwartz et al., 1986). Lead toxicity studies conducted on female animals revealed mostly miscarriages, premature delivery and potent mortality (Tapieau et al., 2000). A concentration of Pb ≈ 0.1 mg/l is detrimental to foetuses and children with possible development of neurological problem (Fatoki et al., 2002).

Comparatively, with regards to the effect of season on heavy metal concentration in the water of the different rivers, concentrations of all the metals were at maximum during the dry season, while minimum concentrations were observed during wet season. This trend could be attributed to the evaporation of water from river during dry season and subsequent dilution due to precipitation and run-off from the surrounding market and farmland during the rainy season. Similar observation has been reported (Patil et al., 2004).

Microbiological report

Table 3 summarizes the results of microbiological studies of water from the various sources. Water sample analyzed from various sources showed that Ogbese river had more microbial load of 439 x 10^6 cfu/100 ml compared with rivers Oluwa, Owena and Ose which has similar range of microbial of 231 x 10^6; 261 x 10 and 259 x 10^6 cfu/100 ml respectively. This is consistent with the study of Ajayi and Akonai (2003) which shows the variation in microbial population of water bodies based on some ecological conditions.

A total number of fifty one bacterial isolates were encountered during the study and identified by standard microbiological technique. Considering the indiscriminate nature of wastes (e.g. human and animal feces) disposal coupled with agricultural activities around the study area, particularly around Ogbese, the level of micro-organisms detected is not surprising. Presence of some microorganisms like *Streptococcus* sp and *E. coli* signified contamination of the water from feacal sources. Other organism present could also emanate from domestic and agricultural activities. These pathogens may pose a special health risk for infants, young children and people with severely compromised immune systems.

River Ogbese is thickly populated with various species of microorganism such as *Micrococcus* sp*, Bacillus* sp and some coliforms like *E. coli*, compared with sample sources from rivers Oluwa, Owena and Ose. Some of these organisms can serve as etiologic agents for disease spread thereby resulting to epidemics if care is not taken. This has some relevance to the study of Jarvis (1990) which shows the opportunistic nature of some microorganisms in aquatic environment.

Despite the levels of microorganism obtained in the study, previous studies have shown evidence for the inadequacy of microorganisms as indicators from the published climatological or regional differences found in

Table 4. Sample locations and sediment characterization (Mean ± S.D) during the both seasons [#].

Locations	pH_{KCl}	C_{org} (%)	$CaCO_3$	Sand (%)	Clay (%)	Silt (%)
Oluwa	7.9 ± 1.2	1.28 ± 0.11	16.9 ± 2.3	80.4 ± 6.9	15.2 ± 3.3	4.4 ± 1.2
Owena	7.3 ± 0.8	1.04 ± 0.24	11.4 ± 1.9	74.2 ± 6.1	20.2 ± 3.2	5.6 ± 2.0
Ogbese	8.3 ± 1.1	1.59 ± 0.42	20.4 ± 4.8	76.1 ± 9.7	18.4 ± 4.2	5.4 ± 2.2
Ose	8.9 ± 1.3	1.10 ± 0.16	24.2 ± 3.1	74.5 ± 5.3	18.1 ± 2.9	2.4 ± 0.8
Control	7.6 ± 0.3	1.72 ± 0.42	32.4 ± 6.3	82.4 ± 8.5	14.2 ± 8.3	3.4 ± 2.3

[#] Values are mean of the two seasons; S.D: standard deviation.

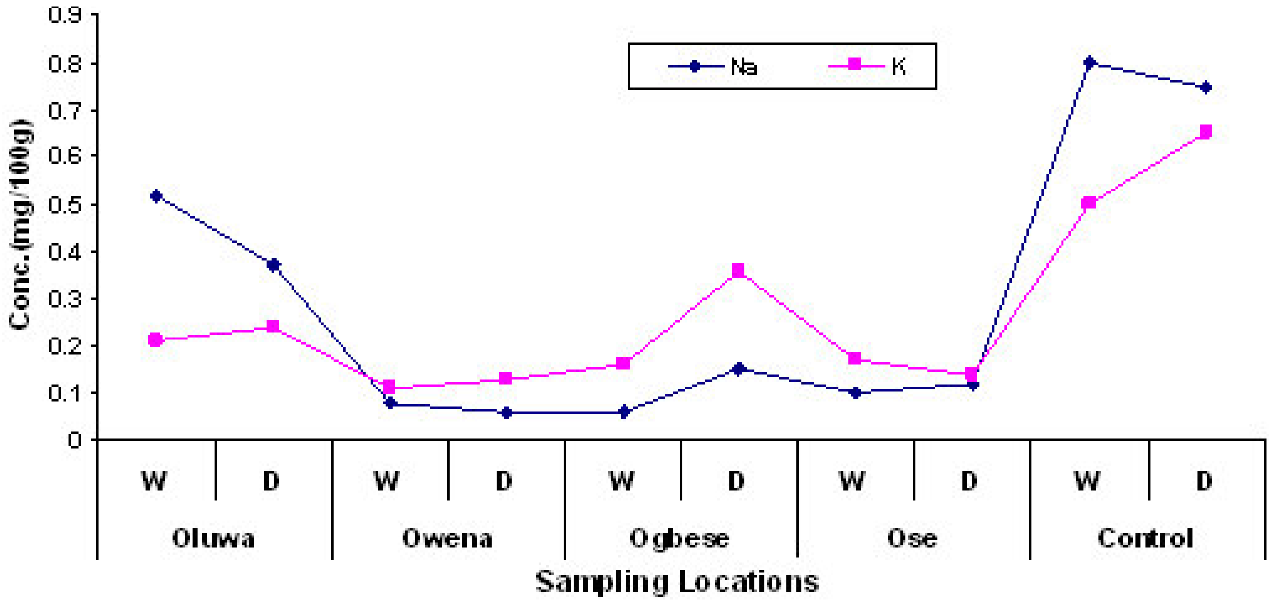


Figure 4a. Seasonal distribution pattern of mineral elements (Na and K).

epidemiology studies. The different indicators correlate with disease outcome depending upon whether or not the study was conducted in fresh or marine waters. As it applies in the present study (that is, freshwater), it has been shown, for instance, that faecal streptococci were better indicators for gastrointestinal disease than faecal coliforms (Ferley, 1989). In another study in Hong Kong, *E.coli* (a faecal coliform) was the best indicator found a relationship with gastroenteritis (Cheung et al., 1990). In contrast, it is expected that numbers of a given pathogenic microorganisms will correlate quite well (and consistently) with its associated disease outcome.

Table 3 shows that the rivers recorded different levels of microbial contamination capable of increasing the health risks for all symptoms. The incidence of respiretory, fever, eye, ear and other problems increased with increasing bacterial counts (Corbett et al., 1999). This impact is expected to reflect more on swimmers. It has been reported that those who swam for longer than 30 min were more than 4 times as likely to develop gastrointestinal symptoms compared to non-swimmers or those who swam for shorter periods (Corbett et al., 1999).

Physicochemical properties of sediments

A summary statistics of the physicochemical properties of sediments between the two seasons from the different study area and control sites are presented in Table 4. Across the two seasons for the four rivers, average sediment pH was in between 7.3 and 8.9. The lowest pH (6.4) was noticed at Owena, whereas the highest (9.1) at Ose. The control sites recorded a considerably neutral-alkaline pH (7.2 - 7.9) level generally. Relatively higher pH in sediments of Ose and Ogbese might be due to high $CaCO_3$ content (see Table 4). In general, the pH of the sediments of these rivers was alkaline. Results of the particle size analysis over the two seasons indicated that highest clay content was found in Owena (20.2%) followed by Ogbese (18.4%), Ose (18.1%) and Oluwa (15.2%). The silt content values averaged over the two seasons revealed that the silt content ranged from 4.4 (Oluwa) to 7.4% (Ose).

For the two seasons, averaged values of sand content from the different rivers (Table 4) indicated that the highest sand content was found in Oluwa (80.4%

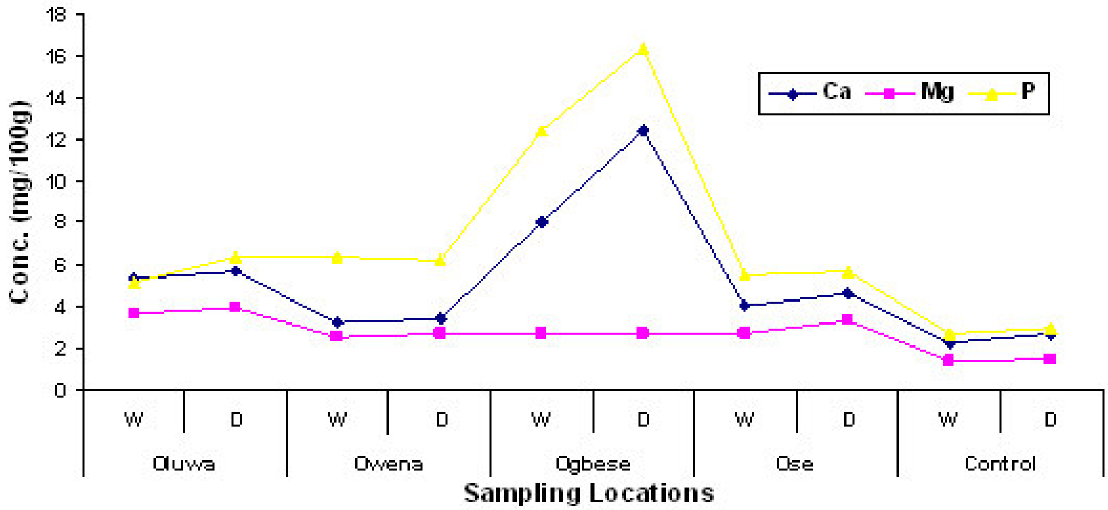


Figure 4b. Seasonal distribution pattern of mineral elements (Ca, Mg and P).

followed by Ogbese (76.1%), Ose (74.5%) and Owena (74.2%). Averagely, the highest $CaCO_3$ equivalent was found in Ose (24.2%) followed by Ogbese (20.4%), Oluwa (16.9%) and Owena (11.4%). The carbonate content of the river sediments indicated the dominance of carbonate minerals at Ose from where eroded materials and runoff bring mineral solids and a possible generation of insoluble carbonates in aquatic environment rich in alkaline earth metals. This is quite visible considering the geological basement rock around this river. Mineral element composition shows that the contents of sodium and potassium are very low (less than 1.0 Cmol/kg, Figure 4a). Available phosphorus formed, though higher than those of Na and K, was equally low (< 6.5 Cmol/kg) except for samples from Ogbese where concentration of 12.75 Cmol/kg) was recorded: Calcium and Magnesium were recorded at low concentration with highest values of 6.00 and 3.70 Cmol/kg respectively, both at Oluwa river (Figure 4b). Comparatively, levels of Na and K at the control site are much higher than levels in rivers studied while those of Ca, Mg and P are much lower than in sediments from the rivers studied (Figures 4a and b).

Average concentrations of inorganic contaminants from sediments (n = 6) are illustrated in Table 5. Variations were observed in the levels of heavy metals in sediments. The contents (in mg/kg) of total Cd, Cu, Pb and Zn during the dry season (wet season in brackets) ranged from; nd - 4.8 (nd - 1.09) Cd; 2.6 - 9.3 (2.1 - 6.1) Cu; 0.38 - 2.50 (0.08 - 1.48) Pb and 0.01 - 8.31 (0.33 - 4.93) Zn. Contamination of heavy metals in the sediments were in the following order: Zn > Pb > Cu > Cd. Generally, concentrations of all the metals at the study sites were observed to be lower compared with levels obtained at the control site. This is indicative of anthropogenic metal input. The levels of metals at each site demonstrate the extent to which each river receives anthropogenic wastes. It is therefore not surprising the increased level of metals recorded at Ogbese in the study. This may be attributed to the myriads of pollutant sources already highlighted above.

The increased level of metals dry season is of environmental significance. This is because, it indicates the continual impute/increase in anthropogenic metal burden into the environment majority of which may persist and thus become toxic not only to aquatic lives but also humans who are at the top of the food chain. In a pattern which parallels the trend in water, river Ogbese recorded the highest concentrations of all the metals in sediments. It was observed that sediments from Ogbese are characterized by a high content of organic matter (Table 4), which plays other important roles in the sorption of organic and inorganic xenobiotics such as heavy metals. In addition, natural (run-off from various sources identified above under introduction) and human related activities are major contributing factors to higher metal loading at the site. However, the levels obtained above are considerably lower than concentrations obtained in some studies within and outside Nigeria (De Carlo et al., 2005; Ololade et al., 2007a; Nuria et al., 2008). Apart from Cd which recorded average concentration (2.7 mg/kg dw, Table 5) during the dry season, all other metals were recorded at concentration below World average river and soils (Li, 2000; Pais and Jones, 1997). Significant positive correlation ($p = 0.05, 0.01$) were also noticed between the levels of metals in water and the sediment (Table 6): Cadmium and Cu concentrations in water were observed to be positively correlated ($p = 0.05$) with concentrations of all the metals in sediments except between Cd in water and Zn in sediment. The levels of Pb in water equally correlates positively ($p = 0.01$) with the levels in sediment ($r = 0.951$).

Assessment of the level of sediment contamination was

Table 5. Metals Concentration# (Mean ± S.D, mg/kg dry weight, n = 6) in Sediments and PACS-2 SRM.

Locations	Cd	Cu	Pb	Zn
SRM*				
Tue value	NI	310	183	364
Recovery	-	319	169.1	372
Sediment				
Oluwa	nd	4.2 ± 1.1	1.5 ± 0.8	8.3 ± 0.3
	nd	(3.8 ± 1.3)	(0.5 ± 0.1)	(4.9 ± 0.4)
I_{geo}	0.0	1.81(1.93)	2.91 (2.91)	4.79 (2.29)
Owena	nd	4.6 ± 0.9	1.5 ± 0.1	3.4 ± 1.3
	nd	(2.1 ± 0.5)	(0.7± 0.4)	(1.4 ± 0.6)
I_{geo}	0.0	1.94(1.07)	2.91 (2.81)	3.50 (0.49)
Ogbese	4.8±0.3	9.3 ± 0.4	2.5 ± 0.1	6.7 ± 0.4
	(1.1±0.1	(6.1 ± 0.1)	(1.5 ± 0.3)	(2.4 ± 0.1)
I_{geo}	0.0	2.95(2.61)	3.64 (3.91)	4.48 (1.26)
Ose	0.6±0.1	4.4 ± 1.3	0.9 ± 0.1	0.3 ± 0.1
	(0.2±0.1)	(2.1± 0.6)	(0.38 ± 0.3)	(nd)
I_{geo}	0.0	1.86 (1.07)	2.17 (1.93)	np
Control	nd	1.2 ± 0.2	0.2 ± 0.1	0.3 ± 0.1
	nd	(1.0 ± 0.3)	(0.1 ± 0.1)	nd
Mean ± S.D				
Dry	2.7 ± 0.2	5.6 ± 0.9	1.6 ± 0.3	4.7 ± 0.3
Wet	0.65 ± 0.1	3.5 ± 0.6	0.78 ± 0.1	2.9 ± 0.1
TEL/ERL[a]	0.6	35.7	35.0	123
PEL/ERM[a]	3.5	197	91.3	315
WAR[b]	1.0	100	100	350
World soils[c]	1.0	5 - 20	2 - 200	10 - 300

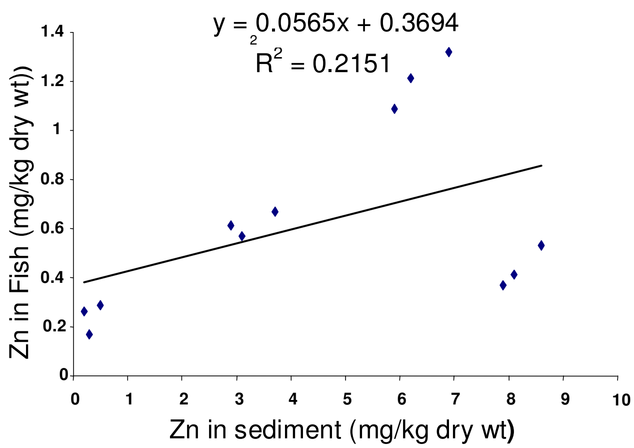
#: Concentrations are mean of triplicate analysis. Values in parenthesis are results of the wet season; SRM: standard reference materials; NI: not indicated; TEL/ERL: threshold effect level/effect range low (PEL/ERM: probable effect level/effect range median. I_{geo}: geoaccumulation Index; nd: not detectable. np = not possible WAR: world average river
[a] MacDonald et al., 2000); [b] Li (2000); [c] Pais and Jones (1997).

based on sediment quality guidelines (MacDonald et al., 2000; Wiotke et al., 2003). These guidelines relate to the potential impact of contaminant on biota and are derived from analyses of relationship between benthic community health and sediment metal concentrations. Two guidelines are given; the effect range low or threshold effect level (ERL/TEL) which represent concentrations of contaminant below which there is a very low probability of effects on the biota and the effect range maximum or probable effect level (ERM/PEL) which represent concentrations above which there is a high (> 50%) probability of adverse effect on the biota. Based on the limited available data (Table 5), apart from Cd which exceeds both the TEL and PEL at Ogbese river, all the other rivers recorded concentrations of the metals at levels far below the TEL and PEL. The increased level of Cd in dry over the wet season couples with the concentration above the PEL calls for proper monitoring because of the associated toxic effects. In order to assess the degree of contamination, the I_{geo} was calculated (Table 5). Applying the classification by previous authors (Muler, 1969; Forstner et al., 1993; Reddy et al., 2004), the tested sediment may be described as moderately contaminated with Cu and Pb but very heavily contaminated with Zn due to mean metal contents especially during the dry season. The I_{geo} seems to be a more objective tool for assessing contamination. Thus, the order of increasing anthropogenic input is Cd < Cu < Pb < Zn.

Bioaccumulation of metals in fish

The results of fish physico-chemical characteristics and heavy metal contents are presented in Table 7. Size, which is related to age, remains an important factor in determining the rate of metals absorption by fish. It has been reported and even recently that certain element either decrease or increase with body length (Evans et al., 1993; Ololade et al., 2007b). In the present study, it was observed that the concentration of Cu in the fish

(a)



(b)

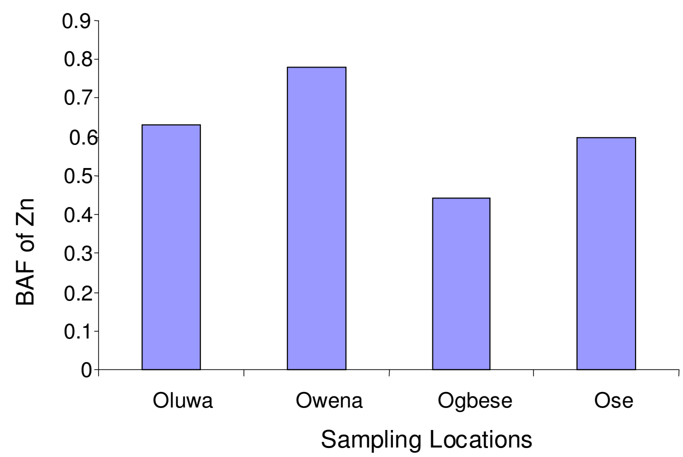
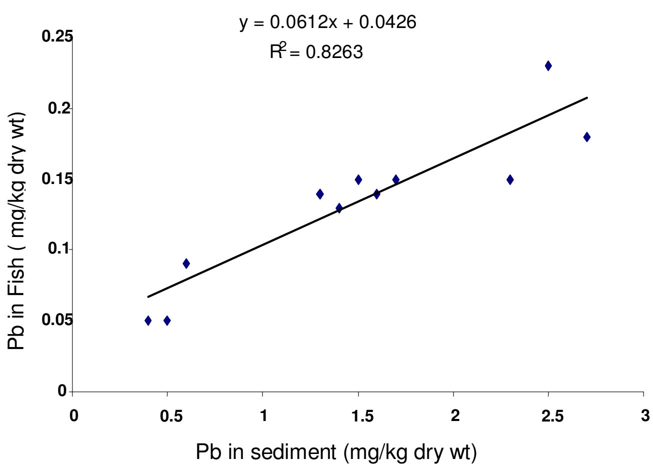


Figure 5a. Plot of Zn (a) and their bioavailability future (b).

(a)



(b)

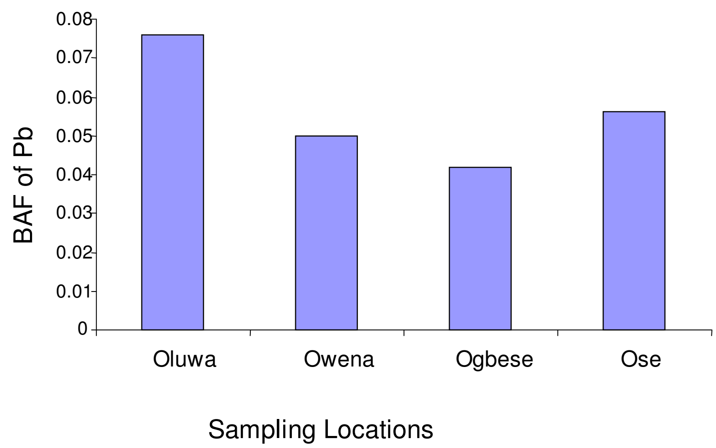


Figure 5b. Plot of Pb (a) and their bioavailability future (b).

flesh decreases with length while concentrations of other metals determined in the study increases with increasing fish length.

Correlation relationships and the bioaccumulation factor (BAF; based on dry weight concentration in fish water) were calculated (Figures 5a - 5d). Apart from Cd and Pb, where significant correlations (R^2 = 0.876 and 0.826 respectively) was recorded, the other two metals did not display any significant correlation (R^2 = 0.798 and 0.215 for Cu and Zn respectively). The BAF for Pb (Fig. 5a) was generally observed to be the least while highest BAF was recorded with Cu (Figure 4b). The study showed that, though, metals like Cd and Pb were detected reasonably in water, the extent of their intake into fish were not very significant as compared with the other two metals.

In this study, Cd was least bioaccumulated (Figure 5c) followed by Zn (Figure 5d) while pronounced sensitivity was observed with Cu. Previous studies supported this conclusion and showed that metals such as Cd bioaccumulate poorly in fish (Bradley and Morris, 1986; Ololade et al., 2007a). In addition, Cd has been shown to record low concentration in tissues (Roesijadi, 1996). The results suggested that bioaccumulation of heavy metals in

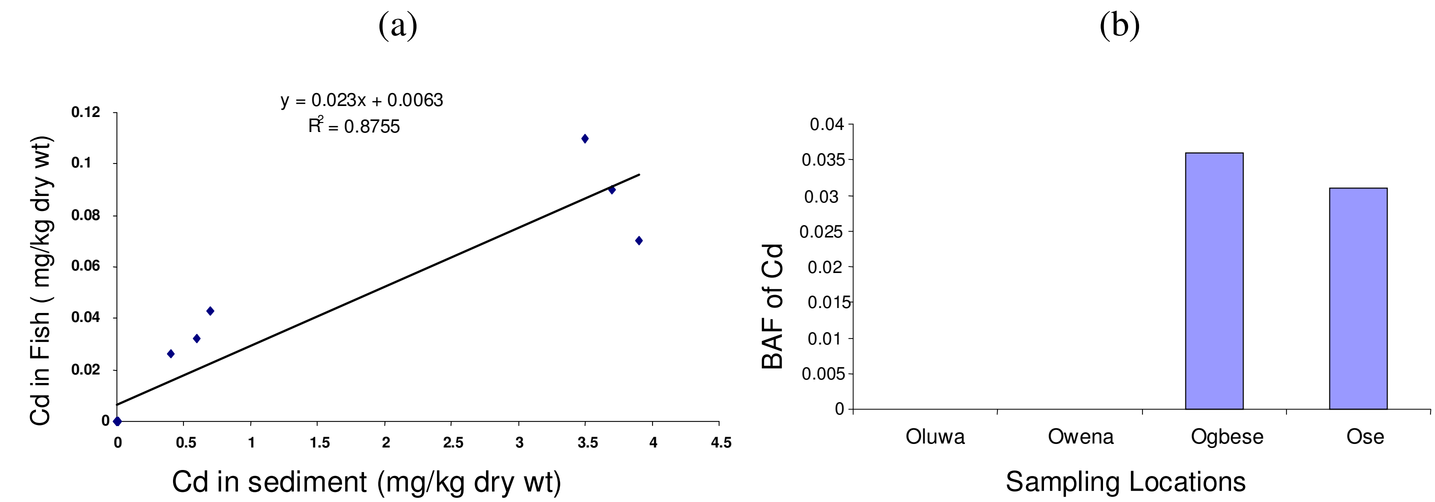


Figure 5c. Plot of Cd (a) and their bioavailability future (b).

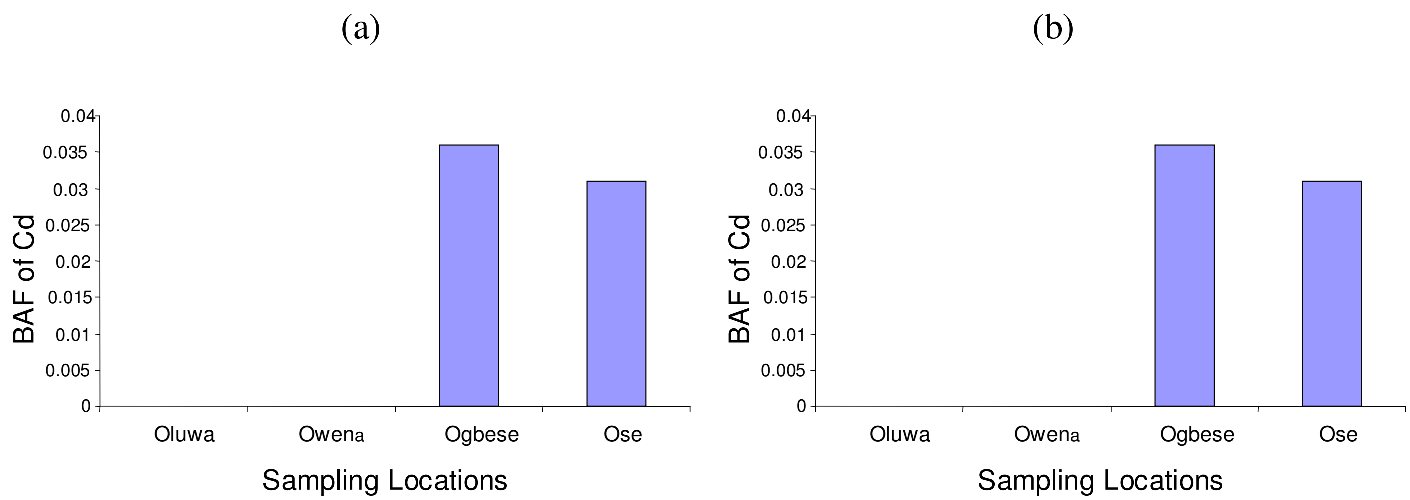


Figure 5d. Plot of Cu (a) and their bioavailability future (b).

Table 6. Correlation matrix of metals in water and sediment[a] (n = 4).

	Cu_s	Pb_s	Cd_s	Zn_s
Cu_w	0.765*	0.768*	0.773*	0.731*
Pb_w	0.550	0.951**	0.584	0.622
Cd_w	0.785*	0.813*	0.784*	0.571
Zn_w	0.002	0.547	0.095	0.281

*Significant at p = 0.05; **Significant at *p*= 0.01; s = sediment; w = water.
[a] mean values of both seasons.

fish varies depending upon their chemical properties. Generally, Cd can get into human body through eating of contaminated fisheries resources such as fish and drinking of water. However, only about 5 to 10% of ingested Cd is actually absorbed by the body, the majority is passed out of the body in feaces (Agency for Toxic Substance and Disease Registry, ATSDR, 1999). As it appears in the study (Table 7), Cd concentration ranged from; nd - 0.09 mg/kg; which is considered higher at some locations like Ogbese and Ose, than the health guidelines in fish. The oral health guideline for Cd is based on a toxicokinetic model which predicts that an adverse health effect would result in people chronically exposed to 0.01 mg/kg/day of Cd in their food (National Academy of Science, NAS, 2001). Consequently, with exposure frequency of almost 365days/year for a population that eat fish seven (7) times a week, the levels obtained at Ogbese and Ose thus become a matter of

Table 7. Physico-Chemical Characteristics and Concentrations (Mean ± S.D, mg/kg dw, 7 ≤ n ≤ 10) of Metals in Fish.

Site	MWW*	ML*(cm)	Cd	Cu	Pb	Zn
Oluwa	65.9 ± 2.5	19.4 ± 0.5	nd	0.86 ± 0.13	0.11 ± 0.03	0.47 ± 0.12
Owena	70.3 ± 3.6	21.6 ± 0.3	nd	0.42 ± 0.04	0.13 ± 0.04	0.63 ± 0.06
Ogbese	67.4 ± 3.1	18.1 ± 0.6	0.09 ± 0.03	3.14 ± 0.07	0.19 ± 0.05	1.28 ± 0.07
Ose	66.2 ± 2.7	14.3 ± 0.2	0.03 ± 0.01	2.11 ± 0.27	0.07 ± 0.12	0.21 ± 0.08
Control	64.3 ± 3.8	18.6 ± 0.2	nd	0.01 ± 0.01	nd	0.01 ± 0.01

*mean ± standard deviation, ML = mean length, MWW = mean wet weight.

concern especially for a growing child. In addition, the World Health Organization (WHO) has established a provisional tolerable weekly intake (PTWI) for Cd at 7 µg/kg of body weight. This PTWI weekly value corresponds to a daily tolerable intake level of 70 µg of Cd for the average 70 kg man and 60 µg for the average 60 kg woman. From Table 7, the daily Cd intake for the generalpopulation from the fish analyzed in the study (nd - 0.09 mg/kg) particularly from Ogbese and Ose is well above the guidelines established by WHO.

Copper is an essential element for good health because it aids in the absorption and utilization of iron and in the production of haemoglobin (NAS, 2001). However, even when the body is very good at regulating how much copper enters the bloodstream, very large single or daily intake can cause harmful effects (NAS, 2001). With the level obtained in the study which ranged from 0.42 - 3.14 mg/kg, consumption of the average concentration of Cu from the various sources may result in daily dose increase.

Zinc is an essential nutrient that is needed by the body for several reasons. It is considered as one of the most abundant trace metal in the body. Based on recommended daily dietary allowance of 5mg/day in infants and 10/15 mg/day in children/adults kg (NAS, 2001), the concentration range in fish (0.21 - 1.28 mg/kg) as obtained in this study is not expected to cause any harm to the body. The muscle and bone contain about 90% (60 and 30% respectively) of the total amount of Zn in the body (ATSDR, 1994). Zinc was detected below health guidelines across the entire study areas. Consequently, eating fish from the various rivers on a daily basis would not result in harmful health effects due to Zn.

Accumulation of Pb in fish is of serious environmental concern. Age among human remains a major factor in determining the extent of Pb absorption. More lead has been reported to enter bloodstream of children than adults through the consumption of Pb-contaminated fish (ASTDR, 1999). This is probably due to higher rate of detoxification (≈ 99%) of the metal in adults through the urine and feaces compared to 65% being detoxified in children. The range of mean concentrations of Pb obtained in the study (0.07 - 0.19 mg/kg) across all the rivers between the two seasons is of serious concern. This is based on the fact that the tolerable daily intake of Pb is 25 µg/kg body weights which are very far below the range of Pb concentrations observed in fish in the study.

Conclusion

In developing countries like Nigeria, where large population may be dependent on raw water for drinking purpose without any treatment whatsoever, especially of significance to human health, the level of some of the water quality parameters at some of the sampling locations as obtained in this report deserves urgent attention. There is therefore an urgent need for a holistic concept of water management, including the ecosystem approach in solving the deteriorated state at some locations, the service of which cannot be avoided at the moment.

The bacterial quality of urban receiving waters is usually of great interest because of the very high levels of indicator microorganisms that occasionally are detected and the elevated levels that are commonly detected as observed in this study. It is therefore important that additional data be collected and that sources of pathogens, along with their fates, are identified in the various rivers so that accurate risk assessments and control strategies can be developed. This is especially critical as children are the ones most likely to be exposed to these contaminated waters during casual play activities such as swimming.

Consequent upon the result of the study, particularly at Ogbese river, there is the need for the development of biocriteria that expresses water quality criteria qualitatively in terms of the resident aquatic community structure and functions. The biocriteria in this concept are measures of biological "integrity" that can be used to asses cumulative ecological impact from multiple services and stress agents as observed in the present study. Our method could be improved by increasing the number by toxins analyzed and by extending the metal analysis to other fish species and other edible marine organisms such as crabs and periwinkles. It is also hoped that metal generation in sediment through speciation analysis will be more informative on the level of bioavailable metal.

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