



Research Article

Phosphorus Speciation and Heavy Metal Levels in Ogun River Sediments at Different Anthropogenic Locations in Abeokuta, Ogun State

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Abstract

Phosphorus (P) is an essential nutrient for phytoplankton growth in water bodies and an important element in biochemical processes. Also, excessive P in river causes eutrophication which endangers aquatic organisms while sediment acts as sink for inorganic and organic pollutants and nutrients. To assess the availability of P and heavy metals (HMs) in Ogun River, surface sediment samples were collected at twelve anthropogenic sites for three months. The surface sediment samples were sequentially extracted to determine five phosphorus fractions [loosely-sorbed P (LS-P), iron-bound P (Fe-P), authigenic apatite, biogenic apatite and CaCO₃-bound P (CFA-P), detrital apatite (Det-P) and other inorganic P (IP) as well as organic P (OP)] and levels of selected HMs (Pb, Cr and Zn). Phosphorus fractions were determined spectrophotometrically and HMs were determined using atomic absorption spectrophotometer (AAS) after wet digestion. The average percentages of fractions of P in surface sediments were Det-P (34.66±1.00%) > Fe-P (27.67±0.02%) > OP (18.11±2.00%) > authigenic apatite, biogenic apatite and CaCO₃-bound P (14.38±4.56%) > LS-P (5.18±0.78%). It was observed that IP was dominant (86.38%) of the total phosphorus (TP) compared to OP (13.62%). One of the sites, Garri processing, had highest TP (710 µg P g⁻¹) which was above the standard values for Chinese Environmental Dredging (500 µg P g⁻¹) and Canadian Province of Ontario (600 µg P g⁻¹) Sediment Quality Guidelines (SQG). The mean concentrations of HMs determined in sediments were below the SQG values except Zn in some sites. The results revealed moderate pollution of P and Zn and also, accumulation of these pollutants overtime might pose threat to aquatic organisms. The results obtained would serve as baseline values for P speciation in Ogun River.

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Introduction

Phosphorus (P) is an important element in the global biogeochemical cycle [1–2]. It is largely introduced anthropogenically into streams, rivers and lakes through urban activities, intensive land use and disposal of agricultural, industrial and domestic wastes; thus affecting benthos as well as chemistry and communities of the water bodies through a variety of direct and indirect processes including eutrophication, reduced

light penetration, suffocation of aquatic habitat, introduction of pollutants like pesticides, metals and nutrients, proliferation of diverse aquatic plants and also acceleration of biochemical processes [3–4]. Important macro-nutrients like nitrogen and phosphorous are continuously being interchanged between sediment and overlying water [5–6]. Studies have revealed that sediments found in water bodies can act as internal source of phosphorus as well as other nutrients and an

understanding of its form can assist in evaluating its cycling and potential impact on water quality [7]. Also, physical, chemical, and biological conditions of sediment like granulometric composition and changes in conditions can induce transformation and release of nutrients like inorganic and organic phosphorus from river sediments [8]. Such P can be in several chemical forms [9] and have been measured by different sequential extraction schemes (phosphorus fractionations), which ultimately allocate phosphorus cycle and bioavailability in rivers [7, 9]. Information on composition of P fractions in sediments is necessary to understand its bioavailability, how excess of it can cause eutrophication in rivers and how it affects diversity of microbial community [10].

A wide range of contaminants are continuously being introduced into the aquatic environment mainly due to increased industrialization, technological development, growing human population, oil exploration and exploitation, as well as agricultural and domestic wastes run-off [11–12]. Among these contaminants, heavy metals (HMs) constitute one of the most dangerous groups because of their persistent nature, toxicity, tendency to accumulate in organisms, food chain amplification potential and non-degradability [13]. Besides, heavy metal pollution has drawn much attention due to its potential health effects on humans living in rural and urban areas as well as the environment [14]. Ogun River cuts across three States characterized by massive population and immense industrial development. Many dwellers without easy access to clean water depend on this River for various life-sustaining activities such as fishery, bathing and recreation. However, these valuable but vulnerable ecosystems are highly impacted by increasing human activities that enrich the river with nutrients which can result to algal blooms [17]. Studies have investigated levels of selected metals and nutrients like phosphate and nitrate in sediment of Ogun River

[15–16]. However, no studies have been done on P speciation in Ogun River except the study conducted in sediments of rivers in Ibadan, South-Western Nigeria [29]. The objective of this study was to determine the speciation of P and assess the levels of selected heavy metals (Pb, Cr and Zn) in sediment of Ogun River in Abeokuta, Ogun State, Nigeria. It was expected that results obtained, especially for phosphorus speciation, would be reference values for further studies in Ogun River.

Materials and methods

1) Description of the study area

Ogun River, part of which was studied, rose near Shaki, Oyo State, at latitude $8^{\circ}33' N$ to $8^{\circ}41' N$ and longitude $3^{\circ}22' E$ to $3^{\circ}28' E$ and flowed through Ogun State into Lagos Lagoon, Lagos State. It had a total area of 22.4 km^2 and a fairly large flow of about $393 \text{ m}^3 \text{ sec}^{-1}$ during wet season [17]. Its source was Igaran Hills, at about 530 m above the mean sea level and it flowed directly southwards over a distance of about 480 km. The River was crossed by Ikere Gorge Dam at Iseyin Local Government Area of Oyo State. Ogun River is underlain by sedimentary Abeokuta formation which consists mostly of sandstone of medium to coarse grain, poorly sorted and micaceous. There are clay and mudstone intercalations; cross bedding is common and the rock is soft and friable, except where cemented locally by ferruginous materials. The main sedimentary rocks are the alluvial deposits and coastal plain sands both of quaternary age. It supported major artisanal fishery activities, especially in Ogun and Lagos States of Nigeria. It served as a route for traders carrying goods by canoe between Abeokuta and Lagos Colony and was used as a means of transportation within the area. In densely populated areas, it was used for bathing. Figure 1 shows the map of study area.

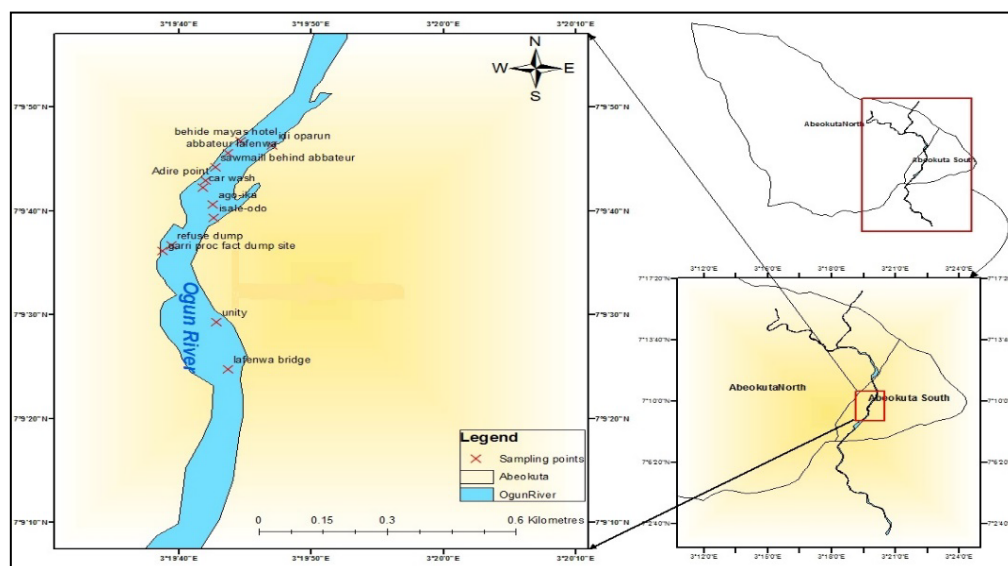


Figure 1 Map of study area showing sampling points.

2) Sample collection, preparation and analysis

2.1) Collection

A total of two hundred and sixteen (216) surface sediment samples were collected from 12 different sites along Ogun River at a depth of 10 cm using a Van Veen grab sampler into labelled polyethylene bags. The sampling period covered three months (November, 2013 – January, 2014), spanning through dry season; a period characterised by easier access to river sediment than wet season due to a decrease in water level. The samples were then transported to the laboratory, air-dried at room temperature, homogenized and sieved through 2 mm mesh sieve to remove refuse and small stones. The code for sample from each site and the main anthropogenic usage are IDO (Idi-Oparun)- Locust bean processing, AGI (Ago-Ika)- Locust bean processing, LAB (Lanfenwa)- Abattoir, MAH (Behind Mayas Hotel)- Abattoir, BEA (Beside abattoir)- Sawmill, LAD (Lanfenwa)- Adire (Tyeing and Dyeing), LCW (Lanfenwa)- Carwash, ISO (Isale-Odo)- Locust bean processing, RED- Refuse dumpsite, LGP- Garri processing dumpsite, LNB- Lanfenwa bridge, UNI (Unity)- Locust bean processing.

2.2) Sequential extraction procedure for sediment sample

Two gram (2 g) of dry surface sediment was sequentially extracted using extraction scheme of Ruttenberg et al. [18]. This involves a five-step extraction scheme separating the major sedimentary P into five fractions namely: loosely-sorbed P (LS-P), iron-bound P (Fe-P), authigenic apatite, biogenic apatite and CaCO_3 -

bound P (CFA-P), detrital apatite (Det-P) and organic P (OP). A schematic presentation of the extraction procedure is given in Figure 2. All supernatants were filtered through a 1.50 μm GF/C filter membrane. Phosphorous in each sample was determined by the molybdenum blue/ascorbic acid method [18] and phosphorus in each fraction was measured spectrophotometrically at 725 nm.

2.3) Heavy metals analysis

Heavy metals (HMs) concentration in the sediment samples were determined as this. One gram (1 g) sediment sample was weighed into a 250 mL conical flask and 30 mL of a mixture of concentrated nitric acid, perchloric acid and sulphuric acid in ratio 3:2:1 was added. The content was boiled till a colourless solution was observed and then allowed to cool. The digest was then filtered into a pre-cleaned plastic bottle using a 5 mm Whatman filter paper according to the method of Woitke et al. [19]. HMs were analyzed using Buck Scientific 210 Model atomic absorption spectrophotometer (AAS) at the most sensitive analytical spectral lines of the metals (Zn-213.9 nm; Cr-357.9 nm and Pb-283.3 nm). A recovery study of the analytical procedure was carried out by spiking and homogenising already analysed solid sample. Samples of 3 g each were randomly selected from among the 12 samples collected from different anthropogenic locations and spiked with appropriate amounts of standard solution of the metals and then analysed. Average recoveries obtained were $92.25 \pm 1.30\%$ Zn, $94.34 \pm 5.12\%$ Cr and $97.60 \pm 3.50\%$ Pb.

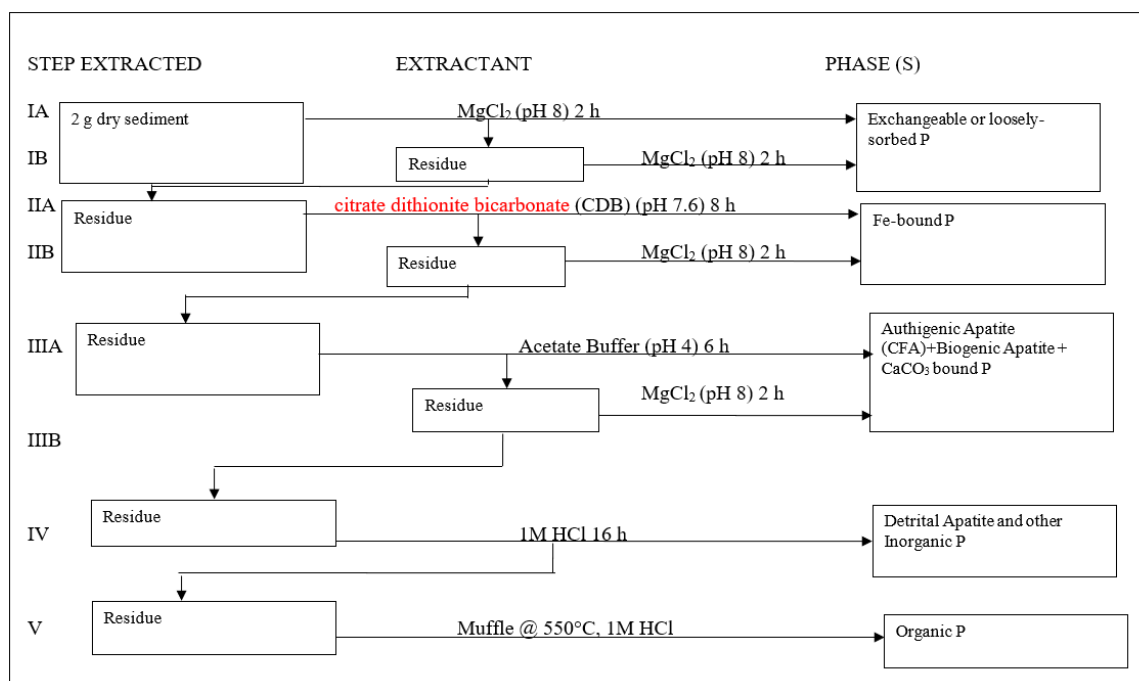


Figure 2 Schematic diagram of the extraction process for speciation of inorganic and organic phosphorus.

2.4) Calculation of pollution indices

Pollution load index (PLI), contamination factor (CF) and Geo-accumulation index were got using Eq. 1, 2 and 3 respectively and computed with Microsoft Excel 2007 version.

$$P_{LS-P} = \frac{(C_{Pb} \times C_{Zn} \times C_{Cr})^{\frac{1}{3}}}{C_{Pb} \times C_{Zn} \times C_{Cr}} \quad \text{Eq. 1}$$

Contamination factor (CF) expresses the level of contamination of heavy metals in sediments while Pb = Lead, Zn = Zinc and Cr = Chromium.

CF is derived from background or baseline concentration of the element of interest in an unpolluted area [20,21] and is expressed by Eq. 2.

$$CF = \frac{C_{metal} (mg\ kg^{-1})}{C_{background\ value} (mg\ kg)^{-1}} \quad \text{Eq. 2}$$

Where $CF < 1$ means low contamination; $1 \leq CF < 3$ indicates moderate contamination; $3 \leq CF \leq 6$ represents considerable contamination and $CF > 6$ means very high contamination. C_{metal} sample concentration and $C_{background}$ is background concentration ($mg\ kg^{-1}$) value.

Geo-accumulation Index (I_{geo}) quantitative approach was used to quantify the degree of anthropogenic contamination in sediments. I_{geo} values enable assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers. The I_{geo} for each analysed metal was calculated using the Eq. 3.

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right) \quad \text{Eq. 3}$$

where C_n = the measured concentration of element in sediment, B_n = the element's content in average shale (background concentration) [22] and 1.5 is a constant.

3) Statistical analysis

Data were analyzed using the Statistical Package for Social Scientists (SPSS 16) software, one-way ANOVA, Duncan's multiple range tests and Pearson's correlation index.

Results and discussion

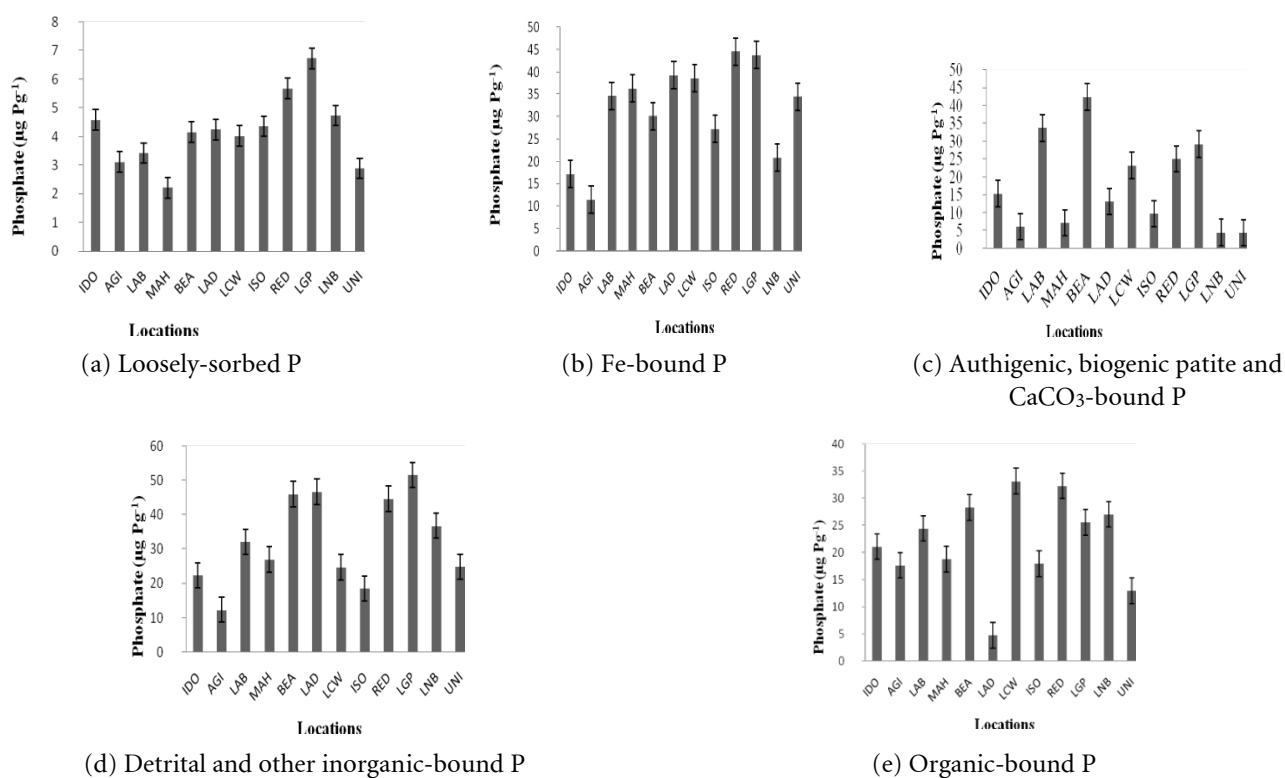
1) Phosphorus speciation

Mean concentrations of the forms of phosphorus at different sites are shown in Figures 3(a-e). LGP

had highest LS-P ($6.73 \pm 4.11\ \mu g\ P\ g^{-1}$) while MAH was lowest ($2.21 \pm 0.36\ \mu g\ P\ g^{-1}$) (Figure 3a). A considerable fraction of loosely-sorbed P is potentially bioavailable and it can be easily released into the water column through desorption processes. On average, the LS-P accounted for $5.18 \pm 0.78\%$ of total phosphorus (TP) and lowest fraction of P obtained. LS-P was the lowest fraction agreed with the findings of [7] and [23] and this value 5.18% of TP was within the range (1.01–15.6%) observed by [23]. It however disagreed with 0.8–2.0% reported by [24] in a similar work. This was probably due to the rocky nature of Ogun River which could make the granulometric composition different. The extent of such release depends on the phosphate concentration as well as other environmental conditions, such as temperature and salinity [24].

Iron-bound P (Fe-P) concentration ranged from (11.47 ± 2.34 to 44.55 ± 9.54) $\mu g\ P\ g^{-1}$ (Figure 3b). Fe-P fraction represents the redox-sensitive P fraction which is mainly bound to iron (Fe), and was considered as potentially mobile pool of P [25]. Due to its low solubility in aquatic environments, Fe is predominantly found in the colloidal and particulate forms. Among the various types of natural particles, iron hydroxide and iron oxides have strongest adsorption capacity for phosphate [24]. The average concentration for all locations was $30.57 \pm 12.55\ \mu g\ P\ g^{-1}$ and it was second in abundance after the detrital apatite P with $27.67 \pm 0.02\%$ of TP. The average concentration of Fe-P obtained in this study was within the value ($33.2\ \mu g\ P\ g^{-1}$) found in Daya Bay, China [23]. Iron hydroxide content in sediments and suspended matter might be an important factor in regulating phosphorus retention capacity of sediments.

The authigenic apatite, biogenic apatite and $CaCO_3$ -bound P at the 12 sites varied (Figure 3c). It was observed that the mean concentration of CFAP was highest ($42.37 \pm 16.95\ \mu g\ P\ g^{-1}$) at BEA and lowest ($4.48 \pm 2.41\ \mu g\ P\ g^{-1}$) at LNB. Authigenic phases such as carbonate are formed from phosphate released during the mineralization processes or the dissolution of iron oxides. The CFAP was $14.38 \pm 4.56\%$ of TP. Its mean concentration for all samples was $15.88 \pm 9.21\ \mu g\ P\ g^{-1}$, whereas Maslukah et al. [10] reported this fraction as the most abundant in a similar study. Since this fraction is generally derived from residual bones and teeth of dead marine organisms, it was low in this study probably due to the composition of the deposit and the type of rock formation in the area [26].



Figures 3(a-e) Concentrations of forms of phosphorus at different sampling sites.

Average concentration of detrital apatite P for all points was $38.28 \pm 12.78 \mu\text{g P g}^{-1}$ and it ranged from $12.32 \pm 0.73 \mu\text{g P g}^{-1}$ to $57.59 \pm 3.00 \mu\text{g P g}^{-1}$ (Figure 3d). The average percentage of Det-P was $34.66 \pm 1.00\%$, representing the largest fraction of the TP. It was highest in LGP and lowest in AGI sites of Ogun River. It is basically due to the parent material, however, it may be enhanced by various anthropogenic activities. The result of this study agreed with that of Yuan et al. [27] who reported this fraction as the largest P pool, but was within the values reported by Liu et al. [24] that ranged from 35–66%. The lower values obtained in this study might be due to rock formation as well as difference in geological locations [26].

Any P in the remaining solid residue (after the HCl extract had dissolved all inorganic forms of P) was considered to be refractory organic phosphorus (ROP). This ranged from 4.71 – $33.14 \mu\text{g P g}^{-1}$. On average, this constituted 18.11% of total sedimentary phosphorus and was the third largest pool of TP. The % value obtained in this study was below the organic P (OP) of 30% in Bohai and Yellow Seas reported by Liu et al. [24]. The concentrations of OP at all sites are presented in Figure 3e. The highest ($33.14 \pm 14.97 \mu\text{g P g}^{-1}$) fraction of organic P was found at LCW and lowest ($4.71 \pm 0.75 \mu\text{g P g}^{-1}$) at LAD. The mean concentration was $20.00 \pm 6.36 \mu\text{g P g}^{-1}$.

Inorganic and organic phosphorus

IP was the sum of LS-P, Fe-P, Det-P and CFAP and found to be the major constituent of TP at all sampling

sites and the major constituent of the total extractable phosphorus from 11 of the 12 sites. Average P concentration in sediment and range of concentrations of TP and IP obtained in this study compared to the concentrations reported in similar rivers from some parts of the world are presented in Table 1. IP and OP ranged from 161 to $633 \mu\text{g P g}^{-1}$ and 14.12 to $99.42 \mu\text{g P g}^{-1}$ respectively; the former was much higher than OP which could be due to a high rate of mineralization of OP. The general trend was that the IP concentrations from all sampling sites were higher than maximum value obtained for OP at LCW. IP has been found to be an important source of bioavailable P in sediments [7]. The results of this study showed that IP was the most available form of P, representing 86.38% of the TP. The IP of this study can be categorized into three different anthropogenic activities based on their concentrations. The first categories were: LGP, RED, BEA and LAB and concentrations ranged from $527 \mu\text{g P g}^{-1}$ at LAB to $633 \mu\text{g P g}^{-1}$ at LGP. The second categories were: ISO, UNI, MAH, LCW and LAD. Their concentrations ranged from $304 \mu\text{g P g}^{-1}$ at ISO to $480 \mu\text{g P g}^{-1}$ at LAD. The third categories were: AGI, IDO and LNB with mean concentrations of 161, 290, and $291 \mu\text{g P g}^{-1}$ respectively. High IP has been attributed to different P sources, integration and development in time [4]. Besides, it could be due to both internal and external factors of calcite formation and phosphorus precipitation as well as human activities at the various sites. The % of IP obtained in this study was within the % values of 51.0–89.9% and 83.4–

93.4% of TP respectively in sediments of Daya Bay, China, and basin of Marcus-Wake Seamounts, Western Pacific Ocean reported by Liao et al. [23] and Liao et al. [27].

Bioavailable phosphorus

The LS-P, Fe-P and organic P are easily released from the sediments to the water column therefore, they were considered as bioavailable forms of P for phytoplankton uptake. The bioavailable P in this study constituted by LS-P, Fe-P and OP, represented 50.96% of total sedimentary P pool in Ogun River. The value obtained in this study was within the range value (34–60%) of TP reported by Gurung et al. [7].

Concentration of OP ranged from 14.12 $\mu\text{g P g}^{-1}$ to 99.42 $\mu\text{g P g}^{-1}$ at LAD and LCW respectively. The concentration of OP was low compared with the concentration ranges of Fe-P, CFAP and Det-P. Percentage concentration (13.62%) of OP found in this study was within the concentration of 15.10% reported by Zhang et al. [28] in Erhai Lake but lower than 23.77–30.63% and 25.5% reported Maryland Coastal Bay, Daya and Bohai and Yellow Seas [7, 23–24]. Supplementary Material (SM) 1 shows the correlation of different P fractions. There was a significant positive correlation of detrital apatite and other inorganic P with loosely-sorbed P and also with Fe-bound P ($r = 0.625$ and $r = 0.643$ at $p \leq 0.05$). Inorganic P had a significant positive correlation with Fe-bound P and authigenic apatite, biogenic apatite and CaCO_3 -bound P ($r = 0.794$ and $r = 0.807$ at $p \leq 0.01$), suggesting a common source [27].

Total phosphorus

The total phosphorus (TP) concentrations resulting from natural and anthropogenic sources could lead to excess P and cause eutrophication [31]. Canadian Province of Ontario Sediment Quality Guidelines (CSQG) and the Chinese Environmental Dredging Standard (CEDDS) were used to compare results in the sediment [29–30]. Forty-two percent (42%) of the sampling sites had their concentrations higher than threshold for clean sediment values 600 $\mu\text{g P g}^{-1}$ and 500 $\mu\text{g P g}^{-1}$ respectively. The value of TP was lowest (214.24 $\mu\text{g g}^{-1}$) in sample from Ago-Ika (AGI) characterised by locust bean processing and highest (710.23 $\mu\text{g g}^{-1}$) at Garri processing dumpsite (LPG) (Table 1). The sites with high TP values were LAB, BEA, LCW, RED and LGP with concentrations, in $\mu\text{g P g}^{-1}$, of 600, 683, 570, 682 and 710, respectively (Table 1). This showed that there could be high level of ecological toxicity of P to organisms inhabiting sediment at various sites [30]. Yuan et al. [27] and Onianwa et al. [29] had reported high TP values in accordance with the results of this study while the concentrations obtained in this study were within the range of 291.9–1,653.4 mg kg^{-1} observed by Barik et al. [25]. The concentrations of TP and IP obtained in this study compared well with concentrations reported in similar rivers from some parts of the world (Table 1). Also, the values reported in this study were within Maryland Coastal Bays, USA and Chilika Lake, India values. Percentage recovery of TP ranged from 90.64 to 94.70% and had a mean of $93.10 \pm 1.89\%$.

Table 1 Concentration of the forms of phosphorus at the sampling sites and comparison of concentrations of P speciation found in literature for some coastal / river sediments and this present study

Sampling sites	IP ($\mu\text{g P g}^{-1}$)	OP ($\mu\text{g P g}^{-1}$)	TP ($\mu\text{g P g}^{-1}$)	Anthropogenic sites
IDO	290.47	63.32	353.78	Locust beans processing
AGI	161.30	52.94	214.24	Locust beans processing
LAB	527.05	73.30	600.35	Abattoir
MAH	355.89	56.35	412.23	Abattoir
BEA	598.12	84.92	683.05	Sawmill
LAD	480.43	14.12	494.55	Adire
LCW	469.42	99.42	568.84	Carwash
ISO	304.25	53.85	358.10	Locust beans processing
RED	585.91	96.88	682.79	Refuse Dump site
LGP	633.43	76.80	710.23	Garri processing dumpsite
LNB	291.11	81.15	372.26	Lanfenwa Bridge
UNI	325.56	38.85	364.41	Locust beans processing
CSQG	600			
CEDS	500			
Study area		TP ($\mu\text{g P g}^{-1}$)	IP ($\mu\text{g P g}^{-1}$)	Reference
Maryland Coastal Bays, U.S.A.		153.6-1668.8	135.3-1113.2	[7]
Andong Salt Marsh, China		91.30-196.99	86.67-188.41	[9]
Daya Bay, China		290.3-521.1	294.5	[23]
Southern Baltic Sea, Europe		233-512	174-481	[30]
Chilika Lake, India		243.97-2150.55	115.04-1730.44	[31]
Ogun River, Abeokuta, Nigeria		214-710	161-633	Present Study

Remark: IP = Inorganic phosphorus; OP = Organic phosphorus; TP = Total phosphorus

2) Levels of heavy metals in sediment

Mean concentration of heavy metals in sediment samples is presented in Table 2. Pb ranged from $4.80 \pm 0.12 \text{ mg kg}^{-1}$ at LNB to $22.04 \pm 0.00 \text{ mg kg}^{-1}$ at RED. The United States Environmental Protection Agency (USEPA) has classified Pb as being potentially hazardous and toxic to most forms of life. The value was below the limit of 300 mg kg^{-1} by European Commission (EC), Probable Effect Limit of 91.3 mg kg^{-1} set by Canadian Freshwater Sediment Guidelines and 48 mg kg^{-1} given as World River Sediment Background Concentration reported by [33–34]. Pb concentration ($22.04 \pm 0.01 \text{ mg kg}^{-1}$) was highest at RED where Fe-bound fraction was also highest. Pb therefore was possibly associated with Fe-bound fraction as observed by [35]. Similar works have reported lower concentrations of Pb ($0.449\text{--}3.330 \text{ mg kg}^{-1}$) in sediment of Jeneberang Waters [36] and ($12.3 \pm 5.0\text{--}16.6 \pm 3.80 \text{ mg kg}^{-1}$) in reservoir of Gda sk, Poland [35]. Pb concentration obtained in this study disagreed with higher concentration of Pb ($25\text{--}70 \text{ mg kg}^{-1}$) reported in Inaouene Watershed, Northern Morocco [37]. Besides, mean concentration of Pb in this study was below the Threshold Effect Level (TEL) of 35 mg kg^{-1} [38] and was significantly different ($p \leq 0.05$) across the sampling sites. Highest ($11.68 \pm 0.26 \text{ mg kg}^{-1}$) Cr was obtained at LCW while lowest ($4.42 \pm 0.08 \text{ mg kg}^{-1}$) was at ISO. The highest concentration could be as a result of the use of detergents. Total average concentration

of Cr was below threshold effect of Sediment Quality Guideline (SQG) for metals as stated by [38]. Concentrations of Cr obtained for some sites in this study were higher than those reported by [38] who assessed level of heavy metals contamination of surface water and sediment of a tropical manmade lake, Southwestern Nigeria. The results obtained for this study were however generally lower than those ($13.08 \pm 0.58\text{--}97.09 \pm 2.39 \text{ mg kg}^{-1}$) reported by [39] in Raohe Basin, China.

TEL, threshold effect level; ERL, effects range low and LEL, lowest effect level [38].

There was also significant difference ($p \leq 0.05$) in the concentrations of Cr through different sites. Zinc ranged from 7.48 ± 0.01 to $291.84 \pm 0.60 \text{ mg kg}^{-1}$ at LAB and RED respectively. Mean concentrations of Zn in mg kg^{-1} , at three different sites: LAD- 243, RED- 291 and LGP- 252 were two-fold higher than threshold limit of zinc in sediment 123 mg kg^{-1} . Low concentrations of zinc observed in this study in some sites corroborated the report of [39]. Also this finding agreed with that of [40] who reported lower concentration of Zn at Kara abattoir, Ogun River. Sediment from RED had higher concentration of Zn and Pb than other sites. As a refuse dumpsite, waste disposed there could vary widely in type, source, composition and concentration. The levels of Zn and Pb in samples from this site could be due to the waste dump.

Table 2 Mean concentration of heavy metals in sediment (mg kg^{-1})

Location	Lead (Pb)	Chromium (Cr)	Zinc (Zn)
IDO	10.46 ± 0.02^e	6.46 ± 0.04^g	95.57 ± 1.99^e
AGI	10.45 ± 0.05^e	4.94 ± 0.29^h	25.27 ± 0.04^g
LAB	10.03 ± 0.01^f	7.14 ± 0.01^f	7.48 ± 0.01^j
MAH	10.98 ± 0.19^d	8.46 ± 0.02^d	29.34 ± 0.51^f
BEA	6.40 ± 0.12^i	8.32 ± 0.05^d	95.68 ± 0.22^e
LAD	14.62 ± 0.34^b	10.54 ± 0.06^b	243.44 ± 0.07^c
LCW	9.92 ± 0.36^f	11.68 ± 0.26^a	20.16 ± 0.04^i
ISO	6.97 ± 0.07^h	4.42 ± 0.08^i	21.08 ± 0.57^h
RED	22.04 ± 0.01^a	9.88 ± 0.10^c	291.84 ± 0.60^a
LGP	12.48 ± 0.45^c	7.20 ± 0.06^f	252.00 ± 1.73^b
LNB	4.80 ± 0.12^j	8.00 ± 0.00^e	101.28 ± 0.54^d
UNI	7.65 ± 0.27^g	4.76 ± 0.15^h	20.06 ± 0.59^i
TEL ¹	35	37.3	123
ERL	35	80	120
LEL ²	31	26	120

*Mean \pm SD are values of three replicates. Different superscripts in the same column indicate significant difference at $p \leq 0.05$.

Values of contamination factor (CF), pollution load index (PLI), geo-accumulation Index (Igeo) and their corresponding contamination concentration for heavy metals in sediments at different sites as well as Muller's Classification for Igeo are presented in Table 3. Eight (8) out of twelve (12) sites studied for Pb had CF values ranged from 0.56 (LNB) to 2.59 (RED) indicating Pb metal enrichment. Similarly, CF values of Zn ranged from 0.11 (LAB) to 4.11 (RED) indicating Zn metal enrichment. Both Pb and Zn CF values showed moderate contamination and it could be deduced from anthropogenic activities at RED, LAD and LGP that contributed to the higher values of CF. For Cr, CF values in all sites ranged from 0.13 to 0.33, showing no Cr metal enrichment and low contamination. PLI values ranged from 0.30 at LAB to 2.61 at LAD. This confirmed that the River sediments were unpolluted at some sites to moderately polluted at some other sites. This provided a simple comparative means for assessing

the quality: a value of 0.0 indicated perfection; a value of 1.0 indicated only baseline levels of pollutants present and values > 1.0 were indicative of progressive deterioration or pollution of the river quality [20]. The PLI could reveal the quality of a component in the environment to the public and show the trend over time. Besides, it also provides valuable information and advice for the policy and decision makers on the pollution level of the area. Moreover, the Igeo value for Pb ranged from -1.41 to 0.79 at LNB and RED while the Igeo value for Cr ranged from -3.57 to -2.17 at ISO and LCW. Also, the Igeo value for Zn was lowest at LAB (-3.83) and highest at ISO (2.34). The results of Igeo for Pb, Cr, and Zn were classified according Muller's scale (Table 3) which showed that the sediment ranged from uncontaminated to moderately contaminated. Over time and with continuous discharge of wastes into Ogun River, the Igeo of Pb and Zn studied might move from moderately contaminated to strongly contaminated.

Table 3 Contamination factor, pollution load index and Igeo values for sediment samples from different anthropogenic activities along Ogun River, Abeokuta as well as Muller's classification for Igeo

Sampling sites	Contamination factor (CF)			PLI	Igeo values		
	Pb	Cr	Zn		Pb	Cr	Zn
IDO	1.23	0.18	1.35	0.67	-0.29	-3.02	-0.16
AGI	1.23	0.14	0.36	0.40	-0.29	-3.41	-2.08
LAB	1.18	0.20	0.11	0.30	-0.35	-2.88	-3.83
MAH	1.29	0.24	0.41	0.50	-0.22	-2.63	-1.86
BEA	0.75	0.24	1.35	0.62	-0.99	-2.66	-0.15
LAD	1.72	0.30	3.43	2.61	0.20	-2.32	1.19
LCW	1.17	0.33	0.28	0.48	-0.36	-2.17	-2.40
ISO	0.82	0.13	0.30	0.32	-0.87	-3.57	2.34
RED	2.59	0.28	4.11	1.43	0.79	-2.41	1.45
LGP	1.47	0.21	3.55	1.03	-0.03	-2.87	1.24
LNB	0.56	0.23	1.43	0.57	-1.41	-2.71	-0.07
UNI	0.90	0.14	0.28	0.33	-0.74	-3.46	-2.41
Average					-0.38	-2.84	-0.95
Igeo class					0	0	0-2
Min.	0.56	0.13	0.11	0.30	-1.41	-3.57	-3.83
Max.	2.59	0.33	4.11	2.61	0.79	-2.17	2.34
Igeo value	Class	Sediment Quality					
0	0	Uncontaminated					
0-1	1	Uncontaminated to moderately contaminated					
1-2	2	Moderately contaminated					
2-3	3	Moderately to strongly contaminated					
3-4	4	Strongly contaminated					
4-5	5	Strongly to extremely contaminated					
6	6	Extremely contaminated					

Remark: IDO (Idi-Oparun)- Locust bean processing, AGI (Ago-Ika)- Locust bean processing, LAB (Lanfenwa)- Abattoir, MAH (Behind Mayas hotel)- Abattoir, BEA (Beside abattoir)- Sawmill, LAD (Lanfenwa)- Adire (Tyeing and Dyeing), LCW (Lanfenwa)- Carwash, ISO (Isale-Odo)- Locust bean processing, RED- Refuse dumpsite, LGP- Garri processing dumpsite, LNB- Lanfenwa bridge, UNI (Unity)- Locust bean processing

Conclusion

Among the five species of P, detrital apatite and other inorganic P was the largest fraction of TP which could be attributed to parent rock and also human activities. Zinc concentration in sediment at LAD, RED and LGP sites were higher than threshold effect level, while other metals were below. From the study, it could be deduced that human activities contributed to the concentration of P fractions and Zn in the River. In addition, accumulation of P and these heavy metals over time may lead to eutrophication and water pollution. Therefore, there is need for relevant authorities to properly manage the Ogun River by ensuring that industries treat their effluents before discharging into rivers. This study would serve as baseline values for P speciation in Ogun River and provide valuable information for policy and decision makers. However, further study to cover both rainy and dry seasons and monitor effect of a high level of flowing water.

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