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Assessment of Sediment Particle Sizes in Relation to Heavy Metal Contamination in the Lagos Lagoon System

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Abstract

Sediments are important in the geochemical cycles of marine and estuarine ecosystems with the ability to influence ecological processes and inhabiting biota. This study assessed sediment particle sizes of the Lagos Harbour and Lagoon system with a view to determine their diversity and influence on heavy metal levels. Samples were collected using Van veen grabs, *viz*; Dry Season 2013 (DS^{-1}), Wet Season 2013 (WS) and Dry Season 2014 (DS^{-2}) for a period of 18 months in the Lagos Lagoon system. The sediments collected were analysed according to the British Standard (BS 1377-2, 1990) at the instrument Physical Geography Laboratory, University of Portsmouth. The mean clay, silt, coarse and sand were found to be 6.67 ± 4.51, 6.0 ± 3.0, 9.17 ± 3.25 and 0.37 ± 3.06 respectively. The particle size in relation with total metals/metalloids concentration in the sediment revealed positive correlation with significant differences ($p<0.05$) between clay and Fe ($r=0.391^*$), clay and Pb ($r=0.40^*$). While the particle size in relation and recoverable metals/metalloids concentration in the sediment revealed positive correlation with significant differences ($p<0.05$) between clay and Mn ($r=0.416^*$), silt and Mn ($r=0.414^*$). The particle size in relation with bioavailable metals/metalloids concentration in the sediment revealed positive correlation with were significant differences ($p<0.05$) between silt and Pb ($r=0.426^*$). This implies that the widespread dredging of the lagoon sediments and artisanal sand mining has had its toll on the structural integrity of the substratum. The strong correlation between the finer particle sizes with total, recoverable and bioavailable fractions of Fe-Mn-Pb in the sediment samples is notable and implies increased chances of retention of pollutants in the sediment matrix.

Keywords: Sustainability • Harbour dredging • Sediment texture • Heavy metal/metalloid • Aquatic pollution

Introduction

Sediments form the physical boundary of depth in water bodies. It is said that marine sediments are products of weathering of pre-existing basement rock aggregates of different types which settle at the bottom of the sea *via* river depositions, wave and wind action [1]. They remain in flux being also deposited by coastal erosion [2] and removed by strong currents into beaches [3].They are well recognized as a main reservoir for many of the persistent organic and inorganic chemicals introduced into the aquatic environment by atmospheric deposition, erosion of the geochemical substrate and from anthropogenic sources [4]. Sediment is known to act as a pollutant sink in aquatic ecosystems [5] and have been noted as stores of hydrophobic pollutants in rivers [6]. They also, are potential sources of pollution for the surrounding water as well as benthic flora and fauna by releasing sorbed contaminants back to the overlying water column should re-mobilization occur through any disturbance [4,7].

Investigation of marine sediments provides important information in marine, environmental and geochemical study about pollution of the marine environment [8]. Sediment is a matrix of materials consisting of detritus, inorganic and organic particles and is relatively heterogeneous in terms of its physical, chemical and biological characteristics [4] and they consist of a varied range of particle sizes, including gravels, sand, silt and clay [9]. The grain sizes and organic matter content are key determinants of presence and availability of heavy metals and trace metals in the sediment [10].

Sediments play a useful role in the assessment of heavy metal contamination [11]. The partitioning behavior of heavy metals is such that they tend to accumulate in sediments to levels that are several orders of magnitude higher than in the surrounding water [12]. The relative texture of sediments affects their respective surface areas and therefore their ability to bid metals with the support of organic complexes they are associated with an understanding of sediment particle sizes in a water body is crucial and a significant factor influencing relative heavy metals distribution, transport and ecological risks.

In furtherance to understanding the complexes which influence total, recoverable and bioavailable metal concentrations in the Lagos Harbor (LH) and associated Lagos Lagoon system, this study therefore is aimed at investigating the relative sediment particle size distributions and the relationship between particle size and the concentration of various heavy metals in the Lagos harbor and Lagos lagoon.

Materials and Methods

Study area

Sampling sites were selected on the basis of the activities such as shipping, sand mining, sawmill industries and recreational/residential within the major sections of the Lagos Lagoon system (i.e Lagos Harbor, urbanized western Lagos Lagoon and Apese Lagoon)as the need for spread to reflect the true picture of the sediment structure (Figure 1). GPS coordinates of each sampling site was taken and recorded; Lagos Harbor (E 003°201 and N 6°261), Lagos Lagoon (E 003°221 and N 6°251), and Apese Lagoon (E 003°271 and N 6°251) in order to produce the spatial distribution maps. Twenty-six sampling sites were established within the study area and across the LH (sites: 1-16), LG (sites: 17-23), and APL (sites: 24-26).Sites were sampled in three seasons,

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namely: Dry Season-1 2013 (DS^{-1}), Dry Season-2 2014 (DS^{-2}) and Wet Season 2013 (WS).

Sampling operations: Sediment samples were collected at the selected sites using a 0.1 m^2 Van-Veen Grab (wt. 25 kg; height-20 cm) and the coordinates marked with the use of a GPS kit (Magellan, Sport rack PRO MARINE [IEC-IPX7 Model]). A composite sediment sample (3 successful grab hauls) were collected for each site. A portion of the top 1-5 cm of the haul was preserved for physical, chemical and other analyses. The labeled samples were placed in Poly-Tetra-Fluoro-Ethylene (PTFE) bottles, bagged and stored in an ice chest cooler at 4°C.

Sample analysis: The stored frozen samples were removed and allowed to defrost on a clean laboratory bench and the analyses for their respective particle sizes. The method used was developed and modified in the School of Earth and Environmental Sciences (SEES), at the University of Portsmouth in line with British Standard (BS 1377-2, 1990) and analyzed using a MASTERSIZER 2000 Laser instrument manufactured by Malvern Instruments, at the Physical Geography Laboratory, University of Portsmouth. This instrument analyses particle size ranges from 0.02 to 2000 µm using a diffraction model based on Mie Theory. Samples were prepared by defrosting to room temperature, with 100 g placed into a glass beaker. Ten mL of H_2O_2 was added to each sample in a beaker to completely remove organic materials. A solution of Hexa-Meta Phosphate (SHMP) and Sodium Hydrogen Carbonate (SHC) added to the samples in each beaker in order to separate the particles.

Heavy metal analysis: The details of the metal analysis protocol are as outlined [13]. Total metal concentrations in sediment samples were analysed using X-ray Fluorescence (XRF) technique based on the method described in the US-EPA Method 6200 (1998) [14]. The extraction of recoverable metals from the sediment samples with aqua regia was carried out using the method described by the National Water Research Institute (NWRI) and analysis was done using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Bioavailable metals were determined using a 1M HCl extraction and (Inductively Coupled Plasma Mass Spectrometry ICP-MS) analysis, as described by Snape, et al. [15].

Geospatial mapping of sediment particle size: The mean value for the measured particle size were estimated and used in the sampled locations of the Lagos harbour, Lagos lagoon and Apese lagoon to perform a geospatial kriging interpolation in the ArcGIS 10.8 software. This gave rise to a spatially explicit map showing the mean particle size of the soil types.

Statistical analysis: The results obtained were presented as mean standard error and differences in particle sizes at the respective zones were compared using two-way Analysis of Variance (ANOVA) SPSS Version 21. Significant differences were set at $p<0.05$ while LSD was used in post-hoc analysis to separate significant means. Pearson's correlation coefficient was done using normalized data to determine relationship between particle sizes and determined heavy metal concentrations.

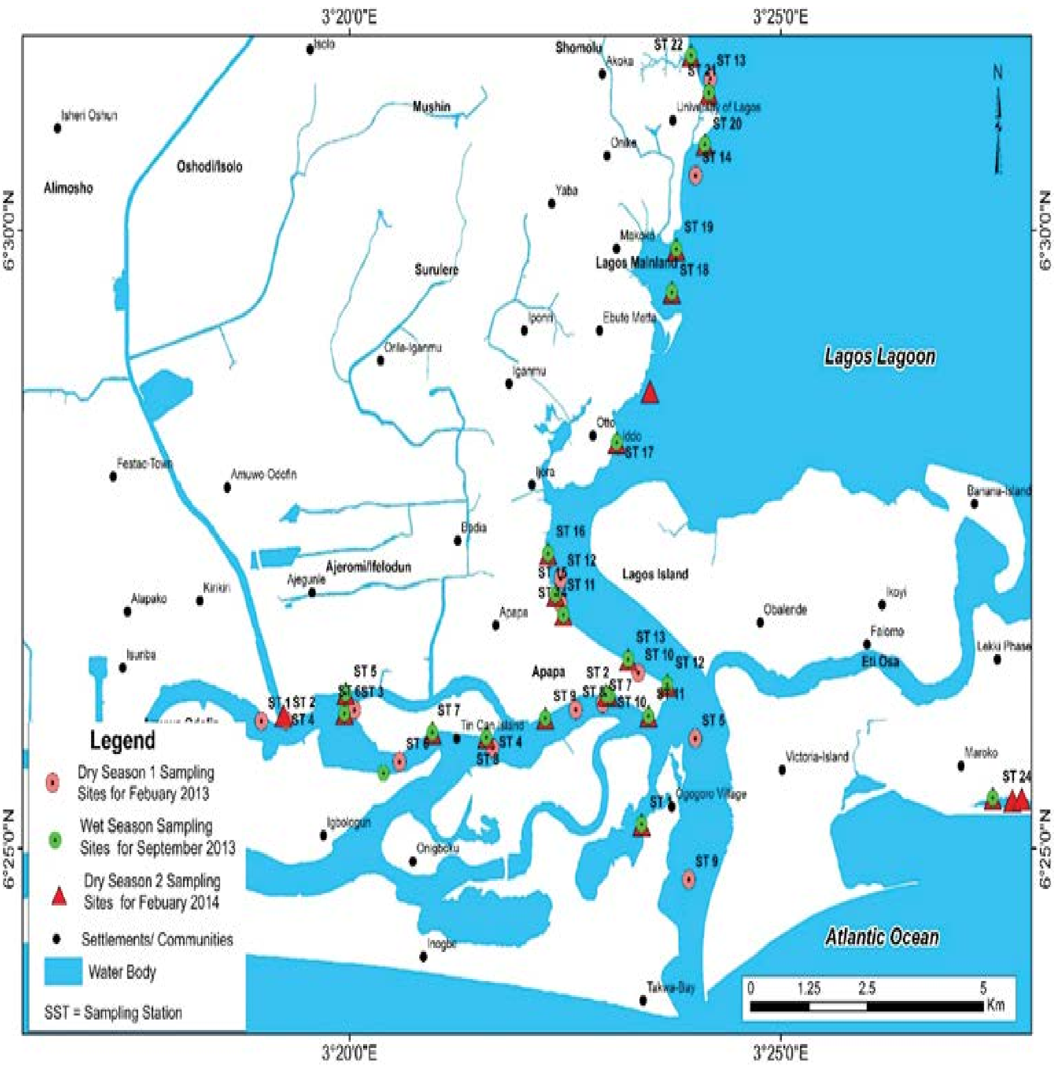


Figure 1. Sampling locations within the Lagos Lagoon system toxicity analysis.

Note: Dry Season 1 Sampling sites for February 2013, Wet season sampling sites for september 2013, Dry season 2 sampling sites for February 2014, Settlements/ Communities, Water Body, SST= Sampling Station

Results

Distribution of sediment particle sizes

The measured particle sizes were categorized as clay, very fine silt, fine silt, medium silt, coarse silt, very fine sand, and fine sand, medium sand and coarse sand. However, analysis was focused on the main categories being clay, silt, coarse and sand particles.

The mean clay, silt, coarse and sand were found to be 6.67 ± 4.51, 6.0 ± 3.0, 9.17 ± 3.25 and 0.37 ± 3.06 respectively (Figure 2). There was significant difference ($p<0.05$) between clay and sand constituents in the sediments with the former being significantly higher. Likewise, coarse and sand particles were also significantly different in distribution.

Distribution of grain particle size: The distribution of the sand particle grain size in the three distinct sample locations, the Lagos harbour, Lagos Lagoon and Apese Lagoon varied geographically. The Lagos harbour was observed to have a mean particle size of 10.77 µm, which was the lowest and increased progressively toward the Lagos lagoon and Apese lagoon, with the mean particle size of 14.305 µm and 15.368 µm respectively. Furthermore, the distribution of the silt particle grain size in the three sample sites varied with Apese lagoon mean measured at 5.37 µm. The spatial explicit map shows the progressive increase in mean particle size away from Apese lagoon towards the Lagos lagoon and Lagos harbour with mean values of 8.8 µm and 10.87 µm respectively. Finally, the clay soil had a mean particle grain size of 1.63 µm at Apese lagoon and exponentially increased to 7.53 µm at the Lagos lagoon and further increased to 10.84 µm at the Lagos harbour (Figure 3).

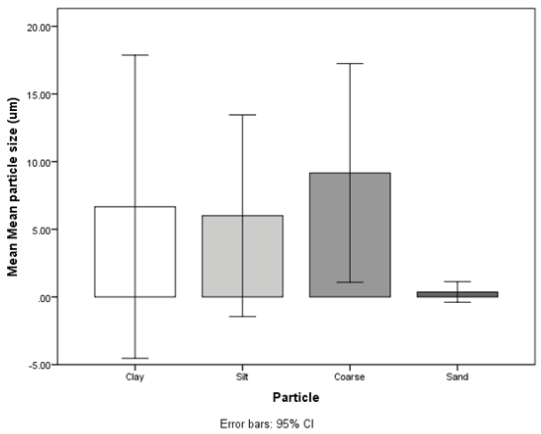


Figure 2. Comparison of different mean particle size distributions across the Lagos Lagoon system the bars on the figure represent +/-2 standard error.

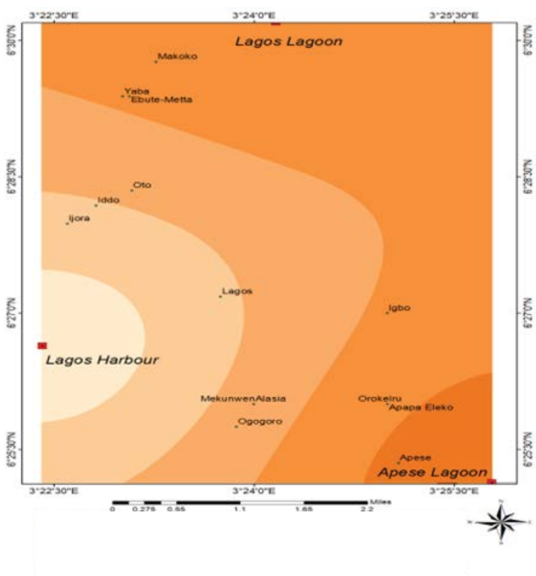


Figure 3a. Mean sand grain particle size (µm) across the Lagos Harbour, Lagos Lagoon and Apese Lagoon.

Note: Sand Particle size 10.78-11.69 11.7-12.61 12.62-13.53 13.54-14.45 14.46-15.37

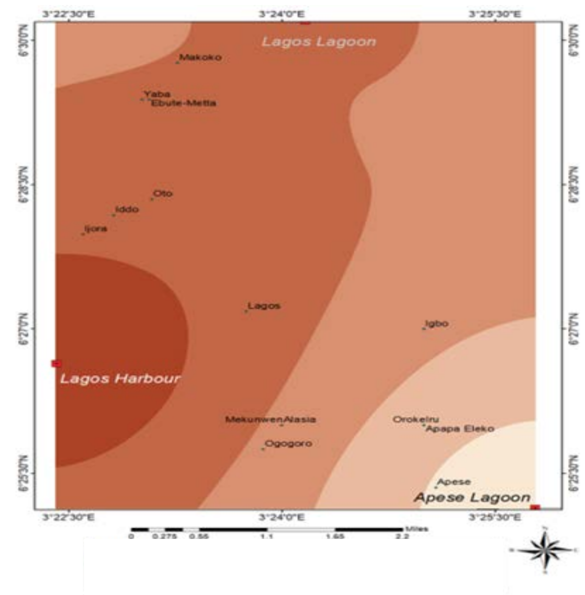


Figure 3b. Mean silt grain particle size (µm) across the Lagos Harbour, Lagos Lagoon and Apese Lagoon.

Note: Slit Particle size 6.37-6.47 6.48-7.57 7.58-8.07 8.08-9.77 9.78-10.87

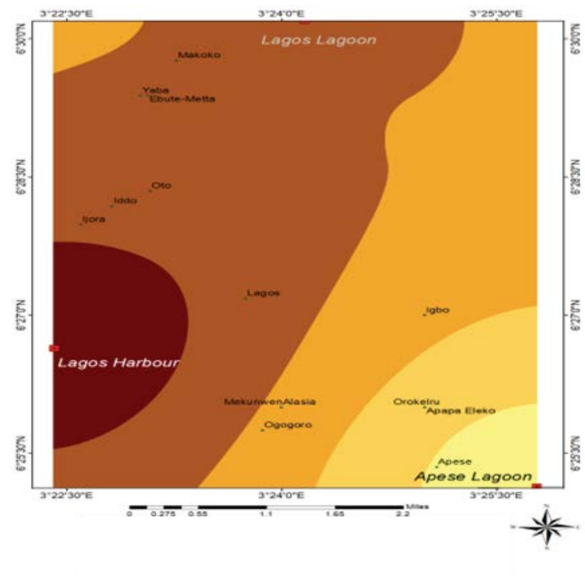


Figure 3c: Mean clay grain particle size (µm) across the Lagos Harbour, Lagos Lagoon and Apese Lagoon.

Note: Clay Particle Size 1.63-3.47 3.48-5.31 5.32-7.15 7.16-8.99 9-10.83

Mean metal and metalloid concentrations in sediment samples: The results of the sediment metal and metalloid concentrations indicated that bioavailable metal concentration was least for all metals with the exception of Cd and Pb. Analysis of variance indicated that the differences in the concentrations of the fractions were however not significant (p>0.05). Overall, Al and Fe had the highest concentrations in the sediment samples while Cd was the least (Table 1).

Spatial distribution of metal/metalloid fractions in sediment across lagos and apese lagoons and lagos harbour: Figure 4, the sand sediment particle sizes increases progressively from the Lagos harbour to the Lagos lagoon and the control site, Apese lagoon.

During the dry season (Figure 4a); Al, As and Cu were significantly distributed at high concentrations in sediment at the Lagos Harbour; Fe, Mn and Zn were significantly distributed at high concentrations in sediment at the Lagos Lagoon. However, during the wet season (Figure 4b); Al were observed to be distributed at high concentration at Apese Lagoon; the metalloid (As) were significantly distributed in Lagos Harbour; Fe, Mn and Zn were significantly distributed at high concentrations in sediment at the Lagos Lagoon.

Correlation of sediment particle sizes and metal concentrations: A correlation analysis was conducted to assess the inter-relationship between

Table 1. Mean concentrations of total, recoverable and bioavailable metals and metalloids (mg/kg) detected in the sediment of the Lagos Lagoon system.

Metal/metalloid Fractions	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
Total	67176	3	0	36	42023	547	0	148
Recoverable	3701	7	0	31	9582	595	11	53
Bioavailable	1544	2	0	9	5819	265	13	58

Table 2. Correlation between sediment particle size and total metals/metalloids concentration in the sediment samples of the Lagos Lagoon system.

	Clay	Silt	Coarse	Sand
Clay	1.00			
Silt	0.965**	1.00		
Coarse	0.644**	0.697**	1.00	
Sand	-0.27	-0.24	-0.14	1.00
Al	0.1	0.04	-0.15	-0.09
As	0.409*	0.37	0.06	0.06
Cd	-0.09	-0.04	-0.01	0.03
Cu	0.08	0.06	-0.06	-0.06
Fe	0.391*	0.33	0.14	-0.15
Mn	0.531**	0.535**	0.32	-0.17
Pb	0.400*	0.36	0.04	0.06
Sn	-0.04	-0.04	-0.12	0.12
Zn	0.01	0	-0.13	0.02

Note: * Indicates correlation with significant difference (p<0.05)
** Indicates correlation with significant difference (p<0.01)

Table 3. Correlation between sediment particle size and recoverable metals/metalloids concentration in the sediment samples of the Lagos Lagoon system.

	Clay	Silt	Coarse	Sand
Clay	1			
Silt	0.965**	1		
Coarse	0.644**	0.697**	1	
Sand	-0.27	-0.24	-0.14	1
Al	0.08	0.04	-0.22	-0.1
As	0.11	0.06	-0.18	-0.19
Cd	0.12	0.19	0.3	-0.11
Cr	0.11	0.12	0.03	-0.15
Cu	-0.06	-0.12	-0.23	-0.16
Fe	0.31	0.31	0.07	-0.18
Mn	0.416*	0.414*	0.15	-0.21
Pb	0.11	0.16	0	0.04
Sn	-0.19	-0.15	-0.11	-0.06
V	0.32	0.31	0.03	-0.12
Zn	0.07	0.1	-0.08	-0.03

Note: *Indicates correlation with significant difference (p<0.05)
**Indicates correlation with significant difference (p<0.01)

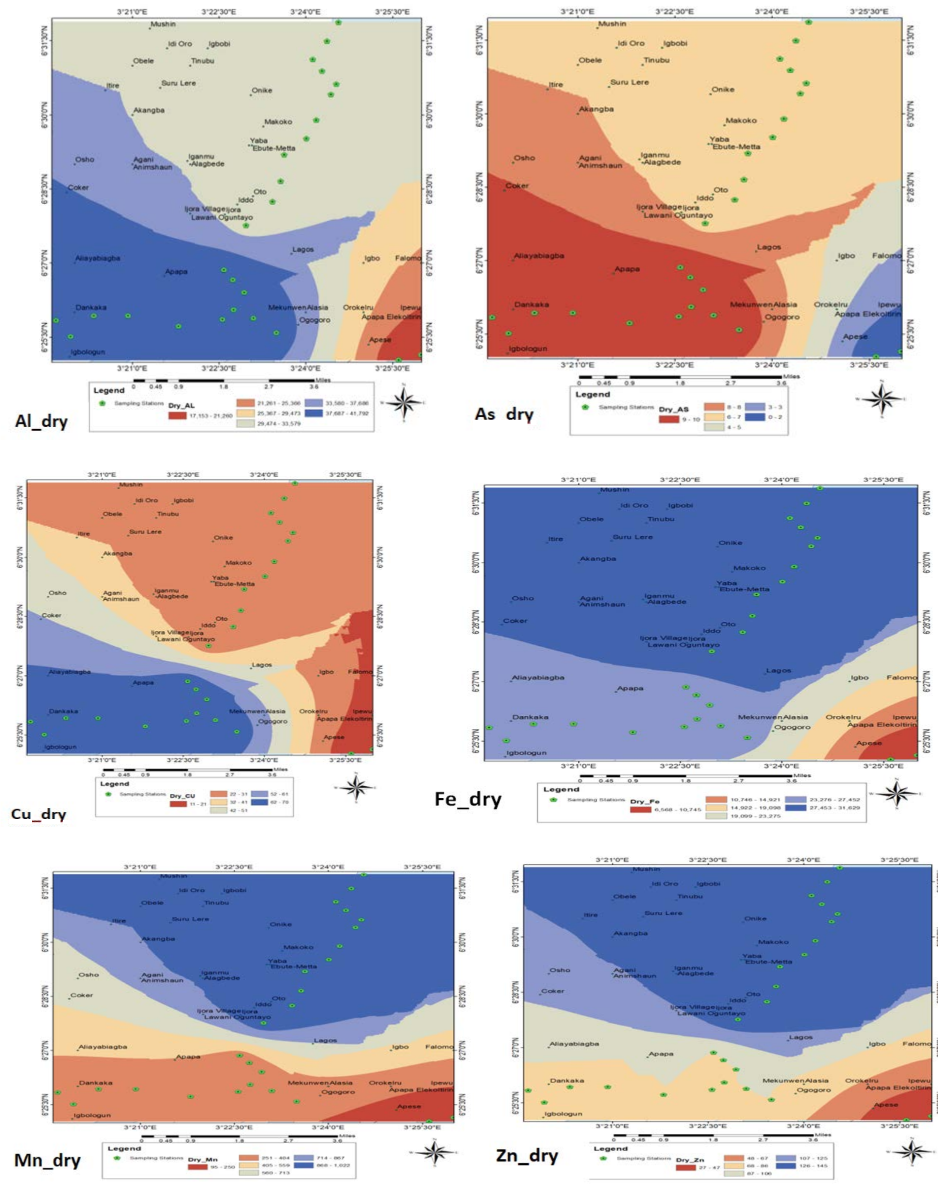
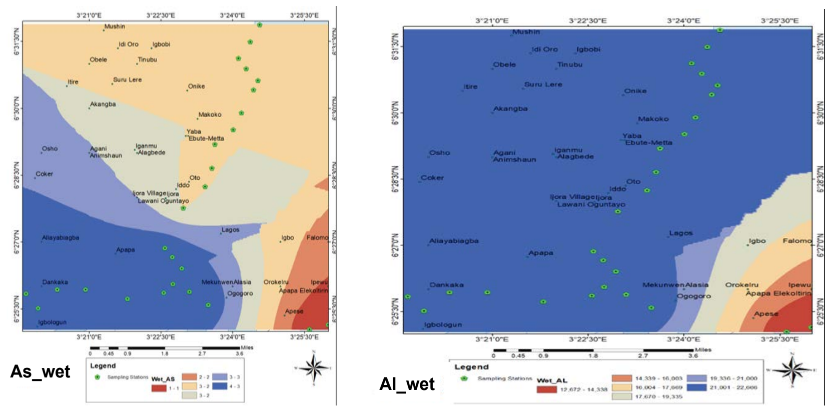


Figure 4a. Spatial distribution of metals/metalloid in sediment across Lagos harbour, Lagos lagoon and Apese Lagoon during the dry ason.



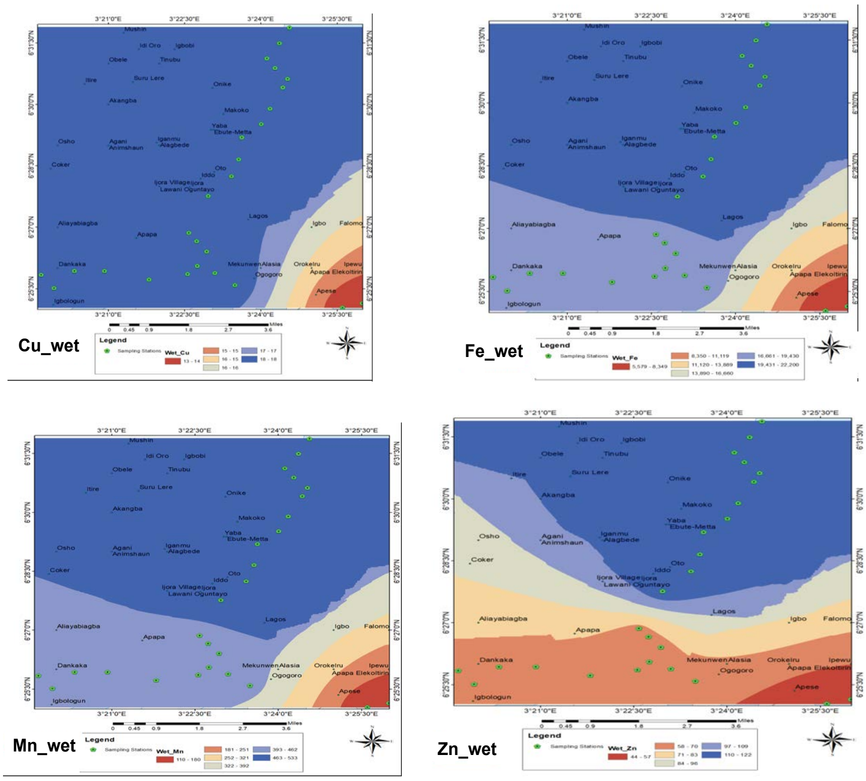


Figure 4b. Spatial distribution of metals/metalloids in sediments across Lagos harbour, Lagoon and Apese Lagoon during the wet season.

Table 4. Correlation between sediment particle size and bioavailable metals/metalloids concentration in the sediment samples of the Lagos Lagoon system.

	Clay	Silt	Coarse	Sand
Clay	1			
Silt	0.965**	1		
Coarse	0.644**	0.697**	1	
Sand	-0.27	-0.24	-0.14	1
Al	0.526**	0.568**	0.27	0.01
As	0.35	0.38	0.04	-0.15
Cd	0.559**	0.612**	0.31	-0.03
Cr	0.15	0.17	0.17	-0.04
Cu	0.19	0.3	0.12	0.02
Fe	0.552**	0.587**	0.28	-0.08
Mn	0.559**	0.557**	0.21	-0.21
Pb	0.32	0.426*	0.24	0.23
Zn	0.1	0.17	0.01	0.22

Note: * Indicates correlation with significant difference ($p<0.05$)

** Indicates correlation with significant difference ($p<0.01$)

the variables of significance towards understanding adsorption, mobility and bioavailability of metals with respect to particle sizes. The results indicated a strong correlation between the sediment particle sizes; clay, silt and coarse (Tables 2-4). Generally, clay, sit and coarse particles showed strong positive correlation compared between themselves but were weakly negatively correlated with sand.

There was significant positive correlation between mean total sediment concentrations of As, Fe, Pb and Mn with the clay constituents across the water bodies. Total Mn concentration also strongly correlated with silt (Table 2).A strong positive correlations was observed between recoverable Mn with silt and clay particles (Table 3).The results also indicated that bioavailable Al, Cd, Fe and Mn showed strong significant positive correlation with Clay and Silt while is Pb components were positively correlated with silt (Table 4).

Discussion

The findings from this study indicated that the overall sediment diversity was low in terms of the particle size. A similar observation was found in the sediment in Lake Kariba [16]. Sediments depend on the parent material available and deposits of materials. The inverse association observed between sand with clay and silt was also reported by Davies and Tawari (2010) [17] from Trans-Okpoka Creek, Upper Bonny Estuary, and Nigeria. The observed nature of the particle sizes in the Lagos Lagoon system can be attributed to sand mining/routine maintenance dredging at the Lagos Harbour as well as drifts from loss of beach shorelines at Apese Lagoon which can be related to the drifts associated with sea water incursion and outflow with tide. Constant dredging can remove the larger aggregates which protect the finer sediment particles and therefore predispose the sediment to greater levels of pollutant uptake.

Particle size plays an important role in many sediment processes such as aggregate stability [18], fluvial morphology [19] and pollution [20]. The coastal plain sand is the youngest within the Dahomey Basin, which is the principal geological formation in the area within which the Lagos Lagoon system lies. It is not rocky but characterized by soils which are soft, poorly sorted clayey sands, pebbly sands, and sandy clays [21]. Given that routine dredging is required to create enough room for navigation of large vessels *via* the LH into the ports, it is apparent that the larger parent surface soil/sediment materials would have been evacuated over the years leaving only finer forms which are typically at lower strata. This has implications for macro-benthic fauna, because such extensive damage would result in drastic alterations of the sediment and loss of organic materials which characterize their typical habitat. Doherty [22] reported very low benthic species diversity around the Apapa port areas which lies within the Lagos Harbour.

Also, heavy metals are usually associated with organic and inorganic complexes which characterize natural sediments of water bodies. Removal of the top surface by dredging invariably leads to release of bound metals from their complexes into the water column. Clay and silts are also known to enhance metal adhesion *via* their surface properties [23]. Thus, their loss would result in the release of the metals, increasing the chances of high concentrations in the sediments due to large amounts of unbound phases. The high clay and silt component of the sediment implies that they have a high risk of heavy metal uptake as noted in Awwal, et al. [13]. Onyena, et al. and Nwankwo, et al. [24,25] reported on the spatio-temporal variations in water and sediment parameters of AbuleAgege, AbuleEledu, Ogbe, and creeks adjoining Lagos Lagoon, Nigeria which indicates high level of contamination due to the increase in human population, industries and influx of contaminants from adjoining creeks. The degree of this contamination can be affected by the seasonal variations in time and space.

Typically, the bottom sediments within aquatic ecosystems serve as efficient natural trap for diverse substances such as nutrients-carbon and nitrogen and other contaminants, and as a natural regulator of the processes that occur under the sea floor. They can store large amounts of organic matter and affect the oxygen content of the bottom water. Bottom sediments also constitute a source of nutrients for the water column above leading to benthic-pelagic coupling and thereby influencing primary productivity [26].

The strong and positive correlation between clay and silt with Fe and Mn is notable. Fe-Monoxide complexes are important in the retention of metals in ligands within sediments while fine particles such as clay minerals provides large surface area for binding of metals compared to larger forms like quartz and feldspar [27,28]. Also Montalvo, et al. [29] reported strong positive correlation between Fe-Mn (r=0.5131), Fe-clay (r=0.5978), Cu-clay (0.8501) and Mn-clay (0.9311) in the Gulf of Mexico, which they attributed to the affinity of the elements to finer sediment particles. The presence of Fe in sediments does not necessarily imply negative consequences. For instance Bruland and Montalvo [29,30] noted that the presence of Fe oxides in sediments increases productivity at shallow coastal regions. However, these oxides enhance the binding of other metals to sediments which is further enhanced by the dominance of particles with large surface areas. The strong and significant positive correlation between bioavailable Cd and clay-silt particles observed in this study is also notable and this raises important toxicological risk in view of the bio-accumulative potential of Cd in aquatic biota and the likely effects of shell fish consumers.

Conclusion

The sediments of the Lagos Lagoon system were found to be mostly dominated by finer particles including clay and silt providing characteristically large surface area for binding of metals and metalloids. This implies that the widespread dredging of the lagoon sediments and artisanal sand mining has had its toll on the structural integrity of the substratum. The strong correlation between the finer particle sizes with total, recoverable and bioavailable fractions of Fe-Mn in the sediment samples is notable and implies increased chances of retention of pollutants in the sediment matrix. There is need for caution in the practice of dredging in the lagoon as this has far reaching effects on pollution transport in the lagoon system and associated food webs.

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