AN INVESTIGATION OF HEAVY METAL SEDIMENTS GEOCHEMISTRY IN LAGOS HARBOUR, NIGERIA

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by

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“Passionate about protecting the Marine Environment for Sustainability”

ABSTRACT

Due to the combination of its restricted water circulation, the rise in shipping intensity and industrial activities, the coastal zone of Lagos Harbour, Nigeria, is vulnerable to contamination with heavy metals. The purpose of this study was therefore to investigate and characterise the concentration of heavy metals in the sediments of Lagos Harbour applying a variety of improved and efficient metal extraction and determination methods.

A total of 26 sampling sites were established for sample collection within Lagos Harbour and Lagos Lagoon, while nearby Apese Lagoon was chosen as a control zone. Surface (1-5 cm) sediment samples were collected using a Van Veen grab on three occasions during the 2013 and 2014 dry seasons, and the 2013 wet season. Total metal concentrations were analysed using X-ray fluorescence (XRF). The sediments were subjected to two acid digestions: *Aqua regia* (AR) and 1 M hydrochloric acid (1 M HCl) following the procedures set out by the Canadian National Water Research Institute (NWRI) and the United States Environment Protection Agency (US-EPA Method 3050B). The results from the metal analysis were computed into GIS for spatial distribution using WinGlink software followed by correlation analysis, Principal Component Analysis (PCA), Cluster analysis of similarities, contamination (C*f*) and enrichment factors (*Ef*).

The significant elements studied in this research were As, Cd, Cr, Cu, Co, Fe, Pb, Mn, Ni, V and Zn. The total analysis (XRF) showed that Cu and Zn significantly exceeded the threshold effect level (TEL), while the *Aqua regia* analysis showed that recoverable As significantly exceeded the TEL across the three sites, and 1 M HCl, however, showed that all the bioavailable metals were below the TEL across all three sites.

The contamination factor (C*f*) indicated that in the 2013 dry season bioavailable Ni had the highest contamination factor at a petroleum products tank farm in Lagos Harbour. In the 2013 wet season XRF showed that the sediments in both Lagos Harbour and Lagos Lagoon were contaminated with Cd and Zn, while *Aqua regia* analysis showed Cu contamination in the sediments from Lagos Lagoon. Results from the 2014 dry season showed a generally higher trend in C*f.*

The enrichment factor of metals in the sediment was measured in the surficial sediments at the three sites in order to identify metals with significant enrichment from anthropogenic sources. Generally, *Aqua regia* analysis showed higher enrichment of metals and metalloids in the sediments in Lagos Harbour than in Lagos Lagoon.

The interrelationship of the metals and grain particle sizes showed (using XRF) that As, Cd, Cu, Mn were significantly loaded in the coarse sand and silt. Using *Aqua regia,* As, Cr, Cd were bioavailable in clay, silt and coarse sand. While 1 M HCl showed that Cr, Cu and Fe were distributed in clay, silt and coarse sand respectively. The factors scores plot showed clusters which indicated that metal concentrations were affected by type of anthropogenic activity, geographical proximity and sea water incursion, but diffused runoff entry during the wet season made the clusters rather weaker. The major identified metal pollution hotspots were the Atlas cove, petroleum tank farm areas and ports in the Lagos Harbour while in the Lagos Lagoon they

include the entry canal points of municipal sewage and runoff, coastal solid waste dump and receiving waters for industrial effluents.

These findings are significant for the development of baseline data to inform the formulation of guidelines for the protection of marine environment within the Nigerian Harbour system. This is in line with the United Nation Sustainable Development Goals #14 and #17: ‘Conserve and sustainably use the ocean, seas and marine resources’ and ‘Strengthen the means of implementation and revitalize the global partnership for sustainable development’. Moreover, these data can be used by the Nigerian authorities to improve harbour life and marine biota, and by other researchers interested in constructing efficacious testing methods.

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My sincere gratitude goes to my team of supervisors, Dr Mike Fowler and Professor Graham Mills for their tremendous support. I would like to thank the Head of School, Dr Michelle Hale and Janet Woodford for their keen interest in helping me all the time.

I would also like to thank everyone who assisted me during my laboratory and fieldwork analysis for the entire period of my studentship: Professor K. Olayinka of the Department of Chemistry, University of Lagos, Mr Douglas Peter of the Central Research Laboratory, College of Medicine of the University of Lagos. Also, my special thanks to Mr Nick Walton (SEES), who at any time was willing to render academic advice, especially with my research field area. Other members of staff who deserved to be acknowledged include Mr James Coyne (Chief Technician) SEES, Mr Joseph Dunlop (SEES), Dr Adil Bakir (SEES), Dr Sarah Reynold (SEES), Mrs Sue Atkins (SEES), Mr Linley Hastewell of Geography Department, all at University of Portsmouth. I am also extending my special appreciations to my very good friends; Auwal Aliyu and Juliana Consul, both of Newcastle University, for their assistance at all time during my study period. Also, to my employer, Nigerian Maritime Administration and Safety Agency (NIMASA), for granting me the opportunity to undertake the PhD programme under the study leave scheme for a period of four years.

Finally, and most importantly, I would like to thank my wife (Benazir), and to my lovely twins (Ayman and Asna), who have been with me throughout the period of the entire study in Portsmouth. This is for their patience, loneliness and endurance, when at times, I am not always at home with them, especially during my fieldwork in Nigeria or when attending academic conferences outside the United Kingdom, and for being there over the last four years.

Dedication

I dedicate this thesis in memory of my late son (**Adam Awwal Bamanga**) who left us in this planet at the age of one, precisely a year ago on the **7th October 2017**. May his gentle soul rest in perfect peace.

Declaration

I affirm that as a registered research student of the University of Portsmouth, for the degree of Doctor of Philosophy, I have not undertaken or registered as a student for another award or pursuing another academic or professional qualification concurrently throughout the entire research period. No part of this work referred to this thesis has been forwarded in relation to the award for another degree or qualification of any other university or institution of higher learning.

Signed ……………………..

Awwal Bamang

Scientific Papers published:

1. The preliminary data obtained prior to detailed investigation in this study was published in the International Journal of Applied Environmental Sciences (IJAES). http://www.ripublication.com. The published paper has the ISSN 0973-6077 and is in Volume 9, Number 6 (2014) pp.2905-2915, and is also available at the above website.
2. Potential Impacts of Urban Development around the Apese Lagoon in the Lagos Metropolis of Nigeria, published in the International Journal of Environmental Sciences (IJES), January 2015. http://ipublishing.co.in/ijesarticles/fourteen/articles/volfive/EIJES51077.pdf

Scientific conferences attended:

While undertaking the research work at the University of Portsmouth, parts of the on-going research data were disseminated in some of the international conferences attended during the study period. The list of the conferences attended, and the type of presentations are stated below.

1. 2014 - 2nd International Conference on Environmental Science and Technology, held from the 14th-17thMay 2014 in Antalya, Turkey. An oral presentation based on the preliminary data obtained was delivered in this conference in a special session on Aquatic Biota and Sediments on the 16th of May 2014. The conference website is available at http://www.icoest.org.
2. 2014 - The 17th International Conference of Heavy Metals in the Environment, held from the 22th to the 26th of September 2014 in Guiyang, China, organised by the Institute of Geochemistry, Chinese Academy of Sciences, the website of the conference is available at http://ichmet2014.gyig.ac.cn; http://english.gyig.cas.cn/. In this conference an oral presentation was offered to the special session on contamination and sediments.
3. 2015 - The Eighth International Conference on Remediation and Management of Contaminated Sediments, held in New Orleans, Louisiana, U.S.A, January 12-15, 2015, organised by Battelle Business Innovative, which can be found at http://www.battelle.org/sedimentscon. In this conference a poster was presented on the results obtained using the hydrochloric acid method.
4. 2015 - International Conference on Environment Sciences and Engineering (ICESE 2015), held from the 24th to the 25th of April 2015 in Istanbul, Turkey, organised by the CBEES.The website of the conference can be found at www.cbees.org
5. 2016 - Chemical Sciences and Technology Enabling Growth in Africa 11-12 February 2016, Lagos Nigeria, organised by RSC-P&G Symposium.The website can be found at www.rsc.org

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Abbreviations

AAS	Atomic Absorption Spectrometry
AF	Anti-fouling
ANOVA	Analysis of Variance
ANZEC	Australian New Zealand Environment and Conservation Councils Guidelines
APHA	American Public Health Association
APL	Apese Lagoon-Lagos
AR	*Aqua regia*
ASTM	American Society for Testing and Materials
BACs	Background Assessment Concentrations
BS	British Standards
CCME	Canadian Council of Ministers of Environment
CEFAS	Centre for Environment Food and Aquatic Services
CEQG	Canadian Environment Quality Guidelines
CRM	Certified Reference Material
CSQGs	Canadian Sediment Quality Guidelines
CTD	Conductivity Testing Devices
DCs	Developing Countries
DS	Dry season
EC	European Community
EEZ	Exclusive Economic Zone
EF	Enrichment Factor
EPA	Environment Protection Agency
EQS	Environmental Quality Standards
ES	Estuarine Sediment
GESAMP	Group of Experts on Science and Marine Pollution
GPS	Global Positioning System
ICESE	International Conference of Environment Science and Engineering
ICHMET	International Conference on Heavy Metals in the Environment
ICOEST	International Conference on Environmental Science and Technology

ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission
IJAES	International Journal of Applied Environmental Sciences
IJES	International Journal of Environmental Sciences
ISQGs	Interim Marine Sediment Quality Guidelines
IMO	International Maritime Organisation
LDC	London Dumping Convention
LH	Lagos Harbour
LG	Lagos Lagoon
MARPOL	Marine Pollution Prevention Convention
MP	Marine Pollution
MPA	Marine Protective Area
NCWRI	National Canada Water Research Institute
n.d	No date
NIST	National Institute of Standards and Technology
BDL	Below Detection Limit
NIMASA	Nigerian Maritime Administration and Safety Agency
NIMET	Nigerian Institute of Meteorological Agency
NPA	Nigerian Ports Authority
OSPAR	Oslo-Paris Commission
RSC	Royal Society of Chemistry
PS	Particle Size
SEES	School of Earth and Environmental Sciences
SOP	Standard Operating Procedure
SPSS	Statistical Package for Social Sciences
ST	Sites
TEL	Threshold Effects Level
UNEP	United Nations Environment Protection
US-EPA	United State Environmental Protection Agency
WHO	World Health Organization
WFD	Water Framework Directive
WS	Wet season
XRF	X-Ray Fluoresence

CHAPTER ONE: INTRODUCTION

1.1 Background

Heavy metal pollution in sediments of marine ecosystems has gained increased attention of many environmental researchers over the past few decades. Heavy metals are natural constituents of sediments and can also be derived from anthropogenic sources, as they are incorporated into sediments as pollutants from industrial or urban releases and wastes (Sakar et al., 2015). Metals settled in sediments may be re-suspended and cause secondary contamination to the aquatic environment (Wardhani et al., 2017).

Sediments act as environmental archives that indicate the timeline of an aquatic environmental contamination (Swarnalatha et al., 2013). While heavy metals may be transferred from water to sediments through settling of particles, their remobilization may occur via aquatic biota, as well as with changes in environmental conditions (Davutluoglu et al., 2011).

It is generally known that marine ecosystems are endangered by various contaminants, mostly untreated sewage, waste oils, plastics and industrial effluents that ultimately affect the sustainability of living resources and pose global environmental as well as public health risk (Naylor et al., 2000; Muduli et al., 2012). There is an assumption that the marine environment has an infinite capacity to absorb these contaminants without being subjected to undue harm (Clark, 2001). However, the continued introduction of wastes into the marine environment may result in measureable rise in the local level of contamination.

Marine pollution, specifically in the coastal zones, has been an issue of growing concern in which much scientific research, for example, Valavanidis & Vlachogianni (2010) have shown that there have been significant ecotoxicological impacts and toxicity to inhabiting biota. Conventionally, these coastal zones have been modified through processes of industrialisation and urbanisation, which include the development of large conurbations, harbours, and associated industrial activities, resulting in the deterioration of water and sediment qualities within the marine environment (Filipkowska et al., 2005; Knox et al., 2014). Among these activities, intensive industrial and shipping are dominant and involve the discharge of fertilizers and pesticides, human sewage, industrial & commercial municipal waste and oil spills into coastal areas (Knox & Paller, 2013). This is of concern since these areas are also intensively used for commerce and leisure as well as fishing activities.

There are concerns about pollutants entering the human food chain through the processes of bio-magnification, direct ingestion or inhalation (Luoma, 1989; WHO, 2002; Clark, 2001). Heavy metals are one of the key elements of concern. Others include hydrocarbon oils and organic compounds, for example, polycyclic aromatic hydrocarbon (PAHs), pesticides and polychlorinated biphenyls (PCBs). Metals including Cd, Cu, Hg, Pb, Ni and Zn and metalloids such as As, are frequently found in harbour sediments and other areas impacted by human activities (Knox & Paller, 2013). The schematic diagram in Figure 1 shows how contaminants are transported from sources and their fate in the marine environment with regards to physical, biological and chemical process.

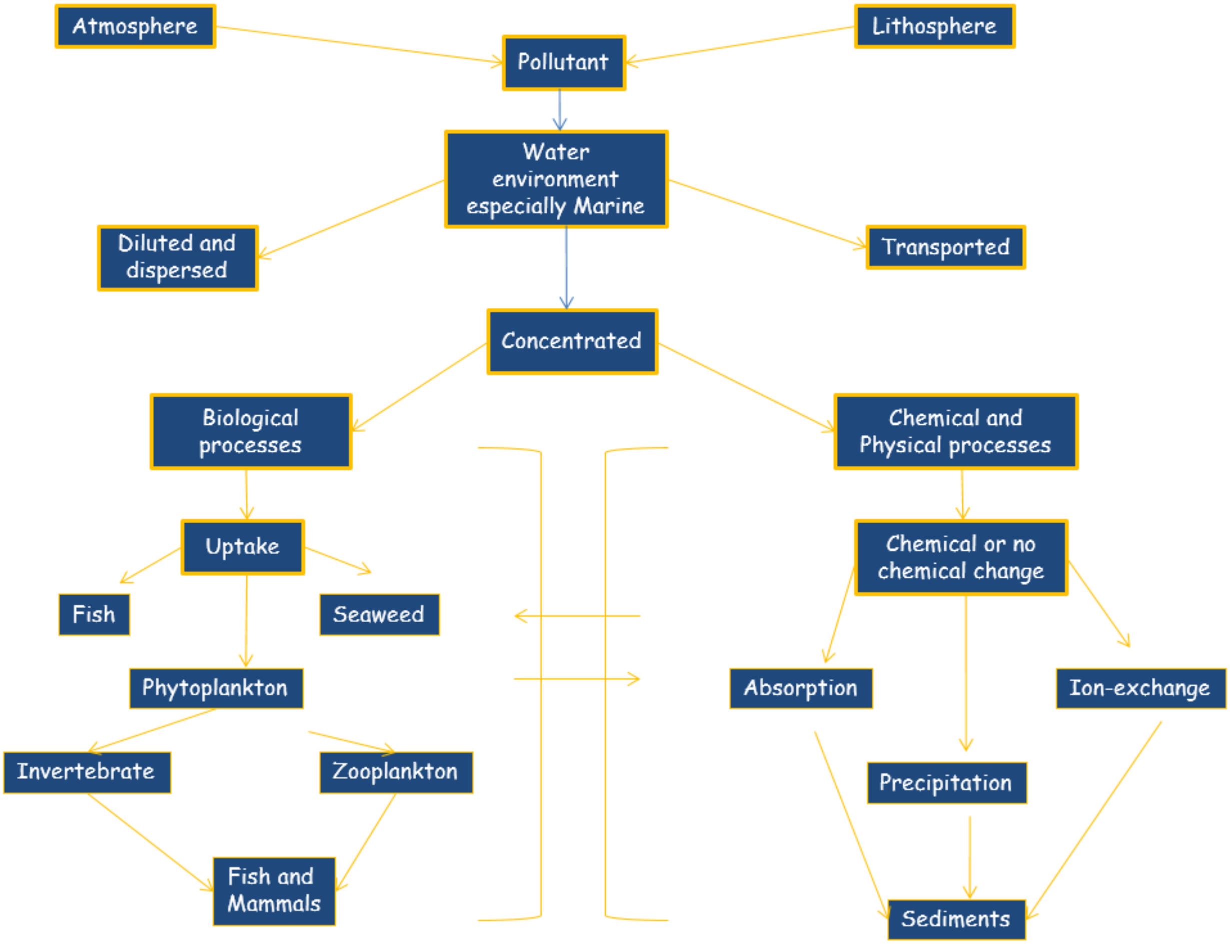


Figure 1: Transport and movement of pollutants into marine environment. (Fergusson, 1990).

Reports have it that heavy metal bioavailability can be influenced by temperature and this is of concern in the face of global warming associated with climate change. Metals such as Cd, Cu & Hg, are influenced by elevated temperature, which leads to higher uptake by organisms (Sokolova & Lannig 2008). Flooding associated with climate change enhances the transport of metals such as As whose realease from contaminated soils are equally increased as a result of the associated temperature increases (Weber et al., 2010). These concerns are likely to rise and pose significant ecological/public health risks in the future (Seitzinger et al., 2010). This is especially a major cause for concern in developing countries (DCs), such as Nigeria, due to a lack of public awareness, inefficient environmental management systems and absence of policies, to ensure effective implementation of guidelines, which promote best practice for a safe marine environment (Howes et al., 2017). Furthermore, the impacts of climate on water resources are among the most important problems facing the management of water resource, including the marine environment (Milly et al., 2008). Variations in the frequency and intensity of precipitation, evaporation and transpiration are now crucial within climate change research (Christensen et al., 2008). Within the context of water resources, especially the hydrological cycle, climate change impacts manifest through decreased infiltration, along with increased runoff and stream flow that lead to groundwater recharge and surface water flooding (Visser et al., 2012). These impacts are linked to heavy metal contamination of the marine ecosystems, and have been discussed extensively, but only qualitatively (Schiedek et al., 2007).

Investigation of marine sediments is important since it helps us understand the overall pollution of the marine environment (Calace et al., 2005). Sediment consists of a matrix of detritus, inorganic and organic particles. They serve as the ultimate sink for many contaminants and as a result, they pose the highest risk to marine life. They are relatively heterogeneous in terms of their physical, chemical and biological characteristics, and contain a varied range of particle sizes, including gravels, sand, silt and clay (Fergusson, 1990; Sarkar et al., 2004). Thus, sediment components are well recognised as a main reservoir for many persistent organic and inorganic chemicals introduced into the aquatic environment by atmospheric deposition, erosion of the geochemical substrate and anthropogenic sources (Sarkar et al., 2004).

Preponderant contaminants include heavy metals, persistent organic pollutants (POPs), oils (hydrocarbon), plastics, nutrients and radioactive substances (UNEP, 1990). Heavy metals are stable and persistent environmental contaminants of coastal sediments (Okoro et al., 2012). In recent years there has been growing concern over increased contamination of estuaries and harbours from various anthropogenic sources (Wepener & Vermeulen, 2005). Heavy metals are especially of major concern due to the fact they exhibit similar behaviour as persistent toxic chemicals. Thus, the investigation of heavy metals in sediment enables detection of contaminants that may be either absent or in low concentrations in water column; and their distribution in coastal sediments provides a record of the spatial and temporal history of pollution in an ecosystem (Binning & Baird, 2001).

The presence of these contaminants requires the characterisation of the chemicals in the environment through scientific investigation to enable proper management of these vulnerable coastal zones (Kesavan et al., 2013). This condition was first noticed in the last century and has become more pronounced in the last two decades (Young, 1994; GESAMP, 2001). Lagos Harbour which is the focus of the present research is likely to experience this kind of pollution due to a wide range of discharges from industrial, commercial, shipping, as well as continued dredging of the harbour area for routine channel maintainance. Continous dredging regularly re-activates, re-suspends settled pollutants in the water column and sediment.

As an objective of the present study, the importance of investigating sediment heavy metals concentrations and distribution in the Lagos Harbour Nigeria is vital to understanding the impacts of shipping activities in this important water body. Lagos is Africa's largest city at 20 million people, and a successful resolution of this marine sediment pollution due to shipping and other industrial related activities within the area will provide helpful lessons for cities all over the world as climate change intensifies.

Incidentally the sediment is home to a veriety of species referred to as benthic fauna which live either on the surface or burrow beneath the surface and some which ocassionally visit to feed before swimming back into water. Their physical structure affects species diversity (Navel et al., 2010), moreso their chemical composition (Richard et al., 2008; Navel et al., 2010). Given their rather stable nature being at the bottom of water, pollutants tend to settle, resulting in a range of acute and chronic toxicity effects on the inhabiting fauna (Hall and Frid, 1995). There has been report of significant negative impact of sediment components on community structure of microbenthic fauna (Brown et al., 2000).This raises key ecotoxicological and public health challenges with respect to toxicity as well as the potential for bioaccumulation and biomagnification of the pollutants such as heavy metals. Given that heay metals which are deliberately or inadavertently released into sediments often include very toxic forms, the threat to sustainable support of biotic life is a key concern which must be addressed by effectively evaluating sediment quality. This is especially important in water bodies such as the Lagos Harbour which is subjected to a range of anthropogenic pressure on a daily basis due to intense shipping activities. Thus the findings from this study will be discussed with respect to potential ecotoxicological concerns in the Lagos Harbour and Lagoon system. To a large extent remediation options would also be proferred for sustainable utilization of this very important aquatic ecosystems

1.2 Statement of the Problem

1. Pollution of marine ecosystem especially as a result of excess contamination within the marine sediments poses significant challenges to both human lives and other ecological factors in the marine areas of Lagos, Nigeria.
2. Anthropogenic activities, which include intensive shipping and industrial activities, discharge of sewage and construction works in the Lagos area has contributed significantly to the pollution of Lagos Harbour in Nigeria and its associated lagoon system.
3. There have been several attempts to identify the sources, types, toxicity and bioaccumulation of heavy metals in the Lagos Lagoon but there is a dearth of information on their spatial distribution and contamination factor in the Lagos Harbour area.

1.3 Structure of the Thesis

Chapter One introduces the problem and the reason for this study. It also gives an overview of the main contaminants under investigation in marine sediments; the data and methodology used; contributions to knowledge and policy suggestions. Chapter Two reviews the literature and established identified knowledge gaps. Chapter Three describes the Lagos Lagoons and the surrounding area. Chapter Four discusses the methodology and the experimental procedure for the physical and chemical analysis of samples. Chapter Five presents the data. Chapter Six discusses the empirical results. Chapter Seven gives a brief summation of the principal findings and finally, Chapter Eight concludes with policy recommendations and suggestions for future research.

1.4 Metals: the main marine contaminants investigated in this study

The accumulation of metals in sediments from both natural and anthropogenic sources follows a similar process, thus making it difficult to identify and determine their origin (Idris et al., 2007).

Moreover, the total concentration of metals often does not accurately represent their characteristics and toxicity. To overcome these problems, it is helpful to evaluate the individual fractions of the metals to fully understand their actual and potential environmental effects (Okoro et al., 2012). Of the heavy metal characteristics, mobility and bioavailability are crucial and depend strongly on the chemical and mineralogical forms in which they occur (Baeyens et al., 2003). Speciation studies are being conducted to determine different forms of heavy metals rather than their total metal content. These studies reveal the level of bioavailability of metals in harbour sediments and confirm that sediments are bio-indicators of heavy metal pollution in marine environments (Wepener & Vermeulen, 2005; Idris et al., 2007; Okoro et al., 2012).

The method of sequential extraction, as based on Tessier method (Tessier et al., 1979) is useful in operational classification of metals into different geochemical fractions. However, the Tessier method was not used in this present study rather a simple combination of different extraction methods with modern instrumental analysis was adopted. The Tessier method requires a longer test time and involves a complicated method of extraction. The techniques employed were used because they require less run time and have also been proven to provide the required measurements by previous researchers (Okoro et al., 2012).

In view of their abundance in the Lagos marine environment, the overall shipping activity in Lagos Harbour and the significant threats which they pose to human health, the elements being investigated in the present study include: As, Cd, Cr, Cu, Co, Fe, Pb, Mn, Ni, Sn, V, and Zn (Owen & Sandhu, 2000; Baptista Neto et al., 2005).

1.4.1 Brief review of heavy metals investigation in Lagos Lagoon

Several studies have documented the occurrence, biogeochemistry, fate, distribution, and ecotoxicological effects of heavy metals in the Lagos Lagoon ecosystem (Ajao 1996; Oyewo 1998; Market & Freise, 2000; Otitoloju, 2000; Don-Pedro et al., 2004; Amaeze et al., 2012; Alo et al., 2014; Bawa-Allah et al., 2017). However, Oyewo (1998) described that gaps and lack of data with no clear picture of the sources, pathways and impacts of these contaminants including quantification and fluxes from local and shipping activities. Further studies have subsequently described the sources of pollutants in the coastal areas of the lagoon (Amaeze et al., 2012). Oftentimes, each coastal section is associated with unique activities which influences the local water quality and sediment ecology. Among these is the Lagos Harbour which is associated with intense shipping activities, refined petroleum products transfer to coastal jetties and industrial activities.

However, a detailed analysis of the ecological risks of heavy metal concentrations in sediments of the Lagos Harbour and Lagos Lagoon using different extraction protocols, or a holistic assessment is still lacking. This study will use combined methods of extraction with advanced analytical techniques such as X-ray fluorescence (XRF), inductively coupled plasma-optical emission (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) to provide a comparative assessment of heavy metal fractions in the sediments. It is intended that the findings of this study will form part of the baseline data development with respect to metal contamination for the harbour system in Nigeria and provide helpful lessons for other marine ecosystems.

1.5 Distinctive Features of Lagos Harbour and Lagos Lagoon System

Unlike the open sea, the coastal zone is most influenced and vulnerable to human exploitation. Enclosed and semi-enclosed areas such as Lagos Harbour are increasingly polluted which in turn, worsens sediment quality. Water quality relates directly to the quality of sediments, serving as the final sink for contaminants such as heavy metals. These contaminants accumulate in sediments and subsequently pollute the water column upon resuspension, thereby negatively impacting the benthic and pelagic flora and fauna of the marine environment.

Lagos Lagoon and Harbour play a significant role for the human community due to prosperous and massive mollusc harvesting, fishing, transportation, shipping and commerce. However, the area has been sensitive to the stress exerted by anthropogenic activities which obviously damages the ecological equilibrium of the marine system.

Lagos, at 20 million inhabitants, is Africa’s most urbanised and industrialised city. Before active industrialisation during the 1960s, urban (including human) waste was the preponderant pollutant in Lagos Lagoon, but industrial wastes are becoming the most important (Okoye et al., 1991). Odiete (1999) opined that at least 2000 industries concentrated in Lagos and neighbouring Ogun State of Nigeria release effluents into the Lagos Lagoon either directly or indirectly. This is expected to have increased over the years as the country countinue to urbanise and industrialise especially around the Lagos-Ogun State axis. The risk of pollution in Lagos Lagoon, due to unsatisfactory waste management in the area, is high (Oyewo, 1998). Human activities within the Harbour area are restricted to a total area of 8.87 km^2 and measuring approximately 23 km in coastal/linear distance with a coastline water depth less than 30 m (Nwankwo, 2004). Currently, plans for countermeasures for the effects of these (increasing) pollutants are inadequate. It can be argued that these activities have been conducted without planning or expansion of the harbour area to accommodate the commensurate increase in both shipping and other related industrial activities.

1.5.1 The Lagos Lagoon system

The Lagos Lagoon system (Figure 2) is comprised three main divisions: Lagos Harbour which represents the central area of the lagoon; the urbanised part of the lagoon which is in the west; and the Epe division in the east. Lagos Harbour is the main inlet from the Atlantic Ocean to the sea ports in Lagos (James & Adejare, 2010), the busiest ports in Nigeria and the largest on the Western coast of Africa. Lagos port also has a major dry-docking facility used by several large fishing fleets and ships. The harbour system was built as a semi-enclosed basin to aid a restricted water circulation, in order to support activities within the sea port area.

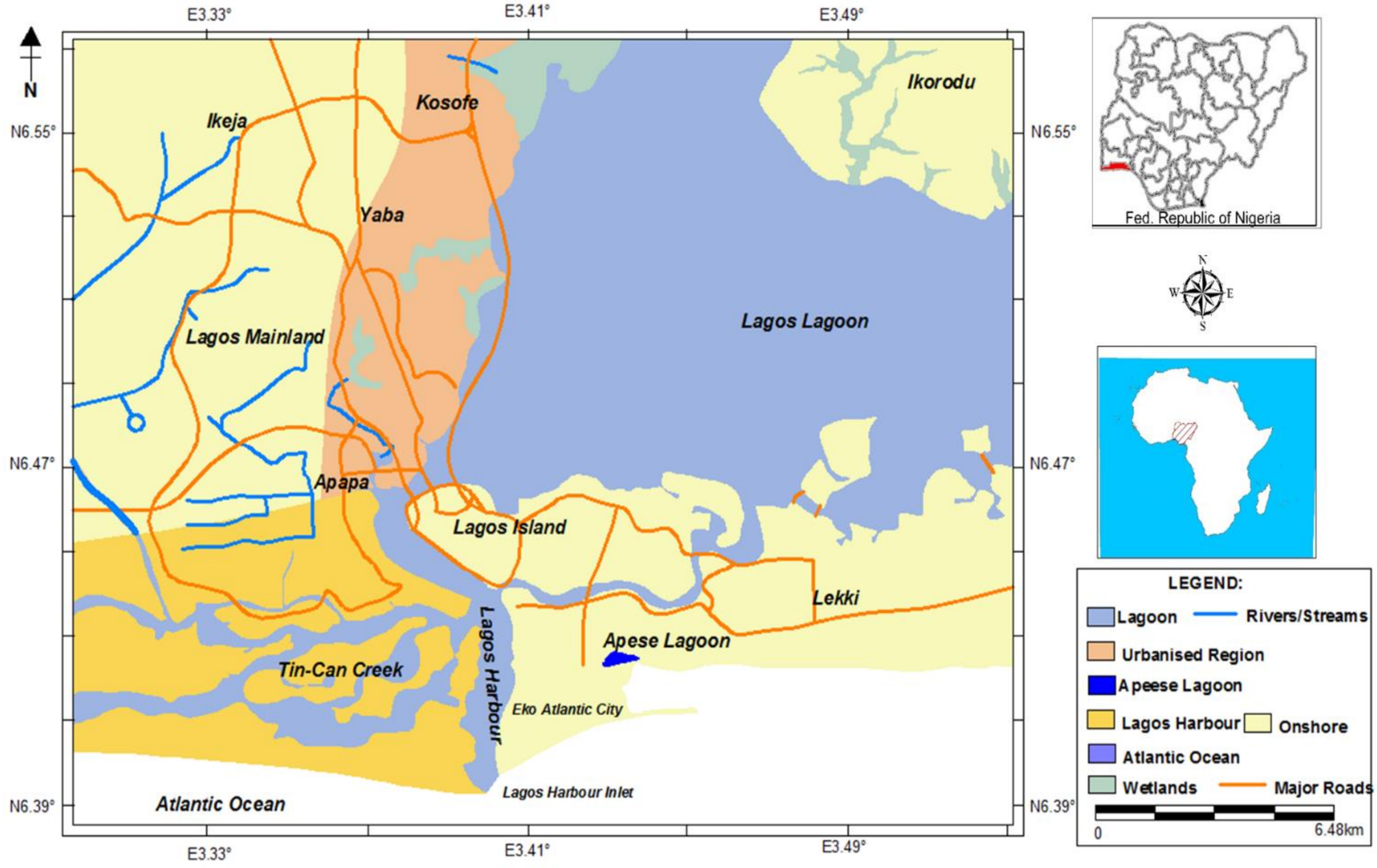


Figure 2: Map of the Lagos Lagoon system comprising Lagos Harbour and Lagoon.

Lagos Harbour is the only natural break of any size with an extended barrier beach from the Volta River to the River Niger and has been established for decades (Hill & Webb, 1958).

The western part of Lagos Lagoon, with a surface area of approximately 200 km^2 (Vijverberg et al., 2012), contains the main metropolitan areas and is characterised by slum settlements, domestic and occasional industrial activities. This part of the Lagoon supports fisheries and transportation and receives domestic and industrial wastewater, sawdust and wood waste, petroleum hydrocarbons, and cooling water from a thermal plant (Agwu, 2013).

1.6 Environmental Legislation

Currently, the primary national guidelines for environmental pollution management in Nigeria is the “Guidelines and Standards for Environmental Pollution Control in Nigeria”, issued by the Federal Environmental Protection Agency (FEPA, 1991) under the aegis of the Federal Ministry of Environment. These guidelines are limited on heavy metal sediment contamination and are basically restricted to water pollution. Another guideline, issued by the Department of Petroleum Resources (DPR) is the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), focuses on the effect of petroleum products on the Nigerian environment. As with FEPA’s guidelines, limits are established by the DPR for contamination of marine ecosystems by both organic and inorganic pollutants. The standards are mostly not updated and hardly reviewed to determine current tolerance thresholds ofaquatic organisms to specific pollutants such as heavy metals. This has necessitated the routine adoption of international standards by investigators in other to adequately provide a background for comparing observed concentration of Pollutants. Apart from being mostly un updated, overall, there is weak enforcement of existing environmental guidelines and standards in the country (Amaeze et al., 2014).

In most developed countries government agencies often use the United States Environment Protection Agency (EPA) guidelines when investigating sources, magnitudes, distributions and environmental impacts of pollutants, as well as establishing maximum allowable limits in the ecosystem. Due to Nigeria’s limited national guidelines and standards, and the lack of consistent investigation of pollutants to serve as a baseline development for guideline formulations, Nigerian studies (including this study) use international standards (Table 1) such as the National Oceanic and Atmospheric Administration (NOAA) and Canadian Sediment Quality Guidelines (CSQGs). The choice for these guidelines (NOAA and CSQGs) are focussed on the specific toxicological threshold effects in water and sediment quality as well as the fact that they possess similar guideline for brackish water and marine environment which is the case for the study area.

Table 1: Limits of sediment concentrations in international guidelines/standards (mg/kg).

Standards	***As***	***Cd***	***Cr***	***Cu***	***Pb***	***Zn***	***Ni***	***Sn***	***V***
NOAA	7.2	0.68	52.3	18.7	30.4	124	15.9	0.048	-
CSQGs	7.24	0.7	52.3	18.7	30.2	124	-	-	-

Note: These standards are for marine sediments.

CSQGs= Canadian Sediment Quality Guidelines | NOAA = National Oceanic and Atmospheric Administration

1.7 Research questions

Following the established knowledge gaps identified in the literature and based on the distinctiveness of the study area (Lagos Harbour and Lagos Lagoon), the proposed study intends to investigate the following research questions:

1. What are the concentration of heavy metals in the sediments of Lagos Harbour, Nigeria?
2. What is the relative spatial distribution of determined heavy metals in the sediment samples of the Lagos Lagoon system and how does this relate to prevailing activities in the respective sections?
3. What are the sources and pathways of contaminants (heavy metals) into the Lagos Harbour?
4. What are the relative comparative of heavy metal concentration within the three different sampling locations (Lagos Harbour, urbanised part of Lagos Lagoon and the relatively undisturbed Apese Lagoon) with the view of establishing the ecological risk posed to their respective sediments?

From these research questions proposed above, the following study objectives were developed as stated in section 1.8.

1.8 Aim and objectives of the study

The primary aim of this study is to investigate heavy metals concentration, spatial distribution and ecological risk in the Lagos Harbour and Lagos Lagoon with relative extraction of a number of heavy metals: As, Cd, Cr, Co, Cu, Fe, Mn, Ni, Sn, Pb, V and Zn, using a three-phase sequential extraction scheme (total, recoverable and bioavailable). The results obtained are compared to sediment quality guidelines (SQGs) such as those issued by the United States National Oceanic and Atmospheric Administration (NOAA) (NOAA, 1999; Kwok et al., 2013), the Canadian Sediment Quality Guidelines (CSQGs) which include the Canadian Councils of Ministers of the Environment (CCME, 2001). This will provide information on the status of the LH with respect to heavy metal distribution in the sediments towards addressing the reseach questions in this study.

Therefore, in order to achieve the overall aim, the objectives of this study include the following:

1. To determine the concentrations of heavy metal within Lagos Harbour area and the Lagoon.

2. To compare the concentrations with International Standards to ascertain the level of heavy metal contamination in the Lagos Harbour area and the Lagoons.

3. To identify the sources, pathways and the extent of contamination using spatial distribution geolochemical contour mapping of heavy metals in marine surficial sediments in relation to prevailing anthropogenic activities.

4. To establish the hotspots for heavy metal contamination in the Lagos Harbour and Lagoon.

5. To determine the ecological risk status of the Lagos Harbour and Lagoon sediments using determined heavy metal concentrations.

1.9 Summary of research methods

The fieldwork and analytical techniques were deployed to determine the anthropogenic sources of the metal contaminants using three sequential extractive methods for total, recoverable, and bioavailable phases. While the total concentrations were analysed after basic physical preparations of the sediment, the recoverable and bioavailable forms were determined after further extraction with *Aqua regia* and IM HCl respectively before analysis. The difference between total and the extractible (receoverable & biovailble) metal analysis lies with the fact that total give the absolute concentration present in the given sediment sample, the latter measures fractions of the metal concentrations based on on geochemical or sedimentary phases -and are related to toxicity and bioaccumulation- often associated with anthropogenic activities. The combination of these methods with the use of advanced analytical techniques including XRF, ICP-MS & ICP-OES for the respective phases and the association of prevailing activities with transport pathways using geochemical contouring mapping to show the spatial distribution of the assessed metals in the Lagos Harbour and Lagoon towards addressing the research questions and objectives of this study are valuable additions to improving baseline data in the study area. The combination of sampling methods and analytical techniues enabled the development of data to make relevant ecotoxicological inference and proposal of suitable remediation techniques.

1.10 Novelty and Relevance of the Study

The Lagos Lagoon system is notable as a water body which receives a diverse range of waste from the densely populated and urbanized city of Lagos, in particular the port areas which make up Lagos Harbour. Heavy metal assessment in the harbour and lagoon system dates back to the works of Ajao (1990 & 1996), Oyewo (1998) and Otitoloju (2000). Each of these investigators, and subsequent ones, have assessed environmental concentrations of the heavy metals using a single extraction process per study as well as single analytical equipment (Don-Pedro et al., 2004; Balogun et al., 2011). There has been no attempt to measure the total metal concentration specifically, rather what is usually measured in the recoverable phases (using *Aqua regia*).

The present study has provided the most comprehensive assessment of sediment heavy metals in a single study in the Lagos Harbour and has provided novel data which will make future research in this important water body easier. Firstly, this study has provided a coherent assessment of the heavy metal contamination of the Lagos Harbour and Lagos Lagoon by integrating the sources, pathways, distribution, concentration and fluxes in order to offer a complete description of the impacts of shipping and related activities that affect the sediment and water quality of the Lagos Lagoon system. This approach was lacking in previous investigations. The integrated nature of the comprehensive data generated from this study helps to indicate the specific sources of metal entry into the Lagos Harbour from various shipping activities and this will guide the scientific community, the government and regulatory bodies, and industry in taking specific actions in the sustainable management of pollution in the harbour system. Don-Pedro et al. (2004) divided the Lagos Lagoon into five zones with respect to geography, with Lagos Harbour making up zone 1. The study noted that zones 1 to 3 received higher levels of industrial effluents compared to 4 and 5, based on measured levels in the environmental components (sediment, surface water and biota). This categorization was based on geography, however, and did not specify the activities at specific sections of the area which could account for the respective heavy metal concentrations, nor was there any attempt to describe the pathways empirically. Also, only one sampling point in that area fell within Lagos Harbour. Amaeze et al. (2012) noted the kinds of anthropogenic activities in the coastal areas of the Lagos Lagoon system including the harbour while Amaeze & Abel-Obi (2015) noted the distribution of coastal solid waste dumps in the lagoon. This present study has added considerable value to available information by extensive sampling of the Lagos Harbour and linking sources with pathways and sediment concentrations.

Also, the design of this investigation, which included sampling in the Lagos Harbour, Lagos Lagoon and Apese Lagoon (as a control) in order to identify the sources of heavy metal contamination, as well as pathways arising from different forms of anthropogenic activities within the respective sections, clearly differentiated the contributions of shipping activities in the harbour areas from the various anthropogenic actions which impact different sections of the lagoon system. Previous studies in the lagoon have not emphasized the impacts of shipping activities, rather they have simply assigned a few sampling points in the harbour area as an overall assessment of the entire lagoon system. This study, therefore, conducted an intensive survey of the harbour with a view to determining its heavy metal pollution status and thus ultimately potential approaches to sustainable management.

The use of geochemical contour mapping for the presentation of the spatial distribution of heavy metals concentrations in the Lagos Harbour and lagoon systems is a novelty in the context of investigations in this water body. The use of this technique has clearly linked the sources and pathways with distribution of specific heavy metals and the prevailing activities within the area and seasons. Results of previous heavy metal investigations in the lagoon system were typically presented as isolated charts and tables without showing clearly the link between sources and distribution over space and time. Previous investigations only indicated sampling points and at best sampling zones in the entire span of Lagos Lagoon (Don-Pedro et al., 2004; Amaeze et al., 2015) with no further information detailing specific distribution of sediments concentrations metals at a glance. The novel use of spatial distribution in this study has therefore helped to indicate the relationship between the sources, pathways and prevailing activities of heavy metal contamination within the Lagos Harbour and lagoon system.

The combined analysis and extraction of total, recoverable and bioavailable concentrations of heavy metals in a single investigation is also a novelty in the context of the study area, given that previous investigations in this lagoon only focused on one extraction technique to obtain recoverable forms (Don-Pedro et al., 2004, Ajagbe et al., 2012) without any effort at comparing the concentrations of different phases of the metals. The present study's novel combination of techniques has revealed a broader view of the phases of metal contamination which is lacking in the previous literature on the Lagos Lagoon system. The importance of this is that it gives a more detailed analytical result which can serve as a more realistic way of presenting the heavy metal baseline data for the area which will enhance the performance of regulatory agencies within the Nigerian maritime and oil industry. The knowledge of the concentrations of the bioavailable fraction of metals in the sediments is particularly germane in the toxicological profiling of the harbour sediment because the sediments have been shown to contain a rich diversity of benthic animals which are important in various ecological processes (Mermillod-Blondin et al., 2005) as well as being local delicacies. This is particularly important for the maritime regulators who are saddled with the responsibility of domesticating IMO regulations and presenting accurate data at international fora, which is currently lacking.

In order to achieve the required measurements, three different instruments (XRF, ICP-OES and ICP-MS) were adopted to analyse the sediment samples from the lagoon system in other to give total, recoverable and bioavailable heavy metal concentrations. In this context, the combination of three instruments is considered as novelty because this has not been previously done in the study area. Previous studies in the Lagos Lagoon system have often employed Atomic Absorption Spectrophotometry (AAS) (Don-Pedro et al., 2004, Ajagbe et al., 2011) with the only published study on analysis of sediments using ICP-OES being that of Olatunji & Abimbola (2010). The relevance of this lies in the comparative advantage of the use of multiple instrumentation rather than just one in accurately presenting concentrations of the various fractions of heavy metals determined in sediment samples. More so, most of the surveys in the lagoon did not emphasize sediment. The focus is mostly on the surface water metal concentrations (Emmanuel & Samuel, 2009, Williams & Edobor-Osoh,2013, Addey et al., 108) using AAS. Nkono et al. (1999) examined heavy metals in the Lagoon's surface water using ICP-OES. A few studies have examined the environmental media (sediment and water) and biota for metal accumulation, using AAS only (Otitoloju, 2000; Aderinola et al. 2009, Olowu et al., 2009) but none have done so in a detailed manner which highlights the respective fractions of the metals analysed.

1.11 Contributions to knowledge and Policy

The principal findings of this study have contributed to knowledge in the following ways.

1. This study contributed to knowledge with respect to the determination of heavy metal concentrations in the sediment of Lagos Harbour and lagoon system, particularly in the use of a combination of methods previously unused in the area for metal determination that provided efficient and improved modes of analysis and extraction.
2. This study was able to outline anthropogenic sources of sediment heavy metal contamination within the Lagos Harbour and Lagoon as being primarily from spillage of petroleum products from coastal tank farms, shipping, routine maintenance dredging, port runoffs, industrial effluents, coastal saw mills and dump sites as well as municipal runoffs from urban canals.

3. The study provided maps to demonstrate the spatial pattern of heavy metal distribution and associate such with prevailing activities in various sections of the studied Lagos Lagoon system.
4. Therefore, the outcome of this investigation is useful in developing the strategy that will need to be in place for the protection of marine biodiversity, including microbenthic fauna and fish species.

The specific findings from this study will help policy makers and relevant stakeholders with more accurate measurement techniques and up to date data to protect Nigeria's marine environment. This will also be useful in developing sediment quality guidelines for pollution monitoring and management of the harbour system in Nigeria. Furthermore, the outcome of this study will be relevant in identifying strategies to implement some of the key International Maritime Organisation (IMO) Conventions that are specifically designed to protect the marine environment from contaminants emanating from shipping activities which are detrimental to the quality of marine environment. Examples of such IMO Conventions include: Marine Pollution Prevention (MARPOL 73/78), the London Dumping Convention (LDC), the Ballast Water Management Convention (BWMC), Anti-Fouling (AF) and Wreck Removal Convention (WR). These Conventions are relevant to this study, and Nigeria's present status about their ratifications, domestication and implementation are presented in **Appendix 1**. Nigeria, being a member of the maritime nations under the umbrella of IMO, is expected to implement some of these international conventions that focus on the protection of the marine environment from different sources of pollutants including shipping in which they are party to it. Thus, the use of such international guidelines and standards for the assessment of marine pollution is imperative for the development of local guidelines that will ensure compliance to most of these conventions. These conventions are also significant in the prevention, control and management of waste emanating from shipping activities that has direct potential effect on the biodiversity of the marine ecosystem.

The thesis is primarily aimed therefore at measuring current levels of sediment pollution by heavy metals within the coastal environment of Lagos Harbour and the contiguous sections of the Lagos

Lagoon for establishing the trend in distribution, ecological risk and defining their sources in the area.

CHAPTER TWO: HEAVY METAL CONTAMINATION IN THE MARINE ENVIRONMENT: A LITERATURE REVIEW

2.1 Metals, Heavy Metals and Metalloids

Metals are often characterised and distinguished from non-metals by their physical properties, the ability to conduct heat, and an electrical resistance directly proportional to temperature, malleability, ductility and even lustre (Housecraft & Sharpe 2008). Duffus (2002) reviewed thirteen different studies that used lower limits on the density of a "heavy" metal ranging from 3.5 to 7 g/cm^3. Heavy metals are elements with metallic properties and specific weights higher than 5g/cm^3. They do not degrade (Gorhe & Paszkowsi, 2006) but enter the food chain consequently forming complex toxic compounds leading to detrimental effect on biological functions (Lenart & Wolny-Koladka, 2013). In addition, the toxic metalloid arsenic can lead to many health challenges in humans (Abdul et al., 2015). Sharma & Agrawa (2005) reported effects of heavy metals to include;

- Disturbance of electron transport, causing electrons to be transferred to oxygen instead of the natural electron acceptors in chloroplasts and mitochondria,
- Redox-active metals in different oxidation states under physiological conditions can participate in the Fenton and Haber–Weiss reactions (Shaw et al., 2004), producing hydroxyl radicals,
- Inactivation and down-regulation of enzymes of the antioxidant defence system,
- Depletion of antioxidant substrates

Toxic metals can be present in industrial, municipal and urban runoff, and they are harmful to humans and aquatic biota. Increased urbanisation and industrialisation have increased the levels of trace metals, especially heavy metals in water ways. There are over 50 elements that can be classified as heavy metals, but only 17 are considered both very toxic and relatively accessible. Hg, Pb, Cd, Se, Cu, Zn, Ni and Cr, As (metalloid) however, should be given particular attention in terms of water pollution and discharge effects. Toxicity levels depend on the type of metal, its biological role, and the type of organisms that are exposed to it (Okoro et al., 2012). These metals are presented in Table 2 based on their uses and properties.

The history of pollution from heavy metals was reported as early as the 1960s, particularly in the Thames Estuary, UK, where 14 trace elements were studied, including; Al, As, Cd, Cr, Cu, Fe, Pb, Hg, Mn, Ni, Ag, Sn, V and Zn, with their levels compared with other estuaries within the UK (Atrill & Thomes, 1995). Some of these heavy metals, for example As, Cd, Hg, Pb, Cd, Cu and Zn, are regarded as serious pollutants because of their toxicity and their tendency to be incorporated into food chains, and their ability to remain in an environment for a long period of time (Kishe & Machiwa, 2003). Although all trace elements are naturally present, and some are important in small amounts for individual metabolic processes of marine organisms, the heavy metals are considered as an important form of contamination in the marine environment because of their toxicity and accumulation by marine organisms (Ochieng et al., 2008).

Table 2: Present and past uses of some heavy metals and metalloids (Denton et al., 1997).

Metal	Uses of Metals and Compounds
Arsenic	Components of pesticides; wood preservatives; alloys; semi-conductors; medicines; glass and enamels
Cadmium	Electroplating (anticorrosion coatings); thermoplastic stabilizers e.g. PVC; Ni-Cd batteries; alloys; solders; catalysts; engraving; semi-conductors; TV tube phosphorus; pigments in paints and plastics; glass ceramics; biocides
Chromium	Ferrochromium alloys, refractory bricks; electroplating; industrial dyes; ink; tanning; wood preservative; glass making; cement production
Copper	Electrical industry; alloys e.g. brass; chemical catalysts; anti-fouling paint; algaecide; wood preservative
Lead	Storage batteries; leaded gasoline; pigments; red lead paint; ammunition; solder; cable covering; anti-fouling; glazing; PVC stabilizers
Nickel	Steel and other alloys; electroplating; catalysts; rechargeable Ni-Cd batteries
Zinc	Zinc based alloys; brass and bronze; galvanizing; rolled zinc; paints; batteries; rubber; sacrificial anodes on marine water craft

2.2 Marine sediments

Sediment is known to act as a pollutant sink in aquatic ecosystems (Fan & Zhang, 2009). A comprehensive study of the sediments in lagoons and surrounding rivers reveals the transportation patterns of heavy metals from various parts of the land-based sources. Heavy metals exist in different chemical fractions within sediments, and these different fractions have different levels of mobility, bioavailability, and potential toxicity. To study the bioavailability of sediment-based heavy metals, the metal fractions must be quantified. The fractionation of heavy metals within sediment is usually achieved quantitatively using sequential extraction procedures (Zhang et al., 2015).

Investigation of marine sediments provides important information in marine, environmental and geochemical study about pollution of the marine environment (Calace et al., 2005). 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 (Sarkar et al., 2004) and they consist of a varied range of particle sizes, including gravels, sand, silt and clay (Fergusson, 1990). They are well recognised 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 (Sarkar et al., 2004).

Sediments play a useful role in the assessment of heavy metal contamination (Gangaiya et al., 2001). The partitioning behaviour 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 (Denton et al., 1997). Therefore, the analysis of heavy metals in sediments permits detection of contaminants that may be either absent or in low concentrations in water columns, and their distribution in coastal sediments provides a record of the spatial and temporal history of pollution in an ecosystem (Binning & Baird 2001). Therefore, the chemical analysis of sediments is very important from the environmental pollution perspective, because sediments concentrate metals from aquatic systems and represent an appropriate medium for monitoring of environmental pollution (Denton et al., 1997; Sarkar et al., 2004). Sediments 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 remobilisation occur through any disturbance (Sarkar et al., 2004; Adamo et al., 2005).

This study will investigate the concentration of heavy metals in the sediments of the Lagos coastal marine environment. Sediment are important indicators for monitoring longer-term contamination, particularly in an aquatic environment, since contaminant concentrations are orders of magnitude higher than in water and they show less variation in time and space, allowing more consistent assessment of spatial and temporal contamination (Beiras et al., 2003; Pekey, 2006). For these reasons, programmes have been initiated to monitor the concentrations of these contaminants in the environment (sediments), which are often considered vital in the management of the environment in both developed and developing countries (Phillips & Yim, 1981).

The main metals for consideration in this investigation are As, Cd, Cr, Cu, Co, Fe, Pb, Mn, Ni, Sn, V, and Zn. Most of these heavy metals are referred to as the contaminants of concern, and the reason for focussing on them lies with the fact that they are known to be present in marine environment associated with shipping activities within the harbour area and pose significant threats to human health and the environment (Owen & Sandhu, 2000; Baptista Neto et al., 2005). Others such as Fe and Mn, though essential metals in biota are known to have the potential to cause harm at excessively high concentrations of exposure which can result in pollution.

2.2.1 Sources, pathways and sinks of heavy metals

A major natural source of metals is geologic, associated with the weathering process from local rock formations (Riley & Chester, 1971). However, large-scale release of heavy metals to the aquatic environment is often as a result of human intervention (Denton et al., 1997). Coastal regions are some of the most sensitive environments and yet they are subject to human pressure (David, 2003), because of rise in urbanisation, industrial development, and recreational activities. Therefore, pollution levels are often elevated in the coast because of nearby land-based pollution sources (Fergusson, 1990; Angelidis, 1995).

Industrial processes that release a variety of metals into waterways include mining, smelting and refining. Almost all industrial processes that produce waste discharges are potential sources of heavy metals to the aquatic environment (Denton et al., 2001). Domestic wastewater, sewage sludge, urban runoff, and leachate from solid waste disposal sites are also obvious sources of heavy metals into rivers, estuaries and coastal waters (Mance, 1987). Other potential sources include ports, harbours, marinas and mooring sites, also subject to heavy metal inputs associated with recreational, commercial, and occasionally, military, boating, and shipping activities (Denton et al., 1997). This is the underlying importance of this study within the context of Lagos Lagoon, Nigeria, where similar sources of contaminants have been reported since two decades ago as the main input for marine pollution (Ajao & Fagade, 1990; Ajao, 1996).

Table 3 shows the general sources in the area based on point and non-point discharges with associated potential pollutants and is one of the major knowledge base to undertake a proper assessment and management of the lagoon. However, most recent studies in Lagos Lagoon are segmented, without coherent investigations to establishing the pathways and impacts on the ecosystem which this table suggests (Oyewo, 1998). Therefore, identifying the anthropogenic sources of heavy metal contaminants and their concentrations in the specific marine environment of the Lagos Harbour area of Western Nigeria is a primary necessity.

Table 3: General sources of marine pollution (Clark, 2001).

Sources	Point or Diffuse	Potential Pollutants
Effluent discharges	Point or Diffuse	Nitrogen (N) and phosphorus, persistent organic pollutants (POPs), pathogens, organics
Industrial Effluents	Point or Diffuse	Nitrogen (N), chemicals, suspended solids
Oil Storage Facilities	Point or Diffuse	Hydrocarbon
Land fill sites	Point or Diffuse	Nitrogen (N), ammonia, chemicals
Fish farming	Point or Diffuse	Nitrogen (N), phosphorus (P), pathogens, oxygen depleting substances
Organic Waste recycling to land	Diffuse	Nitrogen (N), phosphorus (P), pathogens
Agricultural wastes	Diffuse	Nitrogen (N), Phosphorus (P)
Power generation facility	Diffuse	Nitrogen (N), sulphur, mercury, persistent organic pollutants (POPs), temperature (thermal pollution)
Leaking pipelines	Point or Diffuse	Oil, sewage, hydrocarbons
Mining	Point or Diffuse	Heavy metals, suspended & settleable solids
Shipping activities	Point or Diffuse	Heavy metals, organics, anti-fouling, invasive species

Based on the general sources of marine pollution as shown in Table 3 above, there are six main types of input of pollution into the Lagos marine environment:

- Direct discharge of waste into the sea
- Runoff into the water due to rain
- Ship pollution

- Atmospheric pollution
- Deep sea mining
- Industrial discharges

2.2.2 Toxicity of heavy metals and associated metalloids

Due to the toxicities of heavy metals, they were included as priority substances in the EU Water Framework Directive 2000/60/EC (EC, 2000; DSD 76/464/EC, 1976). For example, concern over mercury in the environment arises from the extremely toxic forms in which mercury can occur. Natural biological processes can cause methylated forms of mercury to form which bio-accumulate over a million-fold and concentrate in living organisms especially fish. These forms of mercury: monomethyl mercury and dimethyl mercury are high toxic causing neurotoxicological disorders. The main pathway for mercury to humans is through the food chain such as fish rather than inhalation (Driscoll et al., 2013).

As: Is a metalloid, rarely found as a free element in the natural environment, but more commonly as a component of sulphur-containing ores in which it occurs as metal arsenides. As is widely distributed in natural waters and is often associated with geological sources, but in some locations, anthropogenic inputs, such as the use of arsenical insecticides and the combustion of fossil fuels, can be extremely important additional sources. As occurs in natural waters in oxidation states III and V, in the form of arsenous acid (H_3AsO_3) and its salts, and arsenic acid (H_3AsO) and its salts, respectively (An, 2006)

Cd: Is also found in soil and water samples. It is a by-product of the mining and smelting of Pb and Zn and is used in Ni-Cd batteries, PVC plastic and paint pigments. It has been reporte to enter the environment via industrial effleunts (Vivian & Massie, 1977; Pan et al., 2010). It can be found in soils because insecticides, fungicides sludge, and commercial fertilizers that use Cd are used in agriculture. Cd has been reported in surface sediments samples (Loska & Wiechuła, 2003) and toxicity for this metal has been reported on marine organisms (Järup & Åkesson, 2009). Cd runoffs were the causal factor of the classical toxicity case study of *Itai Itai* disease in Japan (Nishijo et al., 2017).

Cr: A naturally occurring metal found in rocks, animals, plants and soil. It is among the most environmentally persistent and bioaccumulated element. Although, Cr exists in the oxide form, it can emanate from a variety of sources such as soil erosion, excessive application of fertilizers and the weathering process (Cheng et al., 2012). Chen et al. (2007) reported high enrichment factor for Cr in Kaohsiung Harbour, Taiwan. Due to its bioaccumulatve nature, it poses threats of toxicity to fishes and humans via dietry sources. Its main health hazards include bronchial asthma, lung and nasal ulcers and cancers, skin allergies, reproductive and developmental problems as well as carcinogenic effects (Goulart *et al.* 2005, Shekhawat et al., 2015). There abound reports of respiratory (Dayan & Paine, 2001), dermal (Lewis et al., 2004) effects of Cr excposures in humans as well.

Cu: Is an essential substance to human life, but in high quantities it can cause anaemia, liver and kidney damage and stomach and intestinal irritation. It normally occurs in drinking water from Cu pipes, as well from additives designed to control algal growth. In humans, exposure to Cu can result in a wide range of biological effects depending on the level and duration of exposure (Okoro et al., 2012).

Fe: Is classified as the fourth most abundant element in earth's crust and is an essential element and an important micro-element for physiological functions in living organisms. The anthropogenic source of Fe contamination or pollution in the environment is almost similar to that of other heavy metals: industry, transport, fertilizers and dumping (Szyczewski et al., 2009). Given that Fe is a common and biologically essential metal, living organisms have high capacity to tolerate them. Fe toxicity may arise due to excessive uptake resulting in oxidation via a process called fenton reaction (Winterbourn, 1995).

Pb: Is one of the heavy metal elements with no known biological function. It enters the environment via diverse sources such as: mining, smelting, processing, recycling and the disposal of waste materials such as batteries, cables, pigments petrol (gasoline) and steel products (Gloag, 1981; Duzgoren-Aydin, 2007). Flora et al. (2012) noted that Pb pollution remains a major public health concern particularly in developing countries, which proper pollution management practices are lacking. Pb can find their way into water bodies alongside runoffs where and have been to cause short term and chronic effects on fishes (Davies et al., 1976).

Mn: This mineral element is both nutritionally essential and potentially toxic (Keen et al., 1999). It is physiologically important in the function of enzymes and co-factors (Nielsen, 1999). Together with iron oxide, manganese oxide reduction can be important mineralization pathways in sediments (Ferro, 2003). Reaney et al. (2006) reported Mn (II) induced neurotoxicity in laboratory-exposed mice characterized by increased Gamma amino butyrc acid concentrations in the globus pallidus. There are epidemiologic studies suggested a relationship between exposure to elevated environmental manganese concentration and increased chances occurrence of parkinsonian disturbances in humans (Reaney et al., 2006). These purtends significant risks in water bodies such as the Lagos Harbour and lagoon where the fisheries resources are harvested for domestic consumption.

Ni: This is the fifth most common element on the Earth, after iron, oxygen, silicon and magnesium (Harasim & Filipek, 2014). It is present in the soil, water and air in different form. Ni is essential element for plant in low concentration, but high concentration is toxic (Rathor et al., 2014). It has been reported to occur naturally in soil and surface water with concentration lower than 100 and 0.005 ppm, respectively (McIlveen & Negusanti, 1994). Ni is present in the air, water, soil and biological material emanating from natural and anthropogenic sources (Cempel & Nikel, 2006). The routes of entry of Ni into soil includes waste from metal plating industries, combustion of fossil fuels, nickel mining and electroplating (Khodadoust et al. 2004). In small quantities, it is easily excreted but in larger doses, however, it is toxic and may cause serious health conditions such as contact dermatitis, lung cancer, neurological problems, childhood developmental issues, kidney and liver failure, cardiovascular disease (https://www. Environmental pollution centers.org/nickel/).

Vn: Is a trace element widely distributed in the earth's crust and high levels of V are recognised mainly in basic rocks and minerals (Teng et al., 2006). Its anthropogenic sources include fossil fuel combustion and industrial effluents, tailing dam and coal mining (Teng et al., 2006). The toxicity of V like most other compounds is concentration dependent and this is only likely where large accidental spills or dumping of contaminated ash has occurred. Exposure to Vn has been associated with affects on the central nervous system, respiratory and gastro-intestinal effects (pps.sepa.org.uk/spripa/Pages/SubstanceInformation.aspx?pid=110).

Zn: Is trace element considered essential to plant growth and the physiological function of organisms. Various parts of the body contain Zn, relatively high concentrates are present in the skin, while the visceral organs contain approximately 30-50 µg/g of fresh tissue. Most of the body zinc is in the bones where its concentration is approximately 200 µg/g. Excessive intake of Zn may lead to vomiting, dehydration, abdominal pains, nausea, lethargy and dehydration (ATSDR, 1994).

The ambient load of heavy metals may also have direct ecotoxicological importance (Rainbow, 1995); for example, Cu, Zn and Fe are normal constituents in an organism, but when they exceed certain concentrations, or when additional quantities have been introduced through wastewater discharges or sewage, then the biogeochemical cycles are altered and they become potentially toxic and probably interfere with the ecological balance of the ecosystem (Phillips, 1977). This characteristic has led to concerns over the ecological effects that may be associated with sediment quality. The possible effect of these metals in marine ecosystems is applicable to the dose-response relationship of the metals exceeding the threshold levels of established guidelines for water, sediment and biota, as shown in Figure 3.

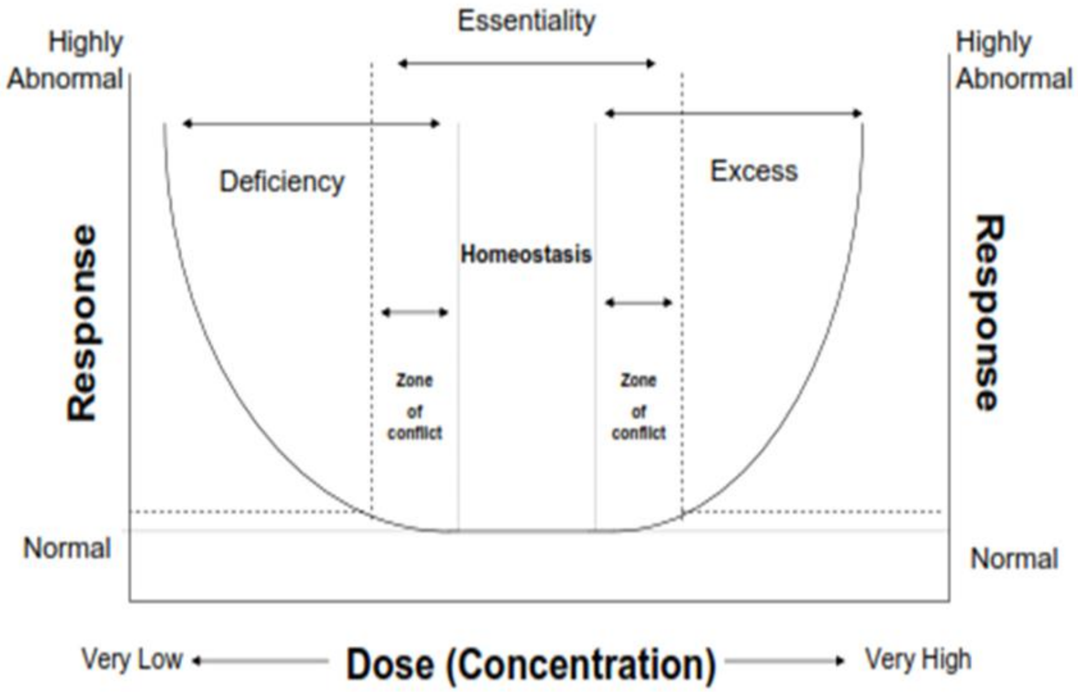


Figure 3: Dose-response curves of the metals exceeding threshold levels (Kapuska et al., 2003).

2.2.3 Speciation of heavy metals

Speciation indicates to the occurrence of a metal in a variant of chemical form which may include free metal ions, metal complexes dissolved in solution and sorbed on solid surface, and metal species that have been co-precipitated in major metal solids or that occur in their own solid phase (Kouassi et al., 2014). The speciation studies of metals in sediments not only show the current quality of the overlaying water but also provide important information on the transportation and fate of pollutants (Chakraborty et al., 2012).

It is widely accepted that total metal content in sediments cannot predict the bioavailability and toxicity of that metal (Chakraborty et al., 2012), rather the physicochemical forms of the metal that establish its bioavailability and toxicity. Thus, the speciation and distribution study of metals in sediments has become one of the most important areas of environmental investigation (Cheng et al., 2009).

Speciation science aims to characterize the forms of the elements in order to understand the transformations between different forms, and to discover the environmental processes controlling these transformations (Gjerde et al., 1993).

Selective chemical extraction removes or dissociates a specific phase with the associated metal bonded to it. The geochemical fractions most commonly analysed are: exchangeable, bound to carbonates, reducible, oxidisable and residual. Among the sequential extraction schemes proposed to investigate the distribution of heavy metals in soil and sediments, the five-step and six step extraction schemes developed by Tessier et al. (1979) and Kersten & Forstner (1986), respectively, are the most widely used. Following these two basic schemes, some modified procedures with different sequences of reagents or operational conditions have been developed (Gomez Ariza et al., 2000), such as those employed for this study.

2.2.4 Heavy metals in sea water

The marine environment is an ecosystem that is vulnerable to pollution. The continental shelf is particularly vulnerable to contaminant loads from sediments transported from coastal and river estuaries (Eruola et al., 2011). The vulnerability of the ocean makes sea water an important environmental medium for these contaminants, including heavy metals. Contaminants first come into contact with the marine environment in sea water process, crucial in determining their fate. The physical and chemical forms of metals in sea water are controlled by several environmental variables such as pH, redox potential, ionic strength, salinity, alkalinity, and the presence of organic and particulate matter, biological activity and the intrinsic properties of the metals. The process involves solution, adsorption, absorption, suspension, flocculation, precipitation, resuspension, oxidation/reduction, siltation, clay-formation, ion exchange. These properties contribute to the bioavailability of heavy metals as well as their possible accumulation in and toxicity to aquatic organisms (Lobban & Harrison, 1997). In coastal waters, concentration of heavy metals decline from river mouths, due to the effects of dilution, and also as a result of the salting–out process of high molecular-weight fractions from the metal speciation and the flocculation of inorganic matter as salinity increases downstream which may adsorb metals and sink in sediments (Lobban & Harrison, 1997).

The concentrations of metals in water are always significantly less than that in sediments, (Nowrouzi et al., 2012). Monitoring of metals in water is less reliable than sediment as a way of identifying pollution due to the latter’s capacity to act as a reservoir for different contaminants.

Arifin et al. (2012), argued that metal concentrations were lower in water and biota than in sediments. This is due to the instability and dilution of these media once they are in water, and the fluctuation of the seawater, which makes them less stable than in sediment.

2.2.5 Heavy metals in marine sediments

Suspended particles adsorb heavy metals from the water column before being deposited as sediment, resulting in the accumulation of higher levels of heavy metals in sediments. In addition, heavy metals may later separate from sediments and re-enter the water column because of changes to environmental factors, such as pH, dissolved oxygen, salinity, and sediment disturbances, increasing aquatic organisms' risks of contamination (Zhang et al., 2015). Thus, heavy metal content in sediments is regarded as a key indicator of aquatic environmental quality. It can reflect the natural geologic background and the effects caused by intensity and time of anthropogenic activities.

Coastal and estuarine sediments in industrial zones serve as the largest reservoir of metal contaminants in the marine ecosystem (Sharifuzzaman et al., 2015). Metals such as Cd,Cu,Hg,Pb and Zn have more substantial effects on the environment than other elements such as Cr, Cu, Mo and Ni (Herut & Sandler, 2006).

Metals typically bind with finer grained sediment particles, such as mud, clay and the organic matter due to their large surface area (Orr et al., 2009). These are then semi-permanently bound until there is a change in the environment which re-mobilises the metals into solution by physical, chemical and biological processes (De Groot et al., 1976).

In the sediments, metals accumulate through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Çevik et al., 2009). Moreover, accumulation or release of metals in sediments is largely controlled by their geochemistry, and the quantities of organic matter, grain size, and cation exchange capacity (Naji & Ismail, 2011). Sediment grain size, mineralogy, reduction/ oxidation state, the adsorption and desorption process, as well as physical movements, all affect the distribution of heavy metal contamination (Buccolieri et al., 2006).

According to Gangaiya et al. (2001), heavy metals transported from the dissolved condition to the particulate phase will lead to the elevation of metal concentrations in estuaries and marine sediments. Hence, concentration of heavy metals is usually higher than those in overlaying water column with several orders of scale (Bryan & Langston, 1992). This is because sediments can accumulate heavy metals and that the concentrations in this medium becomes higher and making it potentially toxic (Bermojo et al., 2003). Therefore, exposure and uptake of even a small size fraction of sediment- bound metal by an organism and where environmental conditions become favourable may lead to bioavailability. This results in increased metal concentrations in pore water which may add meaningfully to the sediment toxicity (Sutherland, 2000).

The evidence of metal-polluted sediments can be assessed by the absence of delicate species or by the development of resistance mechanisms and adjustment in tolerant forms like effective excretory features in organisms (Bryan & Langston, 1992). However, several metals have no established biological function in the marine environment but can symbiotically relate with other chemical species to increase toxicity (Binning & Baird, 2001) in a phenomenon referred to as synergism (Otitoloju, 2000)

Therefore, the possible influences of accumulated levels of heavy metals can be assessed by relating the concentrations of contaminants of interest present in sediments with sediment quality guidelines (SQGs) as reported by Roach (2005).

2.2.6 Major factors affecting metal concentrations in marine sediments

Excessive concentrations of trace metals arising from anthropogenic sources in both estuaries and marine environments is a serious human health and environmental concern. When trace metals are deposited in sediments they undergo a series of physical, biological and chemical processes which determine new chemical phases in the sediment, as reported by Çevik et al. (2009). Understanding the processes affecting trace metals concentration and their fate in sediments is important in measuring suitable plans for sampling and monitoring programmes and planning for appropriate remediation selection process.

2.2.6.1 Texture of sediment

Particle size distribution affects trace metal concentrations in both estuarine and marine sediments (Luoma, 2000). Generally, trace metals are majorly concentrated in the silt/clay sediment fraction, consisting of largely silt/clay fraction with particle size < 0. 063 mm (Williamson & Wilcock, 1994). These enrichments of the silt/clay fraction by anthropogenic trace metals is due to large surface area of this portion and strong adsorptive properties of clay minerals (Williamson & Wilcock, 1994). The clay characteristics which is most important with respect to the trace metals is their ability to absorb metal ions by their outer sheath of hydroxyl groups (Fergusson, 1990). The superficial of clays may be also negatively charged, which is vital in providing possible absorption sites for metal cations (Laszlo, 1987).

In this respect, there is an established relationship of metal concentration and grain size distribution which may be reported as complex, for instance silt/clay particles in estuarine and marine sediments are usually aggregates and particle aggregates that can confuse the association between metal concentration and surface area. Baptista Neto et al. (2006) reported large spartial variations of heavy metals with particle size in the Guanabara Bay, Barazil. Decreasing sediment paricle size has been associated with increasing heavy metal concentrations. In a study conducted by Thorne & Nickless (1981), heavy metal concentrations in the non-residual portion (acid leach) of the sediment was observed to increase with decreasing size of sediment particles. Thorne & Nickless (1981) concluded that "there were significant (99% confidence level) correlations between the amount of less than 20 µm material in the sediment and the concentrations of Fe, Pb, Cu and Mn; lower, but still significant correlations (95% confidence level) were found for Zn, Cd, Ni and Cr".

Another crucial factor in this relationship is the physical and chemical processes which may affect the degree of build-up of metal reactive sediment components on the sediment surface. For example, movement of water across redox boundary may lead to accumulation of iron and manganese oxides (Luoma, 2000).

2.2.6.2 Sediment Transport

The dynamics and sediment characteristics influence the fate and concentration of contaminants, particularly in low energy hydrodynamic conditions which may lead to the tramping of fine particulates. In high areas where high/low hydrodynamics energy occurs, fine particulates are exited (Williamson et al., 2003; Redfern, 2006). Considering this notion, three zones - which are associated with the accumulation of sediments in marine environment - can be distinguished:

1. Zones of accumulation, known as deposition area, this is characterised with fine materials that are persistently deposited, and the wave and current energies are very low in this area.
2. Zones of transportation or movement- In this area fine materials are deposited discontinuously.
3. Erosion zone – The zone is considered as a little area of deposition of fine materials and is characterised by high wave or current energies.

2.2.6.3 Bioturbation

Bioturbation has strong effects on the physical, chemical and biological properties of sediments (Hölker et al., 2015). Biological activities are considered more significant in muddy sediments than sandy sediments where strong physical processes takes place.

Two groups of animals were identified based on their activities at the hight of sediment biological disturbances; (a) large individual groups of predators such as crabs, rays, may move large amount of sediment especially when searching for food, and (b) smaller groups of animals such worms and gastropods may shift small amounts of sediments, but greater population densities make them significant in sediment reoccurrence (Hayward et al., 2004). This process is termed bioturbation and is responsible for the homogenous nature of sediment for at least 60 cm top sediments of Chesapeake Bay (Fergusson, 1990).

The process of bioturbation greatly impacts on the chemistry of muddy sediments. This process is known as oxygen permeation unbioturbated sediments which is extremely limited, and the redox boundary happens a few millimetres below the superficial layer of sediment composition (Williamson & Wilcock, 1994). It is also reported that marine organisms such polychaetes and crabs create a large honeycomb in mud flats of up to 60 cm in depths therefore letting oxygen to be conveyed within sediment through burrowing. The honeycombs formed in turn, provide low tide irrigation of burrow water which maintains oxic conditions when tidal flats are submerged, hence leading to the exchange of solutes between sediments and water. This process turns the sediment to a honeycomb for oxic and anoxic environments (Leong et al., n.d).

2.3 Environmental contamination of Lagos Harbour and Lagoon Systems

Lagos is the most urbanised and industrialised part of Nigeria considering its population of about 20 million people and its city area of 1,171 km^2 (Nichollas & Mimura, 1998). Preceding the active industrialisation starting in the 1960s, urban (including human) wastes were the main sources of contaminants in Lagos Lagoon, but commercial industrial wastes are now most important (Okoye et al., 1991). Odeite (1999) opined that over 2000 industries discharge their wastes directly or indirectly into the Lagos Lagoon. Expectedly this would increase as urbanisation and concentration of industries continues in Lagos and its environs. The risk of pollution in Lagos Lagoon, due to unsatisfactory waste management in the area is high. Human activities within the Lagos Harbour area are restricted to a region not more than a total area of 8.87 km^2 and measuring approximately 23 km in coastal/linear distance associated with a coastline water depth which is less than 30 m. Currently, plans for establishing commensurate countermeasures for the effects of intrusive of human activities into the marine environment are inadequate. It can be argued that these activities have been conducted without planning or expansion of the harbour area to accommodate the commensurate increase in both shipping and other related industrial activities.

The previous studies on the concentrations of heavy metal investigated within the Lagos Lagoon are summarised in Table 4. Most of these metals investigated within the Lagos Lagoon include metals that are similar to those investigated in this study, such as As, Cr, Cu, Fe, Pb, Mn, Ni, V and Zn. These metals were selected based on their toxicity and their potentially harmful effects on various biota and environmental media within the ecosystem. In addition to their toxicities, they are also known to be associated with human induced pollution. The detailed metals and their concentration values are shown in Appendix 2a-c where the summary based on heavy metals studied in Lagos Lagoon within the last three decades. These data were aggregated to identifying the status of the investigated metals and to establish the specific gaps in knowledge that this study needs to address.

Table 4: Previously reported concentrations of heavy metals (mg/kg) studied in Lagos Lagoon within different environmental media.

Serial Number	*Locations*	*Unit*	*As*	*Cd*	*Cr*	*Cu*	*Pb*	*Zn*	*Environmental media (water, sediment or biota)*	*Analytical Methods*	*Instrument Employed*	*References*
1	Lagos Lagoon	mg/kg	2.95-6.69	1.27-2.67	7.36-13.89	14.88-20.81	0.12-0.18	14.23-20.30	Sediment	Analytical (Acid digestion)	Flame Atomic Absorption Spectrophotometer	Bawa-Allah et al. (2017)
2	" "	mg/kg		<0.9	35.8	18.8	25.6	118	Sediment	BCR sequential extraction techniques	ICP-MS	Alo et al. (2014)
3	" "	mg/kg	NA	ND	NA	NA	17.98	13.7	"	Acid digestion	AAS	Williams & Edobor-Osoh (2013)
4	" "	"	NA	ND	NA	12.23	1.47	25.7	"	"	"	"
5	" "	mg/L	NA	ND	NA	NA	ND	0.1	"	"	"	"
6	" "	"	NA	NA	"	"	0.001-0.05	"	Sediment	"	"	"
7	" "	mg/kg	NA	NA	NA	NA	25.46	NA	Biota (fish	Acid Digestion (APHA)	"	Ajagbe et al. (2012)
8	" "	mg/kg	28	3.7	6.0-87	3.0-231	2.0-146	9-32	Sediment	" "	ICP-OES	Olatunji & Abimbola (2010)
9	" "	mg/kg	0.08	1.15	0.62	0.6	0.45	0.73	Sediment	APHA	AAS	Aderinola et al. (2009)
10	" "	mg/kg	NA	0.04-16	2.9–167	1.9-132	NA	7.8-831	Sediment	Acid digestion	AAA	Ajao et al. (1996).
11	" "	mg/kg	NA	16.5	652.1	132.4	483.9	775.9	sediment	Acid digestion	AAA	Okoye et al. (2010)

APHA - American Public Health Association, NA- Not Analysed, ND-Not Detected

2.3.1 Pollution of the Lagos Lagoon system

According to Okoye et al. (2010), pollution of the Lagos Lagoon poses one of the most serious problems for the Lagos metropolis and the city as a whole. This is due to the shallowness of the lagoon and the restriction in water circulation in a micro-tidal environment. The circulation of water in the Lagos Lagoon is characterised by a very low tidal range, sometimes as little as 0.6 m. This leads to narrow and wide expanses of shallow water in the intertidal regions in the creeks and lagoons, inhibiting the movement of sand or mud flats. Due to these features associated with a relatively constant temperature there is highly restricted water circulation in the region, thereby causing the accumulation of organic and inorganic nitrates and phosphates. The absence of vertical movement or circulation within the lagoon results in increased turbidity, during the early rains (Hill & Webb, 1958).

2.3.2 Inorganic compounds as contaminants in Lagos Lagoon system

Inorganic contaminants, such as heavy metals have been investigated in different parts of the Lagos Lagoon (see Table 4). Most of the heavy metals investigated were as segmented study, not coherently considered with the view of determining the sources and effects of these compounds particularly in respect to shipping activities. Furthermore, most studies were centred on effluents and wastes generated from industrial and other sources before they enter the marine environments, and most of these studies were conducted in different environmental media such as water, sediments and marine biota.

The most comprehensive study was conducted in 1996 on trace metal concentrations in Lagos Lagoon as reported by Ajao et al. (1996). The total trace metal levels (mg/kg) recorded in the sediments fell in the ranges of Cd; 0.04 - 16 Co; 0.3 - 103, Cu; 1.9 - 132; Cr; 2.9 – 167, Fe; 1994 - 85548, Mn; 98 - 2757, Ni; 1.6 - 3915, Zn; 7.8 - 831. It is also earlier reported by Okoye et al. (1991), the concentrations of Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn that were determined in the surface sediments of Lagos Lagoon were largely shown to be higher as a result of anthropogenic heavy metal enrichment. This is attributed to the urban industrial wastes as well as run-off water transporting these metals from land-derived wastes (Okoye et al., 1991). Thus, the focus of this study is to provide a coherent study of the distribution of heavy metals within the Lagos Harbour area bearing in mind that there has been an increase in industrialisation since the last major investigation of this kind (Vijverberg et al., 2012).

2.4 Applied techniques for metal evaluation: XRF, ICP-OES and ICP-MS

Previously, heavy metal analysis in the Lagos Lagoon system have been based on Atomic absorption spectroscopy (AAS). The AAS has been used since the 1960s for the quantitative determination of more than 70 elements (Welz & Sperling, 2008), detecting to sub-parts per million (ppm). Recently, modern techniues such as ICP-MS and ICP-OES are now being employed in metal analysis within the lagoon (Table 4).

For this study, the investigation of heavy metals was restricted to only three modern instrumental techniques (ICP-MS, ICP-OES and XRF), this is in line with the research objectives as earlier stated in Chapter 1 of the thesis. These instruments were chosen because of their advantages and wide use worldwide in the analysis of heavy metals within different environmental media (Table 5). Furthermore, advances in understanding of the concentrations and distributions of trace metals in the marine environment have occurred since the mid-1970s (Burton & Statham, 1990). This is mainly due to developments in procedures for contamination-free sampling, the adoption of clean methodologies for handling and analysis of samples, and increased application of improved analytical approaches such as inductively coupled plasma-mass spectrometry (HG-ICP-MS) (Beauchemin, 2010).

2.4.1 Preparation and extraction of heavy metals from environmental media

Different preparations and extraction of heavy metals samples are adopted in different environmental media. Sample preparations for heavy metal analysis are based on the extraction objectives. The preparations of samples for heavy metal analysis are usually undertaken under laboratory conditions involving the thawing of the sediment sample and the grinding of the dry sediment sample used for chemical extraction. These preparations also vary with the methods and aims of the analysis. Preparations of water sample involve filtration, treatment and analysis for dissolved metals according to protocols established for ultra-trace metals analysis in some laboratories, as reported by Braungardt et al. (1998). Extraction tests are commonly used to study the degree of availability under different environmental conditions or affected changes on them. Two types of extraction are considered (single and sequential). The results obtained by the determining the extractable elements are dependent on the extraction procedures applied. But special attention is always paid during extraction particularly on the standard sediment measurements and testing in line with the standards set; for example, European Commission procedures on the preparation of Certified Reference Materials (CRMs) for the extractable heavy metals content (Rauret, 1998). Most single extractions include; acid extraction, chelating agents, buffered salt solution or unbuffered salt solution. The sequential extractions involve the use of extractants of metal fraction bound in different sediment phases that are mor e or less extensively bound. The most common agents applied in sequential extraction include water, carbonate and hydrous oxide (Rauret, 1998).

2.4.2 X-ray fluorescence (XRF)

The X-ray fluorescence (XRF) technique measures the fluorescence spectrum of X-rays emitted when metal atoms are excited by an X-ray source (US-EPA, 1998). The energy or wavelength of emitted X-rays reveals the identity of the metals in the sample and the intensity of emitted X-rays is related to their concentration as described in Method 6200 in US-EPA (1998). XRF spectrometer can analyse a wide range of elements from sulphur through to uranium, with a wide dynamic range, from parts per million (ppm) to percentage (%) levels encompassing typical element levels found in soils and sediments, with detection limits that are different for each element. Metals such as Cu, Pb and Zn have typical detection limits within the range of 50 ppm to 150 ppm (US-EPA, 1998). The XRF instrument is calibrated using several different methods like fundamental parameters determined by the manufacturer. An XRF instrument was used in this study for the determination of total and major elements from the sediment samples collected and analysed.

2.4.3 Inductively coupled plasma optical emission spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) applies plasma energy for analysis of samples, while the component elements (atoms) are excited (Rosenthal et al., 2004). When the excited atoms return to a low energy position, emission rays (spectrum rays) are released and the corresponding photon wavelengths are measured. The element type is determined based on intensity. First, argon carrier gas is supplied to torch oil, and a high frequency electric current is applied to the work coil at the tip of the torch tube. The plasma has high electron density and temperature (10,000 K) and this energy is used in the excitation emission of the sample. Samples solutions are introduced into the plasma in an atomized state through a narrow tube in the centre of the torch (Rosenthal et al., 2004). The ICP-OES consists of a light source unit, a spectrophotometer, a detector, and a data processing unit. This technique was also used in this investigation especially for the analysis of total extractable metals in line with the procedures set out by the National Water Research Institute of Canada, which is simiar to US-EPA recommended method (NWRI, 2006).

For analysis of chemical speciation, different methods have been employed by different researchers such as voltammetry (Ashraf et al.,2012), liquid– liquid extraction (Francis et al., 2001), ion exchange and adsorption columns resins (Pan et al., 2010), gas chromatography (Rodil et al., 2002), liquid chromatography (Juhasz et al., 2002), capillary electrophoresis (CE) (Yin & Wang, 2005) as well as inductively coupled plasma mass spectrometry (ICP-MS) (Butcher, 2007).

2.4.4 Inductively coupled plasma mass spectrometry (ICP-MS)

The inductively coupled plasma mass spectrometry (ICP-MS) technique has been introduced for determination of a wide range of elements in different environmental matrices, including both solid and aqueous samples (Koppenaal et al., 2004; Gabarino et al., 2006). The ICP-MS technique operates based on the use of collision/reaction cell technology to reduce molecular ion interferences (Tanner et al., 2002; USGS, 2006), and the updated version of the ICP-MS can be used in determining elements in the whole-water, biota, sediment and also soil digest fractions (USGS, 2006). ICP-MS instruments have multiple resolution settings available; enabling many commonly encountered spectral interferences to be separated from the analytes of interest (Townsend et al., 2007).

2.4.5 Comparative study of ICP-MS, ICP-OES and AAS

As indicated in the summary of the previous studies in the Lagos Lagoon system in Table 4, the use of AAS in heavy metal analysis has been the common practice since the earliest account of

Ajao et al. (1996) and Oyewo (1998) to the more recent report of Bawa-Allah (2017). Except for a few reports in recent times (Olatunji & Abimbola, 2010; Alo et al., 2014) the use of analytical equipment such as ICP OES and ICP-MS is yet to be integrated in routine monitoring of the lagoon. These modern analytical equipment, apart from having a significantly shorter run time have the ability to provide more pricise results in parts per billion using small samples compared to AAS.

Basically, the sample introduction system and plasma of ICP-OES and ICP-MS look similar. In ICP-OES, the optical spectrum with a typical range of 165-800nm is viewed and measured, either sequentially or simultaneously. The simultaneous ICP-OES can be faster for a large number of elements, but more expensive, than sequential ICP-OES. This greatly depends on the number of elements, and the concentrations required. More recently, several ICP-OES spectrometers are able to reach to 120 nm, thus enabling the determination of Cl at the primary wavelength of 134.664 nm with sub-ppm detection limits.

ICP-MS on the other hand could be a useful tool for sensitive speciation analyses of many environmentally important elements. The analysis of heavy metal species in soil, dust or sediment, can be undertaken by either acid digestion or sequential extraction techniques. Sequential extraction (SE) techniques (Ashraf et al., 2012) use successive chemical extractants of various types in order of greater detective ability and therefore possess greater sensitivity than a single extraction procedure. Speciation, using sequential extraction schemes has been developed for assessing geochemical forms in soil and sediment (Zufiaurre et al., 1998).

ICP-MS extracts the ions produced in the plasma into an interface consisting of a sampler cone followed by a skimmer cone. This configuration enables the pressure to be reduced differentially from atmospheric pressure down to a final pressure of between 10^{-5} to 10^{-7} Torr. The ions, once through the interface, are passed through ion optics, which optimize the ion paths to eliminate neutral species and light, usually by a photon stop. The ions then pass through a mass filter, usually a quadrupole, before the selected ions reach the detector. The ICP-MS provides information for each atomic mass unit (amu), or Da. The ratio of the mass of the ion to its charge, is displayed, and labeled m/z, in the mass region 3-250 Da. The isotope information can be used in several ways; these include isotope ratio measurements, often used for Pb and U that do not have a constant natural abundance, and analysis of samples having unnatural isotope abundances. ICP-MS detection limits are very excellent. Most detection limits are in the 1-10 parts per trillion (ppt) range for solutions. These are as good as, or better than, GF-AAS for most elements in pure water and also cover many more elements. ICP-OES has typically two to three orders of magnitude poorer detection limits than ICP-MS, with most elements in the 1-10 part per billion (ppb) range. Recently, one ICP-OES spectrometer has shown impressive detection limits in the sub-ppb region for some elements using a high-resolution monochromatic with radially viewed plasma. Flame AAS has generally poorer detection limits than ICP-OES except for the alkalis metals, e.g., Na, K. These instruments are described in Tables 5 and 6; summarizing the comparison of the application of these techniques. Draghici et al. (2010) illustrated in Table 5 the techniques, principles, analysis and application of heavy metals determined using different methods. Table 6 presents a comparative assessment of ICP-OES and ICP-MS with AAS which is the commonly used method for metal assessment in the Lagos Lagoon system.

Table 5: Most usual methods applied for heavy metals determination (Draghici et al., 2010).

Technique	Principle	Type of analysis	Applications
Atomic absorption spectrometry (AAS)	Absorption of radiant energy produced, by a special radiation source, by atoms in their electronic ground state	-single element; -multi-element analysis (2-6elements)	widely used
Inductively coupled plasma with atomic emission spectrometry (ICP-AES)	Measures the optical emission from excited atoms	simultaneous multielement analysis	Widely used method for environmental analysis
Inductively coupled plasma with mass spectrometry (ICP-MS)	-argon plasma used as ion source; –used for separating Ions based on their mass-to charge ratio	simultaneous multi-element analysis	-widely used; -isotope determination
Atomic fluorescence spectrometry (AFS)	Measures the light that is re-emitted after absorption	Single element	-mercury, arsenic, and selenium; -complementary Technique to AAS
X-ray fluorescence (XRF)	-X-rays–primary excitation source; -elements emit secondary X-rays of a characteristic wavelength	simultaneous determination of most elements	-non-destructive analysis; -less suitable for analysis of minor and trace elements
Neutron activation analysis (NAA)	-conversion of stable nuclei of atoms into radioactiveones; -measurement of the characteristic nuclear radiation emitted by the radioactive nuclei	simultaneous multielement analysis	-most elements can be determined; -highly sensitive procedure
Electrochemical methods	-controlled voltage or current; -polarography; -potentiometry; - stripping voltammetry;	consecutive analysisof different metal ions	-analysis for transition metals and metalloids (total content or speciation analysis)

Table 6: Simplified comparison of ICP-MS, ICP-OES, Flame AAS, and GF-AAS (Tyler, 2005).

Parameters of interest	ICP-MS	ICP-OES	Flame AAS	GF-AAS
Detection limits	Excellent for most elements	Very good for most elements	Very good for some elements	Excellent for some elements
Sample Throughput	All elements 2 - 6min	5-30 elements/min	15 seconds/element	4 min/element
Linear dynamic Range	10^5 (10^8 with Range extens ion)	10^4 to 10^8	103	102
Precision:				
Shortterm (in-run)	1-3%	0.3-1%	0.1-1%	1-5%
Longterm (4h)	<5%	<3%		
Isotopes	Yes	No	No	No
Dissolved solids max. concentration	0.1-0.4	1-30	0.5-3	>30
No. of elements	>75	>75	>68	>50
Sample usage	Low	Low	Very high	Very low
Semi-quant analysis	Yes	Yes	No	No
Isotope analysis	Yes	No	No	No
Routine operation	Easy	Easy	Easy	Easy
Method development	Skill Required	Skill Required	Easy	Skill Required
Unattended operation	Yes	Yes	No	Yes
Combustible gases	No	No	Yes	No
Operating cost	High	High	Low	Medium
Capital cost	Very high	High	Low	Medium/high

2.5 Sediment quality guideline

One of the first applications occurred in 1989 when the US National Oceanic and Atmospheric Administration (NOAA) proposed screening values for 190 chemicals in sediment as a means of gauging the quality of sediment in marine and freshwater environments (Kwok et al., 2013). The primary intent of the NOAA effects-range-median and -low values (commonly referred to as ER-M and ER-L, respectively) measurments has remained unchanged to the present—to establish a scientific rationale for taking corrective actions to protect aquatic ecosystems from exposure to chemicals in sediment that have the potential to harm aquatic life. NOAA’s SQGs continue to evolve as new knowledge becomes available and have been either adopted directly or used as the foundation for deriving sediment quality values in several countries around the world (Kwok et al., 2013).

The set of NOAA Screening Quick Reference Tables (SQuiRTs) presents screening concentrations for inorganic and organic contaminants in various environmental media. Guidelines for sample preservation and options for laboratory analytical techniques are also included. The SQuiRT cards were developed for internal use by the Coastal Protection and Restoration Division (CPR) of NOAA. The CPR Division identifies potential impacts to coastal resources and habitats likely to be affected by hazardous waste sites. The NOAA Screening Quick Reference Tables for metals in freshwater and sediment are presented in Appendix 3. The NOAA Screening Quick Reference card set is organized into the following sections to streamline analytical objectives for better outcomes due to its broader analytical range in sediment quality guideline:

- Inorganic in Solids (freshwater and marine sediment, plus soil)
- Inorganic in Solids (groundwater and surface water)
- Organics in Water and Solids
- Analytical Methods for Inorganic
- Analytical Methods for Organics
- Guidelines for Sample Collection & Storage (NOAA, 1999)

2.6 Current knowledge gaps

From the literature review, as summarised in Table 4, three key gaps exist:

1. Current research on contamination by heavy metals in the Lagos Lagoon has been uncoordinated, leaving an unclear picture of the level of contamination within the marine environment. The previous studies have assessed heavy metal concentrations across various environmental components such as water, sediments and biota, with data dispersed across several areas within the Lagos Lagoon. Some studies, particularly those conducted within the confined area of the Lagoon, are not coherent in terms of assessing

and establishing the sources and potential ecological effects of these metals on sediment quality.

2. Previous studies on heay metal distribution have presented results as isolated sampling points on maps with no connection to understand spatial distribution and/or levels of the elements in relation to respective sources/ pathways into the lagoon. Thus, as a contribution to knowledge, the spatial distribution of the heavy metals detected in the sediment samples will be developed into appropriate maps for ease of understanding the relative levels in various sections and therefore profer explantaions as to the potential sources of these metals in the lagoon system.
3. Previous investigations of heavy metals conducted within the Lagos Lagoon have only employed one method of digestion per study and analysis has been mostly with AAS (Osibanjo et al., 1994). Previous studies on the sediments of the Lagos Lagoon system have also not compared outcomes of various kinds of analysis using different techniques. Although in recent times, few studies in this area have employed technologies such as ICP-MS and ICP-OES which are specifically designed to measure heavy metals, none has employed these technologies in combination with XRF in other to analyse and extract metals and metalloids in sediment samples for total, recoverable and bioavailable forms.

CHAPTER THREE: DESCRIPTION OF THE STUDY AREA

3.1 Lagos metropolis of Nigeria

Lagos metropolis, Nigeria is Africa's biggest city (20 million people) and one of the fastest growing metropolises in the world. With much of the nation's wealth and economic activities along with 12 % of Nigeria's population, Lagos metropolis is the most heavily urbanised and industrialised city in Nigeria. The city is currently undergoing an extensive programme of expansion and development with the aim of becoming a 'megacity' and major international focus for trade and industry (Howden, 2010). This is part of what contributes to the pollution of the marine environment including harbour and lagoons in the area.

Lagos is built on several floodplains and encompasses a network of marshes, swamps, streams, creeks, rivers and estuaries that receive large quantities of rainwater run-off, municipal effluents, all of which discharge into the Lagos Lagoon. The city also has about 91 waterways (canals). Most of the major markets and industries including *Iddo, Yaba, Oshodi, Mushin, Alaba Rago, Alaba Internatlonal*, generate large quantities of municipal wastes which are either dumped directly into the lagoon or are incinerated at sites that drain into the lagoon. Open waste incineration, in some cases on the shores of Lagos Lagoon, is a very common phenomenon in Lagos.

3.2 Lagos Lagoon

Lagos Lagoon, situated in the western coast of Nigeria, is the largest of the four lagoon systems of the Gulf of Guinea (Onyema, 2013). Its central body is located between longitude 3° 23′ to 3° 40′ E and latitude 6° 22′ to 6° 28′ N. The Lagos Lagoon system is comprised of three main divisions; namely Lagos Harbour which represents the central area of the lagoon, the urbanised part of the lagoon which is in the west, and the eastern division of the lagoon as shown in Figure 4. The Lagos Lagoon has a surface area of about approximately 200 km^2 (Vijverberg et al., 2012). It is characterised by coastal slum settlements, wood saw mills, dump sites, domestic and occasional industrial activities (Amaeze et al., 2012). These activities generate domestic waste and other industrial discharges into it. Thus, it forms the criteria for sites selection as hotspots of pollution source discharged into the Lagos Lagoon and Harbour.

3.3 Lagos Harbour

Lagos Harbour (Figure 4) is the main water inlet from the Atlantic Ocean to the seaports (James & Adejare, 2010). Lagos Harbour has one of the busiest ports in Nigeria, perharps the busiest in Sub-Saharan Africa (Doherty & Otitoloju, 2016). The port also has a major dry-docking facility, used by several large fishing fleets and ships. The harbour system was built as a semi-enclosed basin area generally to aid a restricted water circulation, characterised by low energy levels, in order to support the activities within the seaport area. Existing for many decades, the Lagos Harbour is the only natural break from the Volta River to the River Niger (Hill & Webb, 1958; Addey et al., 2018). The coastal zone is characterised by a tropical climate with April to November comprising the rainy season and December to March the dry season. Due to these climate variations, increases in temperature and humidity cut across wet and dry seasons within the Nigerian climate. This in turn leads to an annual rainfall within the coastal areas totalling between 1500 and 4000 mm (Kuruk, 2004).

Lagos Harbour is part of an extensive estuarine system. The main Harbour entrance and navigation channel connect to a large lagoon and numerous tidal creeks. The Lagos Lagoon has a surface area of approximately 200 km^2, which makes it one of the bigger lagoons of the West African coast. The largest river debouching in the lagoon is the Ogun River. The Commodore Channel is the only significant connection between the Lagos Lagoon and the Atlantic Ocean. The large difference in precipitation between the wet and the dry season causes a significant seasonality in the discharge through the channel (Van Bentum, 2012). Ballendux (2011) showed that the mud in the Commodore and Apapa area mainly contains montmorillonite clays.

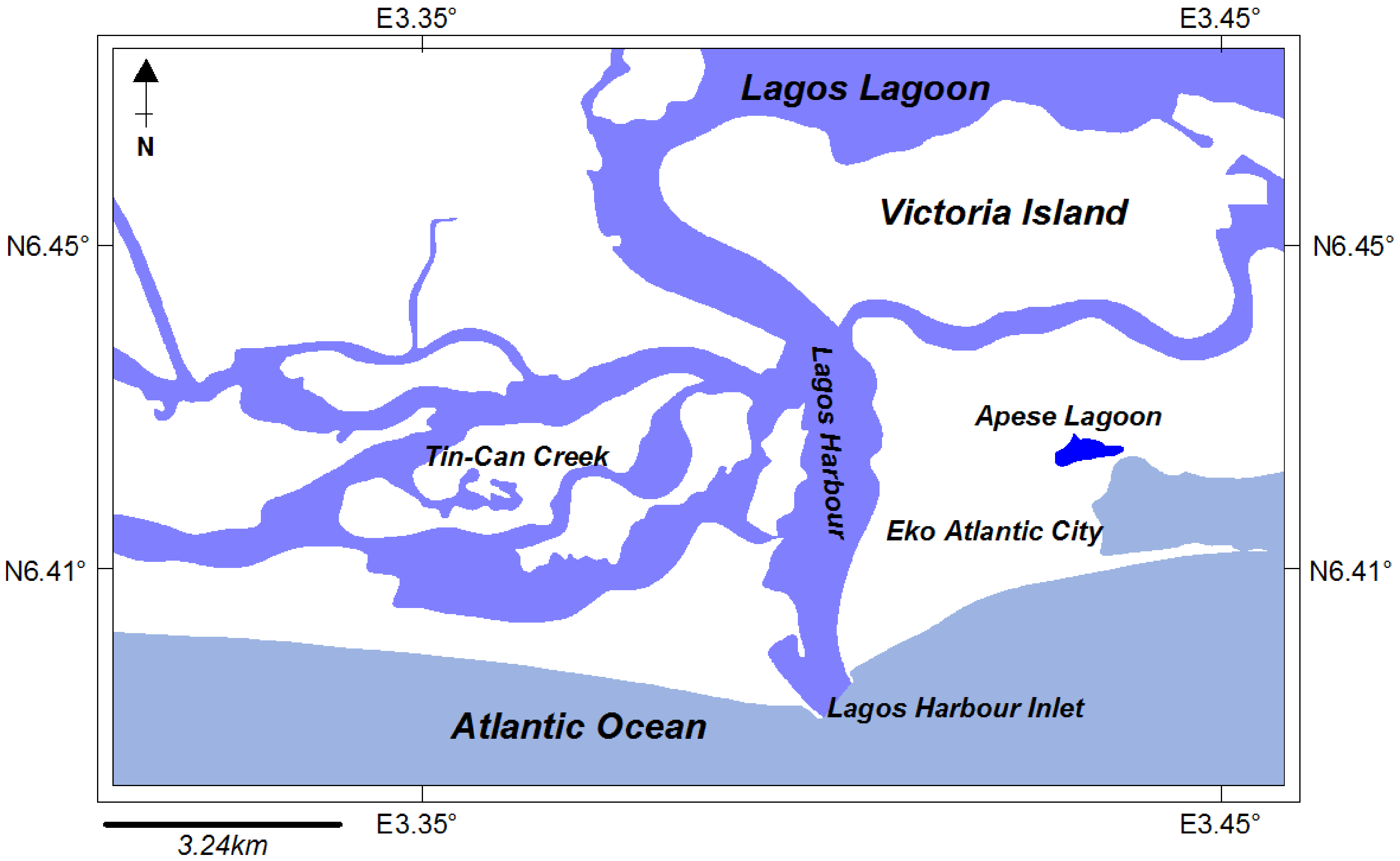


Figure 4: A section of the Lagos Lagoon system showing the Lagos Harbour, parts of the Urbanised sections of the Lagos Lagoon, and Apese Lagoon (Control)

3.4 Apese Lagoon

Apese Lagoon, one of the few lagoons in the south-western Nigeria and claiming the half-part of the divided Kuramo lagoon, is historically referred to as Onijedi lagoon (Edokpayi et al., 2004; Nwankwo et al., 2004). Geographically, Apese Lagoon, located in the eastern side of the Kuramo lagoon, Victoria Island, Lagos, lies within latitudes $6^0$25'20.83''N and $6^0$25'20.29''N and longitudes $3^0$27'57.19''E and $3^0$27'57.19''E and is about 5-6 km linear distance from the Lagos Harbour. As shown in Figure 5, the lagoon is the smallest of the ten lagoons in the region, and measures about 32000km^2 in surface area. The lagoon has a closed irregular-shape figure with its length and widest extremes measuring about 1.3 km and 0.16 km respectively.

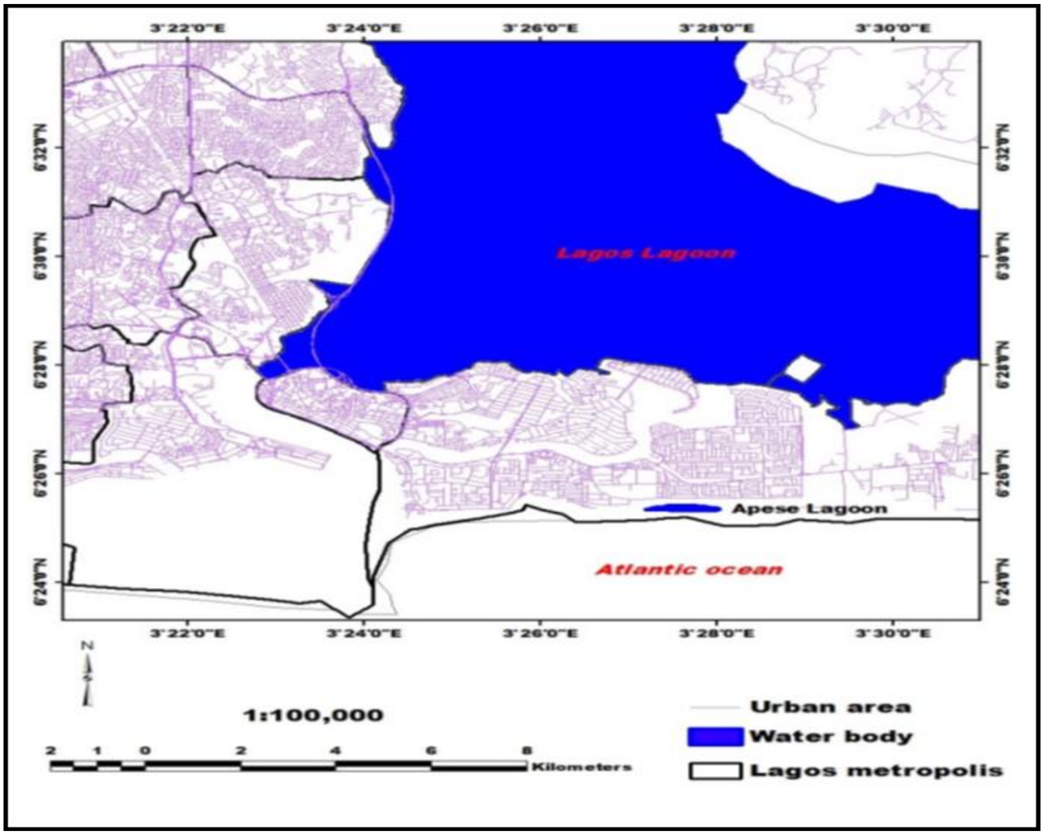


Figure 5: A section of the Lagos marine areas showing Lagos Lagoon and Apese Lagoon(Control)(Nkwunonwo & Bamanga, 2015).

Unlike other lagoons and estuarine water systems in the region, the Apese Lagoon gets seawater inputs chiefly from beach overflows especially at high tide from the Atlantic Ocean (Onyema, 2009 a, b).

The lagoon according Nwankwo, 2004 shows stable physico-chemical properties of water measurements because of less anthropogenic activities. The lagoon was suggested to be a marine protected area by Nwankwo 2004. Therefore, due to the stable condition of the lagoon water that led to the rationale of choosing the lagoon for control zone of the study.

3.5 Geology of Dahomey Basin

The geology of Lagos has been discussed alongside the geology of the Eastern Dahomey Basin (Jones and Hockey, 1964; Billman 1976, Omotsola and Adegoke, 1981; Agagu, 1985; Nton, 2001). The Dahomey Basin (Embayment) is a combination of inland/coastal/offshore Basin that stretches from South-eastern Ghana through Togo and the Republic of Benin to South-western Nigeria. It is separated from the Niger Delta by a subsurface basement high referred to as the Okitipupa Ridge.

3.5.1 Lithostratigraphy of Dahomey Basin

The stratigraphic setting of the Eastern Dahomey Basin has been described in detail in the works of Adegoke (1969); Billman (1976); Ako et al. (1980); Omatsola and Adegoke (1981) and Okosun (1990). These authors reported and described five lithostratigraphic Formations covering the Cretaceous to Tertiary ages. The Formations from the oldest to the youngest (Figure 6 and Table 7) include: Abeokuta Group-Ise, Afowo and Araromi (Cretaceous), Ewekoro Formation (Paleocene), Akinbo Formation (Late Paleocene to Early Eocene), Oshosun Formation (Eocene) and Ilaro Formation (Eocene).

Abeokuta Group: The oldest unit in the Abeokuta Group (Jones & Hockey, 1964) is unconformably overlying the basement complex rocks throughout the Basin. It consists of conglomerate sandstones, sands, siltstones, clays, shales and thin limestone bands (Table 7). It is considered by Omatsola & Adegoke (1981) to be of Neocomian to Paleocene in age and it is the thickest single sedimentary unit in the Basin. Lithostratigraphic Succession of the Abeokuta Group. The group was studied by Billman (1976) but was reviewed by Omatsola & Adegoke (1981) on the basis of new subsurface data.

The group's sedimentary fill was sub-divided into three intervals by Durham & Picket (1966) namely:

a. Sand and sandstones at the base.
b. Alternating sands and shales.
c. Upper shales.

These classifications correspond to this three Formations; Ise, Afowo and Araromi respectively (Omatsola & Adegoke, 1981).

Ise Formation is the oldest Formation and where present, it directly overlies uncomformably the basement complex. It comprises of conglomeratic sands at the base with an upward fining variation into gritty coarse to medium grained loose sands inter-bedded with whitish kaolinitic clays. Quartz is the major constituent of the sands although some other minerals like mica and heavy minerals have been reported in very minor amounts. This Formation has been said to be of Neocomian age.

In **Afowo Formation**, the sediments indicate the commencement of deposition in a transitional environment after the entirely basal and continental Ise Formation. They consist mostly medium to fine grained sandstones inter-bedded with relatively thick siltstones and shales. The sands are tar bearing while the shales are rich in organic matter. They are blackish water shales below and become marine towards the top with abundant fossils. The shaliness generally increases from bottom to top. The Afowo Formation ranges in age from Turonian to Maastrichtian.

The sediments in **Araromi Formation** represent the youngest and topmost sedimentary sequence in Abeokuta Group. It comprises fine to medium grained sands towards the base overlain by siltstones and shales inter-bedded with bands of limestone, sands and lignite towards the top. The shales are dark to grey, mostly marine and are generally rich in organic matter. Both the sands and shales here are bituminous in many places.

Ewekoro Formation was first discovered by Jones and Hockey (1964) and was found to be the unit overlying the Araromi Formation uncomformably (Table 7). It varies from buff – light brown highly fossiliferous limestone at its upper end to dark grey fossiliferous limestone at the lower part of the formation (Adegoke et al., 1980).

Akinbo Formation is characterized by a glauconitic rock band at the base which overlies the Ewekoro formation. The Formational status was established by Ogbe (1972) with a type section at the Ewekoro quarry. It is the same as the upper shale member of Jones 1964. The formation is believed to be the lateral equivalent of the Paleocene – Eocene Nanka Sand (Anambra Basin) and it is overlain by the Oshosun Formation (Omatsola & Adegoke, 1981). It is composed of a well laminated greenish grey to black shales, it varies in thickness and get thinner towards the top of the unit.

The shales of the Akinbo Formation grade into the overlying mudstones and claystones of the **Oshosun Formation**. In its lower part, the Formation is composed of dull brown and brick-red sandy mudstone and claystone with light grey and purplish mottling. Thin pebble beds and coarse pebbly sandstones are locally interbedded. Rare inclusions of phosphatic and glauconitic material occur, becoming more abundant and characteristic in the middle part.

Ilaro Formation includes both marine and continental sediment. It consists of a massive yellow, poorly consolidated sandstone of red and brown weathered surfaces, bands of coarse ferruginized sandstone and ironstone indicating hiatus of depositional environment (Reyment, 1965).

The **Coastal Plain Sands** and **Recent Alluvium** are the youngest sedimentary units in the Eastern Dahomey (Jones & Hockey, 1964). They consist of soft, poorly sorted clayey sands, pebbly sands, sandy clays and rare thin lignite developed to thickness as much as 400 meters towards the coast around the Ise – 2 well (Agagu, 1985). An Oligocene to Pleistocene age has been assigned to this unit and occasionally recent alluvial, littoral and lagoonal deposits that compromise sands, salts and clays cover portions of older units. On top of most sections are the topsoil mostly lateritic clay, sand and pebbles with colour ranging from grey to yellow and brown. In places where laterization is advanced, the predominant colour is reddish brown, which is attributable to prolonged exposure and subsequent oxidation of the materials.

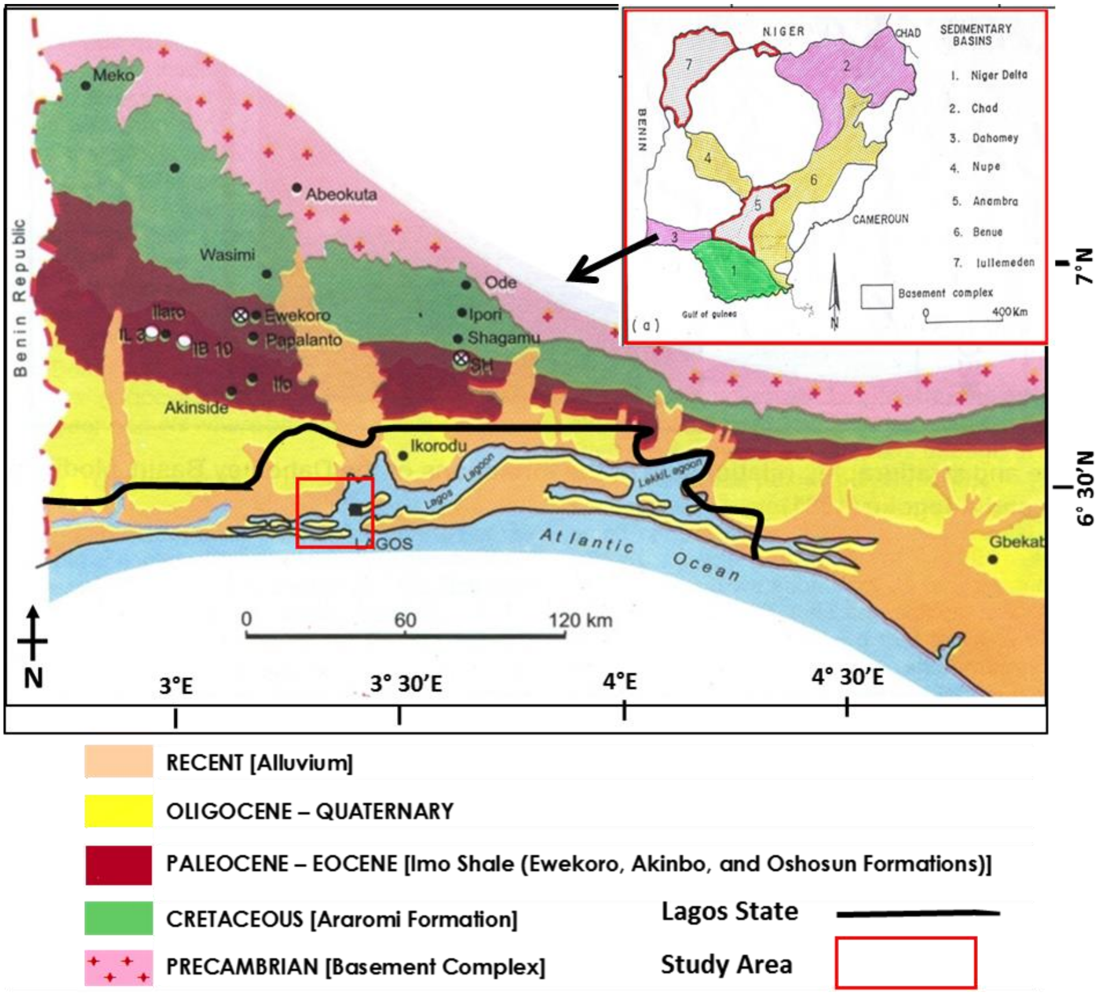
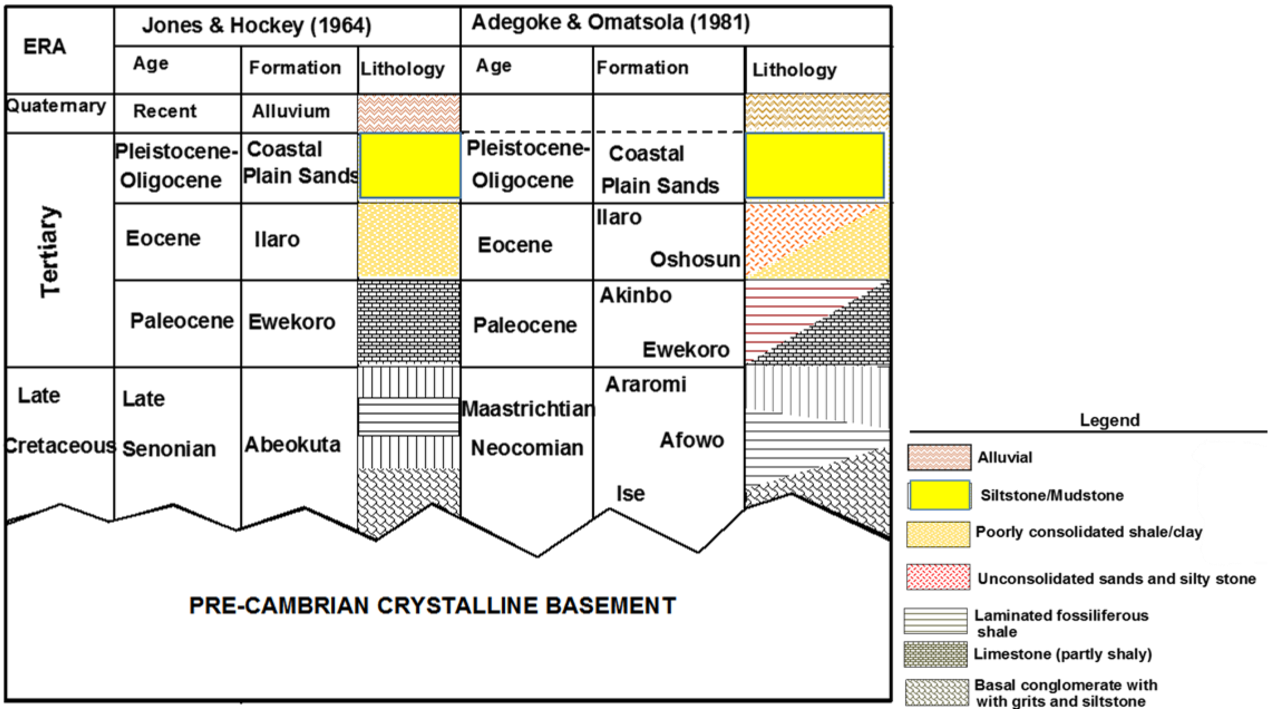


Figure 6: Generalized geological map of Eastern Dahomey Basin (Billman, 1976).

Table 7: The Stratigraphic Chart of Eastern Dahomey Basin (Adegoke & Omatsola, 1981).



IKhane et al. (2012) in their assessment of the petrography and geochemistry of the Dahomey Basin, South West Nigeria determined the major and trace metals which make up the sandstone facies. Their study showed the presence of some major elements (SiO_2, Al_2O_3, Fe_2O_3, CaO, Br, and TiO_2) and trace elements (V_2O_5, SO_3, P_2O_5, CuO, MnO, Rb_2O, and AS_2O_3) respectively. Ajayi et al. (2006) showed that the mean concentrations for Fe was 3.725 wt.% in Oshosun formation in the Western part of the Dahomey Basin of SW Nigeria where the Lagos Lagoon lies. The relatively high Fe content was attributed to accumulation of goethite in the phosphatic shales of the formation. The results from the field investigations will be discussed with due reference to the fact that background levels of naturally high metals would affect the concentrations determined in the Lagos Lagoon system.

3.6 Coastal geomorphology of Nigeria and Lagos Lagoons

The Nigerian coastal and marine area consists of a narrow coastal strip of land bordered by the Gulf of Guinea of the Central Eastern Atlantic. The coastal areas stretch inland for about 15 km in Lagos to about 150 km in the Niger Delta and about 25 km east of the Niger Delta. The Nigerian coastal area is divided into four main geomorphic zones namely:

- Barrier Lagoon Coast
- Mahin Mud Coast
- Niger Delta
- Strand Coastline

The Barrier Lagoon Coastal Complex stretches from Badagry in the east to around Agerige village where the coastline starts a southward inflection. The barrier bar consists of beach ridges fronted by a very narrow beach with a foreshore gradient of about 1:50. Beach crest elevation is between 3-4 m above mean low water tide. The foreshore is backed by narrow and sandy beach ridges, which are aligned parallel with the modern coast. The beaches are subjected to high-energy waves, resulting in the formation of characteristically steep beach profiles. This coastal complex is very fragile, composed of narrow low lying sandy barrier bars backed by the Lagos, Lekki and Yewa lagoons, and linked together by many tortuous creeks (Awosika & Folorunsho, 2000).

The MahinMud Coast is a muddy coastal complex, which lies east of the barrier lagoon coast and stretches to the Benin River in the northwestern flank of the Niger Delta. The coastline is sonamed because of the absence of sandalong the beach and the predominance of silt and clay size sediments. The coastal plain embodying this area stretches about 20 km inland. Relief ranges from sea level along the coast backed by a wide expanse of tidal flat, wide expanse of coastal plain with relief rising gently from 2 m to about 50 m above mean sea level.

The Niger Delta extends over an area of about 75,000 km^2 and accounts for 7.5 % of Nigeria’s land mass covering a coastline of 560 km, about two-thirds of the entire coastline of Nigeria. The Niger delta is rimmed by a chain of sandy barrier islands approximately twenty in number (Allen, 1965). The Niger delta spreads over a number of ecological zones; sandy coastal ridge barriers, brackish or saline mangroves, freshwater permanent and seasonal swamp and lowland forests. The Strand Coast stretches from Imo River eastwards to the Cross-River estuary along the Nigerian Cameroon boundary. The vegetation of the 85 km long strand coast comprises mangrove swamps with species composition similar to those of the Niger Delta zone (Awosika & Folorunsho, 2000).

The Barrier Lagoon complex is backed by the Badagry Creek, the Lagos Lagoon, Lekki Lagoon and numerous other creeks whose only connection to the sea is through the commodore channel in Lagos. The Barrier Lagoon coastal system consists of narrow beach ridges, which are aligned parallel to the coast. Beach sediments along the barrier complex show wide variation in textural characteristics. The sediment compositions are affected by wave/tidal action, littoral current and the petrographical compositions of the shore; hence the grain size distribution of beaches is a function of the hydrodynamic conditions. Sediment distributions along the beach are a result of complex interactions between sediment sources, wave energy level and the general offshore slope on which the beach is constructed. The intensity of the wave action in the littoral zone generally redeposits and sort materials of all grain sizes. Thus, the composition of beach sediment is affectednot only by wave action but depends largely on the amount of plastic material supply to the coast (Abdulkarim et al., 2011).

3.7 Hydrodynamics of coastal lagoon systems

Coastal lagoons are enclosed water basins, with relatively shallow water depths, and situated at the boundary between the land and the ocean. They are usually oriented parallel to the coast and separated from the ocean by a barrier. These lagoons normally have one or a number of streams entering around their perimeter and are connected to the ocean at one or number of inlets. Coastal hydrodynamics of these lagoons are governed by a delicate balance between tidal forces, influxes from the streams, wind stresses, and density induced pressure forces and bottom friction (Sayed & Ahmed, 2014).

Coastal lagoons can be conveniently subdivided into choked, restricted and leaky systems based on the degree of water exchange with the adjacent coastal ocean. The choked lagoons are usually found along coasts with high wave energy and significant littoral drift. They are characterized by at least one and narrow entrance channels, long residence times and dominant wind forcing. Lagos and Lekki lagoons can be categorized as choked lagoons. Lagos Lagoon is a water body in the heart of the Lagos metropolis. Lagos Lagoon cuts across the southern part of the metropolis, linking the Atlantic Ocean in the south. Lagos Lagoon is more than 50 km long and 3 to 13 km wide, separated from the Atlantic Ocean by long sand barrier 2 to 5 km wide, which has swampy margins on the lagoon side. The Nigerian authorities do not permit any opening or outlet to release rainfall storms. Alternatively, outfalls are merely permitted around Lagos and Lekki Lagoons. The drainage of rainfall storm water into the lagoons shall result in water volume retention leading to potential increase in water level (Sayed & Ahmed, 2014).

According to Onyema (2013) there are 10 lagoons in Lagos, Nigeria. These lagoons have been reported in literature and are the Yewa, Ologe and Badagry lagoons (Nwankwo, 2004), Iyagbe Lagoon (Onyema & Nwankwo, 2009), Lagos, Kuramo, Epe, Lekki and Mahin Lagoons (Nwankwo, 2004) and Apese Lagoon (Onyema, 2009 a,b) (Figure 7). Other lagoons in South-western Nigeria are open to the sea via the Lagos Harbour. Unlike all other lagoons and estuarine water systems in the region, the Apese Lagoon receives seawater inputs chiefly from beach overflows especially at high tide from the Atlantic Ocean (Onyema, 2009 a,b).

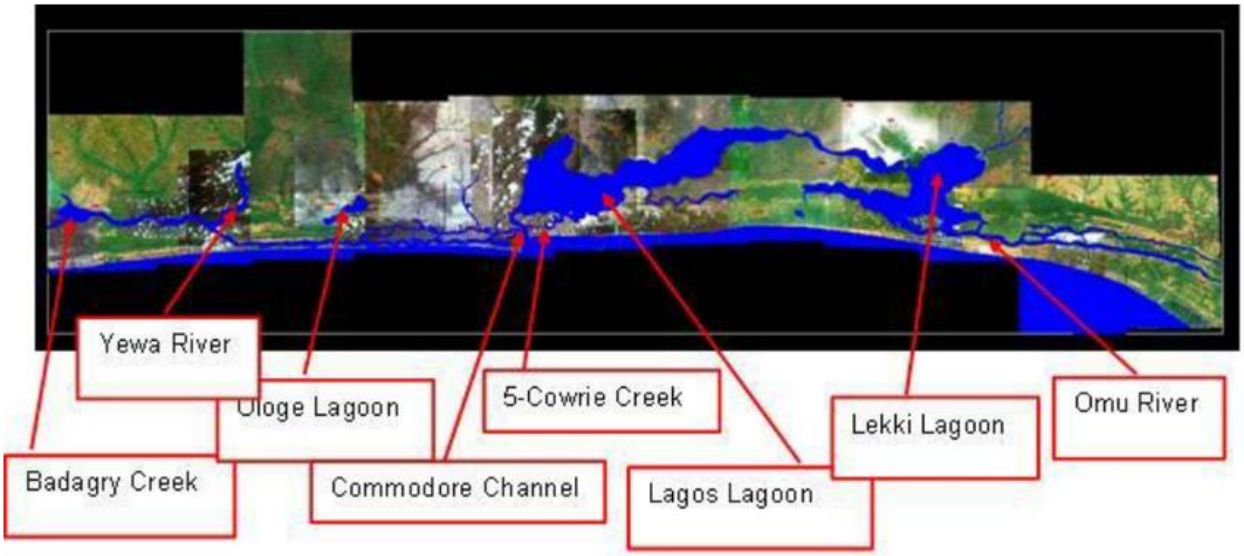


Figure 7: Major water bodies associated with the Lagos Lagoon System (Vijverberg et al., 2012).

3.8 Hydrological features of Lagos Lagoon

The Lagos bathymetric survey carried out in 2008 by the Department of Surveying and Geoinformatics, University of Lagos for Lagos State Government reveals that the water depth of Lagos Harbour ranges from 4m to 20m, with an average depth of 11m. In 2010, another study was conducted by Vijverberg et al., (2012) during which bed levels were measured along Commodore Channel, Apapa Channel and Badagry Creek. Their findings indicated a depth of up to 50m with typical soft mud layer thickness values were found to range from 10 – 30 cm while quays of the Apapa channel has an average soft mud layer of 20 to 30cm (Figure 8). TheLagos Harbour is tidal estuary which is under the influence of enighbouring rivers and the Atlantic Ocean. Its salinity varies with season due mainly to the seasonal rainfall pattern in Nigeria. In the main basin of Lagos Lagoon, salinity is always below 3% during the rainy season. During the dry season however, salinities rise to 30% in Lagos Harbour, and up to 8-10% in the main basin of Lagos Lagoon.

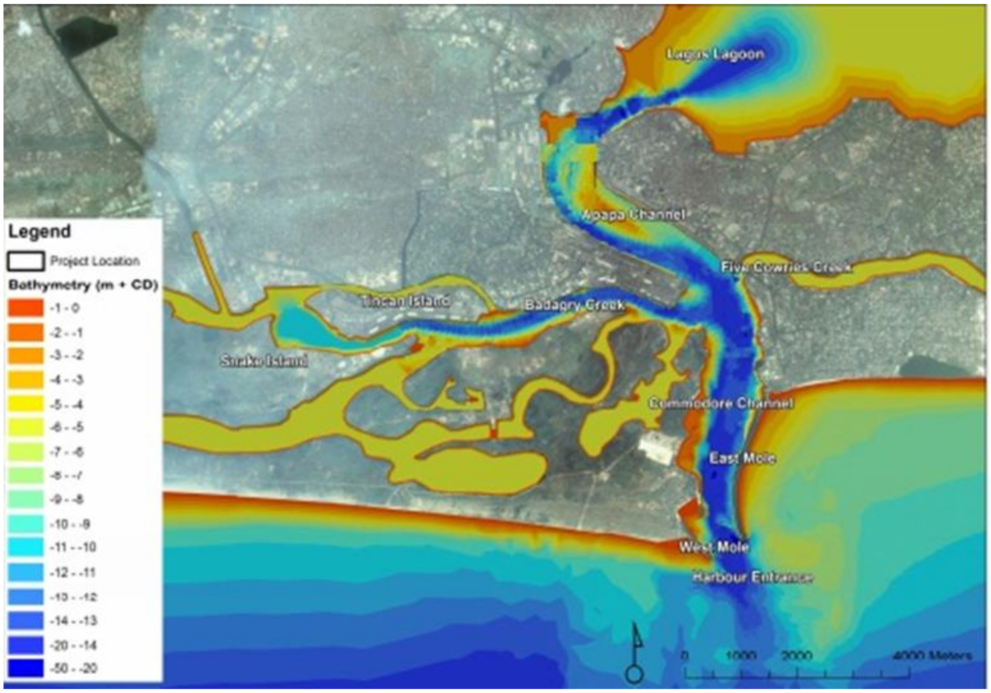


Figure 8: Overview of Lagos Harbour and its bathymetry, including locations of field measurements (Vijverberg et al., 2012).

According to Byun & Wang (2003), sediment transport and its deposition may be strongly affected by horizontal tidal advection, that is, by tide-induced residual currents. Tidal currents are very important factors in sediment transportation along the Nigerian coastline and Niger Delta estuarine waters. The tides off the Nigerian coast have a small range (-0.5 to 0.5m) and generally approach from the southwest and are of the semi-diurnal type (Allen et al., 1980). Tidal currents are strongest at the inlets and can vary from about 2.0 m/s to 5.0 m/s (Dublin-Green et al., 2006), decreasing with distance inland. Allen et al. (1980) reported that fortnightly tidal cycles play a significant role in controlling hydraulic and sedimentology process in Lagos Lagoon. The high sand and low clay fractions at high tide might be traced to the large influx of water from the sea. In estuaries, at high tide, ocean water brings in sediments and leaves them behind when the tide goes out (Davie & Tawari, 2010). Due to seasonal variations of rainfall and occasional flooding, Lagos Lagoon is prone to overspill from land and this may eventually introduce large varieties of detritus and pollutants which will get to the marine environment through the drainage channels and can be taken through water circulation to different parts of the lagoon. The drainage system of Lagos Lagoon receives domestic and industrial effluents from anthropogenic activities in its vicinity. The Five Cowries Creek in central Lagos connects Lagos Lagoon and the Commodore Channel (Van Bentum, 2012). This forms the main outlet for water draining into the lagoon and ultimately into the Atlantic Ocean. Thus, during high tide, the sea water re-enters the harbour and the lagoon, while during low tide the water from both lagoon and harbour is mainly fresh water collected through watershed (Okoye et al., 1991). According to Sandison (1966), water coming into the western part of Lagos Harbour forms the major outlet to the sea for the brackish and fresh water coming through the adjoining lagoon system of South Western Nigeria. This implies that during the rainy season, or after heavy rains, there is an immense volume of fresh water that passes via the harbour and empties out into the sea, while during the dry season (October to March) the flow of fresh water stops, and the rivers run dry. Seawater enters the harbour occasionally, depending on tidal activities, causing changes in marine conditions close to the harbour end, and to the brackish water for about 40 km up to the lagoons and creeks (Hill & Webb, 1958).

There is differential salinity in the lagoon due to the effect of Atlantic Ocean which fluctuates both seasonally and semi-diurnally. Seasonal and diurnal salinity fluctuations are greatest in the Lagos Harbour segment of the lagoon because the influx of water from Atlantic Ocean and the Lagoon. This salinity decreases as distance increases from Atlantic Ocean.

Lagos Harbour experiences high currents at times (raising the water levels up to 0.94 m) the greatest water flow in the area is through the Five Cowrie Creek and is reversed with each tidal cycle. The innermost part of the harbour experiences lower currents (with associated rise in water levels by just up to 0.09 m) and therefore, the deposits of silt, and fine sand will have higher proportions than those at the centre of the lagoon, which is characterised by large amounts of fine sand with fewer coarse grains. The harbour region is influenced by the Guinea-Current, which deflects the tidal water from the harbour to the east, to the extent that finest grain sand and silt is deposited within the harbour region (Hill & Webb, 1958, Onyema, 2009). Figure 9 gives a summary of the physical characteristic of the LH, LG and APL.

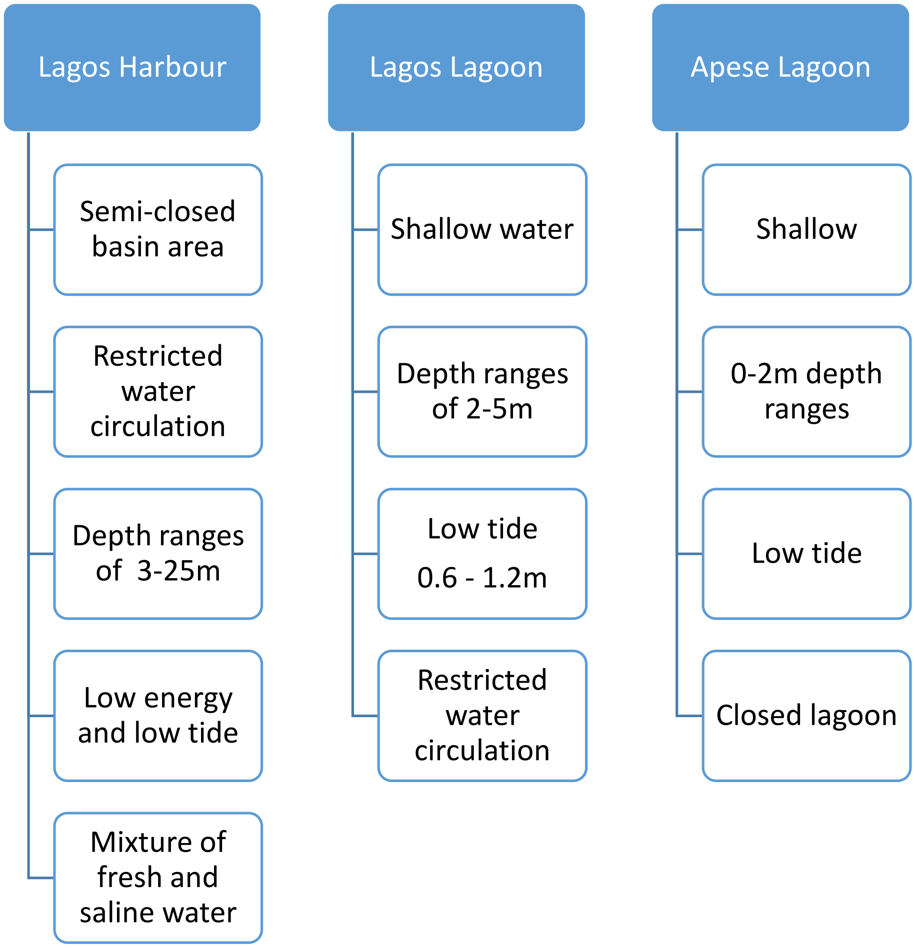


Figure 9: Summary diagram of the physical characteristics of LH, LG & APL.

According to Ajao (1996), Lagos Lagoon has a unique tidal movement within the Gulf of Guinea, having very low tidal ranges of 0.6-1.2 m or less, with limited interconnecting creeks that are very shallow and serve as sites for active silting and mud deposition. The intertidal area within the creeks and lagoons is restricted and is associated with expanses of shallow water in mud flats (Hill & Webb, 1958). Ocean tides around Lagos are semi-diurnal with a periodicity of about 12 h 25 min but with significant diurnal dissimilarities. It was observed that the mean tidal range is between 1 m to 1.5 m (Vijverberg et al., 2012) during extreme spring tides. The wave action across the Nigerian continental shelf is wind produced, with strengths usually determined by the wind velocity, period and time. Waves are predominantly in the barrier lagoon coastline in the west and the Niger Delta region (Dublin-Green et al., 1997). Table 8 provides tidal information for the Lagos Harbour area (tidal levels with varying wave-height expressed in metres) and Table

9 provides information on the water flow velocity measurements of the Lagos Harbour area across four locations.

Table 8: Tide information for Lagos Harbour (Van Bentum, 2012).

Water level (m) HHWS		**Level (m)**
MHWS	Mean High Water Spring (MHWS)	0.94
MHWN	Mean High Water Neap (MHWN)	0.70
MSL	Mean Sea Level (MSL)	0.45
MLWN	Mean Low Water Neap (MLWN)	0.21
MLWS	Mean Low Water Spring (MLWS)	0.09

Table 9: Water flow velocity measurements of the Lagos Harbour area (Van Bentum, 2012).

Location	**Flow velocity (m^3/s), inflow**	**Measurement (m^3 /s), inflow**	**Flow velocity (m^3/s), outflow**	**Measurement (m^3/s), outflow**
Commodore entrance	1.17	10,700	1.09	9,200
Badagry Creek (Tin can Creek)	0.79	2,700	0.59	2,800
Apapa channel (Lagos Harbour)	0.86	6,900	0.81	6,000
Five Cowrie	0.21	400	0.19	400

Vijverberg et al., (2012) also noted the behaviour of suspened sediments concentrations during titadl movement. They noted that about 0.5m thick suspended solids ate transported into the Comandore channels which leads into the Lagos Harbour from the Atlantic Ocean. Specifically, as indicated in Figure 10 below, during ebb (Figure 10a) the flow is negative (outflow) over the whole water column with aconcentration steady at about 200 mg/l. During flood flow (Figure 10b) on the other hand, the upper part of the water column still shows an outflow, whereas near the bed the water flows in.

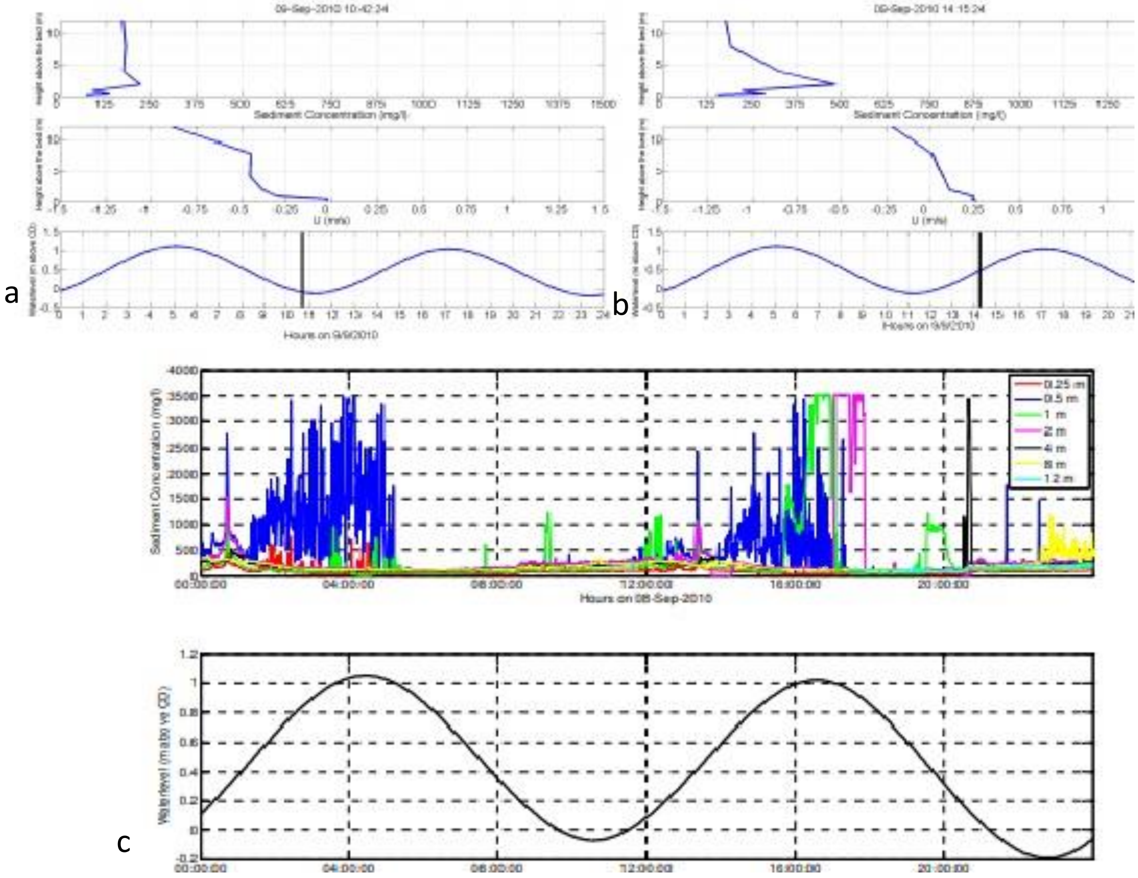


Figure 10a-c: Upper left panel (10a) shows sediment concentration and flow velocity during ebb flow (Sept. 9, 2010, 10:42). Upper right panel (10b) during flood flow (Sept. 9, 2010 14:14). Lower panel (10c) shows sediment concentration and water levels during Sept. 8, 2010. (Vijverberg et al., 2012)

3.9 Geology of the sediment in Lagos Lagoon

The geological substrate of the study area is composed of sediment laid down under fluviatile, lacustrine and marine environments. These sediments grade into one another and are diverse broadly in lateral extent and thickness (Adepelumi & Olorufemi, 2000). The sedimentary area of Nigeria is made of seven basins as shown in Figure 11. Geologically, the Lagos area falls within the eastern part of the Dahomey Basin. The eastern Dahomey Basin is bounded to the north by the Precambrian Basement complex of southwestern Nigeria, the Gulf of Guinea to the south and eastward by the Okitipupa ridge (Olatunji & Abimbola, 2010). The geology of the Lagos area is dominated by a continuous and monotonous repetition of clayey and sandy horizons.

The sediments of Lagos Lagoon typically range from fine, medium and coarse sands to mixtures of silt and clay, supporting a wide variety of habitats (Ajao & Fagade, 1990). The morphology of Lagos Lagoon has been described as coastal dynamics and drainage which is influenced by longshore current actions (Ibe, 1988). This dynamism within the Lagos Lagoon, including the harbour area, will lead to the accumulation of sediment distributions within the Lagos Lagoon system. Although the sediment varies in texture within the Lagos Lagoon, most sediment within the inner harbour is fine grained; but as the sediments move away from the inner part of the harbour towards the open ocean, they tend to coarsen to gravel. The tidal movements in terms of depth, wave action and water circulation influence these changes in appearance.

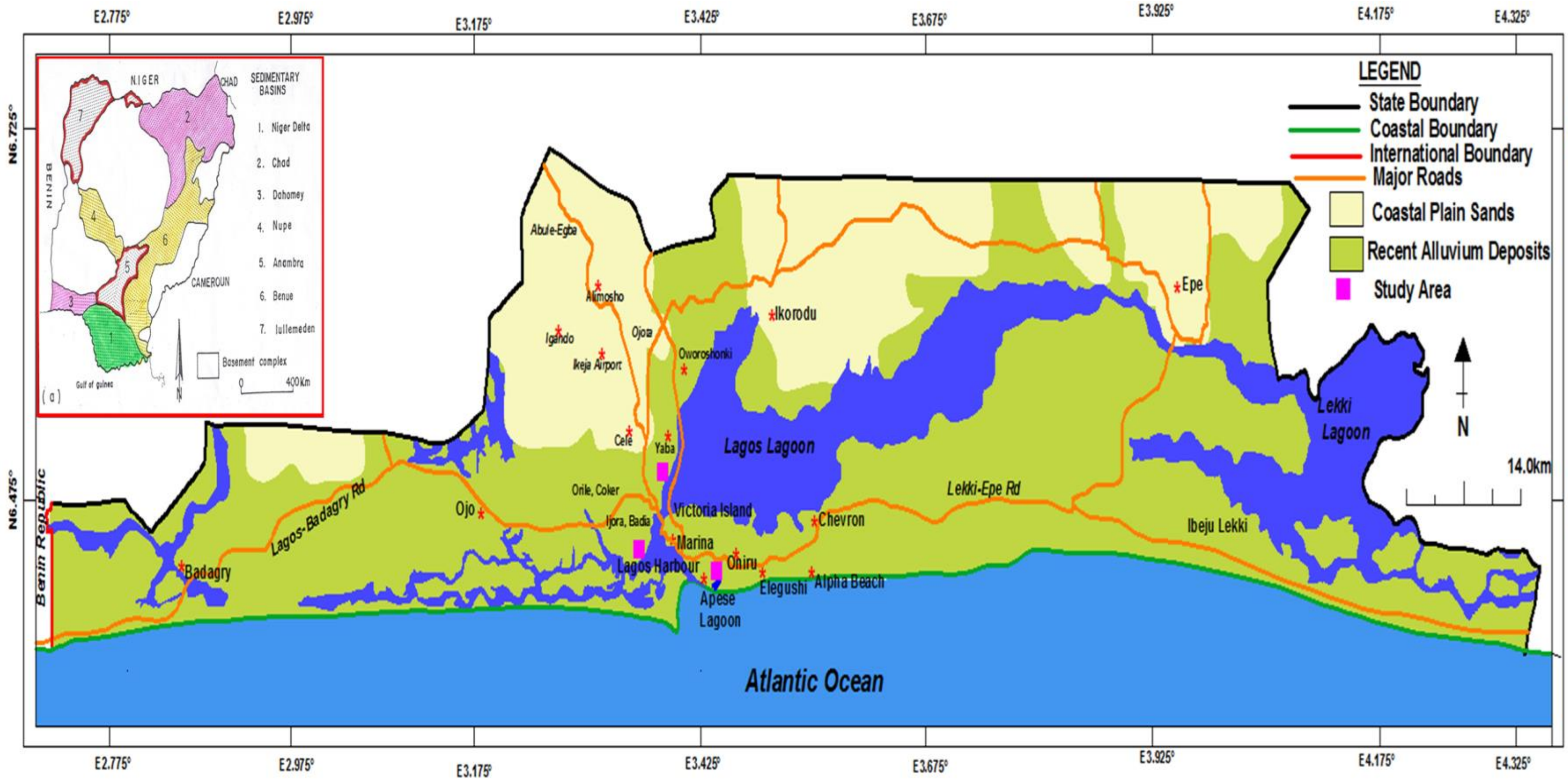


Figure 11: Geological map of Lagos State showing coastal plain sands and recent alluvium deposits. (NGSA, 2006)

CHAPTER FOUR: METHODOLOGY

4.1 Introduction

This section contains two key segments dealings with this study's methodology; fieldwork methods and analytical methods. Fieldwork methods comprise: surveying of the Lagos Lagoon to determine sampling sites, sampling of marine sediments, sites preservations and observations of samples and measurements of the physico-chemical parameters of the lagoon waters. The analytical methods commenced with laboratory handling of the samples, preparation of samples such as grinding of sediments to a fine grain powdered form and determining the grain particle sizes of the sediment samples. This was followed by acid digestion preparations and subsequent analysis of samples using ICP-MS for bioavailable and ICP-OES for recoverable metals, while XRF technique was utilised for total metal analysis.

4.2 Conceptual framework for the methodology

This study was conceptualised in the following design: fieldwork, analysis and data interrogation/handling, data interpretation and identification of sources and pathways of metals to sediment. In order to achieve the assessment of heavy metals concentration in the Lagos Harbour, the fieldwork comprised of surveillance, selection of hotspot sites and collections of samples across the Lagos Lagoon, Lagos Harbour and Apese Lagoon, which served as a control site. To determine the anthropogenic sources of the metal contaminants, analytical involved sample preparation and instrumental analyses for bioavailable, recoverable and total metal concentrations. Particle sizes and total carbon contents were also determined in the marine sediments. The data interrogation and handling facilitate interpretations of the analytical results. This concept is schematically demonstrated in Figure 12.

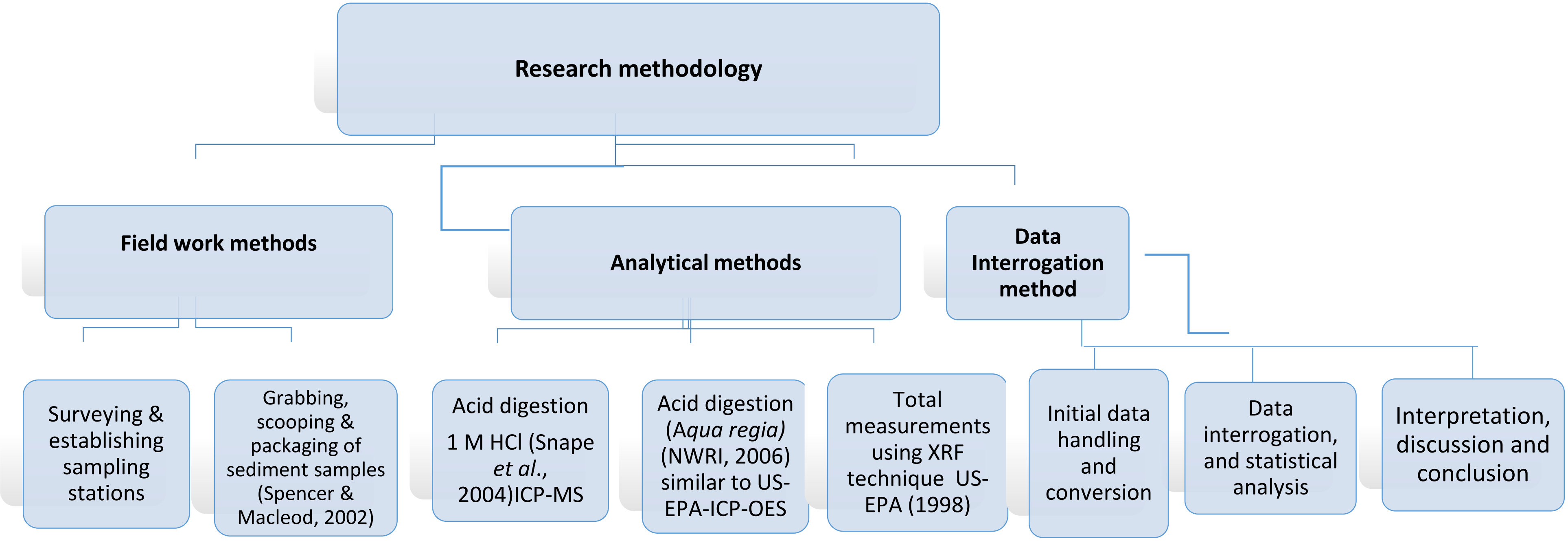


Figure 12: Flow diagram showing the field and analytical methodologies.

4.3 Field work methods

The fieldwork was carried out for a sampling period of three seasons (two dry seasons and a wet season) over one and a half years. The choice of sampling regime was based on the seasonal effects on distributions of the heavy metals (Otitoloju, 2000; Don-Pedro et al., 2004). Sampling was conducted at the peak of dry and rainy seasons to assess the seasonal variations, which agrees with Bawa-Allah et al. (2017). A detailed Gantt chart of the fieldwork program for the sampling regime is shown in Appendix 4; however, Table 10 gives a useful summary.

Table 10: Summary of the fieldwork adopted during the study period.

S/N	Task	Year
1	Preliminary Surveying of Lagos Harbour and Lagoon for the identification of sampling sites for detailed investigation	2012
2	Pilot study of heavy metals investigated within the Lagos Harbour and Lagoon	2012
3	Surveying of Lagos Harbour and Lagoon to generate map for the detailed study area, including a control site	2013
4	First dry season (2013) sampling of sediments within Lagos Harbour and Lagos Lagoon.	2013
5	Wet season sampling (2013) of sediments within Lagos Harbour and Lagoon.	2013
6	Second dry season sampling (2014) of sediments within Lagos Harbour and Lagos Lagoon.	2014

4.3.1 Selection of sampling sites

Activities such as shipping, sand mining, sawmill industries and recreational/residential within the lagoon serving as potential hotspots across the sampling sites were the basis for the selection of sampling sites in this study, as shown in Figure 9. The sampling sites comprised Lagos Harbour, the urbanised western shoreline of Lagos Lagoon, and the separate Apese Lagoon as the control zone. Global positioning system (GPS) coordinates of each sampling site was taken and recorded, 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) as shown in Table 11, whilst Table 12 shows the GPS coordinates and hotspots locations of the selected sampling sites. The sampling sites in the three lagoons are presented in Figure 13. The sampling sites at Apese Lagoon was not established during the dry season-1-2013 sampling regime, hence no data was produced in this location for this season. This is due to a change in the strategy of sampling in line with the main aim and objectives of the study.

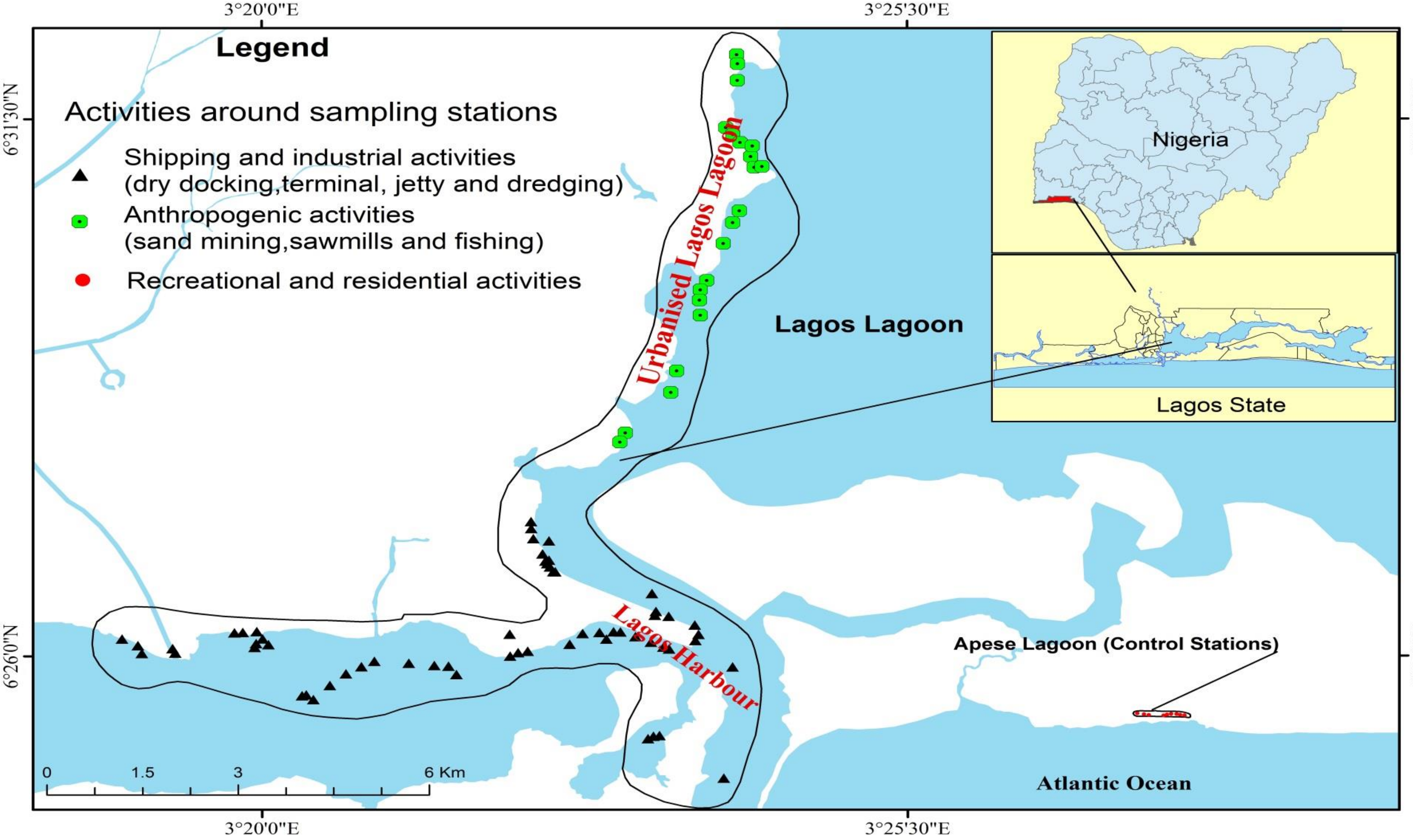


Figure 13: Sampling sites with hotspots, activities around the study areas (Lagos Harbour, urbanised part (western part) of Lagos Lagoon and Apese Lagoon.

Table 11: Established hotspots locations of the selected sampling sites.

Sites	Zone	Observed activities
1	Lagos Harbour	Oil tank farms discharge area
2	ʺ ʺ	Bulk cargo discharge area
3	ʺ ʺ	Bulk cargo discharge area
4	ʺ ʺ	Oil tank farms discharge area
5	ʺ ʺ	Oil tank farms discharge area
6	ʺ ʺ	Vessel discharge area
7	ʺ ʺ	Bulk cargo discharge area
8	ʺ ʺ	Bulk cargo discharge area
9	ʺ ʺ	Oil tank farms discharge area
10	ʺ ʺ	Bulk cargo terminals
11	ʺ ʺ	Container bulk terminal
12	ʺ ʺ	Bulk cargo terminal
13	ʺ ʺ	Bulk cargo terminal
14	ʺ ʺ	Flour mills raw materials terminal
15	ʺ ʺ	Dry docking & ship repair
16	ʺ ʺ	Oil tank farm and discharge areas
17	Lagos Lagoon (urbanised part)	Public sewage & dump sites
18	ʺ ʺ	Saw mills waste & domestic wastes
19	ʺ ʺ	Fish farming and domestic trading
20	ʺ ʺ	Domestic wastes discharge areas
21	ʺ ʺ	Recreational & aquaculture
22	ʺ ʺ	Oyster harvesting, recreational &sand mining
23	ʺ ʺ	Oil tank farms discharge area
24	Apese Lagoon(control)	Recreational & proposed residential development
25	ʺ ʺ	Recreational & proposed residential development
26	ʺ ʺ	Recreational & proposed residential development

Table 12: GPS coordinates and water depth at the sampling sites.

Site	Site Name	Longitude	Latitude	Depth (m)
1	BVS	E003°18' 58.574"	6°26' 1.779"	13.5
2	ATC	E003° 23' 23.1''	6° 25'11.2''	0.7
3	OBT	E003° 19' 15.634"	6° 26' 2.029"	10.5
4	STFM	E003° 22'34.7''	6° 26'10.9''	10.3
5	SFM	E003° 22'59.7''	6° 26'15.0''	7.4
6	GMD	E003° 20' 3.233"	6° 26' 7.144"	11.0
7	ND	E003°20'17.1''	N6° 25'37.2''	6.1
8	JSD	E003° 20'26.2''	N6° 25'33.4''	4.8
9	JDM	E003° 21' 39.324"	6° 25' 48.776"	11.2
10	ORS	E003° 19'13.4''	N6° 26'05.4''	3.2
11	ORD	E003° 19'14.2''	N6° 26'04.8''	1.2
12	TCN6	E003° 24' 0.486"	6° 25' 53.328"	11.5
13	IBJ	E003° 19'57.3''	N6° 26'15.2''	1.3
14	SFX	E003° 20' 34.665"	6° 25' 42.047"	11.8
15	GMD	E003° 19'56.2''	N6° 26'05.5''	9.2
16	GRV	E003° 22' 56.007"	6° 26' 10.474"	12.4
17	SIFX	E003° 20'57.4''	N6° 25'56.9''	9.0
18	APM	E003° 22' 37.253"	6° 26' 7.297"	13.7
19	T6	E003° 21'35.3''	N6° 25'53.9''	7.6
20	FJ	E003° 22'15.8''	N6° 26'03.0''	6.0
21	ENL	E003° 23' 20.826"	6° 26' 25.11"	14.5
22	JSD	E003° 23' 10.9''	N6° 26'12.0''	10.2
23	FM	E003° 22' 26.71"	6° 26' 59.019"	15.4
24	APM	E003° 23' 28.1"	N6° 26' 04.4"	8.7
25	NIPCO	E003° 22' 26.719"	6° 27' 10.905"	11.8
26	BN	E003° 23' 41.2"	N6° 26' 19.1"	8.7
27	ENL	E003° 23' 19.3''	N6° 26'38.4''	10.64

28	FM	E003° 22' 27.2''	N6° 26'54.8''	4.63
29	NPA-DY	E003° 22' 23.4''	N6° 27'02.8''	7.2
30	IDDO	E003° 23' 05.7''	N6° 28'17.2''	1.28
31	OKB	E003° 23' 44.1''	N6° 29'29.4''	1.1
32	MKK	E003° 23' 47.5''	N6° 29'50.8''	1.3
33	UGH	E003° 24' 10.832"	6° 31' 13.438"	1.6
34	UWF	E003° 24'09.9''	N6° 31' 07.0''	1.2
35	UHR	E003° 24' 0.701"	N6° 30' 26.356"	2.5
36	OWSK	E003° 24' 02.8 ''	N6° 32' 09.6 ''	3.1
37	Apese 1agoon 1	E003° 27' 27.4 ''	N6° 25' 24.6 ''	1.0
38	Apese 2	E003° 27' 40.9 ''	N6° 25' 23.4 ''	2.0
39	Apese 3	E003° 27' 47.5 ''	N6° 25' 24.2''	0.8

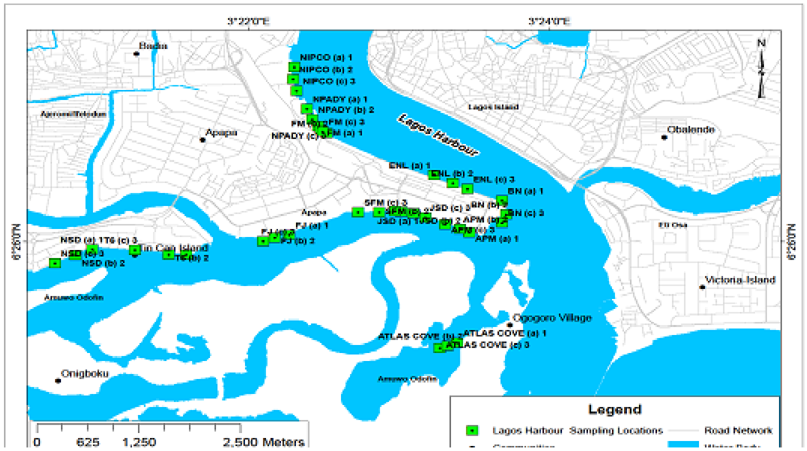


Figure 14a: Map of the Lagos Harbour area showing established sampling locations

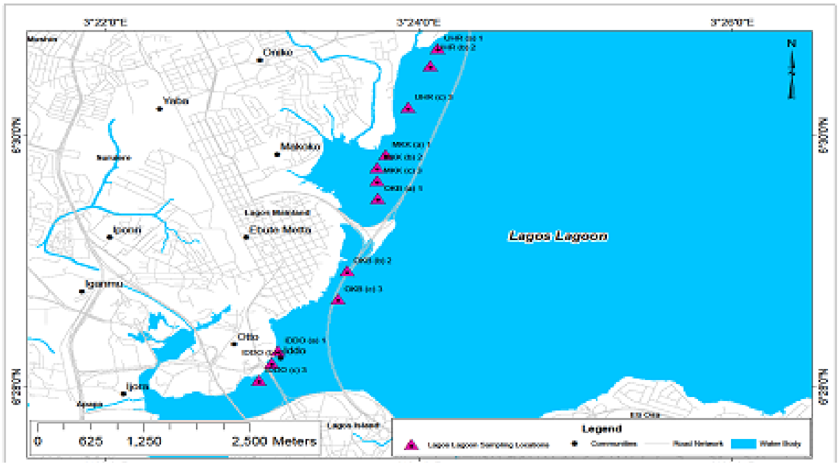


Figure 14b: Map of the Lagos Lagoon area showing established sampling location

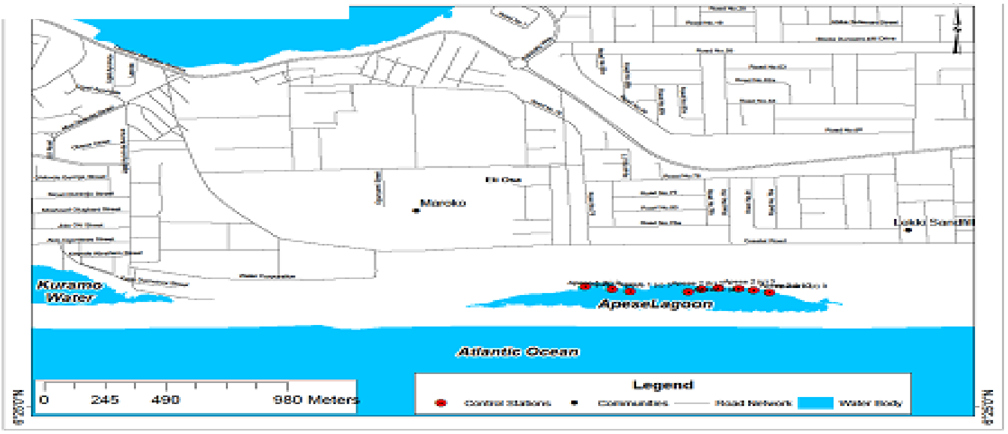


Figure 14c: Map of Apese Lagoon (control) showing established sampling locations

Figure 14: Maps (a-c) showing detailed distribution of different sampling points within different locations of the study area.

4.3.2 Sampling periods

Sampling was carried out in phases across two distinct seasons in Nigeria (dry -(2) and wet (1) seasons). This was to determine the distribution of the investigated metals in two different seasons which are typical of the tropical climate where the study site is located. The fieldwork/sampling of sediments was conducted in February 2013, February 2014 and September 2013 as shown in Table 13 and the sampling spread for the three years is indicated in Figure 15.

Sites sampled in each season are as follows: dry season-1 2013 (sites 1 to 14), dry season-2 2014 (sites-1 to 26) and wet season 2013 (sites-1 to 24), summarised in Table 13. Sampling was also carried out at the control area (Apese Lagoon) across the two distinct seasons (dry and wet). Appendix 5a- 6c gives a more detailed list of the sampling sites, coordinates locations and observed activities.

Table 13: Summary of sampling periods for the study.

S/N	*Sampling seasons*	*Sampling period*	*Sampling time*	*Sampling locations*	No of sampling sites
1	Dry season 1	February, 2013	9 AM-1 PM	Lagos Harbour and Lagos Lagoon	1-14
2	Wet season	September, 2013	ʺ ʺ	Lagos Harbour, Lagos Lagoon and Apese Lagoon	1-24
3	Dry season 2	February, 2014	ʺ ʺ	Lagos Harbour, Lagos Lagoon and Apese Lagoon	1-26

Figure 15: Seasonal sampling points and regimes within the study area.

4.3.3 Collection of sediment samples

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 labelled samples were placed in polytetrafluoroethylene (PTFE) bottles, bagged and stored in an ice chest cooler at 4°C. Table 14 shows the summarised sampling locations, depth ranges and activities at the different sampling zones. Photographs showing sources of contaminants within both Lagos Harbour and the urbanised part of the Lagos Lagoon and the contro, Apese Lagoon during the field work are shown in Figure 16 to 18 (Plates 1, 2 and 3) images.

Table 14: Summarised sampling locations, water depth ranges and activities.

S/N	Zone	Sampling Sites	Water Depth Ranges (m)	Activity
1	Lagos Harbour	1-16	0.2 -15.4	Shipping, dry docking and industrial discharges
2	Lagos Lagoon (urbanised area)	17 – 23	0.2 – 4.5	Domestic activities occasioned by industrial discharges
3	Apese Lagoon (Control)	24- 26	0.2 – 2	Recreational area anthropogenic and housing activities

Figure 16: Plate 1 (a-h) Lagos Harbour - sources of potential contamination from shipping and other industrial activities within the Lagos Harbour area.

(a) Cargo ship discharging within the Lagos Harbour

(b) Flour mills factory facing the lagoon within the Lagos Harbour

(c) Back of the flour mills factory used as a jetty and discharging wastewater direct into the lagoon

(d) Cargo warehouse within the Lagos Harbour area

(e)–(g) Scattered oil tank farms within the Lagos Harbour

(f) Containerised jetty where loading and offloading takes place within Lagos Harbour.

Figure 17: Plate 2 (a-d): Lagos Lagoon- sources of potential contamination from industrial and other anthropogenic activities within the urbanised part of Lagos Lagoon.

- *(a) Slum areas associated with domestic and transportation within the urbanised part of Lagos Lagoon*
- *(b) Marine litter source of contamination within the urbanised part of Lagos Lagoon*
- *(c) Local saw mills industry within the Lagos Lagoon area*
- *(d) Other marine litter within the urbanised part of Lagos Lagoon*

Figure 18: Plate 3 (a-e) Apese Lagoon – showing recreational site and aerial views of the lagoon.
(a) & (e) showing sand bars with dredging activities around Apese Lagoon

(b), (c) & (d) showing side of the lagoon boundary with developmental activity in Apese Lagoon from the part of the city of Lagos.

(f) Open water movement of Apese Lagoon showing the shorelines.

4.3.4 Water quality indicator measurements

Important physico-chemical variables including surface water temperature, pH, conductivity and salinity were analysed simultaneously from the respective sites with the use of conductivity, temperature/depth instruments (YSI-Sonde). The instrument was deployed *in-situ* after the required calibration. Marine waters at each sampling site were measured for water quality determination alongside the sediment sample collection for the sampling sites, the detailed measurements of the physico-chemical parameters are presented in Appendices 7a-d.

4.3.5 Storage and transportation of samples

The collected sediment samples were stored and preserved using ice packs at the point of collection, as recommended by Spencer & Macleod (2002). To preserve the condition of the collected sediment samples, and to reduce volatilisation of any analytes prior to transporting the samples to the laboratory, the samples were kept in cool boxes with ice packs wrapped in polythene bags and stored at -4 ˚C. The cool boxes were covered and sealed to avoid exposure to atmospheric temperature and changes to the stored temperature. Samples were transported to the Central Research Laboratory of the College of Medicine of the University of Lagos for storage, prior to shipping the samples to the UK. The polytetrafluoroethylene (PTFE) bottles were bagged and sealed in plastic transparent bags before being transported to the laboratory for storage. The distance from the sampling sites to the Central Research Laboratory was less than 5 km, so the samples were not subjected to a high degree of disturbance during transportation and the samples were shipped to the UK by a professional courier service. Samples were packed in cool boxes with ice packs to maintain the same storage conditions, with the airline being notified accordingly. Finally, when the samples arrived at the University of Portsmouth, they were kept frozen in the Marine Biogeochemistry Laboratory freezers at -20˚C until they were ready for processing.

4.3.5.1 Permit for sample transportation to the UK

The samples collected in Lagos Nigeria were transported to UK based on the granted permit from the Department of Food, Environment and Rural Affairs (DEFRA) UK. The agency responsible for the issuance of permits to convey samples abroad prohibited under UK (**Licence Number: 115523/217270/0)**. The laboratory was assessed and supervised by Food, Environment and Rural Affairs (FERA) up to the disposal of the sample wastes at the end of analysis.

4.4 Laboratory analysis

This section deals specifically with the handling and the procedures for sample processing in the laboratory, as well as the analysis using different analytical techniques and instrumentation. The samples were processed using different preparations for each analytical purpose, including appropriate quality assurance and quality control procedures.

4.4.1 Sample preparation

The stored frozen samples were removed and allowed to defrost on a clean laboratory bench and emptied into polytetrafluoroethylene (PTFE) beakers for drying. The samples were placed in an oven at 40°C for at least 72 h, for complete dryness. The debris and organic particles were removed from the bulk sediments using a stainless steel or plastic spatula. Samples were disaggregated using a ceramic pestle and mortar ground to a fine powdered homogenised level using a planetary ball mill Fritsch (Pulverisette 7 version) (Harris, 2006). In order to avoid cross contamination between samples, pure silica was ground between each of the samples. The ball mill was then washed with deionised water and dried befor further preparations. All reagents used were of analytical grade, supplied by Fisher Scientific Ltd. All plastic laboratory wares were pre-washed with laboratory grade detergent followed by adequate rinsing using MilliQ water and soaking in a 10% HCl acid solution for over 24 h followed by thorough rinsing with deionised water. The analytical acids used for the digestion were hydrochloric and nitric acids of trace element grade.

4.4.2 Particle size analysis

The particle size method 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 analysed 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_20_2 was added to each sample in a beaker to completely remove organic materials. A solution of hexametaphosphate (SHMP) and sodium hydrogen carbonate (SHC) added to the samples in each beaker in order to separate the particles. It is important to note that Laser Diffraction (LD) provides only volumetric results, whereas the traditional sieving method gives weight percent analysis. The particle size distribution data generated the laser diffractometer is shown in Appendix 7, while the associated diagrams are shown in Appendix 8.

4.4.3 Determination of total carbon and nitrogen contents

Total carbon and nitrogen contents were determined using an in-line Yanaco MT-5 CHN analyser. 1 M HCl was added to the weighed sediment to remove the carbonate fraction. The concentrations of carbon were analysed in percentage terms and later converted to mg/g for both nitrogen and carbon. The mean concentrations of carbon and nitrogen content are shown in Appendix 9 and Appendix 10.

4.4.4 Analysis of metals in sediments

The collected sediment samples were analysed for metals following three procedures as described below.

4.4.4.1 Total metals analysis using XRF spectrometry

Total metal concentrations in marine sediment were analysed using XRF technique. The samples were processed for trace and major elements. The XRF technique used for the total of metals was similar to the method described in the US-EPA Method 6200 (1998). The XRF instrument was calibrated using a variety of international reference standard CRMs powder pills. Powders are prepared for XRF analysis by fusing the sample 5g of sediment, 1g of binder (Cereox wax binder) was added to the sample and mixed thoroughly for the sample to bind. The sediment samples were then put into the pestle mortar and mixed thoroughly to reach homogenised state with the binder. The pestle was pressed together with the sample and then placed into hydraulic tube and pressed again for 20 t/sq. range and left for 45 s. The pestle was then taken out and press turned over and places the metal column on top before placing it back into the hydraulic press to release the pellet. Finally, the samples were labelled with the sample name, date and analyzed using XRF.

4.4.4.2 Recoverable metals (*Aqua regia* – ICP-OES)

For recoverable extraction of metals from the marine sediment samples a method in line with the National Water Research Institute (NWRI, 2006) version 5.7 guidelines for environmentally available recoverable metals was used, similar to the US-Environment Protection Agency (US-EPA) Method 3051 and the Ontario Ministry of the Environment's *Aqua regia* Method HMARSOIL-E3062A.

The procedure for *Aqua regia* extraction was implemented by accurately weighing 0.5 g of sediment, before adding the acids in combination as: 2 mL conc. HCl + 9 mL conc $HN0_3$ + 1 mL 30% hydrogen peroxide and heated at 200 °C for 15 min in a high-pressure microwave oven. The samples were further diluted with deionised water (12 mL) to make it up to 24 mL volume of acids and deionised water and then filtered before finally being analysed using ICP-OES. The instrument was calibrated using a preparation of standard dilution stock solution (100 mg/L). The calibration used was 0, 10, 20, 50 mg/L for low concentration range. International Certified Reference Materials (CRM) HR-1 and PACS - 2 plus acid blanks, were analysed in triplicate using the same procedures as for the samples under investigation, the data is presented in Appendix 14 and Appendices 15a-b for CRM using 1 M HCl and *Aqua regia* respectively

4.4.4.3 Determination of bioavailable metals (1M HCl – ICP-MS)

Bioavailable metals in the marine sediment were determined using a 1 M HCl extraction and ICP-MS analysis, as described by Snape et al. (2004). This method is similar to the one currently adopted in Australia and New Zealand in terms of metal quantification for availability or labile in sediment in order to indicate the sediment quality (Snape et al., 2004). The extraction was based on timing, which was set for 4 h extraction from the time acids were added to the sample. This technique was adopted in order to assess the extraction efficiency using 1 M HCl extraction, except for a minor modification in terms of sediment weight and the reference materials used, which made it faster and more efficient. Approximately 0.5g sediment samples were weighed accurately (to four decimal places) and placed into a 15 mL centrifuge tube 0.5 g.

A triplicate of the acid blank labelled a 15mL centrifuge tube “Blank1M” was used. In the fume cupboard – to each of the 15 mL centrifuge tubes 10mL of 1M hydrochloric acid was added and mixed thoroughly. The lids were secured with the use of Parafilm to prevent leakages. The tubes were loaded in the rotating rack for 4h Samples were filtered through an acid washed pore size filter using a Swinnex filter housing and syringe and collected the sample in a labelled 3 M Sterilin tube. The samples were prepared to a 10 times dillution. Samples were then ready to be analysed using the ICP-MS. All the sediment samples and reference materials, including blanks, were run in triplicate to adhere to quality control procedure. Two independent certified reference materials were analysed with the samples concurrently (Appendix 11 & Appendix 12), which represent excellent reference materials in regional comparisons of marine sediment pollution as demonstrated by Townsend et al. (2007).

4.5 Initial data handling

4.5.1 Data conversion

XRF data requires no conversion, except from oxide to elements and from weight % as appropriate. After the acid preparations were analysed using ICP-MS and ICP-OES, the data generated were reported as quantum data (QD) directly from the instruments, which was in part per billion (ppb) for ICP-MS and mg/L (part per million - ppm) in the case of ICP-OES for the acid digestion methods. The data were converted to mg/kg of the original dried sediment sample in order to arrive at the required unit for this investigation. Similarly, those data obtained using XRF for major elements which were in mass % were converted to mg/kg. Using the formulae for the convertion of the intial data to appropriate units for major elements, Recoverable, Bioavailable and Total Nitrogen and Carbon is indicated in Appendix 13 a – d.

4.6 Chemical normalisation

The results obtained from the extracted aluminium using *Aqua regia* and 1 M HCl data were used to normalise the data. The normalised element was used to estimate the enrichment factor. The formula expressed mathematically for the enrichment factor (EF) is EF = (X/Al) sed divide (X/Al) background value of the controlled sampling site (Ho et al., 2012). Where (X/Al) Sample is the ratio of metal and Al concentrations in the sample, and (X/Al) is the ratio of metal and Al concentrations of a background. The average metal concentrations in sediment from Apese Lagoon (control site) used to provide background metal levels.

$$Ef = {}^{({}^{M}/_{Al})sample}\Big/_{\left({}^{M}/_{Al}\right)background}$$

Figure 19: Enrichment Factor determination of metals in sediment.

4.6.1 Contamination factor (C*f*)

The level of contamination of sediment by metal is expressed in terms of a contamination factor (C*f*) calculated as:

$$\mathrm{C}f = \frac{\mathrm{CmSample}}{\mathrm{CmBackground}}$$

Where, Cm Sample is the concentration of a given metal in river sediment, and Cm Background is value of the metal equals to the world surface rock average given by (Salah et al., 2012). CF values for describing the contamination level are shown in Apendix 24a.

4.7 Data handling: statistical analysis

The data obtained were not normally distributed, hence were log- transformed to correct for normality. The linear association between particle sizes, total nitrogen and organic carbon as well as the respective heavy metals measured were determined using Pearson's correlation coefficients. Each of the above listed parameters were compared in pairs to determine their linear relationships. This is because Pearson's correlation is a statistical tool which provides an easily appreciable information on the relationship between two variables. Significant differences in the mean values at 95% confidence interval were determined using Analysis of Variance (ANOVA) while significant means were separated using LSD post-hoc analysis. All statistical tests were conducted using SPSS (IBM) software, Version 22. Graphical presentation of results was done using bar charts with error bars based on the standard error of the means.

4.7.1 Spatial distribution analysis of the heavy metals

WinGLink version 1.62.08 was used to generate the contour maps. The interpolation radius and gridding values was varied to accommodate and properly represent the data variation and coverage. Meanwhile, the smoothing value was set to zero while the data positions are represented by dots. The generated maps were overlaid to scale on the map of the study area with AutoCAD in order to show the coastal line in relation to the data points.

In other to generate the contour maps concentrations of the metals measured at different sampling sites together with their respective coordinates were computed into the software. The

GIS software sets scacle for the various parameters inputed and uses such to generate contour maps. The contour maps therefore use a range of colours to depict the relative spread of the metal concentrations across the sampled sites of the lagoon system. The maps produced indicated clearly the spatial distribution of the respective metals thereby making it possible to associate concentrations with prevailing activities in the respective locations.

4.7.2 Correlation coefficients analysis

Pearson's correlation matrix was performed to show the correlation coefficients among the variables (heavy metals, total carbon, total nitrogen, and varying particle sizes). The bivariate correlation procedure computes the pair wise associations for a set of variables and displays the results in a matrix. It is useful for determining the strength and direction of the association between two variables. The correlation coefficients computed by bivariate correlation procedure lay in the range −1 (for the cases in which a perfect negative relationship exists) to +1 (for a perfect positive relationship). A value of 0 indicates there is no linear relationship among the variables. For normally distributed variables, the Pearson method can be used to calculate the correlation coefficient (Miller & Miller, 2005).

4.7.3 Principal component analysis

Principal component analysis was used to analyse the interaction between multiple variables such as heavy metals in sediment (XRF, *Aqua regia* and1M HCl), particle size, total carbon and total nitrogen contents. Multivariate data analysis was utilised to identify the correlations among the measured parameters. PCA reduces the dimensionality of data by a linear combination of original data to generate new latent variables which are orthogonal and correlated to each other (Nkansah et al., 2010).

4.7.4 Cluster analysis

Cluster analysis (CA) is a method for dividing a group of variables such as metals into classes of similar metals characteristics. In fact, the groups are not known prior to applying this mathematical analysis and no assumption is made about the distribution of the variables (Miller & Miller, 2005). Cluster analysis grouped the studied heavy metals into clusters based on similarities within a group and variations between different groups. CA was performed on the data using Bray-Curtis method (Miller & Miller, 2005).

CHAPTER FIVE: RESULTS

This section presents and describes the analytical data. The mean concentrations in mg/kg are presented in Appendices 14 a-c for total, Appendices 15 a-c for recoverable and Appendices 16 a-c for bioavailable heavy metals in the analysed sediments. The Certified Reference Materials (CRM) were used to estimate the percentage recovery of extracted metals in order to monitor data quality.

5.1 Data quality

CRMs were used to monitor accuracy and replicate analysis to monitor precision for each analytical technique. The extracted metals for *Aqua regia* and 1 M HCl were monitored with CRMs (HR-1 and PACs-2) for percentage recovery. The analysed CRM data for HR-1 & PACs-2 results from the machine are presented in Appendices 16a–b for both recoverable and bioavailable metals.

The percentage average recoveries for *Aqua regia* method are shown in Table 15 for HR-1. The extracted metal concentrations-As, Co, Cu, Fe, Mn, Ni, Pb and Zn had significantly high percentage recovery while the lowest percentage recovery was recorded for Cd and Al. The metals – As, Pb and Zn exceeded one hundred (100%) percentage recoveries.

Table 16 shows the percentage average recovery for the *Aqua regia.* The metal concentrations – As, Cu, Ni, Pb, Sn and Zn had high percentage recovery. All metals were below one hundred (100%) percentage recoveries with good percentage recoveries above 50% with the exception of Al which is 15%.

Table 15: Measured concentrations of *Aqua regia* extraction and recommended values of HR-1.

Elements	HR-1 (mg/kg)	Measured concentration (n = 3 in triplicate) mg/kg-dry weight	Percentage (%) recovery
Al	30,200	9,792	17
As	6	16	247
Cd	3.83	0.47	12
Co	10.5	9	67
Cr	122	91	72
Cu	81	80	100
Fe	28,289	24,805	81
Mn	511	449	82
Ni	36	35	90
Pb	134	214	154
Sn	9.12	7	71
V	59.6	36	43
Zn	1136	1,305	118

Table 16: Measured concentrations of *Aqua regia* extraction and recommended values of PACS-2.

Elements	PACS-2 (mg/kg)	Measured *concentration* (n = 3) mg/kg-dry weight	Percentage recovery (%)
Al	66,200	9,891	15
As	26.2	25	94
Cd	2.11	BDL	n/a
Co	11.5	9	78
Cr	90.7	49	54
Cu	310	300	97
Fe	40,900	29,914	73
Mn	440	247	56
Ni	39.5	34	86
Pb	183	170	93
Sn	19.8	16	81
V	133	74	56
Zn	364	337	93

Table 17 shows the percentage average extractable for 1 M HCl for HR-1. The metal concentrations – As, Cd, Cr, Cu, Fe, Mn, Ni, and Pb had significantly high percentage recovery. The metals – As, Cd, Fe, Mn and Pb exceeded one hundred (100%) percentage extractable.

Table 18 shows the percentage average extraction for 1 M HCl from PACs-2. The bioavailable metal concentrations –Pb with 81% recorded a highest percentage recovery while Al (3%) was the least recovered. All metals were below one hundred (100%) percentage extraction.

Table 17: Measured concentrations of 1 M HCl extraction and recommended values of HR-1.

Elements	HR-1 (mg/kg)	Measured concentration (n = 3) mg/kg	Percentage (%) recovery
Al	3,235	3,074	95
As	2.3	4.7	205
Cd	3.28	4.4	133
Cr	50	49	97
Cu	60	67	112
Fe	8,015	8,953	112
Mn	266	309.1	116
Ni	15.9	15.3	96
	116	186	160
Zn	1,035	771	74

Table 18: Measured concentrations of 1 M HCl extraction and recommended values of PACS-2.

Elements	PACS-2(mg/kg)	Measured concentration (n = 3) mg/kg	Extraction (%)
Al	66,200	1,920	3
As	26.2	2.9	11
Cd	2.11	0.99	47
Cr	90.7	6.99	8
Cu	310	74.16	24
Fe	40,900	5806	14
Mn	440	94.7	22
Ni	39.5	3.96	10
Pb	183	148	41
Zn	364	68	19

5.2 Water quality parameters

The average surface water physico-chemical parameters of the sampling sites are shown in Figures 20 a to 20 e. The physico-chemical parameters showed significant difference ($p<0.05$) between the sampling locations.

Figure 20 a show that the mean surface water pH for Lagos Harbour (LH), Lagos Lagoon (LG) and Apese Lagoon (APL) were 8.08. 7.87 and 7.94 respectively during the dry season while in the wet season the values were 7.67, 7.40 and 7.67 respectively. The pH was higher in the dry season compared to the wet season across all sampling locations. The pH was highest in the LH in the dry season and lowest at LG in wet season.

Figure 20 b shows that the mean conductivity level at the LH was 49.1 ± 0.8 mS/cm with range of 48.3–49.7 mS/cm, while at the LG recorded value was 39.2 ± 1.2 mS/cm with range of 38 – 40.1 mS/cm. The value at APL was 16.6 ± 3.8 mS/cm with range of 14.1 – 21.0 mS/cm during the dry season. In the wet season, the mean conductivity value in the surface water samples of LH was 28.26 ± 0.66 mS/cm, in the LG it was 9.33 ± 1.48 mS/cm and 36.05 ± 0.98 mS/cm in the APL. The conductivity had highest in LH in the dry season and lowest in LG in wet season.

Figure 20 c shows that the mean salinity recorded was 30.5 ‰ with range of 30–31 ‰ at LH, while at LG the mean salinity was 18.9 ‰ with range of 17.5–20.7 ‰ and 16.16 ‰ with range of 7.8–19.1 ‰ at APL during the dry season. During the wet season, mean recorded salinity value in the LH was 16 .6 ‰ with a range of 12.02 – 23.71, LG was 5.05 ‰ with a range of 0.10 – 10.67 and APL was 21.8 ‰ with a range of 20.19 – 23.05. The salinity was highest in LH in the dry season and lowest in LG in wet season.

Figure 20 d shows that the mean surface water temperature at LH was 29.6°C with range of 29–30°C, while at LG the it was 29°C and 29°C in APL with range of 26–30°C at the dry season. In the wet season recorded mean water temperature was 27.26°C with range of 24.27 – 27.84°C at the LH, 29.29°C with range of 27.80 – 28.87°C in LG and 26.9°C with range 26.6 – 27.14°C in APL. The water temperature had highest value in LH during the dry season and lowest in APL in wet season.

Figure 20 e shows that the mean dissolved oxygen level recorded was 4.1 ± 0.2 mg/L with range of 3.9–4.4 mg/L at LH, while at LG, the mean DO level was 4.0 ± 0.6 mg/L with range of 3.5–4.6 mg/L and 6.5 ± 0.5 mg/L with range of 7.0 mg/L at APL at the dry season. In the wet season, the mean DO at LH recorded 5.13 ± 0.3 mg/L, at LG it was 4.25 ± 0.05 mg/L and 6.82 ± 0.5 mg/L at APL. The dissolved oxygen was highest in APL in wet season and lowest in LG in dry season.

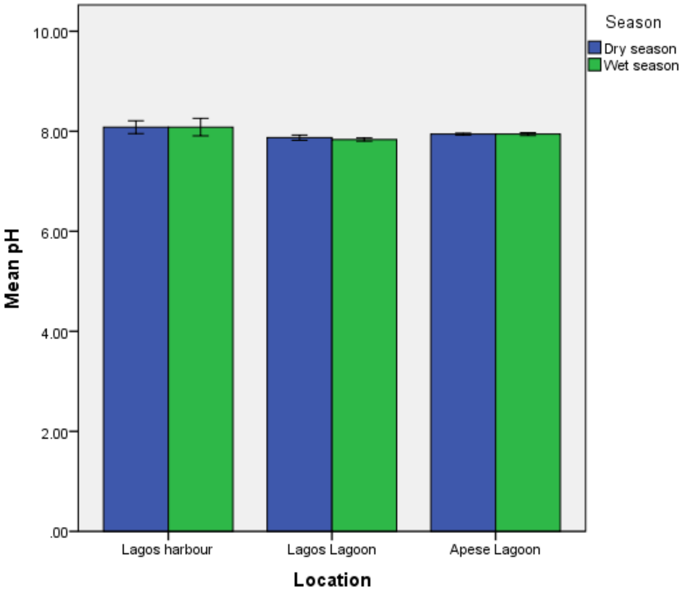


Fig. 20 a: pH variation

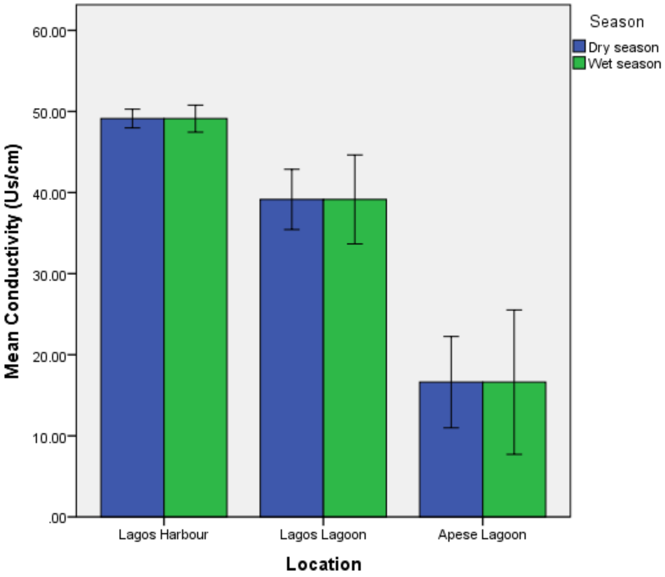


Fig. 20 b: Conductivity variation

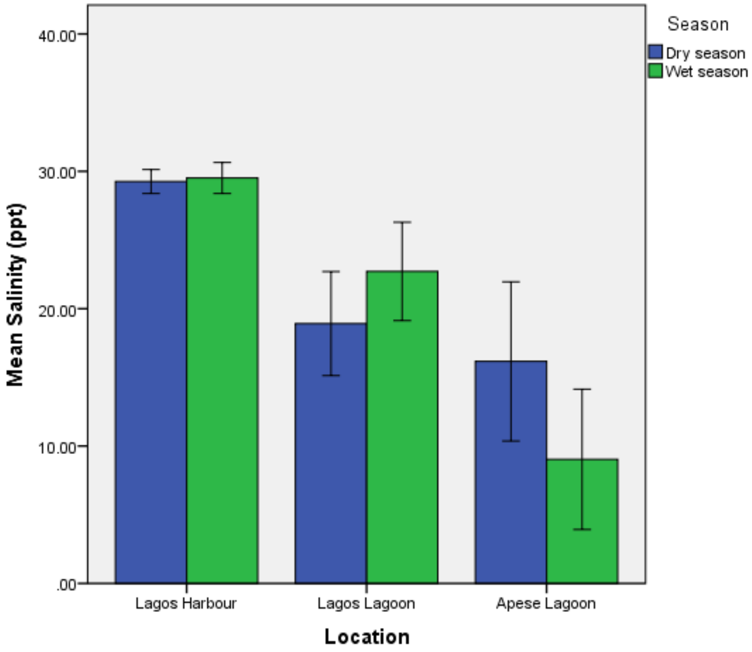


Fig. 20 c: Salinity variation

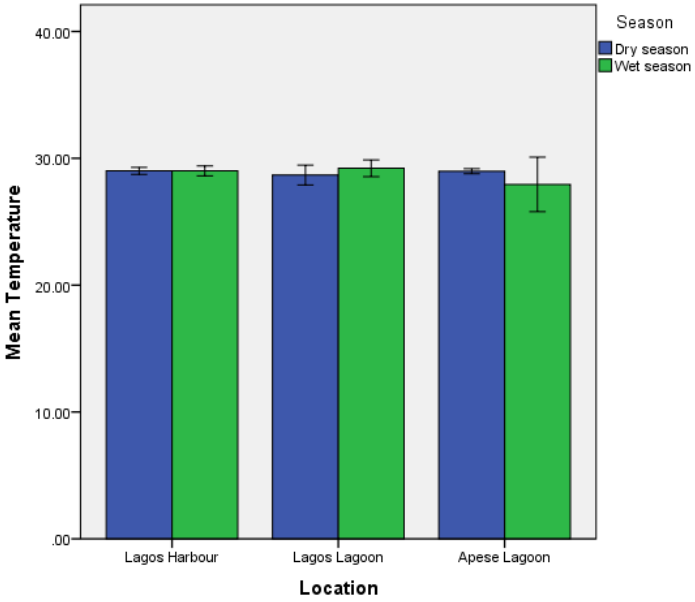


Fig. 20 d: Temperature variation

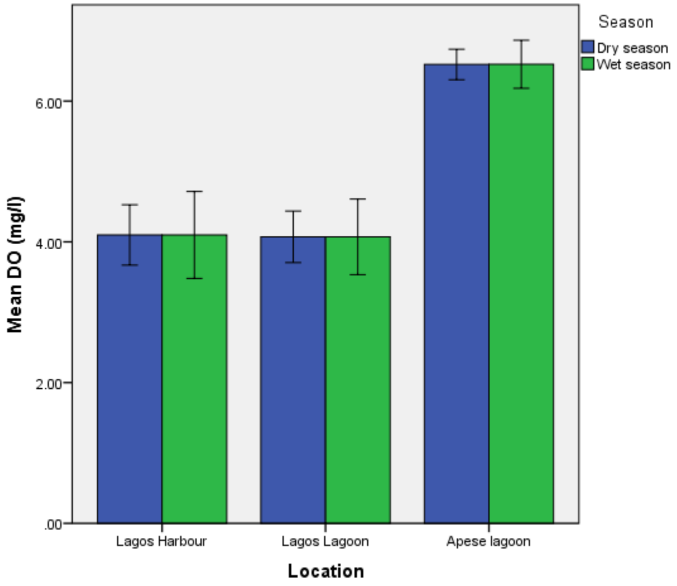


Fig. 20 e: Dissolved oxygen variation

Figure 20: Seasonal variations of the Water quality parameters of Lagos Harbour, Lagos Lagoon and Apese Lagoon. The bars on the figure represent +/- 2 Standard Error.

5.3 Particle size distribution

The average grain particle sizes (in percentage) of the sampling area are presented in Appendix 18. The measured particle sizes were divided into clay, very fine silt, fine silt, medium silt, coarse silt, very fine sand, fine sand, medium sand and coarse sand. Figure 21 shows that the clay and silt sediments have a relatively higher value at LH compared to LG and APL.

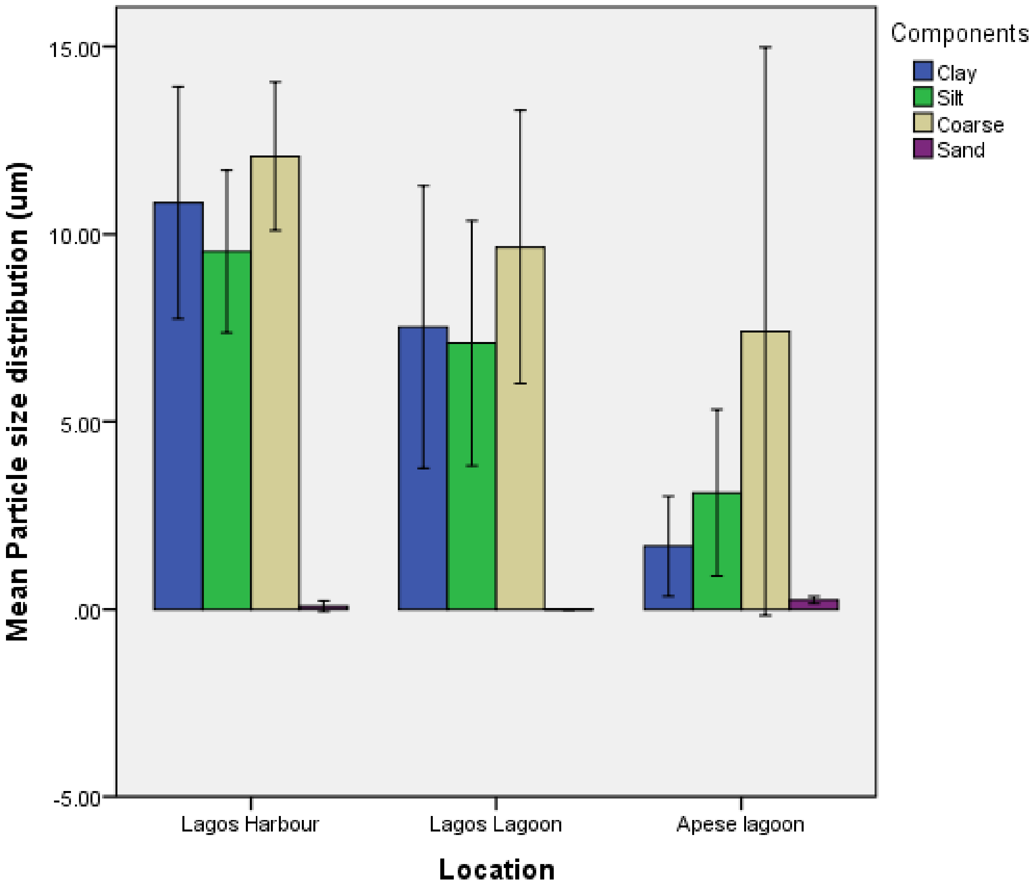


Figure 21: Comparison of different mean particle size distributions across LH, LG & APL. The bars on the figure represent +/- 2 Standard Error.

The coarse silt sediments also have higher values in the LH, followed by LG with the least recorded value at APL. The sand sediments have a higher particle size values at APL that is a control area compared to LH and LG. The coarse sand particle size recorded high level at APL compared to LH and LG. Overall there were significant differences ($P<0.05$) between the particle size distributions in the LH compared to the APL, with the former generally having higher zizes than the latter. There were no significant differences ($P>0.05$) in particle size distribution between Lagos Harbour and Lagos Lagoon as well as between Lagos and Apese Lagoon.

5.4 Total organic carbon and nitrogen contents

The total nitrogen content at the samplings sites, as shown in Figure 22, indicated high concentrations of total nitrogen contents in the wet season in Lagos Harbour with mean value of 1.72 mg/g and least at the Apese Lagoon. In the dry season, the results showed highest mean value of total nitrogen was of 2.19 mg/g in Apese Lagoon and least with mean value of 1.99 mg/g in Lagos Lagoon. The total nitrogen content in the sediment varied significantly ($P<0.05$) with season in the Lagos Lagoon with the dry season having higher values.

Total carbon in the wet season was highest in the Lagos Lagoon with mean value of 42.37 mg/g and least in Lagos Harbour with mean value of 24.38 mg/g. The total carbon recorded highest mean value of 88.67 mg/g in Apese Lagoon and least in Lagos Harbour with mean value of 35.98 mg/g. (Figure 23). Total organic carbon content was significantly higher in the dry season compared to the wet season ($P<0.05$).

There was a significant amount of carbon concentration, highlighting the level of anthropogenic activities, especially in relation to organic matter in the studied area and across the two distinct seasons.

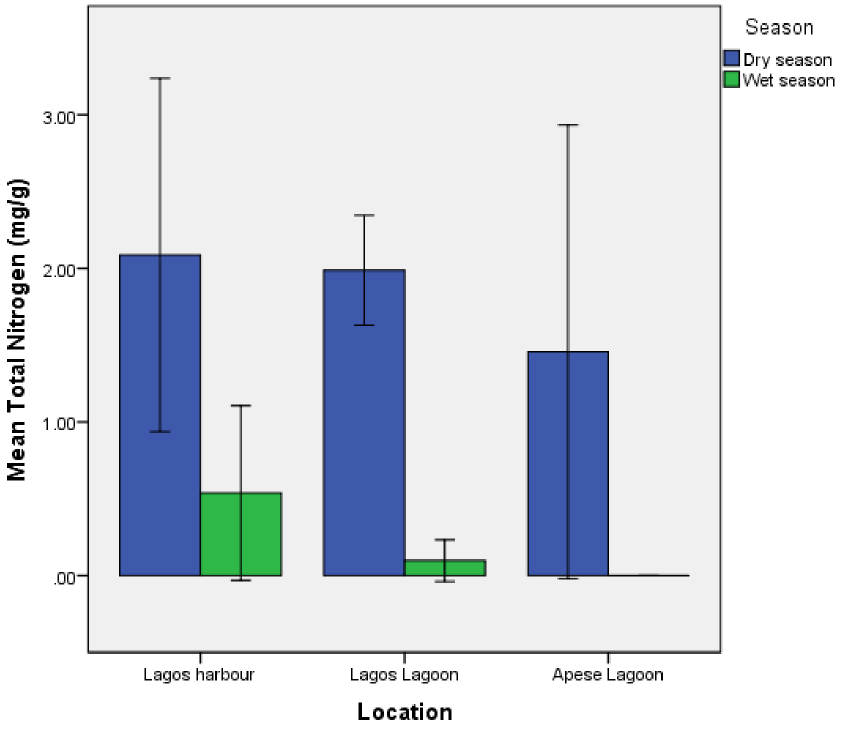


Figure 22: Total nitrogen content for wet (WS) and dry seasons (DS) at sampling locations. The bars on the figure represent +/- 2 Standard Error.

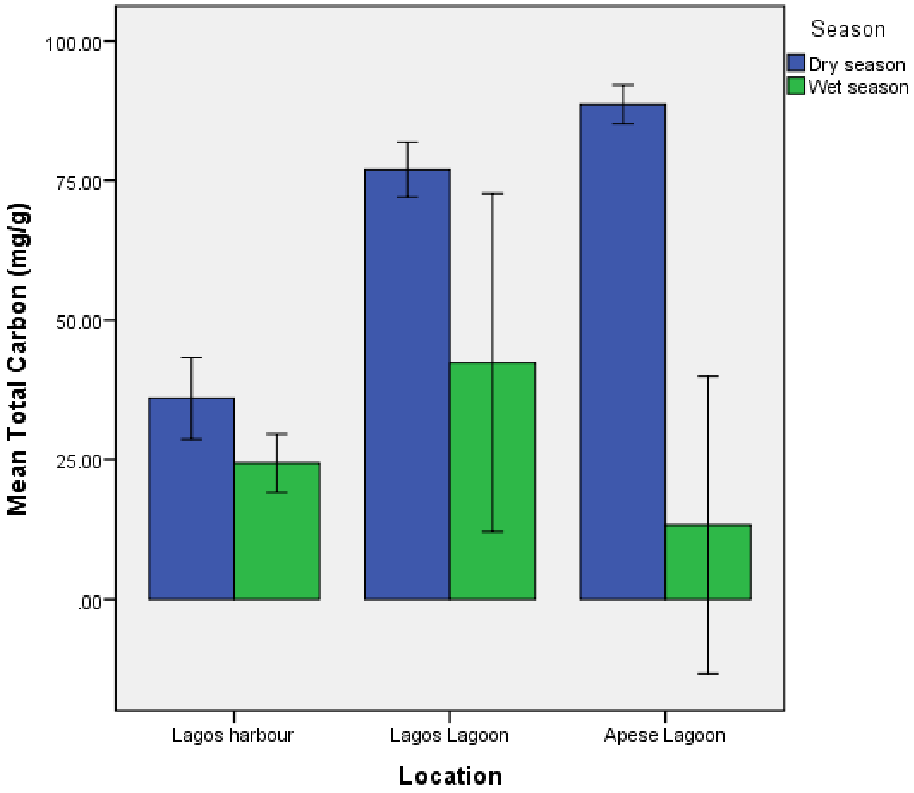


Figure 23: Total organic carbon content for wet (WS) and dry seasons (DS) at sampling locations. The bars on the figure represent +/- 2 Standard Error.

Table 28 shows the concentrations of the total organic carbon and nitrogen and the C:N ratio.

Total carbon recored indicated that there was highest intra seasonal change in the Lagos Lagoon with a range of 5.69 to 128.7 mg/g in the wet season. The LG also recorded the least intra seasonal variation of TC in the dry season (70.06 to 86.17 mg/g).

With respect to total Nitrogen concentration the highest intra seasonal variation was recorded in the dry season in the Lagos Harbour (0.90-8.90 mg/g) while the least was in the LG in the wet season (0.22 -0.46 mg/g). Overall, the largest difference in Carbon -Nitrogen ratio was recorded in the LH (5.10: 55.52) (Table 19).

Table 19: Summarised range of total carbon and nitrogen contents analysed distributions.

S/N	Location	Concentration of Carbon contents (mg/g)	Concentration of Nitrogen contents (mg/g)	Season	C:N Ratio
1.	Lagos Harbour	11.8-61.3	0.90-8.90	Dry season	5.10:55.52
		7.9-47.2	0.35-4.19	Wet season	7.28:43.91
2.	Lagos Lagoon	5.69-128.7	0.22-0.46	Wet season	210.45:279.7
		70.06–86.17	1.23-1.93	Dry season	25.32:60.59
3	Apese Lagoon	86.67-92.13	1.94-2.4	Dry and Wet	38.39:44.927

5.5 Comparative assessment of metal and metalloids concentration with sediment quality guidelines

5.5.1 Total metal concentrations bar charts for DS1, WS and DS2

The total metals analysed and compared with the threshold effect level (TEL) of NOAA and CSQGs are presented in Figure 24–26.

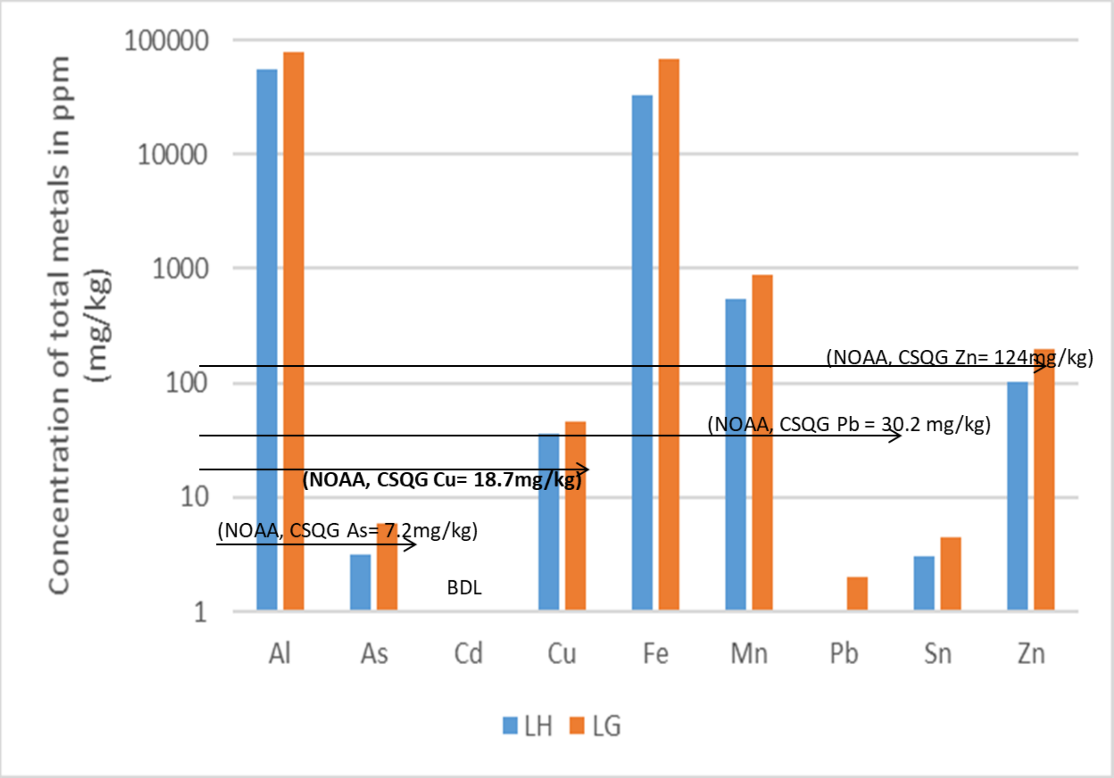


Figure 24: Total metal concentrations (XRF) for DS-1-2013.

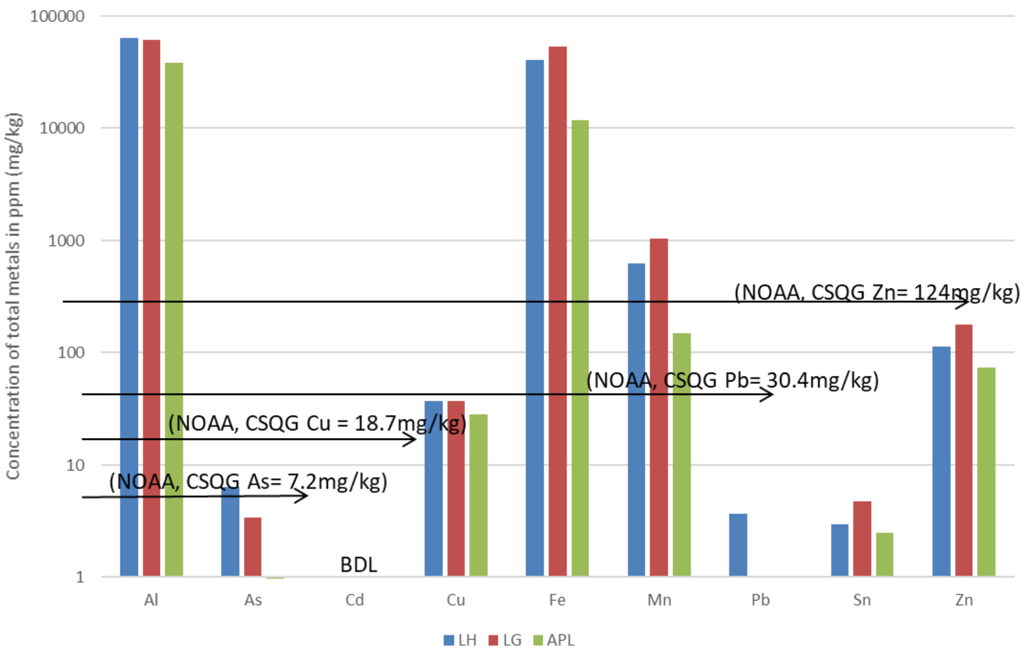


Figure 25: Total metal concentrations (XRF) for WS-2013.

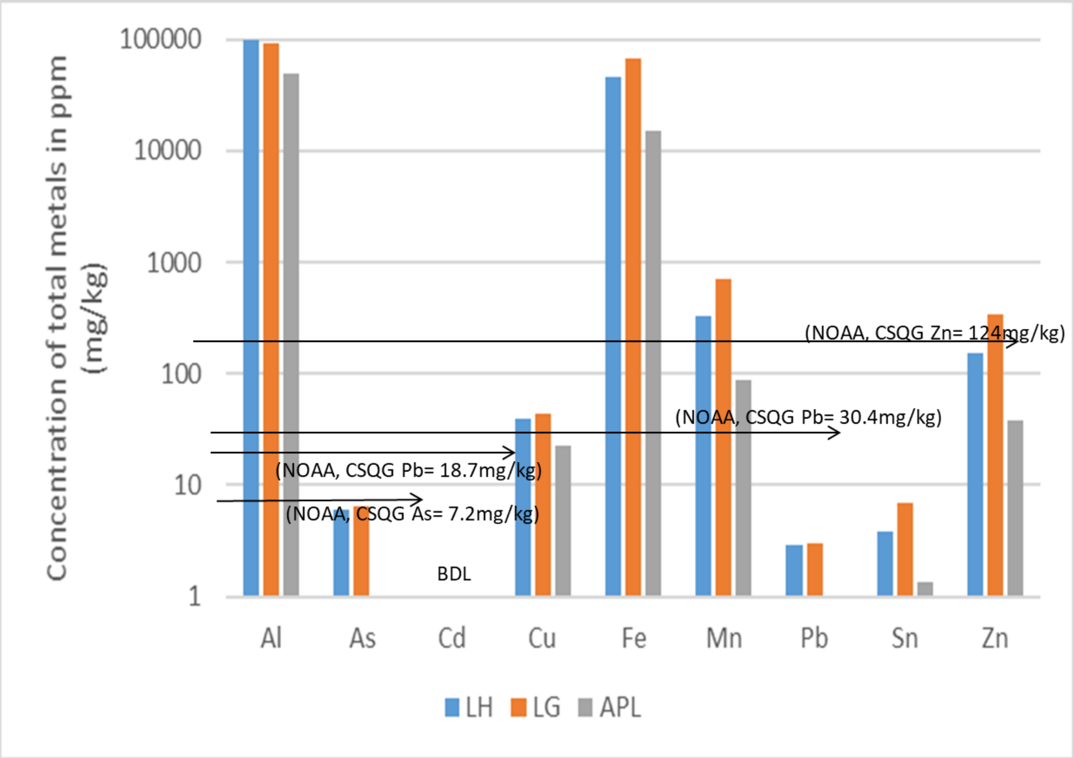


Figure 26: Total metal concentrations (XRF) for DS-2-2014.

Figure 24. Shows the concentrations in each location and comparable with the sediment quality guideline. The total metal concentrations were higher in the LG when compared to LH. The concentrations of Cu exceeded the threshold effect limits in LH and LG, while Zn exceeded the threshold effect limits in LG.

Figure 25. Shows that As concentrations were higher in the LH when compared to LG and APL. The concentrations of Cu exceeded the TEL in LH, LG and APL as well as Zn in LG.

Figure 26. Shows the concentrations of Cu exceeded the TEL in LH, LG and APL as well as Zn in LH and LG.

5.5.2 Recoverable bar charts for DS1, WS and DS2

The recoverable metals concentration compared with the threshold effect level (TEL) of NOAA and CSQGs are presented in Figures 27 – 29.

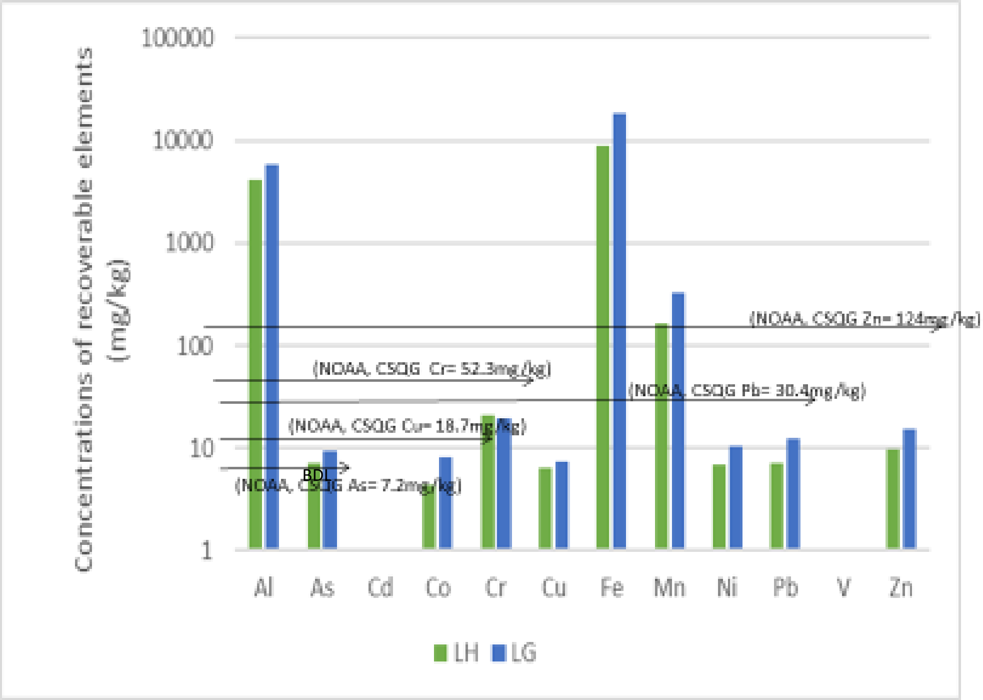


Figure 27: Recoverable elements (*Aqua regia*) for DS-1-2013.

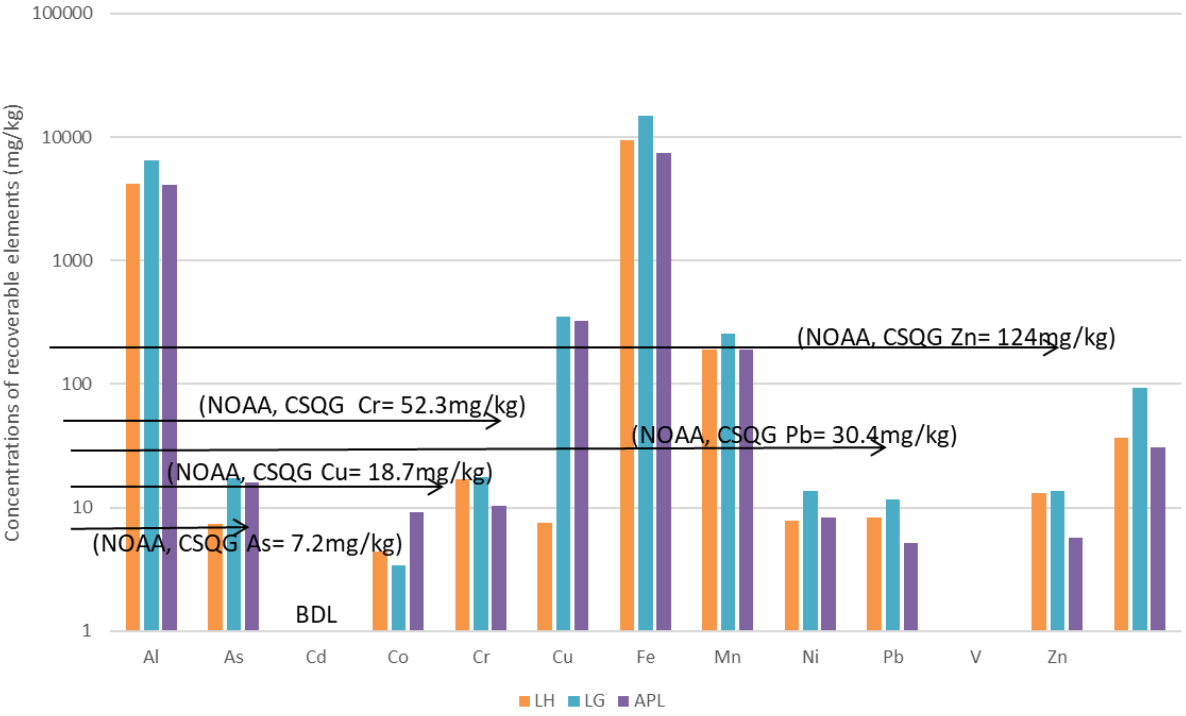


Figure 28: Recoverable elements (*Aqua regia*) for WS-2013.

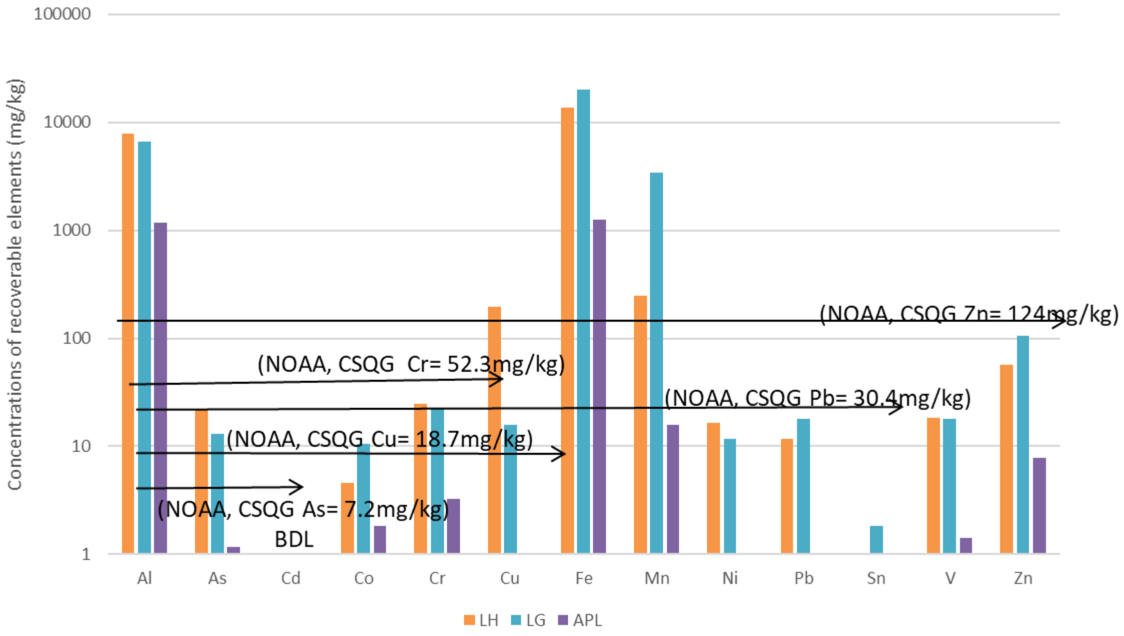


Figure 29: Recoverable elements (*Aqua regia*) for DS-2-2014.

Figure 27. Shows that the metal concentrations were higher in the LG when compared to LH. The concentrations of As exceeded the TEL in LH, LG and APL.

Figure 28 shows that the metal concentrations were higher in the LG when compared to LH. The concentrations of As exceeded the TEL in LH, LG and APL.

Figure 29 shows that the metal concentrations were higher in the LG when compared to LH. The concentrations of As exceeded the TEL of 7.2mg/kg with NOAA and CQGs in LH, LG and APL.

5.5.3 Bioavailable bar charts for DS-1-2013, WS-2013 and DS-2-2014

Bioavailable metals concentration compared with the threshold effect level (TEL) of NOAA and CSQGs are presented in Figure 30–32.

Figure 30. Shows that the bioavailable metal concentrations were higher in the LG when compared to LH. The metal concentrations were below the TEL across the sites- LH and LL, except for Ni that exceeds the TEL in LH.

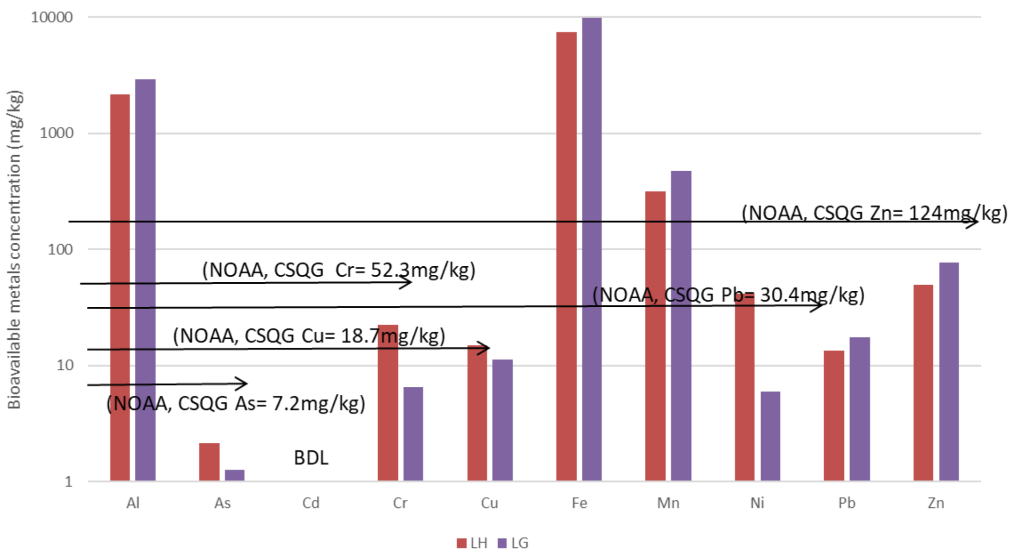


Figure 30: Bioavailable elements (1 M HCl) for DS-1-2013.

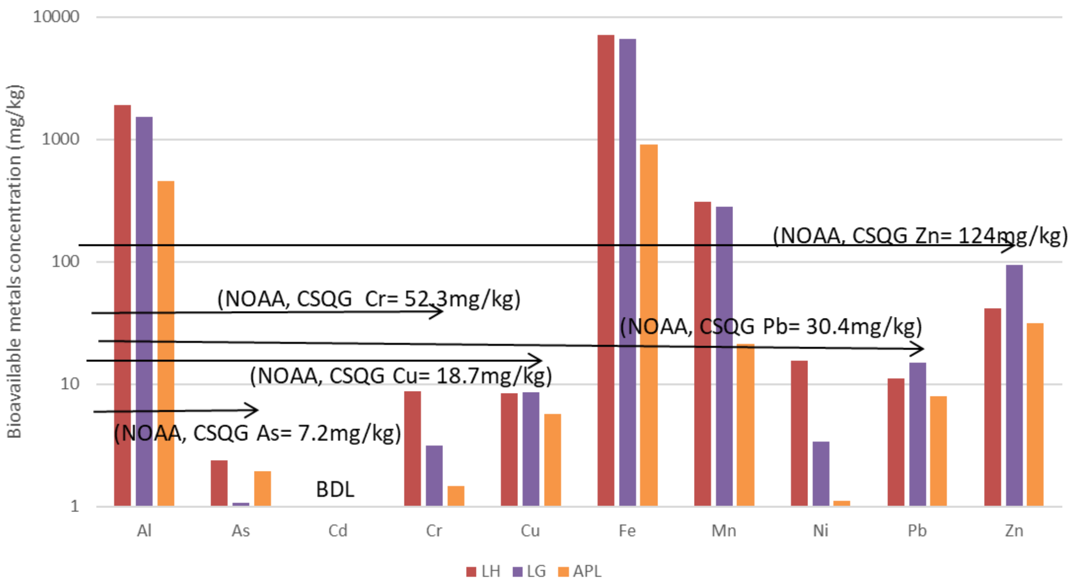


Figure31: Bioavailable elements (1 M HCl) for WS-2013.

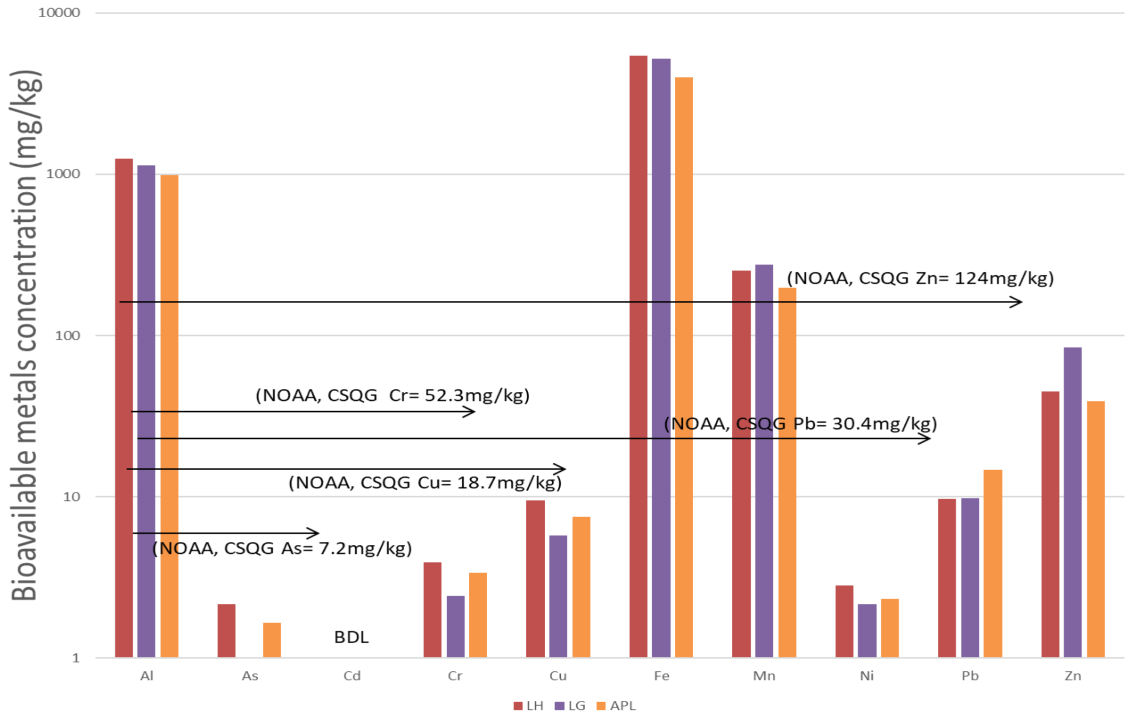


Figure 32: Bioavailable elements (1 M HCl) for DS-2-2014.

Figure 31. Shows that the bioavailable metal concentrations were higher in the LH when compared to LG, exept for Pb and Zn that were higher in LG than LH and APL. The metal concentrations were below the TEL across the sites- LH and LG.

Figure 32. Shows that the bioavailable metal concentrations were higher in the LH when compared to LG, except for Mn and Zn that were higher in LG than LH and APL. The metal concentrations were below the TEL across the sites- LH and LG.

5.5.4 Metal entry pathways and anthropogenic activities in the Lagos Harbour, Lagos and Apese Lagoon

Table 20 presents the list of metal contaminants and their sources within the study areas. The table was contructed based on existing literature and synthesis of the various findings from the filed and laboratory analysis in the present study. The LH was dominated by shipping, industrial and artisanal fishing activities. The LG is characterized mainly by domestic, recreational, industrial and artisanal fishing activity. The control, APL is characterized mainy of recreational activities

Table 20: List of Shipping, Industrial and other associated activities within Lagos Harbour, Lagos Lagoon and Apese Lagoon.

Locations	Activities (Shipping/Industrial & others)	Pathway of Metal Contamination	Intensity of anthropogenic activity
Lagos Harbour	**Shipping** – Oil discharges and air pollution from ships, tank farms, loading and storage, discharge of raw material from bulk cargo, Spillage from ship repairs and dry-docking areas, and continued dredging (metal contaminant- As, Pb &Ni). **Industrial**-Discharges from manufacturing industries (e.g., flour mills, Dangote sugar & flour) located within the Lagos Harbour area (metal contaminant- Pb and Sn) **Fishing**-Abandoned fishing nets and trolleys; use of fishing facilities (metal contaminant- Zn & Cu) (Abiodun & Oyeleke, 2016)	Spills during transfer of petroleum products from vessel to vessel or vessel to coastal tank farms, runoffs from tankfarms and port areas, wastes relaed durting bulk cargo discharges, runoff spills from dry dock activities and industries located within the ports, and shipping activities. Release of Ni from ship exhaust and eventual settling of the air borne Ni into water and sediments. Ilegal ballast waster discharges. Re-suspension of metals due to dredging activities. Leaching of metals from dry docks and wreckages.	Shipping activities are high with frequent docking and offloading of containerized and bulk cargos onto the ports and smaller transfer vessels- Nigeria's busiest port. Petroleum products transfer is frequent. LH is the main entry point of refined petroleum products imported into Nigeria. Industrial activities- Large scale industries are located on the coastline with direct offloading of cargos from vessels being a frequent occurrence. Routine Lagos channel maintenance dredging to remove excess silt from harbour.
Lagos Lagoon	**Transportation**- use of local boats and ferries for fishing (metal contaminant- Cd & Pb). Fishing- Oyster and fish farming and aqua culture **Industria**l –Manufacturing of bevarages, paints and textiles, printing press, sand mining and saw mills (metal contaminant- As, Cu & Cd). **Domestic** – Domestic/Municipal sewage, coastal dumpsites, general waste and water domestic trading (metal contaminant- Zn). (Ajao & Fagade, 1990; Abiodun & Oyeleke, 2016) Recreation- boat clubs, jet ski	General discharge of municipal sewage from canals into the lagoon Industrial. Wastewater stream from large and small-scale industries, leachates from coastal dumpsites, contaminated sediment re-suspension during sandmining Release of petrol, diesel and oils on roads and streets from vehicles and electricity generating sets, transformers and transport in runoffs into canals, creeks and lagoons. Spills of spent engine onto street drainage channels	High release of leachates and municipal wastes during storms in the long-wet season. Daily/Weeky diacharge of effluents from industries into the lagoon either directly or indirectly via canals. Considerable traffic of passanger and logistics ferries/ boats. Daily sand mining activities. Regular burning of sawdust and solid wastes along the coastline. High level of fishing activities.
Apese Lagoon	**Recreational**-boat transportation, associated residential and construction developments around the Lagoon area (metal contaminant- As & Cu). (Abiodun & Oyeleke, 2016)	Proximity to Atlantic Ocean and tidal incursion. New developmental activities, urban storm water and run-off.	Low anthropogenic activities, absence of fishing and high risk of tidal inclusion from the Atlantic Ocean.

5.5.5 Relative occurrence of metals which exceed SQGs in the three study areas (LH,LG and APL)

Overall, these findings indicate that in the three study areas, a number of metals had similar occurences while others were unique in the sense that they were found only in such locations (Figures 33 and 34). The Venn diagrams reveal the spatial distribution and Interrelationship of elements based on SQGs in the study areas (LH, LG & APL). The elements associated with all three zones were As, Cu and Sn, while Cd and Ni exceeding SQG were unique to the LG and LH respectively.

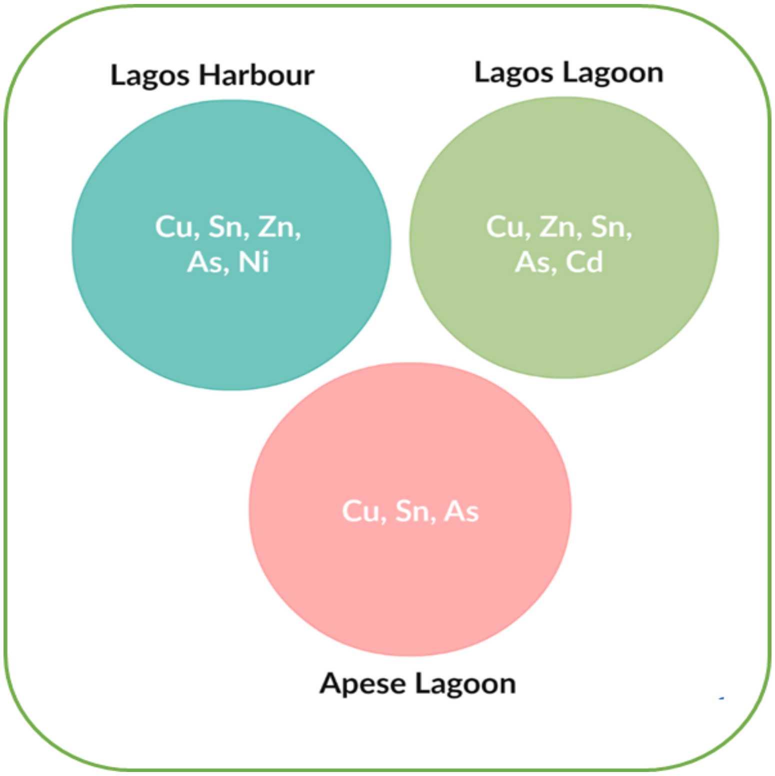


Figure 33: Distribution of elements which exceedance SQGs in the study areas (LH, LG & APL).

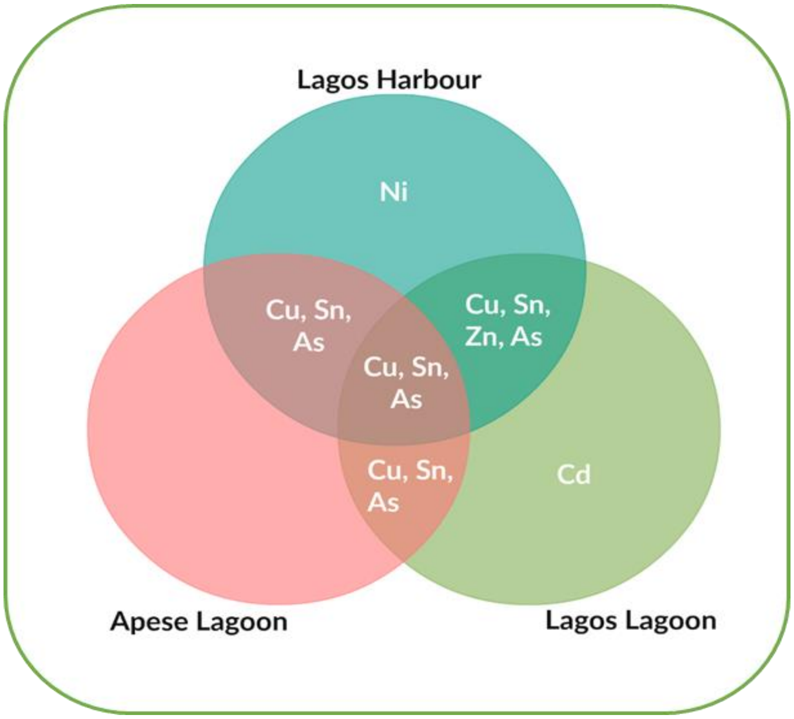


Figure 34: Interrelationship of elements exceedance SQGs within the study areas (LH, LG & APL).

Table 21 below presents and integrated summary of the metals exceeding SQGs and their respective most probable sources based on known metals associated with such activities from existing body of lierature world over. Although relative concentrations could have large ranges between the sampled water bodies (LH.LG and APL), in all cases some metals exceeded NOAA/ CSQGs TEL even in the control (APL) where tidal incursion and stormwater from nearby real estate development sites could be the most probable contributors.

Table 21: Summary of metal contaminants and their sources within the study area and those which exceed SQGs.

Location	**Methods and Elements**									**Sources**	**Comments**
Lagos Harbour	***Total (XRF)***			***Recoverable (Aqua-regia)***			***Bioavailable (I M HCl)***				
	DS1	**DS2**	**WS**	**DS1**	**DS2**	**WS**	**DS1**	**DS2**	**WS**		
	Cu, Sn,	**Cu Sn, Zn**	**Cu Sn**		**As Cu Sn Ni**	**Sn**	**Ni**	**Ni**	**Ni**	**1. Bulk cargo offload/shipping 2. Petrolum products spill 3. Industrial 4. Maintenance dredging**	**Cu, Sn, Zn, Ni and As exceeded the NOAA/ CSQGs TEL**

Lagos Lagoon	***Total (XRF)***			***Recoverable (Aqua-regia)***			***Bioavailable (I M HCl)***				
	DS1	**DS2**	**WS**	**DS1**	**DS2**	**WS**	**DS1**	**DS2**	**W S**		
	Cu Sn Zn	**Cu Sn Zn**	**Cu Sn Zn**	**As Sn**	**As Sn**	**As Cu**	**Cd**		**Ni**	**1. Municipal sewage/runoff 2. Industrial effluents 3. Solid waste leachates 4. Sand mining**	**Cu, Sn, Zn, Ni and As exceeded the NOAA/ CSQGs TEL**

Apese Lagoon	***Total (XRF)***			***Recoverable (Aqua-regia)***			***Bioavailable (I M HCl)***				
	DS1	**DS2**	**WS**	**DS1**	**DS2**	**WS**	**DS1**	**DS2**	**W S**		
	No Sampling	**Cu Sn**	**Cu Sn**	**No Sampling**		**As Cu**	**No Sampling**		**No Significant value**	**1. Tidal incursion 2. Run off from developmental projects. 3. Storm water runoffs**	**Cu, Sn and As exceeded the NOAA/ CSQGs TEL**

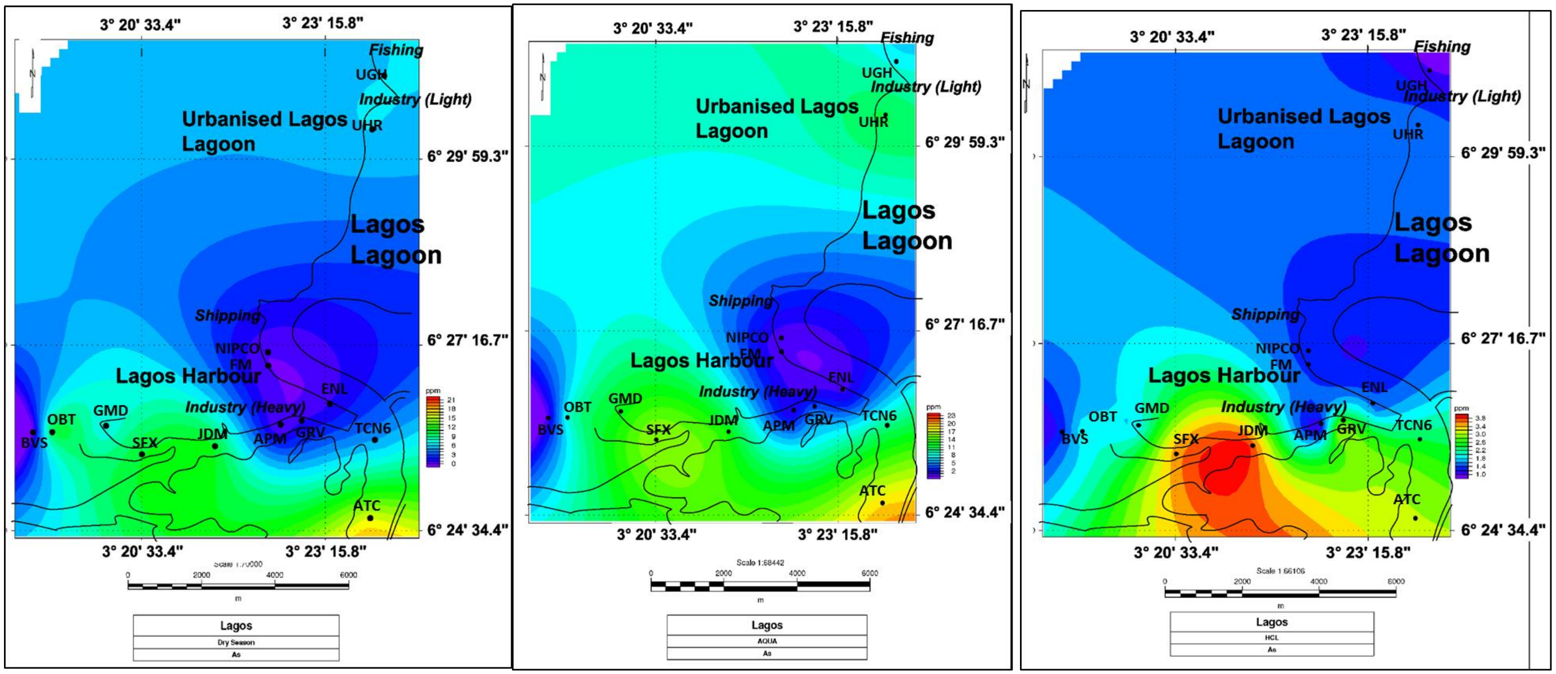
Key: TEL- Threshold effect level, DS- Dry season and WS- Wet season

5.5.6 Geochemical Contour and Spatial Maps of Metal Distributions in LH, LG& APL

The different sites in the Lagoons assessed were found to have a variety of activities associated with them, some unique to them (Table 22, Figures 35-46). The contour maps are represented by the three methods of (XRF, *Aqua regia* and 1 M HCl) analysed and extracted metals and metalloids which are distributed across the LH, LG and APL (control site) as presented in Figures 35 to 46. The contour maps show the spatial variations in the concentration of the metals and metalloids across the study area in each of the method and season based on the sediment quality guidelines as shown in each individual contour map. The significant metals and metalloid presented in the contour maps are: As, Pb, Zn and Fe respectively. The metals were selected due to the fact that they are known metals of health concerns and their sediment concentrations were considerably high, and often higher than the NOAA and CSQGs standards for safe limits of heavy metals in marine sediments. Specifically, the idea was to further evaluate the distribution of two non-biologically relevant metals and two essential ones which are biologically relevant at low concentrations. The contour maps revealed varied concentrations (from very high to low) of the selected heavy distributed in the Lagos Harbour and Lagos Lagoon. The control section (Apese Lagoon) generally showed low to insignificant concentrations of the heavy metals distributed in the sediments for both the wet season (2013) and dry season -2 (2014) (Figures 35 to 46). The summary of activities within respective sampling sites are presented in Table 22.

Table 22: Summary of dominant activities at specific sampling sites in the study locations.

Sites	Names	Zone	Observed activities
1	ATC	Lagos Harbour	Oil tank farms discharge area
2	SFM	Lagos Harbour	Bulk cargo discharge area
3	JSD	Lagos Harbour	Bulk cargo discharge area
4	ORD	Lagos Harbour	Oil tank farms discharge area
5	IBJ	Lagos Harbour	Oil tank farms discharge area
6	GMD	Lagos Harbour	Vessel discharge area
7	SIFX	Lagos Harbour	Bulk cargo
8	T6	Lagos Harbour	Bulk cargo
9	FJ	Lagos Harbour	Oil tank farms discharge area
10	JSD	Lagos Harbour	Bulk cargo terminals
11	APM	Lagos Harbour	Container bulk terminal
12	BN	Lagos Harbour	Bulk cargo terminal
13	ENL	Lagos Harbour	Bulk cargo terminal
14	FM	Lagos Harbour	Flour mills raw materials terminal
15	NPA-DY	Lagos Harbour	Dry docking & ship repair
16	NIPCO	Lagos Harbour	Oil tank farm and discharge areas
17	IDDO	Lagos Lagoon (urbanised part)	Public sewage & dump sites
18	OKB	Lagos Lagoon (urbanised part)	Saw mills waste, domestic wastes, Solid waste dump
19	MKK	Lagos Lagoon (urbanised part)	Fish farming and domestic trading
20	UGH	Lagos Lagoon (urbanised part)	Municipal sewage/Storm canal discharge Domestic wastes discharge areas
21	UWF	Lagos Lagoon (urbanised part)	Recreational & aquaculture
22	UHR	Lagos Lagoon (urbanised part)	Oyster, recreational &sand mining
23	OWS	Lagos Lagoon (urbanised part)	Coastal Dump site, Industrial efflunets
24	AP-1	Apese Lagoon(control)	Recreational & proposed residential development
25	AP-2	Apese Lagoon(control)	Recreational & proposed residential development
26	AP-3	Apese Lagoon(control)	Recreational & proposed residential development

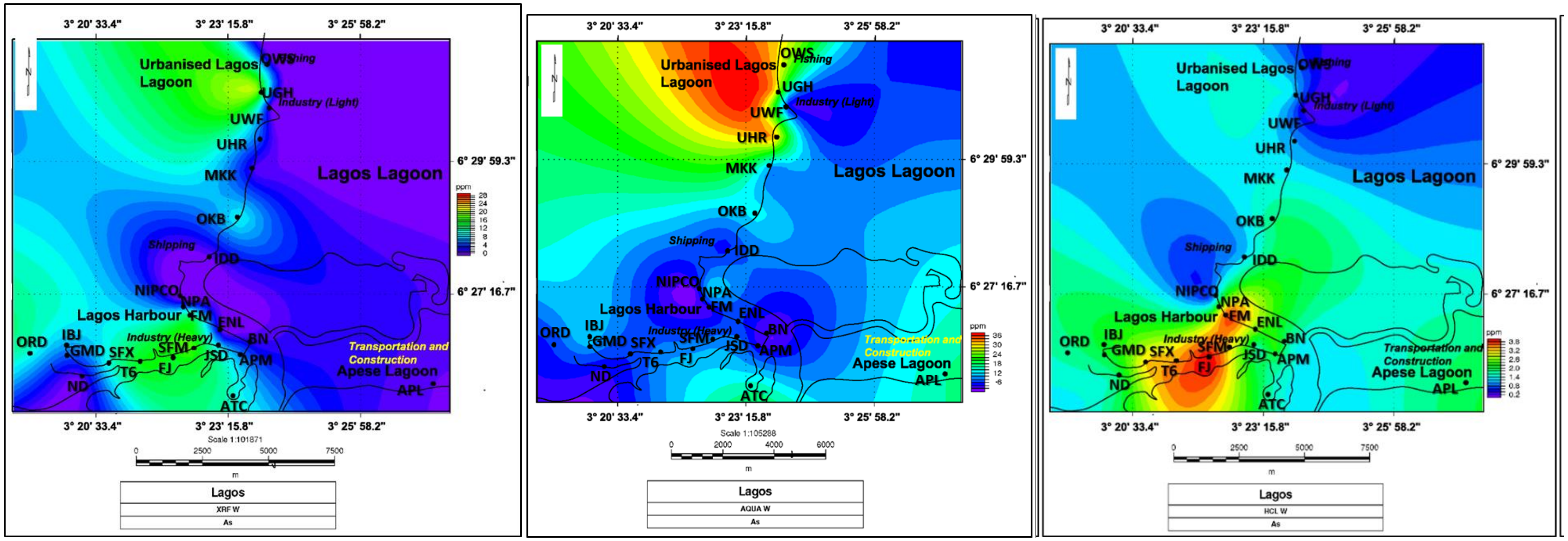


Total As (XRF)

Recoverable As (*Aqua regia*)

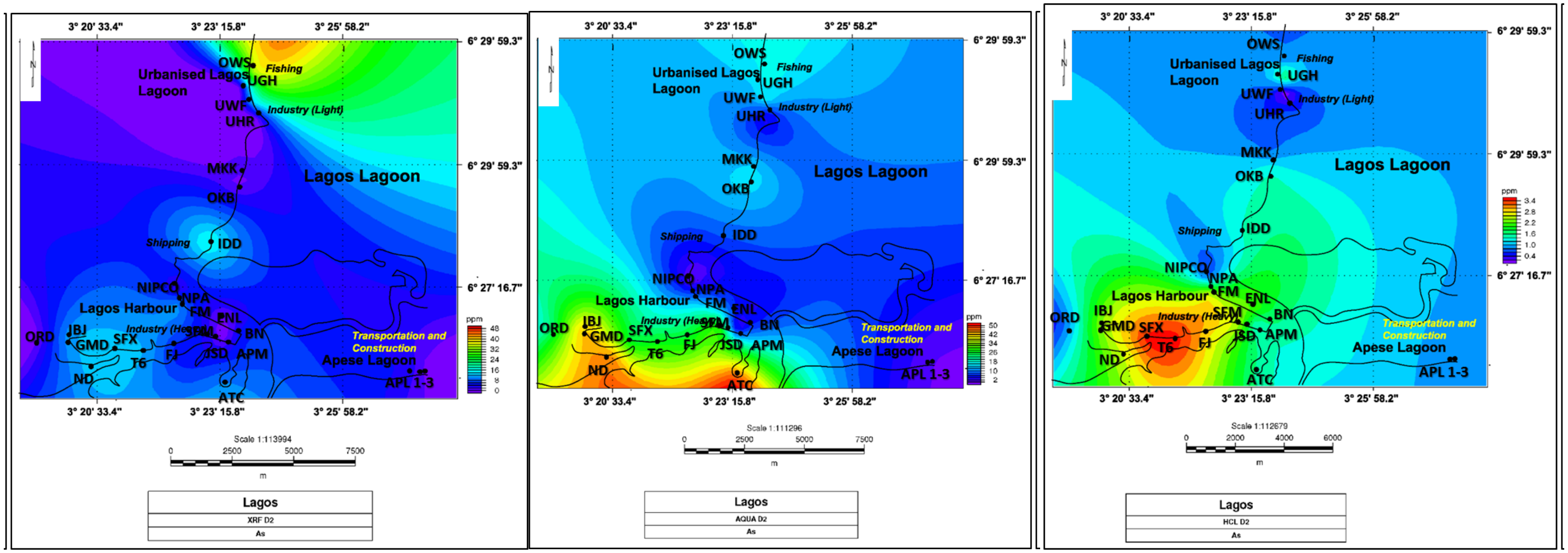
Bioavailable As (1 M HCl)

Figure 35: Spatial variations in the total, recoverable and bioavailable As distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-1 (2013).



Total As (XRF) **Recoverable As (*Aqua regia*)** **BioavailableAs (1 M HCl)**

Figure 36: Spatial variations in the total, recoverable, bioavailable As distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the wet season – 2013.



Total As (XRF)

Recoverable As (*Aqua regia*)

Bioavailable As (1 M HCl)

Figure 37: Spatial variations in the total, recoverable, bioavailable As distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-2 (2014).

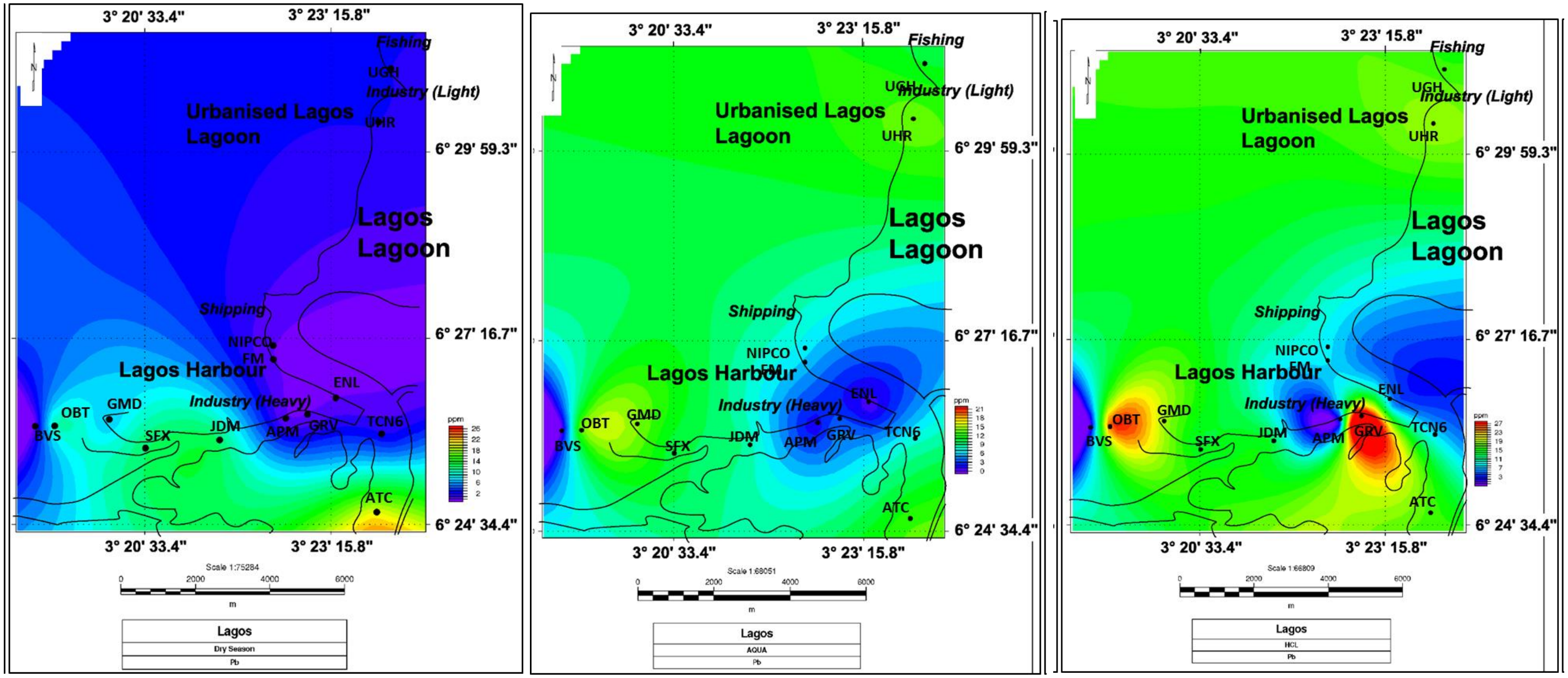
5.5.6.1 Contour map distribution of As in sediment across the study areas (LH, LG, APL)

In the dry season-1 (2013), higher concentrations of bioavailable (1 M HCl) As were much higherin the sediments of Lagos Harbour compared to the LG which shows that activities releasing As are higher in the area and/or the enclosed nature of the harbour allows it collect this metal from shallower areas of the lagoon system (Figure 35). Specifically, the higher bioavailable As concentrations were more distributed around the areas of the harbour where refined petroleum products are trasnsfered onto coastal tank farms.

In the wet season-2013, recoverable (AR) and bioavailable (IM HCl) As concentrations were much higher in spread in the Lagos Habour areas and the LG respectively (Figures 36). With respect to LH, the specific location associated with the high concentrations were the tank farm locations while for the LG it was specifically at areas receiving municipal runoff from the city center (Figure 37).

The total (XRF analysed) As concentrations were much higher in the sediment at the urbanised part of the LG, while the recovereable (AR) and bioavailable (1 M HCl extractable) As were higher in concentration in the sediment of LH during the dry season-2 (2014) as shown in Figure 36. The total As concentrations were higher around the areas receiving municipal runoffs in the LG while the recoverable and bioavailable forms were equally dominant in the areas adjacent the coastal tank farms of the LH.

During the two sampling seasons, As concentration (XRF, AR and I M HCl) were low in concentrations in the APL (control) sediment samples as indicated by the deep and light blue colourations in the contour maps (Figures 35 and 36).

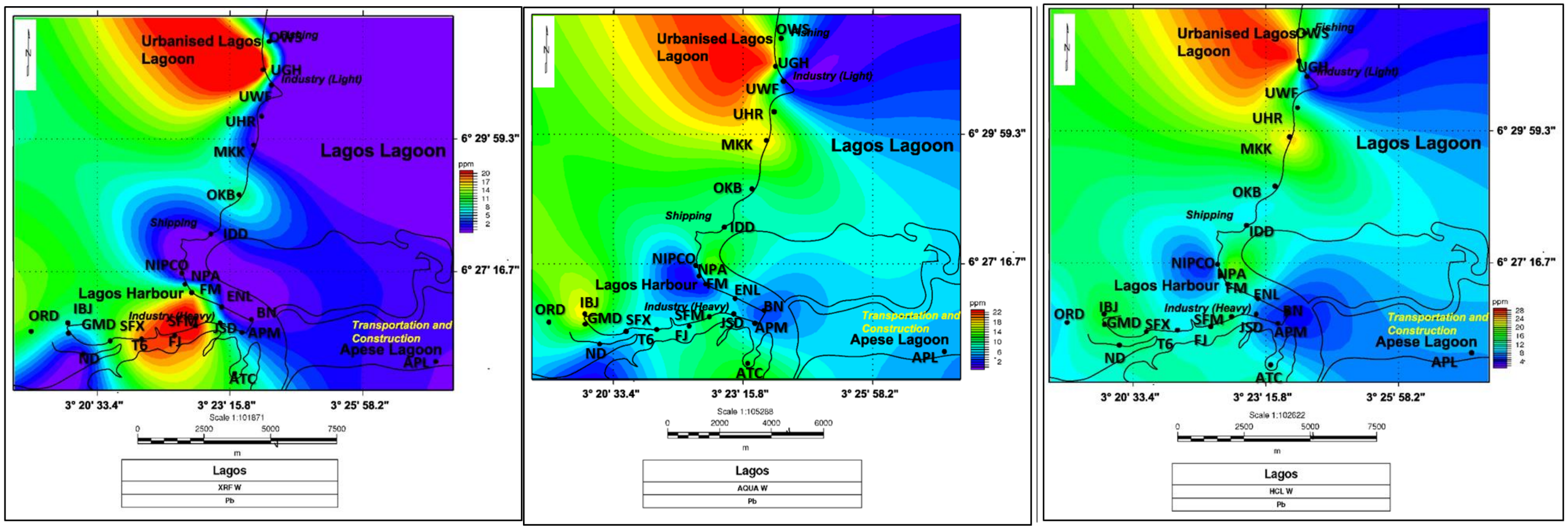


Total Pb (XRF)

Recoverable Pb (*Aqua regia*)

Bioavailable Pb (1 M)

Figure 38: Spatial variations in the total, recoverable, bioavailable Pb distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-1 (2013).

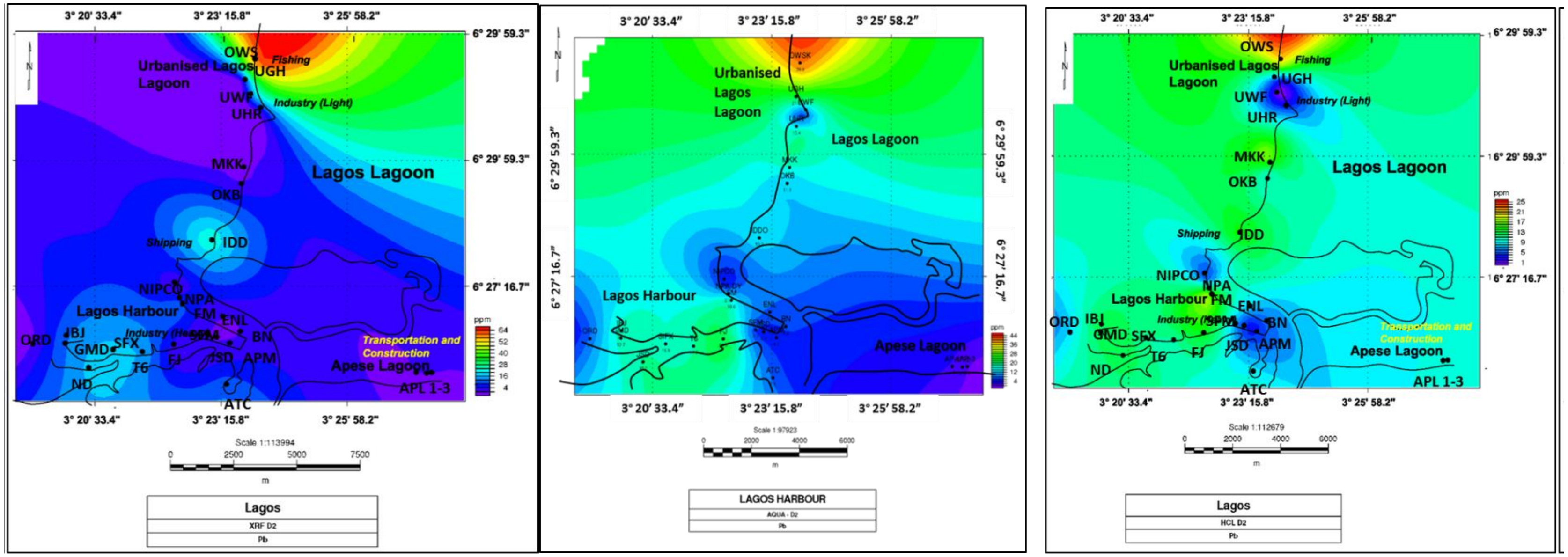


Total Pb (XRF)

Recoverable Pb (*Aqua regia*)

Bioavailable Pb (1 M HCl)

Figure 39: Spatial variations in the total, recoverable, bioavailable Pb distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the wet season – 2013.



Total Pb (XRF)

Recoverable Pb (*Aqua regia)*

Bioavailable Pb (1 M HCl)

Figure 40: Spatial variations in the total, recoverable, bioavailable Pb distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-2 (2014).

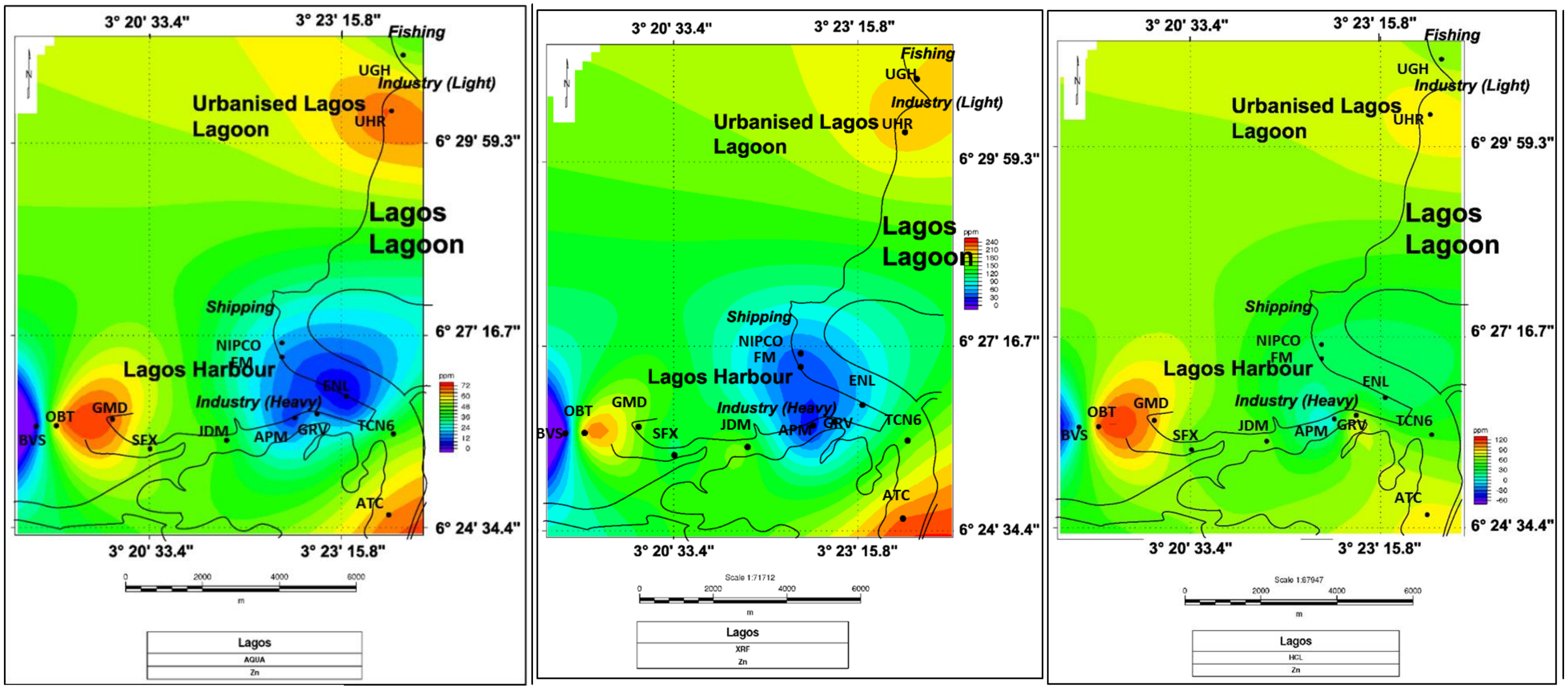
5.5.6.2 Contour map distribution of Pb in sediment across the study areas (LH, LG & APL)

In the dry season-1 (2013), total (XRF) and bioavialable (IM HCl) Pb concentrations were much higher in the sediments of the LH as shown in Figure 38. Specifically, the high concentrations of the total Pb was recorded at the Atlas Cove petroleum products import terminal while the high bioavailable concentrations were recorded around the Cargo offload port area and a section which hosts petroleum products tank farm.

During the WS (2013), the Total (XRF analysed) Pb concentrations were higher in both the sediments at the urbanised part of the LG and the LH, while the recoverable (AR) and bioavailable (1 M HCl) concentrations of Pb were significantly distributed in the sediments at the urbanised parts of the LG during the wet season (Figure 39). The high XRF values were recorded at the petroleum products tank farm area for LH and around the points of discharge of municipal runoffs from the city centers into the LG. The recoverable and bioavailable forms were equally high in this section of the LG.

Also, the total (XRF) and recoverable (digested with 1 M HCl) concentrations of Pb were much higher in the sediments at the urbanised part of the LG, during the dry season-2 (2014) (Figure 40) and this high measurements were around the areas receiving municipal runoffs and coastal settlement which are associated with burning of solid wastes and smoking of fishes using used car tyres as source of fuel/heat This area is also associated with retailing of refined petroleum products to local motorized fishing boat owners.

The Pb concentrations in the sediments at the APL (Control) was equally the lowest compared to LH and LG with values of total, recoverable and bioavailable conentrations being consistently very low to low (Figures 39 and 40).

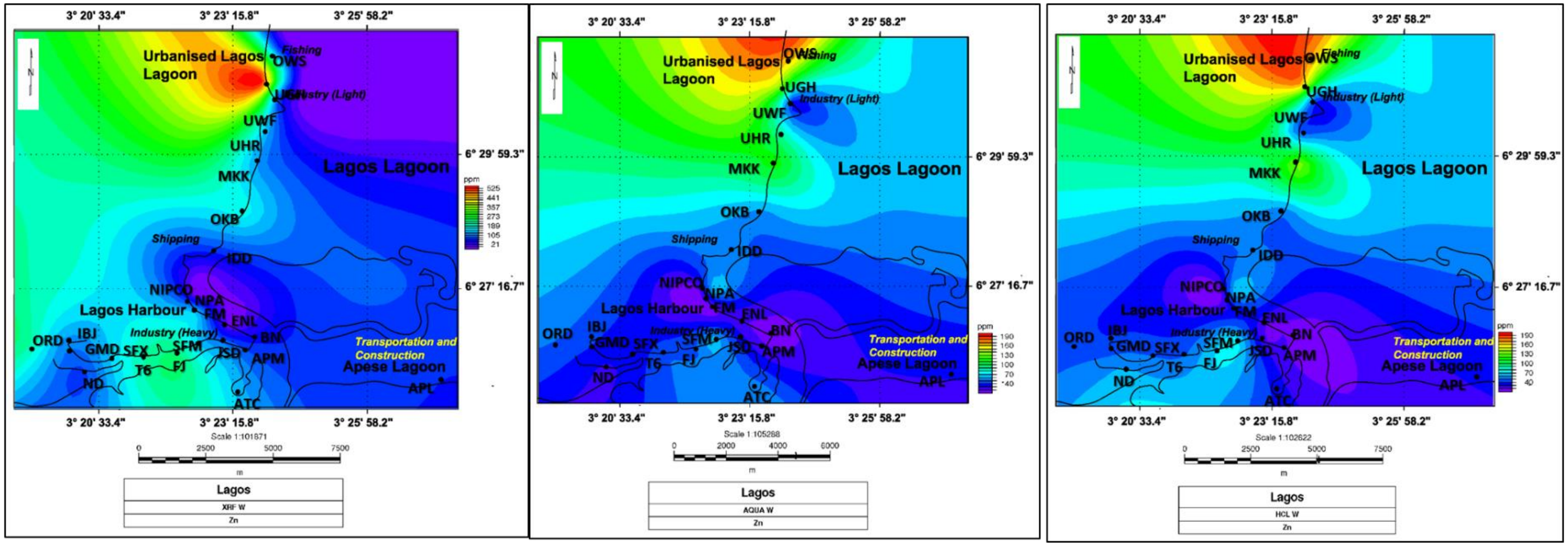


Total Zn (XRF)

Recoverable Zn (*Aqua regia*)

Bioavailable Zn (1 M HCl)

Figure 41: Spatial variations in the total, recoverable, bioavailable of Zn distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-1 (2013).

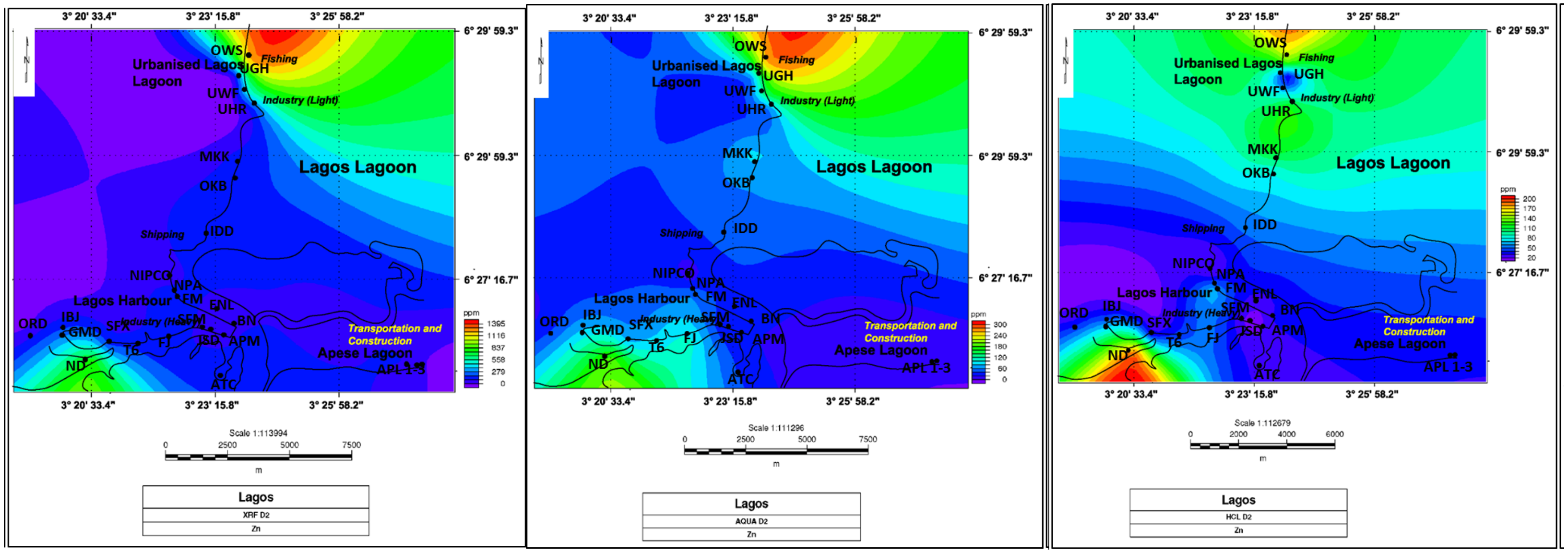


Total Zn (XRF)

Recoverable Zn (*Aqua regia*)

Bioavailable Zn (1 M HCl)

Figure 42: Spatial variations in the total, recoverable, bioavailable of Zn distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the wet sea son (2013).



Total Zn (XRF)

Recoverable Zn (*Aqua regia*)

Bioavailable Zn (1 M HCl)

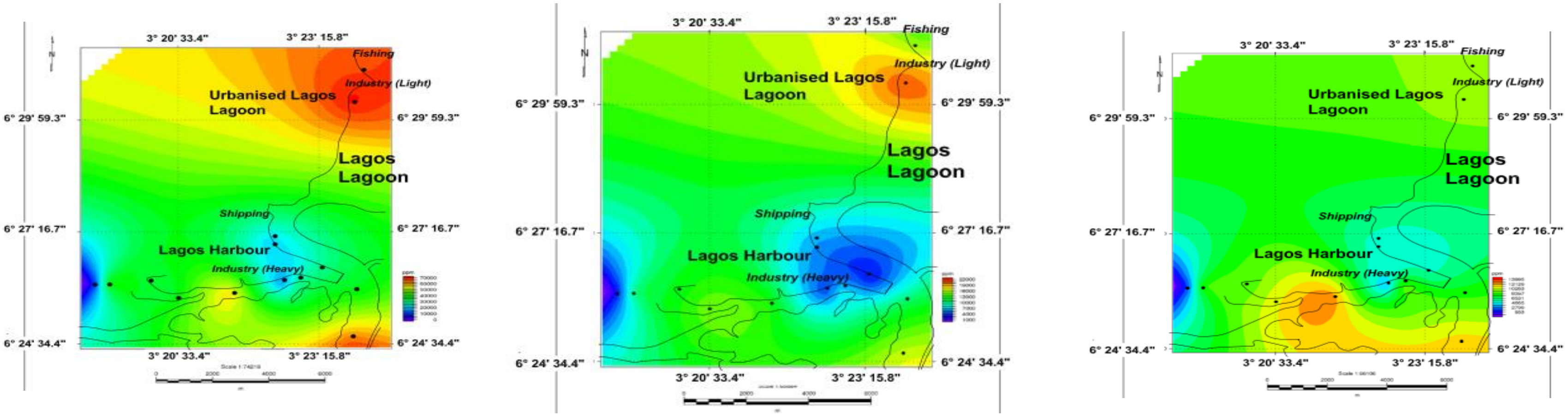
Figure 43: Spatial variations in the total, recoverable, bioavailable of Zn distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-2 (2014).

5.5.6.3 Contour map distribution of Zn in sediment across the study areas (LH, LG, APL)

In the dry season 1 (2013), total (XRF) and recoverable (AR) Zn concentrations were higher in concentration at the urbanised part of the LG. This was also the case in the LH with respect to the bioavailable (1 M HCl) Zn concentration (Figure 41).

The total (XRF), recoverable (AR) and bioavailable (1 M HCl) Zn were much higher in the sediments at the urbanised part of the LG during the wet season-2013 (Figure 42). The APL recorded very low concentrations in the sediment samples for the three forms of Zn analysed.

The total and recoverable Zn concentrations were much higher in the sediment at the urbanised part of the LG specifically in areas where urban runoffs enter the lagoon via cannals. The bioavailable (1 M HCl) Zn concentrations were much higher in the sediments of the LH during the dry season-2 (2014) specifically in areas receiving urban runoffs from the western axis of the harbour. This area also houses a few refined petroleum products tank farms (Figure 43). The control, APL which is associated with mostly recreational activities recorded very low concentrations of the metal in its sediment samples.

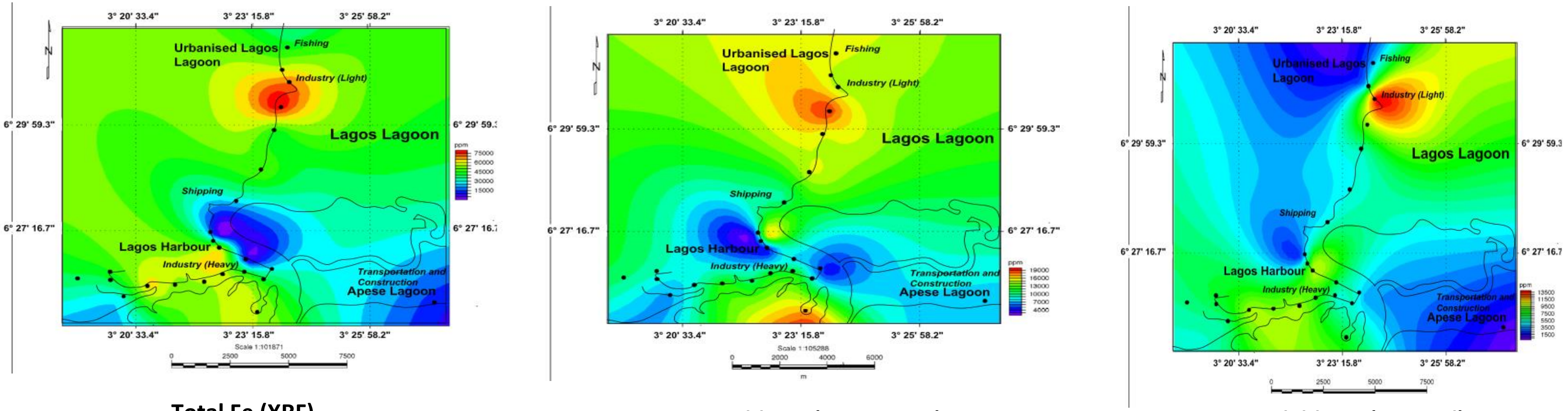


Total Fe (XRF)

Recoverable Fe (*Aqua regia*)

Bioavailable Fe (1 M

Figure 44: Spatial variations in the total, recoverable, bioavailable ofFe distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-1 (2013).

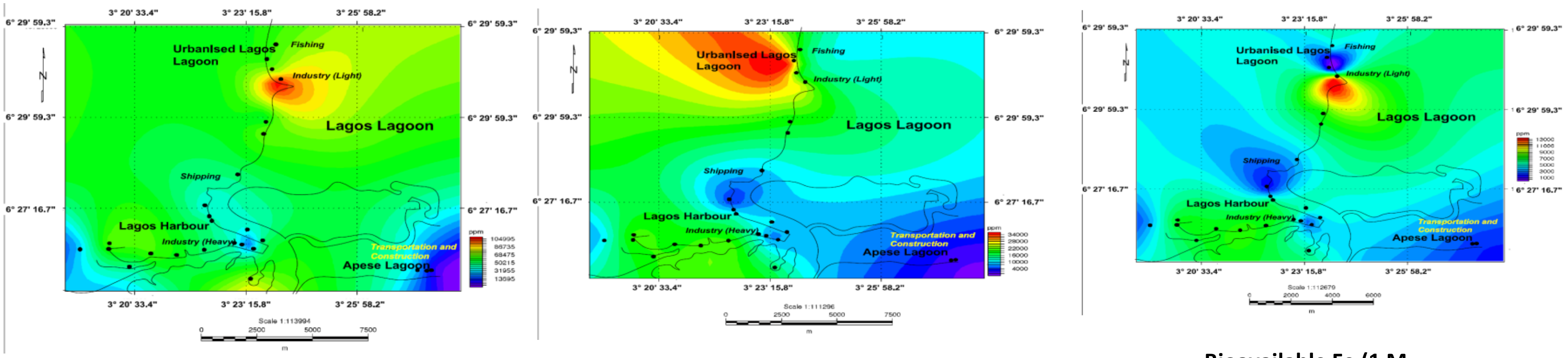


Total Fe (XRF)

Recoverable Fe (*Aqua regia*)

Bioavailable Fe (1 M HCl)

Figure 45: Spatial variations in the total, recoverable, bioavailable of Fe distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the wet season.



Total Fe (XRF)

Recoverable Fe (*Aqua regia*)

Bioavailable Fe (1 M

Figure 46: Spatial variations in the total, recoverable, bioavailable of Fe distributed in sediment across the Lagos Harbour, Lagos Lagoon and Apese Lagoon during the dry season-2 (2014).

5.5.6.4 Contour map distribution of Fe in sediment across the study areas (LH, LG, APL)

In the dry season 1 (2013), Fe concentration was very high in the sediment at the urbanised part of the LG (around areas which receive runoffs from canals which drain major settlements in the city), moderately distributed at the LG with respect to recoverable concentrations (AR) and slightly at Atlas Cove axis of the LH (Figure 44). High Fe concentrations in the LG can also be attributed to inflows from inland rivers which bring in waters and sediments from the hinter lands into the lagoon.

The total (XRF), recoverable (AR) and bioavailable (1 M HCl) concentrations of Fe were high in the sediments at the urbanised part of the LG. Specifically this high reading was in sediment samples obtained from the areas which receive municipal runoffs and also have light industrial activities during the wet season -2013 (Figure 45). The three assessed Fe concentrations were much lower at the AP (control) sampling sites as well during the wet season.

The total (XRF) and bioavailable (1 M HCl) Fe concentration were higher in the sediment samples in the areas receiving urban municipal runoffs into the LG, while recoverable (AR) concentrations showed that the metals were more distributed around the same section of the urbanised part of the Lagos Lagoon during the dry season-2 -2014 (Figure 46). The total (XRF) Fe concentration was moderate in the control sites (AP) while the bioavailable and recoverable forms were low in concentration.

5.6 Correlation coefficients between metals with total organic carbon nitrogen and particle size distributions

A correlation analysis was conducted to assess the inter-relationship between the variables of significance towards understanding adsorption, mobility and bioavailability of metals with respect to particle size, organic carbon and nitrogen. The measured concentrations of the respective elements were computed into MS Excel software to calculate their Pearson's correlation coeficients (using normalized data as indicated in section 4.7) and significance of determined correlations were also generated. The mean measurements obtained in the two dry seasons and those of the single wet season sampling were employed to this effect. The mean data from the two seasons across the sites within the three study locations rather than specific sites were used for this purpose in other to provide a broad view of the correlation among the variables. Sediment physical characteristics is not expected to differ over the distance between sites.

There wase strong correlations between the three sediment particle sizes, i.e clay, silt and coarse. Total nitrogen (TN) in the wet season also correlated significantly with all three particle sizes (Table 23 to Table 25). Table 23 shows the Pearson's correlation coefficient between total metals (XRF) analysed alongside total nitrogen, total carbon and particle sizes. The results indicated that there was significant positive correlation between the metals As, Fe and Pb and the clay constituents of the sediments. The TN concentrationof the wet season correlated significantly with the total As and Pb concentrations. Overall, the total metal concentrations measured showed significant positive correlations across the samples analysed.

Table 24 shows the Pearson's correlation coefficient between recoverable metals (*Aqua regia*) with total nitrogen, total carbon and particle sizes. There was significant positive correction between total carbon (TC) in the wet season with levels of recoverable Fe and Pb in the sediments. In the dry season, there was significant positive correlation between TC and the metals, Ni, Sn and Vn. Similar results obtained for total heavy metal concentrations, the recoverable metals also showed consistent significant correlation in most cases. There were significant positive correlations between Mn with silt and clay particles.

Table 25 shows the Pearson's correlation coefficient between bioavailable (1 M HCl) metals extracted alongside total nitrogen, total carbon and particle sizes. The results indicated that bioavailable Al showed significant positive correlation with TN measured in the dry season as well as Clay, Silt but showed significant negative correlation with TC measured in the dry season as well. The bioavailable forms of As, Fe and Mn showed significant positive correlation with TN values for the dry season. A significant positive correlation was also recorded for Cd with Clay and Silt respectively. Bioavailable concentrations of Fe and Mn were found to be significantly positively correlated with Clay and Silt respectively while the same relationship was reported between bioavailable Pb concentrations and Silt.

Table 23: Correlations coefficient of total metals (XRF), total nitrogen and total carbon and particle size.

	TN_WS	TC_WS	TN_DS	TC_DS	CLAY	SILT	COARSE	SAND	Al	As	Cd	Cu	Fe	Mn	Pb	Sn	Zn
TN_WS	1.00																
TC_WS	0.16	1.00															
TN_DS	-0.28	0.13	1.00														
TC_DS	-0.36	0.09	-0.01	1.00													
CLAY	0.10	0.26	0.37	-0.31	1.00												
SILT	0.09	0.37	0.35	-0.32	.965**	1.00											
COARSE	.414*	0.32	-0.26	-0.34	.644**	.697**	1.00										
SAND	-0.01	-0.04	0.06	-0.13	-0.27	-0.24	-0.14	1.00									
Al	-0.35	0.21	0.11	.548**	0.10	0.04	-0.15	-0.09	1.00								
As	-0.17	0.24	.406*	0.07	.409*	0.37	0.06	0.06	.669**	1.00							
Cd	-0.21	-0.07	-0.09	0.05	-0.09	-0.04	-0.01	0.03	0.21	0.24	1.00						
Cu	-0.23	0.07	0.06	0.08	0.08	0.06	-0.06	-0.06	.593**	.808**	.290*	1.00					
Fe	-0.30	0.16	0.07	0.18	.391*	0.33	0.14	-0.15	.655**	.467**	0.10	.567**	1.00				
Mn	0.04	0.12	0.22	-.408*	.531**	.535**	0.32	-0.17	0.00	0.05	-0.16	0.11	.660**	1.00			
Pb	-0.18	0.21	.412*	0.07	.400*	0.36	0.04	0.06	.651**	.997**	0.24	.796**	.416**	-0.01	1.00		
Sn	-0.16	0.03	0.13	0.11	-0.04	-0.04	-0.12	0.12	.405**	.626**	0.01	.763**	.317*	-0.01	.628**	1.00	
Zn	-0.18	0.04	0.12	0.18	0.01	0.00	-0.13	0.02	.482**	.712**	.337**	.858**	.421**	0.02	.709**	.782**	1.00

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

TN- Total Nitrogen, TC- Total Carbon, WS- Wet season and DS- Dry season.

Table 24: Correlations coefficient of recoverable metals (*Aqua regia*), total nitrogen and total carbon and particle size.

	TN_WS	TC_WS	TN_DS	TC_DS	CLAY	SILT	COARSE	SAND	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sn	V	Zn
TN_WS	1.00																			
TC_WS	0.16	1.00																		
TN_DS	-0.28	0.13	1.00																	
TC_DS	-0.36	0.09	-0.01	1.00																
CLAY	0.10	0.26	0.37	-0.31	1.00															
SILT	0.09	0.37	0.35	-0.32	.965**	1.00														
COARSE	.414*	0.32	-0.26	-0.34	.644**	.697**	1.00													
SAND	-0.01	-0.04	0.06	-0.13	-0.27	-0.24	-0.14	1.00												
Al	-0.34	0.21	0.27	0.38	0.08	0.04	-0.22	-0.10	1.00											
As	-0.24	0.27	0.21	.424*	0.11	0.06	-0.18	-0.19	.919**	1.00										
Cd	-0.06	0.27	-0.22	0.07	0.12	0.19	0.30	-0.11	0.02	0.02	1.00									
Cr	-0.25	0.24	0.08	0.18	0.11	0.12	0.03	-0.15	.527**	.515**	.341**	1.00								
Cu	-0.15	0.04	0.07	0.33	-0.06	-0.12	-0.23	-0.16	.669**	.803**	-0.22	0.17	1.00							
Fe	-0.33	.404*	0.20	0.37	0.31	0.31	0.07	-0.18	.747**	.645**	.484**	.596**	.333**	1.00						
Mn	-0.25	0.30	0.24	0.30	.416*	.414*	0.15	-0.21	0.17	0.04	0.16	0.12	-0.05	.451**	1.00					
Ni	-0.25	0.25	0.17	.398*	0.04	0.02	-0.15	-0.18	.914**	.955**	0.14	.608**	.745**	.705**	0.07	1.00				
Pb	-0.33	.493*	0.14	0.31	0.11	0.16	0.00	0.04	.607**	.536**	.412**	.520**	0.20	.683**	0.12	.594**	1.00			
Sn	-0.18	0.28	-0.07	.711**	-0.19	-0.15	-0.11	-0.06	0.04	0.14	.511**	0.17	-0.03	0.11	0.04	0.21	.448**	1.00		
V	-0.31	.463*	0.29	.414*	0.32	0.31	0.03	-0.12	.704**	.650**	.325**	.673**	0.15	.773**	0.23	.658**	.747**	.313*	1.00	
Zn	-0.27	0.36	0.16	0.34	0.07	0.10	-0.08	-0.03	.585**	.550**	.263*	.404**	.384**	.663**	0.08	.587**	.855**	.263*	.573**	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

TN- Total Nitrogen, TC- Total Carbon, WS- Wet season and DS- Dry season

Table 25: Correlations coefficient of bioavailable metals (1 M HCl), total nitrogen and total carbon and particle size.

	TN_WS	TC_WS	TN_DS	TC_DS	CLAY	SILT	COARSE	SAND	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
TN_WS	**1.00**																	
TC_WS	0.16	1.00																
TN_DS	-0.28	0.13	1.00															
TC_DS	-0.36	0.09	-0.01	1.00														
CLAY	0.10	0.26	0.37	-0.31	1.00													
SILT	0.09	0.37	0.35	-0.32	.965**	1.00												
COARSE	.414*	0.32	-0.26	-0.34	.644**	.697**	1.00											
SAND	-0.01	-0.04	0.06	-0.13	-0.27	-0.24	-0.14	1.00										
Al	-0.14	0.13	.391*	-.509**	.526**	.568**	0.27	0.01	1.00									
As	-0.15	0.35	.533**	0.06	0.35	0.38	0.04	-0.15	.565**	1.00								
Cd	-0.25	0.17	0.24	-0.22	.559**	.612**	0.31	-0.03	.727**	.472**	1.00							
Cr	0.10	-0.01	0.01	-.516**	0.15	0.17	0.17	-0.04	.527**	.300*	0.15	1.00						
Cu	-0.10	0.20	0.16	-0.24	0.19	0.30	0.12	0.02	.538**	.428**	.591**	.390**	1.00					
Fe	-0.20	0.23	.416*	-0.38	.552**	.587**	0.28	-0.08	.832**	.496**	.556**	.387**	.388**	1.00				
Mn	-0.09	0.21	.436*	-0.15	.559**	.557**	0.21	-0.21	.690**	.492**	.448**	.256*	0.19	.881**	1.00			
Ni	0.25	0.15	0.06	-.414*	0.31	0.31	0.19	0.00	.441**	0.20	0.21	.624**	.342**	.279*	.318*	1.00		
Pb	-0.22	0.18	0.16	-0.36	0.32	.426*	0.24	0.23	.472**	.298*	.754**	0.12	.724**	.345**	0.13	0.13	1.00	
Zn	-0.20	0.12	0.17	-0.11	0.10	0.17	0.01	0.22	.282*	-0.05	.561**	0.02	.528**	0.24	0.16	0.10	.579**	1.00

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

TN- Total Nitrogen, TC- Total Carbon, WS- Wet season and DS- Dry season.

5.7 Principal componentanalysis (PCA)

In this section, principal component analysis (PCA), a statistical technique designed to investigate the nature of relationship between variables would be applied to the total metal analysed for XRF, particle sizes, total carbon and total nitrogen. The same would also be repeated to recoverable metals (AR) and bioavailable metals (1 M HCl). The idea is to determine if the variables exhibit patterns of relationships with one another such that they can be broken into subsets of variables tending to be more highly related to others within the subset than to those in other subsets.

The estimated components from the PCA are used for determining the subsets of the metals while the factor scores are used for the various sites.

The factor scores grouped the sites into various subsets based on some common latent characteristics possessed by sites combined within each group. For instance, five clusters were formed for the wet season XRF data based on some latent characteristics of the sites. Two locations from LH sites where shipping (dry-docking) activities were being carried out formed a cluster, and it can therefore be inferred that the impact of those activities affect those sites in some similar measures whereas, in another group, sites characterised by oil terminal and bulk cargo shipping activities within the LH have also been grouped in a cluster. The implication is that within LH, different shipping activities have dissimilar effects on the total metal analysed based on XRF.

5.7.1 Principal component analysis of total metal (XRF), particle sizes, total carbon and total nitrogen in DS-1, WS and DS-2

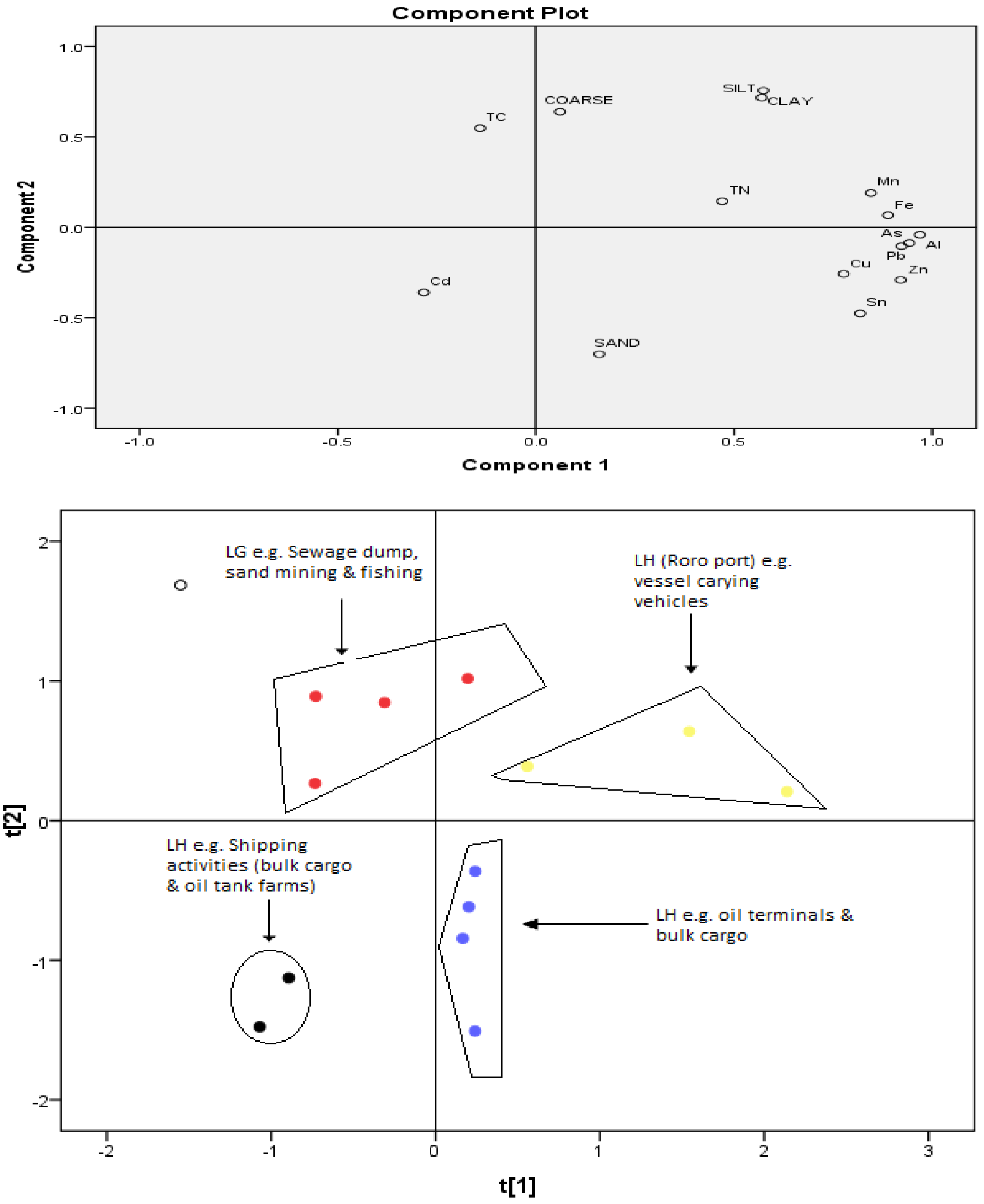


Figure 47: PCA loadings (top) and scores plots (bottom) of total metals analysed in sediment, particle sizes, total nitrogen and total carbon during the dry season-1 (2013).

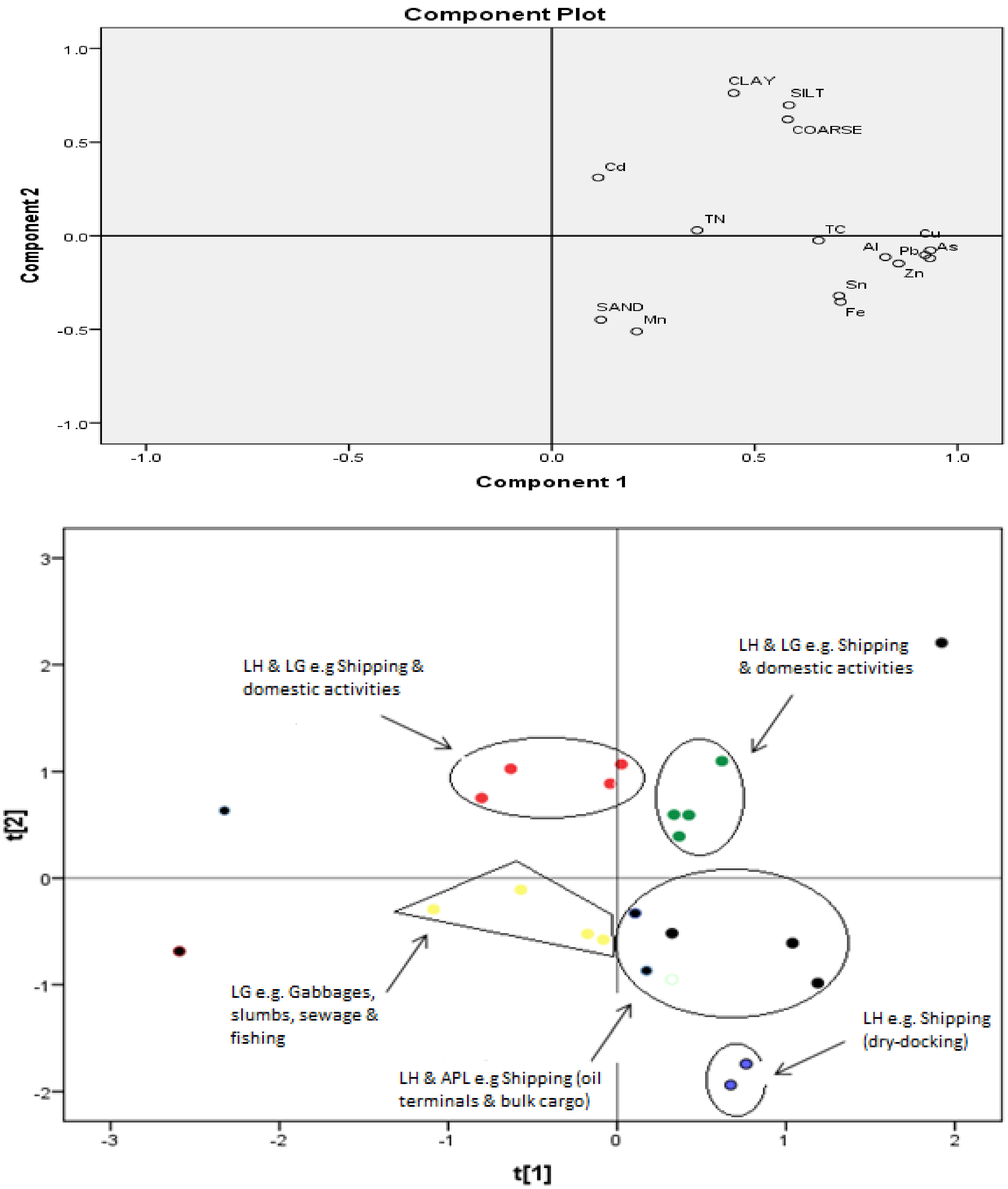
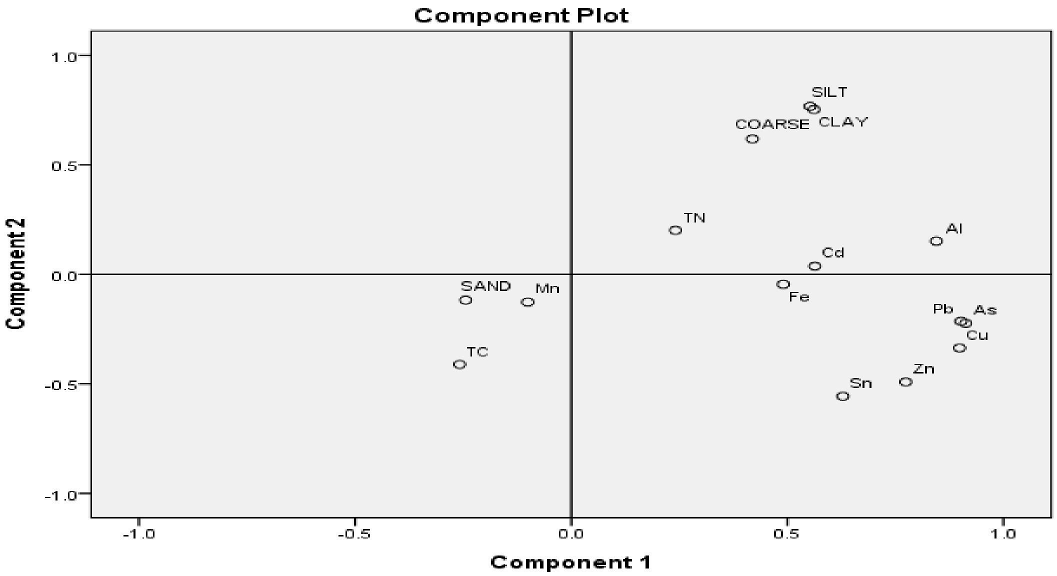


Figure 48: PCA loadings (top) and scores plots (bottom) of total metals analysed in sediment, particle sizes, total nitrogen and total carbon during the wet season (2013).



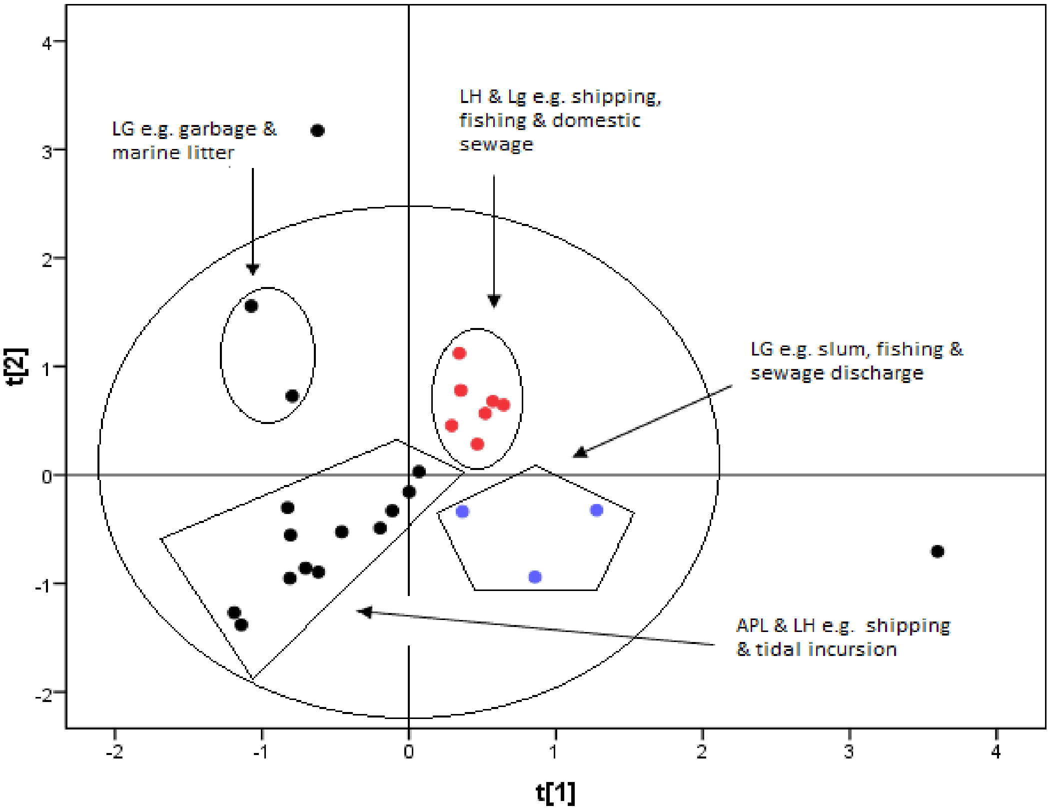


Figure 49: PCA loadings (top) and scores plots (bottom) of total metals analysed in sediment, particle sizes, total nitrogen and total carbon during the dry season-2(2014).

The PCA of the total metals analysed for XRF, particle sizes, total carbon (TC) and total nitrogen (TN) showed that clustered correlation of TN with Mn, and Fe with coarse sand, silt and clay in component 1, while As, Pb, Cu, Zn, Sn and Al were correlated with sand particles at component 2 during the Dry Season-1 of 2013 as shown in Figure 47. The factor scores that present the distinctiveness in the locations, grouped them into four distincti clusters based on similarities in total metal concentrations. The first cluster is composed of four sites in the LG characterized by sewage disposal, sand mining and artisanal fishing activities. The second cluster is composed of three sites within the LH where vessel offload of vehicles at RORo jetties occurs. The LH also formed two more clusters including one with 4 sites where bulk cargo loading onto terminals occurred and another characterized by cargo offloading and Petroleum products tank farm.

Figure 48 shows the PCA plot with correlation between Cd, total nitrogen with clay, silt, coarse sand particles at component 1, while at component 2 the PCA of the total metals - As, Cu, Sn, Zn, Fe, Pb, Mn and Al were correlated with sand particles during the wet season 2013 (WS). The plot of the factor scores is presented in the lower part of the Figure 45, It includes five distinct clusters with respect to total metal concentrations. The first included areas within the LG and LH characterized by shipping activities and domestic activities in coastal settlements. The scores plot also contained a second cluster with sites common to LH and LG with similar trend of total metal concentrations characterized by shipping and domestic activities. A third cluster contained 3 sites within the LG characterized by coastal dumpsites, municipal sewage disposal and artesinal fishing activities. The fourth and fifth clusters contained sites within the LH in which, one cluster there were six sites with similar total metal concentrations characterized by coastal Pteroleum products discharge tank farms as well as bulk cargo offload terminals. The other had 2 sites where shipping and dry-docking activities occur.

Figure 49 shows the PCA with observed correlation cluster between TN, Cd, and Al with coarse sand, silt and clay in component 1, while TC and Mn were correlated with sand particles in component 2 during the dry season - 2 of 2014 (DS-2). The lower part of the figure displays the plot of the factor scores showing four distinct clusters. The largest one contained 12 sites dis tributed across the APL and LH and were characterized by shipping activities and tidal incursions.

This was followed by a second cluster with seven sites spanning the LH and LG and characterized by shipping activities, fishing and discharge of domestic sewage. The third has 3 sites in the LG where coastal slums, fishing activities and municipal sewage discharge occur. Lastly, the fourth cluster was characterized by coastal gabbage dumps and litters in the LG. Appendices for the PCA total variance of total metals analysed using XRF are presented as Appendix 19a, Appendix 19b and Appendix 19c.

5.7.2 Principal component analysis of recoverable metal (*Aqua regia*), particle sizes, total carbon and total nitrogen in DS-1, WS and DS-2

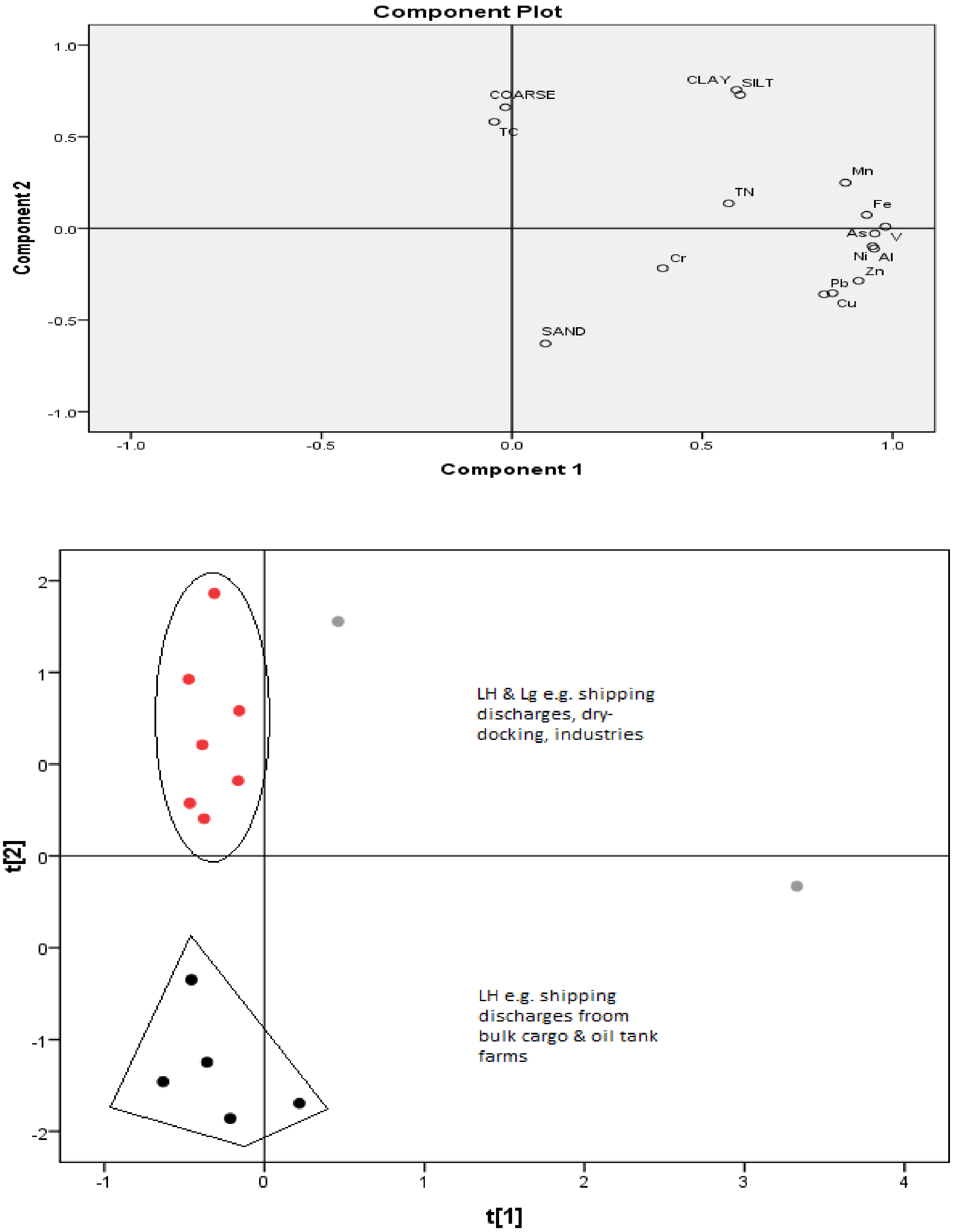


Figure 50: PCA loadings (top) and scores plots (bottom) of recoverable metals extracted in sediment, particle sizes, total nitrogen and total carbon during the dry season-1- (2013).

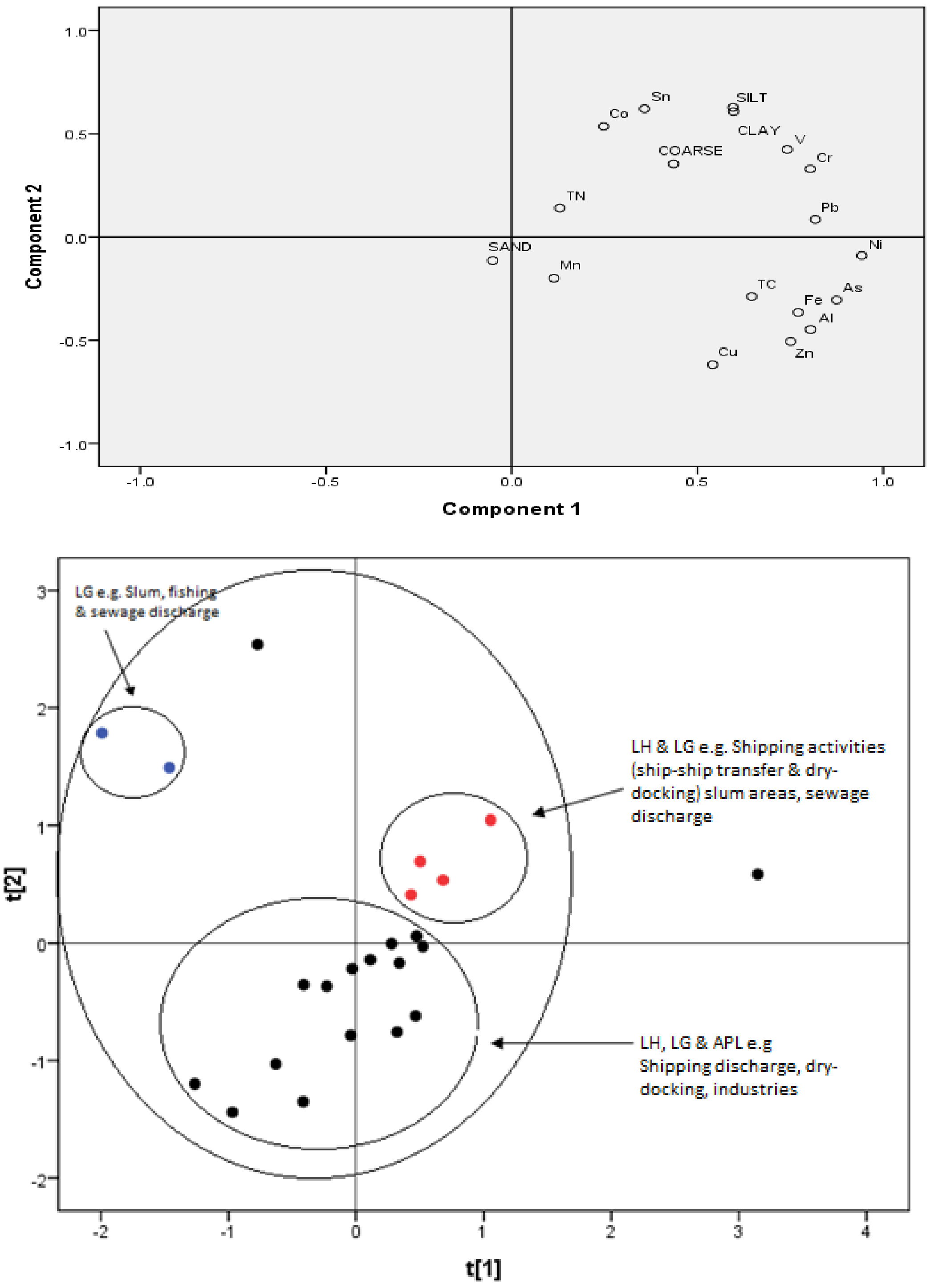


Figure 51: PCA loadings (top) and scores plots (bottom) of recoverable metals extracted in sediment, particle sizes, total nitrogen and total carbon during the wet season – 2013.

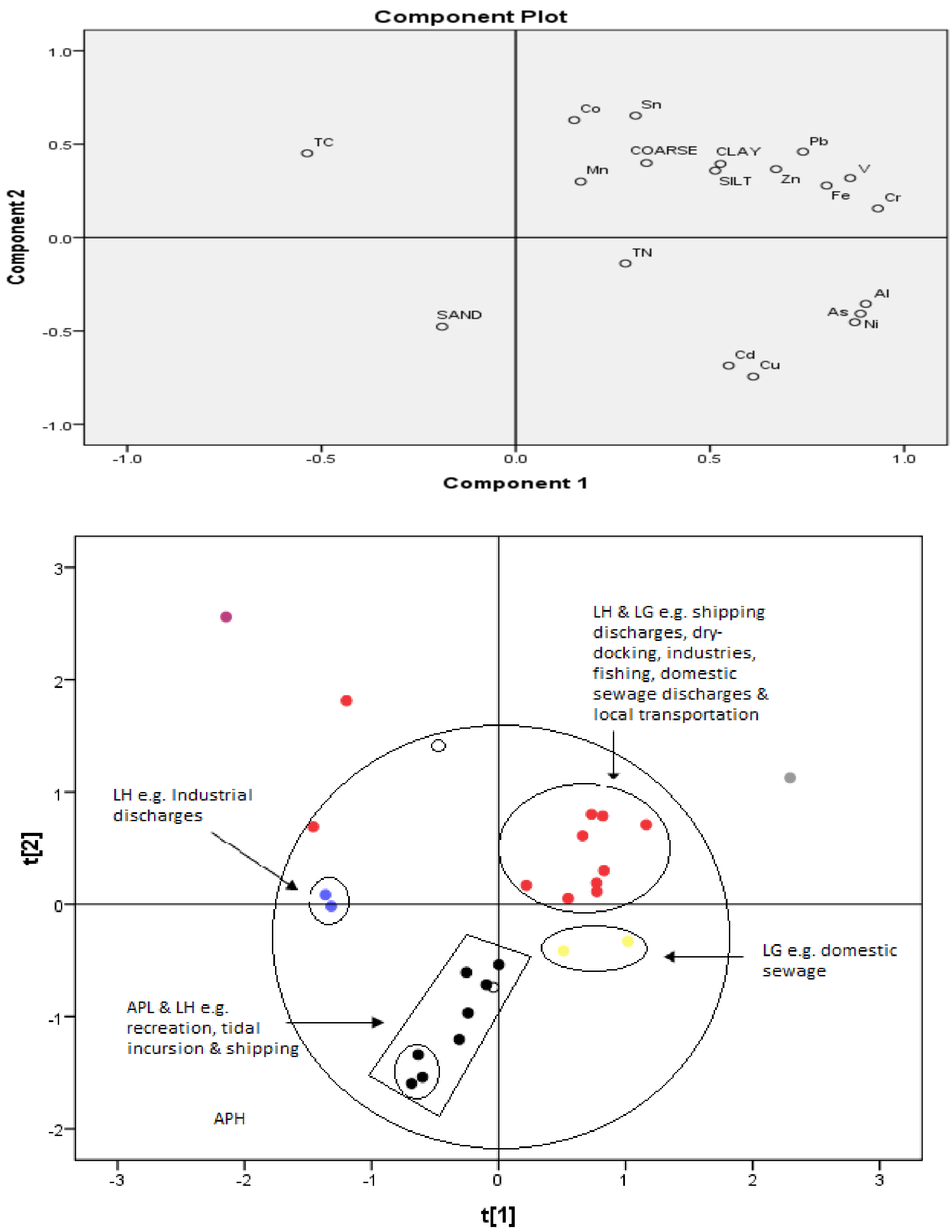


Figure 52: PCA loadings (top) and scores plots (bottom) of recoverable metals extracted in sediment, particle sizes, total nitrogen and total carbon during the dry season-2 (2014).

The PCA of the recoverable metals, Mn, Fe, (TN) and TC showed that clustered correlation with coarse sand, silt and clay in component 1, while As, Pb, Cu, Zn, Ni, and Al were correlated with sand particles at component 2 during the dry season 1 of 2013 (DS-1) as shown in Figure 50. The factor scores plot show two distinct clusters with similar trends in recoverable heavy metal concentrations. The first cluster had seven sites spread within the LH and LG characterised by shipping discharge, dry-docking while the second had five sites characterized by shipping activities, bulk cargo offload and Petroleum products tank farms.

Figure 51. shows the PCA plot with correlation between recoverable Sn, Co, Cr, Pb, V, TN with clay, silt, coarse sand particles at component 1, while at component 2 the PCA of the metals – As, Cu, Zn, Fe, Ni, Mn and Al were correlated with sand particles during the wet season 2013 (WS). The factor scores plot showed three clusters within APL, LH and LG. In the largest cluster, there were 16 sites whose characteristic activities were shipping discharges, dry docking and various coastal industrial activities at the three sampled lagoons. The second had four sites characterized by ship-to-ship transfer of cargo, dry-docking, coastal slumps and municipal sewage discharges at the LH and LG. The third cluster contained sites within the LG characterized by coastal slumps, fishing activities and discharges of municipal sewage.

Figure 52. shows the PCA observed correlation cluster between recoverable concentrations of the metals, Co, Sn, Mn, Cr, Pb, V and Fe with coarse sand, silt and clay in component 1, while TN Al, As, Ni, Cd, and Cu were correlated with sand particles in component 2 during the dry season of 2014 (DS-2). Results of factor scores plot for the dry season indicated four clusters and one sub-cluster. The first cluster had only two sites within the LH where industrial discharges occur. The second comprised eight sites in the LH and LG characterized by vessel discxharges, dry docking, coastal industrial activities, artisanal fishing, discharge of domestic sewage as well as passanger transport in motorized boats. The third cluster had 2 sites within the LG where domestic sewage discharges occur. The fourth cluster also included a sub-cluster. Within the main cluster there are eight sites with similar recoverable metal concentrations within the APL and LH. The activities within the area include recreational and shipping activities as well as tidal

incursion of sea water. In the sub-cluster, there are three sites all within the APL where recreational activities are commonplace.

The PCA analysed showing the percentage variance and Eigen values of recoverable metals for DS-1-2013, WS-2013 and DS-2-2014 are presented in Appendix 20a, A ppendix 20b and Appendix 20c.

5.7.3 Principal component analysis of bioavailable metal (1 M HCl), particle sizes, total carbon and total nitrogen in DS-1, WS and DS-2

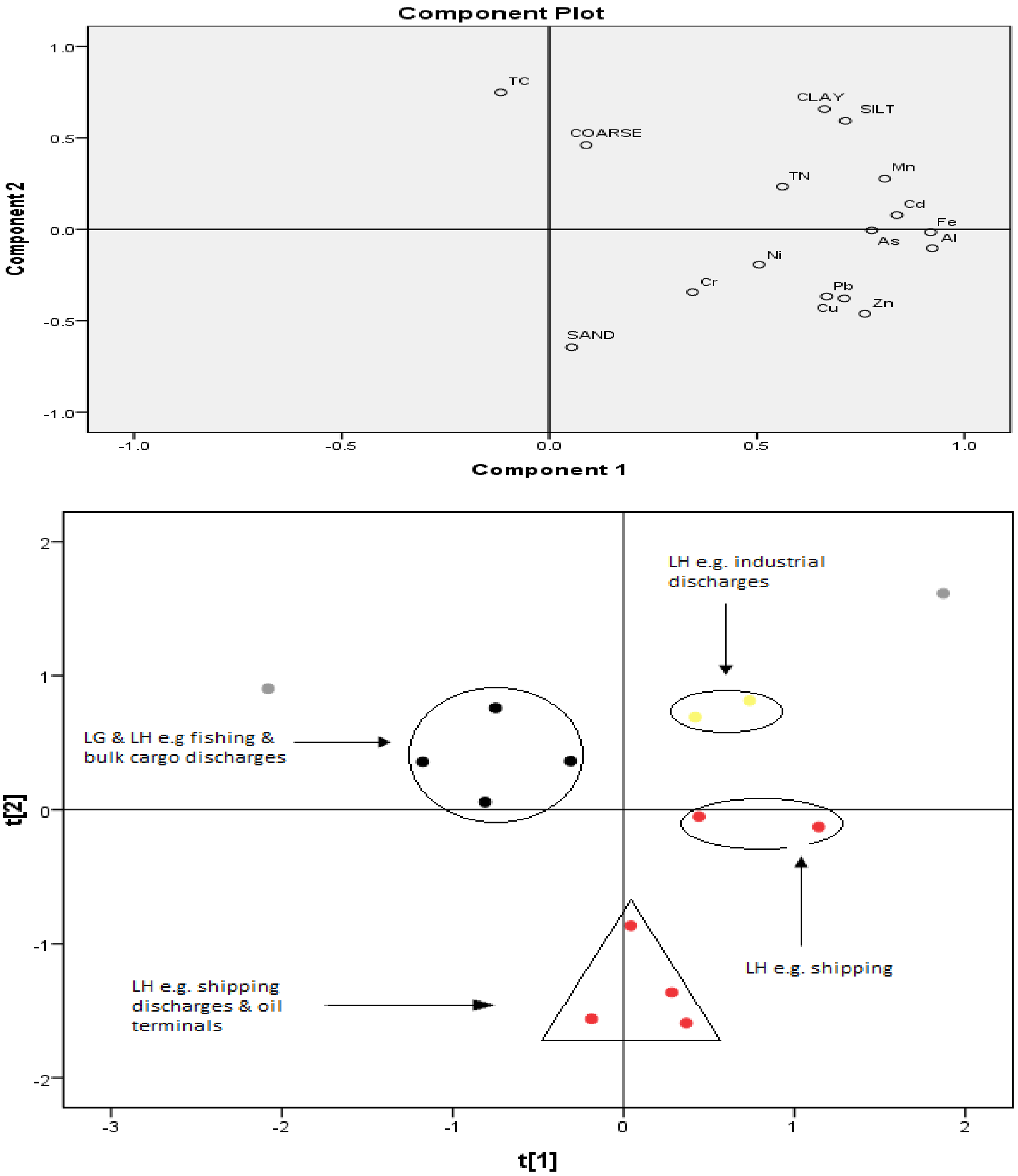
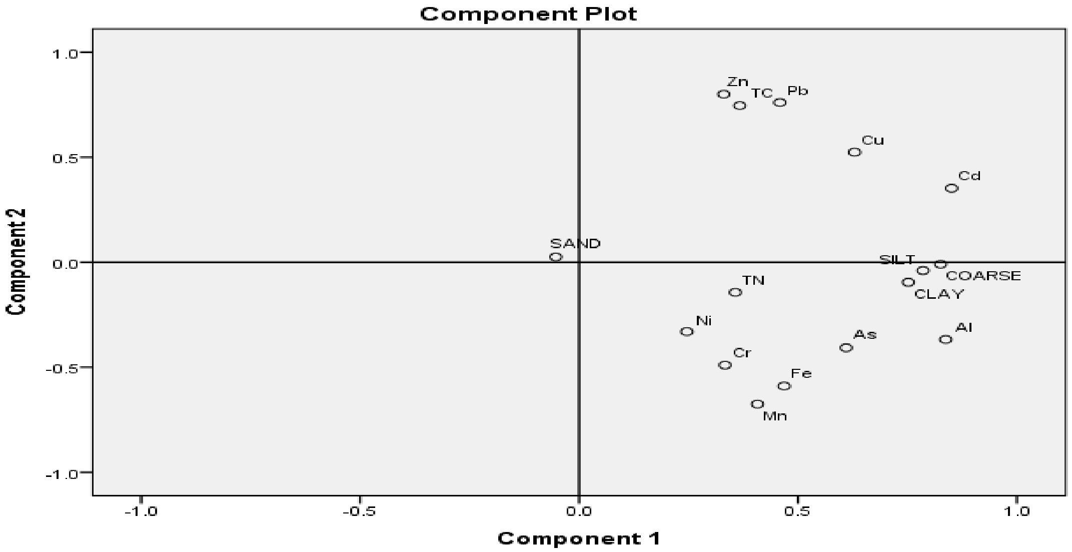


Figure 53: PCA loadings (top) and scores plots (bottom) of bioavailable metals extracted in sediment with particle sizes, total nitrogen and total carbon during the dry season-1(2013).



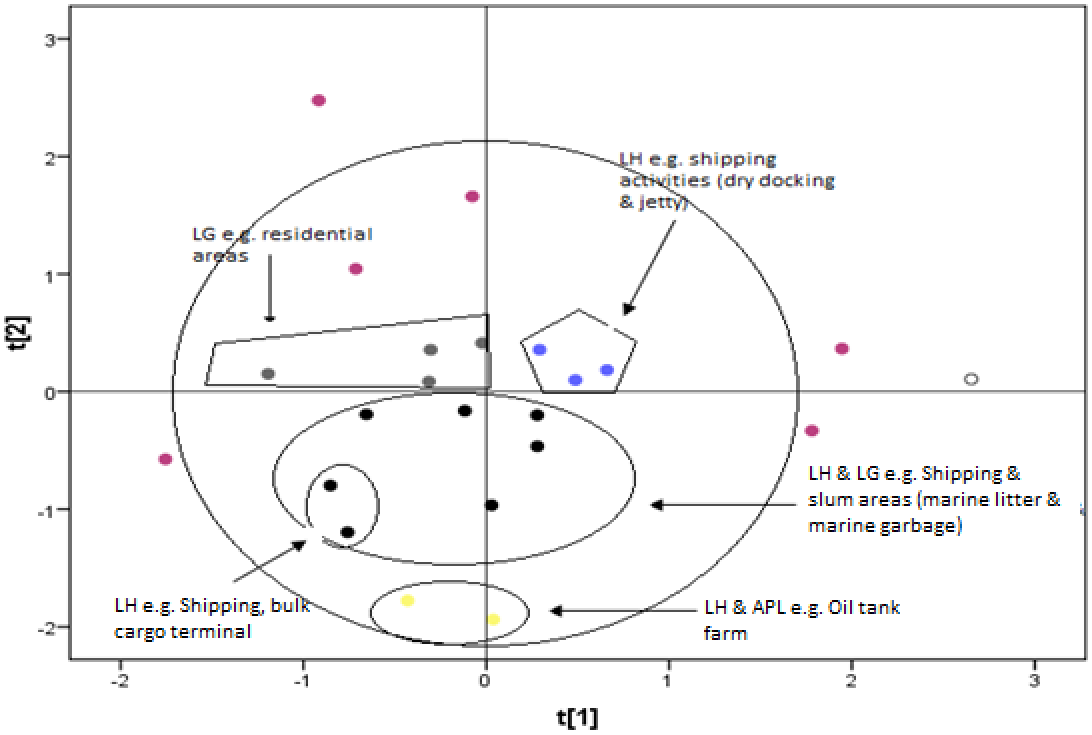


Figure 54: PCA loadings (top) and scores plots (bottom) of bioavailable metals extracted in sediment, particle sizes, total nitrogen and total carbon during the wet season (2013).

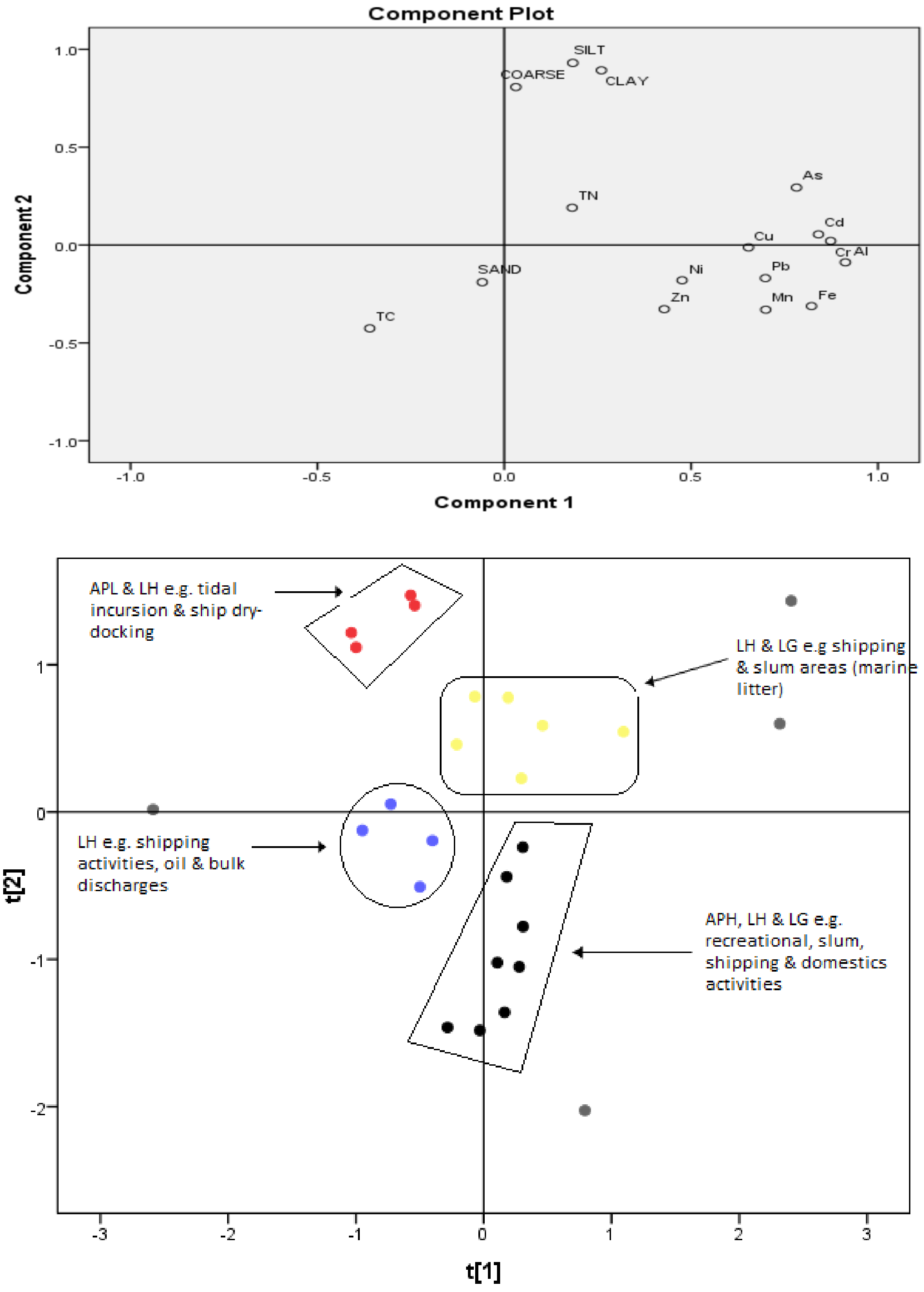


Figure 55: PCA loadings (top) and scores plots (bottom) of bioavailable metals extracted in sediment, particle sizes, total nitrogen and total carbon during the dry season - 2 (2014).

Figure 53 shows the PCA of the bioavailable metals using 1 M HCl - Mn, Cd, Fe, TN and TC showed that clustered correlation with coarse sand, silt and clay in component 1, while As, Pb, Cu, Zn, Ni, and Al were correlated with sand particles at component 2 during the dry season-1 of 2013 (DS-1). The plots of the factor scores showed four distinct clusters in the dry season-1 (2013) analysed sediments with respect to the bioavailable fractions of the metals analysed. The first contain four sites within the LH and LG where fishing activities and bulk cargo offload activities were recorded. The second cluster contains two sites within the LH characterized by industrial discharges from coastal industries located within the port complex. The third cluster was also within the LH with ship berthing and cargo offload being the dominant activities. The fourth cluster contains four sites characterized by shipping activities, discharges from cargo ships and coastal Petroleum products tank farms within the LH.

Figure 54 shows the PCA plot with correlation between bioavialable Cu, Cd, Pb, Zn, TC with sand particles at component 1, while at component 2 the metals - As, Cr, Fe, Ni, Mn, Al and TN were correlated with clay, silt, coarse sand particles during the wet season 2013 (WS). The factor scores formed five clusters based on the various activities in the lagoon system. The first cluster contained four sampling sites with residential areas within the LG coastline. The second cluster contained 3 sites where shipping activities such as dry docking, passanger boat traffic within the LH. The third cluster contained eight sites within LH and LG characterized by shipping activities, coastal slums and dumping of gabbage. This cluster also had a sub-cluster of the LH where shipping activities and bulk cargo terminals were recorded. The fifth cluster had two sites characterized by Petroluem products tank farm within LH and APL.

Figure 55 shows the PCA plot with correlation cluster between metals, As, Cd, Cu and TN with coarse sand, silt and clay in component 1, while, Al, Cr, Pb, Mn, Ni, Zn were correlated with sand particles in component 2 during the dry season of 2014 (DS-2). The factor scores again showed four distinct clusters. The first was characterized by tidail incursion and dry docking in four sites of the APL and LH. The second cluster had six sites within the LH and LG where shipping activities, coastal slums, dumpsites and marine litters are the dominant anthropogenic actiuvities influencing the area. The third cluster had four sites in the LH where the prevailing activities include shipping activities, Petroleum products discharge and cargo offloading. The fourth cluster contained eigth sites within the APL, LH and LG with prevailing activities such as recreation, coastal slums, ship berthing and cargo offload.

The PCA table of percentage variance and the Eigen values for bioavailable metals analysed for DS-1-2013, WS-2013 and DS-2-2014 are presented in Appendix 21a, Appendix 21b and Appendix 21c.

5.8 Cluster analysis of similarities of metals

5.8.1 Analysis of similarities (ANOSM) of total metals analysed with XRF

Cluster analysis was performed to show the intra-relationship amongst variations in parameters from different sampling sites in Lagos Harbour, Lagos and Apese Lagoons which are grouped into clusters of similar water quality features. Cluster analysis of the metals using XRF in sediment revealed ten (10) principal groups of sites of both dry and wet seasons as shown in Figure 56. The clusters were as follows; group 1- LG 25, LG 26, LG 27, group 2- LH 20 and APL 30, group 3- LH 10, LH 12, LG 23 and APL 31, group 4- LH 14, LH 19 and LH 17, group 5- LH 11, LH 16; group 6- LH 18, group 7- LH 13, LH 15 and LH 3, group 8- LG 24; group 9- LH 5 and APL 29; group 10- APL 28 and LH 1; group 11- LH 4, LH 7, LG 22, LH 6, LH 9 and LH 2, group 12- 8 and LG 21.

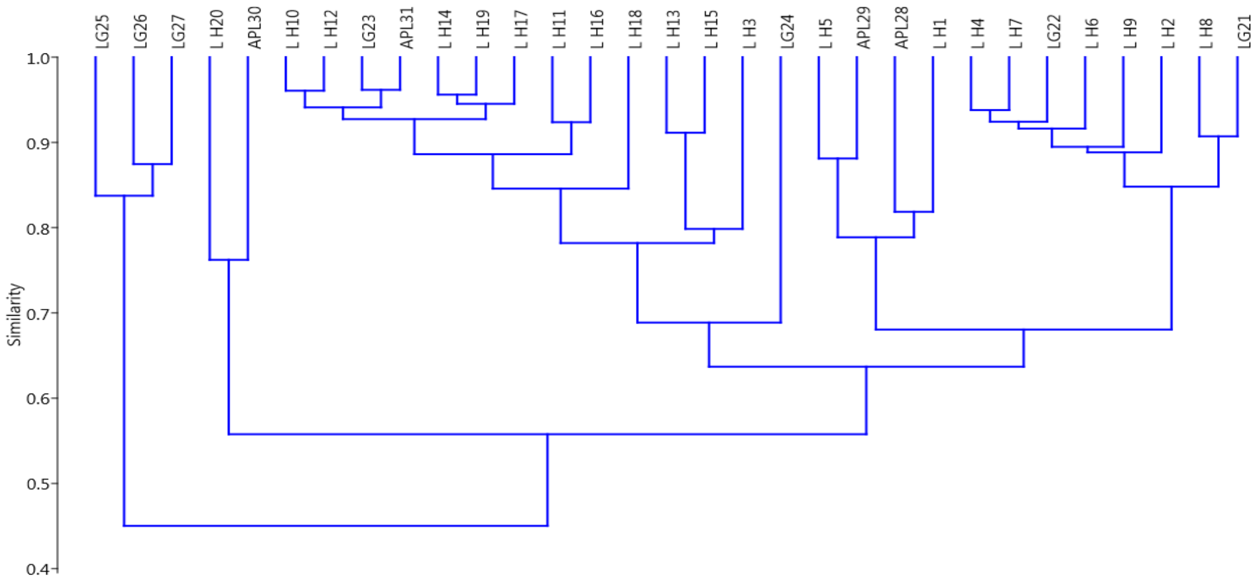


Figure 56: Cluster dendrogram of total metals in sediment using XRF from Lagos Harbour, Lagos and Apese Lagoons.

The respective clusters mostly share ecological or anthropogenic characteristics which reflects on the measured metal concentrations. Others however, have nothing in common other than a similar trend in heavy metal concentrations. For instance, the first cluster- LG 25 to LG 27 are areas characterized by Petroleum products tank farm clusters in the LG. The second cluster on the other hand contains stations which on the one hand is characterized by recreational activities and residential area development in the APL and on the other hand one characterized by Power plants, municipal sewage discharge and land reclamation. The forth cluster, i.e LH 14, LH 17 and LH 19 is composed of areas where rew materials cargo are discharged, municipal sewage and general waste discharge, fishing as well as domestic water supply, thus implying that their only unifying factor is geographical proximity.

5.8.2 Analysis of similarities (ANOSM) of recoverable metals extracted with *Aqua regia*

Cluster analysis of the metals using *Aqua regia* in sediment revealed ten (10) principal groups of sites of both dry and wet seasons as presented in Figure 56. The clusters include; group 1- APL 25 and APL 26, group 2- LG 20, group 3- LH 13, LH 14, LH 15 and LG 19, group 4 – LG 21, LG 22, LG 23, group 5- LH16, APL 24, group 6- LH 10, LH 11, LH 12, group 7- LH 7, LH 8, and LH 9, group 8 – LH 6, LG 18, LG 17, group 9- LH 2, LH 4 and LH 1 and group 10- LH 5 and LH 3.

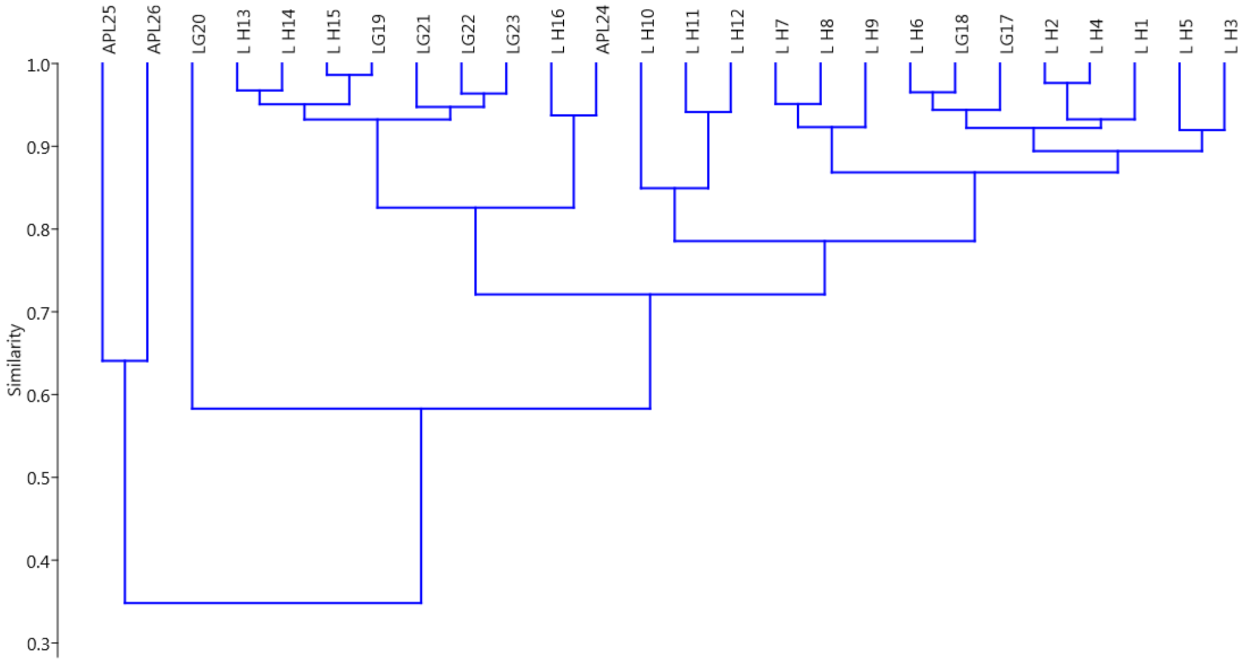


Figure 57: Cluster dendrogram of extractable the metals in sediment using *Aqua regia* from Lagos Harbour, Lagos and Apese Lagoons.

The clusters from the Bray-Curtis similarity index of recoverable heavy metals in the Lagoon system presented in Figure 57 also indicated that relationships based on mostly geographical proximity and similarity of activities. Specifically, the first group, i.e APL 25 and 26 consists of locations that are clustered in Apese Lagoon characterized by mostly recreational activities and proposed residential estate development. The second was a singular location of LG 20 which is characterized by recreational and aquaculture activities. The fourth cluster (LG 21, LG 22, LG 23) was based on geographical proximity as well because of the varied activities occuring in the respective locations including oyster and fish farming, sand mining, coastal residential area, location of electricity power plant (distribution sub-station), discharge point for municipal sewage as well as land reclamation activities. The eight cluster (LH 6, LG17 and LG 18), although characterized by various types of waste discharge activities including ballast water, sewage and leachates from coastal sawmill and dumpsites, are unified by the common fact that these wastes from the sources are mostly organic.

5.8.3 Analysis of similarities (ANOSM) of bioavailable metals extracted with 1 M HCl

Cluster analysis of the metals using 1 M HCl in sediment revealed nine (9) principal groups of sites of both dry and wet seasons as presented in Figure 58. The clusters are as follows; group 1- LH 13, LG 22 and LH 16; group 2 – LH 15 and LG 19; group 3- LG 23; group 4 - LH 14 and LG 20; group 5 - APL 24; group 6 – LG 21; group 7 – APL 25 and APL 26; group 8 – LH 8, LH 9, LH 10 and LH 12; group 9 – LH 1, LH 2, LH 3, LH 4, LH 5, LH 6, LH 7, LH 11, LG 17 and LG 18.

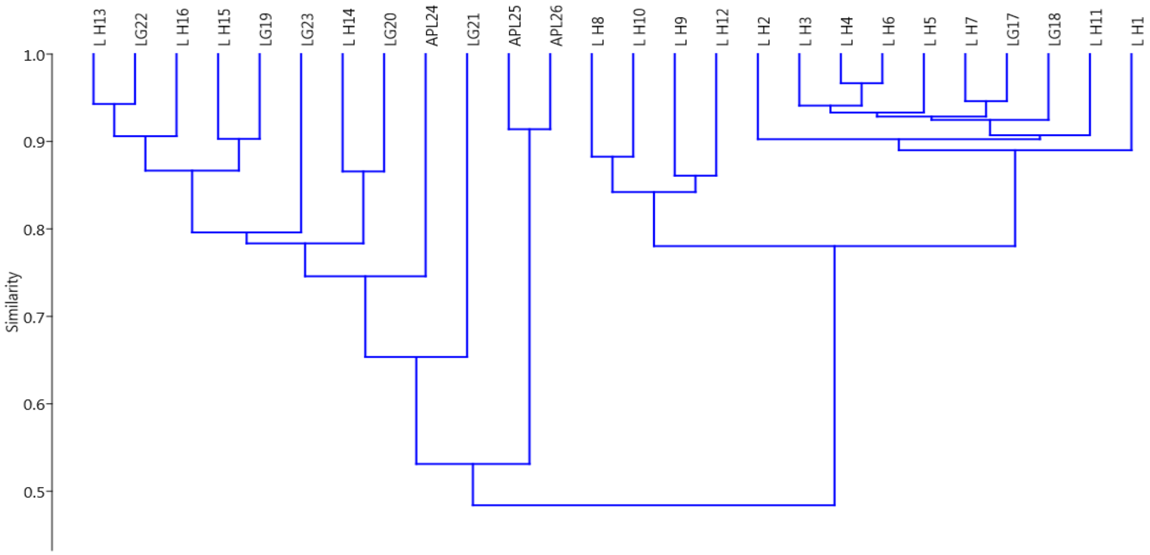


Figure 58: Cluster dendrogram of bioavailable metals in sediment using 1 M HCl from Lagos Harbour, Lagos and Apese Lagoons.

The first cluster (LH 13, LH 16 and LG 22) with similar bioavailable metal contractions were characterized by divergent activities ranging from residential to large bulk cargo discharge and Oil tank farms and discharge area. Whereas LH 13 and 16 had a unifying factor in their geographical proximity and discharge activity, LG 22 on the surface had nothing in common with them. However, the eight cluster (LH 8, LH 9, LH 10 and LH 12) share both geographical proximity and similarity in activities with the common denominator being cargo discharge and apparently ship berthing with associated ballast water discharge. The ninth cluster is rather large and consisted of bioavailable metal concentrations in areas mostly in the LH and some in the LG (i.e LH 1, LH 2, LH 3, LH 4, LH 5, LH 6, LH 7, LH 11, LG 17 and LH 1G) with the unifyng factor being organic wastes discharged at terminals via ship ballast water (LH 1 to LH 11) and those municipal sewage discharges and leachates from coastal sawmill and solid waste dumps (LG 17 and LH 1G).

5.9 Heavy metal contamination factor

This was determined in sample to show the levels of contamination of the sediment samples with total (XRF), recoverable (AR) and bioavailable (1M HCl) metals in the Lagos Harbour and Lagos Lagoon (Figure 59 a-c). The detailed tables showing the respective C*f* figures calculated for the LH, LG and APL are presented in Appendix 24b.

5.9.1 Heavy metal contamination factor (DS-1, 2014)

The contamination level of the elements across each of the stations in relation to their observed activities in the dry season 1 is presented in the Table 26. It can be observed that the level of contamination level varies from low contamination to considerable contamination. Sites where contaminations are high can be easily noticed (Legend is beneath each table). In the Lagos Harbour, some sites with activities such as Oil tank farm discharge and Bulk Cargo discharge have shown considerable to moderate contamination. Meanwhile, sites in the urbanised part of the lagoon have equally shown low to moderate contamination. The contamination levels are not only related to the activities but can possibly be due to the handling of these services in such a way that spillage or other means of discharge into the water bodies can be avoided.

Table 26: Contamination level of the elements at each site in relation to observed activities using the three methods (DS-1, 2013).

Location		XRF					*Aqua regia*	1 M HCl			
LH	Station	As	Cu	Mn	Pb	Zn	As	Cd	Ni	Zn	**Observed activities**
1	ATC	1.23	1.16	1.35	1	2.38	1.45	1.33	5.15	0.88	Oil tank farms discharge area
2	OBT	0.77	0.93	0.46	0.5	2.14	0.62	1.02	0.42	1.13	Oil tank farms discharge area
3	GMD	0.54	0.82	0.4	0.35	1.66	0.96	1.01	0.81	1	Vessel discharge area
4	JDM	0.85	0.98	1.15	0.6	1.55	1	1.08	0.19	0.58	Bulk cargo discharge area
5	TCN6	0.38	0.84	0.91	0.1	1.57	0.77	0.62	0.15	0.49	Bulk cargo
6	SFX	0.85	0.78	0.8	0.6	1.24	1.24	1.29	0.17	0.57	Bulk cargo
7	GRV	0.08	0.67	0.55	0	0.56	0.3	1.74	0.1	0.78	Bulk cargo terminals
8	APM	0	0.51	0.35	0	0.21	0.08	0.13	0.09	0.09	Container bulk terminal
9	BVS	0	0.47	0.28	0	0.03	0.04	0.04	0.04	0.01	Bulk cargo terminal
10	ENL	0.08	0.69	0.76	0	0.71	0.04	0.42	0.04	0.23	Bulk cargo terminal
11	FM	0	0.98	0.51	0	0.74	0.03	0.35	0.16	0.38	Flour mills raw materials terminal
12	NIPCO	0	0.69	0.15	0	0.01	0	0.13	0.02	0.14	Oil tank farm and discharge areas
LG											
13	UGH	0.46	0.98	0.84	0.1	2.06	0.59	1.58	0.08	0.7	Domestic wastes discharge areas
14	UHR	0.46	1.04	1.24	0.1	2.15	0.86	2.04	0.09	0.92	Oyster, recreational &sand mining

🟥 Very high contamination ⬛ Considerable contamination 🟨 Moderate contamination ⬜ Low contamination

5.9.2 Heavy metal contamination factor (WS, 2013)

In the wet season, the Lagos Harbour have shown low to considerable contamination especially in sites with bulk cargo and oil tank farms.

However, very high contaminations of Cu can be observed in site within the urbanised Lagos Lagoon. Cd have shown considerable contamination level across some sites that handles bulk cargo in the harbour area and domestic discharge in the urbanised part of the lagoon (Table 27).

5.9.3 Heavy metal contamination factor (DS-2)

In the second dry season very, high contamination levels can be observed in Cd, Cu and Zn. Some sites with activities such as Oil tank farms and Bulk Cargo discharges have shown moderate to very high contamination level within the Lagos Harbour. Similarly, the urbanised part of the Lagos Lagoon has also shown varying degree of contamination levels. Some hotspots (OWSK and UGH) have shown moderate to very high contamination levels in most of the elements. Apese Lagoon sites (control zone) which have minimal anthropogenic activities have shown low contamination level. It can be deduced that activities and possibly, the handling of such activities pay a prominent role in the contamination level within the Lagos Harbour. Meanwhile, the urbanised region has shown contamination levels that shows that indiscriminate disposal of waste may find its way into water bodies though run-offs and may pose contamination threat to water bodies (Table 28).

Table 27: Contamination level of the elements at each site in relation to observed activities using the three methods (WS- 2013).

		XRF						***Aqua regia***		**1 M HCl**			
LH	**Site Names**	As	Cd	Cu	Mn	Pb	Zn	As	Cu	Cd	Ni	Pb	**Observed activities**
1	ATC	0.77	0	0.89	0.5	0.5	1.46	1.16	0.2	0.69	0.04	0.56	Oil tank farms discharge area
2	STFM	1.31	0	0.93	1.34	1.15	1.53	0.68	0.15	0.95	0.05	0.69	Bulk cargo discharge area
3	ND	0	3.33	0.87	0.38	0	0.82	0.34	0.14	0.76	0.04	0.66	Bulk cargo discharge area
4	ORS	0.77	0	0.98	0.46	0.55	2.09	0.49	0.2	0.8	0.03	0.52	Oil tank farms discharge area
5	IBJ	0	0	0.67	0.22	0	0.67	0.32	0.18	0.69	0.56	1.07	Oil tank farms discharge area
6	GMD	0.92	0	1.02	0.98	0.65	1.6	1.34	0.4	0.91	0.09	0.51	Vessel discharge area
7	SIFAX	0.77	0	1.18	0.88	0.55	1.6	0.47	0.11	1.19	0.14	0.68	Bulk cargo
8	T-6	1.15	3.33	1.09	1.18	0.95	2.2	0.7	0.2	1.16	1.22	0.53	Bulk cargo
9	FJ	1.15	0	1.02	1.28	1	2.46	0.72	0.16	1.6	0.11	0.61	Oil tank farms discharge area
10	JSD	0.62	0	0.76	0.92	0.35	0.99	0.64	0.11	0.59	1.09	0.35	Bulk cargo terminals
11	APM	0.38	0	0.69	0.82	0.1	0.87	0.3	0.06	0.57	0.09	0.28	Container bulk terminal
12	ENL	0.15	0	0.67	0.62	0	0.57	0.14	0.07	0.32	0.04	0.22	Bulk cargo terminal
13	FM	0	0	0.42	0.15	0	0.03	0.48	0.1	0.85	0.04	0.43	Flour mills raw materials terminal
14	FM-AP	1	0	0.91	1.33	0.75	1.49	0.27	0.08	1.16	0.05	0.56	Bulk cargo terminal
15	NPA-DY	0	0	0.44	0.22	0	0.14	0.8	0.4	0.62	0.06	0.86	Dry docking & ship repair
16	NIPC	0	0	0.62	0.44	0	0.52	0.2	0.14	0.3	0.02	0.34	Oil tank farm and discharge areas
LG													
17	IDD	0	0	0.6	0.73	0	0.73	0.43	0.25	0.52	0.04	0.56	Public sewage & dump sites
18	OKB	0.69	0	0.93	0.67	0.45	1.87	0.98	0.29	0.87	0.04	0.59	Saw mills waste & domestic wastes
19	MKK	0.08	0	0.73	0.95	0	1.28	0.75	0.36	1.31	0.05	1.18	Fish farming and domestic trading
20	UWF	0	0	0.62	2.97	0	1.09	0.4	6.58	0.17	0.05	0.18	Recreational & aquaculture
21	OWS	0	0	0.73	0.72	0	1.07	2	14.59	1.21	0.04	0.79	Oil tank farms discharge area
22	UHR	0.38	0	0.93	1.9	0	1.57	2.4	17.95	0.86	0.05	0.67	Oyster, recreational &sand mining
23	UGH	1.46	3.33	1.27	0.59	1.4	5.48	2.33	14.16	1.53	0.08	1.29	Domestic wastes discharge areas
APL													
24	APS-LAG	0	0	0.56	0.14	0	0.66	1.23	7.23	0.22	0.02	0.4	Recreational & proposed residential development

🟥 Very high contamination ▨ Considerable contamination 🟨 Moderate contamination ⬜ Low contamination

Table 28: Contamination level of the elements at each site in relation to observed activities using the three methods (DS-2, 2014).

		XRF					*Aqua regia*						1 M HCl			
LH		As	Cd	Cu	Pb	Zn	As	Cd	Cu	Mn	Pb	Zn	Cd	Pb	Zn	**Observed activities**
1	ATC	0.77	0	0.93	0.5	1.61	3.46	0	14.31	0.17	0.38	0.41	0.58	0.42	0.27	Oil tank farms discharge area
2	SFM	0.23	0	0.78	0	0.79	2.12	0.43	8.64	0.26	0.3	0.3	0.46	0.32	0.23	Bulk cargo discharge area
3	JSD	1	0	1.76	0.85	8	3.47	1.58	14.67	0.3	0.91	1.88	0.81	0.63	1.88	Bulk cargo discharge area
4	ORD	0	0	0.64	0	0.6	1.98	0.72	8.52	0.09	0.41	0.44	0.43	0.4	0.38	Oil tank farms discharge area
5	IBJ	0.92	3.33	1.11	0.65	2.39	4.96	1.65	20	0.24	1.09	0.96	0.92	0.73	0.62	Oil tank farms discharge area
6	GMD	0.77	3.33	1	0.5	1.77	1.53	0	0.41	0.31	0.63	0.66	0.83	0.55	0.48	Vessel discharge area
7	SIFX	1	0	0.96	0.85	1.74	2	0	0.48	0.64	0.8	0.8	0.99	0.55	0.38	Bulk cargo
8	T6	0.92	0	0.87	0.75	1.46	2.06	0	0.53	0.72	0.89	0.91	1.05	0.54	0.46	Bulk cargo
9	FJ	0.46	0	0.82	0.1	1.08	1.93	0	0.98	0.41	1.1	1.04	0.75	0.69	0.56	Oil tank farms discharge area
10	JSD	0	0	0.53	0	0.71	0.82	0	0.17	0.21	0.31	0.32	0.4	0.24	0.22	Bulk cargo terminals
11	APM	0	0	0.56	0	0.42	0.2	0	0	0.17	0.22	0.17	0.16	0.12	0.13	Container bulk terminal
12	BN	0.31	0	0.76	0	0.82	0.39	0	0.05	0.22	0.31	0.24	0.26	0.27	0.32	Bulk cargo terminal
13	ENL	0	0	0.69	0	0.58	0.5	0	0.08	0.26	0.38	0.33	0.69	0.38	0.26	Bulk cargo terminal
14	FM	0.46	0	0.84	0.2	0.91	0.29	0	0.09	0.16	0.5	0.3	0.33	0.54	0.65	Flour mills raw materials terminal
15	NPA-DY	0.92	0	0.93	0.65	2.24	0.98	0	0.34	0.39	1.05	0.77	0.98	1.12	0.6	Dry docking & ship repair
16	NIPCO	0.15	0	0.64	0	0.61	0.03	0	0	0.09	0.19	0.13	0.2	0.23	0.19	Oil tank farm and discharge areas
LG																
17	IDDO	1.23	0	0.98	1.15	1.96	0.63	0	0.26	0.19	0.67	0.53	0.55	0.72	0.56	Public sewage & dump sites
18	OKB	0	3.33	0.71	0	1.51	1.16	0	0.28	0.4	0.59	0.67	0.6	0.48	0.84	Saw mills waste & domestic wastes
19	MKK	0	0	0.76	0	1.36	1.06	0	0.31	0.52	0.81	0.87	0.85	0.81	1.1	Fish farming and domestic trading
20	UWF	0	0	0.69	0	1.72	0.5	0	0.16	1.45	0.4	0.68	0.35	0.23	1.18	Recreational & aquaculture
21	OWSK	2.69	6.67	1.78	2.9	12.62	1.26	0	0.69	0.31	1.99	2.78	1.49	0.95	1.5	Oil tank farms discharge area
22	UHR	0	0	0.6	0	0.92	1.18	0	0.29	24.66	0.77	0.81	0.23	0.21	0.42	Oyster, recreational &sand mining
23	UGH	0.92	3.33	1.24	0.75	4.61	1.17	0	0.47	0.41	1.06	1.4	0.03	0.03	0.64	Domestic wastes discharge areas
APL																
24	APL1	0.23	0	0.58	0	0.85	0.23	0	0.04	0.02	0.08	0.16	0.95	1.28	0.56	Recreational & proposed residential development
25	APL2	0	0	0.44	0	0.11	0.04	0	0	0.02	0.02	0.05	0.3	0.48	0.39	Recreational & proposed residential development
26	APL3	0	0	0.49	0	0.25	0	0	0.01	0.01	0.01	0.03	0.31	0.44	0.29	Recreational & proposed residential development

🟥 Very high contamination ▨ Considerable contamination 🟨 Moderate contamination ☐ Low contamination

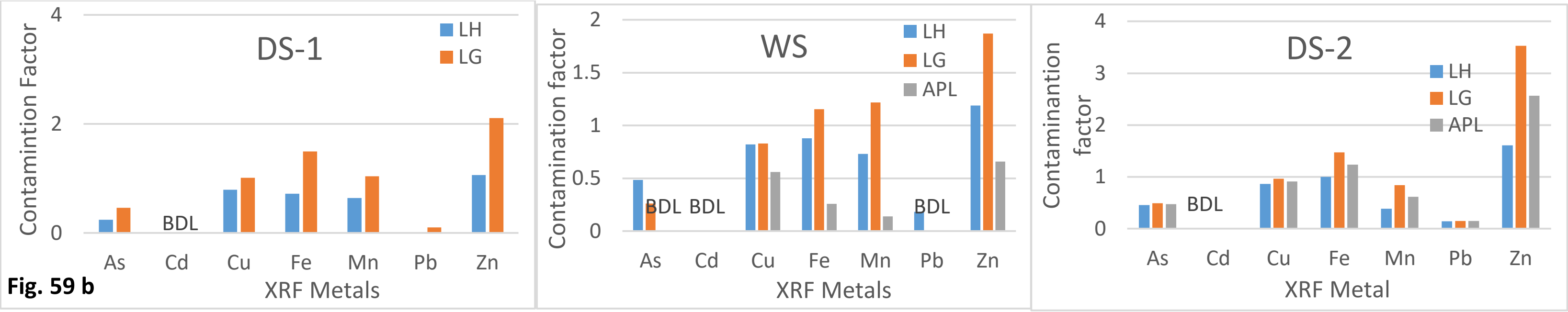


Fig. 59 b

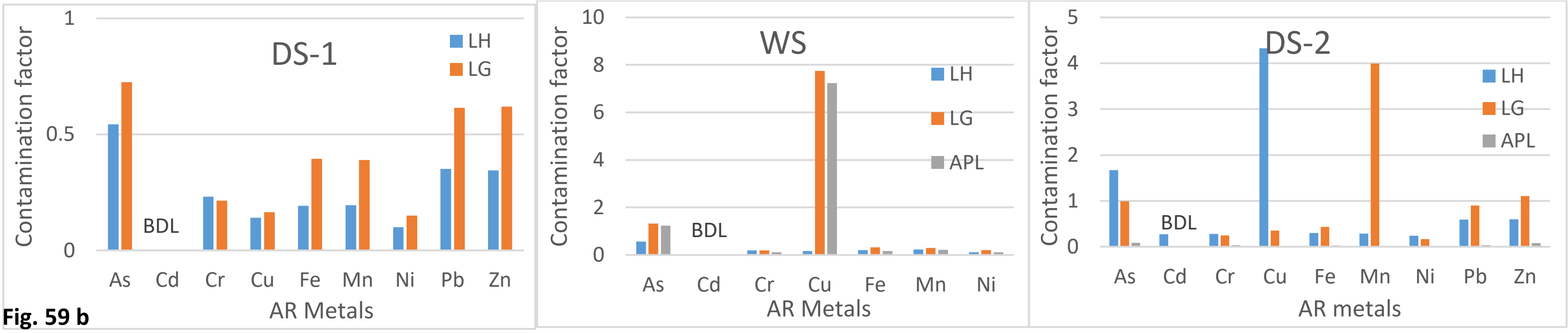


Fig. 59 b

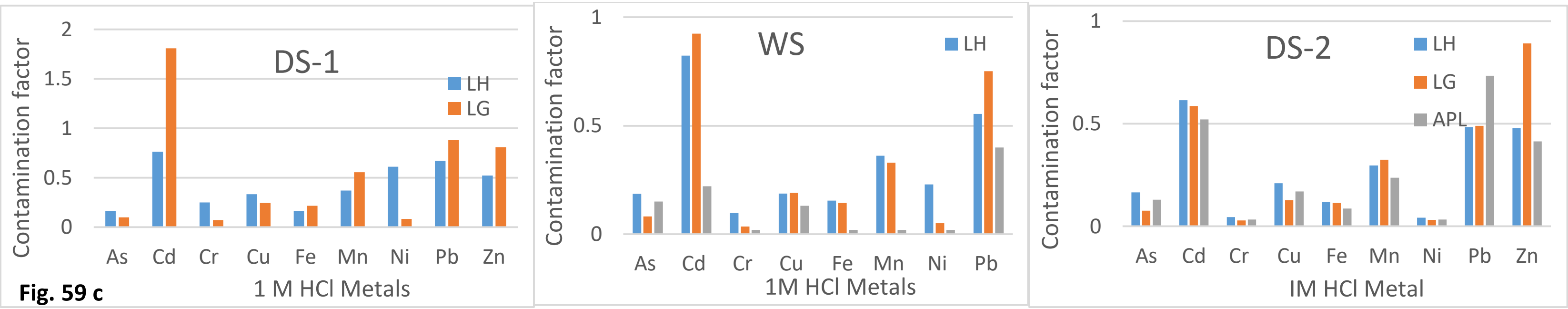


Fig. 59 c

Figure 59a-c: Contamination factor (*Cf*) of heavy metals in sediment using XRF, *Aqua regia* and 1 M HCl during DS - 1, WS and DS - 2.

5.9.4 Contamination factor (C*f*) of total metals (XRF) in the sediments

The contamination factor results for the total metal (XRF) concentrations when compared to historic background levels are presented in Figure 59 a for DS-1 (2013), WS (2013) and DS-2 (2014). The results indicated that the C*f* for most XRF metal concentrations in the DS-1 (2013) had low contamination factor (i.e C *f*< 1) at the LH. On the other hand, Cu, Fe, Mn and Zn showed moderate level of contamination (1 ≤ C*f* < 3) in the same sampling season at the LG indicated that there is considerable imput of those metals from the urbanized sites of the LG. With respect to the quality of sediments collected during WS (2014), the C*f* values for Zn at LH as well as Fe, Mn and Zn at LG had values which were indicative of moderate contamination. In the DS-2 (2014), the calculated values of C*f* only Fe for LG and APL as well as Zn for LH, LG and APL had moderate levels of contamination.

5.9.5 Contamination factor (C*f*) of Recoverable metals (AR) in the sediments

The results of the calculated C*f* of recoverable heavy metal concentrations in the sediment samples of the LH, LG and APL for DS-1, WS and DS-2 are presented in Figure 59 b. Specifically, results of the Cf for total recoverable metals in the DS-1 (2013) indicated that all assessed metals had low levels of contamination for all three lagoon systems. In the WS (2013), As in the LG and APL had moderate levels of contamination while Cu had a very high level of contamination (C*f* > 6) LG and APL. The relatively high level of As and Cu at the LG was contributed specifically by the high recorded in the sediments of samples from the urbanized sections of the LG receiving municipal sewage and industrial effluents from the city centres of Lagos. In the APL the reason can be attributed to the introduction of metal laden sea water at high tides into the lagoon and its relatively landlocked nature which makes it retain metals for longer periods.

However, in the DS-2 (2014), there was considerable (3 ≤ C*f* < 6) to very high contamination (C*f* > 6) of the sediments at the LH with As and Cu. The reason for this could be attributed to the relatively high C*f* between sites 1 to 9 which are characterized by petroleum products tank farms and bulk cargo raw material discharge. Also, Mn and Zn recorded considerable and low levels of contamination respectively at the LG. The high Mn in the LG was attributed to the high levels at site 22 (Cf=24.66) which is an area characterized by receipt of municipal sewage while the Zn levels can be attributed to leachates from coastal solid waste dump at site 21 and 23 of the LG.

Contamination factor (C*f*) of Bioavilable metals (1 M HCl) in the sediments

The results for the C*f* of bioavailable concentrations of heavy metal in the sediment samples are presented in Figure 59 c for DS-1, WS and DS-2 in the LH, LG and APL. The results indicated that bioavailable Cd has moderate levels of contamination with respect to the LG in the DS-1 (2013). All other metals had low levels of contamination for all the Lagoon systems sampled in the DS-1. In the WS and DS-2, the *Cf* of all bioavialble metals were all <1 indicating low levels of contamination.

5.10 Enrichment factor (E*f*) of metals in sediment

Enrichment factor was determined in sample to indicate the level of enrichment and mobility of contaminants at each site. Specifically, E*f* was calculated for the LH and the urbanized sections of the LG using the control (APL) as the background data. The APL data was used for the background rather than the Shale values because of its geographical proximity to LH and LG and it is relatively undisturbed. Figure 59 showed the average enrichment factors of the metals in Lagos Harbour and Lagos Lagoon. The detailed tables showing the E*f* figures calculated for the LH, LG & APL are presented in Appendix 22.

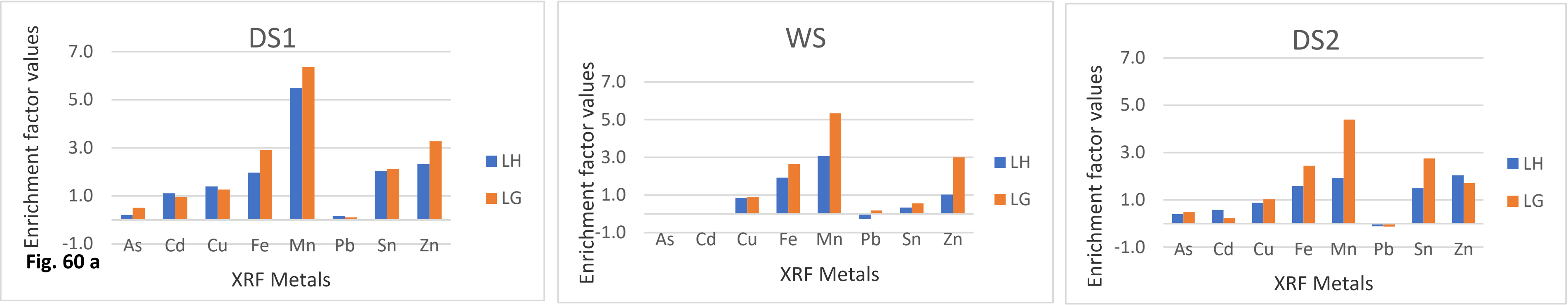


Fig. 60 a

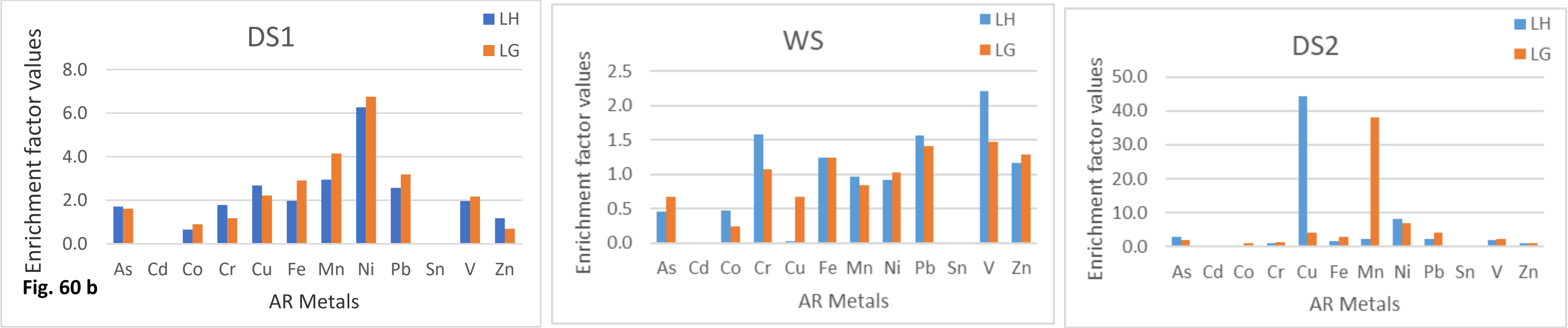


Fig. 60 b

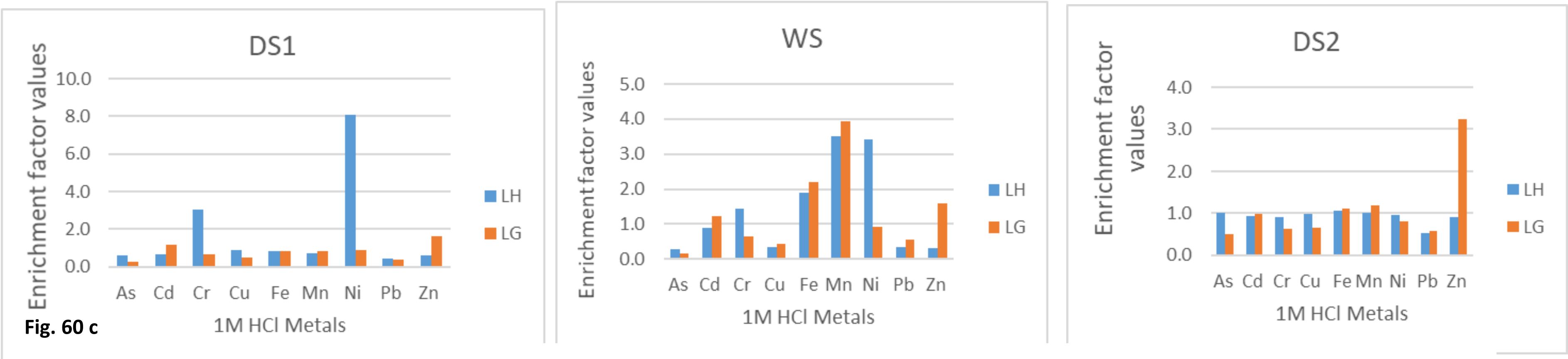


Fig. 60 c

Figure 60a-c: Enrichment factor of heavy metals in sediment using XRF, *Aqua regia* and 1 M HCl during DS - 1, WS and DS - 2.

LH: Lagos Harbour, **LG**: Lagos Lagoon. The enrichment factor was classified with the following standards: EF<2: depletion to minimal enrichment; EF 2–5: moderate enrichment; EF 5–20: significant enrichment; EF 20–40: very high enrichment; and EF > 40: extremely high enrichment.

5.10.1 Enrichment factor of total metals in sediment using XRF

The Enrichment factor (E*f*) of heavy metals analysed with XRF are shown in Figure 60a and reveal As, Cd, Cu, and Pb fell within E*f* < 2 (depletion to minimal enrichment), Fe, Sn and Zn fell within E*f* value of 2-5 (moderate enrichment) and Mn fell within E*f* values of 5-20 (significant enrichment) in both LH and LG during DS-1 (2013). This implies that relative to background levels of expected levels of metals within areas and within the same geo-ecology of the Lagos Lagoon system, Mn has been significantly increased in the sediments.

Likewise, the E*f* values of total (XRF) for As, Cd, Cu, Pb and Sn for both LH and LG, as well as Fe and Zn in LH fell within E*f* <2 (depletion to minimal enrichment), while Fe, Mn and Zn in LG as well as Mn in LH fell within E*f* value of 2-5 (moderate enrichment) during WS (2013).

The E*f* values of total (XRF) for As, Cd, Cu and Pb for both LH and LG, as well as Mn and Sn in LH, and Zn in LG fell within E*f* < 2 (depletion to minimal enrichment), while Fe, Mn and Sn in LG as well as Zn in LH fell within E*f* value of 2-5 (moderate enrichment) during DS-2 (2014).

5.10.2 Enrichment factor of recoverable metals in sediment using *Aqua regia*

The calculated E*f* of heavy metals extractable with *Aqua regia* are shown in Figure 60 b also revealed low level of enrichment of most assessed metals in the sediments. Specifically, the results reveal As, Cd, Co, Cr, Sn and Zn fell within E*f* < 2 (depletion to minimal enrichment), Cu, Fe, Mn, Pb and V fell within E*f* value of 2-5 (moderate enrichment) and Ni fell within E*f* values of 5-20 (significant enrichment) in both LH and LG during DS-1 (2013).

The E*f* values of *Aqua regia* for As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, and Zn for both LH and LG, as well as V in LG fell within E*f* < 2 (depletion to minimal enrichment), while V in LH within E*f* value of 2-5 (moderate enrichment) during WS (2013).

The EF values of *Aqua regia* for Cd, Co, Cr, Sn and Zn for both LH and LG, as well as Fe in LH in LG fell within E*f* < 2 (depletion to minimal enrichment), while As, Pb and V in LH and LG, as well as Cu and Fe, in LG, Mn in LH fell within E*f* value of 2-5 (moderate enrichment) and Ni fell within E*f* values of 5-20 (significant enrichment) in both LH and LG; Mn in LG fell within E*f* 20–40 (very high enrichment) and Cu in LH was above the E*f* > 40 (extremely high enrichment) during DS-2 (2014).

5.10.3 Enrichment factor of bioavailable metals in sediment using 1 M HCl

The E*f* of heavy metals bioavailable in sediment with 1 M H Cl are shown in Figure 60 c and the results revealed that As, Cd, Cu, Fe, Mn, Pb and Zn in LH and LG, as well as Cr and Ni in LG fell within E*f* < 2 (depletion to minimal enrichment). Cr in LH fell within E*f* value of 2-5 (moderate enrichment) and Ni in LH fell within E*f* values of 5-20 (significant enrichment) during DS-1 (2013).

The E*f* values of 1 M HCl for As, Cd, Cr, Cu, Mn, Ni, Pb and Zn for both LH and LG, as well as Fe in LH and Ni in LG were within E*f* < 2 (depletion to minimal enrichment), while Fe in LG and Ni in LH were within E*f* values of 2-5 (moderate enrichment) during WS (2013).

The E*f* values of 1 M HCl for As, Cd, Cr, Cu, Fe, Mn, Ni, and Pbfor both LH and LG, as well as Zn in LH in LH fell within *Ef* < 2 (depletion to minimal enrichment), while Zn in LG fell within E*f* value of 2-5 (moderate enrichment) during DS-2 (2014).

5.10.4 Percentage recovery (*Aqua regia*) and bioavailable (1 M HCl)

Pb was below detection limit with respect to percentage recoverability at the LH during DS-1 as well as LG and APL in the WS and APL during the DS-2. The percentage recovery of the metals across the sampling locations and seasons can be described as follows: Pb > As > Mn > Cu > Zn > Cd (Table 29).

The results of the percentage bioavailability assessment indicated that Cd had low recovery levels being below detection limit across sampling locations and seasons. This was also the case for As in APL during the WS and DS-1. The percentage bioavilability assessment indicated that As, Pb and Zn were below detection limit at the control location (APL) in DS-2. The trend with respect to percentage bioavailability include Mn > Zn > Cu > Cu > Fe > Pb (Table 30).

Table 29: Percentage recoverability of metals detected in Lagos Harbour, Lagos Lagoon and Apese Lagoon.

	Location	Percentage Recoverability							
		Al	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**
DS-1	LH	7.4	233.3	BDL	16.7	26.6	30.4	BDL	31.7
	LG	7.5	150.0	BDL	15.2	26.6	37.1	600.0	29.5
WS	LH	3.0	33.3	BDL	21.6	17.5	49.4	275.0	43.4
	LG	2.5	33.3	BDL	24.3	12.5	26.9	BDL	52.2
	APL	1	BDL	BDL	24	7	18	BDL	49
DS-2	LH	8.0	366.7	BDL	500.0	29.9	75.0	400.0	37.3
	LG	7.2	216.7	BDL	37.2	29.4	473.4	600.0	31.3
	APL	2.4	BDL	BDL	4.3	8.4	18.4	BDL	21.1

BDL: Below Detection Limit; NA- Abnormal result far above 100%

Table30: Percentage bioavailability of metals detected in Lagos Harbour, Lagos Lagoon and Apese Lagoon.

Season	Location	Percentage Bioavailability							
		Al	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**
DS-1	LH	3.9	66.7	BDL	41.7	22.6	58.0	BDL	49.5
	LG	3.7	16.7	BDL	23.9	14.3	53.7	NA	38.5
WS	LH	3.0	33.3	BDL	21.6	17.5	49.4	NA	36.3
	LG	2.5	33.3	BDL	24.3	12.5	26.9	BDL	52.2
	APL	1	BDL	BDL	24	7	18	BDL	49
DS-2	LH	1.3	33.3	BDL	23.1	11.8	77.1	NA	29.4
	LG	1.2	16.7	BDL	14.0	7.7	38.4	NA	25.4
	APL	2.0	BDL	BDL	34.8	27.0	227.6	BDL	NA

BDL: Below Detection Limit; NA- Abnormal result far above 100%

CHAPTER SIX: DISCUSSION OF EMPIRICAL RESULTS

6.1 Introduction

This study was aimed at characterising and identifying the sources and pathways of contaminants (heavy metals), their concentrations and the ecological risk associated with the surveyed metals and metalloids (As, Cd, Cr, Co, Cu, Pb, Sn, Mn, Ni, V and Zn) in sediments. The metals were characterized as total (without extraction), recoverable (with extraction using the *Aqua regia* extraction technique) and bioavailable phases (using IM HCl extraction) with XRF, ICP-OES and ICP-MS analysis respectively. It also intends to compare the measured concentrations (total, recoverable and bioavailable) with International Standards to ascertain the levels of heavy metal contamination in Lagos Harbour (LH), Lagos Lagoon (LG) and a control site, Apese Lagoon (APL). The key focus of the study was to assess the metal sources, pathways of entry, concentrations, distribution and ecological risk in the sediments of LH in order to improve the data available to inform effective management actions. Given the proximity of LH to LG, and the flow of water at low and high tide to and from both water bodies, the LG was also studied extensively, especially the urbanized part. The APL is geographically associated with the others, being one of the lagoons that make up the Lagos Lagoon system, but is strategically isolated from the others by large areas of land. Like LH, the APL is influenced by the Atlantic Ocean via sea water incursion at high tide. The patterns of metal concentrations and associated activities were used to determine hotspots as targets for metal pollution management rather than a non-specific approach as typically suggested in other work, in order to minimize toxic effects on the biota. To this end, a review of existing literature was conducted to identify knowledge gaps with respect to metal pollution and transport in the lagoons. These gaps in knowledge are itemised below:

Current research on contamination by heavy metals in the Lagos Lagoon has been uncoordinated, leaving an unclear picture of the level of contamination within the marine environment. The previous studies have assessed heavy metal concentrations across various environmental components, such as water, sediments and biota, with data dispersed across several areas within the Lagos Lagoon. Some studies, particularly those conducted within the confined area of the Lagoon, are not coherent in terms of assessing and establishing the sources and potential ecological effects of these metals on sediment quality.

Previous studies on heavy metal distribution have presented results as isolated sampling points on maps with no connection to understand spatial distribution and/or levels of the elements in relation to respective sources/ pathways into the lagoon using contouring mapping. Thus, as a contribution to knowledge, the spatial distribution of the heavy metals detected in the sediment samples were developed into appropriate maps in order to make it easy to understand the relative levels in various sections and therefore proffer explanations as to the potential sources of these metals in the lagoon system.

Previous investigations of heavy metals conducted within the Lagos Lagoon have only employed one method of digestion per study, and analysis has been mostly with Atomic Absorption Spectroscopy (Osibanjo et al., 1994). Previous studies on the sediments of the Lagos Lagoon system have also not compared outcomes of various kinds of analysis using different techniques. Although in recent times, a few studies in this area have employed technologies such as ICP-MS (Amaeze, 2015) and ICP-OES (Olatunji & Abimbola, 2010) which are specifically designed to measure heavy metals, none has employed these technologies in combination with XRF in other to analyse and extract metals and metalloids in sediment samples for total, recoverable and bioavailable forms.

From the foregoing, it is apparent that up-to-date and functional information is needed by regulators and researchers to frame the management strategies for the lagoon. In order to obtain the relevant information to bridge these gaps, a number of research questions need to be answered. Coastal environments are crucial in the ecological system since they act as breeding grounds/nurseries for biota, serve as a refuge for a diverse range of species and are a key buffer in preventing sea water incursion into land. In recent years, however, rapid industrialization and excessive mining activities within the Lagos coastal ecosystems (Bawa-Allah et al., 2017) have led to the LH and LG becoming contaminated by different types of pollutants, including heavy metals, thereby threatening their continued capacity to provide valuable ecosystem services in a sustainable manner. To mitigate these challenges, this research sought to provide answers to the following questions:

1. What are the concentrations of heavy metal in the sediments of Lagos Harbour, Nigeria?

2. What is the relative spatial distribution of determined heavy metals in the sediment samples of the Lagos Lagoon system and how does this relate to prevailing activities in the respective sections?
3. What are the sources and pathways of contaminants (heavy metals) into the Lagos Harbour?
4. What are the heavy metal concentrations within the three different sampling locations (Lagos Harbour, the urbanized part of Lagos Lagoon and the relatively undisturbed Apese Lagoon) with a view to establishing the ecological risk posed to their respective sediments?

The following discussion will answer the above questions through a careful scientific analysis of the results.

6.2 Water quality parameters

The physicochemical properties of the surface water samples were assessed to determine the water quality in the sampling sites at the LH, LG and APL. Since water's physical, chemical and biological characteristics may enhance the bioavailability and mobility of trace heavy metals, physicochemical analysis of the water is therefore useful to determine the quality and nature of coastal ecosystems. An increased rate of urbanisation, industrialisation and other forms of modernization have plagued the productive capacities of coastal water bodies in general, threatening their sustainable limits (Addo et al., 2012). In particular, the coastal areas of the Lagos Lagoon have been reported to be dotted with dump sites which release leachates laden with diverse sources of waste into the water and these are potentially acutely toxic to sensitive aquatic animals (Amaeze & Abel Obi, 2015).

The consistency of water temperature readings recorded in both seasons, with an average temperature of 29.6 °C in LH, 28.7 °C in the LG and 28.9 °C in the APL, is linked to the depth of the Harbour, the shallowness of the Lagos Lagoon and regular tidal motions, which ensure the complete mixing of the water. This observation agrees with the findings of Ajao (1990) and Oyewo (1998) in their investigation on the temperature of Lagos Lagoon. The temperature of the surface water over two sampling seasons ranged between 26.6 °C and 31.0 °C which is also in line with the temperature range of 24.5 °C to 31.5 °C recorded by Fagade & Olaniyan (1994).

Rainfall is a major determinant factor of salinity in that it augments the fresh water inflow into the marine environment and reduces the salinity. The salinity range in the Lagos Harbour was found to vary significantly with season, being 30.5 ‰ during the dry season and 16.6‰ during the wet season as a result of rainfall and other fresh water input from rivers, streams and inland creeks. The Lagos and Apese Lagoons, meanwhile, are both brackish, with high salinity values during the dry seasons - 18.9 ‰ and 16.2 ‰, respectively; and low values during the wet season with 5.04 ‰ in both Lagoons. The seasonality of salinity linked with rainfall has been reported by a number of investigators in the lagoon system including Nwankwo (2004) and Oyenma (2009).

Conductivity measurements are used routinely in many industrial and environmental applications as a fast, inexpensive and reliable way of measuring the ionic content of the water (Gray, 2005). The conductivity of the LH increased due to increased salinity and inflow of sea water during the dry season. Similar results have also been noted by Nwankwo (1996).

The low variation in pH, with a range of 8.0–8.3 at LH; 8.0–8.2 at LG; and 7.9–8.0 at APL, agreed with Ayoola & Kuton (2009), who reported high seawater influx and strong tidal currents, due to the high buffering capacity of the system and effective flushing, explain this environment’s relatively stable pH across the sampling sites.

The dissolved oxygen in the surface water is an important parameter in aquatic systems (Manora, 2012). The ability of water to maintain oxygen in a dissolved state decreases with increasing temperature. As a result, colder water can contain more dissolved oxygen than warm water (AWQA, 2012). Dissolved oxygen ranged between 4.09 mg/L at the LH; 4.07 mg/L at the LG; and 6.52 mg/L at APL. This is consistent with the control site (APL) being relatively undisturbed by human activities. The values at the LH and LG were below the minimum permissible limit of the WHO standards (Adejuwon & Adelakun, 2012). This is attributed to human activities on the LH and LG including shipping operations such as offloading and discharging waste, sand mining, and continued dredging.

From the foregoing it is apparent that both natural and anthropogenic factors influence the surface water of LH and LG while then APL has minimal anthropogenic influence, with tidal influx of sea water being the main natural factor influencing it. However, these anthr5opogenic factors are severe enough to drastically alter the water quality as most parameters were within their normal ranges. However, one cannot conclude that the water quality status is not affecting biota of the surface water. In fact, they are if we consider reports of variations in phytoplankton (Nwankwo, 2004) and fish species diversity (Amaeze et al., 2012) in the Lagos Lagoon system. Specifically, Amaeze et al., (2012) reported lower fish species diversity in areas within and around the Lagos Harbour.

6.3 Particle size, total carbon and total nitrogen

This section seeks to discuss that current status of the respective sediment structures in view of the consistent dredging in the LH. Although various degrees of dredging for sand as sand mining occurs in the LG, the scale and consistency of this practice in the harbour leaves room for concern which can be assuaged to some extent by the understanding the particle structure and characteristics in both water bodies as well as the control, APL.

The mean percentage values for sand, clay and silt obtained in this study reflected the sediment texture of the lagoons. The dominant sediment in the study area was very fine sand, comprising 19.78 % of the sediment at the LH; 27.37 % at LG; and 19.26% at APL, indicating the sandy substratum nature of the sampling sites. Overall sediment diversity was low in terms of the particle size. A similar observation was found in the sediment in Lake Kariba (Balogun, 2017). According to Allan (1995), 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 & Tawari (2010) from Trans-Okpoka Creek, Upper Bonny Estuary, Nigeria. The lowest observed particle sizes were the very coarse sand with percentages of 0.5 % at LH and 0.25 % at APL. The observed nature of the particle sizes can be attributed to sand mining/ routine maintenance dredging at the LH as well as drifts from loss of beach shorelines at APL which can be related to the drifts associated with sea water incursion and outflow with tide.

Particle size plays an important role in many sediment processes such as aggregate stability (Zauca et al., 2013), fluvial morphology (Cartacuzencu et al., 2014), and pollution (Karbassi et al., 2014). 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 (Agagu, 1985). 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 microbenthic fauna, because such extensive damage would result in drastic alterations of the sediment and loss of organic materials which characterize their typical habitat. Doherty (2014) reported very low benthic species diversity around the Apapa port areas which lies within the LH. Also, heavy metals are usually associated with organic and inorganic complexes which characterize natural sediments of water bodies (Nissenbaum & Swaine, 1976; Kersten, 2002; Ferro, 2003).

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 (Grabowski et al., 2011). 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 bottom sediments within aquatic ecosystems have an essential role as an 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 (Jorgensen, 1996; Leticia et al., 2003).

The organic carbon content in surface sediments depends on myriad factors such as sedimentary characteristics, rate of microbial degradation, column water productivity and terrestrial inputs. Higher plant organic matter has a lower nitrogen content and thus a higher carbon to nitrogen ratio (C: N). High C: N ratios in marine sediments indicate a terrigenous organic matter contribution (Leticia et al., 2003). The work in this study revealed that there were significantly higher nitrogen concentrations in the sediments compared to carbon, probably due to loss of the latter via dredging, and accumulation from dead decaying animals.

Moreover, the lower TC and TN, recorded in the LH compared to the LG and APL is notable. In fact, APL, being the most remote and least disturbed, often had the highest values compared to LH where dredging and coastal erosion has resulted in loss of surface organic matter. Loss of organic matter, as indicated earlier, would result in increased levels of free metallic ions which can be moved into the water column via subsurface mixing thereby exposing them for uptake by fin and shell fishes.

The C: N ratio for the LH indicates both terrestrial and marine organic matter loadings in the sediment, while at the LG the C:N ratio revealed significantly high organic carbon loadings in the sediments that indicates both terrestrial and marine organic matter across all the sites. The LG receives municipal sewage from the urbanized areas of the Lagos and which can account for the inflow of organic carbon. In the LH, sources of organic carbon may include hydrocarbon spills from tank farms and vessels, ballast water discharge as well as other diffused land base sources.

Stein (1991) suggested that values of C: N ratio lower than 10 are strictly of marine origin, while values around 10 represent both marine and terrestrial organic components in the sediment. Thus, the C: N ratios observed in sediments at the LH, LG and APL reflects mixed origin of the organic matter and sea incursion, especially in the wet season. These are attributed to the input of terrestrial material generated from anthropogenic sources both land based and marine. The high content of total organic carbon at some sampling sites - LH 1, LH 2, LH 12, LH13 and LG 17 – LG 23 are most likely a result of the direct discharge of domestic sewage or insufficiently treated waste from ships as well as illegal coastal ballast water discharges.

The correlation coefficient of the total carbon content and nitrogen with particle sizes showed a significantly positive correlation between total carbon content with clay and silt during the wet season. This indicates that the large surface area of the particle sizes (clay and silt) significantly increased the absorption of the total carbon content and by extension metals at the LH during the wet season. The implication of this is that the LH sediment would more likely hold more pollutants even if all three water bodies have similar pollution exposure. This changes in the nature of the sediment/substratum has been largely brought about by the routine maintenance dredging to allow of increased navigational capacity of the water body.

6.4 Metals and metalloids

6.4.1 Metal concentrations in the LH, LG and APL

This section seeks to discuss the implications of the concentrations of metals determined using XRF, *Aqua regia* and 1 M HCl methods as well as make comparison with International Standards in order to ascertain the level of heavy metal contamination and ecological risk in the Lagos Harbour area and the Lagoons. This particularly provides answers to the first to fourth objectives of this study which seeks to determine the levels of the metals in the LH and compare the values obtained with international standards in order to make deductions regarding the ecological risk status of this section of the Lagos Lagoon system. However, the ecotoxicological implications cannot be determined merely be chemical analysis thus the following section will further elucidate the ecotoxicological implications of these findings by systematically comparing determined concentrations with their toxicological potential based on existing literature. The toxicity of metals to aquatic biota inhabiting the Lagos Lagoon system is well reported (Okoye et al., 1991; Otitoloju, 2002; Otitoloju & Don-Pedro, 2002) and is mainly due to their toxicity and ability to bioaccumulate and biomagnify in food chains, with the added risk of negative health outcomes in humans. Accordingly, activities which enhance their availability is of ecotoxicological concern.

Box 1: Objectives 1 & 2

- To determine the concentrations of heavy metal within Lagos Harbour area and the Lagoon.
- To compare the concentrations with International Standards to ascertain the level of heavy metal contamination in the Lagos Harbour area and the Lagoons.

The XRF analyses conducted for this study consistently yielded higher concentrations of heavy metals compared to extraction by AR and 1M HCl. This is expected, however, because XRF measures the total metal concentrations in the media. In contrast, metal extraction by AR provides the recoverable concentrations while 1M HCl measures the bioavailable concentrations. Ideally, recoverable concentrations should be higher than bioavailable concentrations but that was not always the case in this study. The reason is attributed to the peculiarities of the ligands and complexes which bind some of these metals, which limit very high/effective recovery of analytes.

With respect to the specific extraction and analytical techniques employed, the total metal concentration analysed through XRF always yielded higher concentrations than the *Aqua regia* (recoverable) and 1M HCl (bioavailable) extractions. This can be attributed to XRF being an entirely dry and direct process involving no form of liquid analysis. Liquid in any form can have a diluting effect, no matter how low, thereby reducing the exact amounts of such metals which can be measured from each technique. Although concentrations of metals determined by XRF are typically higher, they have been reported to show excellent correlation with those analysed by the conventional atomic absorption spectroscopy techniques after digestion with *Aqua regia* (Radu & Diamond, 2009). The determined concentrations the recoverable forms, were significantly higher ($P<0.05$) than the bioavailable forms.

The determined concentrations of total recoverable and bioavailable heavy metals and metalloids in sediments of the LH, LG and APL were compared with the SQGs of NOAA using the Screening Quick Reference Table (NOAA, 1999). The concentrations of the total metals (XRF) – Cu, Pb and metalloid As, the recoverable (*Aqua regia*) metals – Cu, Cr, Pb, Zn and As, and the bioavailable (1 M HCl) metals – Cu, Cr and Pb and As – were all above the threshold effect level (TEL) of the NOAA and CSQGs standards. It should be noted that for total, recoverable and bioavailable metals, concentrations of Cu, Pb and As were similarly above compared standards in all three analytical techniques, indicating that the environment has become enriched with these trace elements via various polluting activities. From the forgoing it is apparent that the preponderance of coastal anthropogenic activities in the LH and its environs have resulted in enrichment of the sediments with metals above the TEL. This is of grave concern for the survival of the remaining microbenthic fauna in this water body and has high potential for negative health effects in humans who feed on harvested fin and shell fishes for local delicacies that must have bioaccumulated these metals. Macrobenthic ecology is important in maintaining the structure of substratum, serving as carbon and nutrient sink and protecting the water from pollution (Levin et al., 2001). Sustained disruption of this ecosystem by way of dredging and introduction of toxic metals would result in continued displacement and death of the inhabiting biota together with disruption of ecological processes which they support.

The findings from this study also indicated a particularly high level of Ni in the LH, while Cd was only detected to have higher concentrations than the standards in the LG. The reasons for this distinct pattern can be seen in the specific activities which generate such wastes. With respect to Ni, this metal has been associated with heavy oil used by ships as fuel for their normal operations (Manousakas et al., 2017). Ni is also released alongside V and other air pollutants via the emissions from ships (Manousakas et al., 2017). Thus, its concentration was very high in LH, especially in sites around the ports because of the high level of ship traffic. This implies that there is need to improve ship fuel sources in other to manage Ni levels and protect the LH sensitive microbenthic fauna from harm due to bioaccumulation of this metal. Their hotspots in the harbour were centred around sections with tank farms/coastal depots where transfer of petroleum products routinely occur. Ni together with V are two of the key metals associated with heavy fuel spills (Santos-Echeandía et al., 2008).

The fact that Ni was remarkably high only in the LH might point to a unique or non-dispersed activity around the harbour which could be responsible for such an isolated phenomenon in large water bodies like LH and LG which are in constant interactions under the influence of tides. A study conducted in the port of Shanghai, China, for example, noted very high Ni and V concentrations in aerosol samples compared to other heavy metals. As with this study, these concentrations were attributed to the fact that Ni is a component of heavy oils used by ships and is thus emitted when they are operational (Zhao et al., 2013). Likewise, high concentrations of Ni noted in coastal urban areas of the city of Patras in Greece have been attributed to shipping activities given the low industrial activity in the city (Manousakas et al., 2017).

Cd was also higher than NOAA and CSQG TEL standards in the LG sediment sample and is a very toxic chemical and thus a source of considerable concern. Several decades ago Cd poisoning in a coastal rice farming community in Japan resulted in Itai Itai disease, associated with severe damage to the bones and deformities (Nishijo et al., 2017). The high concentration of this metal observed can be associated with road runoffs from the municipal sewage/canal system. Brake pads of vehicles are known to wear out over time during use, leading to their release onto the road surface resulting in Cd deposition on roads. Rainfall then transports the Cd deposits alongside other contaminates into the lagoon, either directly or via the numerous municipal waste canal systems which drain the City of Lagos into the LG. Cd is also associated with pesticides and fungicides (Chen et al., 2008), thereby making domestic discharges during mosquito and other pest control actions an equally important pathway into the lagoon. Cd, therefore, eventually ends up in the LG sediments where they are adsorbed and easily bioaccumulated by benthic animals such as molluscs. This is of particular public health concern in view of the practice of periwinkle harvesting from the lagoon for the preparation of some Nigerian local dishes.

In respect to the specific metals extracted with *Aqua regia*, As in LH and LG at DS-1 and DS-2 exceeded the stipulated permissible threshold effect level (TEL) of 7.2 mg/kg by NOAA and CSQGs. The As level for total analysed metals (XRF) and digested metals (1 M HCl) in the sediment were below the NOAA/ CSQGs TEL values. The availability of As at a location has been attributed to the unsuitable disposal of electronic waste, industrial effluents, fertilizers and atmospheric depositions (Talbot & Chegwidden in Abiodun & Oyeleke, 2016) notably observed in all the locations. In the present study, however, As was mostly concentrated around petroleum products tank farms and transfer sites in the LH, indicating that spill of imported petroleum products at the ports are important contributors to its distribution in the lagoon.

The levels of Cu detected following analysis with XRF showed significantly higher values in the DS-1, DS-2 and WS across the three zones (LH, LG and APL). The Cu level extracted with *Aqua regia* in DS-2 in Lagos Harbour, WS in Lagos and Apese Lagoons were found to have exceeded the NOAA/ CSQGs TEL value of 18.7 mg/kg. Cu, although an essential metal, becomes toxic at concentrations as low as 20 mg/kg (Wright & Welbourn, 2002). It finds its way into water bodies via mining activities, production of metals and electrical appliances, domestic pesticide use, leather processing and automotive brake pads (Solomon, 2009). Given its abundance in the LG, in a section known for receipt of municipal runoffs, such high concentrations could have emanated from diffused sources such as worn out brake pads and disposal of used pesticide containers for domestic mosquito control. Its concentrations in the LH can be attributed to discharges during bulk cargo offloading as well as leaching of anti-fouling paints (Srinivasan & Swain, 2007). Cu binds easily to sediments and has been known to bioaccumulate in microbenthic fauna (Bradl, 2005). It has also been shown to be many folds more toxic to fishes than mammals (Wright & Welbourn, 2002). As a result, its high concentration in the lagoons is a cause for concern and a major threat to valuable shellfish and the sustenance of fishing communities.

The total analysed Zn level were found to be significantly higher than the TEL of 124 mg/kg in the NOAA/CSQG standards across various sampling seasons. Zn has also been reported to be toxic to aquatic invertebrates at much lower concentrations than the TEL (Clifford & McGeer, 2009). The sources of excess amounts of Zn in the LH and LG therefore need to be clearly identified and prioritized for management actions.

This study showed that the mean concentrations of Pb in the sediments are within the TEL permissible level of 30.2 mg/kg in NOAA/ CSQG across the LH, LG and APL, which corroborates with Abiodun & Oyeleke (2016) who found the level of Pb within the LG to be within the permissible level of 40 mg/kg set by the USEPA. The link between urban activities and Pb can be inferred from the very high recoverable concentrations recorded in the LG in this study. Also, the levels observed in the LH can be attributed to deposition from emissions arising from industries and ships around the harbour. The harbour area in particular has a very high traffic of tug boats and ferries which also contributes to the release of waste associated with the burning of leaded fossil fuels. Sadip et al. (2003) reported that low concentrations of Pb might threaten life in a marine environment compared to most other heavy metals which elicit toxicity only at high exposure concentrations

From the forgoing it is apparent that the LH sediments contain metals from anthropogenic sources some of which were at levels above safe limits which can pose considerable harm to biota. Heavy metal contamination in sediment is of major concern particularly in Nigeria due to its diffuse sources, toxicity to shellfish, persistence, its bio-accumulative nature as well as weak regulations and poor enforcement of waste discharge permits. The metal concentrations observed in LH and LG in the wet season were due to the influx of waste from various point and non-point sources across the sites which enter via shipping and petrol tank farm operational activities along with urban runoffs, municipal sewage, industrial effluents and a host of other pollutants into the water. The environmental fluxes in the rainy season influence the metal concentration and mobility. Mobility and bioavailability of metals depends directly not just on concentration but also the environmental properties such as pH, organic matter concentration, silt and clay concentration, salinity, and dissolved oxygen concentration (Abiodun & Oyeleke, 2016).

6.4.2 Spatial distributions of metals and metalloids

In view of the current knowledge gaps with respect to the distribution and entry pathway of metals into the LH, this study used the determined concentrations of total, recoverable and bioavailable to generate geochemical contouring maps to provide a descriptive assessment of the status of the LH and adjourning LG as well as APL (control) sediments with a view to associating them with location specific activities and establish unique hotspots of metal entry pathways.

Box 2: Objectives 3 & 4

- To identify the sources, pathways and the extent of contamination using spatial distribution geochemical contour mapping of heavy metals in marine surficial sediments in relation to prevailing anthropogenic activities.
- To establish the hotspots for heavy metal contamination in Lagos Harbour and Lagoon

The contour maps showed the spatial variations in the concentration of selected metals and metalloids in relation to the activities within the regions of the study area. These maps were used to show at a glance, the differences in sediment concentrations and the spread of respective metals in the sediments. This cannot be clearly and simply understood by just analysing metals and discussing the entire mean of a large area as the LH, LG or APL. These spatial maps have aided in understanding the spread of hotspots of certain metals thus aiding easy linking of major pathways of the respective metals into the water bodies.

Very high concentrations of total As in the DS-1, as well as recoverable As in the DS-1 and 2, were distributed at the Atlas Cove section around the harbour entrance from the sea where large vessels which cannot enter into the port discharge petroleum products to smaller collection vessels for onward shipment to the tank farms. Discharge of petroleum products from vessels into coastal tank farm storage systems at all sampling seasons is the major pathway of entry since As is a component of petroleum hydrocarbon and is one of the heavy metals highlighted in the Environmental Guidelines and Standards for Petroleum Industry in Nigeria (EGASPIN, 2002). Thus, incidental spills during routine petroleum products transfer, which is likely to occur at least occasionally at the tank farm locations, coupled with surface runoffs during rainfall, and occasional accidental spills, could be attributed as likely reasons for the remarkably high As concentration and distribution in these sections of the LH. Other areas of the LH which equally have high vessel traffic for discharge of large containerized and bulk cargo, as well as coastal industries did not record such high values. This therefore implies that the petroleum products tank farm is a hotspot for As discharge into the LH. Baptista Neto et al. (2006) reported anomalous spatial distribution of heavy metals in the harbour area of Guanabara Bay, South-eastern Brazil and areas which are the main outlets of most polluted rivers, municipal waste drainage systems and a major oil refinery. This is very similar to the results obtained in this study with respect to the LH and the LG since the former is a harbour which is also a centre for receipt of refined petroleum products. LH and LG, however, also receive considerable amounts of municipal waste and industrial effluent from other sections of the city.

During DS-1, very high concentrations of bioavailable Pb were distributed around the bulk cargo offload area and a section with tank farms and dockyards, which also receive municipal sewage from creeks draining waste from sections of the city of Lagos into the LH. This was also the case for total (XRF) metals in the wet season. In the WS and DS-2 an equally very high concentration of all forms of Pb were detected in the urbanized sections of the LG, particularly in areas known to receive municipal sewage and effluents. The high levels of Pb in the LH, therefore, can be attributed mainly to bulk cargo transport activities, discharges from industries located at the port and municipal sewage laden with urban runoffs while in the LG urban runoffs into the municipal sewage systems, together with industrial effluents, can be described as the hotspots for Pb contamination. The release of Pb, particularly in urban areas, are associated with vehicular emissions which can settle onto roads and then enter into water bodies alongside runoffs after rainfalls. High concentrations of Pb has been reported by Amaeze et al. (2015) in runoffs from the Third-Mainland Bridge in Lagos, one of the longest and busiest bridges in Africa. The consistently very high concentrations of Pb detected during the WS in the urbanized sections of the LG receiving municipal sewage and effluents can be explained by high rainfalls during the WS which creates runoffs into the lagoon laden with a diverse range of urban pollutants. High concentrations of Pb in sediment samples of the LG has been reported by Idowu et al. (2012) in sediment samples at Yaba, an area within the periphery of the LG. Amaeze & Abel-Obi (2015) also recorded high Pb concentrations in leachate samples at Oworoshoki, an area within the LG with a coastal dumpsite.

Likewise, widespread distribution of high concentrations of Zn were observed around the vicinity of LH especially where there are petroleum products transfer operations and in the LG in areas receiving municipal runoff/sewage. This was particularly the case for DS-1 but during subsequent sampling such high levels were distributed mainly around similar sections of the LG.

It is noteworthy that concentrations of the metal and metalloids are relatively low in distribution within the Apese Lagoon (APL). The area around the APL is relatively remote and sparsely populated, with the most dominant activities being recreational. Although construction of residential estates has begun around this location, the most significant source of the variation in the APL's ecosystem results from sea water incursion due to its proximity to the ocean.

The spatial distribution maps have provided visual evidence of variations in concentration of selected metals and metalloids across the three seasons within the study areas. In conjunction with observed activities, these maps have also helped to describe the pathways of these metals into the LH and surrounding lagoons. The findings from this study has clearly identified petroleum products tank farms at the port areas and the Atlas cove petroleum products vessel-to vessel transfer area as hotspots for As and Zn supply into the LH given as evident in the orange to deep yellow colouration of the contours. For Pb, the hotspots for supply into the LH include bulk cargo discharge operations, spills from coastal tank farms and dry dock operations. Municipal sewage/runoff discharge and possibly operations of an electricity sub-station beside the University of Lagos guest house (UGH) and Oworoshoki (OWS) are the hotspots for discharge of As, Pb and Zn into the LG.

6.5 Correlation coefficient of the metals and particle size

The assessment of the relationship of specific metals with particle size distribution and total carbon and nitrogen relationships in sediment provides information on metal sources and pathways in the geo-environment (Dragovic et al., 2008). The discussion here is therefore aimed at further explaining the third objectives of the study.

The total, recoverable and bioavailable metal concentrations correlated significantly between themselves, indicating that they occur mostly in ligands as metal complexes such that detection of one implies a high chance of a detecting another. The total analysed metals – As and Fe as well as total nitrogen – exhibited a significant positive correlation with clay and with coarse sand particles. The recoverable Mn with *Aqua regia* as well as total nitrogen had a strong positive and significant correlation with clay and silt particles in wet season. Furthermore, the bioavailable metal – Pb as well as total nitrogen – was correlated with silt particles. This study corroborates the finding of Yang et al. (2014) that metals such as Pb and Cu that are correlated with total organic carbon may be associated with the effect of local urbanisation and industrialisation. This is particularly evident since levels of these metals (Cu and Pb) were particularly high in urbanized sections of the LG receiving municipal waste via canals as well as industrial effluents via creeks and rivers which discharge into the lagoon.

The extent of the input of metals into LH and LG with the physicochemical characteristics of sediment could have a core role in the inter-site accumulation of the heavy metals, as has been reported elsewhere by Zhang et al. (2007) and Sohrabi et al. (2010). Of particular interest is the interactions between Fe and Mn and fine sediment particles such as clay and silt in that recoverable Fe, Mn and Fe were always correlated significantly with clay and silt. A expected, Fe_2O_3 and MnO, are major trace metals of the coastal plain sands of the Dahomey Basin of the South Western Nigeria and much of West Africa (Ikhane et al., 2012). The coastal plain sand is characterized by soft, poorly sorted clayey sands, pebbly sands, sandy clays due to the fact that it is the youngest sedimentary units in the Eastern Dahomey (Jones & Hockey 1964). Fe concentrations are particularly linked to the accumulation of goethite in the phosphatic shales of the Oshosun formation of the Dahomey Basin. This indicates a long-standing relationship with the geological materials in the lagoon. Also, CuO is a trace metal associated with this basin and their occurrence together with the former are expected to show significant correlation with the lithographical components analysed. Fe and Mn are intricately tied to the biogeochemistry of marine sediments and regulate nutrient cycling in marine sediments, especially with respect carbon, phosphorous and sulphur (Burdije, 1993). Thus, the significant correlation established between them and the clay-silt components of the sediments in this investigation restates that importance in the lagoon systems' ecology. This also brings to the fore the negative effects of dredging which causes the loss of these metals from the sediments' surfaces as they are naturally conformed, thereby disrupting the sediment ecology and the animals which it supports in its anoxic high nutrient state.

6.6 Principal component analysis (PCA) of heavy metals and metalloids

PCA was performed to ascertain clustered inter-relationships between metals in sediment, particle sizes, total carbon and total nitrogen from sources within the locations across different seasons. This was done in combination with a factor scores plot in order to group specific sites in the lagoon with similar concentrations of total, recoverable and bioavailable metals to show how these are based on prevailing activities, geographical and other factors. This will further strengthen the response to the research questions and provide evidence for objectives three and four.

Box 3: Objectives 3 & 4

- To identify the sources, pathways and the extent of contamination using spatial distribution geocheming contour mapping of heavy metals in marine surficial sediments in relation to prevailing anthropogenic activities.
- To establish the hotspots for heavy metal contamination in the Lagos Harbour and Lagoon.

Different contamination behaviours were observed in LH, LG and APL. As shown in the previous chapter, there were two principal components (PC1 and PC2) for sedimentary variables at the LH, LG and APL.

Overall, the two principal components (loadings and scores plots) for XRF, AR and 1 M HCl methods were characterized by, respectively, 67.8%, 71.8% and 60.1% of the accumulative contribution rate for the metals, TC, TN and silt, sand and clay for the dry season-1 (2013). The contribution of PC1 and PC2 of the metals analysed and extracted showed positive load contributions of the metals, particle sizes (sand, coarse sand, silt and clay) and total nitrogen. This inter-relationship could be attributed to industrial effluent (shipping and heavy industries) entering the Lagos Harbour and domestic/municipal sewage as well as industrial effluents (entering the urbanized parts of Lagos Lagoon).

Similarly, two principal components for XRF, AR and 1 M HCl methods were characterized by, respectively, 58.8%, 56.8% and 55.3% of the accumulative contribution rate for the metals, TC, TN and silt, sand and clay for the wet season (2014). The contribution of PC1 and PC2 of the metals analysed and extracted showed positive load contributions of the metals, particle sizes (coarse sand, silt and clay), total carbon and total nitrogen, indicating that these metals originated from anthropogenic activities. Finally, the two principal components for XRF, AR and 1 M HCl methods were characterized by, respectively, 55.2%, 59.8% and 54.5% of the accumulative contribution rate for the metals, TC, TN and silt, sand and clay for the dry season-2 (2014). The contribution of PC1 and PC2 of the metals analysed and extracted showed positive load contributions of the metals, particle sizes (coarse sand, silt and clay) and total nitrogen.

Previous studies found that the input of Cd and Cu to the oceans was dominated by riverine sources (Yang et al., 2014). This kind of input also occurs in the Lagos Lagoon system through the discharge of inland rivers such as the Ogun, Ose and Yewa into the lagoon. Anthropogenic sources were of greater environmental significance in the context of the Lagos Lagoon, however. The sources of pollution into the Lagos Lagoon system are diverse, including point and non-point sources. This is compounded by inadequate central sewage systems across the city of Lagos and weak enforcement of waste management regulations including port waste management. The few sewage treatment facilities across the city are mostly basic with no chemical treatment unit, thus treated effluents discharged into the lagoon system continue to receive considerable amounts of pollutants. Dockyards observed during the field data gathering exercise were found to have basic construction with no waste management system for preventing runoffs directly into the lagoon. Ships docked at the ports were found discharging ballast water into the harbour despite it being illegal to do so. The concentration of industries at the port areas including petroleum tank farms is notable. Diesel oil handling by small fishing vessel owners are typically crude involving the use of drums from which spills are inevitable during transfers. These sources are coupled with the preponderance of coastal dumpsites (Amaeze & Abel-Obi, 2015) which release heavy metals into the lagoon system alongside their leachates. These diverse polluting activities, which occur along most of the coastline of the harbour and urbanized sections of the LG, provide diffuse sources of pollutants into the water bodies. Nevertheless, certain locations exist where prevailing activities particularly result in large scale discharges of metal laden wastes, referred to as hotspots in the context of this study. Focusing on these hotspots presents an opportunity to reduce pollution in the LH and LG significantly, given that they contribute the largest amounts of metals as indicated by the relative contours on the maps in Chapter 5 above and the site-specific contamination and enrichment factors below.

The Eigenvalues showed that As, Cd, Cu analysed with XRF, As, Cr, Cu, extracted with AR and 1 M HCl in DS-1 (2013), were significantly loaded in the sediment with scores greater than 1. The eigenvalues during the WS showed that As, Cd, Cu, Mn analysed with XRF, AR and 1 M HCl were strongly loaded in the sediment with scores greater than 1. During the DS-2 (2014), meanwhile, As, Cd, Cu and Mn analysed with XRF, As, Cd, Cr, Cu, extracted with AR and bioavailable with 1 M HCl were significantly loaded in the sediment with scores greater than 1. Given that high concentrations of these metals are associated with anthropogenic sources there is concern over their continued input into the LH and LG. This is particularly in view of their abilities to bioaccumulate and biomagnify along food chain due to their non-biodegradability. Thus, there is need for concerted efforts by respective concerned regulators in managing the sources of these metals in other to ensure sustainable protection of aquatic biota. The results obtained from this study should be juxtaposed with those from bioassays using local species from the lagoon system in establishing environmental quality standards (EQS) which should stipulate limit of various metals in industrial effluents that can be discharged into the LH and LG. These would include improvement of safety practices across the harbour which would ensure only treated wastes with levels of metals within safe limits based on EQS are permitted to be discharge while diffused sources are curtailed using a broad urban waste management framework which includes construction of waste water treatment plants for urban runoffs prohibition of coastal solid waste dumps and restoration of existing dumpsites.

As for the results of the factor scores, the plots based on each season and method showed distinctive and interesting characteristics of the studied locations based on the type of activities being carried out there and proximity of the respective locations to themselves. For the XRF metals, there was a different clustering based on activities with unique to the LH. Also, there were clustering based on similar environmental conditions with respect to LH and APL which experience incursion of seas water at high tide. In the wet season there were also clusters of XRF metal levels which were simply based on similarity of concentrations of respective metals in different locations. This is because areas which did not have similar activities but which had similar metal concentrations were clustered. Classically sites in the LH and LG are dominated by shipping activities and discharge of domestic sewage respectively. Thus clustering of these sites can only be based on similarity of concentrations.

Similarly, different patterns of clusters were obvious from the *Aqua regia* analysis. Whereas in the first dry season, the clusters formed were all based on aggregation of areas with similar activities having a similar range of recoverable metal concentrations in the dry season; in the wet season, however, some areas with different kinds of activities were clustered together.

With respect to the bioavailable metals (1M HCl), clusters were mostly smaller in the dry seasons compared to the wet season. Also, in the wet season, several locations were unclustered, implying very different ranges of the metal concentrations across the sampled lagoons. This is very plausible in view of the disruptions and turbulence caused by rainfall and irregular tidal activities associated with the wet season. In the second dry season sampling, various kinds of clusters were observed, including those clustered by similar ecological factors (sea water incursion), similar activities and proximity as well as different activities.

It can be concluded that the clusters were generally defined by geographical proximity, similarity in prevailing activities, occurrence of sea water incursion and season. In the wet season, it was more likely to see clusters of areas with different activities and large geographical distance separating them. This may be explained by the fact that the wet season causes perturbation of the water columns due to more turbulence and wind action, which causes mixing and dividing of bottom sediments at the surface. Also diffused sources provide inflow of runoff into the lagoon system during the wet season thereby changing established patterns. During the wet season, high rainfall intensity and volume leads to widespread washing of the soil from industrial, port, urban and domestic sectors of the city and the runoffs laden with assorted pollutants move en masse through the adjourning creeks and canals into the lagoon, particularly in the urban sections of the LG.

6.7 Contamination factor of metals in sediment

The prioritisation of pollution management is typically incumbent on the ability to demonstrate the toxicological properties of the target pollutants. Among the non-invasive techniques employed in the establishment of the negative environmental impacts of pollutants is the demonstration of ecological risks as outlined in the fifth objective of this study. To this end, the contamination and enrichment factors of the determined sediment metal concentrations were calculated with the former, discussed particularly based on site specific activities at various identified hot spots.

Box 4: Objective 5

- To determine the ecological risk status of the Lagos Harbour and Lagoon sediments using the determined heavy metal concentrations.

Low to very high contamination was detected across the sampling area- LH, LG and APL as indicated by the calculated metal contamination factor (C*f*). Specifically, C*f* values were higher in the areas around the ports and tank farms in the LH and in the urbanized LG which receives municipal waste and industrial effluent from the city centre. As expected, a higher contamination factor was recorded using XRF because its calculation was based on total rather than phases which are recoverable and bioavailable. It is noteworthy that considerable contamination was recorded with respect to XRF metal concentrations at a petroleum products tank farm in the LH. Considerable contamination was also recorded for Cd through XRF at the bulk cargo transfer areas of the ports, and this is indicative that shipping activities contribute to Cd enrichment of the LH and the pathway for this might be through accidental and inadvertent discharges of debris and wastes during transfer of cargo.

The findings from this study have also showed that contamination with excessively high concentrations of Cu occurs in the urbanized sections of the LG which receives a range of waste types from the city centres. Abrahim & Parker (2007), reported high contamination factor in Tamaki Estuary, New Zealand and concluded that the sediments have suffered systematic heavy metal contamination following catchment urbanisation. This aligns with the findings of the present study which showed that sediments within the urbanized sections of the LG had a very high degree of metal contamination. Despite their usefulness however, environmental risk factors cannot be used alone to make judgements but should instead be used in combination with other environmental considerations, as has been done in this study and that of Zhang et al. (2007) in the western Xiamen Bay, China.

6.8 Enrichment factor of metals in sediment

The enrichment and contamination factor were assessed so as to determine the extent of contamination of heavy metals in sediment from the study areas. The results of the calculated enrichment factor (E*f*) of total metals analysed (XRF) indicated that As, Cd, Cu, and Pb were minimally enriched while Sn, Zn, Mn were significantly enriched in the sediment and this could possibly be attributed to anthropogenic sources in the LH and LG during the dry season. Chen et al. (2007), who investigated enrichment factors for Hg, Pb, Cd, Cr, Cu, Zn and Al in Kaohsiung Harbour, Taiwan, noted that the enrichment factor was particularly high for Cr, and that the physicochemical properties of the sediment correlated strongly with metal concentrations, suggesting the influence of industrial and municipal wastewaters discharged from the neighbouring industrial parks and river basins.

The metals, As, Cd, Cu, Pb and Sn indicated minimal enrichment, while Fe, Mn and Zn showed moderate enrichment in the sediment of LH and LG during the wet season. This study corroborates the findings of Bawa-Allah et al. (2017) who found that most of the heavy metals (Co, Zn, Cu, Cr, Ni, and Pb) were minimally enriched and As was significantly enriched in the sediments of five zones of the Lagos Lagoon and this was attributed to anthropogenic sources.

The recoverable metals – As, Cd, Co, Cr, Sn and Zn – were minimally enriched in the sediment samples, while Cu, Fe, Mn, Pb and V were moderately enriched in the LH and LG during the dry season of 2013 and 2014 respectively. Recoverable Ni concentrations were significantly enriched in the LH. The high Ni enrichment is expected in the LH in view of the significantly high concentrations measured due to shipping activities. During the wet season, the E*f* of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, and Zn were low, showing minimal enrichment, while V was moderately enriched in the sediment of LH.

The calculated enrichment factor (E*f*) from bioavailable metals – As, Cd, Cu, Fe, Mn, Pb and Zn – were minimal; Cr was moderate, while Ni was significantly enriched in sediment of LH and LG during the dry season-1 (2013). Bioavailable As, Cd, Cr, Cu, Fe, Mn, Ni, and Pb were minimally enriched, while Zn showed moderate enrichment during the dry season 2014. During the wet season As, Cd, Cr, Cu, Mn, Pb and Zn were minimally enriched, Fe and Ni were moderately enriched at the LH and LG. The difference in E*f* values for the respective metals in the sediments may be due to the differences in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediment (Ghrefat et al., 2011). The calculated enrichment factor was in line with concentrations of measured metals, indicating a linear relationship between both factors. The importance of calculating *Ef*, however, lies in the fact that such would provide information of prevalent levels relative to background levels.

Invariably, metals tend to be more enriched in sediments during the dry season, indicating that *Ef* associated with the flux of the lagoon in the wet season could impact measured concentrations and therefore lower/minimal enrichment factor would be calculated. The specific locations contributing to the moderate enrichment of metals in the LH and LG remains principally the same, being isolated to petroleum tank farms, port/shipping activities and influx of municipal wastes respectively.

6.9 Ecotoxicological implications of the findings

From the foregoing it is apparent that some of the heavy metals detected in the LH, LG and APL exceed safe limits for sediment quality. The notable metals exceeding sediment quality guidelines (SQGs) include As and Cd, which, according to Jarup (2003), are of particular concern to human health. Luo et al. (2010) also reported high pollution with As and other metals, including Cd and Pb, in the coastal and estuarine areas of the northern Bohai and Yellow Seas, China. As is a known toxicant to fish with the capability to accumulate in fish gills, muscle, brain and liver (Lian & Wu, 2017). USFDA (1993) stated that fish and other sea foods are the key sources of As exposure. Although low levels can be found in biological systems, high levels as detected in the sediment samples are associated with a range of toxic effects. Mamindy-Pajany et al. (2013) reported in a study involving sediment toxicity assessment using the microtox solid phase test with *Vibrio fischeri* that the toxicity of whole sediment samples was proportional to their arsenic content. The levels of bioavailable As in the assessed sediments from the three study areas (LH, LG & APL) peaked at 2 mg/kg and, at this level, benthic animals are at risk of uptake and histopathological effects, especially due to the fact that their movements can disturb the surficial sediments thereby re-suspending them into the water column. Acute exposure of crabs to 96 hours LC_{50} concentration of arsenite has been associated with histopathological lesions in crab hepatopancrease (Neff, 1997) Inorganic arsenic, in the form of arsenite ions, has been associated with carcinogenicity based on the report of Agency for Cancer Research (IARC,1987), thus, uptake in fish via bioaccumulation poses a risk to humans who feed on them.

With respect to establishing order of toxicity of metals to benthic fauna (*Clibanarius africanus, Tympanotonus fuscatus and Sesama huzardi*) inhabiting the Lagos Lagoon sediment, a study conducted by Otitoloju and Don-Pedro (2002) found Cd to be the second most toxic metal after Hg. Sediment association with Cd was reported to enhance the latter's toxicity to new born estuarine amphipods, *Leptocheirus plumulosus* (Dewitt et al., 1996). Bioavailable Cd concentration measured in the present study peaked at 1 mg/kg in the Lagos Lagoon, above the SQGs for this metal, indicating that the lagoon sediment is a reservoir for the metal. This calls for concern since there are many edible forms of benthic molluscs in the lagoon, especially *T. fuscatus* and *Graphea gazar*, which are routinely harvested as fish for local delicacies. Another metal exceeding SQGs is Cu, the bioaccumulation of which in Cu rich sediments of reservoirs in the Brazilian state of Paulo has been associated with toxic effects to macrobenthic fauna including oligochaes and chironiomid larvae, resulting in deformation of their mouthparts (de Souza Beghelli et al., 2016).

The Lagos Lagoon system is home to an array of fin and shell fishes which are at risk of taking up high concentrations of such heavy metals, thereby posing significant health risks to humans who consume fishes from the Lagoon. This risk is exacerbated by continuous inputs of heavy metals from a range of sources, as observed in this study. Don-Pedro et al. (2004) noted a 2 to 200-fold increase in metal concentrations in the Lagos Lagoon over a 7– years period. It is extremely unlikely that conditions with respect to urban and industrial waste management have improved in that time, given the urban expansion of Lagos and the lack of evidence of improved regulation over the years (Amaeze et al. 2015). Ajagbe et al. (2012) noted that Pb concentrations in the shellfish *Mytilus edulis, Penaeus notialis* and *Callinectes amnicola* inhabiting the Lagos lagoon were 8 to 24 times higher than the WHO safe limit for consumption. Specifically, Ajagbe et al. (2012) recorded a mean of 6.5 mg/kg of Pb in the Lagos Lagoon sediments, compared to 10-13 mg/kg, 10-18 mg/kg and 8-15 mg/kg in the LH, LG and APL in this study, signifying that this metal continues to increase in concentration and therefore ecological risk in the Lagos Lagoon system.

Ni also exceeded SQGs in the harbour area, implying that at their current levels of occurrence, they pose a considerable threat to biota. This is especially noteworthy owing to their bioavailable concentrations of 42 mg/kg. Brix et al. (2004) reported acute toxicity of Ni with LC_{50} of 20.8 mg/l and sub-lethal effects in the gills of rainbow trout's (*Oncorhynchus mykiss*). In natural environments like lagoons, chronic exposures to sub-lethal concentrations are more likely due to dilution factors. The fact that operational discharges of petroleum products during transfers in jetties like those in the LH are typically low, they often go un noticed despite the relatively high frequency of occurrence, therefore posing long term risks to biota. The consistency of these transfers given the importance of refined petroleum products imports to Nigeria makes it a major cause for concern. In another investigation, Ni was found to be accumulated in the gills, kidneys and plasma of fish at sub-lethal concentrations of 384 µg Ni l(-1) and 2034 µg Ni l(-1) over 42 days (Pane et al., 2004). Ni is a known genotoxic agent capable of inducing oxidative stress and DNA damage to cells of living organisms (Latvala et al., 2016) with far-reaching consequences of mutagenicity. Although sediment release during dredging, ship movements and natural bioturbation are typically low, the consistency of these events enhances the chances of occurrence and therefore the risk of accumulation and toxicity to biota. Guerra-García & García-Gómez (2005) reported the presence of Ni (0.008–0671 mg/kg) among other metals in the sediments of the harbour of Ceuta, North Africa, and concluded that there was moderate pollution in the area. This value is much lower than what was reported in this study for bioavailable Ni (i.e 3.0-42.0 mg/kg), a reason which can be attributed to the closed nature of the Lagos Harbour, having only one entrance compared to the harbour of Ceuta which has tow entrance, and the fact that it has been made deliberately deeper than the rest of the lagoon system to allow for the movement of large vessels towards the ports. The prevailing environmental conditions in the Lagos Lagoon system, which includes a moderate to high pH (Okoye, 2007; Poopola et al., 2017), could also enhance the bioavailability or toxicity of the Ni, as was reported in the study of Schubauer-Berigan et al. (1993) which comparatively assessed the impact of pH on the toxicity of selected metals to *Ceriodaphnia dubia, Pimephales promelas, Hyalella azteca* and *Lumbriculus variegatus.* These findings are particularly worrisome in view of the fact that the Lagos Harbour and lagoon system is a major fishing hub and a source of fish which end up in Lagos markets. Continuous consumption of these contaminated fish, if the pollution levels remain unabated, will lead to chronic exposures which might result in changes in the incidence of diseases such as cancers among others. This is particularly of concern in view of the notable effects of heavy metals on public health. Mahurpawar (2015) reviewed the clinical manifestation of effects of exposure and uptake of a range of heavy metals including those that exceeded SQGs reported in the present study. The author noted the target organs of the toxic onslaught of these metals to include pulmonary, nervous, skeletal, connective tissues, excretory and circulatory systems.

Dredging also enhances the transport of metals into the water column, resulting in far-reaching disruption of the natural sediment ecology and the trophic relationships they support. Removal of surface sediments results in the dislodgement of macrobenthic fauna from their natural habitat and this can often cause irreplaceable damage. Macrobenthic fauna play important roles in fixing nutrients and metals into the substratum and their gradual flux into water column in a sustainable way (Karlson et al., 2007). Loss of these valuable species weakens the sediment structure because the biofilms which hold the sediments in place are lost, thereby increasing the rate of erosion into the sea.

6.10 Sustainable remediation and management of contaminated sediments

With due consideration of the levels of heavy metal contamination in the harbour and the Lagos Lagoon system, and the risk which they pose, the need for sustainable management action is quite evident. It is noteworthy that there are currently technologies and processes available for *in situ* and *ex situ* remediation of heavy metal contamination (Peng et al., 2009). The findings from the present study are indicative of the need for remediation, particularly of metals such as As, Cd, Ni, Pb, Sn and Zn which were found to exceed the USEPA SQGs. In view of the nature of the pollution spread in the Lagos Harbour and the lagoon system, both *in situ* and *ex situ* methods are recommended. This is feasible in so far as this study has identified hotspots of these metals in the sediments. Remediation action combined with source reduction activities such as waste water treatment before discharge, enforcement of IMO convention requirements such as ballast and bilge management, prevention of unregulated dumping of refuse and dredge spoil, among others, is germane in sustainable heavy metal pollution management in this system. A key factor in source reduction also lies in public enlightenment and effective enforcement of extant maritime laws of Nigeria.

In view of the busy nature of the ports in the Lagos Harbour and the fact that dredging is often done to restore depth, a combination of *in situ* and *ex situ* remediation is advised. This would involve restoration of dredged spoil using techniques such as *ex situ* washing which is augmented with chelating agents and biosurfactants which has been reported to be effective in removal of metals such as Cd, Cu, Ni, Pb and Zn (Pollettini et al., 2006; Dahrazma and Mulligan; 2007). The choice of soil washing also lies with the relative ease with which this can be done, taking account of the technological challenges in Nigeria and the fact that the coarse component of the sediments is considerable (Peng et al., 2009) noted that this technique is suitable for sediments rich in sand and gravel). After *ex situ* sand washing, the clean sand can them be applied for various other uses such as construction in urban areas where sand is an important resource.

Given that the dredging exposes the sediment such that metals trapped underneath are subsequently resuspended into the water column, it will also be important to incorporate *in situ* sediment amendment using materials such as apatite, zeolites, steel shot, or beringite to lower metal mobility and bioavailability in sediment by precipitation or sorption, thereby decreasing their solubility (Peng et al., 2009). Limestone capping of sediments have been reported to be effective in stabilizing metals such as Zn (Park et al., 2018) and given the considerably high concentrations of Zn detected in the sediment samples of the LH, this technique is advised. The same authors noted the ability of activated carbon to stabilize the sediments from release of Cd and Pb and interrupts the release of Cr, Cu, Ni & Zn. Although this technique does not efficiently trap heavy metals, it reduced their bioavailability and rate of mobility prior to another round of dredging. Other efficient amendment agents include alkaline organic treatments using lime-stabilized biosolid (LSB) and N-Viro Soil (NV) (Basta et al., 2001).

In addition, phytoremediation should be conducted in the shallower areas where plants may be able to take root. This is very feasible because these areas are out of reach of large vessels and can remain relatively undisturbed during remediation. The plants in conjunction with microorganisms inhabiting the rhizosphere area around their roots will enhance metal removal from coastal sediments (Khan, 2005). Also, it has been reported that plants are important in making dredged sediments suitable for soil-bed leaching, thereby augmenting the rate of metal uptake, with good success rate in solubilizing Ni, Cu and Cr (Loser et al.,2001). Their result also noted that sediment conditioning with plant *Phragmites australis* caused similar metal solubilisation with long-term store sediments (Loser et al.,2001)

The challenge with the various remediation techniques often lies with the specificity of remediation technique for few metals. Thus remediation process is often experimental and laborious with huge costs prohibiting their application. The selective nature of these remediation chemicals implies that there is a risk of complication of the chemical characteristics of the environment if not methodically applied by experts. Thus notwithstanding the importance of remediation in restoring environmental status, a better management system for metals is waste reduction at source. It is incumbent on State and Federal regulators to enforce extant laws and continually evolve new ones to protect our valuable aquatic resources.

6.11 Limitations of the study

6.11. 1 Scientific limitations

The scientific limitations identified in this study are outlined below.

- The non-uniformity in sample site numbers limits the application of several statistical analysis in respect to the distributions of heavy metal concentrations. More sampling sites were established in the LH, being the main focus of this study, followed by the LG, while the size of APL also limited the possible number of sampling points due to its significantly smaller volume and low levels of associated anthropogenic disturbances. This led to a wide-range of variations statistically in data that were distributed in the sampling sites, locations and seasons. However, the data were normalized before analysis.
- This study was also limited by unequal sampling patterns in terms of seasons. Two dry seasons (DS-1 and DS-2) and one wet season (WS) were sampled over an eighteen-month period. This was due to the time and logistical constraints during the program involving sampling in Lagos and conveying samples abroad for analysis (i.e. to the University of Portsmouth).

- The frequency of sampling was limited to once per season. A more effective sampling regime would have involved frequent sampling for monitoring.
- There were no updated local standards which set environmental quality objectives for marine areas such as harbours. Thus, international standards were adopted for the study.
- The study did not involve field or laboratory ecotoxicology assessment, rather inference was drawn from results of chemical analysis.

6.11.2 Administrative and logistics challenges

The other limitations to this study include:

- As a result of the large sample size and surface area of the Lagos Harbour and Lagoons, sample collection across all points from non-selected sites in this investigation are limited. Nonetheless, this study utilized the most sampling points of any study in Lagos Harbour and thus is able to offer more comprehensive data than in any previous work.

- More time was expended identifying hotspots, which led to time constraints, due to the limited time given for field work overseas.

- Availability of resource materials to undertake the field work were one of the main challenges faced. If additional resources were available, frequent sampling would have been undertaken, instead of seasonally. In practice, the sampling was carried out three times over eighteen months.

- Protocol and procedures involved in bringing samples from abroad also presented administrative challenges, due to UK regulations.

CHAPTER SEVEN: SUMMARY

7.1 Introduction

This chapter: (1) highlights the concentration of heavy metals in different locations with respect to their different sources; (3) assesses the results and their implications; (4) offers recommendations for future studies; and (4) recommendations for Nigerian regulatory agencies responsible for the monitoring and management of marine pollution as well as harbour management systems.

7.2 Quality assurance- certified reference materials

The CRMs allow excellent representations of the varying environmental conditions observed at LH, LG and APL. The extraction with *Aqua regia* certified with HR-1 and PACS-2 is more efficient than extraction with 1 M HCl. This showed that metals contained in sediment that were extracted with *Aqua regia* were digested with high percentage recoveries. The most significant metals extracted from sediment by *Aqua regia* were As, Pb, Zn and Cu . When 1 M HCl was used to extract metals from the sediment the most effectively recovered and significant labile metals were As, Pb, Cd, Mn, Fe, Cr and Ni, with the highest percentage recoveries, certified by HR-1 and PACs-2. The 1 M HCl and *Aqua regia* methods measured with HR-1 and PACs-2 can therefore provide researchers with reassurance about the general measurement procedure, as well as indicate accuracy and precision, allowing comparability between methods over time.

7.3 Water quality parameters

The water quality parameters revealed significantly low levels of dissolved oxygen at LH and LG; findings that are associated with shipping, oil tank farms, large vessel discharge, recreation and aquaculture activities. The lowest dissolved oxygen levels were in the coastal areas of LH and LG, which can be attributed to anthropogenic activities, in comparison to the moderate dissolved oxygen levels at APL (control), indicating minimal anthropogenic influence. Variations in salinity indicated direct seawater incursion into LH; in contrast, LG is further inland and is therefore recharged by inflows of water from inland rivers and creeks which mixes with seawater to become a brackish water estuary. During the rainy season salinity values for the most inland sections of the LG remain at 0 ppt for a few months of the year.

7.4 Particle sizes and total organic carbon and nitrogen

The particle sizes were comprised of clay, silt and coarse sand particulates, with the largest percentage of clay, silt and coarse sand in LH where routine maintenance dredging to create room for large cargo carrying vessels has led to the loss of most of the surface layers of the substratum. High percentages of sand and coarse sand particulates were found in APL (control) being under tidal influence of the Atlantic Ocean which washes salt water alongside sand from coastal beaches into the lagoon. The C: N ratio indicated that the LG had a higher organic content than LH and APL. The relatively higher C: N ratio can be attributed to being a recipient of sewage and nutrient rich waters from municipal canals, dumpsites and inland rivers and creeks respectively.

7.5 Comparative assessment of metal concentrations in sediments of Lagos Harbour, Lagos Lagoon and Apese Lagoon using Sediment Quality Guidelines

The significant elements studied in this research were As, Cd, Cr, Cu, Co, Fe, Pb, Mn, Ni, V and Zn, which were analysed and extracted from the three sites (Lagos Harbour, Lagos and Apese Lagoons). The XRF analysis showed that in both LH and LG, Cu and Zn significantly exceeded the threshold effect level (TEL) set by the National Oceanic and Atmospheric Administration (NOAA)/Canadian sediment quality guidelines (CSQGs), compared to the control site (Apese Lagoon) where only Cu exceeding the TEL. As, measured by *Aqua regia* extraction, also significantly exceeded the TEL across the three sites- LH, LG and APL. While, the bioavailable metals (measured by 1 M HCl) were below the TEL across the three sites. The trend for the metal concentrations were (in decreasing order): XRF > *Aqua regia* > 1 M HCl for all three water bodies.

7.5.1 Anthropogenic sources and pathways of metals within the Lagos Lagoon

The concentrations of heavy metals were found to be associated with anthropogenic activities. This was my motivation for the initial investigation, especially within LH and the urbanised part of LG, where human activities are most intense (such as shipping, petroleum products tank farm operations, industrial discharges, dredging, sand mining, saw milling, domestic activities, fishing, transportation, mobile industries, stormwater run-off, municipal sewage solid waste dumps and coastal slump settlements). The metals find their way into the LH and LG through petroleum products spills at the harbour, discharges associated with cargo transfers, port runoffs, resuspension of sediments during Lagos Harbour channel maintenance dredging operations, leaching of anti-fouling paints and rusted metals from vessels and wrecks, inflows from coastal runoffs, leachates from coastal dumpsites, discharge of domestic and municipal sewage, especially after heavy rainfall, as well as poorly treated industrial effluents from large and small scale industries. Figure 61 below describes the major anthropogenic pathways of metals into the investigated water bodies of Lagos Lagoon.

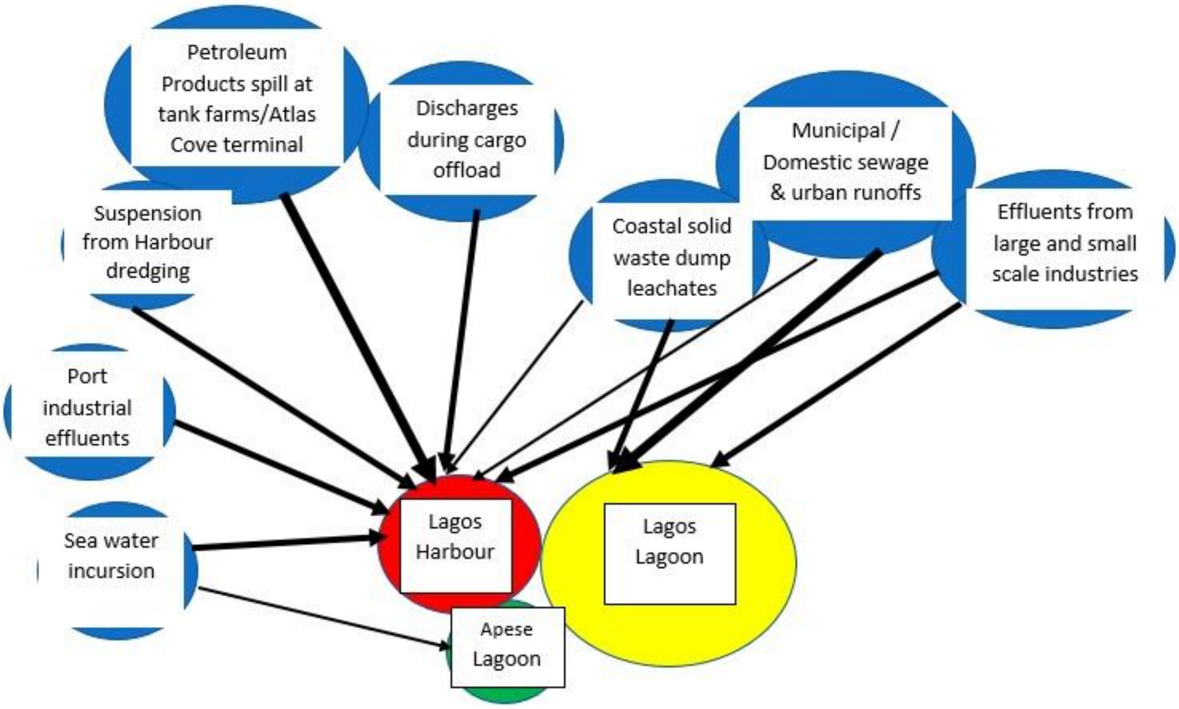


Figure 61: Conceptual diagram showing the intensity of metals pathways in the Lagos Harbour (LH), Lagos Lagoon (LG) and control, Apese Lagoon (APL) based on anthropogenic activities.

From the results, it is apparent that the Lagos Harbour and its associated lagoons are recipients of diverse forms of contamiants which are associated with respective coastal activities or remote activities which are affliated with the caostline. These contaminants eventually end up in receptors- water, sediment and biota - as conceptualized in Figure 62.

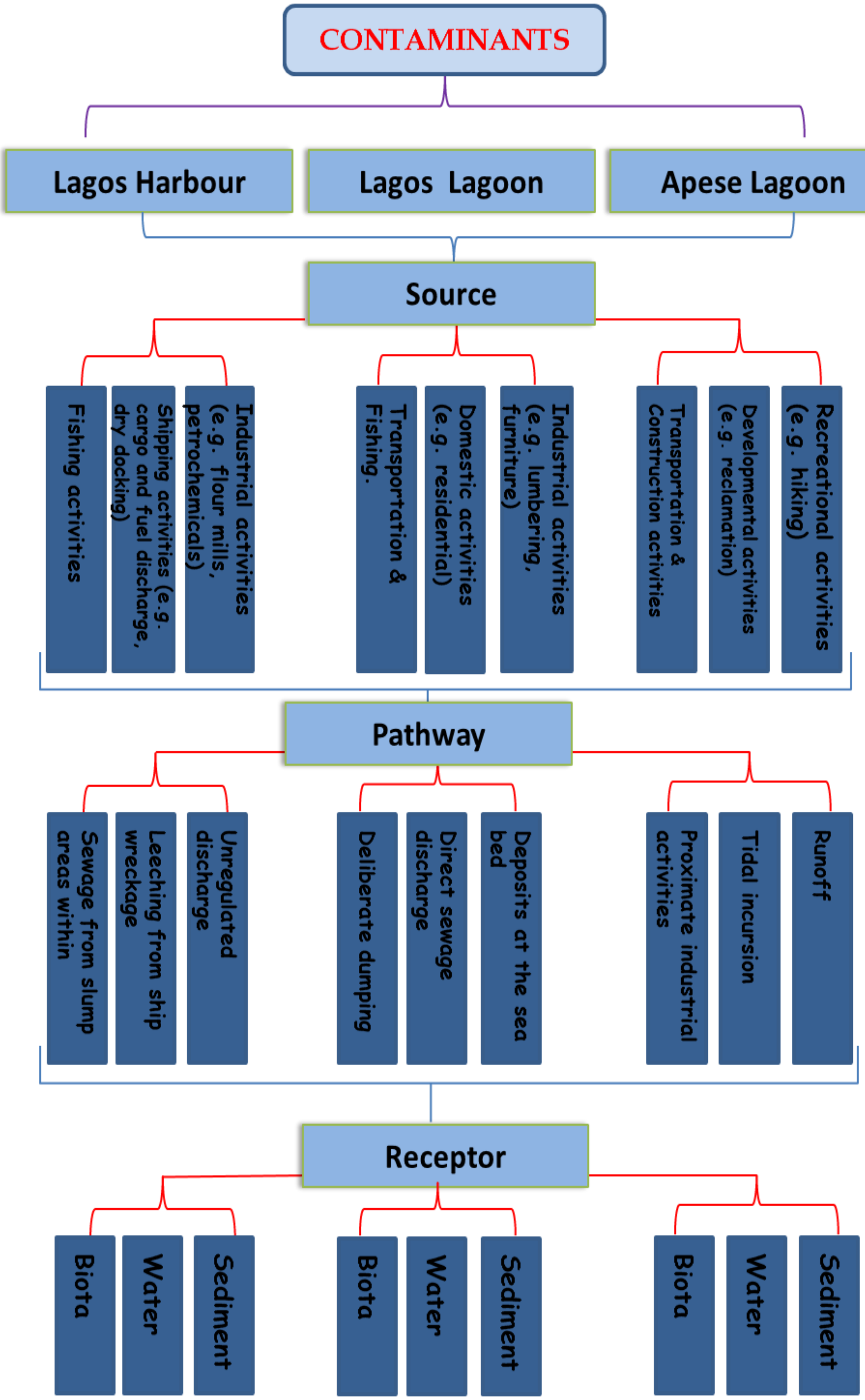


Figure 62: Conceptual model of sources, pathways and receptors of contaminants in the study and surrounding areas of Lagos Lagoon.

7.6 Contamination factor of metals in sediments

The calculated contamination factor (C*f*) indicated low to very high levels of contamination in LH as well as most of the LG and, occasionally, in the APL sediments compared to historic levels. The highest contamination factor in DS-1 (2013) was for bioavailable Ni (C*f*=5.5) at a Petroleum products tank farm in LH. In WS (2013) XRF analysis revealed sediments that were highly contaminated with Cd at two sites in LH and one site in the LG. *Aqua regia* analysis also revealed high levels of Cu contamination in the sediments from LG (C*f*, from 6.58 to 17.95) and APL (C*f*=7.23) during the WS. Results from the DS-2 (2014) showed generally higher levels of C*f.* For XRF metals, Cd showed considerable contamination at some sites in LH and LG as well as very high contamination for LG. Total (XRF) Zn had moderate contamination at many sites across the LH and LG and very high contamination at two sites in LG. Sediment samples with AR extraction showed very high contamination with Cu at several sites in LH and at a site in LG.

7.7 Enrichment factor of metals in sediments

The enrichment factor of metals in the sediment was measured in the surficial sediments from LH and LG in order to identify metals with significant enrichment from anthropogenic sources. The elements with minimal enrichment were As, Cd, Cu, Ni, Pb, while those with moderate enrichment were Fe, Mn and Zn, analysed with XRF. *Aqua regia* analysis, meanwhile, indicated that the metals with minimal enrichment were As, Cd, Co, Cr, Sn and V, and those with moderate enrichment were Fe, Mn and Zn; while Ni was significantly enriched; and Cu was extremely enriched. 1 M HCl analysis indicated that bioavailable metals with minimal enrichment were As, Cd, Cu, Fe, Mn, Pb and Zn; while Cr had moderate enrichment. The most effective method to determine high levels of enrichment of metals and metalloids in the sediment was *Aqua regia* in the following order: LH > LG, with the metals of APL used as background.

7.8 Interpretations of the relationship and interactions of the elements

1 M HCl analysis showed that the correlated significant elements at the labile phase in the sediment were Pb and total nitrogen distributed in silt and coarse sand, predominantly in Lagos Harbour. *Aqua Regia* analysis revealed that Mn and total nitrogen were significantly

accumulated in the silt and clay*;* while XRF showed that As and Fe were largely distributed in the clay and coarse sand. Oxides of Fe and Mn are typical components associated with the basement materials in this area and this was used to explain their importance in the nutrient retention and ecology of the substratum, particularly in LG where extensive dredging has not damaged most of the substratum unlike LH where the harbour management operations have destroyed most of the substratum and displaced the microbenthic fauna. The total carbon was significantly deposited in the sediment of the Lagos Lagoon. The cluster analysis revealed similar sources of discharge emerging from sections of LH in the form of heavy shipping and industrial activities, as well as in the urbanised parts of the LG and APL (control site). These findings indicate similar sources of pollution from anthropogenic activities, except for shipping and bulk cargo transfer operations which are unique to the harbour.

Using XRF, the interrelationship of the metals and particle sizes showed that As, Cd, Cu, Mn were significantly loaded in the coarse sand and silt. With *Aqua Regia,* As, Cr, Cd were bioavailable in clay, silt and coarse sand. While 1 M HCl measured elements of significance such as, Cr, Cu and Fe, distributed in clay, silt and coarse sand respectively. The factors score plot showed clusters which indicated that metal concentrations were determined/ affected by type of anthropogenic activity, geographical proximity and sea water incursion, although during the wet season diffused runoff entry makes the clusters rather weaker.

7.8.1 Overall assessment of the study locations

The overall assessment of this investigation revealed that LH and LG are susceptible to pollution from heavy metal contamination. This is due to persistent anthropogenic activities within the different regions of the lagoon; activities that are increasing due to industrialisation and urbanisation. This is particularly the case for As, Cr, Cu, Pb and Zn, each of which exhibited a significant increase in concentration when measured using the 1 M HCl and *Aqua Regia* methods. For LG, Pb showed a consistent rise in concentrations, which corroborated the previous preliminary investigation (Bamanga et al., 2014), and this increase resulted from an established source within the LG. The LH and LG waters are at risk, given indication linking the concentrations of toxic heavy metals to reduced levels of marine biota in Lagos Harbour. The threat posed by the growth in industrialisation, however, includes increased volumes of shipping and fishing activities within the LG. This is assuming a critical dimension in view of the uncertainties arising from unrestricted discharges into the Lagos Lagoon, which affect marine waters, and marine biota such as fish and birds.

Metal concentrations were higher in the dry season than in the wet season. This is linked to the increase in water volume during the wet season which dilutes concentrations, as well as the influx of water from rivers and other tributaries around the Lagos area, and salinity changes.

7.8.2 Comparison of metal analysis using XRF, *Aqua Regia* and I M HCL

This study was intended to investigate and characterise heavy metal on the Lagos Lagoon system by employing a combination of extraction techniques and highly efficient analytical equipment. To this end, the sediment samples were analysed using XRF to obtain the total values of the metals in the environment as well as extracted with either *Aqua Regia* and 1 M HCl in other to measure recoverable/extractible and bioavailable concentrations. The latter are more important than XRF measurements because XRF provides a measure of the total concentrations of metals inherent in the environment, in practice a good percentage of such analytes cannot be recovered by available technologies. Hence measurement of recoverable and bioavailable concentrations is more important because they give an idea of the amounts of the measured metals which are actually accessible or available for uptake by biota.

From the results obtained, XRF analysis yielded the highest concentrations for the metals analysed, as can be observed in Section 6.5. Typically, XRF analysis involves a dry process whereby the total metal in the soil/sediment samples is analysed without digestion. This is unlike the case of extraction with AR which uses a combination of two acids to extract metals from organic and inorganic complexes which they form and 1M HCl system which uses only a weak acid to extract bioavailable components of the soil/ sediment profile. Thus, the typical recovery efficiency for metals with the three analyses were as follows: XRF> *Aqua Regia*>1 M HCl. There are occasional situations, however, where higher concentrations can be obtained with 1M HCl extraction compared to *Aqua Regia*. For instance, in the DS-1 (2014) samples, higher concentrations of Ni were detected using 1M HCl in sediments from the LH.

7.8.3 Bioavailability and bioaccessibility of metals in the LH

The metals from the *Aqua regia* extraction represent the bioaccessible forms, which is the maximum amount that can be extracted for quantification. Considerable amounts of these metal species were measured in the harbour. High concentrations of the metals were also recovered using 1M HCl with no significant differences ($P<0.05$) with respect to values from the AR extraction. This implies that much of the recoverable metals are bioavailable, meaning that there is a high risk of metal uptake by the biota which are already under displacement stress from routine dredging of the channel. Two factors will moderate the bioaccessibility of the metal, however; specifically, the extensive damage to the substratum means that much of the surface organic matter have been lost and thus retention of accessible metals is reduced. On the other hand, the routine dredging will ensure the continuous re-suspension of the metals into the water column, making them accessible for uptake by benthic and pelagic fauna.

7.8.4 Implications of the findings

The implication of these findings is that sediments in areas experiencing high levels of shipping and urbanisation are faced with a potential threat of contaminants from inorganic compounds, depending on the intensity of human activities. The few significant heavy metals (bioavailable and recoverable) detected have shown a significant increase in concentration levels in both LH and LG sediments, which shows that the sediments of these areas are at risk of continuously getting contaminated; and possibly, of becoming polluted, depending on the concentrations. This has implications for water quality, and for the sustainability and quality of fisheries resources. The release of metals from sediments will result in their uptake in shellfish, pelagic fin fishes as well as planktons followed by transport up the aquatic food chain through biomagnification.

The implications of increased sediment pollution could also lead to revenue loss, particularly from foreign vessels that patronise the Lagos Ports, including tourism due to loss in aesthetics and biodiversity. The potential impacts are particularly high in humans because of the practice of direct harvesting of shellfish such as periwinkles and oysters in the lagoon for local delicacies. Further economic loss could come from declining fishing activities, particularly in the harbour and urbanised part of the lagoon where fishing is a source of subsistence and income. In the past 10-15 years there used to be substantial fishing activities within the Lagos Harbour area; however, fishermen now have to go beyond their initial fishing territory (harbour area) in order to obtain substantial catch. Osae-Addo & Abigail (1992) earlier reported drastic reductions in fish catch from 1,000,000 kg/year in 1980 to 100,000 kg/year in 1990 more than two decades ago, amounting to a decline by almost 90 %. This study has elucidated the unsustainable uses to which the Lagos Lagoon has been subjected to. The study therefore provides an update on current concentrations with evidence of their distribution and transport pathway and risk implications. The findings herein which provide resources for fact-based regulation by port safety officers and novel information to researchers who seek to increase our knowledge of bio-geo-ecological processes in Lagos Harbour and the entire lagoon system.

CHAPTER EIGHT: CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion

The main objectives of this study were to assess sediment geochemistry in Lagos Harbour, Nigeria, for selected heavy metals and metalloids (As, Cd, Cr, Co, Cu, Pb, Sn, Mn, Ni, V and Zn). The total (XRF), recoverable/extractable (AR) and bioavailable (1 M HCl) concentrations were researched in order to understand the spatial distribution of these elements and to determine their pathways, as well as the ecological risks they pose. As earlier identified, the rationale for the study was anchored on the need to determine the impacts of shipping and other activities within the LH on sediments in LG together with a relatively undisturbed control site at Apese Lagoon (APL). Based on the results obtained from the respective analyses conducted, ecotoxicologically relevant inferences were drawn as justification for remediation exercises to ensure that the harbour and the associated lagoon are sustainably utilized, and it remains capable of sustaining viable biota populations.

The findings indicated significant concentrations of extractible and bioavailable metals (As, Cd, Cu, Ni, Zn and Pb) in LH sediments compared to the international guidelines of NOAA and CSQG. The distribution of heavy metals showed higher concentrations in the LH sediments, followed by the urbanized part of LG, with minimal or low concentrations in the control zone (APL). The data obtained using the XRF (As, Cd, Cr, Cu, and Mn), AR (As, Cr, Cu and Zn) and 1M HCl *(*As, Cd and Cu) indicated significant variations across seasons in LH, with the dry season generally recording higher concentrations. The results showed that the distributions of heavy metals are influenced by anthropogenic activities, with petroleum tank farm operations and cargo offload being the primary contributors of spills and discharges through which the metals enter the substratum in the LH. These distributions also correlated with different particle size fractions, with greater accumulations of heavy metals in clay and silt than in sand and coarse sandy sediments, which indicates pollution from human activities as the main source. The measured concentrations of metals in the sediments were found to have low to very high contamination factors, at odds with the historic background concentrations. As, Cd, Cu, Mn, Ni and Zn showed considerable to very high contamination factors in some hotspots in LH and LG. Most metals exhibited minimal to moderate enrichment factors in the sediments, while Ni was significantly enriched in the sediment of LH and LG during dry season-

1 (2013). The *status quo* is unsustainable and portends present and future threats to human and ecosystem health. The continuous dredging of the LH poses a particularly unsustainable threat to the macrobenthic fauna communities which are vital to maintaining the utility and elasticity of the sediment, especially with respect to the ability of the water body to recycle nutrients and support important trophic relationships. Many of the measured heavy metals have been reported to be acutely toxic to aquatic animals and have equally been shown to have sub-lethal effects even in cases of continuous release at low concentrations.

Urgent regulatory action is advised to mitigate the rate of metal inflow. This includes source reduction, public engagement and enforcement of extant laws, in combination with both *in situ* and *ex situ* remediation techniques to ensure sustainable support of life forms in the water body and protection of public health, especially of those whose delicacies include sediment dwelling molluscs.

Hitherto, studies involving heavy metals in the Lagos Harbour and lagoon system did not present coherent data which were able clearly to indicate pathways of metal entry and link them with the distribution of the respective metals. This study has been able to do so using geochemical contour mapping to elucidate relationship between sources, pathways and hotspots for specific metals. Such precise information presented in the thesis would guide understanding of the scope of the threat to biota and formulation of effective remediation programmes for this water body.

8.2 Recommendations for the development of policy and guidelines

It is recommended that policy and guidelines are developed and put in place for the protection of the marine environment and in particular the harbour management system in Nigeria:

1. This study recommends the need for further investigation through periodic follow-up testing of Lagos Harbour sediments. This should entail a more frequent sampling of marine sediments. This strategy will enhance monitoring and provide more detailed information, especially for the determination of bioavailability data and ecological risk

of heavy metal concentrations in marine sediments when compared to international standards.

2. Due to the combined (and more informative) methods of extracting the heavy metals components from the sediments, the results of this study are recommended as baseline data that will be useful for the ongoing monitoring of water and sediment quality of Lagos Harbour and Lagoon.
3. Given the constant dredging of Lagos Harbour, the dredged materials must be tested for chemical characterisation, especially for heavy metals and organic pollutants, to establish their concentrations before disposal options and decisions are taken.
4. The synthesis and adoption of the findings from this study will also help in the implementation of the London Dumping Convention (LDC) on the prohibition of dumping of any kind of waste materials, including dredged materials, either at the sea or on shore, without appropriate permission from regulatory authorities. The monitoring option is to ensure compliance and enforcement in line with the International Maritime Organisation (IMO) Convention. This is binding on IMO member states, and Nigeria is a member of the IMO and signatory to most of these Conventions including the LDC.
5. Given the ecological risks posed by the constant dredging of Lagos Harbour in order to maintain a navigational channel for large vessels, dredging exercises must be minimised to not more than 2-3 times in a year or when it is expedient. This is recommended in order to reduce the unnecessary disturbance of the bottom sediments, which increases the release of contaminants within the water column, putting them in a free-state that will result in their bioavailability and the pollution of the water column.
6. It is recommended that the regulatory bodies responsible for managing and regulating harbour activities in Nigeria, such as the Nigerian Ports Authority (NPA) and the Nigerian Maritime Administration and Safety Agency (NIMASA) should put in place basic waste management and monitoring measures, and strengthen the enforcement of existing laws regarding marine pollution; while also ensuring the provision of adequate port reception facilities in order to minimise the further contamination of Lagos Harbour from shipping activities.

7. The Nigerian government agencies responsible for the management of the harbour area should consider funding research of this nature to develop guidelines that would protect the ecosystem and help in remediating the already polluted sediments in other to ensure marine environment sustainability across all ports in the nation.

8.3 Future research

Investigation of heavy metals in the marine sediments of Lagos Harbour area was part of an initial process of baseline development for this study area. Hence, further research is required for a more detailed assessment of the Lagos Harbour sediments, including:

1. Investigation of organic pollutants, for example, total hydrocarbon contents (THC) and polycyclic aromatic hydrocarbons (PAHs) in Lagos Harbour sediments which may serve as potential sources of pollution, and which could have a direct source/link with heavy metal pollution.
2. Determination of heavy metal concentrations in the tissues of marine biota of Lagos Harbour and Lagoon waters needs to be extensively conducted in order to ascertain the fate of the assessed metals. This is in view of the health implications of the accumulation of heavy metals in marine biota, such as fish and shellfish, that are consumed by humans, given that the combination of accumulation and consumption can lead to bio-magnification (Okoye, 2015).
3. Determination of the nutrients within the sediments in Lagos Harbour is also recommended, given currently limited data on nutrient concentrations and transport. This will also be helpful for understanding the links between the high concentrations of nutrients entering the Lagoon as a result of the numerous discharges of wastewaters within the municipality of Lagos, and the associated seasonal algal blooms in the Lagoon.
4. Investigating marine anti-fouling compounds, such as organotin (e.g., tributyltin (TBT), in Lagos Harbour sediments is also recommended for future work. Anti-fouling paint is associated with shipping activities which uses organotin in the painting of ships hulls in order to minimize attachment by invasive species and the growth of organisms found in ballast water and sediment discharges. Recently, the use of such anti-fouling paints has been banned by the IMO (IMO, 2002) because of its effect on marine biota, sediment and water quality.

5. Determination of the sedimentation rate of the Lagos Harbour system is important in order to determine the rate of sediment movement, particularly from the river and estuarine environments into the Lagos Harbour area. This would provide a scientific basis for channel maintenance dredging rather than the current practice of regular dredging even when this may be unnecessary.
6. In view of the findings with respect to sediment heavy metals which exceeded SQGs in the various section of the Lagos Harbour and Lagoon system, there would be need for further research detailing the ecotoxicological effects of these metal concentrations on the biota inhabiting the sediments. This should be focused on the mechanisms by which the metals are released from sediments into the water column, the methods of trophic transfers and depuration rates among species which accumulate them (assuming the causal factors of their release are controlled). A study comparing the relative contribution of natural transports and anthropogenic activities on metal distribution in the Lagoon will also add value to available data.
7. There is need to conduct research into the development of locally feasible and appropriate remediation techniques to manage the levels of heavy metals and other pollutants in the sediments of the Lagos Harbour and other sections of the Lagoon systems as may be required. This should include a review of all available remediation techniques in this context, cost- benefit analysis, laboratory pilot studies, ecological modelling among others. Also, the role of microbial communities in metal disposition in sediments needs to be elucidated.

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APPENDICES:

Appendix 1: Relevant IMO Conventions with respect to marine pollution as applied to Nigerian state.

Serial /No.	IMO Conventions	Applications/purposes	Nigerian Status	Remarks
1.	MARPOL 73/78 (Annexes 1-6)	Marine pollution prevention	Domesticated	Not fully Implemented
	a) Annex I	Prevention of oil pollution from ships	Domesticated	Partially implemented
	b) Annex II	‘Prevention of noxious substance in bulk from ships	Domesticated	Not implemented
	c) Annex III	Prevention of harmful substance in packaged form from ships	Domesticated	Not implemented
	d) Annex IV	Prevention of sewage discharges from ships.	Domesticated	Partially implemented
	e) Annex V	Prevention of garbage from ships	Domesticated	Fully implemented
	f) Annex VI	Prevention of air emissions from ships	Domesticated	Not implemented
2	London Dumping Convention (LDC)	Prohibition of dumping of wastes in marine environment	Domesticated	Partially implemented
3	Ballast Water and Sediment (BWM)	Control of ships ballast water and sediment	Ratified	Partially implemented
4.	Wreck Removal Convention	Wreck removal convention	Ratified	Partially implemented
5.	Anti-fouling paint Convention	Prohibits use of harmful organotin in anti-fouling system.	Domesticated	Not implemented

Source: www.imo.org

Appendix 2a: Previous investigations of heavy metals in Lagos Lagoon.

Serial Number	*Locations*	*Unit*	As	Al	Cd	Cr	Cu	Fe	Hg	Pb	Zn	*Environmental media (water, sediment and biota)*	*Analytical Methods*	*Instrument employed*	*References*
1	*Lagos Lagoon*	mg/kg	NA	NA	0.04-15.5	2.9-167	1.9-132	NA	NA	NA	NA	Sediment	Analytical (Acid digestion)	AAS	Ajao *et al,* 1996
2	" "	mg/L	NA	17	0.39	0.33	23.8	1.57	NA	10.6	0.143	Water (wet season)	Analytical (Acid extraction)	1CP-OES	Nkono *et al,* 1999
		mg/l	NA	214.9	1.98	40.2	19.9	1.57	NA	13.7	0.234	Water (Dry season)	"	"	Aderinola *et al,* 2009
3	" "	mg/kg	0.08	NA	1.15	0.62	0.6	19	NA	0.45	0.73	Sediment	APHA	AAS	"
4	" "	" "	0.36	NA	0.27	0.07	0.38	3.58	NA	0.06	0.08	Biota (fish)	"	"	"
5	" "	mg/L	0.01	NA	0.35	0.06	0.2	1.41	NA	0.26	0.53	Water	"	"	"
6	" "	mg/L	NA	NA	0.17	0.039	NA	NA	NA	0.043	0.107	Water	Analytical method	"	Williams & Edobor-osoh,2013
7	" "	mg/kg	NA	NA	ND	NA	NA	19.02	NA	17.98	13.66	"	Acid digestion	AAS	"
8	" "	"	NA	NA	ND	NA	12.23	12.23	NA	1.47	25.72	"	"	"	"
9	" "	mg/L	NA	NA	ND	NA	NA	1.17	NA	ND	0.1	"	"	"	"
10	" "	mg/kg	NA	NA	NA	NA	NA	NA	NA	25.46	NA	Biota (fish	Digestion (APHA)	"	Ajagbe *et al,* 2012
11	" "	"	NA	NA	NA	"	"	NA	NA	0.001-0.05	"	Sediment	"	"	"
12	" "	"	"	"	"	"	"	"	"	0.008-0.035	"	Water	"	"	"
13	" "	mg/L	NA	NA	NA	NA	NA	NA	0.27-0.40	NA	NA	Water	Acid digestion	"	Emmanuel & Samuel,2009
14	" "	mg/kg	28	NA	3.7	6.0-87	3.0-231	ND	NA	2.0-146	9-366	Sediment	" "	ICP-OES	Olatunji & Abimbola, 2010

NA-Not available, **ND**-Not detected

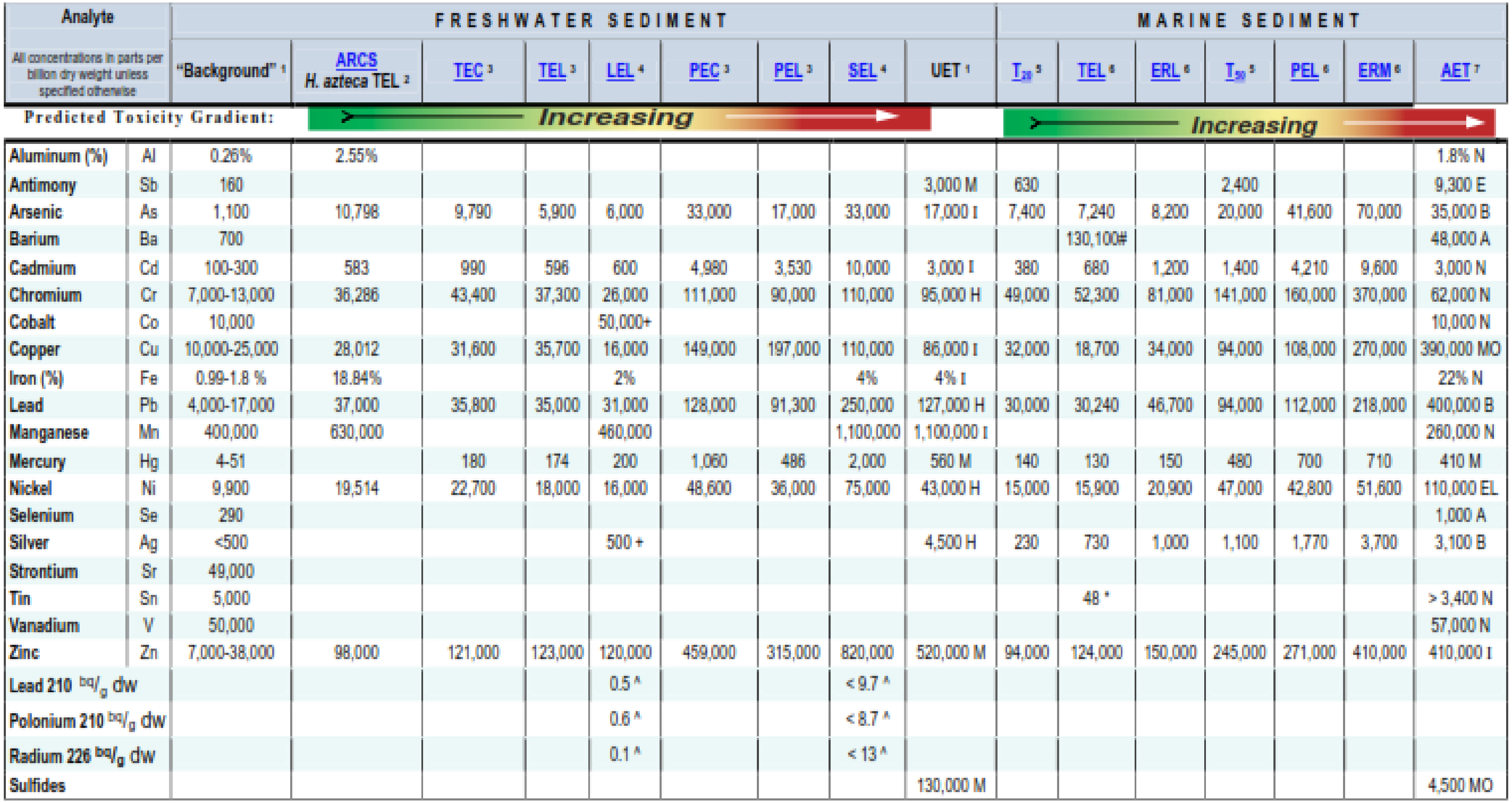
Appendix 2b: Previous investigations of heavy metals in Lagos Lagoon (continued).

Serial No.	*Locations/ Zone*	Unit	Cu	Cr	Zn	Pb	As	Cd	Hg	Fe	Al	*Environmental media (water, sed. or biota)*	*Analytical Methods*	*Instrument employed*	*References*
15	Lagos Lagoon University of Lagos	mg/kg	NA	5.65	NA	17.75	NA	13.4	NA	44.68	NA	Sediment	Acid digestion	AAS	Uaboi-Egbemi et al.,2010
16	Ebute-metta	mg/kg	NA	6.81	NA	22.25	NA	14.63	NA	38.75	NA	Sediment	Acid digestion	AAS	Uaboi-Egbemi et al.,2011
17	Ijora	mg/kg	NA	9.06	NA	20.5	NA	12.62	NA	12.62	NA	Sediment	Acid digestion	AAS	Uaboi-Egbemi et al.,2012
18	Lagos Lagoon	mg/kg	132.4	672.1	775.5	483.9	NA	16.5	NA	93.1	NA	"	"	"	Okoye *et al* ., (1991)
19	Lagos Lagoon	mg/L	NA	8.065	1.055	BDL	NA	0.074	NA	8.065	NA	Water	APHA	AAS	Lawson E.O (2011)
20	Lagos Lagoons (canal waters.	mg/L	NA	0.30-0.60	N/A	1.08-9.40	NA	ND	N/A	N/A	N/A	Waters (Sea, water & canal)	APHA	AAS	Ajibola *et al(2005)*
21	Lagos Lagoons (water samples	mg/L	NA	0.42	N/A	1.97	N/A	N/D	N/A	N/A	N/A	Waters (Sea, water & canal)	APHA	AAS	Ajibola et al. *(2005)*
22	Lagos Lagoon(Sea water samples)	mg/L	NA	0.48	N/A	4.24	N/A	N/D	N/A	N/A	N/A	Waters (Sea, water & canal)	APHA	AAS	Ajibola et al. *(2005)*
23	Lagos metropolis	mg/kg	0.11-0.27	5,285.10	702.2	2,258.60	N/A	537.8	N/A	161,717.90	NA	Industrial effluents	Survey data	Qualitative	Oyewo & Don-Pedro (2003)
24	Chemical allied sources	mg/kg	0.011-0.27	ND	ND	ND	NA	NA	0	1.82-4.4	NA	Chemical allied effluents	" "	" "	Oyewo & Don-Pedro (2003)
25	Lagos metropolis	mg/kg	3.0-231	6 -87.0	9-366	2.0146	28	3.7	NA	ND	NA	Sediment	Acid digestion	ICP-OES	Olatunji & Abimbola *et al* ,2010

Appendix 2c: Previous investigations of heavy metals in Lagos Lagoon (continued).

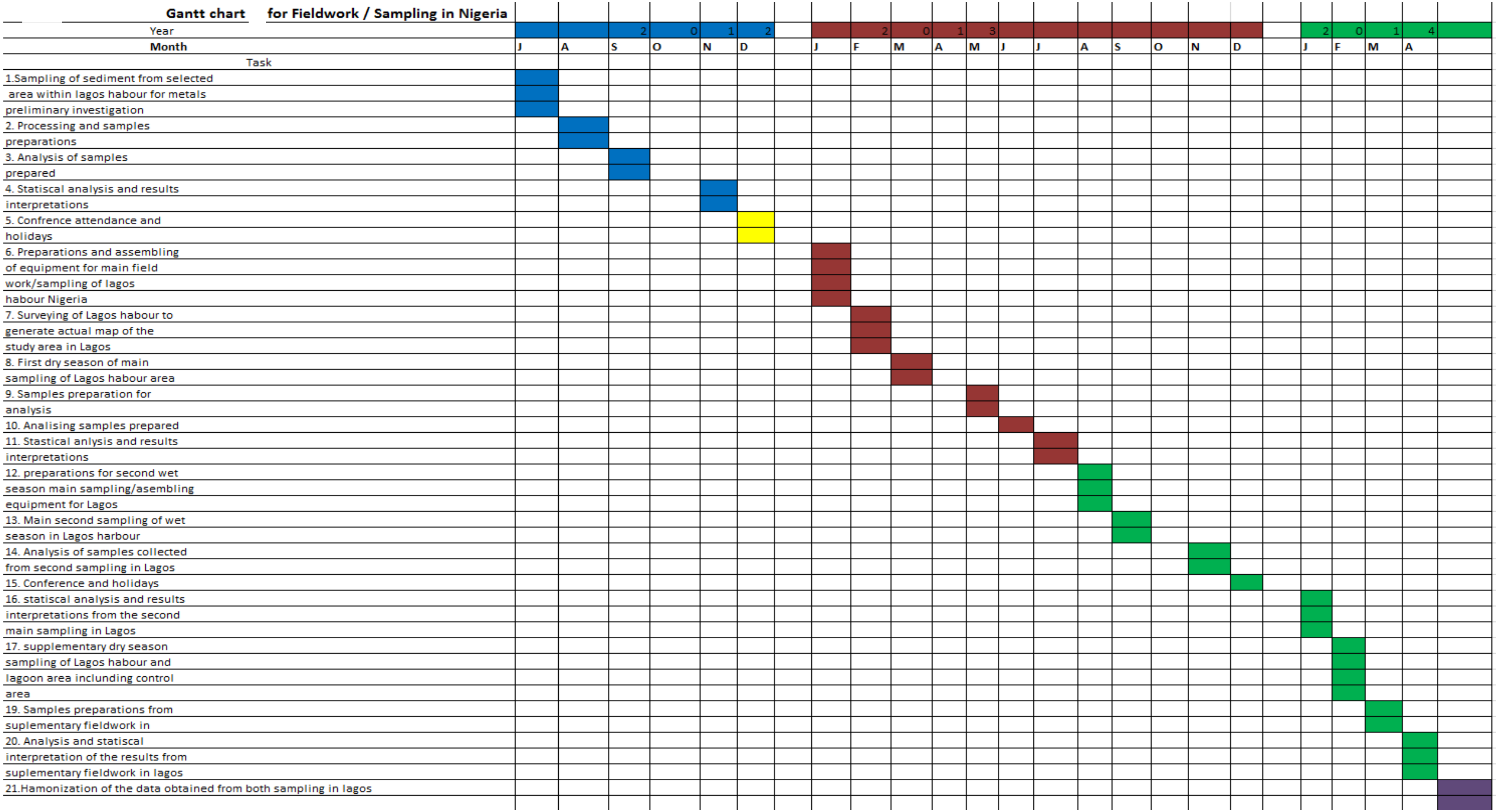
Serial numbers	Locations/ Zone	Unit	Cu	Cr	Zn	Pb	As	Cd	Hg	Fe	Al	Environmental media (water, sed. or biota)	Analytical Methods	Instrument employed	References
26	Chemical allied sources	mg/kg	0.16	ND	0.02-0.118	0.01-0.08	ND	ND	NA	4.20-43.67	NA	Water	Acid digestion	ICP-OES	Olatunji & Abimbola et al ,2011
26	Lagos (Ologe Lagoon)	mg/kg	0.15±0.02-0.34±0.06	NA	2.14±0.53-2.13±053	0.29±0.03-2.39±0.16	NA	0.12±0.03-1.56±0.03	NA	20.64±4.70,70-212±19	NA	Sediment	APHA	AAS	Kumolu-Johnson & Ndimele,2012
27	Lagos Lagoon	mg/L	NA	NA	NA	NA	NA	NA	0.27-0.40	NA		Water	Acid digestion	AAS	Emmanuel & Samuel.,2009
28		mg/kg	NA	NA	NA	NA	NA	NA	0.95	NA	NA	Sediment	Acid digestion	AAS	Emmanuel & Samuel.,2010
29	Lagos Harbour	mg/L	4.53-5.55	0.03-0.60	NA	0.22-0.61	NA	0.02	NA	0.67-1.41	NA	Water	APHA	AAS	Balogun , 2017
30	Lagos Lagoon	mg/L	23.8	40.2	0.234	13.7	NA	1.98	NA	1.57	214.1	Water	Acid digestion	ICP-OES	Nkono et al.,1999
31	" "	mg/kg	11.48	NA	15.36	173.95	NA	0.58	NA	NA	NA	Biota	" "	AAS	Otitoloju & Don-Pedro,2002
32	Lagos Lagoon	mg/kg	54.82±13.88	NA	52.8±4.01	9.18±7.18	NA	0.83±0.20	NA	NA	NA	Biota	Acid digestion	AAS	Adedeji &Okocha,2011
33	Lagos Harbour-Control-	mg/kg	NA	NA	NA	76.52	NA	NA	NA	NA	NA	Sediments	Acid digestion	AAS	Ihenyen (1991)
34		mg/kg	NA	NA	NA	13.91	NA	NA	NA	NA	NA	Sediments	Acid digestion	AAS	” ”
35	Lagos Harbour & Lagoon	mg/kg	317	817	ND	471	NS	NS	NA	NS	NA	Sediments	Acid digestion	ICP-MS & XRF	Bamanga et al, 2014
36	Lagos Lagoon	mg/kg	22.4125	39.725	113.375	24.275	ND	2.35	NA	ND	NA	Sediments	" "	AAS	Oyeyiola et al.,2014

Appendix 3: NOAA Screening Quick Reference Tables.



Analyte		FRESHWATER SEDIMENT									MARINE SEDIMENT						
All concentrations in parts per billion dry weight unless specified otherwise		"Background"[1]	ARCS *H. azteca* TEL[2]	TEC[3]	TEL[3]	LEL[4]	PEC[3]	PEL[3]	SEL[4]	UET[1]	T_{20}[5]	TEL[6]	ERL[6]	T_{50}[5]	PEL[6]	ERM[6]	AET[7]
Predicted Toxicity Gradient:			Increasing →								Increasing →						
Aluminum (%)	Al	0.26%	2.55%														1.8% N
Antimony	Sb	160								3,000 M	630			2,400			9,300 E
Arsenic	As	1,100	10,798	9,790	5,900	6,000	33,000	17,000	33,000	17,000 I	7,400	7,240	8,200	20,000	41,600	70,000	35,000 B
Barium	Ba	700										130,100#					48,000 A
Cadmium	Cd	100-300	583	990	596	600	4,980	3,530	10,000	3,000 I	380	680	1,200	1,400	4,210	9,600	3,000 N
Chromium	Cr	7,000-13,000	36,286	43,400	37,300	26,000	111,000	90,000	110,000	95,000 H	49,000	52,300	81,000	141,000	160,000	370,000	62,000 N
Cobalt	Co	10,000				50,000+											10,000 N
Copper	Cu	10,000-25,000	28,012	31,600	35,700	16,000	149,000	197,000	110,000	86,000 I	32,000	18,700	34,000	94,000	108,000	270,000	390,000 MO
Iron (%)	Fe	0.99-1.8 %	18.84%			2%			4%	4% I							22% N
Lead	Pb	4,000-17,000	37,000	35,800	35,000	31,000	128,000	91,300	250,000	127,000 H	30,000	30,240	46,700	94,000	112,000	218,000	400,000 B
Manganese	Mn	400,000	630,000			460,000			1,100,000	1,100,000 I							260,000 N
Mercury	Hg	4-51		180	174	200	1,060	486	2,000	560 M	140	130	150	480	700	710	410 M
Nickel	Ni	9,900	19,514	22,700	18,000	16,000	48,600	36,000	75,000	43,000 H	15,000	15,900	20,900	47,000	42,800	51,600	110,000 EL
Selenium	Se	290															1,000 A
Silver	Ag	<500				500 +				4,500 H	230	730	1,000	1,100	1,770	3,700	3,100 B
Strontium	Sr	49,000															
Tin	Sn	5,000										48 *					> 3,400 N
Vanadium	V	50,000															57,000 N
Zinc	Zn	7,000-38,000	98,000	121,000	123,000	120,000	459,000	315,000	820,000	520,000 M	94,000	124,000	150,000	245,000	271,000	410,000	410,000 I
Lead 210 $^{bq}/_{g}$ dw						0.5 ^			< 9.7 ^								
Polonium 210 $^{bq}/_{g}$ dw						0.6 ^			< 8.7 ^								
Radium 226 $^{bq}/_{g}$ dw						0.1 ^			< 13 ^								
Sulfides										130,000 M							4,500 MO

Appendix 4: Gantt chart showing field work for dry and wet seasons sampling in Nigeria.



Gantt chart for Fieldwork / Sampling in Nigeria

Year	2012							2013													2014				
Month	J	A	S	O	N	D		J	F	M	A	M	J	J	A	S	O	N	D		J	F	M	A	
Task																									
1.Sampling of sediment from selected area within lagos habour for metals preliminary investigation	🟦																								
2. Processing and samples preparations		🟦																							
3. Analysis of samples prepared			🟦																						
4. Statiscal analysis and results interpretations					🟦																				
5. Confrence attendance and holidays						🟨																			
6. Preparations and assembling of equipment for main field work/sampling of lagos habour Nigeria								🟥																	
7. Surveying of Lagos habour to generate actual map of the study area in Lagos									🟥																
8. First dry season of main sampling of Lagos habour area										🟥															
9. Samples preparation for analysis												🟥													
10. Analising samples prepared													🟥												
11. Stastical anlysis and results interpretations														🟥											
12. preparations for second wet season main sampling/asembling equipment for Lagos															🟩										
13. Main second sampling of wet season in Lagos harbour																🟩									
14. Analysis of samples collected from second sampling in Lagos																		🟩							
15. Conference and holidays																			🟩						
16. statiscal analysis and results interpretations from the second main sampling in Lagos																					🟩				
17. supplementary dry season sampling of Lagos habour and lagoon area inclunding control area																						🟩			
19. Samples preparations from suplementary fieldwork in																							🟩		
20. Analysis and statiscal interpretation of the results from suplementary fieldwork in lagos																								🟩	
21.Hamonization of the data obtained from both sampling in lagos																									🟪

Appendix 5: Sampling sites name, coordinates locations and observed activities.

Appendix 5a: February 2013 (Dry season)

Serial number	Sites Number	Sites Name	Longitude	Latitude	Depth (m)	Zone	Observed activities around the sampling sites
1	9	ATC	3° 23' 55.94"	6° 24' 44.944"	13.9	Lagos Harbour	Ship bunkering fuel station and discharges
2	2	OBT	3° 19' 15.634"	6° 26' 2.029"	10.5	″	″ ″ ″ ″ ″ ″ ″ ″
3	3	GMD	3° 20' 3.233"	6° 26' 7.144"	11.0	″	Ro-Ro vessels jetty and discharge areas
4	4	JDM	3° 21' 39.324"	6° 25' 48.776"	11.2	″	Bulk Cargo discharge terminal
5	5	TCN6	3° 24' 0.486"	6° 25' 53.328"	11.5	″	″ ″ ″ ″
6	6	SFX	3° 20' 34.665"	6° 25' 42.047"	11.8	″	″ ″ ″ ″
7	7	GRV	3° 22' 56.007"	6° 26' 10.474"	12.4	″	″ ″ ″ ″
8	8	APM	3° 22' 37.253"	6° 26' 7.297"	13.7	″	Containerized foreign vessels terminal
1	1	BVS	3° 18' 58.574"	6° 26' 1.779"	13.5	Lagos Harbour	Oil tanker farms discharges and loading station
10	10	ENL	3° 23' 20.826"	6° 26' 25.11"	14.5	″	General and Bulk cargo discharge terminal
11	11	FM	3° 22' 26.71"	6° 26' 59.019"	15.4	″	Bulk cargo discharge terminal
12	12	NIPCO	3° 22' 26.719"	6° 27' 10.905"	11.8	″	Oil tanker farms discharges and loading
13	20	UGH	3° 24' 10.832"	6° 31' 13.438"	1.6	Lagos Lagoon	Unilag Ferry jetty & domestic activities.
14	21	UHR	3° 24' 0.701"	6° 30' 26.356"	2.5	″	Unilag High rise area and domestic activities

Appendix 5b: February 2014 (Dry season).

Serial number	Sites name	Sites Sample Code	Coordinates (Latitude and Longitude)		Depths (m)	Zones	Observed Activities around the sampling sites
1	1	ATC(a) 1	N6° 25'11.2''	E003° 23' 23.1''	0.7	Lagos Harbour	Oil tank farms for discharging oils, loading and storage
2	1	ATC (b) 2	N6° 25'10.7''	E003° 23'20.0''	2.8	″	″
3	1	ATC (c) 3	N6° 25'09.3''	E003° 23'17.2''	1.7	″	″
4	2	SFM (a) 1	N6° 26'15.0''	E003° 22'59.7''	7.4	″	Bulk cargo raw material discharge area
5	2	SFM (a) 2	N6° 26'14.5''	E003° 22'52.5''	8.1	″	″
6	2	SFM (a) 3	N6° 26'13.9''	E003° 22'43.9''	8.7	″	″
7	3	JSD (a) 1	N6° 25'33.4''	E003° 20'26.2''	4.8	″	Bulk cargo discharge area
8	3	JSD (b) 2	N6° 25'36.3''	E003° 20'22.6''	5.4	″	″
9	3	JSD (c) 3	N6° 25'35.8''	E003° 20'20.4''	6.7	″	″
10	4	ORD (a) 1	N6° 26'04.8''	E003° 19'14.2''	1.2	″	Oil tank farm and discharge area
11	4	ORD (b) 2	N6° 26'06.6''	E003° 18'56.5''	1.35	″	″
12	4	ORD (c) 3	N6° 26'10.6''	E003° 18'48.4''	3.5	″	″
13	5	IBJ (a) 1	N6° 26'15.2''	E003° 19'57.3''	1.3	″	Oil tank farms and discharge area
14	5	IBJ (b) 2	N6° 26'14.7''	E003° 19'50.1''	2.1	″	″
15	5	IBJ (c) 3	N6° 26'14.5''	E003° 19'45.8''	2.82	″	″
16	6	GMD (a) 1	N6° 26'05.5''	E003° 19'56.2''	9.2	″	Large vessel discharge area (Ro-ro terminal)
17	6	GMD (b) 2	N6° 26'07.8''	E003° 19'56.9''	8.7	″	″
18	6	GMD (c) 3	N6° 26'10.7''	E003° 20'00.3''	1.13	″	″
19	7	SIFX (a) 1	N6° 25'56.9''	E003° 20'57.4''	9.01	″	Bulk cargo discharge area
20	7	SIFX (b) 2	N6° 25' 53.6"	E003° 20' 50.8"	10.5	″	″

21	7	SIFX (c) 3	N6° 25' 49.2"	E003° 20' 42.8"	10.65	″	″
22	8	T6 (a) 1	N6° 25'53.9''	E003° 21'35.3''	7.6	″	Bulk cargo discharge area (containerized)
23	8	T6 (b) 2	N6° 25'54.3''	E003° 21'28.0''	11.1	″	″
24	8	T6 (c) 3	N6° 25'55.7''	E003° 21'15.0''	10.1	″	″
25	9	FJ (a) 1	N6° 26'03.0''	E003° 22'15.8''	6.04	″	Oil tank farms discharge area
26	9	FJ (b) 2	N6° 26'02.2''	E003° 22'10.9''	2.8	″	″
27	9	FJ (c) 3	N6° 26'00.1''	E003° 22'06.8''	7.8	″	″
28	10	JSD (a) 1	N6° 26'12.0''	E003° 23' 10.9''	10.23	″	Bulk cargo discharge area
29	10	JSD (b) 2	N6° 26'13.5''	E003° 22' 06.6''	9.71	″	″
30	10	JSD (c) 3	N6° 26'14.9''	E003° 23'03.2''	9.5	″	″
31	11	APM (a) 1	N6° 26' 04.4"	E003° 23' 28.1"	8.7	″	Container terminals (bulk)
32	11	APM (b) 2	N6° 26'05.6''	E003° 23' 25.2''	9.6	″	″
34	11	APM (c) 3	N6° 26'08.5''	E003° 23' 18.8''	8.85	″	″
35	12	BN (a) 1	N6° 26' 19.1"	E003° 23' 41.2"	8.7	″	Bulk cargo discharge area
36	12	BN (b) 2	N6° 26' 13.36"	E003° 23' 43.1"	5.7	″	″
37	12	BN (c) 3	N6° 26' 09.6"	E003° 23' 41.5"	6.1	″	″
38	13	ENL (a) 1	N6° 26'38.4''	E003° 23' 19.3''	10.64	″	Large bulk cargo terminal discharge area
39	13	ENL (b) 2	N6° 26' 27.4"	E003° 23' 21.4"	8.9	″	″
40	13	ENL (c) 3	N6° 26' 24.5"	E003° 23' 27.9"	5.65	″	″
41	14	FM (a) 1	N6° 26'54.8''	E003° 22' 27.2''	4.63	″	Raw materials cargo discharge area
42	14	FM (b) 2	N6° 26' 52.0"	E003° 22' 28.9"	4.72	″	″
45	14	FM (c) 3	N6° 26'51.8''	E003° 22' 29.9''	6	″	″
46	15	NPA-DY (a) 1	N6° 27'02.8''	E003° 22' 23.4''	7.2	″	Ship repairs and dry docking area

47	15	NPA-DY (b) 2	N6° 26' 58.5"	E003° 22' 24.9"	7.3	“	“
48	15	NPA-DY (c) 3	N6° 26' 56.9"	E003° 22' 25.8"	5.72	“	“
49	16	NIPCO (a) 1	N6° 27' 22.7"	E003° 22' 17.5"	3	“	Oil tank farms and discharge area
50	16	NIPCO (b) 2	N6° 27' 18.4"	E003° 22' 17.6"	3.11	“	“
51	16	NIPCO (c) 3	N6° 27' 12.3"	E003° 22' 18.7"	3.82	“	“
52	17	IDDO (a) 1	N6° 28'17.2''	E003° 23' 05.7''	1.28	Lagos Lagoon	Public sewage dumpsite & general waste
53	17	IDDO (b) 2	N6° 28'11.5''	E003° 23'03.0''	1.32	“	“
54	17	IDDO (c) 3	N6° 28'01.7''	E003° 25' 52.8''	0.93	“	“
55	18	OKB (a) 1	N6° 29'29.4''	E003° 23' 44.1''	1.11	“	Sawmills waste and domestic activities
56	18	OKB (b) 2	N6° 28'55.3''	E003° 23' 32.0''	1.28	“	“
57	18	OKB (c) 3	N6° 28'42.0''	E003° 23' 29.0''	1.1	“	“
58	19	MKK (a) 1	N6° 29'50.8''	E003° 23' 47.5''	1.25	“	Fishing & domestic water trading
59	19	MKK (b) 2	N6° 29'45.0''	E003° 23' 44.1''	1.19	“	“
60	19	MKK (c) 3	N6° 29'38.7''	E003° 23' 43.7''	1.12	“	“
61	20	UWF (a) 1	N6° 31' 07.0''	E003° 24'09.9''	1.18	“	Recreation and aquaculture
62	20	UWF (b) 2	N6° 31'0.33''	E003° 24' 11.8''	1.2	“	“
63	20	UWF (c) 3	N6° 31'00.9''	E003° 24' 15.7''	1.17	“	“
64	21	OWSK (b) 1	N6° 32' 09.6 ''	E003° 24' 02.8 ''	3.1	“	Oyster &fish farming, sand mining
65	21	OWSK (b) 2	N6° 32' 04.0 ''	E003° 24' 03.3''	2.24	“	“
66	21	OWSK (c) 3	N6° 31' 53.7 ''	E003° 24' 03.1''	1.48	“	“
67	22	UHR (a) 1	N6° 30'41.3''	E003° 34'07.4''	1.2	“	Residential area
68	22	UHR (b) 2	N6° 30'33.6''	E003° 24'04.2''	1.22	“	“

Serial number	Sites number	Sites Sample Code	Coordinates (Latitude and Longitude)		Depths (m)	Zones	Observed Activities around the sampling stations
66	21	OWSK (c) 3	N6° 31' 53.7 ''	E003° 24' 03.1''	1.48	ʺ	ʺ
67	22	UHR (a) 1	N6° 30'41.3''	E003° 34'07.4''	1.2	ʺ	Residential area
68	22	UHR (b) 2	N6° 30'33.6''	E003° 24'04.2''	1.22	ʺ	ʺ
69	22	UHR (c) 3	N6° 30'13.59''	E003° 23' 55.9''	1.53	ʺ	ʺ
70	23	UGH (a) 1	N6° 31' 24.8 ''	E003° 23' 57.2''	0.9	ʺ	Power plants, municipal sewage &land reclamation
71	23	UGH (b) 2	N6° 31' 20.5 ''	E003° 24' 00.9''	0.9	ʺ	ʺ
72	23	UGH (c) 3	N6° 31' 15.6 ''	E003° 24' 04.5''	1.3	ʺ	ʺ
73	24	Apese 1agoon (a) 1 (control)	N6° 25' 24.6 ''	E003° 27' 27.4 ''	1	Apese Lagoon	Recreation and proposed residential development areas
74	24	Apese 1 (b) 2	N6° 25' 24.1 ''	E003° 27' 30.9 ''	2	ʺ	ʺ
75	24	Apese 1 (c) 3	N6° 25' 23.7 ''	E003° 27' 33.3 ''	0.7	ʺ	ʺ
76	25	Apese 2 (a) 1	N6° 25' 23.4 ''	E003° 27' 40.9 ''	2	ʺ	ʺ
77	25	Apese 2 (b) 2	N6° 25' 23.9 ''	E003° 27' 42.6 ''	1.7	ʺ	ʺ
78	25	Apese 2 (c) 3	N6° 25' 24.3 ''	E003° 27' 44.7 ''	0.5	ʺ	ʺ
79	26	Apese 3 (a) 1	N6° 25' 24.2''	E003° 27' 47.5 ''	0.8	ʺ	ʺ
80	26	Apese 3 (b) 2	N6° 25' 23.8 ''	E003° 27' 49.3''	0.9	ʺ	ʺ
81	26	Apese 3 (c) 3	N6° 25' 23.4 ''	E003° 27' 51.6''	0.8	ʺ	ʺ

Appendix 5c: September 2013 (Wet season).

Serial numbers	**Sites name**	**Sites Sample Code**	**Coordinates (Latitude and Longitude)**		**Depths (m)**	**Zones**	**Observed Activities around the sampling stations**
1	1	ATC (a)	N6° 25'11.9''	E003° 23' 22.2''	1.4	Lagos Harbour	
2	1	ATC(b)	N6° 25'10.3''	E003° 23'18.7''	1.4	″	
3	1	ATC (c)	N6° 25'04.7''	E003° 23'14.0''	1.4	″	
4	2	STFM (a)	N6° 26'10.9''	E003° 22'34.7''	10.3	″	
5	2	STFM (b)	N6° 26'07.5''	E003° 22'26.9''	10.3	″	
6	2	STFM (c)	N6° 26'07.1''	E003° 22'23.4''	3.3	″	
7	3	ND (a)	N6° 25'37.2''	E003° 20'17.1''	6.1	″	
8	3	ND (b)	N6° 25'35.8''	E003° 20'24.4''	7.9	″	
9	4	ORS (a)	N6° 26'05.4''	E003° 19'13.4''	3.2	″	
10	4	ORS (b)	N6° 26'06.5''	E003° 18'57.3''	1.5	″	
11	4	ORS (c)	N6° 26'10.2''	E003° 18'49.4''	4.2	″	
12	5	IBJ (a)	N6° 26'15.4''	E003° 19'58.7''	3.5	″	
13	5	IBJ (b)	N6° 26'15.1''	E003° 19'51.1''	3.5	″	
14	5	IBJ (c)	N6° 26'13.7''	E003° 19'44.9''	3.4	″	
15	6	GMD (a)	N6° 26'02.8''	E003° 19'59.1''	11.3	″	
16	6	GMD (b)	N6° 26'06.6''	E003° 19'56.1''	11.3	″	
17	6	GMD (c)	N6° 26'09.9''	E003° 19'58.3''	11.3	″	
18	7	SIFAX (a)	N6° 25'53.2''	E003° 20'50.3''	10.2	″	
19	7	SIFAX (b)	N6° 25' 49.7''	E003° 20' 44.8"	13.6	″	
20	7	SIFAX (c)	N6° 25' 45.0"	E003° 20' 37.7"	13.6	″	
21	8	T-6 (a)	N6° 25'55.1''	E003° 21'28.6''	9.4	″	
22	8	T-6 (b)	N6° 25'55.0''	E003° 21'22.3''	11.8	″	
23	8	T-6 (c)	N6° 25'55.9''	E003° 21'15.2''	12.4	″	
24	9	FJ (a)	N6° 25'59.2''	E003° 22'09.3''	9.5	″	
25	9	FJ (b)	N6° 25'59.2''	E003° 22'04.3''	4.5	″	
26	10	JSD (a)	N6° 26'14.1''	E003° 23' 05.0''	13.7	″	
27	10	JSD (b)	N6° 26'14.9''	E003° 22' 53.5''	10.1	″	
28	10	JSD (c)	N6° 26'13.9''	E003° 22'45.4''	10.1	″	
29	11	APM (a)	N6° 26' 2.5"	E003° 23' 31.6"	12.5	″	
30	11	APM (b)	N6° 26'05.8''	E003° 23' 25.1''	13.4	″	
31	11	APM (c)	N6° 26'10.9''	E003° 23' 12.7''	13.7	″	
32	12	ENL (a)	N6° 26' 18.3"	E003° 23' 43.2"	8.6	″	
33	12	ENL (b)	N6° 26' 30.6"	E003° 23' 14.7"	3.8	″	

34	12	ENL (c)	N6° 26' 4.3"	E003° 23' 35.9"	6.2	″
35	13	FM (a)	N6° 26'33.4''	E003° 23' 07.1''	6	″
36	13	FM (b)	N6° 26' 32.0"	E003° 23' 11.0"	5.5	″
37	13	FM (c)	N6° 26' 30.6"	E003° 23' 14.7"	6.5	″
38	14	FM-AP (a)	N6° 26'51.5''	E003° 22' 30.3''	6	″
39	14	FM-AP (b)	N6° 26' 50.3"	E003° 22' 32.7"	6	″
40	15	NPA-DY (a)	N6° 27'01.9''	E003° 22' 22.2''	3.8	″
41	15	NPA-DY (b)	N6° 26' 59.6"	E003° 22' 26.0"	6.33	″
42	15	NPA-DY (c)	N6° 26' 56.5"	E003° 22' 26.7"	3.8	″
43	16	NIPC (a)	N6° 27' 15.5"	E003° 22' 18.3"	3.21	″
44	16	NIPC (b)	N6° 27' 12.9"	E003° 22' 18.5"	2.5	″
45	16	NIPC (c)	N6° 27' 18.1"	E003° 22' 19.2"	3.2	″
46	17	IDD (a)	N6° 28'02.9''	E003° 22' 54.3''	0.3	Lagos Lagoon
47	17	IDD (b)	N6° 28'04.3''	E003° 22' 57.4''	0.3	″
48	17	IDD (c)	N6° 27'58.1''	E003° 22' 50.5''	4.5	″
49	18	OKB (a)	N6° 28'50.8''	E003° 23' 29.0''	0.4	″
50	18	OKB (b)	N6° 28'48.4''	E003° 23' 27.3''	0.4	″
51	18	OKB (c)	N6° 28'42.0''	E003° 23' 29.0''	3.5	″
52	19	MKK (a)	N6° 29'51.3''	E003° 23' 47.7''	0.5	″
53	19	MKK (b)	N6° 29'47.6''	E003° 23' 44.4''	0.5	″
54	19	MKK (c)	N6° 29'39.3''	E003° 23' 42.7''	0.5	″
55	20	UWF (a)	N6° 31' 05.1 ''	E003° 24' 09.2''	0.4	″
56	20	UWF (b)	N6° 31' 03.7 ''	E003° 24' 11.7''	0.3	″
57	20	UWF (c)	N6° 31' 08.0 ''	E003° 24' 08.7''	0.3	″
58	21	OWS (a)	N6° 31' 58.5 ''	E003° 24' 07.1 ''	0.4	″
59	21	OWS (b)	N6° 31' 53.31 ''	E003° 24' 1.2''	1.2	″

60	21	OWS (c)	N6° 32' 13.3 ''	E003° 24' 02.6''	1.5	ʺ
61	22	UHR (a)	N6° 30' 26.9''	E003° 23' 57.6''	0.2	ʺ
62	22	UHR (b)	N6° 30' 23.9''	E003° 23' 57.2''	0.2	ʺ
63	22	UHR (c)	N6° 30'18.1''	E003° 23' 56.1''	0.2	ʺ
64	23	UGH (a)	N6° 31' 24.0 ''	E003° 23' 59.5''	0.2	ʺ
65	23	UGH (b)	N6° 31' 24.6 ''	E003° 23' 57.9''	0.2	ʺ
66	23	UGH (c)	N6° 31' 25.3 ''	E003° 23' 55.3''	0.2	Apese Lagoon
67	24	APS-LAG (A)	N6° 25'25''	E003° 27'28.4''	0.2	ʺ
68	24	APS-LAG (B)	N6° 25'24.1''	E003° 27'30.1''	0.5	ʺ
69	24	APS-LAG (C)	N6° 25'23.8''	E003° 27'50.4''	1	ʺ
70	24	APS-LAG (D)	N6° 25'24''	E003° 27'48.0''	0.8	ʺ

Appendix 6: Water quality measurements for Ds-2013, DS 2013& DS-2014

Appendix 6a: Water quality measurements for February 2013 (Dry Season).

Sites name	Sites numbers	Zones	pH	DO%	DO mg/L	Conductivity mS/cm	Salinity g/kg	Temperature 0C	TDS mg/L
BOVAS/SWIFT OIL (Tincan)	1	Lagos Harbour	7.19	64.8	4.2	46.45	27.01	30.35	27.44
OBAT/RAHAMANIYA (Tincan)	2	Lagos Harbour	7.08	57.7	3.75	45.68	26.36	30.46	26.88
PTMLGRIMALDI JETTY (Tincan)	3	Lagos Harbour	7.23	70.4	4.52	48.12	28.02	30.3	28.4
JOSEP DAM (Tincan)	4	Lagos Harbour	7.39	80	5.14	50.46	29.63	30.2	29.85
5 STAR LOG (Tincan)	5	Lagos Harbour	7.44	70.6	4.84	47.77	27.84	30.1	28.28
SIFAX TERMINAL (Tincan)	6	Lagos Harbour	7.31	79	5.11	46.71	27.14	30.21	27.61
GREENVIEW (Apapa)	7	Lagos Harbour	7.28	82.7	5.32	49.59	29.05	30.1	29.31
AP MOLLER (Apapa)	8	Lagos Harbour	7.62	102.8	6.51	54.95	32.75	29.91	32.65
ATLAS COVE (Apapa)	9	Lagos Harbour	7.68	115.7	7.31	55.78	33.39	29.81	32.2
ENL JETTY (Apapa)	10	Lagos Harbour	7.67	115.6	7.28	56.26	33.67	29.88	33.45
ABTL JETTY(Flour mills-Apapa)	11	Lagos Harbour	7.5	113.5	7.15	55.96	33.39	30.02	33.2
NIPCO (Apapa)	12	Lagos Harbour	7.65	115.4	7.25	55.97	33.41	29.95	33.21
UNILAG 1(Control) Lagoon	13	Lagos Lagoon	7.42	76.4	5.09	36.77	20.83	30.22	21.75
UNILAG 2(Control) Lagoon	14	Lagos Lagoon	7.1	71.6	4.8	37.28	21.21	30.06	22.1

Appendix 6b: Water quality measurement for February 2013 (Wet season).

Sites Name	Site numbers	Zones	pH	D0 %	DO mg/L	Conductivity mS/cm	Salinity g/kg	Temperature ^{0}C	TDS mg/L
Atlas Cove A	1	Lagos Harbour	7.9	63	4.15	47.4	28.01	29.06	28.36
Atlas Cove B	1	Lagos Harbour	7.93	65.4	4.29	47.22	28.09	29.16	28.44
Atlas Cove C	1	Lagos Harbour	7.95	66.5	4.37	47.25	28.12	29.12	28.46
Standard Flower Mill A	2	Lagos Harbour	8.12	66.2	4.3	49.67	29.71	20.17	29.9
Standard Flower Mill B	2	Lagos Harbour	8.11	68.2	4.44	49.61	29.63	29.18	29.84
Standard Flower Mill C	2	Lagos Harbour	8.02	57	3.74	48.86	29.07	29.27	29.34
Niger dock A	3	Lagos Harbour	7.89	54.1	3.54	46.24	27.71	29.15	28.09
Niger dock A	3	Lagos Harbour	7.89	53.3	3.51	46.95	27.86	29.19	28.25
Niger dock B	3	Lagos Harbour	7.78	44.6	2.93	44.16	26.8	29.19	26.27
Obat, Rahamaniyya& Swift Oil Terminal A	4	Lagos Harbour	7.68	29.3	1.91	44.96	26.42	29.44	26.92
Obat, Rahamaniyya&Swift Oil Terminal B	4	Lagos Harbour	7.7	34.4	2.24	45.38	26.66	29.44	27.14
Obat, Rahamaniyya& Swift Oil Terminal C	4	Lagos Harbour	7.72	38.7	2.58	45.42	26.77	29.35	27.19
Ibru Jetty A	5	Lagos Harbour	7.72	33.9	2.23	45.03	26.53	29.32	27.01
Ibru Jetty B	5	Lagos Harbour	7.73	38.3	2.51	46.07	27.18	29.34	27.64
Ibru Jetty C	5	Lagos Harbour	7.76	41.2	2.69	46.61	27.56	29.35	27.97
Grimaldi A	6	Lagos Harbour	7.72	33.1	2.19	45.09	26.7	29.16	27.16
Grimaldi B	6	Lagos Harbour	7.69	37.7	2.48	44.74	26.46	26.94	26.94
Grimaldi C	6	Lagos Harbour	7.71	39.8	2.65	44.95	26.65	29.2	27.08
Sifax A	7	Lagos Harbour	7.91	52.3	3.43	47.62	28.37	29.13	28.69
Sifax B	7	Lagos Harbour	7.87	53.9	3.53	47.19	28.09	29.1	28.44
Sifax C	7	Lagos Harbour	7.88	52.2	3.43	47.55	28.33	29.11	28.65
Tincan 6 A	8	Lagos Harbour	7.93	51.8	3.38	48.42	28.97	29.05	29.22
Tincan 6 B	8	Lagos Harbour	7.86	41.6	2.69	49.3	29.1	29.76	29.36
Tincan 6 C	8	Lagos Harbour	7.93	51.8	3.97	48.95	29.28	29.76	29.49

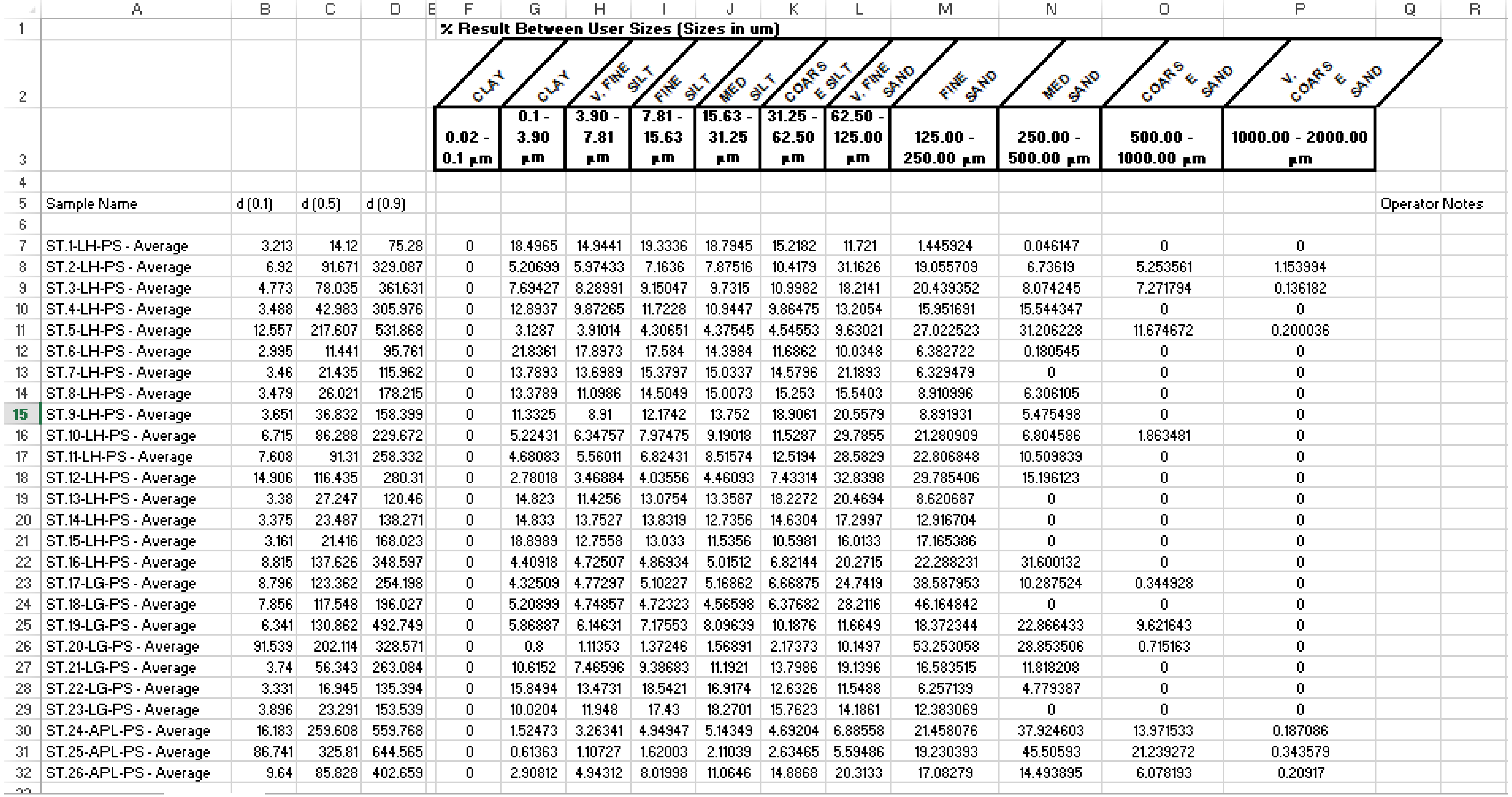
Appendix 6c: Water quality measurement for February 2014 (Dry season).

Sites name	Sites No's (Triplicates)	Zone	pH	D0 %	DO mg/L	Conductivity mS/cm	Salinity g/kg	Temperature ^{0}C
Folawiyo Jetty A	9	Lagos Harbour	7.86	42.4	2.81	47.79	28.57	28.96
Folawiyo Jetty B	9	Lagos Harbour	78.4	42.7	2.8	47.87	28.61	29.04
Folawiyo Jetty C	9	Lagos Harbour	7.91	56	3.67	47.63	28.47	28.98
Joseph Dam A	10	Lagos Harbour	8.09	64.7	4.21	48.72	29.13	29.18
Joseph Dam B	10	Lagos Harbour	8.03	60.5	3.96	48.81	29.14	29.22
Joseph Dam C	10	Lagos Harbour	8.1	64.4	4.1	49.59	29.61	29.27
APM A	11	Lagos Harbour	8.22	74.5	4.84	50.52	30.68	29.11
APM B	11	Lagos Harbour	8.25	76.3	4.93	51.52	30.81	29.1
APM C	11	Lagos Harbour	8.1	70.5	4.58	40.15	29.38	29.14
Bullnose A	12	Lagos Harbour	8.27	86.5	5.54	54.23	32.88	29.08
Bullnose B	12	Lagos Harbour	8.27	90.8	5.8	55.16	33.52	29.05
Bullnose c	12	Lagos Harbour	8.6	88.1	5.64	54.18	32.83	29.06
ENL Jetty A	13	Lagos Harbour	8.27	89.3	5.7	54.8	32.9	29.9
ENL Jetty B	13	Lagos Harbour	11.28	90.2	5.76	54.89	33.32	29.07
ENL Jetty C	13	Lagos Harbour	8.2	88	5.63	54.74	33.35	29.06
Flour Mills A	14	Lagos Harbour	8.28	89.8	5.76	54.3	33.97	29.01
Flour Mills B	14	Lagos Harbour	8.26	87.8	5.63	54.17	32.95	29.93
Flour Mills C	14	Lagos Harbour	8.17	87.6	5.59	54.1	32.9	29.23
NPA Dockyard A	15	Lagos Harbour	8.19	82.1	5.29	51.68	30.97	29.35
NPA Dockyard B	15	Lagos Harbour	8.17	81.8	6.24	50.94	30.4	29.3
NPA Dockyard C	15	Lagos Harbour	8.09	8.12	5	50.6	30.26	29.41
NIPCO A	16	Lagos Harbour	8.17	85	5.4	52.68	31.6	29.39
NIPCO B	16	Lagos Harbour	8.19	82.4	5.31	52.06	31.1	29.37
NIPCO C	16	Lagos Harbour	8.19	83	5.34	52.07	31.2	29.35
Iddo A	17	Lagos Lagoon	8.04	63.2	4.06	51.25	30.33	29.87
Iddo B	17	Lagos Lagoon	8.11	75.5	4.86	51.49	30.71	29.49

Appendix 6d: Water quality measurement for February 2014 (Dry season).

Sites name	Sites numbers (Triplicates)	Zones	pH	D0 %	DO mg/L	Conductivity mS/cm	Salinity g/kg	Temperature ^{0}C
Iddo C	17	Lagos Lagoon	8.11	74.5	4.81	50.94	30.42	29.39
Okobaba A	18	" "	7.69	34.8	2.33	40.23	23.37	29.36
Okobaba B	18	Lagos Lagoon	7.91	52	3.38	47.66	28.33	29.22
Okobaba C	18	" "	8.01	65	4.24	47.38	28.7	29.27
Makoko A	19	Lagos Lagoon	7.79	58.6	3.92	40.37	23.3	29.35
Makoko B	19	" "	7.83	54	3.66	42.13	24.65	29.25
Makoko C	19	Lagos Lagoon	7.8	54.1	3.61	42.64	25.15	29.25
Unilag Water Front A	20	Lagos Lagoon	7.86	76.4	5.17	33.31	18.86	29.55
Unilag Water Front B	20	Lagos Lagoon	7.82	71	4.91	33.36	18.95	29.49
Unilag Water Front C	20	Lagos Lagoon	7.85	77.3	53.4	33.59	19.12	29.51
Oworoshoki A	21	Lagos Lagoon	7.81	50	3.5	32.16	18	29.99
Oworoshoki B	21	Lagos Lagoon	7.81	38.7	2.65	32.07	17.79	30.02
Oworoshoki C	21	Lagos Lagoon	7.79	42.4	2.85	32.84	18.47	30.2
Unilag High Rise A	22	Lagos Lagoon	7.82	68.1	4.63	36.69	20.86	29.38
Unilag High Rise B	22	Lagos Lagoon	7.79	65.9	4.46	37.36	21.57	29.34
Unilag High Rise C	22	Lagos Lagoon	7.8	62.4	4.82	39.85	23.31	23.31
Unilag Guest House A	23	Lagos Lagoon	7.99	59.3	3.99	32.05	18.24	29.35
Unilag Guest House B	23	Lagos Lagoon	7.79	63.4	4.38	32.29	18.34	29.4
Unilag Guest House C	23	Lagos Lagoon	7.88	85.3	5.86	32.53	18.43	29.56
Apese Lagoon 1 A	24 A-1	Lagos Lagoon	7.92	92	6.78	0.22	0.13	20.27
Apese Lagoon 1 B	24B-2	" "	7.96	95.8	7.48	2.09	0.12	28.55
Apese Lagoon 1 C	24C-3	Lagos Lagoon	7.94	75.3	5.5	20.83	11.5	28.6
Apese Lagoon 2 A	25A-1	Lagos Lagoon	8.04	89	6.41	21.08	11.6	28.25
Apese Lagoon 2 B	25B-2	Lagos Lagoon	8.08	86.6	6.29	21.04	11.61	28.9
Apese Lagoon 2 C	25C-3	Lagos Lagoon	7.79	81.9	5.89	21.01	11.56	29.04
Apese Lagoon 3 A	26A-1	Lagos Lagoon	7.87	91.7	6.45	21.09	11.56	29.12
Apese Lagoon 3 B	26B-2	Lagos Lagoon	7.99	98.3	7.04	21.22	11.6	29.33
Apese Lagoon 3 C	26C-3	Lagos Lagoon	7.9	95.3	6.85	21.02	11.57	29.35

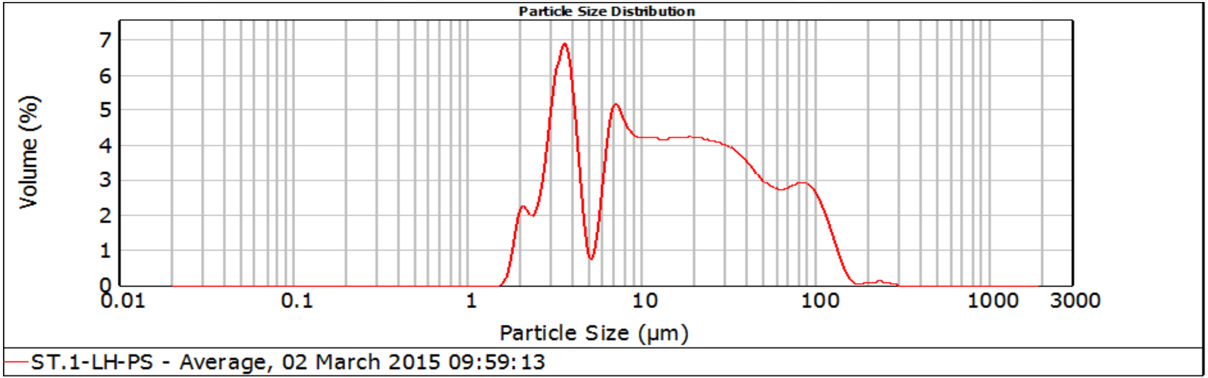
Appendix 7: Results of particle size distributions generated from the Laser machine readings analysed.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1						% Result Between User Sizes (Sizes in um)												
2						CLAY	CLAY	V. FINE SILT	FINE SILT	MED SILT	COARSE SILT	V. FINE SAND	FINE SAND	MED SAND	COARSE SAND	V. COARSE SAND		
3						0.02 - 0.1 µm	0.1 - 3.90 µm	3.90 - 7.81 µm	7.81 - 15.63 µm	15.63 - 31.25 µm	31.25 - 62.50 µm	62.50 - 125.00 µm	125.00 - 250.00 µm	250.00 - 500.00 µm	500.00 - 1000.00 µm	1000.00 - 2000.00 µm		
4																		
5	Sample Name	d (0.1)	d (0.5)	d (0.9)													Operator Notes	
6																		
7	ST.1-LH-PS - Average	3.213	14.12	75.28		0	18.4965	14.9441	19.3336	18.7945	15.2182	11.721	1.445924	0.046147	0	0		
8	ST.2-LH-PS - Average	6.92	91.671	329.087		0	5.20699	5.97433	7.1636	7.87516	10.4179	31.1626	19.055709	6.73619	5.253561	1.153994		
9	ST.3-LH-PS - Average	4.773	78.035	361.631		0	7.69427	8.28991	9.15047	9.7315	10.9982	18.2141	20.439352	8.074245	7.271794	0.136182		
10	ST.4-LH-PS - Average	3.488	42.983	305.976		0	12.8937	9.87265	11.7228	10.9447	9.86475	13.2054	15.951691	15.544347	0	0		
11	ST.5-LH-PS - Average	12.557	217.607	531.868		0	3.1287	3.91014	4.30651	4.37545	4.54553	9.63021	27.022523	31.206228	11.674672	0.200036		
12	ST.6-LH-PS - Average	2.995	11.441	95.761		0	21.8361	17.8973	17.584	14.3984	11.6862	10.0348	6.382722	0.180545	0	0		
13	ST.7-LH-PS - Average	3.46	21.435	115.962		0	13.7893	13.6989	15.3797	15.0337	14.5796	21.1893	6.329479	0	0	0		
14	ST.8-LH-PS - Average	3.479	26.021	178.215		0	13.3789	11.0986	14.5049	15.0073	15.253	15.5403	8.910996	6.306105	0	0		
15	ST.9-LH-PS - Average	3.651	36.832	158.399		0	11.3325	8.91	12.1742	13.752	18.9061	20.5579	8.891931	5.475498	0	0		
16	ST.10-LH-PS - Average	6.715	86.288	229.672		0	5.22431	6.34757	7.97475	9.19018	11.5287	29.7855	21.280909	6.804586	1.863481	0		
17	ST.11-LH-PS - Average	7.608	91.31	258.332		0	4.68083	5.56011	6.82431	8.51574	12.5194	28.5829	22.806848	10.509839	0	0		
18	ST.12-LH-PS - Average	14.906	116.435	280.31		0	2.78018	3.46884	4.03556	4.46093	7.43314	32.8398	29.785406	15.196123	0	0		
19	ST.13-LH-PS - Average	3.38	27.247	120.46		0	14.823	11.4256	13.0754	13.3587	18.2272	20.4694	8.620687	0	0	0		
20	ST.14-LH-PS - Average	3.375	23.487	138.271		0	14.833	13.7527	13.8319	12.7356	14.6304	17.2997	12.916704	0	0	0		
21	ST.15-LH-PS - Average	3.161	21.416	168.023		0	18.8989	12.7558	13.033	11.5356	10.5981	16.0133	17.165386	0	0	0		
22	ST.16-LH-PS - Average	8.815	137.626	348.597		0	4.40918	4.72507	4.86934	5.01512	6.82144	20.2715	22.288231	31.600132	0	0		
23	ST.17-LG-PS - Average	8.796	123.362	254.198		0	4.32509	4.77297	5.10227	5.16862	6.66875	24.7419	38.587953	10.287524	0.344928	0		
24	ST.18-LG-PS - Average	7.856	117.548	196.027		0	5.20899	4.74857	4.72323	4.56598	6.37682	28.2116	46.164842	0	0	0		
25	ST.19-LG-PS - Average	6.341	130.862	492.749		0	5.86887	6.14631	7.17553	8.09639	10.1876	11.6649	18.372344	22.866433	9.621643	0		
26	ST.20-LG-PS - Average	91.539	202.114	328.571		0	0.8	1.11353	1.37246	1.56891	2.17373	10.1497	53.253058	28.853506	0.715163	0		
27	ST.21-LG-PS - Average	3.74	56.343	263.084		0	10.6152	7.46596	9.38683	11.1921	13.7986	19.1396	16.583515	11.818208	0	0		
28	ST.22-LG-PS - Average	3.331	16.945	135.394		0	15.8494	13.4731	18.5421	16.9174	12.6326	11.5488	6.257139	4.779387	0	0		
29	ST.23-LG-PS - Average	3.896	23.291	153.539		0	10.0204	11.948	17.43	18.2701	15.7623	14.1861	12.383069	0	0	0		
30	ST.24-APL-PS - Average	16.183	259.608	559.768		0	1.52473	3.26341	4.94947	5.14349	4.69204	6.88558	21.458076	37.924603	13.971533	0.187086		
31	ST.25-APL-PS - Average	86.741	325.81	644.565		0	0.61363	1.10727	1.62003	2.11039	2.63465	5.59486	19.230393	45.50593	21.239272	0.343579		
32	ST.26-APL-PS - Average	9.64	85.828	402.659		0	2.90812	4.94312	8.01998	11.0646	14.8868	20.3133	17.08279	14.493895	6.078193	0.20917		

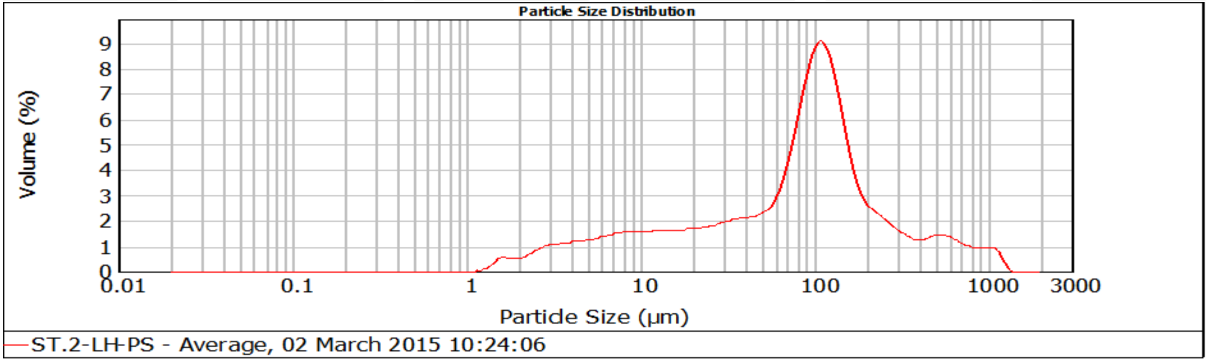
Appendix 8: Chromatographs generated by Laser Machine for particle size distribution for sites 1-26(DS-2-2014) across LH, LG and APL.

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	14.94	15.630	18.79	63.000	11.72	250.000	0.05	1000.000	0.00
0.100	18.50	7.810	19.33	31.250	15.22	125.000	1.45	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



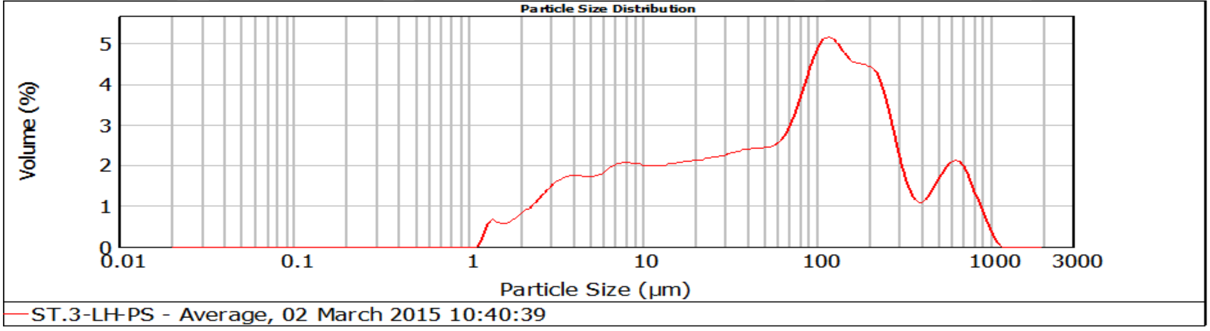
ST.1-LH-PS - Average, 02 March 2015 09:59:13

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	5.97	15.630	7.88	63.000	31.16	250.000	6.74	1000.000	1.15
0.100	5.21	7.810	7.16	31.250	10.42	125.000	19.06	500.000	5.25	2000.000	
3.900		15.630		63.000		250.000		1000.000			



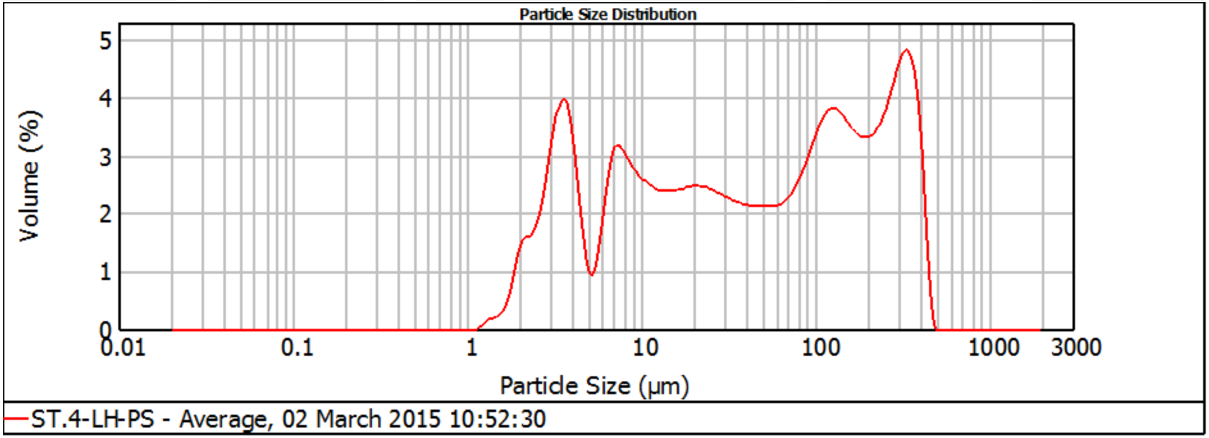
ST.2-LH-PS - Average, 02 March 2015 10:24:06

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	8.29	15.630	9.73	63.000	18.21	250.000	8.07	1000.000	0.14
0.100	7.69	7.810	9.15	31.250	11.00	125.000	20.44	500.000	7.27	2000.000	
3.900		15.630		63.000		250.000		1000.000			

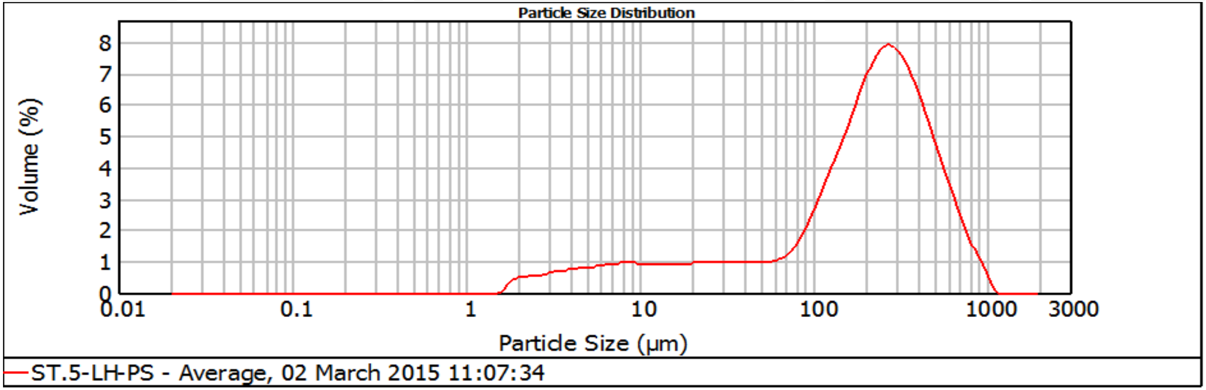


ST.3-LH-PS - Average, 02 March 2015 10:40:39

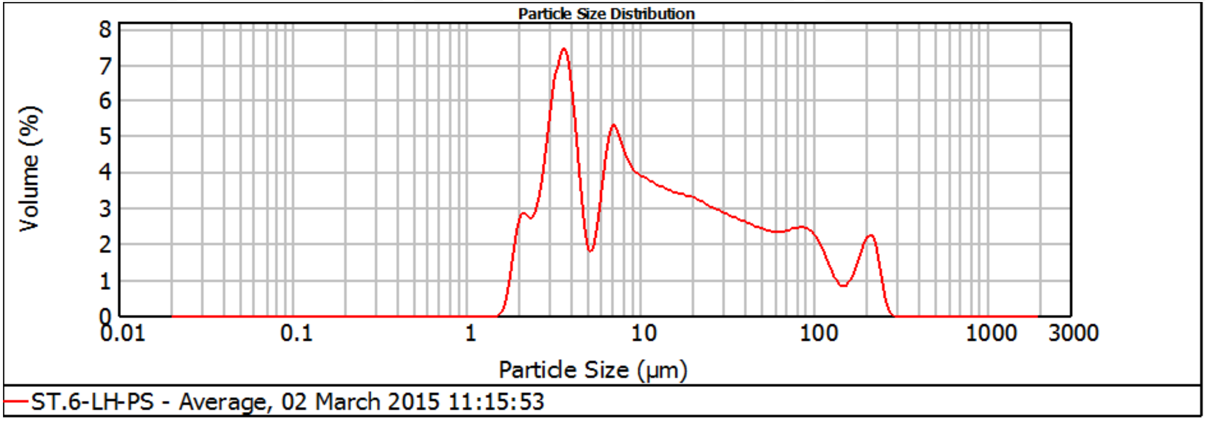
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	9.87	15.630	10.94	63.000	13.21	250.000	15.54	1000.000	0.00
0.100	12.89	7.810	11.72	31.250	9.86	125.000	15.95	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



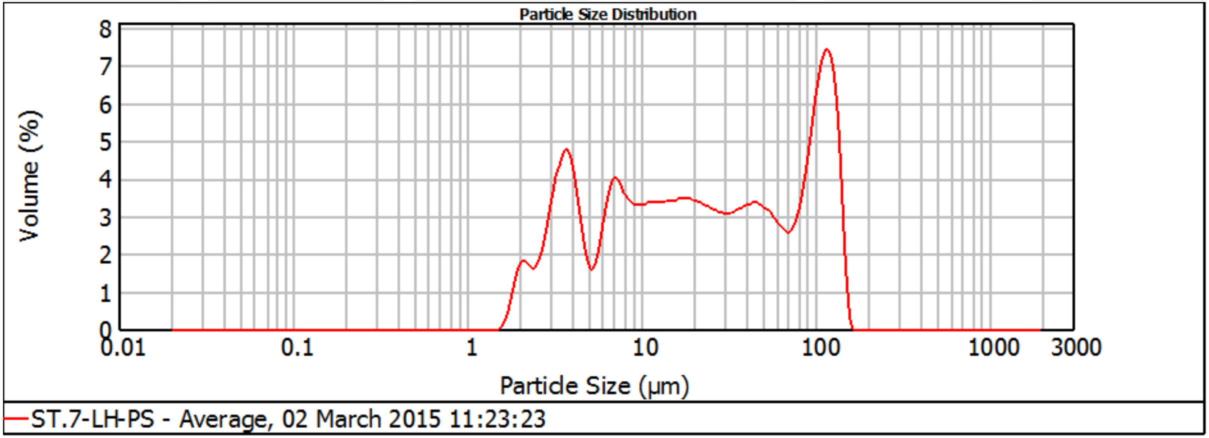
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	3.91	15.630	4.38	63.000	9.63	250.000	31.21	1000.000	0.20
0.100	3.13	7.810	4.31	31.250	4.55	125.000	27.02	500.000	11.67	2000.000	
3.900		15.630		63.000		250.000		1000.000			



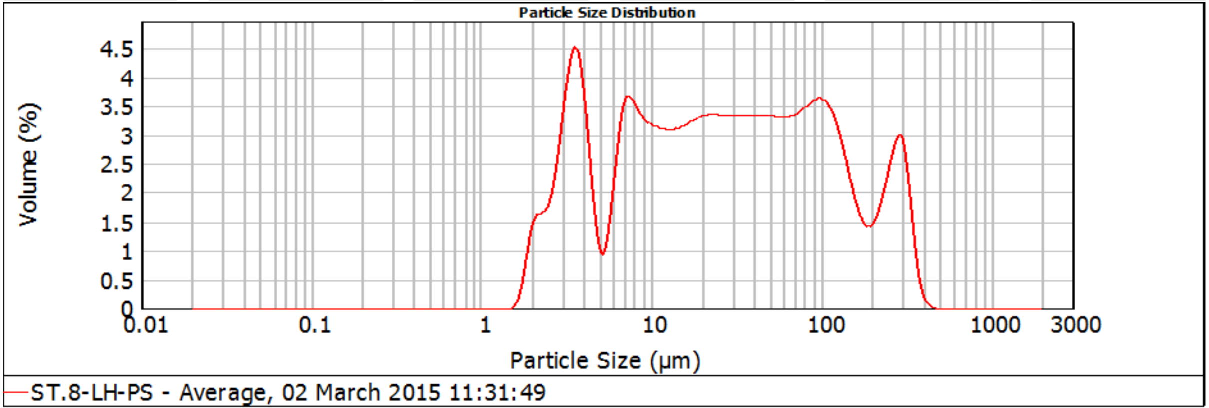
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	17.90	15.630	14.40	63.000	10.03	250.000	0.18	1000.000	0.00
0.100	21.84	7.810	17.58	31.250	11.69	125.000	6.38	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



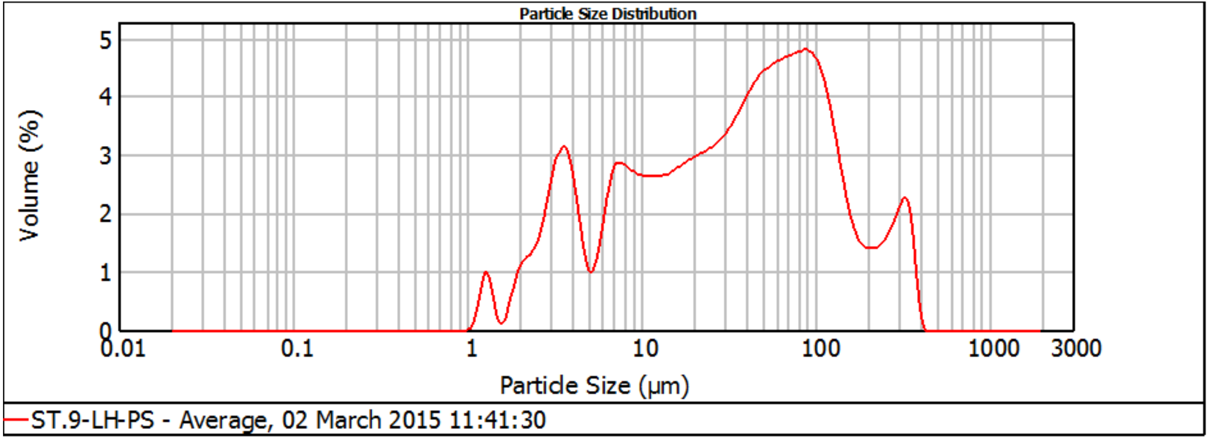
Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020		3.900		15.630		63.000		250.000		1000.000	
	0.00		13.70		15.03		21.19		0.00		0.00
0.100		7.810		31.250		125.000		500.000		2000.000	
	13.79		15.38		14.58		6.33		0.00		
3.900		15.630		63.000		250.000		1000.000			



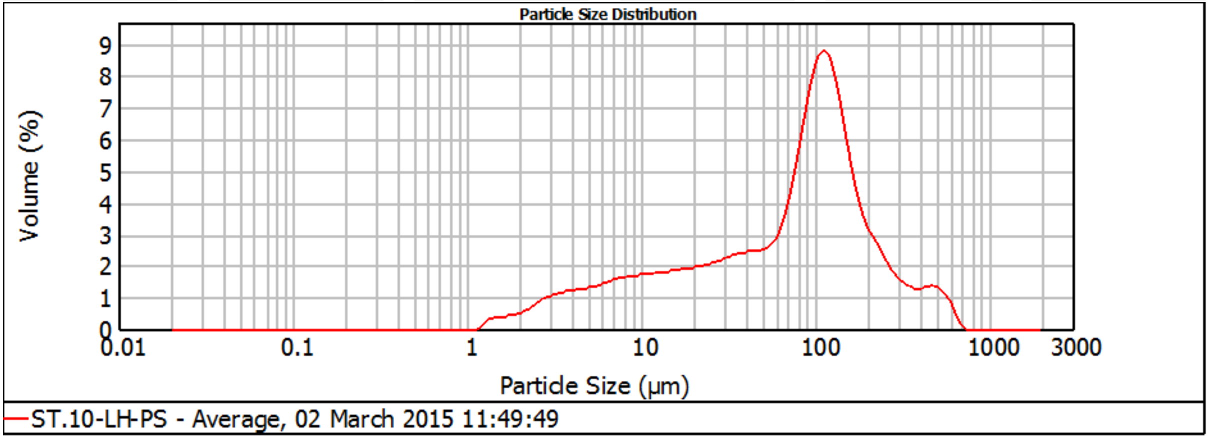
Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020		3.900		15.630		63.000		250.000		1000.000	
	0.00		11.10		15.01		15.54		6.31		0.00
0.100		7.810		31.250		125.000		500.000		2000.000	
	13.38		14.50		15.25		8.91		0.00		
3.900		15.630		63.000		250.000		1000.000			



Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020		3.900		15.630		63.000		250.000		1000.000	
	0.00		8.91		13.75		20.56		5.48		0.00
0.100		7.810		31.250		125.000		500.000		2000.000	
	11.33		12.17		18.91		8.89		0.00		
3.900		15.630		63.000		250.000		1000.000			

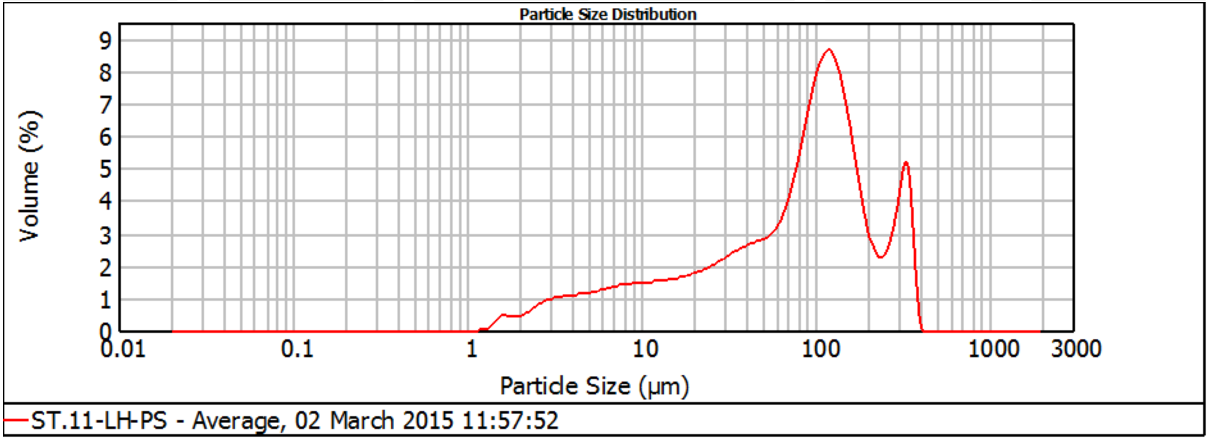


Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	6.35	15.630	9.19	63.000	29.79	250.000	6.80	1000.000	0.00
0.100	5.22	7.810	7.97	31.250	11.53	125.000	21.28	500.000	1.86	2000.000	
3.900		15.630		63.000		250.000		1000.000			



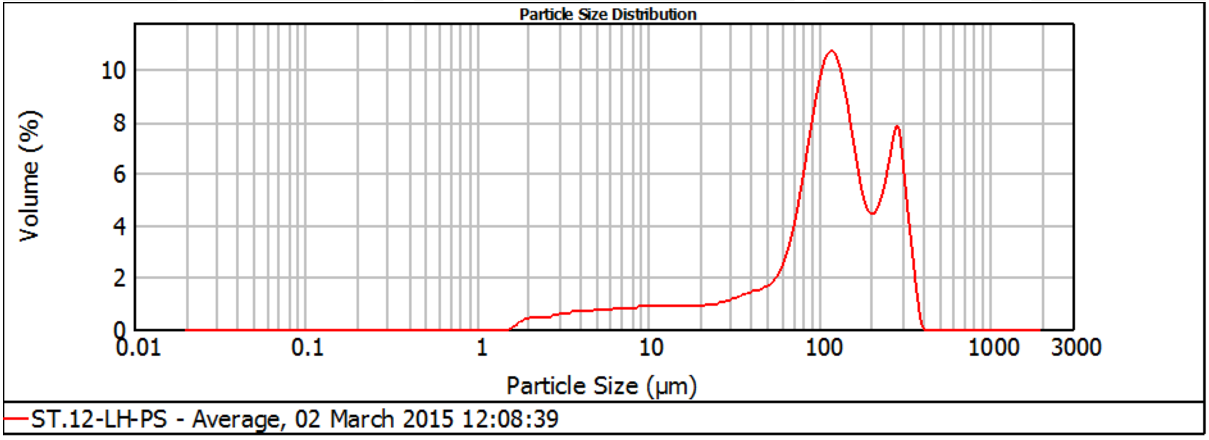
ST.10-LH-PS - Average, 02 March 2015 11:49:49

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	5.56	15.630	8.52	63.000	28.58	250.000	10.51	1000.000	0.00
0.100	4.68	7.810	6.82	31.250	12.52	125.000	22.81	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



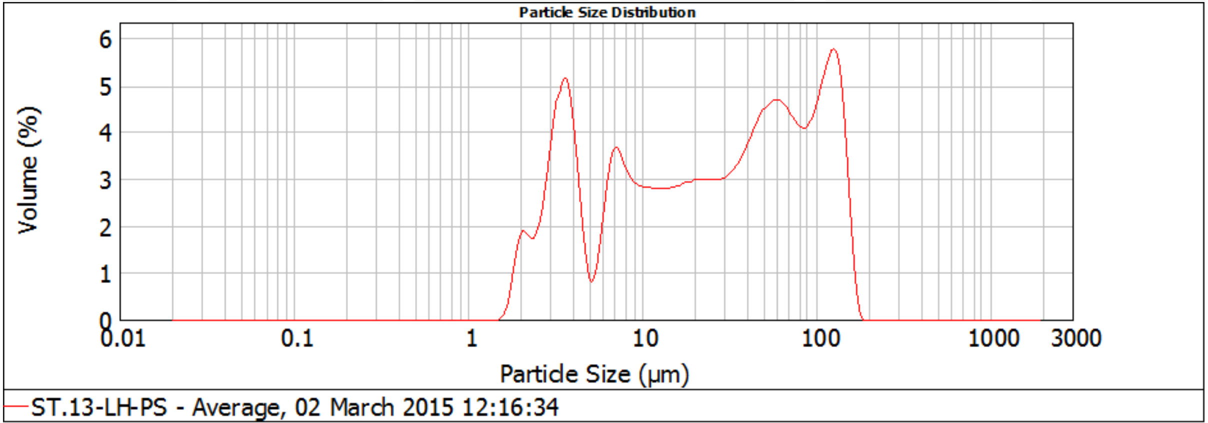
ST.11-LH-PS - Average, 02 March 2015 11:57:52

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	3.47	15.630	4.46	63.000	32.84	250.000	15.20	1000.000	0.00
0.100	2.78	7.810	4.04	31.250	7.43	125.000	29.79	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			

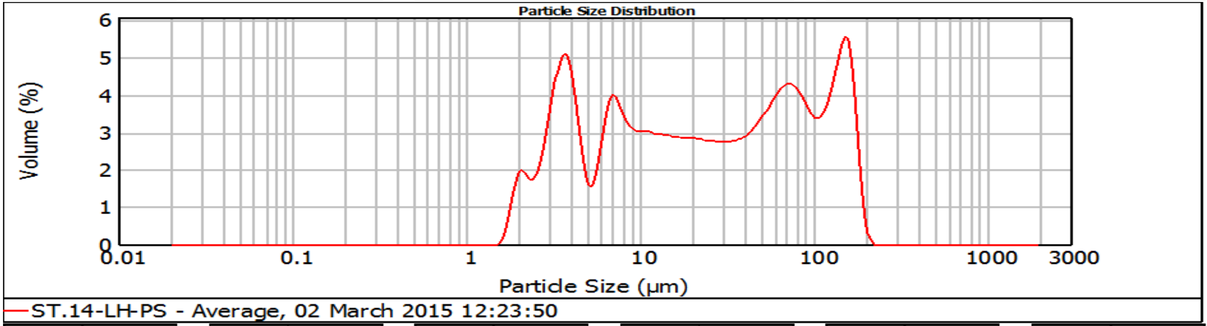


ST.12-LH-PS - Average, 02 March 2015 12:08:39

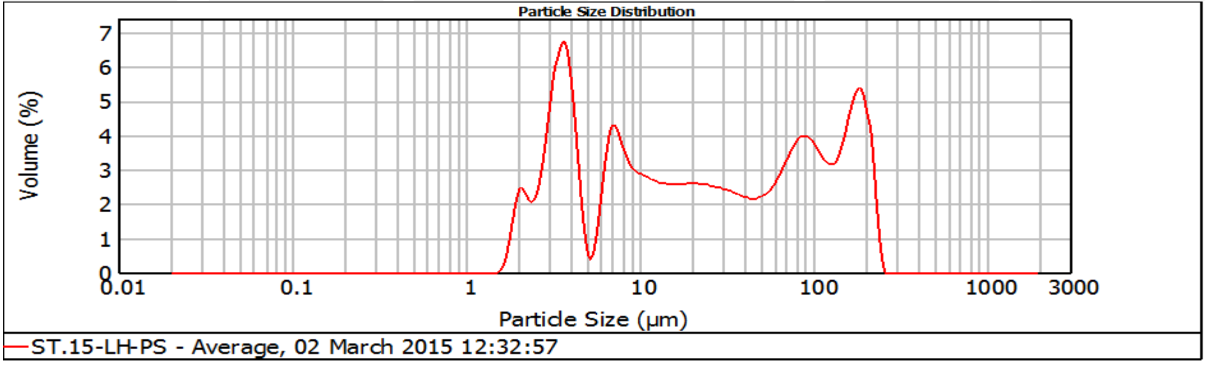
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	11.43	15.630	13.36	63.000	20.47	250.000	0.00	1000.000	0.00
0.100	14.82	7.810	13.08	31.250	18.23	125.000	8.62	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



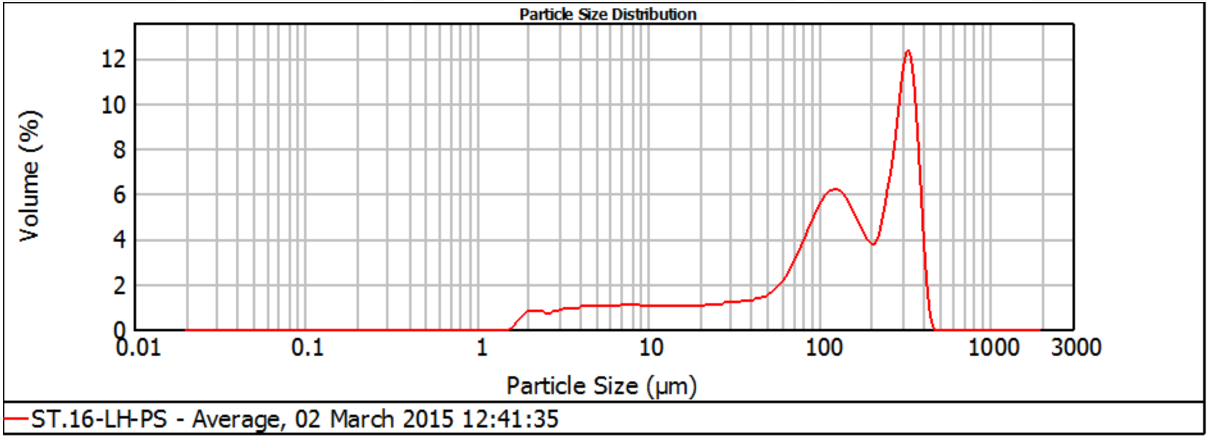
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	13.75	15.630	12.74	63.000	17.30	250.000	0.00	1000.000	0.00
0.100	14.83	7.810	13.83	31.250	14.63	125.000	12.92	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	12.76	15.630	11.54	63.000	16.01	250.000	0.00	1000.000	0.00
0.100	18.90	7.810	13.03	31.250	10.60	125.000	17.17	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			

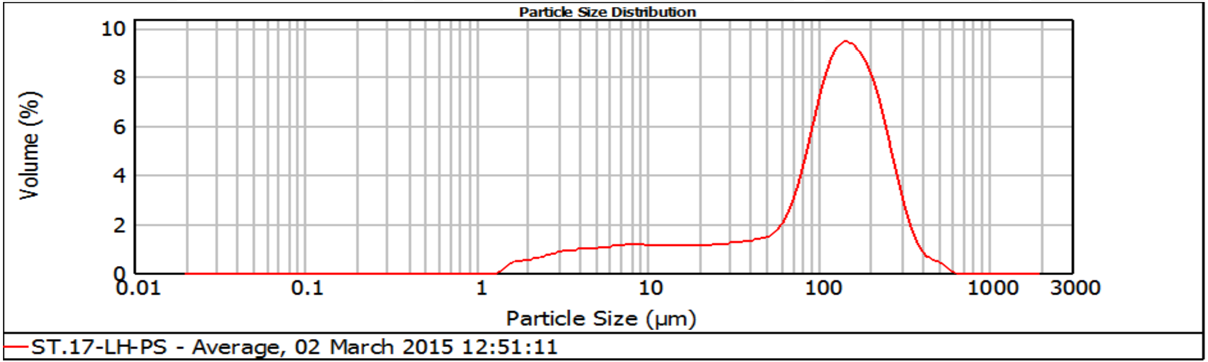


Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	4.73	15.630	5.02	63.000	20.27	250.000	31.60	1000.000	0.00
0.100	4.41	7.810	4.87	31.250	6.82	125.000	22.29	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



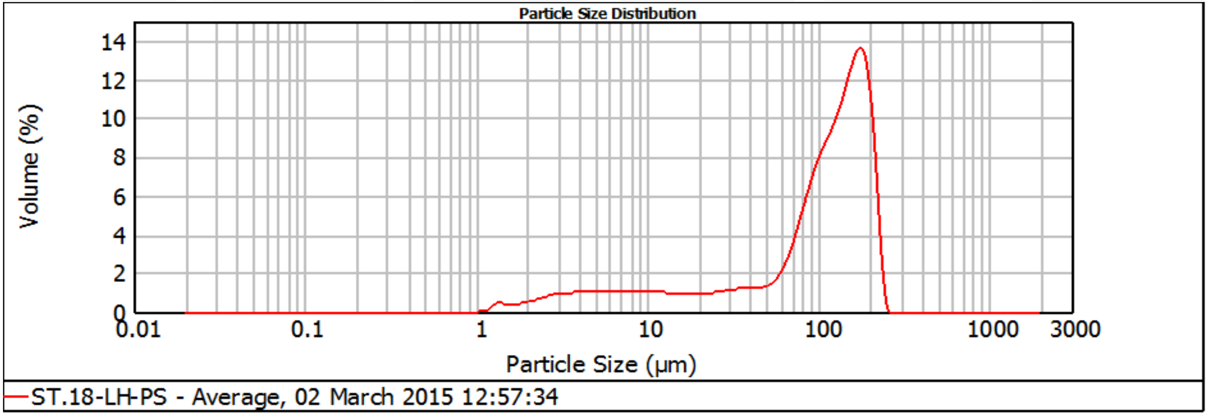
ST.16-LH-PS - Average, 02 March 2015 12:41:35

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	4.77	15.630	5.17	63.000	24.74	250.000	10.29	1000.000	0.00
0.100	4.33	7.810	5.10	31.250	6.67	125.000	38.59	500.000	0.34	2000.000	
3.900		15.630		63.000		250.000		1000.000			



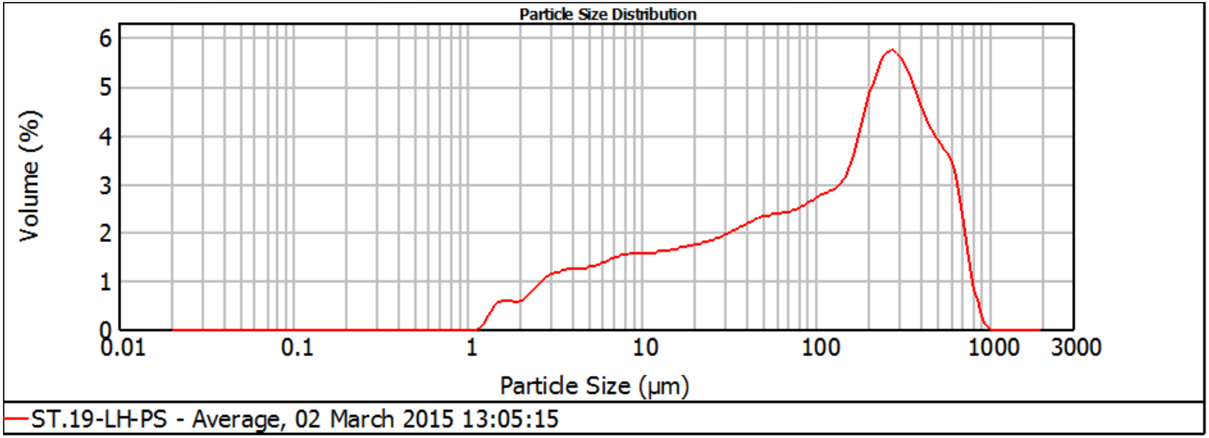
ST.17-LH-PS - Average, 02 March 2015 12:51:11

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	4.75	15.630	4.57	63.000	28.21	250.000	0.00	1000.000	0.00
0.100	5.21	7.810	4.72	31.250	6.38	125.000	46.16	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			

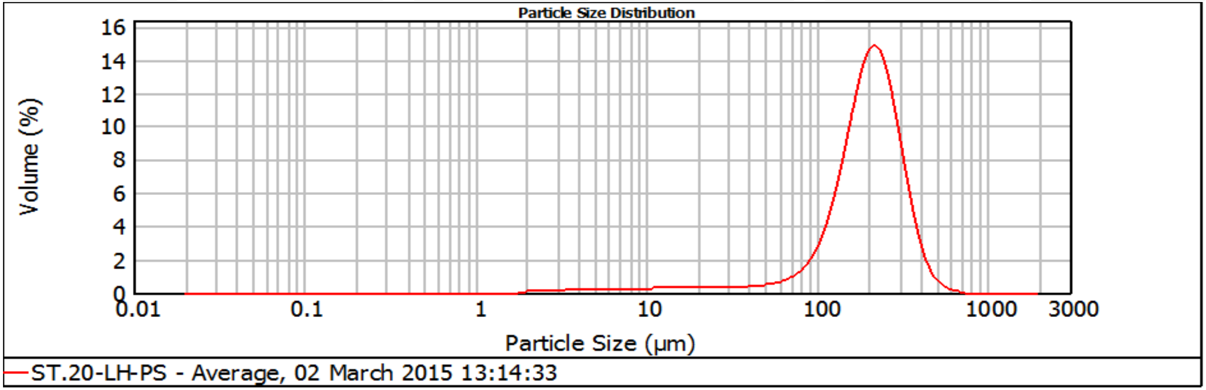


ST.18-LH-PS - Average, 02 March 2015 12:57:34

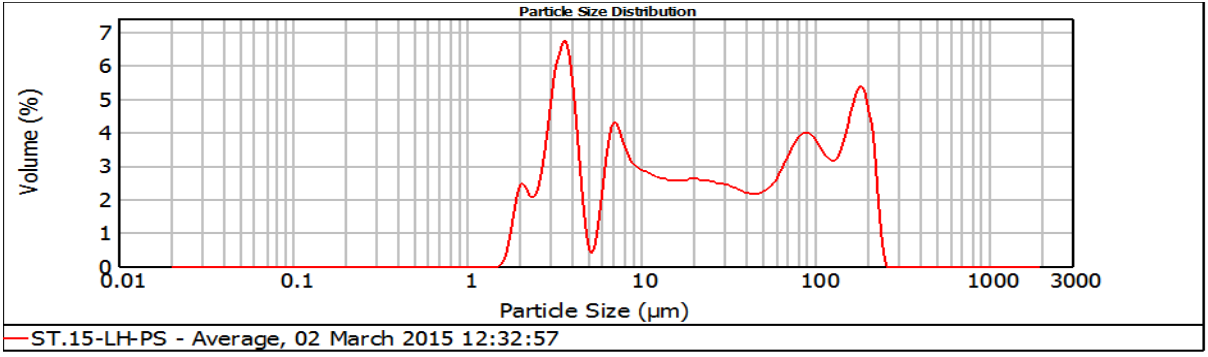
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020		3.900		15.630		63.000		250.000		1000.000	
	0.00		6.15		8.10		11.66		22.87		0.00
0.100		7.810		31.250		125.000		500.000		2000.000	
	5.87		7.18		10.19		18.37		9.62		
3.900		15.630		63.000		250.000		1000.000			



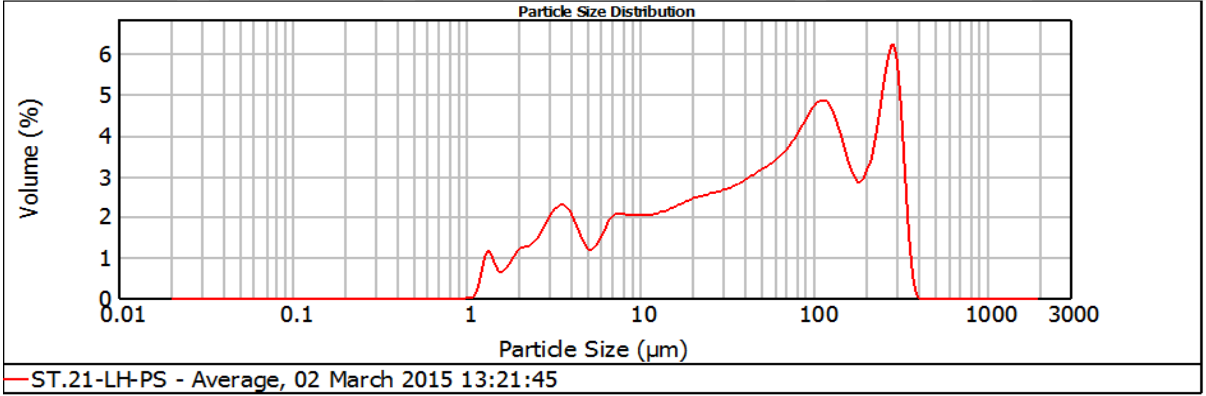
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020		3.900		15.630		63.000		250.000		1000.000	
	0.00		1.11		1.57		10.15		28.85		0.00
0.100		7.810		31.250		125.000		500.000		2000.000	
	0.80		1.37		2.17		53.25		0.72		
3.900		15.630		63.000		250.000		1000.000			



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020		3.900		15.630		63.000		250.000		1000.000	
	0.00		7.47		11.19		19.14		11.82		0.00
0.100		7.810		31.250		125.000		500.000		2000.000	
	10.62		9.39		13.80		16.58		0.00		
3.900		15.630		63.000		250.000		1000.000			

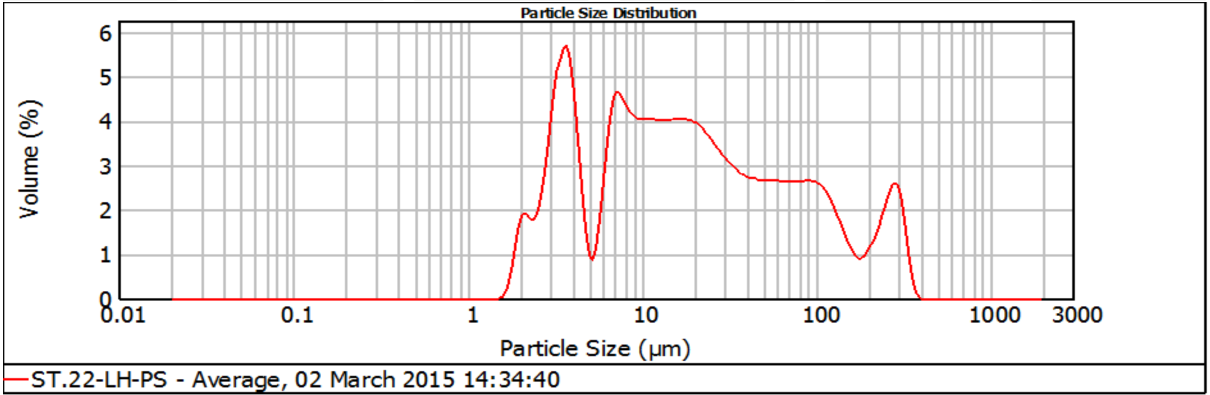


Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	13.47	15.630	16.92	63.000	11.55	250.000	4.78	1000.000	0.00
0.100	15.85	7.810	18.54	31.250	12.63	125.000	6.26	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



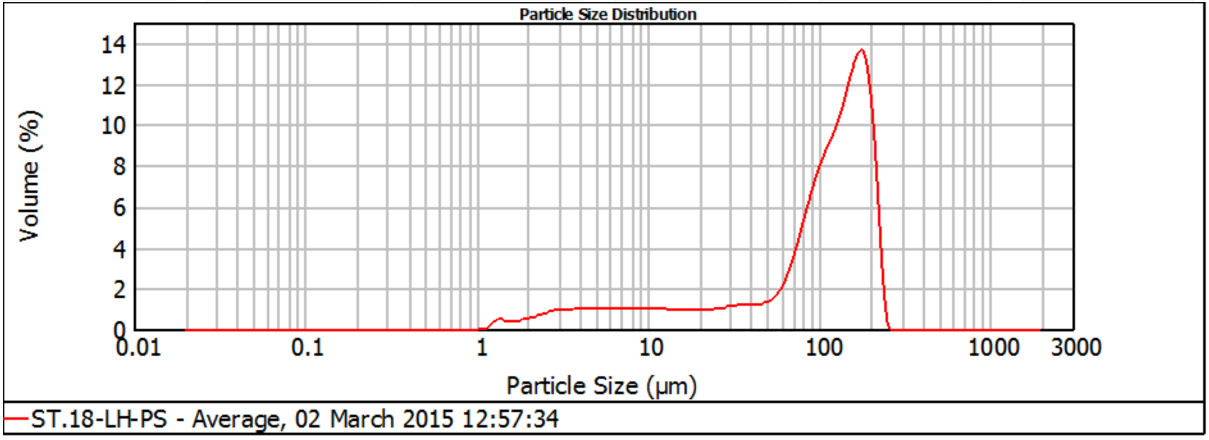
ST.21-LH-PS - Average, 02 March 2015 13:21:45

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	4.75	15.630	4.57	63.000	28.21	250.000	0.00	1000.000	0.00
0.100	5.21	7.810	4.72	31.250	6.38	125.000	46.16	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			



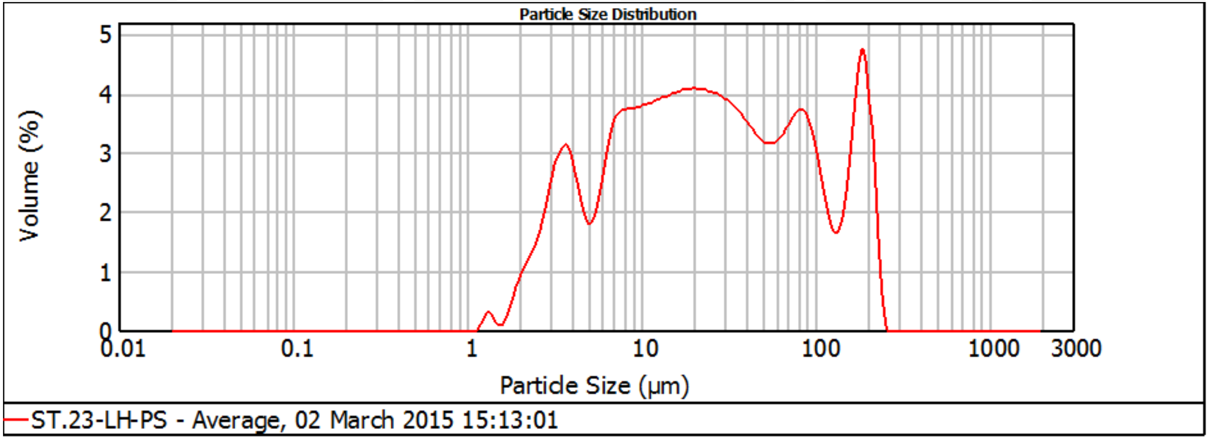
ST.22-LH-PS - Average, 02 March 2015 14:34:40

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	11.95	15.630	18.27	63.000	14.19	250.000	0.00	1000.000	0.00
0.100	10.02	7.810	17.43	31.250	15.76	125.000	12.38	500.000	0.00	2000.000	
3.900		15.630		63.000		250.000		1000.000			

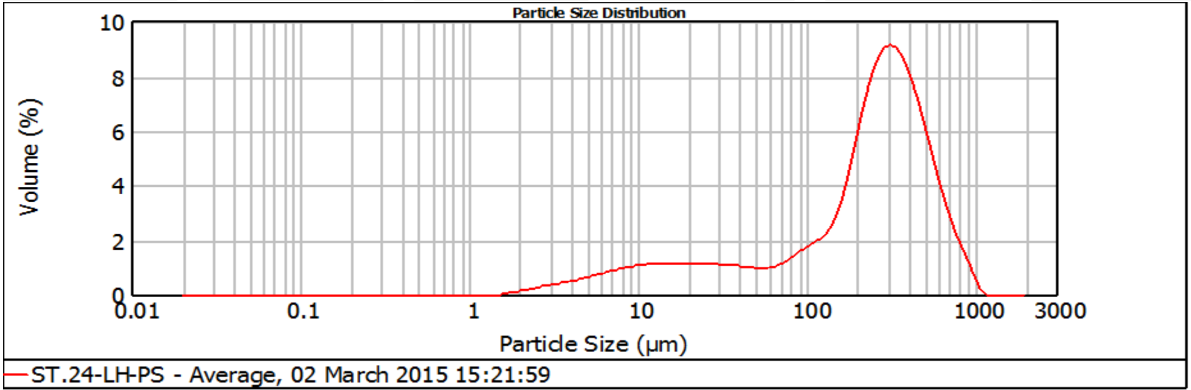


ST.18-LH-PS - Average, 02 March 2015 12:57:34

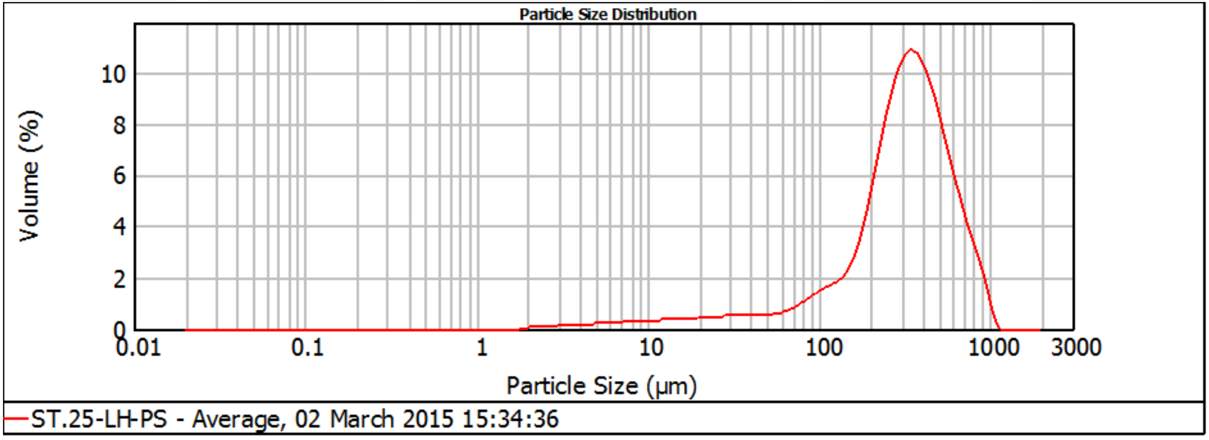
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	3.26	15.630	5.14	63.000	6.89	250.000	37.92	1000.000	0.19
0.100	1.52	7.810	4.95	31.250	4.69	125.000	21.46	500.000	13.97	2000.000	
3.900		15.630		63.000		250.000		1000.000			



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	1.11	15.630	2.11	63.000	5.59	250.000	45.51	1000.000	0.34
0.100	0.61	7.810	1.62	31.250	2.63	125.000	19.23	500.000	21.24	2000.000	
3.900		15.630		63.000		250.000		1000.000			



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	3.900	4.94	15.630	11.06	63.000	20.31	250.000	14.49	1000.000	0.21
0.100	2.91	7.810	8.02	31.250	14.89	125.000	17.08	500.000	6.08	2000.000	
3.900		15.630		63.000		250.000		1000.000			



Size (µm)	Volume In %
0.020	0.00
0.100	1.52
3.900	

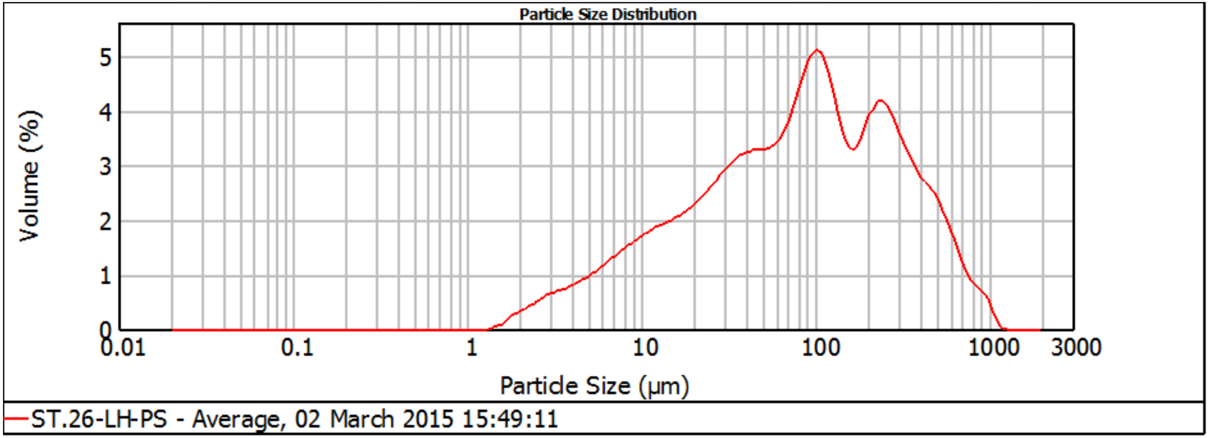
Size (µm)	Volume In %
3.900	3.26
7.810	4.95
15.630	

Size (µm)	Volume In %
15.630	5.14
31.250	4.69
63.000	

Size (µm)	Volume In %
63.000	6.89
125.000	21.46
250.000	

Size (µm)	Volume In %
250.000	37.92
500.000	13.97
1000.000	

Size (µm)	Volume In %
1000.000	0.19
2000.000	



Size (µm)	Volume In %
0.020	0.00
0.100	1.52
3.900	

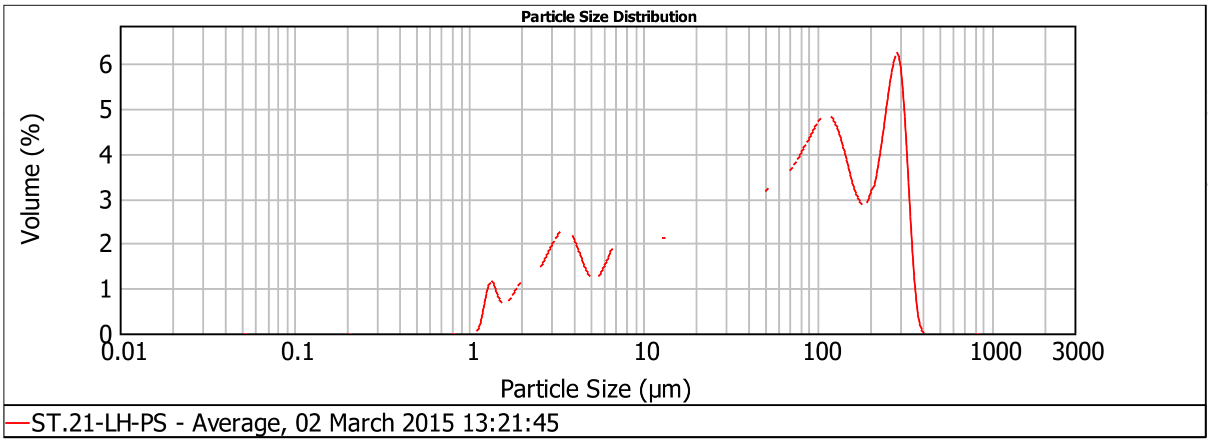
Size (µm)	Volume In %
3.900	3.26
7.810	4.95
15.630	

Size (µm)	Volume In %
15.630	5.14
31.250	4.69
63.000	

Size (µm)	Volume In %
63.000	6.89
125.000	21.46
250.000	

Size (µm)	Volume In %
250.000	37.92
500.000	13.97
1000.000	

Size (µm)	Volume In %
1000.000	0.19
2000.000	



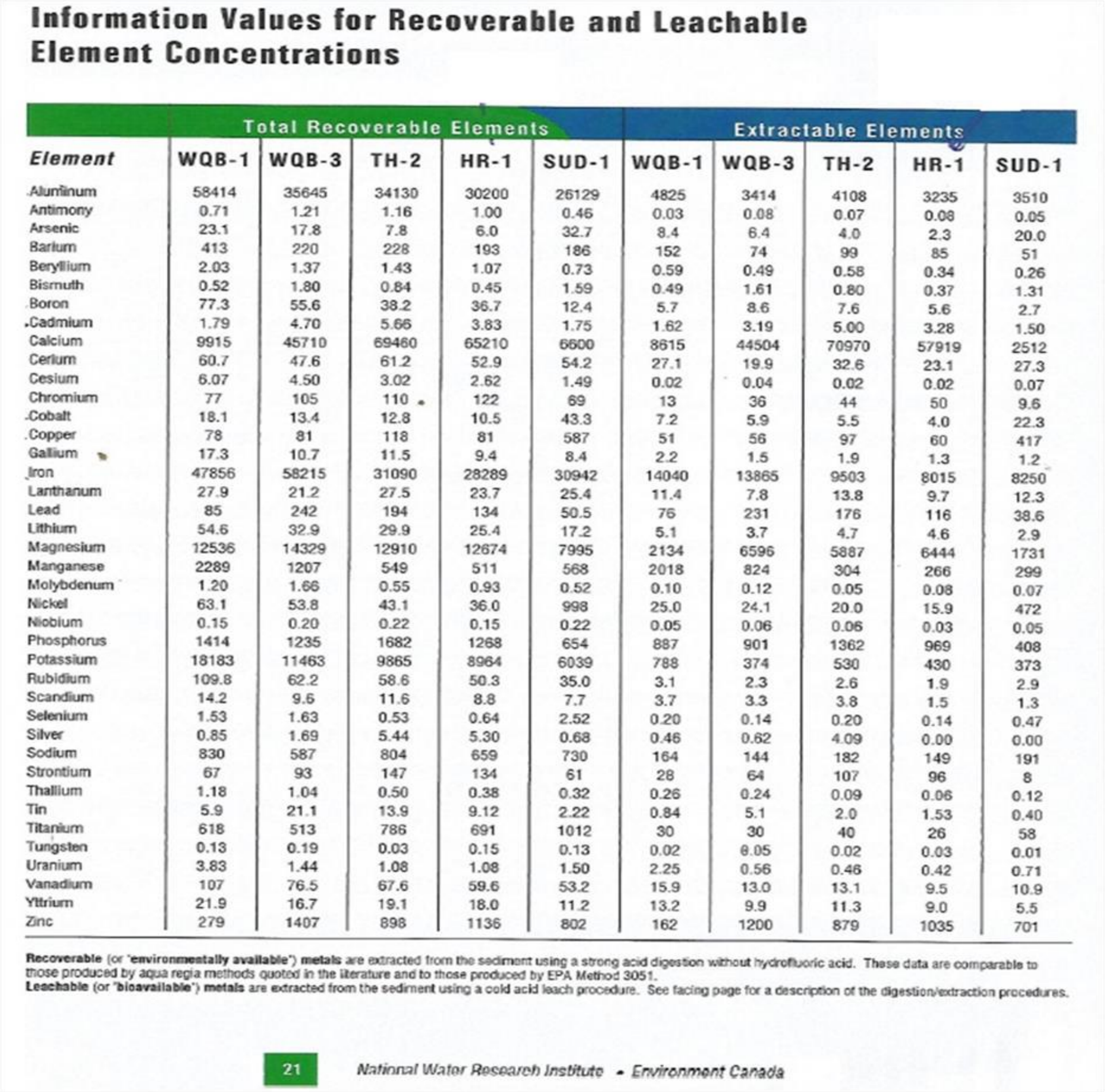
Appendix 9: Total organic Carbon and Nitrogen contents concentrations (N and C) in marine sediments of LH, LG and APL in percentage and mg/g (WS 2013).

	N%		**C%**		
Sites number	Mean	mg/g	Mean	mg/g	Location
1	0.15	1.54	4.72	47.19	Lagos Harbour
2	0.06	0.59	3.60	35.96	' "
3	0.00	0.00	1.27	12.73	' "
4	0.00	0.00	3.32	33.19	' "
5	0.00	0.00	2.24	22.38	' "
6	0.00	0.00	3.02	30.23	' "
7	0.00	0.00	2.45	24.52	' "
8	0.00	0.00	2.60	25.98	' "
9	0.42	4.16	3.03	30.27	' "
10	0.20	1.97	2.58	25.83	' "
11	0.03	0.35	1.54	15.37	' "
12	0.00	0.00	1.05	10.47	' "
13	0.00	0.00	1.41	14.10	' "
14	0.00	0.00	3.07	30.73	' "
15	0.00	0.00	2.33	23.28	' "
16	0.00	0.00	0.79	7.91	' "
17	0.00	0.00	2.23	22.32	Lagos Lagoon
18	0.00	0.00	2.88	28.77	' "
19	0.02	0.22	4.63	46.30	' "
20	0.00	0.00	0.57	5.69	' "
21	0.00	0.00	3.63	36.30	' "
22	0.00	0.00	2.85	28.50	' "
23	0.05	0.46	12.87	128.70	' "
24	0.00	0.00	3.99	39.90	Apese Lagoon

Appendix 10: Total Carbon & Nitrogen contents concentrations (N and C) in marine sediments of Lagos Harbour, Lagos Lagoon and Apese Lagoon in percentage and mg/g (dry season-2-(2014).

Sites	N%	mg/g	C%	mg/g	Area
1	0.23	2.32	1.18	11.84	Lagos Harbour
2	0.29	2.87	1.72	17.18	' "
3	0.15	1.47	1.54	15.38	' "
4	0.47	4.70	3.06	30.57	' "
5	0.35	3.47	2.94	29.38	' "
6	0.89	8.90	5.26	52.63	' "
7	0.20	1.97	3.05	30.54	' "
8	0.22	2.17	3.46	34.61	' "
9	0.00	0.00	3.00	30.00	' "
10	0.00	0.00	3.33	33.33	' "
11	0.00	0.00	3.67	36.67	' "
12	0.00	0.00	4.00	40.00	' "
13	0.00	0.00	4.33	43.33	' "
14	0.09	0.90	5.00	49.97	' "
15	0.25	2.47	5.90	59.04	' "
16	0.22	2.17	6.13	61.28	' "
17	0.23	2.33	8.62	86.17	Lagos Lagoon
18	0.28	2.77	7.01	70.14	' "
19	0.18	1.83	7.01	70.06	' "
20	0.19	1.90	7.36	73.63	' "
21	0.12	1.23	7.45	74.52	' "
22	0.19	1.93	8.04	80.42	
23	0.19	1.93	8.38	83.76	' "
24	0.20	1.97	8.72	87.21	Apese Lagoon
25	0.24	2.40	9.21	92.13	' "
26	0.00	0.00	8.67	86.67	' "

Appendix 11: HR-1 reference material.

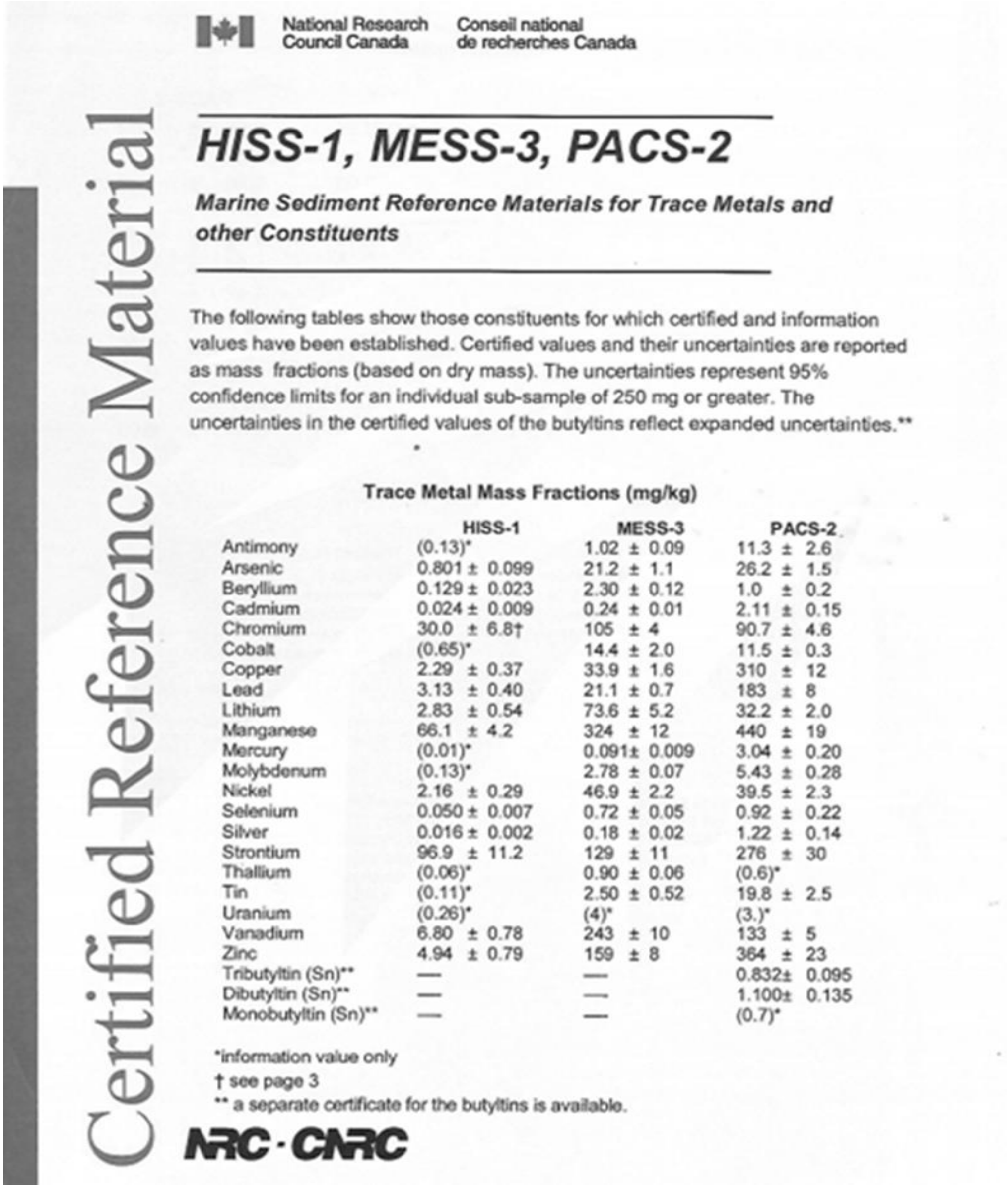


Information Values for Recoverable and Leachable Element Concentrations

Element	Total Recoverable Elements					Extractable Elements				
	WQB-1	WQB-3	TH-2	HR-1	SUD-1	WQB-1	WQB-3	TH-2	HR-1	SUD-1
Aluminum	58414	35645	34130	30200	26129	4825	3414	4108	3235	3510
Antimony	0.71	1.21	1.16	1.00	0.46	0.03	0.08	0.07	0.08	0.05
Arsenic	23.1	17.8	7.8	6.0	32.7	8.4	6.4	4.0	2.3	20.0
Barium	413	220	228	193	186	152	74	99	85	51
Beryllium	2.03	1.37	1.43	1.07	0.73	0.59	0.49	0.58	0.34	0.26
Bismuth	0.52	1.80	0.84	0.45	1.59	0.49	1.61	0.80	0.37	1.31
Boron	77.3	55.6	38.2	36.7	12.4	5.7	8.6	7.6	5.6	2.7
Cadmium	1.79	4.70	5.66	3.83	1.75	1.62	3.19	5.00	3.28	1.50
Calcium	9915	45710	69460	65210	6600	8615	44504	70970	57919	2512
Cerium	60.7	47.6	61.2	52.9	54.2	27.1	19.9	32.6	23.1	27.3
Cesium	6.07	4.50	3.02	2.62	1.49	0.02	0.04	0.02	0.02	0.07
Chromium	77	105	110	122	69	13	36	44	50	9.6
Cobalt	18.1	13.4	12.8	10.5	43.3	7.2	5.9	5.5	4.0	22.3
Copper	78	81	118	81	587	51	56	97	60	417
Gallium	17.3	10.7	11.5	9.4	8.4	2.2	1.5	1.9	1.3	1.2
Iron	47856	58215	31090	28289	30942	14040	13865	9503	8015	8250
Lanthanum	27.9	21.2	27.5	23.7	25.4	11.4	7.8	13.8	9.7	12.3
Lead	85	242	194	134	50.5	76	231	176	116	38.6
Lithium	54.6	32.9	29.9	25.4	17.2	5.1	3.7	4.7	4.6	2.9
Magnesium	12536	14329	12910	12674	7995	2134	6596	5887	6444	1731
Manganese	2289	1207	549	511	568	2018	824	304	266	299
Molybdenum	1.20	1.66	0.55	0.93	0.52	0.10	0.12	0.05	0.08	0.07
Nickel	63.1	53.8	43.1	36.0	998	25.0	24.1	20.0	15.9	472
Niobium	0.15	0.20	0.22	0.15	0.22	0.05	0.06	0.06	0.03	0.05
Phosphorus	1414	1235	1682	1268	654	887	901	1362	969	408
Potassium	18183	11463	9865	8964	6039	788	374	530	430	373
Rubidium	109.8	62.2	58.6	50.3	35.0	3.1	2.3	2.6	1.9	2.9
Scandium	14.2	9.6	11.6	8.8	7.7	3.7	3.3	3.8	1.5	1.3
Selenium	1.53	1.63	0.53	0.64	2.52	0.20	0.14	0.20	0.14	0.47
Silver	0.85	1.69	5.44	5.30	0.68	0.46	0.62	4.09	0.00	0.00
Sodium	830	587	804	659	730	164	144	182	149	191
Strontium	67	93	147	134	61	28	64	107	96	8
Thallium	1.18	1.04	0.50	0.38	0.32	0.26	0.24	0.09	0.06	0.12
Tin	5.9	21.1	13.9	9.12	2.22	0.84	5.1	2.0	1.53	0.40
Titanium	618	513	786	691	1012	30	30	40	26	58
Tungsten	0.13	0.19	0.03	0.15	0.13	0.02	0.05	0.02	0.03	0.01
Uranium	3.83	1.44	1.08	1.08	1.50	2.25	0.56	0.46	0.42	0.71
Vanadium	107	76.5	67.6	59.6	53.2	15.9	13.0	13.1	9.5	10.9
Yttrium	21.9	16.7	19.1	18.0	11.2	13.2	9.9	11.3	9.0	5.5
Zinc	279	1407	898	1136	802	162	1200	879	1035	701

Recoverable (or "**environmentally available**") **metals** are extracted from the sediment using a strong acid digestion without hydrofluoric acid. These data are comparable to those produced by aqua regia methods quoted in the literature and to those produced by EPA Method 3051.
Leachable (or "**bioavailable**") **metals** are extracted from the sediment using a cold acid leach procedure. See facing page for a description of the digestion/extraction procedures.

Appendix 12: PACS -2 reference material.



National Research Council Canada
Conseil national de recherches Canada

Certified Reference Material

HISS-1, MESS-3, PACS-2

Marine Sediment Reference Materials for Trace Metals and other Constituents

The following tables show those constituents for which certified and information values have been established. Certified values and their uncertainties are reported as mass fractions (based on dry mass). The uncertainties represent 95% confidence limits for an individual sub-sample of 250 mg or greater. The uncertainties in the certified values of the butyltins reflect expanded uncertainties.**

Trace Metal Mass Fractions (mg/kg)

	HISS-1	MESS-3	PACS-2
Antimony	(0.13)*	1.02 ± 0.09	11.3 ± 2.6
Arsenic	0.801 ± 0.099	21.2 ± 1.1	26.2 ± 1.5
Beryllium	0.129 ± 0.023	2.30 ± 0.12	1.0 ± 0.2
Cadmium	0.024 ± 0.009	0.24 ± 0.01	2.11 ± 0.15
Chromium	30.0 ± 6.8†	105 ± 4	90.7 ± 4.6
Cobalt	(0.65)*	14.4 ± 2.0	11.5 ± 0.3
Copper	2.29 ± 0.37	33.9 ± 1.6	310 ± 12
Lead	3.13 ± 0.40	21.1 ± 0.7	183 ± 8
Lithium	2.83 ± 0.54	73.6 ± 5.2	32.2 ± 2.0
Manganese	66.1 ± 4.2	324 ± 12	440 ± 19
Mercury	(0.01)*	0.091± 0.009	3.04 ± 0.20
Molybdenum	(0.13)*	2.78 ± 0.07	5.43 ± 0.28
Nickel	2.16 ± 0.29	46.9 ± 2.2	39.5 ± 2.3
Selenium	0.050 ± 0.007	0.72 ± 0.05	0.92 ± 0.22
Silver	0.016 ± 0.002	0.18 ± 0.02	1.22 ± 0.14
Strontium	96.9 ± 11.2	129 ± 11	276 ± 30
Thallium	(0.06)*	0.90 ± 0.06	(0.6)*
Tin	(0.11)*	2.50 ± 0.52	19.8 ± 2.5
Uranium	(0.26)*	(4)*	(3.)*
Vanadium	6.80 ± 0.78	243 ± 10	133 ± 5
Zinc	4.94 ± 0.79	159 ± 8	364 ± 23
Tributyltin (Sn)**	—	—	0.832± 0.095
Dibutyltin (Sn)**	—	—	1.100± 0.135
Monobutyltin (Sn)**	—	—	(0.7)*

*information value only

† see page 3

** a separate certificate for the butyltins is available.

NRC·CNRC

Appendix 13: Procedural convertion of the data obtained for the instrumental analysis

Appendix 13a: Procedural steps and formulae for the conversion of data obtained from ICP-MS.

Quantum Data QD(ppb) ICP-MS	(ng/ml) = QD X 4 (DF)	Corrected ng/ml = ng/ml - Mean blank	Corrected ng/ml X 20 ml (Volume of digest)	(ng/ml)/Mass of the sediment (g) = ng/g divided by 1000	mg/kg (ppm) or µg/g in dried sediment sample

DF-dilution factor**, QD-**Quantum machine generated data**, ng-**nanogram**, ppm-**parts per million**, µg-**microgram**, ppb-**parts per billion**, g-**gram**, mg-**milligram**, kg-**kilogram**, ICP-MS-** inductively coupled plasmamass spectrometry.

Appendix 13b: Procedural formulae for the conversion of data obtained from ICP-OES for *Aqua regia.*

ICP-OES readings (mg/l) = blankcorrected	mg/L x 10 (DF)	mg/L x 24 mL volumes digest in litre	Divided by mass of the sediment approximately	Divided by /1000 = mg/kg	Final conc. unit is in mg/kg of dry weight sediment sample

ICP-OES-Inductively coupled plasma optical emission spectrometry, mg/L-milligram per litre, mg/kg-milligram per kilogram

In Appendix 13a and 13b, DF is represented as dilution factor and mg/L, is milligram per litre; the data obtained using the XRF technique are represented in ppm for trace metals, and percentage mass oxides for major elements, are converted intomg/kg for metals.

Appendix 13c: Procedural conversion of major oxides data to elements in mg/kg.

Metals	XRF Trace metals		Metal (mg/kg)
Major oxides	Mass percentage of major oxides divided by the conversion factors	values obtained from dividing the mass % by the conversion factor is multiplied by 10000	Metal (mg/kg)

XRF-X-ray fluorescence.

For CHN data, the data were converted to mg/g as the dry weight samples that were analysed for total carbon contents also generated in % mass which were then converted into mg/g X 10,000 as presented in Table 20.

Appendix 13d: Procedural conversion of CHN data for heavy metals and major elements to mg/g.

CHN data	mass % x 10,000	mg/g	

Appendix 14a: Mean total metal concentrations (XRF)-mg/kg-DS-1-2013 for LH, LG & APL.

Site No	Location	Al	As	Cd	Cu	Fe	Mn	Pb	Sn	Zn
		ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)
Site 1	Lagos Harbour	88453.72	16	-2	52	62914	1146.196	20	5	226
Site 2	″	64034.08	10	0	42	37223.82	394.9731	10	7	203
Site 3	″	67648.86	7	1	37	35475.24	340.7611	7	5	158
Site 4	″	73788.17	11	-1	44	54087.15	975.8158	12	4	147
Site 5	″	64865	5	-1	38	38161.06	774.457	2	3	149
Site 6	″	68913.77	11	0	35	38685.64	681.5222	12	4	118
Site 7	″	49977.17	1	0	30	28480.91	464.6742	- 7	2	53
Site 8	″	42255.4	-3	-1	23	17031.19	294.2937	- 12	1	20
Site 9	"	29436.94	-4	-1	21	11141.97	240.0817	- 15	-	- 3
Site 10	″	58249.37	1	0	31	29942.73	642.7993	- 7	3	67
Site 11	″	36137.26	-9	0	44	34069.38	433.6959	- 26	2	70
Site 12	″	30532.49	-8	0	31	9316.448	131.6577	- 22	1	1
Mean effects		**56191**	**3**	**0**	**36**	**33044**	**543**	**-2**	**3**	**101**
Site 13	Lagos Lagoon	74476.2	6	-1	44	67215.51	712.5004	2	**5**	**196**
Site 14	″	83547.56	6	0	47	70300.01	1053.262	2	4	204
Mean effects		**79012**	**6**	**-1**	**46**	**68758**	**883**	**2**	**5**	**200**

Appendix 14b: Mean total metal concentrations (XRF) mg/kg WS-2013 for LH, LG & APL.

Sites	**Location**	**Al**	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Sn**	**Zn**
		ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)
Site 1	Lagos Harbour	83569	10	0	40	54968	**426**	10	4	139
Site 2	"	74698	17	-1	42	58284	1138	23	5	145
Site 3	"	52025	0	1	39	29628	325	-8	2	78
Site 4	"	60626	10	-1	44	38364	387	11	4	199
Site 5	"	52909	-2	-1	30	25354	186	-11	3	64
Site 6	"	84336	12	0	46	58920	836	13	4	152
Site 7	"	77625	10	0	53	61172	751	11	4	152
Site 8	"	78768	15	1	49	52975	999	19	4	209
Site 9	"	74942	15	0	46	55178	1084	20	4	234
Site 10	"	67924	8	-1	34	43337	782	7	1	94
Site 11	"	62325	5	0	31	36853	697	2	2	83
Site 12	"	63325	2	0	30	29894	527	-4	3	54
Site 13	"	29707	-7	0	19	9170	124	-19	0	3
Site 14	"	75900	13	-1	41	57738	1131	15	4	142
Site 15	"	28288	-6	0	20	9079	186	-19	2	13
Site 16	"	58667	-1	0	28	26557	372	-11	1	49
Mean effects		**64102**	**6**	**0**	**37**	**40467**	**622**	**4**	**3**	**113**
Site 17	Lagos Lagoon	**60303**	0	-1	27	28705	620	-7	5	69
Site 18	"	71703	9	0	42	**49981**	573	9	5	178
Site 19	"	57397	1	-2	33	44162	805	-7	4	122
Site 20	"	39133	-7	0	28	69454	2525	-23	2	104
Site 21	"	58583	-3	0	33	43323	612	-16	3	102
Site 22	"	70687	5	-2	42	78497	1611	-1	5	149
Site 23	"	71385	19	1	57	57976	503	28	9	521
Mean effects		**61313**	**3**	**-1**	**37**	**53157**	**1036**	**-2**	**5**	**178**
Site 24	Apese Lagoon	36719	0	0	25	12086	116	-8	5	63
Mean effects		**36719**	**0**	**0**	**25**	**12086**	**116**	**-8**	**5**	**63**

Appendix 14c: Mean total metal concentrations (XRF) mg/kg DS-2-2014 for LH, LG & APL.

Sites	Location	Al	As	Cd	Cu	Fe	Mn	Pb	Sn	Zn
		ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)	ppm (mg/kg)
Site 1	Lagos Harbour	126708.91	10.00	0.00	42.00	73111.05	279.31	**10.00**	4.00	153.00
Site 2	"	85647.20	3.00	0.00	35.00	39166.34	344.77	-3.00	1.00	75.00
Site 3	"	87552.36	13.00	-1.00	79.00	43757.05	257.49	17.00	20.00	760.00
Site 4	"	66866.62	-3.00	-1.00	29.00	29777.37	100.38	-13.00	2.00	57.00
Site 5	"	115270.18	12.00	1.00	50.00	64220.17	322.95	13.00	4.00	227.00
Site 6	"	127738.94	10.00	1.00	45.00	62999.86	414.60	10.00	4.00	168.00
Site 7	"	123742.74	13.00	0.00	43.00	63888.11	628.45	17.00	4.00	165.00
Site 8	"	101182.81	12.00	0.00	39.00	57902.75	610.99	15.00	1.00	139.00
Site 9	"	103792.73	6.00	0.00	37.00	47750.06	353.50	2.00	3.00	103.00
Site 10	"	72070.97	-1.00	-2.00	24.00	25028.93	183.30	-11.00	2.00	67.00
Site 11	"	72961.59	-2.00	-1.00	25.00	25468.91	213.85	-11.00	1.00	40.00
Site 12	"	94847.75	4.00	0.00	34.00	45641.48	336.04	-1.00	3.00	78.00
Site 13	"	95436.34	-2.00	0.00	31.00	35588.40	213.85	-11.00	2.00	55.00
Site 14	"	76547.33	6.00	-1.00	38.00	28789.50	183.30	4.00	3.00	86.00
Site 15	"	104141.23	12.00	0.00	42.00	56682.44	532.43	13.00	4.00	213.00
Site 16	"	94112.01	2.00	-2.00	29.00	36659.29	270.58	-4.00	4.00	58.00
Mean effects		**96789**	**6**	**0**	**39**	**46027**	**328**	**3**	**4**	**153**
Site 17	Lagos Lagoon	100330.90	16.00	-2.00	44.00	47667.04	305.49	23.00	16.00	186.00
Site 18	"	88404.27	-3.00	1.00	32.00	67681.88	763.74	-15.00	1.00	143.00
Site 19	"	90727.64	1.00	-1.00	34.00	56972.99	480.06	-8.00	3.00	129.00
Site 20	"	72891.89	-9.00	-1.00	31.00	103079.35	2203.93	-30.00	4.00	163.00
Site 21	"	126538.53	35.00	2.00	80.00	64826.18	192.03	58.00	14.00	1199.00
Site 22	"	62219.88	-7.00	-1.00	27.00	62261.03	741.92	-22.00	2.00	87.00
Site 23	"	107812.16	12.00	1.00	56.00	72148.08	331.68	15.00	8.00	438.00
Mean effects		**92704**	**6**	**0**	**43**	**67805**	**717**	**3**	**7**	**335**
Site 24	Apese Lagoon	67935.37	3.00	0.00	26.00	26846.95	91.65	-2.00	2.00	81.00
Site 25	"	41077.20	-6.00	-1.00	20.00	11215.29	100.38	-18.00	**1.00**	**10.00**
Site 26	"	39714.15	-6.00	0.00	22.00	6450.24	69.83	-18.00	1.00	24.00
Mean effects		**49576**	**-3**	**0**	**23**	**14837**	**87**	**-13**	**1**	**38**

Appendix 15a: Mean recoverable metal concentrations (*Aqua regia*) mg/kg DS-1-2013 for LH, LG & APL .

Site No	Location	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sn	V	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Site 1	Lagos Harbour	7182.25	18.80	0.00	5.11	33.22	12.98	16405.99	367.18	15.07	12.58	0.00	23.98	64.28
Site 2	"	5575.76	8.10	0.00	3.63	18.14	9.65	9845.23	110.86	7.45	13.49	0.00	11.79	59.15
Site 3	"	6493.57	12.42	0.00	5.82	24.50	10.84	12327.58	133.90	10.66	14.14	0.00	16.96	67.94
Site 4	"	6263.15	12.94	0.00	4.18	24.00	9.16	12800.39	299.41	10.79	8.50	0.00	16.87	41.34
Site 5	"	5680.78	9.99	0.00	4.41	19.15	6.62	10471.61	247.62	7.72	7.46	0.00	11.95	42.69
Site 6	"	6821.33	16.09	0.00	4.39	29.14	9.18	14566.09	328.73	13.05	10.34	0.00	21.45	48.27
Site 7	"	3824.66	3.90	0.00	2.54	11.23	3.83	6670.14	133.68	3.77	3.57	0.00	7.01	17.85
Site 8	"	2434.09	0.98	0.00	1.25	6.19	0.27	4274.26	91.35	1.11	1.30	0.00	2.74	9.14
Site 9	Lagos Harbour	1044.12	0.51	0.00	2.91	3.29	0.00	3334.68	65.00	0.13	0.00	0.00	0.77	2.71
Site 10	"	1176.20	0.58	0.00	5.02	2.77	1.80	2901.20	39.50	0.32	0.45	0.00	0.32	2.83
Site 11	"	1682.93	0.33	0.00	9.39	74.68	11.12	8699.27	105.51	10.27	3.88	0.00	2.50	19.67
Site 12	"	1931.29	0.00	0.00	3.37	4.28	0.45	3377.38	57.59	0.84	8.32	0.00	1.23	13.87
Mean effects		**4176**	**7**	**0**	**4**	**21**	**6**	**8806**	**165**	**7**	**7**	**0**	**10**	**32**
Site 13	Lagos Lagoon	5550.28	7.61	0.00	6.16	17.28	5.91	15774.62	210.22	8.45	10.97	0.00	13.90	49.81
Site 14	"	6264.99	11.16	0.00	10.45	21.67	8.95	20809.13	446.62	12.20	13.56	0.00	16.80	68.22
Mean effects		**5908**	**9**	**0**	**8**	**19**	**7**	**18292**	**328**	**10**	**12**	**0**	**15**	**59**

Appendix 15b: Mean recoverable metal concentrations (*Aqua regia*) mg/kg WS-2013 for LH, LG & APL.

Sites	Zone	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Site 1	Lagos Harbour	2257.59	1.64	0.21	5.41	7.71	7184.56	144.70	2.73	11.14	35.36
Site 2	"	1525.43	3.19	0.28	7.84	8.10	8129.26	389.50	3.66	13.87	73.52
Site 3	"	1896.91	1.83	0.23	5.52	13.12	6446.63	230.84	2.70	13.11	61.22
Site 4	"	1816.46	1.69	0.24	5.09	11.34	6168.80	150.60	2.36	10.50	45.38
Site 5	"	1714.14	1.69	0.21	6.99	11.99	6068.01	159.20	38.25	21.37	48.11
Site 6	"	2215.13	2.40	0.27	5.86	8.69	8111.08	313.88	5.86	10.26	36.98
Site 7	"	2610.71	3.22	0.36	8.59	9.19	9673.03	493.11	9.52	13.59	49.59
Site 8	"	3154.98	3.39	0.35	24.12	12.96	9112.42	518.02	82.76	10.64	48.85
Site 9	"	2436.83	3.97	0.48	9.11	10.22	9553.24	515.23	7.55	12.28	71.13
Site 10	"	1359.32	1.75	0.18	28.77	6.12	5371.08	193.62	73.87	6.97	23.48
Site 11	"	1297.65	2.21	0.17	6.11	3.45	5520.06	279.26	6.25	5.57	22.30
Site 12	"	1322.08	1.68	0.10	5.10	4.52	4449.35	188.05	2.92	4.50	15.77
Site 13	"	1680.80	2.50	0.26	5.74	4.82	6563.76	351.43	2.51	8.59	21.00
Site 14	"	2199.04	3.72	0.35	6.73	7.18	9903.90	552.79	3.37	11.29	33.16
Site 15	"	1882.90	2.44	0.19	5.59	12.05	7853.28	335.44	4.17	17.13	56.74
Site 16	"	946.59	0.98	0.09	2.90	3.17	3043.74	95.79	1.69	6.81	16.28
Mean effects		**1895**	**2**	**0**	**9**	**8**	**7072**	**307**	**16**	**11**	**41**
Site 17	Lagos Lagoon	1183.13	1.23	0.15	3.60	6.56	5134.29	218.79	2.39	11.14	51.55
Site 18	"	1488.17	1.77	0.26	3.77	8.06	5002.60	199.98	2.95	11.89	52.78
Site 19	"	1652.19	1.30	0.39	3.79	13.94	5694.76	195.80	3.26	23.61	131.68
Site 20	"	1598.03	0.31	0.05	3.05	0.98	13451.44	666.29	3.09	3.51	42.46
Site 21	"	1641.93	0.69	0.36	2.41	10.01	4028.25	80.20	2.78	15.72	165.62
Site 22	"	1841.17	1.03	0.26	3.62	6.60	9304.16	524.41	3.56	13.38	44.97
Site 23	"	1327.25	1.16	0.46	1.70	13.43	3846.29	70.86	5.51	25.86	165.36
Mean effects		**1533**	**1**	**0**	**3**	**9**	**6637**	**279**	**3**	**15**	**93**
Site 24	Apese Lagoon	458.02	1.93	0.07	1.46	5.68	900.73	21.22	1.10	7.97	31.33
Mean effects		**458**	**2**	**0**	**1**	**6**	**901**	**21**	**1**	**8**	**31**

Appendix 15c: Mean recoverable metal concentrations (*Aqua regia*) mg/kg DS-2-2014 for LH, LG & APL.

Sites	Location	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sn	V	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Site 1	Lagos Harbour	12250.59	44.99	0.00	0.19	29.78	644.17	15117.28	148.48	23.66	7.65	0.00	20.97	39.30
Site 2	″	8188.16	27.50	0.13	0.34	20.67	388.86	11184.36	217.90	15.54	6.04	0.00	12.23	28.73
Site 3	″	13182.49	45.14	0.47	2.88	32.10	660.20	19896.45	255.33	40.37	18.22	1.65	18.50	178.30
Site 4	″	8830.94	25.68	0.21	2.26	16.65	383.44	11065.11	74.65	21.25	8.10	0.00	9.15	41.58
Site 5	″	19169.34	64.44	0.49	3.63	40.03	900.11	25776.04	202.71	52.64	21.87	0.00	29.16	90.85
Site 6	″	6860.74	19.88	0.00	5.44	30.66	18.61	14946.20	261.91	13.90	12.68	0.88	24.52	62.72
Site 7	″	6932.34	25.96	0.00	10.01	38.35	21.62	19204.54	543.63	17.60	15.94	1.01	31.31	75.89
Site 8	″	7334.13	26.84	0.00	8.55	41.47	23.85	21036.61	608.03	19.38	17.83	1.22	34.42	86.74
Site 9	″	7326.87	25.14	0.00	8.04	38.46	43.92	20285.03	350.95	18.03	21.92	1.44	32.15	99.16
Site 10	″	5234.31	10.62	0.00	3.90	17.68	7.63	9057.17	179.81	6.61	6.14	0.28	14.32	30.14
Site 11	″	4235.06	2.64	0.00	3.61	11.69	-0.83	6587.26	142.39	3.29	4.33	0.67	7.99	16.51
Site 12	″	4834.98	5.10	0.00	4.09	14.95	2.24	8946.00	185.83	5.69	6.17	0.81	12.82	23.01
Site 13	″	5620.93	6.54	0.00	4.89	18.25	3.41	10251.88	217.70	7.24	7.64	0.83	14.60	31.43
Site 14	″	4997.21	3.73	0.00	5.19	15.23	4.17	7548.28	134.63	4.71	10.05	0.61	9.17	28.41
Site 15	″	6731.91	12.80	0.00	6.70	26.60	15.20	14958.32	329.98	12.96	21.08	2.13	20.13	73.06
Site 16	″	2900.33	0.37	0.00	3.91	7.11	-0.79	4263.40	76.42	1.90	3.77	0.48	4.61	12.68
Mean effects		**7789**	**22**	**0**	**5**	**25**	**195**	**13758**	**246**	**17**	**12**	**1**	**19**	**57**
Site 17	Lagos Lagoon	5174.83	8.16	0.00	4.63	16.34	11.78	9562.16	165.31	6.21	13.33	2.59	12.33	50.48
Site 18	″	7001.18	15.14	0.00	9.72	24.81	12.50	16899.81	340.96	12.06	11.89	1.35	19.34	63.66
Site 19	″	6661.37	13.78	0.00	10.34	22.44	13.81	18224.48	439.82	12.25	16.25	1.57	17.88	82.95
Site 20	″	4492.35	6.56	0.00	20.32	11.80	7.31	24340.30	1236.62	9.84	7.94	0.88	6.53	65.05
Site 21	″	7509.17	16.42	0.00	9.30	27.14	30.95	18663.43	265.26	14.55	39.89	4.41	25.38	263.92
Site 22	″	9099.50	15.30	0.00	8.17	29.40	13.03	32476.41	20960.01	14.22	15.36	1.11	26.99	76.54
Site 23	″	6761.27	15.20	0.00	10.75	24.80	21.17	19375.89	349.51	12.99	21.24	0.82	17.35	133.04
Mean effects		**6671**	**13**	**0**	**10**	**22**	**16**	**19935**	**3394**	**12**	**18**	**2**	**18**	**105**
Site 24	Apese Lagoon	2291.74	2.93	0.00	1.35	5.38	1.61	2571.12	16.66	0.91	1.69	0.00	3.26	15.09
Site 25	″	735.61	0.54	0.00	2.74	2.72	0.15	884.36	19.59	0.00	0.33	0.00	0.96	4.89
Site 26	″	507.62	0.00	0.00	1.43	1.75	0.24	301.72	11.06	0.00	0.28	0.00	0.00	3.29
Mean effects		**1178**	**1**	**0**	**2**	**3**	**1**	**1252**	**16**	**0**	**1**	**0**	**1**	**8**

Appendix 16a: HR-1 and PACs-2 analysed data for *Aqua regia* extraction.

		As	Zn	Fe	Cd	Cr	Cu	Pb	Ni	Al	Sn	V	Co	Mn
HR1 A (ug/g)		15	1273	23900	0.47	88	80	210	34	9530	7	34	9	435
Certified values (ug/g)	**mean**	6.29	1105	30579	3.88	126	79.9	139	39.4	59250	9.87	84.1	14	549
	SD	1.16	173	7435	1.24	45	11.4	37	15.4	22778	0.47	33.8	3.9	83
	mean - SD	5.13	932	23144	2.64	81	68.5	102	24	36472	9.4	50.3	10.1	466
	mean + SD	7.45	1278	38014	5.12	171	91.3	176	54.8	82028	10.34	117.9	17.9	632
recovery	**mean**	239	115	78	12	70	100	151	87	16	67	41	64	79
	- SD	292	137	103	18	108	116	206	143	26	70	68	88	93
	+ SD	201	100	63	9	51	87	119	62	12	63	29	50	69

		As	Zn	Fe	Cd	Cr	Cu	Pb	Ni	Al	Sn	V	Co	Mn
HR1 B (mg/kg)		16	1305	24805	0	91	80	214	35	9792	7	36	9	449
Certified values (ug/g or mg/kg)	**mean**	6.29		30579	3.88	126	79.9	139	39.4	59250	9.87	84.1	14	549
	SD	1.16	173	7435	1.24	45	11.4	37	15.4	22778	0.47	33.8	3.9	83
	mean - SD	5.13	932	23144	2.64	81	68.5	102	24	36472	9.4	50.3	10.1	466
	mean + SD	7.45	1278	38014	5.12	171	91.3	176	54.8	82028	10.34	117.9	17.9	632
recovery	**mean**	247	118	81	12	72	100	154	90	17	71	43	67	82
	mean - SD	303	140	107	18	113	117	209	147	27	75	71	93	96
	mean + SD	208	102	65	9	53	88	121	64	12	68	30	53	71

		As	Zn	Fe	Cd	Cr	Cu	Pb	Ni	Al	Sn	V	Co	Mn
Liquid CRM (multi-element standard as a test)	<x>	0.935	1.011	1.014	0.1	0.099	0.091	0.098	0.095	0.098	< - 0.005	0.09	0.105	0.098
	sd	0.003	0.001	0.005	0	0	0.001	0	0.001	0.001	0	0.002	0.001	0
		93.5	101.1	101.4	10	9.9	9.1	9.8	9.5	9.8	na	9	10.5	9.8
Certified value mg/L		100	100	100	10	10	10	10	10	10	na	10	10	10

Recovery	**94**	**101**	**101**	**100**	**99**	**91**	**98**	**95**	**98**	**na**	**90**	**105**	**98**

Appendix 16b: HR-1 and PACs-2 analysed data for 1 M HCl extraction.

Elements		**27(mg/kg)**	**CRM**	**Cr (53)**	**CRM**	**Mn(55)**		**Fe (57)**	**CRM**	**Ni(60)**		**Cu (63)**		**Zn(66)**		**As(75)**		**Cd (111)**		**Pb (208)**	
Ref	Mean	**Al** Al(mg/kg)	CRM	Cr (mg/kg)	CRM	Mn (mg/kg)	CRM	Fe (mg/kg)		Ni (mg/kg)	CRM	Cu (mg/kg)	CRM	Zn (mg/kg)	CRM	As (mg/kg)	CRM	Cd (mg/kg)	CRM	Pb (mg/kg)	CRM
SLRS-5 A		48.75	49.5	-0.1563	0.208	4.004	4.33	164.7	91.2	0.3987	0.476	18.38	17.4	4.484	0.845	0.3987	0.413	0.0147	0.006	0.0493	0.081
SLRS-5 B		48.53		-0.125		3.993		164.5		0.3547		18.2		3.442		0.3589		0.0064		0.0522	
SLRS-5 C		50.65		-0.1347		3.96		161.7		0.3588		17.97		0.0148		0.4046		0.0104		0.0493	
	Mean	49.31		-0.13867		3.985667		163.6333		0.370733		18.18333		2.646933		0.3874		0.0105		0.050267	
	SD	1.165676		0.016023		0.022898		1.677299		0.024306		0.205508		2.338276		0.020296		0.004151		0.001674	
	% RECOVERY	99.61616		-66.6667		92.04773		179.4225		77.88515		104.5019		313.2465		93.80145		175		62.05761	
HR-1A-REF		3287.271	3235	52.01352	50	334.7777	266	9629.167	8015	16.21775	15.9	71.54539	60	1164.405	1035	4.9598	2.3	4.725584	3.28	197.5708	116
HR-1B-REF		3127.178		49.1934		311.4517		8976.227		15.50924		67.46904		952.1446		4.876982		4.368661		188.067	
HR-1C-REF		2808.252		44.48826		282.1331		8253.642		14.10892		62.07301		197.2364		4.371346		3.993618		172.792	
	Mean	3074.234		48.56506		309.4542		8953.012		15.27864		67.02915		771.262		4.736043		4.362621		186.1433	
	SD	243.8588		3.801775		26.37908		688.0563		1.073161		4.751487		508.3234		0.31854		0.36602		12.50091	
	%RECOVERY	95.03041		97.13012		116.3362		111.7032		96.09205		111.7152		74.51807		205.9149		133.0067		160.4683	
PACS-2-A-REF		2631.95	66200	9.119166	90.7	38.51383	440	6709.425	40900	5.397357	39.5	120.4744	310	161.7363	364	3.743108	26.2	1.584829	2.11	121.4189	183
PACS-2-B-REF		2092.022		7.223408		31.05526		5269.673		4.406309		95.9056		32.59145		2.977933		1.262319		95.91857	
PACS-2-C-REF		1038.618		4.63812		214.6608		5439.841		2.09196		6.096782		10.21683		2.066339		0.117403		6.151178	
	Mean	1920.863		6.993565		94.7433		5806.313		3.965209		74.15893		68.18153		2.929127		0.988184		74.49622	
	SD	810.3383		2.249348		103.9185		786.7323		1.696272		60.21003		81.78953		0.839449		0.771166		60.54626	
	%RECOVERY	2.901606		7.710656		21.53257		14.19636		10.0385		23.92223		18.73119		11.17987		46.83335		40.70831	

Appendix 17a: Mean bioavailable metal concentrations (1 M HCl) mg/kg DS-1-2013 for LH, LG & APL.

Site No	Zone	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Site 1	Lagos Harbour	3735.86	3.02	0.40	59.69	27.96	11625.86	743.13	350.04	16.55	83.45
Site 2	“	2463.87	1.92	0.31	12.59	19.22	7792.59	201.97	28.82	25.36	107.78
Site 3	“	2636.13	1.87	0.30	36.13	17.46	8654.93	209.67	54.82	18.96	95.35
Site 4	“	3153.31	3.80	0.32	25.09	16.39	12497.96	634.77	13.07	13.25	54.78
Site 5	“	2945.19	2.39	0.19	15.84	9.91	7958.43	407.76	9.99	8.71	46.95
Site 6	“	3193.04	3.53	0.39	16.01	13.19	10959.65	620.59	11.44	14.03	53.70
Site 7	“	2370.24	2.80	0.52	9.44	43.52	8053.77	204.27	6.48	38.19	73.83
Site 8	“	889.74	1.13	0.04	4.36	2.18	3978.57	148.44	5.96	2.35	8.18
Site 9	Lagos Harbour	544.50	1.31	0.01	5.26	0.50	2191.41	110.23	3.05	0.80	1.34
Site 10	“	1332.16	1.48	0.13	5.29	10.46	5424.64	229.77	2.92	5.99	21.67
Site 11	“	2183.31	2.08	0.10	77.72	17.19	8306.50	195.77	11.11	10.07	35.78
Site 12	“	559.29	0.54	0.04	3.31	2.39	2054.72	79.01	1.29	6.27	13.21
Mean effects		**2167**	**2**	**0**	**23**	**15**	**7458**	**315**	**42**	**13**	**50**
Site 13	Lagos Lagoon	2380.30	1.01	0.47	6.62	9.66	9619.40	316.86	5.67	16.32	66.73
Site 14	“	3475.46	1.53	0.61	6.50	12.78	10063.76	630.60	6.24	18.88	87.40
Mean effects		**2928**	**1**	**1**	**7**	**11**	**9842**	**474**	**6**	**18**	**77**

Appendix 17b: Mean bioavailable metal concentrations (1 M HCl) mg/kg WS-2013 for LH, LG & APL.

Sites	Location	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Site 1	Lagos Harbour	2257.59	1.64	0.21	5.41	7.71	7184.56	144.70	2.73	11.14	35.36
Site 2	"	1525.43	3.19	0.28	7.84	8.10	8129.26	389.50	3.66	13.87	73.52
Site 3	"	1896.91	1.83	0.23	5.52	13.12	6446.63	230.84	2.70	13.11	61.22
Site 4	"	1816.46	1.69	0.24	5.09	11.34	6168.80	150.60	2.36	10.50	45.38
Site 5	"	1714.14	1.69	0.21	6.99	11.99	6068.01	159.20	38.25	21.37	48.11
Site 6	"	2215.13	2.40	0.27	5.86	8.69	8111.08	313.88	5.86	10.26	36.98
Site 7	"	2610.71	3.22	0.36	8.59	9.19	9673.03	493.11	9.52	13.59	49.59
Site 8	"	3154.98	3.39	0.35	24.12	12.96	9112.42	518.02	82.76	10.64	48.85
Site 9	"	2436.83	3.97	0.48	9.11	10.22	9553.24	515.23	7.55	12.28	71.13
Site 10	"	1359.32	1.75	0.18	28.77	6.12	5371.08	193.62	73.87	6.97	23.48
Site 11	"	1297.65	2.21	0.17	6.11	3.45	5520.06	279.26	6.25	5.57	22.30
Site 12	"	1322.08	1.68	0.10	5.10	4.52	4449.35	188.05	2.92	4.50	15.77
Site 13	"	1680.80	2.50	0.26	5.74	4.82	6563.76	351.43	2.51	8.59	21.00
Site 14	"	2199.04	3.72	0.35	6.73	7.18	9903.90	552.79	3.37	11.29	33.16
Site 15	"	1882.90	2.44	0.19	5.59	12.05	7853.28	335.44	4.17	17.13	56.74
Site 16	"	946.59	0.98	0.09	2.90	3.17	3043.74	95.79	1.69	6.81	16.28
Mean effects		**1895**	**2**	**0**	**9**	**8**	**7072**	**307**	**16**	**11**	**41**
Site 17	Lagos Lagoon	1183.13	1.23	0.15	3.60	6.56	5134.29	218.79	2.39	11.14	51.55
Site 18	"	1488.17	1.77	0.26	3.77	8.06	5002.60	199.98	2.95	11.89	52.78
Site 19	"	1652.19	1.30	0.39	3.79	13.94	5694.76	195.80	3.26	23.61	131.68
Site 20	"	1598.03	0.31	0.05	3.05	0.98	13451.44	666.29	3.09	3.51	42.46
Site 21	"	1641.93	0.69	0.36	2.41	10.01	4028.25	80.20	2.78	15.72	165.62
Site 22	"	1841.17	1.03	0.26	3.62	6.60	9304.16	524.41	3.56	13.38	44.97
Site 23	"	1327.25	1.16	0.46	1.70	13.43	3846.29	70.86	5.51	25.86	165.36
Mean effects		**1533**	**1**	**0**	**3**	**9**	**6637**	**279**	**3**	**15**	**93**
Site 24	Apese Lagoon	458.02	1.93	0.07	1.46	5.68	900.73	21.22	1.10	7.97	31.33
Mean effects		**458**	**2**	**0**	**1**	**6**	**901**	**21**	**1**	**8**	**31**

Appendix 17c: Mean bioavailable metal concentrations (1 M HCl) mg/kg DS-2-2014 for LH, LG & APL.

Sites	Location	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Site 1	Lagos Harbour	1425.62	1.57	0.18	3.41	5.11	5510.17	135.68	2.09	8.49	25.64
Site 2	″	1040.49	2.42	0.14	4.05	6.27	5700.81	264.45	2.40	6.34	21.39
Site 3	″	1524.48	2.64	0.24	4.67	37.42	6862.35	336.16	3.38	12.53	179.05
Site 4	″	883.61	0.98	0.13	2.19	8.04	3653.16	79.07	1.59	8.09	35.81
Site 5	″	1689.45	2.25	0.28	4.18	13.86	7857.00	203.68	2.75	14.54	58.51
Site 6	″	1465.71	2.50	0.25	4.03	10.45	6200.65	292.25	2.22	11.05	45.31
Site 7	″	1852.55	3.44	0.30	5.32	8.48	7240.56	506.98	2.65	11.07	36.45
Site 8	″	1799.43	3.47	0.31	5.61	8.68	7801.64	512.35	3.12	10.86	43.25
Site 9	″	1478.87	2.90	0.23	4.44	16.73	7186.86	289.28	2.62	13.72	52.90
Site 10	″	773.41	1.97	0.12	5.70	4.27	3857.49	180.54	10.52	4.76	20.45
Site 11	″	498.42	1.02	0.05	1.62	1.81	2091.32	105.12	0.91	2.41	12.32
Site 12	″	1301.24	1.66	0.08	3.16	4.22	4301.92	194.57	1.78	5.46	30.00
Site 13	″	1319.47	2.19	0.21	4.07	5.23	5494.57	289.69	2.07	7.50	24.92
Site 14	″	875.46	1.60	0.10	3.25	7.00	3831.79	163.00	1.93	10.86	61.33
Site 15	″	1546.98	3.16	0.30	5.76	12.20	7675.65	407.04	4.25	22.47	57.43
Site 16	″	497.23	0.72	0.06	1.47	2.04	1602.99	80.66	0.99	4.63	17.58
Mean effects		**1248**	**2**	**0**	**4**	**9**	**5429**	**253**	**3**	**10**	**45**
Site 17	Lagos Lagoon	1035.67	1.41	0.16	3.23	8.22	3819.88	161.55	2.07	14.38	53.05
Site 18	″	1534.67	1.44	0.18	3.73	6.89	6894.03	269.99	2.63	9.66	80.23
Site 19	″	1545.53	0.98	0.26	3.30	8.83	7413.62	318.82	2.98	16.13	104.28
Site 20	″	1668.97	0.45	0.10	2.77	1.37	12788.21	881.57	3.49	4.67	111.82
Site 21	″	1283.53	0.87	0.45	2.48	12.23	4424.99	256.39	2.66	18.92	142.24
Site 22	″	711.77	1.53	0.07	0.94	2.47	942.64	25.42	1.05	4.18	39.83
Site 23	″	175.89	0.19	0.01	0.58	0.26	144.93	8.66	0.32	0.63	60.94
Mean effects		**1137**	**1**	**0**	**2**	**6**	**5204**	**275**	**2**	**10**	**85**
Site 24	Apese Lagoon	1604.94	3.19	0.28	5.83	12.43	7716.28	396.12	4.33	25.68	53.22
Site 25	″	594.92	0.88	0.09	2.09	4.94	2278.08	100.02	1.29	9.66	36.63
Site 26	″	753.41	0.91	0.09	2.19	5.18	2035.35	98.38	1.39	8.84	27.82
Mean effects		**984**	**2**	**0**	**3**	**8**	**4010**	**198**	**2**	**15**	**39**

Appendix 18: Mean Percentage of particle size distributions in fractions of the sediment in LH, LG & APL.

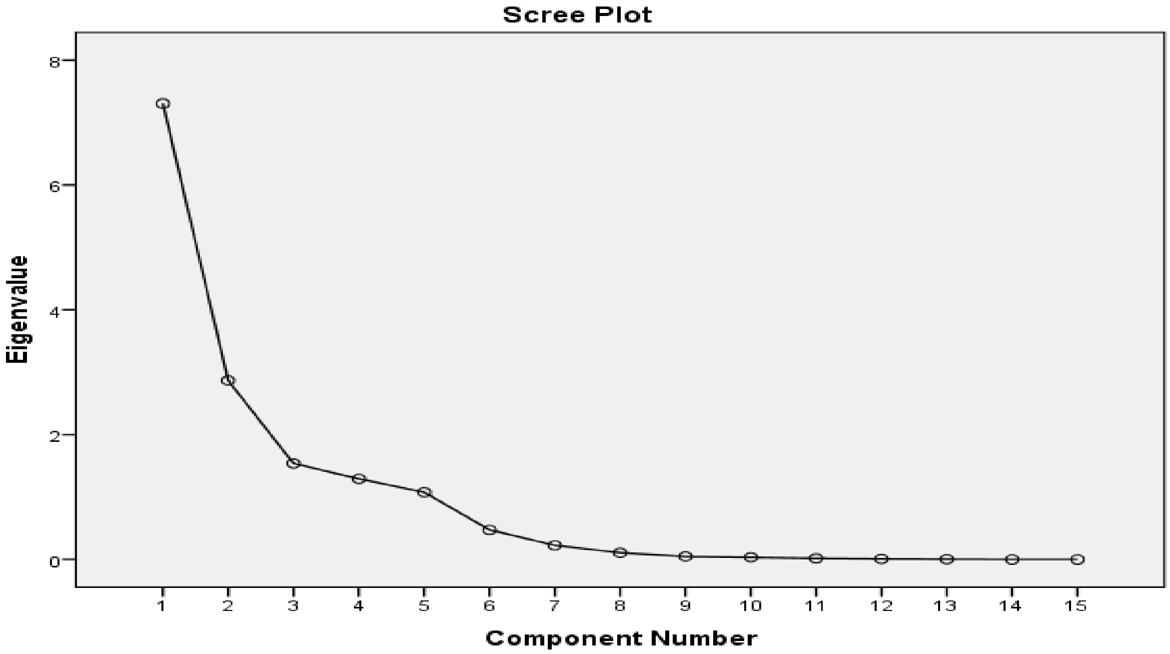
Locations	*Sites*	*Clay*	*V. Fine Silt*	*Fine Silt*	*Medium Silt*	*Coarse Silt*	*V. Fine sand*	*Fine sand*	*Medium sand*	*Coarse sand*	*V. Coarse sand*
Sizes (µm)		**0.1-3.90**	**3.9-7.81**	**7.81-15.63**	**15.63-31.25**	**31.25-62.50**	**62.50-125.0**	**125.0-250.0**	**250.0-500.00**	**500.0-1000.0**	**1000.0-2000.0**
Lagos Harbour	1-16	10.84	9.54	10.94	10.92	12.08	19.78	15.58	11.47	6.52	0.50
Lagos Lagoon (urbanised)	17-23	7.53	7.10	9.10	9.40	9.66	17.09	27.37	11.23	1.53	0.00
Apese Lagoon	24-26	1.68	3.10	4.86	6.11	7.40	10.93	19.26	32.64	13.76	0.25

Appendix 19a: DS-1-1-2013: PCA of total metals in sediment, particle sizes, total nitrogen and total carbon and Eigen value.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.304	48.697	48.697	7.304	48.697	48.697
2	2.868	19.117	67.814	2.868	19.117	67.814
3	1.538	10.256	78.070			
4	1.292	8.612	86.683			
5	1.077	7.178	93.860			
6	.474	3.162	97.023			
7	.226	1.506	98.528			
8	.108	.718	99.246			
9	.048	.323	99.569			
10	.033	.222	99.791			
11	.019	.124	99.915			
12	.009	.062	99.977			
13	.003	.023	100.000			
14	1.536E-016	1.024E-015	100.000			
15	-3.108E-016	-2.072E-015	100.000			

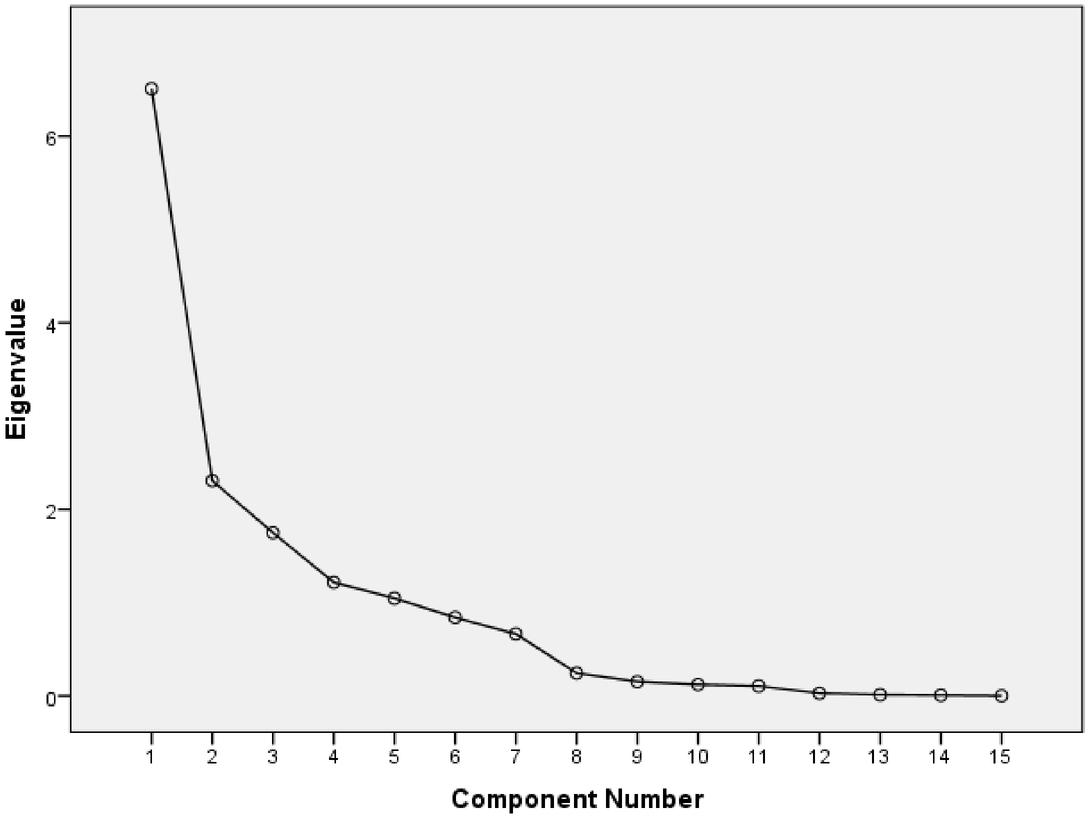
Extraction Method: Principal Component Analysis.



Appendix 19b: PCA of total metals in sediment, particle sizes, total nitrogen and total carbon and Eigen value for WS-2013.

Total Variance Explained

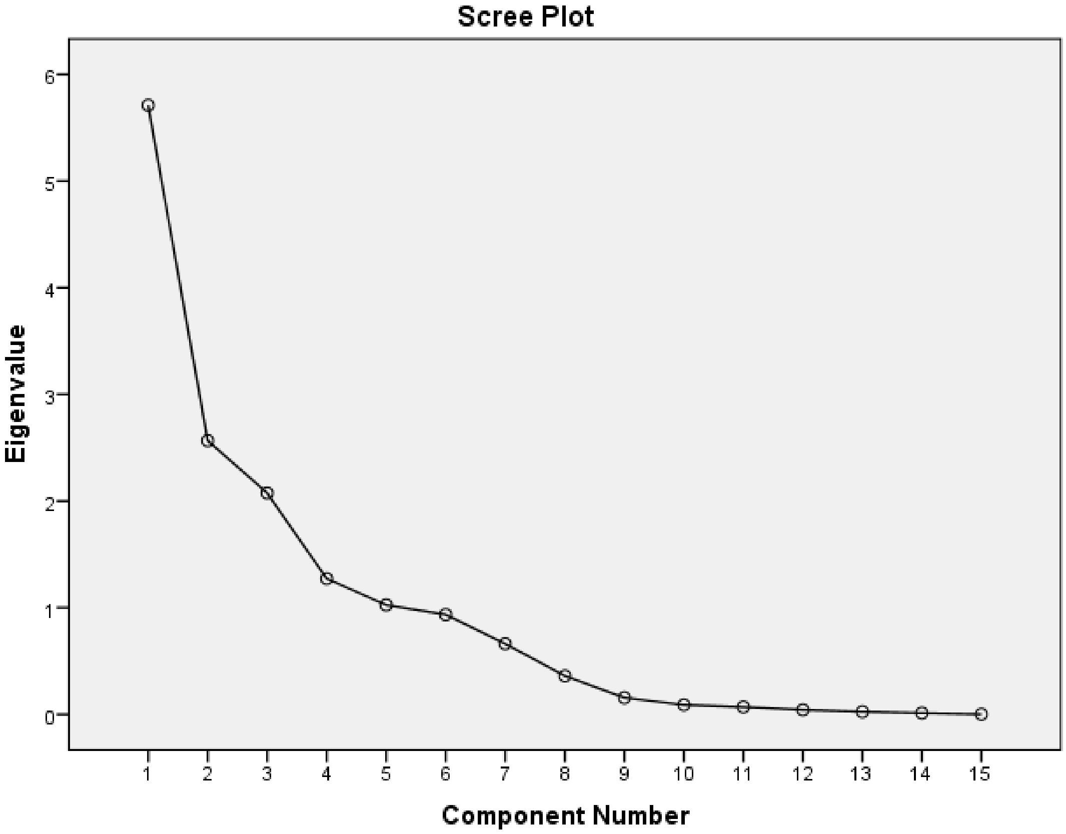
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.509	43.390	43.390	6.509	43.390	43.390
2	2.306	15.374	58.764	2.306	15.374	58.764
3	1.748	11.655	70.419			
4	1.217	8.112	78.531			
5	1.045	6.970	85.501			
6	.840	5.602	91.103			
7	.664	4.428	95.531			
8	.244	1.627	97.157			
9	.152	1.014	98.172			
10	.121	.808	98.980			
11	.105	.700	99.680			
12	.028	.188	99.868			
13	.012	.078	99.946			
14	.007	.049	99.995			
15	.001	.005	100.000			



Appendix 19c: DS-2-2014: PCA of total metals in sediment, particle sizes, total nitrogen and total carbon and Eigen value.

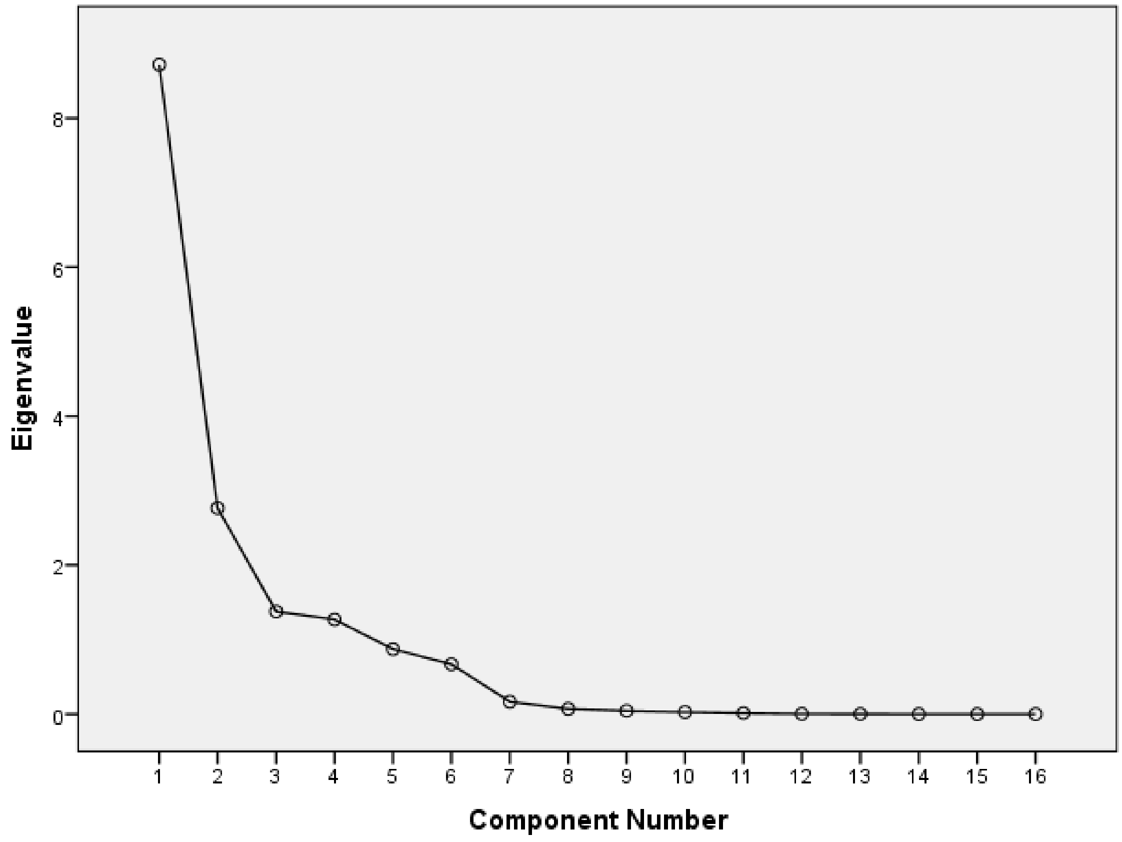
Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.711	38.072	38.072	5.711	38.072	38.072
2	2.566	17.105	55.177	2.566	17.105	55.177
3	2.075	13.834	69.011			
4	1.272	8.483	77.494			
5	1.025	6.836	84.330			
6	.936	6.237	90.566			
7	.662	4.413	94.979			
8	.360	2.403	97.382			
9	.156	1.037	98.419			
10	.089	.591	99.009			
11	.069	.460	99.469			
12	.043	.284	99.753			
13	.024	.162	99.916			
14	.012	.081	99.996			
15	.001	.004	100.000			



Appendix 20a: PCA of recoverable metals (*Aqua regia*) analysed for DS-1-2012.

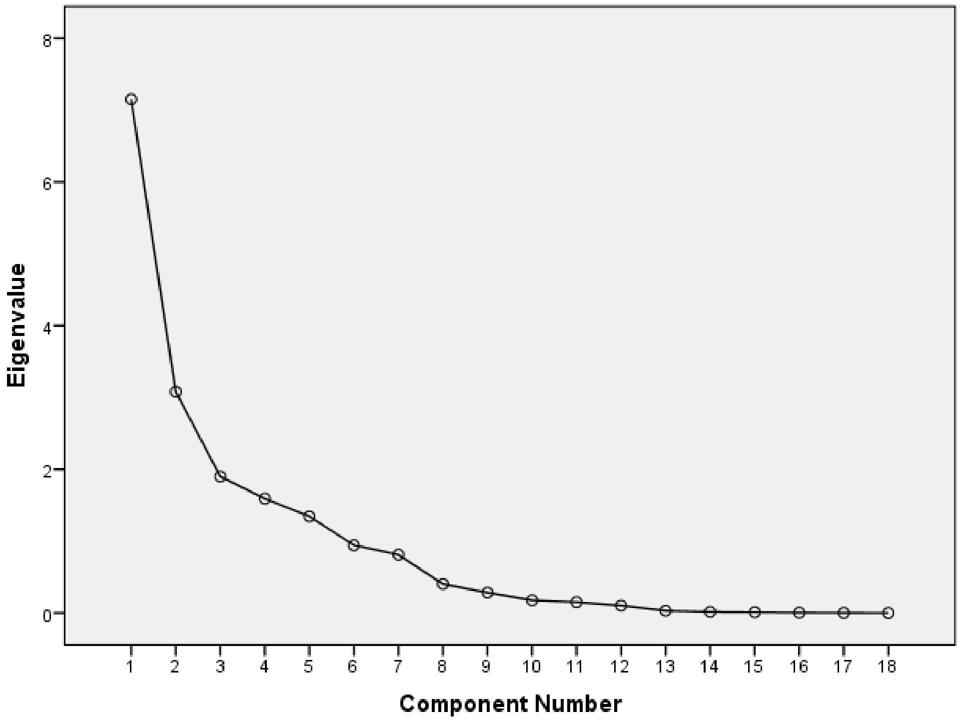
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.719	54.492	54.492	8.719	54.492	54.492
2	2.765	17.280	71.771	2.765	17.280	71.771
3	1.377	8.608	80.380			
4	1.270	7.935	88.315			
5	.873	5.454	93.769			
6	.669	4.183	97.952			
7	.166	1.040	98.993			
8	.071	.443	99.436			
9	.044	.272	99.708			
10	.028	.173	99.881			
11	.014	.089	99.970			
12	.003	.019	99.989			
13	.002	.011	100.000			
14	1.293E-016	8.078E-016	100.000			
15	-5.830E-017	-3.644E-016	100.000			
16	-2.103E-016	-1.314E-015	100.000			



Appendix 20b: PCA and Eigen value for recoverable metals analysed for WS-213.

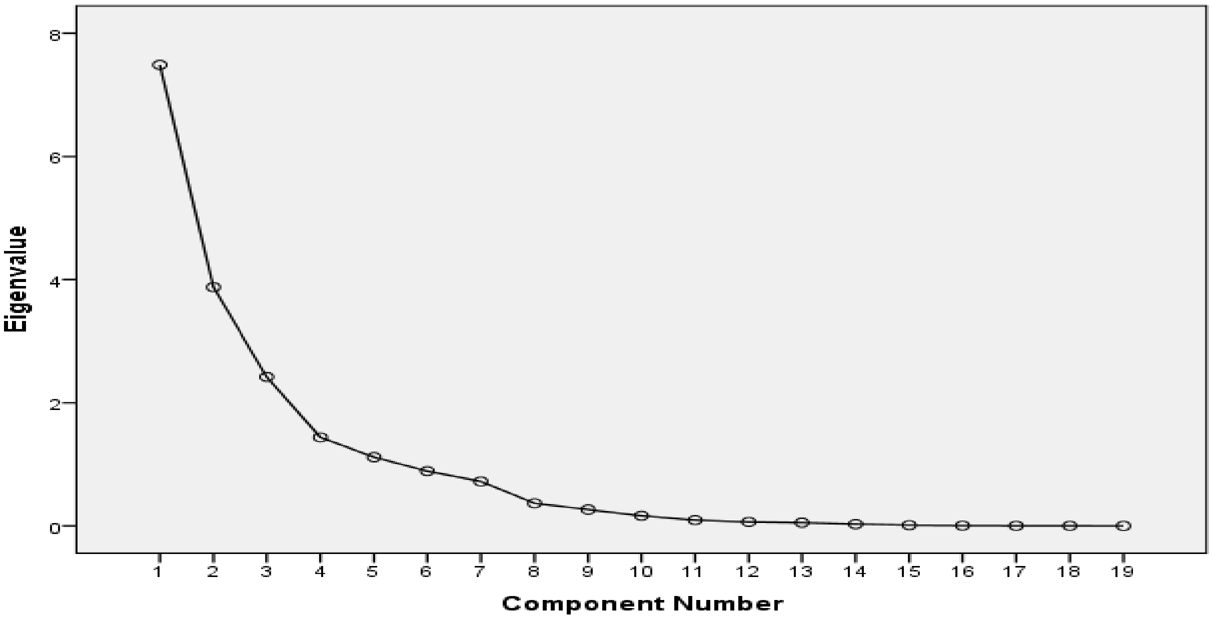
Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.151	39.727	39.727	7.151	39.727	39.727
2	3.080	17.109	56.836	3.080	17.109	56.836
3	1.901	10.559	67.395			
4	1.591	8.840	76.235			
5	1.344	7.469	83.704			
6	.943	5.242	88.946			
7	.812	4.510	93.456			
8	.403	2.238	95.694			
9	.283	1.572	97.266			
10	.176	.978	98.244			
11	.151	.837	99.081			
12	.103	.571	99.652			
13	.031	.173	99.826			
14	.015	.084	99.910			
15	.011	.060	99.970			
16	.003	.018	99.988			
17	.002	.011	99.999			
18	.000	.001	100.000			



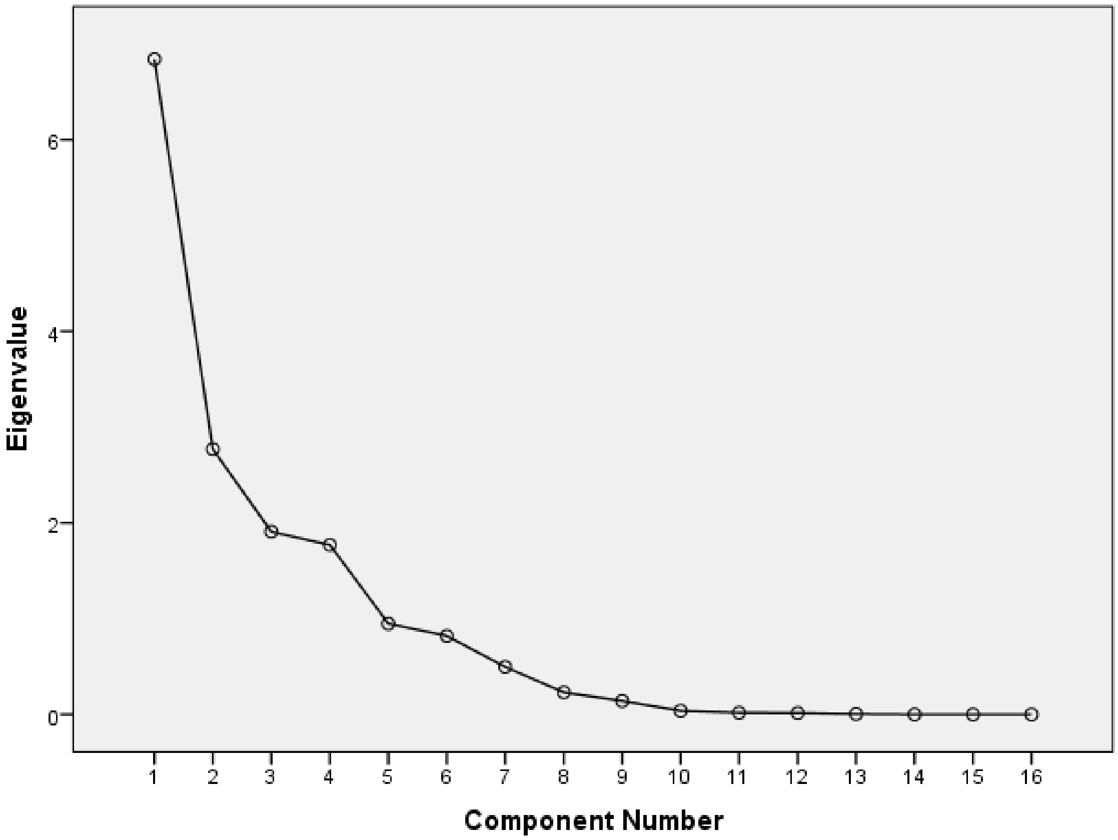
Appendix 20c: PCA and Eigen value for recoverable metals analysed for DS-2-014.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.486	39.400	39.400	7.486	39.400	39.400
2	3.876	20.399	59.800	3.876	20.399	59.800
3	2.419	12.731	72.530			
4	1.438	7.568	80.098			
5	1.115	5.870	85.968			
6	.890	4.684	90.652			
7	.721	3.796	94.448			
8	.367	1.929	96.377			
9	.265	1.395	97.772			
10	.166	.873	98.645			
11	.094	.492	99.137			
12	.064	.338	99.475			
13	.052	.274	99.749			
14	.028	.149	99.897			
15	.012	.062	99.959			
16	.005	.025	99.983			
17	.002	.008	99.992			
18	.001	.007	99.998			
19	.000	.002	100.000			



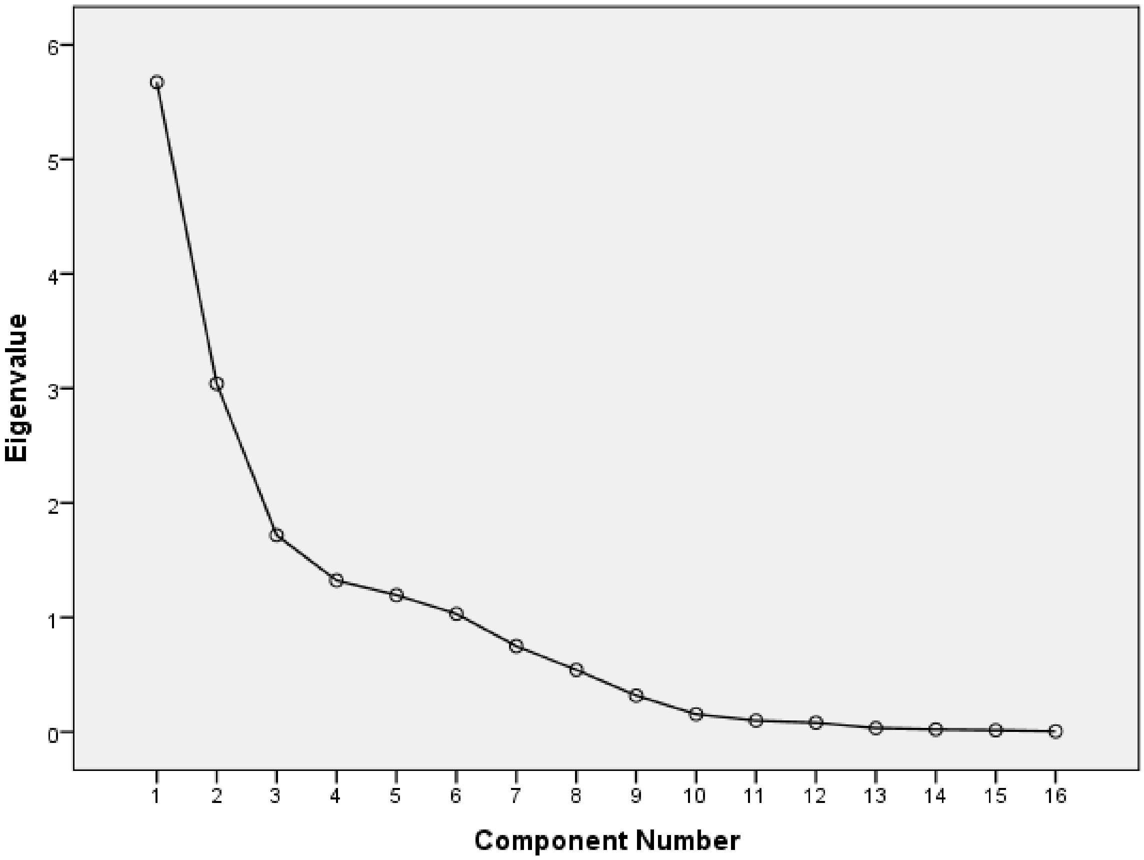
Appendix 21a: PCA for bioavailable metals (I M HCl) analysed for DS-1-2013.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.840	42.749	42.749	6.840	42.749	42.749
2	2.769	17.308	60.057	2.769	17.308	60.057
3	1.908	11.923	71.980			
4	1.770	11.061	83.041			
5	.948	5.922	88.964			
6	.820	5.124	94.088			
7	.497	3.104	97.192			
8	.231	1.445	98.637			
9	.141	.881	99.518			
10	.038	.238	99.756			
11	.019	.117	99.873			
12	.015	.095	99.968			
13	.005	.032	100.000			
14	7.047E-017	4.404E-016	100.000			
15	-1.073E-016	-6.707E-016	100.000			
16	-2.649E-016	-1.656E-015	100.000			



Appendix 21b: PCA for bioavailable metals (I M HCl) analysed for WS-2013.

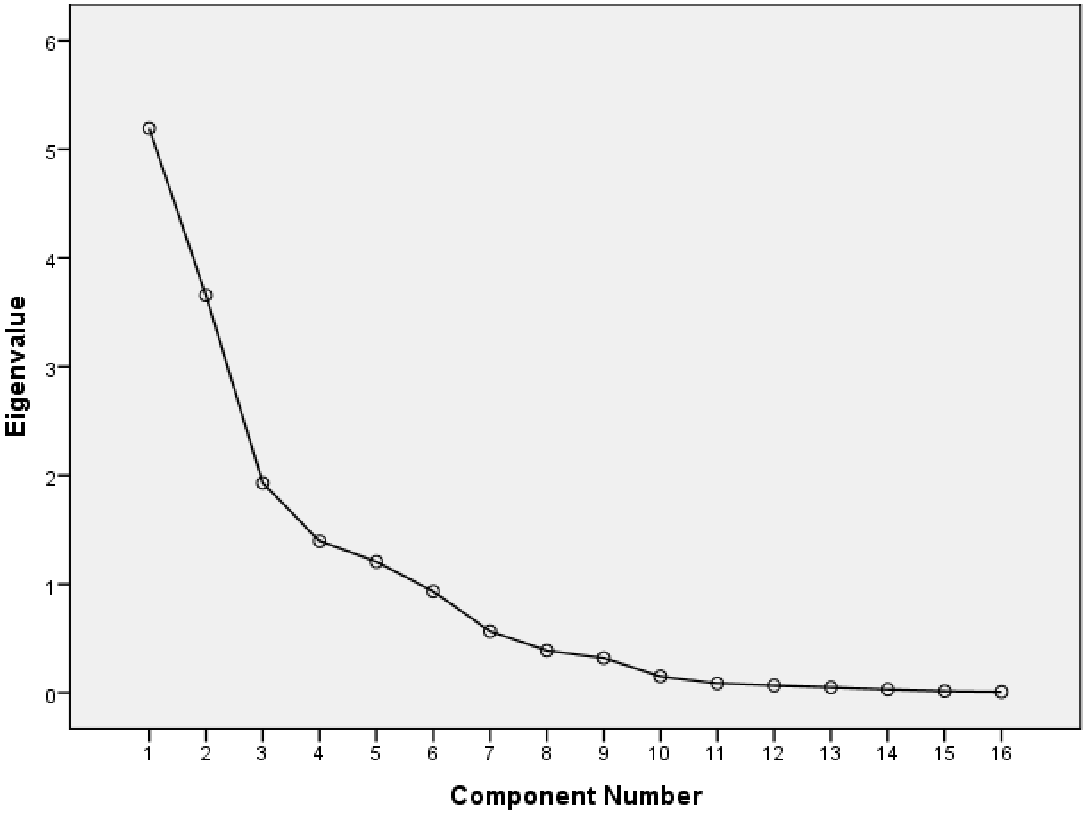
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.674	35.462	35.462	5.674	35.462	35.462
2	3.041	19.003	54.466	3.041	19.003	54.466
3	1.718	10.734	65.200			
4	1.323	8.269	73.469			
5	1.194	7.462	80.931			
6	1.031	6.445	87.376			
7	.749	4.678	92.054			
8	.543	3.391	95.445			
9	.317	1.980	97.425			
10	.154	.964	98.389			
11	.099	.618	99.007			
12	.081	.509	99.516			
13	.034	.211	99.727			
14	.023	.141	99.868			
15	.015	.096	99.964			
16	.006	.036	100.000			



Appendix 21c: PCA for bioavailable metals (I M HCl) analysed for DS-2-2014.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.195	32.466	32.466	5.195	32.466	32.466
2	3.658	22.861	55.327	3.658	22.861	55.327
3	1.931	12.070	67.397			
4	1.396	8.723	76.120			
5	1.206	7.538	83.658			
6	.933	5.833	89.491			
7	.566	3.539	93.030			
8	.388	2.428	95.458			
9	.320	1.999	97.457			
10	.150	.938	98.395			
11	.086	.540	98.935			
12	.067	.422	99.357			
13	.049	.306	99.663			
14	.030	.191	99.854			
15	.015	.093	99.947			
16	.009	.053	100.000			



Appendix 22: Enrichment factor for total, recoverable and bioavailable metals for DS1, WS and DS-2 at the LH, LG and APL

Total (XRF)

DS1								
Location	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Sn**	**Zn**
LH	0.0	1.1	1.4	2.0	5.5	0.2	2.0	2.3
LG	0.0	0.9	1.3	2.9	6.3	0.0	2.1	3.3
DS2								
Location	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Sn**	**Zn**
LH	0.0	0.6	0.9	1.6	1.9	0.0	1.5	2.0
LG	0.0	0.2	1.0	2.4	4.4	0.0	2.8	1.7
WS								
Location	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Sn**	**Zn**
LH	0.0	0.0	0.8	1.9	3.1	0.0	0.3	1.0
LG	0.0	0.0	0.9	2.6	5.3	0.2	0.6	3.0

Recoverable (*Aqua regia*)

DS1												
Location	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Sn**	**V**	**Zn**
LH	1.7	0.0	0.7	1.8	2.7	2.0	3.0	6.3	2.6	0.0	2.0	1.2
LG	1.6	0.0	0.9	1.2	2.2	2.9	4.2	6.8	3.2	0.0	2.2	0.7
DS2												
Location	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Sn**	**V**	**Zn**
LH	2.8	0.0	0.4	1.2	44.2	1.7	2.4	8.2	2.3	0.0	2.0	1.1
LG	2.0	0.0	1.0	1.2	4.2	2.8	38.0	6.8	4.1	0.0	2.3	1.1
WS												
Location	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Sn**	**V**	**Zn**
LH	0.4	0.0	0.5	1.6	0.0	1.2	1.0	0.9	1.6	0.0	2.2	1.2
LG	0.7	0.0	0.2	1.1	0.7	1.2	0.8	1.0	1.4	0.0	1.5	1.3

Bioavailable (1 M HCl)

DS1									
Location	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LH	0.6	0.7	3.0	0.9	0.8	0.7	8.1	0.4	0.6
LG	0.3	1.2	0.7	0.5	0.8	0.8	0.9	0.4	1.6
DS2									
Location	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LH	1.0	0.9	0.9	1.0	1.1	1.0	1.0	0.5	0.9
LG	0.5	1.0	0.6	0.7	1.1	1.2	0.8	0.6	3.2
WS									
Location	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LH	0.3	0.9	1.4	0.4	1.9	3.5	3.4	0.3	0.3
LG	0.2	1.2	0.6	0.4	2.2	3.9	0.9	0.6	1.6

LH: Lagos Harbour, LG: Lagos Lagoon and APL: Apese Lagoons. **EF<2: depletion to minimal enrichment; EF 2–5: moderate enrichment; EF 5–20: significant enrichment; EF 20–40: very high enrichment; and EF > 40: extremely high enrichment**

Appendix 23a: Contamination factor (CF) and level of contamination (Hakanson, 1980).

Contamination Factor (CF)	Contamination Level
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF > 6	Very high contamination

Appendix 23b: Contamination factor for total, recoverable and bioavailable metals for DS1, WS and DS-2 at the LH, LG and APL

XRF DS-1-13

Location		As	Cd	Cu	Fe	Mn	Pb	Zn
LH								
1	ATC	1.23	-6.67	1.16	1.37	1.35	1.00	2.38
2	OBT	0.77	0.00	0.93	0.81	0.46	0.50	2.14
3	GMD	0.54	3.33	0.82	0.77	0.40	0.35	1.66
4	JDM	0.85	-3.33	0.98	1.18	1.15	0.60	1.55
5	TCN6	0.38	-3.33	0.84	0.83	0.91	0.10	1.57
6	SFX	0.85	0.00	0.78	0.84	0.80	0.60	1.24
7	GRV	0.08	0.00	0.67	0.62	0.55	-0.35	0.56
8	APM	-0.23	-3.33	0.51	0.37	0.35	-0.60	0.21
9	BVS	-0.31	-3.33	0.47	0.24	0.28	-0.75	-0.03
10	ENL	0.08	0.00	0.69	0.65	0.76	-0.35	0.71
11	FM	-0.69	0.00	0.98	0.74	0.51	-1.30	0.74
12	NIPCO	-0.62	0.00	0.69	0.20	0.15	-1.10	0.01
LG								
13	UGH	0.46	-3.33	0.98	1.46	0.84	0.10	2.06
14	UHR	0.46	0.00	1.04	1.53	1.24	0.10	2.15

Aqua regia DS-1-13

Location		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LH										
1	ATC	1.45	0.00	0.37	0.29	0.36	0.43	0.22	0.63	0.68
2	OBT	0.62	0.00	0.20	0.21	0.21	0.13	0.11	0.67	0.62
3	GMD	0.96	0.00	0.27	0.24	0.27	0.16	0.16	0.71	0.72
4	JDM	1.00	0.00	0.27	0.20	0.28	0.35	0.16	0.43	0.44
5	TCN6	0.77	0.00	0.21	0.15	0.23	0.29	0.11	0.37	0.45
6	SFX	1.24	0.00	0.32	0.20	0.32	0.39	0.19	0.52	0.51
7	GRV	0.30	0.00	0.12	0.09	0.15	0.16	0.06	0.18	0.19
8	APM	0.08	0.00	0.07	0.01	0.09	0.11	0.02	0.07	0.10
9	BVS	0.04	0.00	0.04	0.00	0.07	0.08	0.00	0.00	0.03
10	ENL	0.04	0.00	0.03	0.04	0.06	0.05	0.00	0.02	0.03
11	FM	0.03	0.00	0.83	0.25	0.19	0.12	0.15	0.19	0.21
12	NIPCO	0.00	0.00	0.05	0.01	0.07	0.07	0.01	0.42	0.15
LG										
13	UGH	0.59	0.00	0.19	0.13	0.34	0.25	0.12	0.55	0.52
14	UHR	0.86	0.00	0.24	0.20	0.45	0.53	0.18	0.68	0.72

1 M HCl DS-1-13

Location		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LH										
1	ATC	0.23	1.33	0.66	0.62	0.25	0.87	5.15	0.83	0.88
2	OBT	0.15	1.02	0.14	0.43	0.17	0.24	0.42	1.27	1.13
3	GMD	0.14	1.01	0.40	0.39	0.19	0.25	0.81	0.95	1.00
4	JDM	0.29	1.08	0.28	0.36	0.27	0.75	0.19	0.66	0.58
5	TCN6	0.18	0.62	0.18	0.22	0.17	0.48	0.15	0.44	0.49
6	SFX	0.27	1.29	0.18	0.29	0.24	0.73	0.17	0.70	0.57
7	GRV	0.22	1.74	0.10	0.97	0.18	0.24	0.10	1.91	0.78
8	APM	0.09	0.13	0.05	0.05	0.09	0.17	0.09	0.12	0.09
9	BVS	0.10	0.04	0.06	0.01	0.05	0.13	0.04	0.04	0.01
10	ENL	0.11	0.42	0.06	0.23	0.12	0.27	0.04	0.30	0.23
11	FM	0.16	0.35	0.86	0.38	0.18	0.23	0.16	0.50	0.38
12	NIPCO	0.04	0.13	0.04	0.05	0.04	0.09	0.02	0.31	0.14
LG										
13	UGH	0.08	1.58	0.07	0.21	0.21	0.37	0.08	0.82	0.70
14	UHR	0.12	2.04	0.07	0.28	0.22	0.74	0.09	0.94	0.92

XRF WS-13

		As	Cd	Cu	Fe	Mn	Pb	Zn
LH								
1	ATC	0.77	0.00	0.89	1.19	0.50	0.50	1.46
2	STFM	1.31	-3.33	0.93	1.27	1.34	1.15	1.53
3	ND	0.00	3.33	0.87	0.64	0.38	-0.40	0.82
4	ORS	0.77	-3.33	0.98	0.83	0.46	0.55	2.09
5	IBJ	-0.15	-3.33	0.67	0.55	0.22	-0.55	0.67
6	GMD	0.92	0.00	1.02	1.28	0.98	0.65	1.60
7	SIFAX	0.77	0.00	1.18	1.33	0.88	0.55	1.60
8	T-6	1.15	3.33	1.09	1.15	1.18	0.95	2.20
9	FJ	1.15	0.00	1.02	1.20	1.28	1.00	2.46
10	JSD	0.62	-3.33	0.76	0.94	0.92	0.35	0.99
11	APM	0.38	0.00	0.69	0.80	0.82	0.10	0.87
12	ENL	0.15	0.00	0.67	0.65	0.62	-0.20	0.57
13	FM	-0.54	0.00	0.42	0.20	0.15	-0.95	0.03
14	FM-AP	1.00	-3.33	0.91	1.26	1.33	0.75	1.49
15	NPA-DY	-0.46	0.00	0.44	0.20	0.22	-0.95	0.14
16	NIPC	-0.08	0.00	0.62	0.58	0.44	-0.55	0.52
LG								
17	IDD	0.00	-3.33	0.60	0.62	0.73	-0.35	0.73
18	OKB	0.69	0.00	0.93	1.09	0.67	0.45	1.87
19	MKK	0.08	-6.67	0.73	0.96	0.95	-0.35	1.28
20	UWF	-0.54	0.00	0.62	1.51	2.97	-1.15	1.09
21	OWS	-0.23	0.00	0.73	0.94	0.72	-0.80	1.07
22	UHR	0.38	-6.67	0.93	1.71	1.90	-0.05	1.57
23	UGH	1.46	3.33	1.27	1.26	0.59	1.40	5.48
APL								
24	APL-LAG	0.00	0.00	0.56	0.26	0.14	-0.40	0.66

***Aqua regia* WS-13**

		As	Cd	Cr	Cu	Fe	Mn	Ni
LH								
1	ATC	1.16	0.00	0.34	0.20	0.37	0.18	0.21
2	STFM	0.68	0.00	0.23	0.15	0.25	0.30	0.12
3	ND	0.34	0.00	0.13	0.14	0.15	0.13	0.07
4	ORS	0.49	0.00	0.19	0.20	0.22	0.14	0.10
5	IBJ	0.32	0.00	0.15	0.18	0.19	0.13	0.08
6	GMD	1.34	0.00	0.30	0.40	0.19	0.21	0.28
7	SIFAX	0.47	0.00	0.15	0.11	0.19	0.25	0.09
8	T-6	0.70	0.00	0.22	0.20	0.26	0.38	0.13
9	FJ	0.72	0.00	0.21	0.16	0.23	0.31	0.13
10	JSD	0.64	0.00	0.22	0.11	0.25	0.36	0.12
11	APM	0.30	0.00	0.14	0.06	0.18	0.26	0.08
12	ENL	0.14	0.00	0.09	0.07	0.11	0.13	0.04
13	FM	0.48	0.00	0.17	0.10	0.17	0.24	0.10
14	FM-AP	0.27	0.00	0.09	0.08	0.10	0.13	0.05
15	NPA-DY	0.80	0.00	0.24	0.40	0.33	0.31	0.17
16	NIPC	0.20	0.00	0.11	0.14	0.10	0.11	0.04
LG								
17	IDD	0.43	0.00	0.18	0.25	0.22	0.24	0.09
18	OKB	0.98	0.00	0.27	0.29	0.33	0.27	0.16
19	MKK	0.75	0.00	0.23	0.36	0.33	0.27	0.14
20	UWF	0.40	0.00	0.06	6.58	0.31	0.57	0.10
21	OWS	2.00	0.00	0.19	14.59	0.34	0.14	0.26
22	UHR	2.40	0.00	0.23	17.95	0.41	0.45	0.35
23	UGH	2.33	0.00	0.21	14.16	0.33	0.16	0.29
APL								
24	APL-LAG	1.23	0.00	0.11	7.23	0.16	0.22	0.12

1 M HCl WS-13

Location		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb
LH (Location)	Sites name								
1	ATC	0.13	0.69	0.06	0.17	0.16	0.17	0.04	0.56
2	STFM	0.25	0.95	0.09	0.18	0.18	0.46	0.05	0.69
3	ND	0.14	0.76	0.06	0.29	0.14	0.27	0.04	0.66
4	ORS	0.13	0.80	0.06	0.25	0.13	0.18	0.03	0.52
5	IBJ	0.13	0.69	0.08	0.27	0.13	0.19	0.56	1.07
6	GMD	0.18	0.91	0.07	0.19	0.18	0.37	0.09	0.51
7	SIFAX	0.25	1.19	0.10	0.20	0.21	0.58	0.14	0.68
8	T-6	0.26	1.16	0.27	0.29	0.20	0.61	1.22	0.53
9	FJ	0.31	1.60	0.10	0.23	0.21	0.61	0.11	0.61
10	JSD	0.13	0.59	0.32	0.14	0.12	0.23	1.09	0.35
11	APM	0.17	0.57	0.07	0.08	0.12	0.33	0.09	0.28
12	ENL	0.13	0.32	0.06	0.10	0.10	0.22	0.04	0.22
13	FM	0.19	0.85	0.06	0.11	0.14	0.41	0.04	0.43
14	FM-AP	0.29	1.16	0.07	0.16	0.22	0.65	0.05	0.56
15	NPA-DY	0.19	0.62	0.06	0.27	0.17	0.39	0.06	0.86
16	NIPC	0.08	0.30	0.03	0.07	0.07	0.11	0.02	0.34
LG									
17	IDD	0.09	0.52	0.04	0.15	0.11	0.26	0.04	0.56
18	OKB	0.14	0.87	0.04	0.18	0.11	0.24	0.04	0.59
19	MKK	0.10	1.31	0.04	0.31	0.12	0.23	0.05	1.18
20	UWF	0.02	0.17	0.03	0.02	0.29	0.78	0.05	0.18
21	OWS	0.05	1.21	0.03	0.22	0.09	0.09	0.04	0.79
22	UHR	0.08	0.86	0.04	0.15	0.20	0.62	0.05	0.67
23	UGH	0.09	1.53	0.02	0.30	0.08	0.08	0.08	1.29
APL									
24	APL-LAG	0.15	0.22	0.02	0.13	0.02	0.02	0.02	0.40

XRF DS-2-14

		As	Cd	Cu	Fe	Mn	Pb	Zn
LH								
1	ATC	0.77	0.00	0.93	1.59	0.33	0.50	1.61
2	SFM	0.23	0.00	0.78	0.85	0.41	-0.15	0.79
3	JSD	1.00	-3.33	1.76	0.95	0.30	0.85	8.00
4	ORD	-0.23	-3.33	0.64	0.65	0.12	-0.65	0.60
5	IBJ	0.92	3.33	1.11	1.40	0.38	0.65	2.39
6	GMD	0.77	3.33	1.00	1.37	0.49	0.50	1.77
7	SIFX	1.00	0.00	0.96	1.39	0.74	0.85	1.74
8	T6	0.92	0.00	0.87	1.26	0.72	0.75	1.46
9	FJ	0.46	0.00	0.82	1.04	0.42	0.10	1.08
10	JSD	-0.08	-6.67	0.53	0.54	0.22	-0.55	0.71
11	APM	-0.15	-3.33	0.56	0.55	0.25	-0.55	0.42
12	BN	0.31	0.00	0.76	0.99	0.40	-0.05	0.82
13	ENL	-0.15	0.00	0.69	0.77	0.25	-0.55	0.58
14	FM	0.46	-3.33	0.84	0.63	0.22	0.20	0.91
15	NPA-DY	0.92	0.00	0.93	1.23	0.63	0.65	2.24
16	NIPCO	0.15	-6.67	0.64	0.80	0.32	-0.20	0.61
LG								
17	IDDO	1.23	-6.67	0.98	1.04	0.36	1.15	1.96
18	OKB	-0.23	3.33	0.71	1.47	0.90	-0.75	1.51
19	MKK	0.08	-3.33	0.76	1.24	0.56	-0.40	1.36
20	UWF	-0.69	-3.33	0.69	2.24	2.59	-1.50	1.72
21	OWSK	2.69	6.67	1.78	1.41	0.23	2.90	12.62
22	UHR	-0.54	-3.33	0.60	1.35	0.87	-1.10	0.92
23	UGH	0.92	3.33	1.24	1.57	0.39	0.75	4.61
APL								
24	APL1	0.23	0.00	0.58	0.58	0.11	-0.10	0.85
25	APL2	-0.46	-3.33	0.44	0.24	0.12	-0.90	0.11
26	APL3	-0.46	0.00	0.49	0.14	0.08	-0.90	0.25

Aqua regia **DS-2-14**

		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LH										
1	ATC	3.46	0.00	0.33	14.31	0.33	0.17	0.35	0.38	0.41
2	SFM	2.12	0.43	0.23	8.64	0.24	0.26	0.23	0.30	0.30
3	JSD	3.47	1.58	0.36	14.67	0.43	0.30	0.59	0.91	1.88
4	ORD	1.98	0.72	0.19	8.52	0.24	0.09	0.31	0.41	0.44
5	IBJ	4.96	1.65	0.44	20.00	0.56	0.24	0.77	1.09	0.96
6	GMD	1.53	0.00	0.34	0.41	0.32	0.31	0.20	0.63	0.66
7	SIFX	2.00	0.00	0.43	0.48	0.42	0.64	0.26	0.80	0.80
8	T6	2.06	0.00	0.46	0.53	0.46	0.72	0.29	0.89	0.91
9	FJ	1.93	0.00	0.43	0.98	0.44	0.41	0.27	1.10	1.04
10	JSD	0.82	0.00	0.20	0.17	0.20	0.21	0.10	0.31	0.32
11	APM	0.20	0.00	0.13	-0.02	0.14	0.17	0.05	0.22	0.17
12	BN	0.39	0.00	0.17	0.05	0.19	0.22	0.08	0.31	0.24
13	ENL	0.50	0.00	0.20	0.08	0.22	0.26	0.11	0.38	0.33
14	FM	0.29	0.00	0.17	0.09	0.16	0.16	0.07	0.50	0.30
15	NPA-DY	0.98	0.00	0.30	0.34	0.33	0.39	0.19	1.05	0.77
16	NIPCO	0.03	0.00	0.08	-0.02	0.09	0.09	0.03	0.19	0.13
LG										
17	IDDO	0.63	0.00	0.18	0.26	0.21	0.19	0.09	0.67	0.53
18	OKB	1.16	0.00	0.28	0.28	0.37	0.40	0.18	0.59	0.67
19	MKK	1.06	0.00	0.25	0.31	0.40	0.52	0.18	0.81	0.87
20	UWF	0.50	0.00	0.13	0.16	0.53	1.45	0.14	0.40	0.68
21	OWSK	1.26	0.00	0.30	0.69	0.41	0.31	0.21	1.99	2.78
22	UHR	1.18	0.00	0.33	0.29	0.71	24.66	0.21	0.77	0.81
23	UGH	1.17	0.00	0.28	0.47	0.42	0.41	0.19	1.06	1.40
APL										
24	APL1	0.23	0.00	0.06	0.04	0.06	0.02	0.01	0.08	0.16
25	APL2	0.04	0.00	0.03	0.00	0.02	0.02	0.00	0.02	0.05
26	APL3	0.00	0.00	0.02	0.01	0.01	0.01	0.00	0.01	0.03

1 M HCl DS-2-14

Location	Sites name	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
LH										
1	ATC	0.12	0.58	0.04	0.11	0.12	0.16	0.03	0.42	0.27
2	SFM	0.19	0.46	0.05	0.14	0.12	0.31	0.04	0.32	0.23
3	JSD	0.20	0.81	0.05	0.83	0.15	0.40	0.05	0.63	1.88
4	ORD	0.08	0.43	0.02	0.18	0.08	0.09	0.02	0.40	0.38
5	IBJ	0.17	0.92	0.05	0.31	0.17	0.24	0.04	0.73	0.62
6	GMD	0.19	0.83	0.04	0.23	0.13	0.34	0.03	0.55	0.48
7	SIFX	0.26	0.99	0.06	0.19	0.16	0.60	0.04	0.55	0.38
8	T6	0.27	1.05	0.06	0.19	0.17	0.60	0.05	0.54	0.46
9	FJ	0.22	0.75	0.05	0.37	0.16	0.34	0.04	0.69	0.56
10	JSD	0.15	0.40	0.06	0.09	0.08	0.21	0.15	0.24	0.22
11	APM	0.08	0.16	0.02	0.04	0.05	0.12	0.01	0.12	0.13
12	BN	0.13	0.26	0.04	0.09	0.09	0.23	0.03	0.27	0.32
13	ENL	0.17	0.69	0.05	0.12	0.12	0.34	0.03	0.38	0.26
14	FM	0.12	0.33	0.04	0.16	0.08	0.19	0.03	0.54	0.65
15	NPA-DY	0.24	0.98	0.06	0.27	0.17	0.48	0.06	1.12	0.60
16	NIPCO	0.06	0.20	0.02	0.05	0.03	0.09	0.01	0.23	0.19
LG (Location)	Sites name									
17	IDDO	0.11	0.55	0.04	0.18	0.08	0.19	0.03	0.72	0.56
18	OKB	0.11	0.60	0.04	0.15	0.15	0.32	0.04	0.48	0.84
19	MKK	0.08	0.85	0.04	0.20	0.16	0.38	0.04	0.81	1.10
20	UWF	0.03	0.35	0.03	0.03	0.28	1.04	0.05	0.23	1.18
21	OWSK	0.07	1.49	0.03	0.27	0.10	0.30	0.04	0.95	1.50
22	UHR	0.12	0.23	0.01	0.05	0.02	0.03	0.02	0.21	0.42
23	UGH	0.01	0.03	0.01	0.01	0.00	0.01	0.00	0.03	0.64
APL (Control)	Sites numbers									
24	APL1	0.25	0.95	0.06	0.28	0.17	0.47	0.06	1.28	0.56
25	APL2	0.07	0.30	0.02	0.11	0.05	0.12	0.02	0.48	0.39
26	APL3	0.07	0.31	0.02	0.12	0.04	0.12	0.02	0.44	0.29