

**CHEMOMETRIC ANALYSIS, SPECIATION AND
REMEDICATION OF POTENTIALLY TOXIC METALS IN
THE SEDIMENTS OF THE LAGOS LAGOON SYSTEM**

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BY

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UNIVERSITY OF LAGOS**

CERTIFICATION

This is to certify that the Thesis:

**"CHEMOMETRIC ANALYSIS, SPECIATION AND REMEDIATION OF
POTENTIALLY TOXIC METALS IN THE SEDIMENTS OF THE LAGOS
LAGOON SYSTEM"**

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is a record of original research carried out

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DEDICATION

To God Almighty the Fountain of Knowledge, and to my late parents-Edward Adesoji Adedeji and Lydia Olayemi Adedeji, who kindled the flame.

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ABSTRACT

The Lagos lagoon system is the main water body in Lagos State and it is highly polluted. It receives enormous amount of domestic and industrial wastes from rivers and creeks. In this study, three main Lagos trans-urban streams Odo-Iyaaloro, Shasha and Ibeshe creeks that empty into the Lagos Lagoon were examined. For the study, samples were collected bimonthly for a year and the physicochemical properties of both the water and sediments were determined. The pseudototal heavy metal concentrations in surface sediments were determined and the quality of the data were checked with two standard reference materials-CRM BCR 143 and GLAURM.

Odo-Iyaaloro was observed to be a polluted water body, with high concentrations of Pb, Cu, Cd, and Zn, with mean concentrations of 21.3 mg/kg, 138.7 mg/kg, 118.6 mg/kg, and 777 mg/kg respectively at point 5, and 34.4 mg/kg, 184.8 mg/kg, 153.5 mg/kg and 1044 mg/kg respectively at point 6. In Ibeshe creek, Cu showed the highest concentration of 332 mg/kg at point B which is a point close to a shoreline textile industry. Enrichment factors, using Fe as a normalizer, showed that Pb, Cd, Zn and Cu in sediments of Odo-Iyaaloro and Shasha creeks, and Cu in Ibeshe creek, were products of anthropogenic sources. It also showed that Cr in the Lagos Lagoon sediments was of natural origin. Principal component analysis showed that organic matter builds aggregates and flocs, which effectively concentrate potentially toxic metals and sink down to form a 'fluffy layer.'

In order to determine the potential mobility and bioavailability of these metals, speciation of the metals was carried out using sequential extraction. Three different

sequential extraction procedures (Tessier's method, Original BCR and modified BCR) were compared, and the modified BCR was then used. The quality of the data in this determination was also checked with standard reference materials: BCR 701 and GLAURM. Analyte recoveries from the direct aqua regia digestion utilized were acceptable. Generally, Cd and Zn were found to be mostly present in the acid exchangeable fraction with a range of 40.3-77.2%, and 17.6-87.3% respectively. Cr and Cu were found to be distributed between the oxidisable fraction and the residual fraction. Pb was found to be mostly associated with the Fe and Mn oxides and hydroxides, and significantly present in the residual fraction, with values ranging from 13-70% and 14-66% respectively.

Potential techniques for the remediation of the PTMs were explored. Four of the most polluted samples were used. Sequential extraction was performed on the samples to determine the fractionation pattern of the metals, and to predict the efficiency of remediation. The efficiency of batch extraction and column leaching of the metals from the sediments using EDTA were compared. The removal of Cd, Cr, Cu, Pb and Zn, were 48-87%, 3-7%, 18-48%, 8-73% and 8-80% respectively for the batch extraction, while in the column leaching technique, 46-66%, 3-7%, 15-57%, 10-59%, and 9-47% of Cd, Cr, Cu, Pb, and Zn respectively were removed. EDTA was able to remove metals in the acid exchangeable and the reducible fractions effectively. This study has proved that heap leaching is a promising approach for the remediation of metal polluted sediments after dredging.

CHAPTER ONE

INTRODUCTION AND REVIEW OF LITERATURE

1.0 Introduction

Environmental pollution from potentially toxic metals is of concern because the latter exhibit behaviour consistent with those of persistent toxic chemicals. Unlike many organic contaminants that lose toxicity with biodegradation, metals cannot be degraded and their toxic effects can therefore be long lasting (Clark, 1992). Although their concentration in biota can increase through bioaccumulation, some heavy metals are known to have toxic effects even at very low concentrations (Davey et al., 1973). When metals are present above threshold concentration limits, they become toxic to plants and animals and the hazards they cause in humans may be acute or chronic. The metals may also act in subtle ways, causing cancer and other secondary effect diseases or even damage to a foetus.

Increasing industrialization and the growth of large urban centres have been accompanied by increases in the pollution stress of the aquatic environment. Over the past 50 years, industries have released more wastes into the aquatic environment than the whole of preceding centuries (Carrasco et al., 2003). Following industrialization, unnatural quantities of metals such as arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and zinc (Zn) have been released into the aquatic

environment through storm water and wastewater discharges (Haynes and Johnson, 2000).

The total concentration of potentially toxic elements in the environment does not provide information about the distribution, mobility and potential bioavailability of elements. Consequently, the identification of the geochemical phases to which the metals are bound and the knowledge of the strength of bonds between the metals and sediments, are necessary to evaluate the availability and the capacity of mobilization of the potentially toxic metals (PTMs) in the sediments. To acquire this information, 'operationally defined speciation' is necessary. This can be carried out by sequential extraction (Mester et al., 1998 and Filgueiras et al., 2002). The heavy metal distribution in soils and sediments normally serves as the indices of the potential harm to the environment. Heavy metals can occur in several forms in water, sediments and soils. There is increasing interest in techniques that relate the degree of mobility of the metals with risk assessment (i.e. the more mobile the metal is, the more the risk associated with it (Bourg, 1995). Hence the necessity for characterizing the form the metals exist (speciation).

Speciation has been identified as a useful tool in predicting the remediation efficiency of extractants used in remediation of soils and sediments, as this allows for an accurate estimation of the effectiveness and the cost of removal. There is therefore a need to identify not only the total metal concentration, but the species in which the metals are present. As far as we are aware, no study has ever been conducted on the

speciation of potentially toxic metals in the sediments of the Lagos Lagoon even with the increased importance of the Lagoon in the socio-economic life of Lagos State. The Lagos lagoon in the Southwest Nigeria is a huge storehouse of living resources that contribute to the food security of about fifteen million inhabitants of Lagos and beyond. It is also home to the biggest port complex and more than 80% of the industries in Nigeria. Some studies on the total metal concentrations in water and sediments of the Lagos Lagoon have been conducted (Bhalero and Adeeko, 1981; Lori, 1991; Ukwé and Alo, 1998): however speciation and/or remediation of these metals have not been studied. Metal toxicity to both terrestrial and aquatic life and the associated risks and dangers have led to the development of techniques for the treatment or remediation of contaminated sediments. The remediation of soils and sediments polluted by heavy metals has been a challenge facing regulators and the scientific community.

1.1 POTENTIALLY TOXIC METALS ("HEAVY METALS") IN SEDIMENTS

Potentially toxic metals are commonly referred to as heavy metals. The term "heavy metal" is ambiguous, since it is defined in different ways by different researchers. The term "heavy metal" is imprecise but it is widely used, although others such as "toxic metals", "trace metals" or better still, "potentially toxic metals" are possible alternatives.

According to Alloway (1990), the term "heavy metals" refer to metals with an atomic density $>6 \text{ g cm}^{-3}$ which occurs naturally in rocks and are extracted into soils and sediments in high concentrations and cause contamination. However, according to Elson (1980), heavy metals are defined as those metals having a density at least five times greater than that of water, while the Concise Chemical and Technical Dictionary defines them as: "metals of atomic weight greater than sodium and this includes magnesium and calcium" (Bennet, 1986).

Toxicity is usually a function of the concentration to which a human or organism is exposed to. Therefore essential elements such as Zn and Cu can become toxic when their concentration levels exceed those required for correct nutritional response (Forstner and Wittman, 1981). Any element can be toxic to humans and organisms depending on the concentration to which they are exposed. The term "potentially toxic metal" has therefore become more appropriate, but this term has been used interchangeably with the term "heavy metal".

The potentially toxic metals (PTMs) of interest in this research include cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn). Increases in industrial and human activities have resulted in increases in release of these pollutants to the environment. Some of the activities which discharge metals into the environment include: leather tanning, metal working, electroplating, energy and fuel production, use of fertilizers, vehicular emissions, mine tailings and metal smelting. Effluents from these activities eventually find their way into the waterbody and finally, the sediments. One of the important properties of these metals is that they are non-biodegradable and can therefore persist in the environmental matrices for a long time (Ellis et al., 1989).

1.2 TOXICITY OF THE HEAVY METALS

- **Cadmium:** Cadmium is a naturally occurring metallic element used for electroplating and galvanizing processes. It is also used in the production of pigments, batteries, as a chemical reagent and in miscellaneous industrial processes (ATSDR, 1989). It is the middle member of the periodic sub-group consisting of Zn, Cd, and Hg, and therefore reveals intermediate properties (Forstner and Wittman, 1981). Cadmium is more efficiently absorbed from the lungs than from the gastrointestinal tract. The absorption efficiency is a function of solubility of the specific cadmium compound as well as its exposure, concentration and route (ATSDR, 1989). Cadmium is transported in the blood by red blood cells and high-molecular-weight proteins such as albumin (Goyer, 1991).

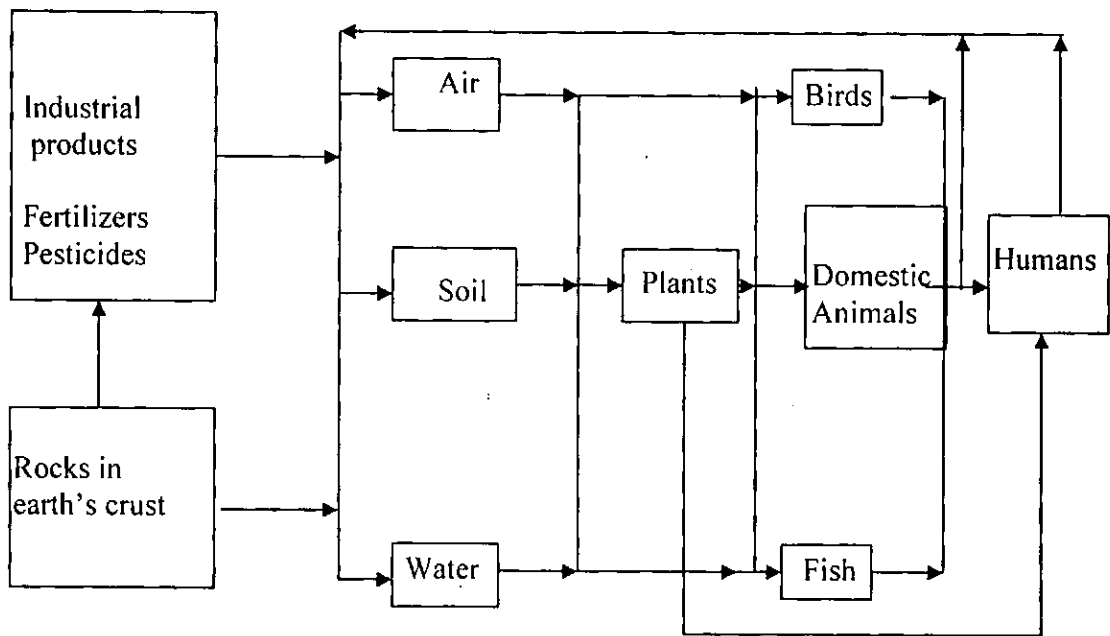
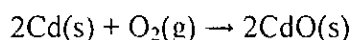


Figure 1.1 Pathway of metals from the environment to humans (Purves, 1985)

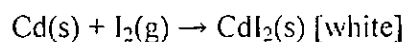
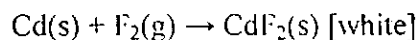
All three elements (Zn, Cd, and Hg) display a profound capacity of combining with -SH groups and imidazole-containing ligands. The stability of such complexes increase in the order of $\text{Zn} < \text{Cd} < \text{Hg}$. Cd and Hg compete with and displace Zn in a number of Zn-containing metalloenzymes by irreversibly binding to active sites and destroying the normal metabolism (Forstner and Wittman, 1981). The primary targets of Cd include the kidney, gastrointestinal tract and the lungs. The liver, bones, testes and cardiovascular systems have also been shown to be affected to various degrees by Cd. Doses of 1,500 to 8,900 mg of cadmium (20 to 30 mg/kg of body weight) have resulted in human fatalities. High doses are known to cause gastrointestinal irritation resulting in vomiting, abdominal pain and diarrhoea (ATSDR, 1989). Dietary intake of Cd has also been implicated in osteomalacia, osteoporosis and spontaneous fractures, conditions collectively called "itai-itai (ouch-ouch) disease (Friberg, 1950).

Inhalation of Cd fumes or dust may result in a wide range of effects, including a metallic taste, headache, chest pains, cough with foamy or bloody sputum, muscular weakness and other respiratory tract infections (USAF, 1990).

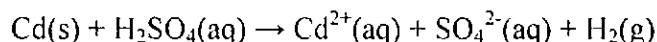
Reactions: -Cadmium metal burns in air to form cadmium(II) oxide.



-Cadmium reacts with halogens as stated below:



- Cadmium metal dissolves slowly in dilute sulphuric acid to form solutions containing the aquated Cd(II) ion together with hydrogen gas, H₂. In practice, the Cd(II) is present as the complex ion [Cd(OH₂)₆]²⁺.



The reacts of cadmium with oxidizing acids such as nitric acid, HNO₃, are complex and depend upon precise conditions.

- **Chromium :-** Chromium enters the air, water and soil mostly as Cr (III) and Cr(VI). While Cr (VI) is toxic, Cr (III) is not. Chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat. It is not a strong oxidizer and the human's natural body acidity is enough for the chromium to keep to this Cr (III) state (Corrosion Doctors, 2008).

Cr (VI) is toxic because it is a very strong oxidizing agent, and one of its reduction products is chromium (V). Cr (V) is a known carcinogen and lodges in any tissue to form cancerous growths. Reports indicate that Cr (V) is a factor leading to premature senility in parts of Russia. In the body, the acidity and action of enzymes on Cr (VI) will promote the formation in small quantities of Cr (V) which is able to lodge in the kidneys, intestine and lungs. Breathing in high levels of Cr (VI) can cause irritation to the nose, such as runny nose, nosebleeds, ulcers and holes in the nasal septum. Ingesting large amounts of Cr (VI) can cause stomach upsets and ulcers, convulsions, kidney, liver damage and even death.

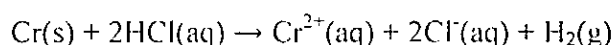
Skin contact with certain Cr (VI) compounds can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have also been reported (corrosion Doctors, 2008).

Reactions: Chromium reacts directly with fluorine, F_2 , at $400^\circ C$ and 200-300 atmospheres to form chromium(VI) fluoride, CrF_6 . $[Cr(s) + 3F_2(g) \rightarrow CrF_6(s)]$

Under milder conditions, chromium(V) fluoride, CrF_5 , is formed. $[2Cr(s) + 5F_2(g) \rightarrow 2CrF_5(s)]$

-Chromium metal dissolves in dilute hydrochloric acid to form solutions containing the aquated Cr(II) ion together with hydrogen gas, H_2 . In practice, the Cr(II) is present as the complex ion $[Cr(OH_2)_6]^{2+}$. Similar results are seen for sulphuric acid but pure samples of chromium may be resistant to attack.

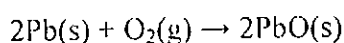
Chromium metal does not react with nitric acid, HNO_3 and in fact is passivated.



- **Lead :-** This metal resembles the divalent Group IIA alkaline earth metals in chemical behaviour more than its own group IVA metals. It differs from group IIA metals in the poor solubility of lead salts such as hydroxides, sulphates, halides, and phosphates. Metabolism of Pb and Ca are similar both in their deposition in and mobilization from the bone. Since Pb can remain immobilised for years, metabolic disturbance can remain undetected (Forstner and Wittman, 1981).

Lead inhibits the synthesis of haemoglobin and also shortens the life span of erythrocytes. The ultimate effects of these is anaemia. It also affects the central nervous system. Psychopathological symptoms include restlessness, dullness and memory loss. The disease caused by lead poisoning is known as plumbism (Forstner and Wittman, 1981). A large affinity of Pb^{2+} for thiol and phosphate containing ligands inhibit the biosynthesis of heme and therefore affects membrane permeability of kidney, liver and brain cells. This results in either reduced functioning or complete breakdown of these tissues, since lead is a cumulative poison (Forstner and Wittman, 1981).

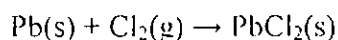
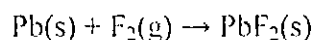
Reactions : The surface of metallic lead is protected by a thin layer of lead oxide, PbO . Only upon heating lead to $600\text{-}800^\circ\text{C}$ does lead react with oxygen in air to form lead oxide, PbO .



Finely divided lead powder is pyrophoric, however, meaning it is a fire risk.

-The surface of metallic lead is protected by a thin layer of lead oxide, PbO . It does not react with water under normal conditions.

-Lead metal reacts vigorously with fluorine, F_2 , at room temperature and chlorine, Cl_2 , on warming to form the poisonous dihalides lead(II) fluoride, PbF_2 , and lead(II) chloride, PbCl_2 , respectively.

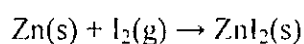
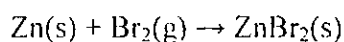


-The surface of metallic lead is protected by a thin layer of lead oxide, PbO. This renders the lead essentially insoluble in sulphuric acid, and so, in the past, a useful container of this acid. Lead reacts slowly with hydrochloric acid and nitric acid, HNO₃. In the latter case, nitrogen oxides are formed together with lead(II) nitrate, Pb(NO₃)₂.

- **Zinc** :-This is one of the most abundant trace elements in the human body. It is a constituent of all cells and several enzymes depend on it as a cofactor (Forstner and Wittman, 1981). Zinc is essential for a healthy immune system, production of certain hormones, wound healing, bone formation, and clear skin. It is required in very small amounts and is thus known as a trace mineral (Hershinkel et al., 2007). Though zinc is an essential requirement for a healthy body, too much of it can be harmful. Excessive absorption of zinc can suppress copper and iron absorption, thereby resulting in anaemia. Other symptoms of Zn toxicity include fever, cough, abdominal pain, nausea, vomiting, diarrhea, drowsiness, restlessness and gait abnormalities. In pregnant women, zinc toxicity can result in premature birth and sometimes still birth (Hershinkel et al., 2007).

Reactions: Zinc metal tarnishes in moist air. Zinc metal burns in air to form the white zinc(II) oxide, a material that turns yellow on prolonged heating. $\{2\text{Zn(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{ZnO(s)}\}$

-Zinc dibromide, zinc(II) dibromide, ZnBr_2 , and zinc diiodide, zinc(II) diiodide, ZnI_2 , are formed in the reactions of zinc metal and bromine, Br_2 , or iodine, I_2 .



-Zinc metal dissolves slowly in dilute sulphuric acid to form solutions containing the aquated Zn(II) ion together with hydrogen gas, H_2 . In practice, the Zn(II) is present as the complex ion $[\text{Zn}(\text{OH}_2)_6]^{2+}$. $[\text{Zn(s)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{H}_2(\text{g})]$

-The reacts of zinc with oxidizing acids such as nitric acid, HNO_3 , are complex and depend upon precise conditions.

-Zinc metal dissolves in aqueous alkalis such as potassium hydroxide, KOH , to form zincates such as $[\text{Zn}(\text{OH})_4]^{2-}$. The resulting solutions contain other species as well.

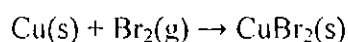
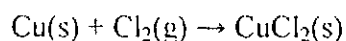
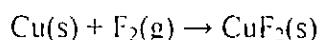
- **Copper :-** This is an essential metal that is found in all living organisms and it has been the cause of some food-borne intoxications. Symptoms of copper poisoning include coppery eructations and taste. Fatal cases are generally terminated by convulsions, palsy and insensibility.

A significant portion of the toxicity of copper comes from its ability to accept and donate single electrons as it changes oxidation state. This catalyses the production of very reactive radical ions such as hydroxyl radical. Too much copper in the water has been found to damage marine life. The observed effects of these higher

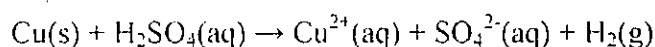
concentrations in fish and other creatures are damages to gills, liver, kidneys and the nervous system. Studies have found that people with mental illness such as schizophrenia showed heightened levels of copper in their systems. (Wikipedia, 2007).

Reactions: -Copper metal is stable in air under normal conditions. At red heat, copper metal and oxygen react to form Cu_2O . $[4\text{Cu(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Cu}_2\text{O(s)}]$

-The reaction between copper metal and the halogens fluorine, F_2 , chlorine, Cl_2 , or bromine, Br_2 , affords the corresponding dihalides copper(II) fluoride, CuF_2 , copper(II) chloride, CuCl_2 , or copper(II) bromide, CuBr_2 respectively.



-Copper metal dissolves in hot concentrated sulphuric acid to form solutions containing the aquated Cu(II) ion together with hydrogen gas, H_2 . In practice, the Cu(II) is present as the complex ion $[\text{Cu}(\text{OH}_2)_6]^{2+}$.



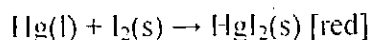
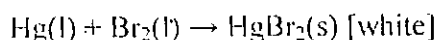
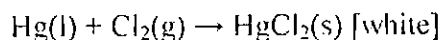
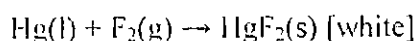
-Copper metal also dissolves in dilute or concentrated nitric acid, HNO_3 .

Some other potentially toxic metals of interest include;

- **Mercury** : This is a heavy metal which occurs in several forms, all of which can produce toxic effects in high enough doses. Its zero oxidation state Hg^0 exists as vapor or as liquid metal, its mercurous state Hg^+ exists as inorganic salts, and its mercuric state Hg^{2+} may form either inorganic salts or organomercury compounds; the three groups vary in effects. Toxic effects include damage to the brain, kidney, and lungs. Mercury poisoning can result in several diseases, including acrodynia (pink disease), Hunter-Russell syndrome, and Minamata disease (Davidson et al., 2004).

Reactions: Mercury metal reacts in air at about 350°C to form mercury(II) oxide.
$$[2\text{Hg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{HgO}(\text{s})]$$

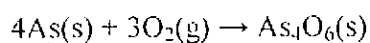
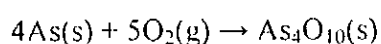
-Mercury metal reacts with fluorine, F_2 , chlorine, Cl_2 , bromine, Br_2 , or iodine, I_2 , to form the dihalides mercury(II) fluoride, HgF_2 , mercury(II) chloride, HgCl_2 , mercury(II) bromide, HgBr_2 , or mercury(II) iodide, HgI_2 , respectively.



-Mercury does not react with non-oxidizing acids but does react with concentrated nitric acid, HNO_3 , or concentrated sulphuric acid, H_2SO_4 , to form mercury(II) compounds together with nitrogen or sulphur oxides. Mercury dissolves slowly in dilute nitric acid to form mercury(I) nitrate, mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$.

- **Arsenic** :This is a notoriously poisonous metalloid Arsenic and its compounds are used as pesticides, herbicides, insecticides and various alloys. The most common oxidation states for arsenic are -3 (arsenides: usually alloy-like intermetallic compounds), +3 (arsenates(III) or arsenites, and most organoarsenic compounds), and +5 (arsenates(V): the most stable inorganic arsenic oxycompounds). Arsenic also bonds readily to itself, forming, for instance, As-As pairs in the red sulfide realgar and square As_4^{3-} ions in the arsenide skutterudite. In the +3 oxidation state, the stereochemistry of arsenic is affected by possession of a lone pair of electrons (Emsley, 2001).

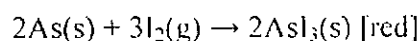
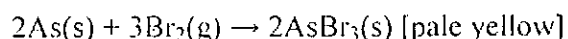
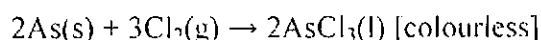
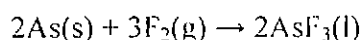
Reactions: Arsenic is stable in dry air, but the surface oxidizes slowly in moist air. When heated in air, arsenic ignites "arsenic trioxide" - actually tetraarsenic hexaoxide, As_4O_6 . This is accompanied by phosphorescence under some conditions. When heated in oxygen, arsenic ignites in oxygen to form "arsenic pentoxide" - actually tetraarsenic decaoxide, As_4O_{10} , and As_4O_6 .



-Arsenic reacts with fluorine, F_2 , to form the gas pentafluoride arsenic(V) fluoride. $[2\text{As(s)} + 5\text{F}_2(\text{g}) \rightarrow 2 \text{AsF}_5(\text{g})]$

-Arsenic reacts under controlled conditions with the halogens fluorine, F_2 , chlorine, Cl_2 , bromine, Br_2 , and iodine, I_2 , to form the respective trihalides

arsenic(III) fluoride, AsF_3 , arsenic(III) chloride, AsCl_3 , arsenic(III) bromide, AsBr_3 , and arsenic(III) iodide, AsI_3 . [



1.3 SEDIMENTS

Sediments are loose particles of sand, clay, silt and other substances of geological origin that have been transported before settling at the bottom of a water body. They are formed from weathered rocks and decomposing plants and animals (USEPA, 2006). Once in water, these sediments are dispersed by wave action and currents and then deposited at the bottom and later resuspended again. Upon re-suspension, it is dispersed by wave action and currents, a series of events that continues until the sediments are transported out of the system or until they become a permanent part of bottom sediments through diagenesis (Dickson et al., 1984).

Sediments are important carriers of trace metals in the hydrological cycle. They also play an important role as indicators of the quality of the system, as well as the historical development of certain hydrological and chemical parameters. Comparative analysis of total concentrations of longitudinal profiles and sediment cores can be performed to determine metal anomalies in zones of mineralization as well as from pollution sources (Forstner and Wittman, 1979). Depending on the environmental

conditions; sediments may be either a sink or a source for trace metals in the surface water. They are not fixed permanently by the sediments but can be recycled through biological and chemical agents, both within the sedimentary compartment and also back into the water column (Salomons and Forstner, 1984).

Heavy metals are dangerous because they bioaccumulate. They bioaccumulate in aquatic organisms, thereby entering the food chain and having deleterious effects on animals and human beings. Sediments play a useful role in the assessment of heavy metal contamination (Elson, 1980). This is because in unperturbed environments, heavy metals are preferentially transferred from the dissolved to the particulate phase. As a result, metal concentrations in sediments are generally much higher than the overlying water and therefore more easily detected (Bryan and Langston, 1992). The advantage of using sediments then is that analytical problems associated with the detection of low but significant amounts of metals in water do not have to be addressed. Also, continuous monitoring of water is not necessary as sediment concentrations indicate contamination loads over long periods of time (Forstner, 1989).

1.3.1 Composition of Sediments

In view of their behaviour in nature, sediments can be classified into:

- fine sediments with particles size smaller than about 5×10^{-5} m
- coarse sediments with grains exceeding 5×10^{-5} m and subdivided into sands and gravels

Fine sediments mainly consist of clay minerals, organic matter and fine grained quartz, carbonate and feldspar particles. Organic matter play an important role in the transport of trace metals, since they are able to bind trace metals and they take part in diagenetic processes after deposition. There is also increasing evidence that suspended particles in natural waters are covered with organic films which determine to a large extent their hydrodynamic behaviour as well as their adsorption characteristics (Salomons and Forstner, 1984).

The mineralogy of coarse sediments consists mainly of quartz with admixture of feldspar. They also consist of rounded particles, while the shape and size of fine particles is diverse. The fine particles are charged, the charge depending on the ionic strength and the surface coating. The surface charge is also responsible for the cohesion characteristics of fine grained sediments (Salomons and Forstner, 1984).

1.3.2 Transport of sediments

The main processes of sediments transport include:

- erosion of the sediments from a bottom or a bank,
- vertical transport of the particles in the body of the water in which it is carried,
- horizontal transport by the flow,
- deposition on the bottom, and
- compaction (consolidation) of the deposit.

All these phenomena vary in space and time. In general, for sediment particles to start moving, the flow of water must exceed a certain critical velocity. Also, deposition occurs when these characteristics of the flow decrease below another critical value. This behaviour depends on the grain size of the sediments. Compared to coarse sediments, a relatively strong current is needed for the erosion of fine cohesive sediments, while for the deposition of the small particles it requires very fine conditions (Salomons and Forstner, 1984).

After deposition, consolidation of the sediments under their own weight and under the weight of the overlying sediments, results in the expulsion of pore water. The particles of coarse sediments form a rather rigid structure already at the moment of deposition. Further deformation is relatively small and is reached very rapidly. Fine sediments, specifically the flocculated, form a very loose fabric with a very high porosity and low permeability. Consolidation progresses slowly, and may cause a 50 % reduction of the volume (Salomons and Forstner, 1984).

1.4 ANTHROPOGENIC INFLUENCES ON METAL CONCENTRATIONS IN SEDIMENTS

1.4.1 Background Concentration

In order to determine the extent of pollution in an aquatic system by means of the heavy metal loads in sediments, it is of primary importance to establish the natural level of these substances i.e the 'pre-civilizational' level. The pollution levels are then obtained by subtracting it from existing values for metals concentration in order to

derive the total enrichment caused by anthropogenic influences (Salomons and Forstner, 1984).

Also in order to obtain an ideal comparative basis for environmental studies, the following criteria should be fulfilled so as to achieve representative values for metal concentrations: (a) a large number of sediment samples must be analysed which correspond with recent deposits in their (i) grain size distribution, (ii) material composition (iii) conditions of origin (iv) samples must be uncontaminated by civilization influences (Salomons and Forstner, 1984).

According to Salomons and Forstner (1984), in order to establish background values for trace metals in sediments, several possibilities have been explored.

1. average shale composition as a global standard value;
2. fossil aquatic sediments from defined environments as a standard, taking into consideration natural allochthonous and autochthonous factors as well as regional influences;
3. recent deposits in relatively unpolluted areas;
4. short dated sedimentary cores which provide a historical record of events occurring in the watershed of a particular estuary (Salomons and Forstner, 1984).

1.4.2 Quantification of Environmental Impact

A first attempt to quantify the extent of heavy metal pollution in sediments on a more global scale was made by Forstner and Muller (1973) by comparing heavy metal consumption with the natural concentration of the respective elements in unpolluted sediments. This is then recorded in the “Index of Relative Pollution Potential”. It has been found that this index proves to be particularly high for Zn, Pb, Hg and Cd.

A similar approach was used by Niki-Forova and Smirnoova (1975) by calculating the “technogenic migration” of a metal and the degree of its utilization through its “Technophility Index” (TP) that is, the ratio of the annual output of a metal to its mean concentration in the earth’s crust. The higher the TP of a metal, the more intensively it is involved in technologic migration. The TP of some metals at the beginning of the 20th century was found to be as stated below:

$$\begin{array}{cccccccccccc} \text{Mn} & = & \text{Fe} & < & \text{Ni} & < & \text{Cr} & < & \text{Zn} & < & \text{Cu} & < & \text{Hg} & = & \text{Pb} & < & \text{Cd} \\ 5 & & 5 & & 10 & & 20 & & 50 & & 100 & & 150 & & 150 & & 700 & \text{ (all values } \times 10^7 \text{)} \end{array}$$

The TP varies with time, and thus each metal can be characterized by its own rate of TP growth. The TP of Pb for example, has grown two and a half times from the beginning of the 20th century up to 1975 and has further increased four and a half times by the year 2000.

A quantitative measure of the metal pollution in aquatic sediments has been introduced by Muller (1979) which is called the “Index of Geoaccumulation”:

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

C is the measured concentration of the element “n” in the sediment fraction and B_n is the geochemical background value in argillaceous sediment (average shale), the factor 1.5 is used because of possible variations of the background data due to lithogenic effects.

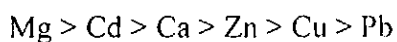
1.5 ADSORPTION OF METAL IONS BY SOILS/SEDIMENTS

Sorption of metal ions can be by several mechanisms which include cation exchange (non-specific adsorption), specific adsorption, organic complexation, chemisorption of metals, co-precipitation and precipitation.

1.5.1 Cation Exchange

Cations are adsorbed onto negatively charged surfaces in the soil/sediment colloidal fraction which are made up of the alumino-silicate clay minerals, hydrous oxides of iron and manganese and humic organic material. Above a pH of 7.0, Fe oxides are negatively charged and adsorb cations. Soil organic matter also has a pH-dependent negative charge which can adsorb cations. At pH 4.5 and above, the carboxyl and phenolic groups dissociate, giving rise to negative charges. Clay minerals have permanent negative charges created by charge imbalance where isomorphous substitution of major constituent (e.g. Al^{3+} replacing Si^{4+} , or Mg^{2+} replacing Al^{3+}) has occurred in the crystal lattice of the mineral during its formation (Alloway, 1982).

Cation exchange occurs where a higher concentration of cations is held in the zone of attraction of the negative charges on the soil colloidal surfaces than in the bulk of the solution. There is a general order of replacement whereby it is found that those ions which are most strongly attracted replace other cations in the zone of attraction. For clay minerals, the order of increasing selectivity as given by Bittel and Miller (1974) as:



1.5.2 Specific Adsorption

This occurs where metals such as Cd, Cu, Ni and Zn form complex ions (MOH^+) on surfaces that contain hydroxyl groups, especially hydrous oxides of Fe, Mn and Al. These complex ions do not undergo cation exchange but can be displaced by strong acids or complexing agents. Specific adsorption is strongly pH dependent and is responsible for the retention of larger amounts of metals than cation exchange (Alloway, 1982).

1.5.3 Organic Complexation of Metals

This route of metal sorption occurs when the solid state humic material binds metals into a ring structure most commonly a chelate. Humic compounds with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination complexes with metals. The stability constant of humic complexes tend to decrease (Alloway, 1982) in the order:



1.5.4 Chemisorption of Elements

Scenarios where the element is incorporated into the structure of the compound is a mechanism of metal sorption. The most common example of this is when metals, such as Cd, replace Ca in the mineral structure of calcite (CaCO_3) (Alloway, 1982).

1.5.5 Co-precipitation of Elements

This is the simultaneous precipitation of an ion in conjunction with other elements. The elements found co-precipitated with secondary minerals in the soil include (Alloway, 1982):

Fe oxides: V, Mn, Cu, Zn and Mo;

Mn oxides: Fe, Co < Ni, Zn, Pb;

Calcite: V, Mn, Fe, Co, Cd;

Clay minerals: V, Ni, Co, Cr Cu, Pb, Ti, Mn, Fe

1.5.6 Precipitation

In metal sorption, cases where the concentration of metals and accompanying ions exceed the solubility product of insoluble forms, such as CdCO_3 and CdS , precipitation occurs. The redox status of the polluted sediment plays an important role in the behaviour of such pollutants. The status determines whether there will be an appreciable concentration of sorptive Fe and Mn oxides present, and, some elements such as Cd which readily form insoluble sulphide precipitates (CdS) under strongly reducing conditions will be immobile in anoxic sediments. However, if these

sediments become aerated, the sulphide will oxidize to form sulphuric acid and so the liberated Cd^{2+} ions will be highly mobile and available for uptake by the aquatic organisms (Alloway, 1982).

1.6 FACTORS AFFECTING METAL RETENTION IN SEDIMENTS

- **pH-:** The pH of a soil/sediment applies to the H^+ ion concentration in the solution present in the sediment pores which is in dynamic equilibrium with the predominantly charged surface of the soil/sediment particles. Hydrogen ions are strongly attracted to the surface negative charges, and they have the power to replace most other cations (Wild, 1988). The sediment pH is the most important physico-chemical parameter controlling the sorption-desorption of ions in sediments (Alloway, 1982).
- **Organic matter-:** Carbon compounds are added to soils/sediments as the products of photosynthesis in roots, stems, leaves, woody material, faeces and sewage sludges. These materials decompose slowly, and because of its low specific gravity, they are called the light fraction of soil organic matter. Organic matter also consists of humus, which is made up of fulvic acid, humic acid and humin. Humus has pH-dependent negative charges due to the presence of $-\text{COOH}$ and $-\text{OH}$ groups which dissociate and therefore able to react with metals (Wild, 1988)

- **Cation Exchange Capacity (CEC)**:- This is a measure of soil/sediments ability to hold cations by electrical attraction. It also provides an indication of the capacity of sediment to bind and exchange positively charged substances, including contaminants. This is determined by the amount of clay and/or humus that is present. Cations are held by negatively charged particles of clay and humus called colloids. If there is a concentration of a particular cation in the soil water, those cations will force other cations off the colloid and take their place. The stronger the colloid's negative charge, the greater its capacity to hold and exchange cations (Wiklander, 1964). Cation exchange capacity of a soil increases with a rise in pH (Alloway, 1982)

1.7 REVIEW ON METHODS OF CHEMICAL ANALYSIS OF HEAVY METALS IN SEDIMENTS

For determining trace metals in sediments, it is necessary to dissolve the samples by a chemical attack. The more current procedures include:-

- (i) total decomposition by hydrofluoric acid
- (ii) strong acid digestion
- (iii) weak acid extraction (Adami et al., 1999)

The choice of the attack procedure depends on the information required by the analyst: i.e., the geochemical characterisation does not require a hydrofluoric attack giving the total content of each metal, while the assessment of the degree of trace metal pollution to which the sediment dwelling organisms are exposed can be better obtained by a milder attack (Adami et al., 1999).

In soil analysis, five mineral acids namely, hydrochloric, nitric, sulphuric, perchloric and hydrofluoric acids have been used. For the simultaneous extraction of a large number of metals, sulphuric acid has a disadvantage, owing to the formation of some insoluble sulphates (Maxwell, 1968). Hydrofluoric acid has the notable property of dissolving silicates, and so it has been used in conjunction with nitric, hydrochloric or perchloric acid in the total decomposition of silicates. Nitric acid has been used separately or in conjunction with hydrochloric acid or perchloric acid. Such acids provide a high degree of metal extraction, but do not dissolve silicates completely; they dissolve organic matter, dissolve all precipitated and adsorbed metals, and leach out certain amount of metals from the silicate lattice.(Agemian and Chau, 1976)

Agemian and Chau (1976) made a study of the extractability of a large number of metals from sediments using different extractants. The extracting efficiency for the ten metals determined was found to be in the order, HF -HClO₄-HNO₃ mixture > boiling HClO₄-HNO₃ mixture > boiling aqua-regia > boiling nitric acid solution > cold 0.5 N hydrochloric acid solution > cold 1.0 N hydroxylammonium chloride plus 25% acetic acid solution > and 0.5 N ethylenediaminetetraacetic acid solution. Two exceptions to this order were boiling HClO₄-HNO₃ when used for chromium and cold 1 N hydroxylammonium chloride plus 25% acetic acid solution when used for copper. It was discovered that chromium was lost by volatilisation when boiling HClO₄-HNO₃ was used, while copper in the form of organic complexes was not extracted.

Concentrations of acid leachable heavy metals and total metal concentration in sediments of a lake in Ibadan was compared, using X-ray fluorescence. It was discovered that > 90% of the iron and manganese, 80% of the zinc, 60% of the lead and 30% of copper and nickel in sediments were acid leachable. According to Ajayi and Mombeshora (1989), these concentrations could be regarded as having environmental implications.

Nine partial decomposition procedures and a total digestion treatment were applied to road-deposited sediments (Sutherland et al., 2004). The objective was to define a parsimonious, time-efficient decomposition procedure that (1) has limited impact on the alumino-silicate matrix/or and refractory-associated fractions, (2) has metal recoveries independent of CaCO_3 content and (3) produces high anthropogenic signals for known contaminants (e.g, Cu, Pb and Zn). The nine extractants used varied from weak single reagents (0.11 M acetic acid) to strong multi-step procedures (BCR 3-step plus aqua-regia). The 1 hr extraction with cold HCl digestion was said to be the most appropriate for use with road sediments. This was based on the assessment criteria such as- minimal removal of Al from alumino-silicate matrix, metal recoveries not being based on CaCO_3 content, high metal content obtained for the contaminants, and simple, time efficient and cost effective technique. The two weakest decomposition procedures considered- 0.05 M EDTA and 0.11 M acetic acid removed negligible amount of Al from the lattice. However the recoveries were quite low, and Al, Co and Cu were dependent on CaCO_3 content (Sutherland et al., 2004).

1.8 REVIEW OF STUDIES ON HEAVY METALS IN SEDIMENTS

Larceda et al. (1991) in their study observed that heavy metals were commonly retained within mangrove sediments and indicated that the anoxic, fine grained and organic rich mangrove sediments reduce the potentially deleterious effects of metal contamination because of the low availability of metals accumulated within the sediments, thereby reducing remobilization and biotic uptake.

The degree of retention of heavy metals in sediments is said to be affected by sediment characteristics, in particular, the type and quantities of organic matter, grain size, cation exchange capacity and mineral constituents (Vertacnik et al., 1995). Large amounts of metals were shown to be bound to the fine grained fraction (<63 μm) of the sediment mainly because of its high surface area-to-grain size ratio and humic substance content (Bourg, 1995). Oyeyiola et al., (2006) reported a good correlation between cation exchange capacity and Cd, Cr, Cu, Pb and Zn in sediments, and also between these metals and % organic matter.

Ong et al. (2006) analysed surface sediments collected from estuarine mangrove forests of Terengauuanu in Malaysia, and a statistical analysis of the results using Pearson correlation matrix proved that there was a significant relationship between the metal concentration, the organic carbon content as well as the grain size. The concentrations of Pb, Cr and Zn was observed to decrease with increase in particle mean size and organic carbon, suggesting that there was association with the fine fraction of the sediments. Also the calculated Index of geoaccumulation (Igeo) suggested that all the metals were considered to be dominantly terrigenous in origin.

Ramessur and Ramjeawon (2002) determined the concentrations of Pb, Cr and Zn in sediments from an urbanized river in Mauritius. The mean concentrations of the metals were found to be $105 \pm 30 \text{ mg kg}^{-1}$, $167 \pm 30 \text{ mg kg}^{-1}$ and $14 \pm 7 \text{ mg kg}^{-1}$ for Cr, Zn and Pb respectively, and these were well below the limits of 600, 2500 and 700 mg kg^{-1} quoted for contaminated sediments (24% clay and 10% organic matter by weight) adopted from the draft standards from Netherlands. Pb and Zn in the river were found to be significantly positively correlated indicating a common source for Pb and Zn contamination. A significant negative correlation was found for Pb and Zn with dissolved oxygen in summer along the river, and this indicated that the presence of anoxic waters influenced the trappings of Zn and Pb in the sediment phase. Pb was significantly lower in the estuary in summer compared to winter and this was said to indicate a significant change in organic profile by resuspension/deposition of cleaner background sediments and removal of organic rich sediments in the estuary during the periods of heavy rains in summer.

Glasby et al., (2004) studied heavy-metal pollution of $< 63 \mu\text{m}$ fraction of sediments from Szczecin Lagoon and the Gdansk Basin, Poland, using ICP-MS, ICP-AES and XRF methods. It was discovered that sediment samples from the Szczecin lagoon displayed a somewhat higher concentration of P, Mn, Cr, Cu Cd, Pb and Zn in those collected in October 1997 after the exceptional flooding of Oder River (which drains into the Szczecin Lagoon), than those collected in December 2000. This was said to be due to enhanced transport of redox-sensitive and anthropogenic elements in the

Oder River and their subsequent redeposition in the western part of the Lagoon. Factor analysis of the data showed that sediments from western part of the Szczecin Lagoon were more enriched with Cd, Ni, Pb, Zn, Co, Cu, Al, Fe, Sb, Mn and V. It was concluded that clay minerals and organic matter build aggregates and flocs, which effectively concentrate trace metals and sink down to form a 'fluffy layer'.

Distribution and normalisation of heavy metal concentrations in mangrove and Lagoonal sediments from Mazatlan harbour in California was carried out by Soto-Jimenez and Paez-Osuna (2004). Al and Li were used as reference elements to normalise concentration for the metals, and this normalization technique confirmed that Co, Cr, Ni, V, Al, Fe, Li and Mn were mainly of natural origin whereas Cd, Zn, Cu, and Pb were anthropogenic and directly associated with point discharges from municipal, dock and industrial activities.

In order to verify whether pollution was increasing or decreasing in the lagoon of Venice, Bernardello et al. (2006) analysed sediments from the Lagoon at three different times (in 1987, 1993 and 1998) over a 12-year period, during which the lagoon environment underwent substantial changes. Some of the heavy metals determined (Zn, Cd, Pb, Cu, Co and Hg) were found to be correlated, and statistical analysis showed a high positive loading for these metals on PC1. This indicated that these metals were associated with anthropogenic inputs. Compared with the background values, mercury was found to be the metal with the highest concentration in sediments, and this showed its anthropogenic origin. It confirmed the results of

previous studies as the main source of Hg contamination had been reported to be a large chloroalkali plant in Porto-Marghera using Hg cathodes since the 1950s. A decrease in the concentration over the years was observed for the metals determined, and this decrease in contamination was attributed to a decrease in the intensity of sources, erosion process which cause the selective loss of the finest fraction of the sediments and also intensive harvesting of clams with hydraulic dredges.

Morrison and Brown (2003), in their study of trace metals in Fanga'uta Lagoon, Kingdom of Tonga, found that Cd was within the range of $<0.1-0.9 \mu\text{g g}^{-1}$, $<1-31 \mu\text{g g}^{-1}$ for Pb, $6-208 \mu\text{g g}^{-1}$ for Zn and $<2-25 \mu\text{g g}^{-1}$ for Ni. These values were said to be within the range normally found in unpolluted sediments. A strong positive correlation was found between Sn with P and Pb. The association of Pb and Sn is said to be commonly found, and there is a strong correlation between Pb and P in volcanic soils in the Pacific Island soils due to the formation of plumbogummite minerals. Ca and Sr were also found to mirror each other, as would be expected of unpolluted sediments.

Monterroso et al., (2003) in their study of Cd, Cu, Pb and Zn in sediments of Ria de Aveiro lagoon, a lagoon on the north western coast of Portugal, found the sediments to exhibit a broad range of metals i.e: copper, cadmium, zinc and lead, with concentrations varying between 3.0-46, 0.10-1.6, 51-589 and $6.0-26 \mu\text{g g}^{-1}$ respectively. Zn and Cd concentrations in sediments from the northern area of the Lagoon were found to be higher than the values recorded in the southern areas, and were 3-5 times higher than background values. In order to minimize the variation of

metal concentration with particle size, values were normalized to Al. Zn/Al, Cd/Al and Cu/Al ratios were found to be highest in the northern area of the lagoon, and this reflected the anthropogenic sources of metals discharged in the northern region of the Lagoon.

Seasonal evolution of heavy metal concentrations in the surface sediments of two Mediterranean *Zostera marina* L. beds at Thau Lagoon (France) and Venice Lagoon (Italy) were investigated by Rigollet et al. (2004). The concentrations and seasonal changes of the heavy metals and organic carbon in the sediments underlying the bed were measured monthly during a year. Thau Lagoon sediments were found to show concentrations of Cu ($18.7 \pm 3.9 \mu\text{g g}^{-1}$) and Pb ($13.8 \pm 3.8 \mu\text{g g}^{-1}$) with average concentrations two fold higher than Venice lagoon- (Cu: $8.4 \pm 4.8 \mu\text{g g}^{-1}$; Pb: $6.1 \pm 0.70 \mu\text{g g}^{-1}$). The organic carbon concentration was higher at Thau ($1.0 \pm 0.3 \text{ mg g}^{-1}$) than at Venice ($0.7 \pm 0.2 \text{ mg g}^{-1}$). A significant seasonal fluctuation was found for Zn, Cu, Ni and Cr in both Lagoons. At Thau, the concentrations of Fe, Mn, Zn, Cu, Cr and Ni increased at the end of summer and in autumn and this corresponded to immediately after the *Zostera* peak. This was said to be probably due to the fact that *Zostera* debris and the organic matter present could have increased the number of sorption sites for heavy metals which would be released when the organic fraction is mineralized.

Table 1.1

Average metal concentrations found in sediments from different regions of the world

Location	Cd	Cu	Pb	Zn	Cr	Reference
Puerto Rico						Acevedo-Figueora et al (2006)
San Jose Lagoon	1.8	105	219	531	*	
Joyuda Lagoon	0.10	22	7.6	52	*	
Italy						Bernardello et al (2006)
Lagoon of Venice (1987)	0.62-3.1	13-51	19-56	186-433	28-51	
Lagoon of Venice (1993)	0.69-1.3	12-36	19-43	72-251	29-45	
Lagoon of Venice (1998)	0.59-2.0	14-32	19-42	71-255	61-107	
Thau lagoon, France	0.28	18.7	13.8	36.1	21.8	Rigollet et al (2004)
Sidi Moussa Lagoon	*	30.4	*	49.8	96.9	Maanan et al (2004)
Kingdom of Tonga						Morrison and Brown (2003)
Fanga' uta Lagoon	<0.1-2.4	2-180	<1-31	6-208	*	
Mauritius						Ramessur and Ramjeawon (2002)
St. Louis River	*	*	14	167	105	
Califonia						Soto-Jimenez and Paez-Osuna (2001)
Mazatlan Harbour	*	7.7-90.9	*	46.4-348	7.6-42.5	
Fiji						Morrison et al (1997)
Great Astrolabe lagoon	<0.2-3.3	22-28	4-17	10-164	17-36	
Florida						Trocine and Trefry (1996)
Indian River Lagoon	0.16	24	7.1	54	28	
Mexico						Vazquez et al (1999)
Pom-Atasta Lagoon	6.42	3.80	8.2	46.4	83.1	

Concentrations are in µg/g.

* Not determined.

1.9 SPECIATION

Speciation is defined as (a) the process of identifying the different, defined species, forms or phases present in a material; or (b) the description of the amounts and kinds of these species, forms or phases present. The species can be defined (i) functionally, (ii) operationally, or (iii) as specific chemical compounds or oxidation states (Ure et al., 1993a; Ure and Davidson, 1995).

It is increasingly being acknowledged that the distribution, mobility and biological availability of chemical elements depend not only on their concentrations, but, critically, on the chemical and physical associations which they undergo in natural systems (Ure and Davidson, 1995; Ure et al., 1995). Some variations of the chemical and physical conditions in the environment can accelerate to some extent the release of toxic metals into it, thus causing contamination (Filgueiras et al., 2002). Some of the more important controlling factors include pH, temperature, organic matter decomposition, redox potential and availability of "reactive species" such as complexing ligands (both organic and inorganic), particle phases for adsorption, and colloidal matter (Ure and Davidson, 1995; Kennedy et al., 1997). For example, a decrease in pH of rainwater resulting from the burning of sulphur-rich fossil fuels can increase the leachability of aluminium from aluminosilicate minerals in soils, resulting in detrimental effects including in extreme cases, fish kills in receiving waters (Ure and Davidson, 1995).

Functionally defined speciation is exemplified by the 'plant available' species, in which specific reagents are used to extract from soil that portion of an element known from empirical observations, to correlate plant availability (Ure and Davidson, 1995).

In operationally defined speciation, the physical or chemical fractionation process applied to the sample defines the fraction obtained. For example, sequential extraction procedures are commonly used to isolate separately, metals associated with the 'water/acid soluble', 'exchangeable', 'reducible', 'oxidisable', and 'residual' fractions of sediments. Physical procedures such as the division of a solid sample into particle sized fractions or the isolation of soil solution or sediment pore water by filtration, centrifugation or dialysis are also examples of operational speciation (Ure and Davidson, 1995).

The third form of speciation, that in which the precise chemical form of an element is measured or defined is the hardest to achieve since analytical methodology of great selectivity and, generally, sensitivity is required. Some success has been achieved in the analysis of waters where, by judicious choice of absorbent and/or reagents, specific oxidation states of elements (for example chromium (III) and chromium (IV)) may be distinguished and quantified (Ishiaka et al., 1989). For solid samples, this narrowly defined type of speciation is seldom possible since specific extraction procedures tend to change the speciation and direct, non-destructive methods are only sensitive enough for major element constituents. Direct methods may be able to identify the species, but are unable to quantify it without resort to associated

separation procedures. Resorting to separation or extraction of element species present the problem of maintaining the speciation unchanged during the extraction or separation procedure (Ure and Davidson, 2001; Filgueiras et al., 2002).

1.9.1 Chemical Fractionation/ Sequential Extraction

This is also known as 'operational speciation' and has been defined as the quantification and identification process of different species, forms or phases of an element, present in a sample, or the description and the types of them (Ure and Davidson, 1995; Ure et al., 1995; Filgueiras et al., 2002). Fractionation is usually performed by a sequence of 'selective chemical extraction techniques, which include the successive removal of these phases and their associated metals, hence the name sequential extraction (Ure and Davidson, 2001).

The main goal of the studies on operational speciation is to convert the metals bound in the solid phases into soluble forms with the extractants used at each step (Tokalioglu et al., 2000). The general applications of sequential extraction schemes can be summarised as follows:

1. Characterisation of pollution sources
2. Evaluation of metal mobility and bioavailability
3. Identification of binding sites of metals for assessing metal accumulation, pollution and transport mechanisms

Sequential extraction results have proved useful to distinguish between anthropogenic and geochemical sources of most metal species in sediments (Gouws and Coetzee,

1997). Sequential extraction schemes provide information on the potential bioavailability and mobility of sediment bound metals (Stone and Marsalek, 1996), design of remediation processes, short and long term soil radionuclide and heavy metal bioavailability (Kennedy et al., 1997).

For the design of sequential extraction schemes, the extraction sequence must be chemically homogenous and ecologically meaningful, so that the role of each fraction in the environment can be readily interpreted. Most of SES (sequential extraction schemes) includes a number of stages between 3 and 8. (Table 1.2). One of the first, and most applied, sequential extraction procedure proposed is a 5-step procedure published by Tessier et al (1979). Several other procedures followed the Tessier procedure, and there is now a wide variety of sequential extraction procedures available based on different sequence of extractants and different operational conditions (Table 1.1). Most procedures involve the chemical separation into “metal soluble in water and acid medium”, “exchangeable”, “reducible or associated with Fe and Mn oxides”, “oxidizable or associated with organic matter and sulphur”, and “residuals or associated silicates”. Typical draw backs inherent in these methodological approaches are the lack of selectivity of chemical reagents so that a specific association form is isolated and the critical influence of operational conditions such as pH, temperature, leaching time, reagent concentration, stirring system, particle size of the solid, the ratio of solid to volume of extractants (Forstner, 1993; Hursthouse, 2001)

Table 1.2

Some common sequential extraction schemes

Phases							Scheme
A	B	C	D	E	F	G	
CaCl ₂	HOAc	-	K ₄ P ₂ O ₇	NH ₄ Ox/HOx	-	DCB	McLaren and Crawford (1973)
MgCl ₂	NaOAc	-	-	NH ₂ OH.HCl/HOAc	H ₂ O ₂ /NH ₄ OAc	-	Tessier et al. (1979)
Mg(NO ₃) ₂	-	NH ₂ OH.HCl	NaOCl	NH ₄ Ox/HOx	-	-	Shuman (1983)
NH ₄ OAc	NaOAc	NH ₂ OH.HCl	-	NH ₄ Ox/HOx	H ₂ O ₂ /NH ₄ OAc	-	Salomons and Forstner (1984)
-	HOAc	NH ₂ OH.HCl	-	-	H ₂ O ₂ /NH ₄ OAc	-	Ure et al. (BCR) (1993)
-	HOAc	NH ₂ OH.HCl	-	-	H ₂ O ₂ /NH ₄ OAc	-	Sahuquillo et al. (Modified BCR) ^a (1999)

Phases: A, Exchangeable; B, acid-soluble; C, easily reducible (i.e Mn oxides); D, easily oxidisable (i.e humic and fulvic acids); E, moderately reducible (i.e amorphous Fe oxides); F, oxidisable oxides and sulphides; G, poorly-reducible (i.e crystalline Fe-oxides). ^aThis scheme differs from that of Ure et al in terms of the concentration of hydroxylamine hydrochloride concentration (0.5 instead of 0.1 mol dm⁻³), and also in terms of the pH (1.5 instead of 2)

1.9.2 Target phases in sequential extraction schemes

1.9.2a Water-soluble fraction

Trace elements extracted by water are relatively labile and thus may be potentially bioavailable. In any sequential extraction scheme, this fraction of a soil or sediment is usually the first to be brought into solution and is usually negligible (Hall et al., 1996). This phase contains the water-soluble species made up of free ions and ions complexed with soluble organic matter and other constituents. It constitutes the most mobile and potentially, the most available metal and metalloid species (Filgueiras et al., 2002).

The use of water as an extractant has a number of analytical problems in that the efficiency of the aqueous extraction for trace metals is too low and therefore the dissolved concentration may be outside the range of determination limits of available routine analytical methods (FAAS, ICP-AES) (Filgueiras et al., 2002).

However, the water soluble fraction may be obtained in two ways, by sampling sediment pore water solution using insitu filtration, dialysis tubes or bags, or by leaching procedure in the laboratory (Gleyzes et al., 2002). Normally, this fraction is usually determined together with the exchangeable fraction.

1.9.2b Exchangeable fraction

This fraction includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction; metals that can be released by ion-exchange

processes and metals that can be coprecipitated with carbonates present in many types of sediments (Filgueiras et al., 2002).

Exchangeable metal ions are a measure of those metals which are released most readily into the environment. According to Stone and Droppo (1996), in relation to the total trace metal content, the exchangeable fractions are a minor component (generally less than 4%), and vary slightly with grain size. Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilization of metals from this fraction (Ure and Davidson, 1995).

Reagents commonly used for this purpose are electrolytes in aqueous solution, such as salts of strong acids and bases, or salts of weak acids and bases at pH 7 (Rauret, 1998). The most popular reagent used is MgCl_2 (1.0 mol l^{-1}), which combines the rather strong Mg^{2+} ion-exchange capacity with the weak complexing ability of Cl^- (Gleyzes et al., 2002). This reagent does not attack organic matter, silicates or metal sulphides. Some slight dissolution of carbonates was observed, but could be avoided by shortening the extraction time (Tessier et al., 1979). Other solutions include KNO_3 , MgNO_3 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, NH_4NO_3 and NH_4Cl .

In a study on effects of drying on the measurement of exchangeable fractions in sediments by sequential extraction, it was found that the exchangeable fraction was the most affected in the drying technique (Bordas and Bourg, 1998).

1.9.2c Acid –soluble fraction

This fraction contains the metals which are precipitated or coprecipitated with carbonate (Clevenger, 1990). Carbonate can be an important adsorbent for many metals when organic matter and Fe-Mn oxides are less abundant in the aquatic system (Stone and Droppo, 1996). The carbonate form is a loosely bound phase and may change with environmental conditions (Stone and Marsalek, 1996). This fraction is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5 (Gleyzes et al., 2002).

The reagent which is most widely used in Sequential Extraction Schemes (SES) for releasing the metal fraction bound to carbonates is the sodium acetate-acetic acid buffer at 1 mol l⁻¹ concentration and pH 5. This reagent is well adapted to dissolve calcium carbonates but dissolution of dolomite is not total. Moreover, when the pH of the extracting solution is lowered from 7 (pH of the extracting solution in the first two stages) to 5, the remaining specifically-sorbed trace metals ions that escaped extraction in the previous step would be released (Tessier et al., 1979).

Significant percentages of Fe and Mn have been found in some extracts originating from sediments after treatment with NaOAc-HOAc. This can be attributed to solubilization of FeCO₃ and MnCO₃ (Fe and Mn are in reduced state) in acidic solution of acetate rather than attack of the Fe/Mn oxides (Tessier et al., 1979).

Generally, heavy metals in the exchangeable and acid soluble fractions are considered to be readily and potentially bioavailable, while the reducible and oxidisable fractions are relatively stable under normal soil conditions (Wong et al., 2002).

1.9.2d Reducible Phase

Iron and manganese oxides are present in large amounts in soils and sediments (Emmerson et al., 2000), and they are excellent scavengers of metals (Gleyzes et al., 2002). Under anoxic conditions, Fe(III) and Mn(IV) can be reduced, and followed by subsequent dissolution, adsorbed trace metals could be released (Clevenger, 1990). The reagents used to target the reducible phase include hydroxylamine, oxalic acid and dithionite (Gleyzes et al., 2002).

The use of 0.2 molL^{-1} oxalic acid, together with 0.2 molL^{-1} oxalate solution at ambient temperature in the dark has been used to target the amorphous iron oxides. Adding a strong reducing agent such as ascorbic acid, and also extracting in the light provides sufficiently severe conditions to dissolve even the crystalline iron oxide (Smith, 1994). Though oxalate forms stable complexes with most metals, it can also form sparingly soluble oxalates salts with Ca and Pb, and this can lead to low recoveries of lead in solution (Gleyzes et al., 2002).

Sodium citrate/sodium dithionite buffer (DCB) is a strong reducing agent, that can dissolve even well crystallised Fe oxides, and this has been used in some sequential extraction schemes (Harrington et al., 1998). The presence of metal impurities and

blockages during analysis are the main drawbacks of this reagent. Dithionite has been known to be easily contaminated with zinc and its purification by a chelation – extraction procedure proves difficult. DCB has also been known to attack silicates (Tessier, 1979).

Hydroxylamine hydrochloride in nitric acid is the preferred reagent for leaching the reducible fraction in sediments (Filgueiras et al., 2002). It uses the reducing power of the hydroxylamine to dissolve the different metallic oxides, and this depends chiefly on the pH (Smith, 1994). When the pH falls below 1.5, the reagent may partly release the metal content associated with the silicates (Tessier et al., 1979).

1.9.2e Oxidisable Fraction

This fraction refers to metals which are associated with various forms of organic material such as living organisms, detritus or coatings on mineral particles (Tokalioglu, et al., 2000). Organic substances have been known to exhibit a high degree of selectivity for divalent ions compared to monovalent ions, and the probable order of binding strength being $Hg > Cu > Pb > Zn > Ni > Co$ (Jonasson, 1977; Stone and Marsalek, 1996).

This form of metals are assumed to remain in the soil or sediment for longer periods but may be mobilised by decomposition processes (Kennedy et al., 1997). The organic fraction released in the oxidisable phase is not considered very mobile or

available since it is thought to be associated with stable high molecular weight humic substances that release small amounts of substance in bits (Miragaya and Sosa, 1994). Under oxidizing conditions, these organic materials tend to be degraded, leading to the release of sorbed metals, so oxidising reagents such as H_2O_2 or $NaClO$ are frequently used to extract metals associated with this fraction. However, some oxidising agents also tend to simultaneously oxidise any sulphides presents, so this step is commonly called "oxidisable fraction" (Stone and Droppo, 1996).

Generally, hydrogen peroxide, applied to a heated medium (at a temperature of $85^\circ C$) for several hours is the preferred reagent for dissolving organic matter, as a compromise between a complete attack of organic matter and minimum alteration of silicates (Tessier, 1979). The shortcoming of this reagent is metal readsorption on the residual fraction, and this has been reportedly overcome by the additional extraction stage with ammonium acetate at pH 2. The hydrogen peroxide/ammonium acetate prevents readsorption of the extracted metals onto the oxidized substrate, and this reagent has been adopted by many sequential extraction schemes for leaching metals associated with organic matter and sulphides.

1.9.2f Residual fraction

Metals extracted in this fraction are those in the lattice of primary and secondary minerals. In this case, possible changes in environmental conditions would have no effect on the release of such metals from this fraction on a time-scale of several years

(Perez, and Valiente, 2005). Extraction of trace metals in this phase is achieved by digestion with strong acids such as HF, HClO₄, HCl and HNO₃ (Gleyzes et al., 2002).

1.9.3 The BCR Sequential Extraction Scheme

The lack of uniformity of the extraction schemes and the lack of reference material had hindered the comparison of the schemes and the validation of the procedures. Owing to the likelihood of the many pitfalls which may occur, it was expected that the use of extraction schemes would be progressively abandoned (Quevauviller et al., 1993). Consequently, the Community Bureau of Reference (BCR, now Standards, Measurements and Testing Programme) organized a series of intercomparisons on extractable trace metal determination and a workshop on Sequential Extraction Techniques in sediments and soils to discuss results of intercomparisons and establish a common procedural scheme. This project led to the optimization of a 3-step procedure based on acetic acid extraction (step 1), hydroxylammonium chloride extraction (step2) and hydrogen peroxide/ammonium acetate extraction (step 3). It also led to the production of a reference material (BCR 601) (Quevauviller et al., 1993; Quevauviller et al., 1997).

The original BCR procedure has been used with good reproducibility within laboratories. The use of a sediment standard reference material showed excellent reproducibility, except for analytes which were close to detection limits.

Mester et al. (1998), observed good reproducibility for all the metals except for Cu in the third step, and all the results obtained in their laboratory overlapped with the certified values except for Cd in step 3. Svete et al. (2001), also observed good reproducibility in the result of the reference material (BCR 601) used. The original BCR procedure was tested on sewage sludge (Perez-Cid et al., 1996), river sediments (Svete et al., 2001), car park dust (Tokalioglu et al., 2003), street dust (Stone and Marsalek, 1996), soil (Ho and Evans, 1997) and compost (Greenway and Song, 2002).

Tokalioglu et al. (2003), compared the original BCR SES with schemes by Benitez and Dubois (1999), and Hall et al., (1996) on car park dusts. A comparison was done using a student's t-test among the total metal concentration acquired from the three sequential extraction procedures, and it was observed that there was no significant difference observed for Cu, Pb and Zn at 95% confidence level. Contrarily, a significant difference at 95% confidence level was observed for Cd, Fe, Mn and Ni. Fe and Ni in the original BCR procedure, was found to be lower than those found in the other two procedures. It was thus concluded that SES and reagents have substantially different effectiveness for extracting and /or partitioning of metals from the car park dusts. That is, the extractable metal content can be altered depending on the operational conditions. It was therefore concluded that if the aim of the work is to quantify the fraction of metal characterised by mobility and bioavailability, the BCR procedure is recommended instead of the other long and difficult procedures, while, on the contrary, if the aim of the work is to obtain more knowledge about the

fractions of the metals bound to different phases of the sample, the 5-step procedures would be preferred.

Perez-Cid et al. (1996), compared the Tessier scheme and the original BCR scheme in the partitioning of Cu, Cr, Pb Ni and Zn in sewage sludges. It was discovered that both schemes yielded similar performances except in the case of lead when extraction efficiencies were compared, but matrix effects caused by concomitants was less pronounced in the BCR scheme in comparison with the Tessier scheme.

Partitioning of Cd, Pb and Zn was done on river sediments from a lead and zinc mining area by Svete et al. (2001) using the original three step sequential extraction procedure. Zn was found to prevail in the most sparingly soluble fraction and is also distributed between the organic matter and sulphides, whereas a smaller proportion was found in the easily soluble fraction. Pb was distributed between the organic matter and sulphides whereas Cd was predominantly associated with the most sparingly soluble fraction.

The BCR (original) scheme was tested in a first interlaboratory trial on BCR 601 on the extraction of Cd, Cr, Cu, Ni, Pb and Zn, and the results showed that while promising, improvements were necessary due to the fact that only 60% of the extractable metals were certifiable (Ure et al., 1993a). The remaining metals could not be certified due to the high variability between the results obtained by the different laboratories, and this was attributed to small variations in the pH of the

hydroxylamine hydrochloride. It was also reported by Davidson et al. (1999), that when three analysts prepared their own reagent and performed sequential extraction independently and on a different day, results showed significant inter-analyst variability. The main difference was found to be in the amount of metal extracted in the second step, using $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ acidified with nitric acid. The probable cause of the variability was as a result of small differences in pH. It was reported that although each analyst used a calibrated pH meter to adjust the extractant, it was discovered that each found a slightly different volume of HNO_3 required to reach pH 2.0.

The BCR scheme was therefore improved with respect to the second step by the addition of a fixed amount of nitric acid and the concentration of hydroxyl ammonium chloride was increased from 0.1M to 0.5M, and a reference material (BCR701) was certified. The modified protocol also recommended the inclusion of an additional step, residual extraction stage (step 4) to allow comparison with pseudo total digestion results for validation purposes (Pueyo et al., 2001)

The original and the modified BCR sequential extractions have been compared (Rauret et al., 1999; Mossop and Davidson, 2003; Brunori et al., 2004; Joksic et al., 2005). Mossop and Davidson, (2003) observed that increasing the concentration of hydroxylamine hydrochloride in step 2 had little effect on Fe, but the influence of the extractant pH was more important. This was also the case for copper and lead, while

it was observed that the zinc partitioning was relatively unaffected by the changes in the sequential extraction scheme.

It has been reported by Joksic et al. (2005), that when the original BCR scheme was used, <10% of the total Pb and Cu were associated with the residual phase (step 2), while in using the modified BCR protocol, the percentage of Pb and Cu in step 2, increased to about 30-70% of the total metal present. A similar trend was also reported for Zn and Ni.

Rauret et al., (1999) compared the original and modified protocols on CRM 601. For the modified protocol, it was observed that Cr and Zn values were similar to the certified/indicative values, while for Cd, Ni and Pb, larger standard deviation values were observed, but were also consistent with the certified/indicative values. When the modified BCR protocol was used for the second step for Cu, the amount extracted was higher and there was good reproducibility of result between the different laboratories. This was attributed to the increase in reagent concentration and decrease in pH, which caused a more effective attack on the more refractory, crystalline oxyhydroxides in addition to the amorphous forms.

The modified BCR sequential extraction scheme has been used on soils, sediments and soil reference materials of different origin (Morrison and Vicente-Beckett, 2002; Zemberyova et al., 2006). Zemberyova et al. (2006), reported satisfactory accuracy, when the sum of elements contents in the three fractions plus the *aqua-regia*

extractable content of the residue was compared to the *aqua-regia* extractable content of the elements in the original soils.

1.9.4 Limitations of Sequential Extraction

The main criticisms of sequential extraction schemes are the problems of readsorption and sample pre-treatment.

(a) Readsorption

Readsorption may lead to a significant underestimation of potential bioavailability of metals, especially at high contamination (Howard and Vandenbrink, 1999). Natural sediments spiked with a known amount of metal have been used for testing readsorption. Application of this to the readsorption studies of Cd and Zn during sequential extraction with the BCR procedure showed that the extent of this phenomenon was less than previously suspected and was not so important, whereas, readsorption effect for Pb and Cu was suspected to be more important (Davidson et al., 1999).

It was observed that addition of complexing agents such as criptand and multidentate chelating agents to extractants of both the BCR and Tessier SES proved to counteract readsorption, and the amount of complexing agent depends on the type of soil or sediment (Raksataya et al., 1997; Howard and Vandenbrink, 1999). Attempts to prevent readsorption using a chelating agent have been reported by Howard and Shu, (1996). The addition of nitrilotriacetic acid (NTA) to the reagents used in the Tessier

extraction method was found to reduce re-adsorption. Authors observed an improved recovery of 18% lead, 30% nickel and 19% zinc, and this improvement was attributed to the prevention of re-adsorption by the NTA used. Samples with high organic matter content were also found likely to be more susceptible to greater re-adsorption problems.

(b) Sample pre-treatment

The original distribution of the metals should not be disturbed during sample pre-treatment, as this could be an additional source of error. Wet storage of oxidised soils and sediments at ambient temperature is inadequate because of the rapid microbial induced shift from oxidising to reducing conditions in the stored samples (Filgueiras et al., 2002).

The effect of drying methods (freeze drying, air drying and oven drying at 105°C) on the distribution of metals was studied on superficial sediments (Bordas and Bourg, 1998). Compared to fresh sediments, none of the drying methods completely preserved the distribution of Cu, Pb, Zn, and Cd in the geochemical fractions, especially when the metal content is low.

Davidson et al. (1999) in a study of industrially contaminated soil for assessment of variability sources found that repeatability was higher for air-dried samples than for field moist samples, but larger amount of metals were extracted. This suggests alterations in the metal distribution during drying. Davidson et al. (1999) also

reported that Cd and Pb differ in their responses to different treatment. Air drying markedly reduced the total amount of Cd in the four steps, suggesting redistribution into forms inaccessible even to pseudo-total digestion with aqua regia. Oven drying was reported to have little effect on the fractionation of Cd, whereas freeze drying produced a large increase in oxidisable Cd. The phase distribution of Pb was observed to be generally less affected by sample treatment than that of Cd, the largest change occurring with oven drying.

Quevauviller et al.(1993) concluded that sequential extraction should be conducted on wet, sieved sediment immediately after sampling, so that environmentally relevant information can be obtained. Since this recommendation cannot always be followed, freeze drying or air drying has been suggested (Bordas and Bourg, 1998).

1.10 REMEDIATION OF CONTAMINATED SOILS AND SEDIMENTS

Remediation of contaminated soils and sediments are based on two principles:

1. immobilisation of the metal's rate of mass transfer
2. removal of the metals from the soil matrix (Di Palma et al, 2005)

Remediation technologies are divided into two categories

1. In-situ treatment:- This refers to the treatment of soils or sediments at location
2. Ex-situ treatment: - This involves the treatment of contaminated soils or sediments at another location (Kosteckii and Calabrese, 1989).

Sediment remediation may involve either in-situ or ex-situ, but in-situ remediation alternatives are somewhat limited and generally involve a single technology such as capping (USEPA, 1994).

Capping is a technique for the control of polluted sediment with metals and organic compounds. It refers to the placement of a covering or cap over an in situ deposit of contaminated sediment. The cap could be non-polluted (clean) sediments, gravel, or sand. It may also involve a more complex design with liners and multiple layers (Zoumis et al., 2001). The layer is usually about 30-40 cm thick to prevent biological mixing of the capped contaminated sediment. The capping material is usually coarser than the polluted sediment to prevent mixing or disruption of the cover by wind, wave or current. This method of remediation is rarely used because of the difficulty in placing a uniform cover in the sub-aqueous environment (UNEP, 2007).

Azcue et al. (1998) demonstrated in situ capping in Hamilton Harbour Lake Ontario, Canada, and it was shown to be successful.

Ex-situ remediation involves dredging the sediments, removal to another location and treatment. Remediation options of such dredged sediments or soils include (Mulligan et al., 2001a)

- Solidification/stabilization
- Vitrification
- Chemical Oxidation
- Thermal extraction
- Electrokinetics
- Bioremediation
- Phytoremediation
- Soil washing

(a) Solidification/stabilization

Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization). Agents include lime, flyash, cement, bitumen, asphalt and soluble phosphates. Solidification/stabilization process is effective for metal contamination as destructive techniques available for metals is few (Mulligan et al., 2001a).

Seaman et al. (2001) conducted batch experiments to evaluate the ability of hydroxylapatite to reduce the solubility of metals in contaminated sediments. Hydroxylapatite was effective at reducing the solubility of U, and to a lesser extent, Ni. It was also effective at reducing the solubility of Al, Ba, Cd, Co, Mn and Pb. Sequential extraction indicated that the apatite transferred the metals from more chemically labile forms such as the water-soluble and exchangeable fractions to the less labile forms.

The use of low-cost and environmentally safe techniques for the in situ immobilization of heavy metals in soils have been investigated (Guo et al., 2006). Agricultural wastes such as bark sawdust, bagasse, ricehulls and poultry manure have been used. According to Bailey et al., (1999), bark sawdust was effective in the immobilization of Cd, Pb, Hg and Cu, while Bagasse successfully immobilized Pb. Bark, sawdust were also used by Olayinka et al., (2005) in the remediation of metal pollutants from industrial effluents and up to 99.4 % and 100 % of Zn and Cr respectively were removed. Other low cost agricultural wastes used by Olayinka et al., (2007) include waste tea, coconut husk, coconut husk and teak tree bark.

(b) Vitrification

This is another type of immobilization technique. It involves the insertion of electrodes into the soil which must be able to carry a current and then to solidify as it cools. This process has been applied on sediments, but costs are too high because of

the high moisture content which can sometimes be above 20%. Efficiency is also decreased by high organic contents in the sediments (Mulligan et al., 2001a).

(c) Chemical oxidation/reduction

Oxidation/reduction of potentially toxic elements is another method for remediation of ex-situ sediments. This involves the percolation of organic and inorganic chemicals to reduce the metals to their lowest valence states and form stable organometallic complexes. A common chemical for this purpose is sodium polythiocarbonate that forms a precipitate, which becomes less soluble with time. The metals in the treated soil/sediment, then becomes no longer leachable (Mulligan et al., 2001a).

Chemical treatments are usually for soils before solidification. For example, reduction of Cr(VI) is usually performed before solidification/stabilization. Oxidation is less commonly used as these reactions are not specific; therefore there is a risk of converting other metals into more toxic or mobile forms. Arsenic is most applicable for chemical oxidation since As(V) is less toxic than As(III) (Mulligan et al., 2001b).

(d) Electrokinetics

This involves passing a low intensity electric current between a cathode and an anode imbedded in the contaminated sediments. Ions and small charged particles, in addition to water, are transported between the two electrodes. Anions move towards the positive electrodes while cations move to the negative electrode. Movement are by electromigration (charged chemicals movement), electro-osmosis (movement of

fluids), electrophoresis (charged particles movement), and electrolysis (chemical reactions due to electric field), and these is initiated by an electric gradient (Mulligan et al., 2001a).

This technology has been used in North America, and it is currently being used in Europe, for the removal of copper, zinc, lead, arsenic, cadmium, chromium and nickel. Ions such as cyanide and nitrate and radionuclides such as uranium and strontium can also be treated by electrokinetics (Mulligan et al., 2001a).

Cundy and Hopkinson (2005) used a technique called FIRS (Ferric Iron Remediation and Stabilization), which is a low-tech, low-energy contaminant reduction technique for the remediation of sediments. This technique involved the use of a low magnitude direct electric potential between two or more sacrificial Fe-rich, electrodes placed in, or either side of a contaminated soil or sediment. The electric potential was used to generate a strong pH (and E_h) gradient within the soil column (pH 2-13), and force the precipitation of Fe-rich barrier in the soil between the two electrodes. This technique was able to significantly reduce the Arsenic, due to its solubility under the high pH conditions generated near the cathode.

(e) Bioremediation

This involves the use of microorganisms for the treatment of contaminated soils or sediments. This method has been effective in the treatment of PAHs and metal contaminated soils. Bioleaching involves the use of *Thiobacillus* sp. Bacteria, which reduces sulphur containing compounds under aerobic and acidic conditions, and at

temperatures between 15 and 55°C. Leaching can be done either by direct or indirect means. Indirect means involves the acidification of sulphur compounds to produce sulphuric acid, which then desorbs the metals on the soils/sediments by exchanging with the protons. The direct leaching involves solubilizing the sulphides by oxidation to metal sulphates (Mulligan et al., 2001a). When tested in the laboratory, *Thiobacilli* were able to remove 70-75% of heavy metals from sediments (with the exception of lead and arsenic) (Karavaiko et al., 1988)

Microorganisms have also been known to oxidize and reduce metal contaminants. Mercury and cadmium can be oxidized, while arsenic and iron can be reduced by microorganisms. This process is called mercurites. It has been developed and tested in Germany at concentrations greater than 100 ppm. Since the mobility is influenced by its oxidation state, these reactions can affect the contaminant mobility (Mulligan et al., 2001a).

(f) Phytoremediation

Plants such as *Thlaspi*, *Urtica*, *Chenopodium*, *Polygonum sachalase* and *Alyssim* have been known to accumulate cadmium, copper, lead, nickel and zinc, and can therefore be used in the removal of these metals from soils/sediments (after dredging) (Baker et al., 1991)

Phytoextraction involves the uptake of metals by trees, grasses, and crops, while phytostabilization is a process of excreting components from the plants to decrease

the pH of the soil and form metal complexes, thereby immobilising the contaminants. In the case of phytoextraction, the plants should be disposed of in an appropriate fashion. Some techniques for disposal include drying, incineration, gasification, pyrolysis, acid extractions, and anaerobic digestions (Mulligan et al., 2001a).

The main disadvantage of this method is the length of time required. Longer times are required for remediation, compared to other methods. Phytoremediation has the advantage of its low cost of implementation (Gonzalez and Gonzalez-Chavez, 2006).

Plants for phytoextraction should possess the following characteristics:

- tolerance to high levels of the metal,
- accumulate reasonably high levels of the metal in their above-ground tissues,
- rapid growth rates, (iv) produce relatively high biomass in the field (Santos et al., 2006).

According to Baker et al, (1991) hyperaccumulators are able to grow on metalliferous soils, and they complete their life cycle without any symptoms of metal toxicity. Unfortunately, these plants usually produce less biomass than other plant species.

Salix dasyclados has been found to effectively remove As, Cd, Pb and Zn from soils, and its effectiveness is found to be comparable to *Arabidopsis halleri* and *Thalassia caerulescens* (Fischerova et al., 2006).

Chelate-induced metal has been used, with the aim of desorbing metals from soil, thus making it easier for plants to take up the metals. The effect of two chelating agents - Ethylenediaminetetracetic acid (EDTA) and ethylenediaminedisuccinate EDDS on metal phytoextraction of *Brachiara decumbens* has been studied. Although EDTA was generally more effective in soil metal solubilization, EDDS, a chelate less harmful to the environment, was more efficient in inducing metal accumulation in shoots (Santos et al., 2006).

(g) Soil Washing

Soil washing is the separation of contaminants from soil or sediment solids by solubilizing them in a washing solution. It is generally an ex situ method. When the solubilization in a solution is done *insitu*, it is called soil flushing (Mulligan et al., 2001a; Mulligan et al., 2001b).

Factors affecting soil washing include

- Clay content. This makes it difficult to remove contaminants
- Complex waste mixtures- This affects the formulation of appropriate wash liquids
- High humic contents- This inhibits contaminant removal
- Particle size distribution- This affects the removal of wash liquids
- Wash solution- This may be difficult to recover or dispose. (USEPA, 2006)

Soil washing usually employs acids, bases, chelating agents, surfactants, alcohols, water and reducing agents as the extracting agent. After chemical treatments, the

washed soil/sediment, is rinsed with water, and returned to site. Acid extraction relies on ion exchange and soil matrix dissolution to solubilize metals. Acids are good as washing solution because they generally increase the solubility of metals, but strong acids may destroy the basic nature of the soil, thus leaving it unsuitable for revegetation (Robert, 1999).

A chelant for soil washing is a ligand that contains two or more electron donor groups so that more than one bond is formed between the metal ion and the ligand. Ethylenediaminetetracetic acid (EDTA) forms 1:1 molar ratio complexes with several metal ions. Acids and chelating agents are generally employed as wash solutions, because they remove a wide range of metals, but the particular reagent used, depends both on the metal to be removed, and also on the specific metal compounds or species involved (Robert, 1999),

Inorganic acids have been used in the removal of metals from sludges obtained from a central wastewater treatments plant in California, USA. The sludges were dosed with 1N sulphuric acid to effect metal solubilization. The results revealed that the most difficult metal to be released was Cu, and therefore concluded that part or all of the Cu in the sludge, exists as an organic complex (Babel and del Mundo Dacera, 2006). The shortcoming of using acids in the remediation of soils/sediment is that acids have been known to attack and degrade the soil crystalline structure as well as alter the chemical, physical and biological properties of the soil when the contact time is extended, (Tuin and Tels, 1990) and chelating agents such as diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA) (Elliot and

Brown, 1989), oxalic acid (Elliot and Shastri, 1999) and ethylenediamine tetraacetic acid (EDTA) (Yu and Klarup, 1994; Olayinka and Odiwe, 2007) have been used in place of mineral acids, because they have less damaging effects.

Teik-Thyne et al. (2004) compared the heavy metal extraction by chelating agents (sodium ethylenediaminetetraacetic acid, sodium nitrilotriacetic acid, and calcium trisodium diethylenetriaminepentaacetic acid) with those of HNO_3 , CaCl_2 , and deionised water. Their results showed that the chelating agents were more efficient in extracting Pb and Cd from the acidic soils used than HNO_3 , and the extractable Pb and Cd were removed from the soil within 15 min of extraction with the chelating agent. The chelating agents however, demonstrated a poor Cr extraction, and the extraction efficiency was found to be dependent on the heavy metal speciation in the solid phase.

The efficiencies of neutral salts, strong acids and chelates were tested on the extraction of Cd from three soils. It was discovered that the higher the selectivity of the cations of the added neutral salts toward the soil adsorption sites, the lower the pH in the extracts and the more the soil Cd that could be extracted. Calcium chloride and iron(III) chloride were selected as wash chemicals to restore Cd-contaminated soil insitu. Washing with calcium chloride led to the formation of cadmium chloride complexes, enhancing Cd extraction from the soils. The washing also substantially decreased soil levels of exchangeable and acid-soluble Cd, which are the major forms of bioavailable Cd (Makino et al., 2006).

EDTA is the most widely used chelating agent because it forms stable complexes with a wide range of metals, over a wide pH range. Papassiopi et al. (1999) used EDTA for the extraction of metals from soils contaminated with heavy metals from mining and smelting activities. The percentage removal was found to range between 50-98% for Pb and 50-100% for Zn. The tetrasodium salt was found to be less effective for metals removal compared to the disodium salt.

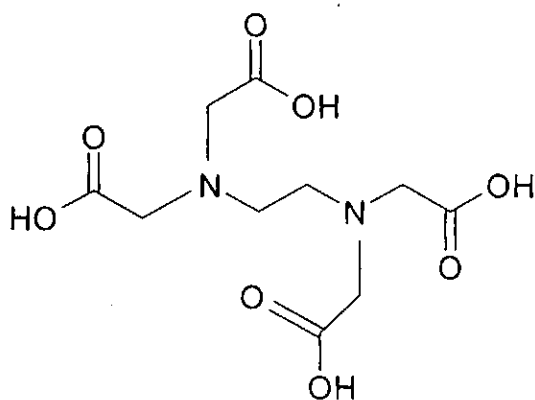
Elliot and Brown, (1989) compared nitrilotriacetic acid and ethylenediamine tetraacetic acid for their ability to solubilize Pb from highly –contaminated soils collected from a battery recycling facility. For chelant concentrations below 0.04 M, EDTA released 10-30% more Pb than NTA. It was also discovered that Pb recovery progressively increased with higher EDTA concentrations, although the additional Pb release with each EDTA increment became smaller. The disadvantage of NTA in the removal of metals from soils and sediment is that it is toxic.

Most studies of soil washing with EDTA have been done using batch extraction (Singh et al., 1998; Papassiopi et al., 1999). Although this method could be upscaled to treat larger amounts of soil or sediments, it may be more practical and economical to leach the soil using either column or heap leaching (Heil et al., 1999; Sun et al., 2001). Heap leaching is used in the mining industry for the extraction of precious metals, and it has the potential for the economical treatment of relatively large amount of soils or sediments. Laboratory column leaching has been done by few

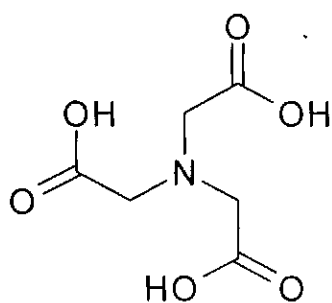
researchers, while a few others have compared the efficiency of column leaching and batch extraction.

Sun et al. (2001) studied the extraction of Zn, Cd, Cu, and Pb by 0.01M EDTA from four contaminated soils using batch and column experiments. In the batch experiment, the heavy metals were extracted as 1:1 metal-EDTA complexes, and the ratios of the metals extracted were similar to those in the soils, suggesting that EDTA extracted the four heavy metals with similar efficiency. Different elution pattern was observed for these metals in the column experiment. Cu was the most mobile of the four heavy metals, while Pb was the least mobile. Sequential fractionation of the leached and unleached soils showed that the heavy metals in various operationally defined fractions contributed to their removal by EDTA.

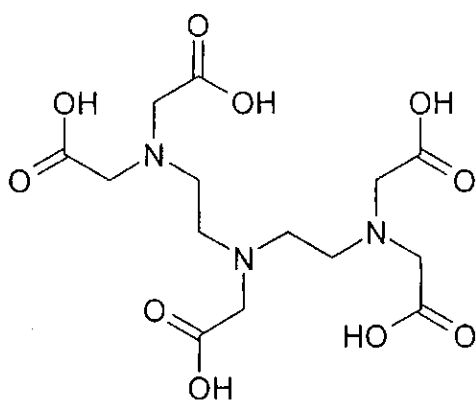
The distribution of Pb, Ni and Zn in two contaminated soils was determined before and after treating the soils with an EDTA solution. After the EDTA extraction, the proportion of Pb in the acid-exchangeable fraction considerably increased, which was related to the degree of metal extraction from other fractions. This was said to be probably due to the fact that the chelating agent may form stable water-soluble complexes which are weakly adsorbed to soil particles (Yu and Klarup, 1994). EDTA was also found to extract Pb, Zn, Ni from the silicate matrix, which implied that the extractable amounts were not so strongly fixed to the residual fraction (Barona et al., 2001).



Ethylenediaminetetracetic acid (EDTA)



Nitrilotriacetic acid (NTA)



Diethylenetriaminepentaacetic acid (DTPA)

Fig. 1.2 structures of some chelating agents

There have been studies on the influence of parameters such as pH, concentration of EDTA, ratio of mass of sediment to volume of EDTA (m/V) and lability of the metals in soil, on the effect of metal extraction by EDTA. Fangueiro et al. (2002), in a laboratory batch extraction observed that the higher the EDTA concentration, the higher the release of metal, until a plateau was reached at the EDTA concentration of 0.05M, and that the metal extracted by EDTA did not depend on the mass/volume ratio (Fangueiro et al., 2002).

The high cost of EDTA has hampered its wide use for the remediation of metal contaminated soils or sediments. Also the procedure generates large volume of wastewater containing metal-EDTA complexes that need to be disposed. This problem has been solved by a few researchers. Hong et al., (1999) discovered that the extractant can be removed after washing by reacting the complex with Na_2S , and also by substituting the metal-complex with Fe (III) ions at low pH followed by precipitation of Pb ions either with phosphate or sulphate ions (Kim and Ong, 1999). 91.6% of EDTA was known to be recovered by evaporation, followed by the addition of sulphuric acid (Di Palmer et al., 2005).

1.11 METHODS OF QUANTIFICATION OF POTENTIALLY TOXIC METALS

Some of the methods of quantifying metals include

- Atomic Spectrometry,
- Molecular Spectrometry
- Electroanalytical Techniques

1.11.1 Atomic Spectrometry

It was discovered in 1860 that the interactions of electromagnetic radiations with atoms can be related to the atom concentration. This led to the development of three main types of spectrophotometric methods for determining elements present in samples of matter, as well as their concentration. These include

- a. Optical spectrometry (Atomic emission (AE), Atomic fluorescence (AF) and Atomic Absorption)
- b. Mass Spectrometry
- c. X-ray Spectrometry

In optical spectrometry, the elements present in a sample are converted to gaseous atoms by a process called atomization, where the UV/Visible absorption, emission or fluorescence of the atomic species is then measured. In atomic mass spectrometry, samples are also atomized, but in this case, the gaseous atoms are converted to positive ions (usually singly charged), and separated on the basis of their mass to charge ratios. In X-ray spectrometry, atomization is not required because X-ray

spectra for most elements are largely independent of how they are chemically combined in a sample. Measurement is then based on the direct measurement of the fluorescence, absorption, or emission spectrum of the sample.

Compared with Atomic Absorption and Atomic Emission Spectrometry, Atomic fluorescence spectroscopy, which involves the measurement of re-emitted radiation by atoms in the excited state, has not gained widespread general use for routine elemental analysis, therefore no atomic fluorescence instruments are marketed commercially (Skoog et al., 1998).

Atomic absorption spectrometry has been the most widely used method for the determination of single elements in analytical samples. There are several methods of atomization methods which includes the flame, electrothermal atomisation, glow discharge atomization, cold-vapour atomization, and hydride atomization. In terms of reproducible behaviour, the flame atomization method is the most superior of all the other atomization methods; however, other atomization methods are better in terms of sampling efficiency and thus sensitivity (Skoog et al., 1998). Electrothermal atomizers have the advantage of unusually high sensitivity, with detection limits in the range of 10^{-10} to 10^{-13} g of analyte, however, they have the disadvantage of being slow, and also the analytical range is low. Consequently these non-flame methods are applied when flame atomization provides inadequate detection limits. Electrothermal atomization method can be used for the direct analysis of solid samples. Generally, AAS has the advantages of simple procedure and less expensive equipment, lower

operating cost and greater precision, while it has the disadvantage of interferences (Skoog et al., 1998).

Zhang and O'Connor (2005), in their study of heavy metal concentrations in 1,884 sediments analysed by two different methods – instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS), found that although INAA detected the total concentration of elements, it had a higher detection limit when compared to AAS. According to the researchers, the lower results obtained by the AAS technique could be due to the incomplete digestion prior to analysis. In all, the average differences were 20-30% for Co, Cr, Fe, Ni, and Zn.

Atomic emission spectrometry, involves the measurement of intensity of radiation emitted by excited state atoms. The excitation method could be the flame, arc and spark, or plasma. The plasma, or the arc and spark emission spectroscopy has several advantages when compared with the flame and electrothermal absorption methods, in that there is less interelement interference, which is due to the higher temperatures used. Furthermore, they permit the determination of low concentration of elements that form refractory compounds, and multielement analysis of very small samples can be done. Despite these advantages, the plasma, or the arc and spark emission spectroscopy cannot completely displace the flame and the electrothermal AA methods because the spectra obtained from plasma, arc and spark sources are often highly complex, since they are made up of hundreds or even thousands of lines,

which consequently require higher resolution and more expensive equipment (Skoog et al., 1998).

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used by Sandroni and Smith (2002) for the analysis of trace metals in different standard reference materials. The results obtained were in agreement with the certified values, and this showed that the analytical method was precise and accurate.

1.11.1a Atomic Absorption Spectrometry

This involves the absorption of electromagnetic radiation by ground state atoms, and the intensity of frequency of the electromagnetic radiation is decreased. When atom is irradiated, absorption becomes probable if and only if the energy difference between the ground state and one of the higher energy states of the atom matches exactly the energy of the photon. The extent of absorption is proportional to the number of ground state atoms present. The wavelength of a transition between two specific energy levels is unique and can be determined in terms of the difference in energy levels (ΔE) (Christian, 1994).

$$\Delta E = E_I - E_0 = h\nu$$

Absorption of electromagnetic radiation causes excitation of an electron from the from a lower energy level (often the ground state) to a higher energy level (excited state)

After a brief period (10^{-6} to 10^{-9} s), the excited electron loses all or part of the excitation energy by emission of radiant energy and the electron returns to its original state. Thus it is also possible to perform quantitative analysis by measuring the intensity of emission. There are different excitation states for an element; the emission spectra involve not just transitions from the excited state to ground state, e.g. E_3 to E_0 , but also transition from E_3 to E_1 , E_3 to E_2 , E_2 to E_1 e.t.c, thus the emission spectrum of a given element may be quite complex. In theory, absorption of radiation by already excited state may also occur, but the ratio of excited to ground state atom is extremely small, so absorption spectrum of a given element is much simpler since it is usually only thought to be associated with transitions from the ground state to higher energy states (Jeffery et al., 1989)

The relationship between the ground and excited state populations is given by the Boltzman equation

$$N_1/N_0 = (g_1/g_0)e^{-\Delta E/KT}$$

Where g_1 and g_0 are the statistical weights of the excited and ground states respectively, ΔE is the excitation energy, k is the Boltzman constant, and T is the absolute temperature. From the equation the ratio N_1/N_0 depends on both the excitation energy and temperature, thus at high temperatures and low ΔE , the ratio N_1/N_0 will be high. From calculations, it shows that only a small fraction of the atoms are excited even under the most favourable conditions (i.e high temperature and low

excitation energy). Due to the high proportion of ground state to excited state atoms, atomic absorption spectroscopy is more sensitive than flame emission spectroscopy.

In atomic absorption spectrometry (AAS) radiation from an external source is absorbed by atoms in their free states. The intensity of the light absorbed increases as the number of atoms increase, thus the concentration of analyte can be determined quantitatively by measuring the absorbance (Skoog et al., 2001).

The Lambert-Beer law gives the relationship between absorbance measured and the concentration of the atom

$$A = \log_{10} [I_0/I] = \epsilon c l$$

Where ϵ is the molar absorptivity and has the unit $\text{L cm}^{-1} \text{ mol}^{-1}$, c is the concentration in mol L^{-1} and l is the path length of the radiation through the absorbing medium.

1.11.2 Molecular Spectrometry

These include UV/Visible Molecular Absorption spectrometry, Molecular Luminescence spectrometry, Infrared spectrometry, Molecular Emission spectrometry, Raman spectrometry, Nuclear Magnetic Resonance spectroscopy and surface characterization by spectroscopy and Microscopy (such as Laser- Microbe Mass spectrometry, Scanning electron Microscopy, Scanning Tunnelling Microscopy). Of all these, only the UV-Visible can be used for the quantitative analysis of metals either directly or indirectly (Skoog et al., 1998).

Molecular Absorption Spectrometry is based on the measurement of transmittance (T) or absorbance of (A) of solutions contained in transparent cells having a path length of b cm. The concentration of an absorbing analyte is linearly related to absorbance as represented by the equation.

$$A = -\log T = \log \frac{P_0}{P} = Ebc$$

UV/ Visible Molecular Absorption Spectrometry is useful in the analysis of compounds that are capable of absorbing ultraviolet or visible radiation. The absorption of this radiation generally results from excitation of bonding electrons; as a consequence, the wavelengths of absorption peaks can be correlated with the types of bonds in the species under study. Some molecules which absorb ultraviolet radiation include aromatic compounds, organic compounds that are conjugated, Inorganic anions such as nitrate, carbonate, nitrite, phosphate e.t.c, lanthanide and Actinide ions, elements of the first and second row transition metal series (Skoog et al., 1998).

For non absorbing species such as lead and copper, reagents can react selectively with them to yield products that absorb strongly in the ultraviolet or visible region. Examples include *o*-phenanthroline for the determination of iron, dimethyl-glyoxime for nickel, diethyldithiocarbamate for copper, and diphenyldithiocarbazon for lead. The disadvantage of this technique over the Atomic spectrometry is its sensitivity, which is not as good (Skoog et al., 1998).

1.11.3 Electroanalytical Techniques

These encompass a group of quantitative analytical methods which are based on the electrical properties of a solution of the analyte when it is made part of an electrochemical cell. Examples of electroanalytical techniques include Potentiometry, Coulometry and Voltammetry (Skoog et al., 1998). These techniques are specific for a particular oxidation state of a compound and the instrument is relatively inexpensive. The disadvantage of these techniques is that they provide information on the activities of chemical species rather than concentrations. (Skoog et al., 1998)

Anodic stripping voltammetry was used for the determination of zinc in environmental samples. (Lau and Cheng, 1998) The recovery of zinc in three real samples and two synthetic sea water samples spiked with 10 trace metals ranged from 98 % to 102 %, and the precision of the method was found to be 1.6 %. According to the researchers, the method was found to be simple, efficient and accurate and can be used for the determination of zinc in natural water, wastewater, air, oyster tissue, sewage sludge and sediment samples. Wang et al. (1994) employed stripping analysis (SA) for field verification of metal contaminants in soils and sediments at hazardous waste sites. An adsorptive stripping voltammetric scheme was used for monitoring total chromium and for chromium speciation, while the conventional anodic stripping voltammetry and potentiometric stripping analysis were used for the measurement of cadmium, zinc, copper and lead. They observed that the concentration values measured by the SA techniques correlated well with the atomic and mass spectroscopy methods. It was therefore decided that the sensitivity, portability, low

power need, and low cost of SA makes it an attractive choice for on site characterization activities.

1.12 MICROWAVE - ASSISTED DIGESTION

As environmental analysis has become increasingly routine, with a subsequent increase in the number of samples requiring analysis, methods which allow for the accelerated extraction of solid matrices have been developed (Morales-Munoz et al., 2003). Microwave assisted digestion (MAD) has been used for determination of metals in soils (Chen and Ma, 2001; Sandroni et al., 2003), sediment (Sandroni et al., 2003; Lo and Sakamoto, 2005), sewage sludge (Sandroni and Smith 2002), and particulate matter (Sandroni et al., 2003).

There have been several comparisons of MAD and open decomposition methods. Chen and Ma (2001), compared three digestion methods- the hotplate aqua regia, microwave aqua regia and the microwave aqua regia and HF for the digestion of three reference materials and twenty soil samples. Microwave aqua regia + HF was found to be the best, with elemental recovery of 94%, followed by the microwave aqua-regia with a recovery of 80%. The hotplate aqua regia digestion, gave the least recovery of 74%.

The main advantages of MAD are the short reaction times required, complete decomposition of samples, low reagent volumes used, reduction of blank values, reduction of reagent costs, no loss of volatile elements and more uniformed heating of samples (Anton-Paar, 2006).

1.12.1 Theory of microwave digestion

Microwaves are electromagnetic radiation with wavelengths of 1 mm to 1 m. To prevent interferences there are microwave frequencies which are reserved for specific domestic, industrial and scientific purposes. Of these, 2.45 GHz is the most frequently used. Electromagnetic waves are interconnected electric (B) and magnetic fields (E) which change over time and propagate at the speed of light (c) through space. (Fig 1.3) (Anton-Paar, 2006).

Microwaves show the same effects as light i.e Diffraction, interference, refraction, reflection and polarizability. Which of these effects occur depends on the wavelength and molecular structure. Microwaves are reflected by non-polar metals, they pass through ceramic, glass and porcelain, they are absorbed by organic materials, and they are not an ionizing radiation, neither mutagenic nor carcinogenic.

Low microwave frequencies can be produced using electron tubes or transistors, while high and very high frequencies (> 100 MHz) are produced by Klystrons, magnetrons or travelling wave tubes. In decomposition instruments such as the one used, microwaves are produced using magnetrons.

A magnetron is a metallic vacuum tube, consisting of a cathode and an anode, which is surrounded by a permanent magnet frame. High voltage is applied to a heated rod (cathode) to produce electrons, and these electrons are drawn into a circular path by the applied magnetic field. These electrons hit the outer wall of the tube (anode), which is cut at regular intervals radially to the chamber (resonator). Within these

incisions the polarity of the electrical field reverses with the desired frequency and produces microwaves. These are emitted through an antenna, e.g in the microwave oven (Anton-Paar, 2006).

The capacity of a substance to absorb microwave energy is expressed by its dielectric loss factor ($\tan \delta$), which is represented by the dielectric loss (ϵ'') and the dielectric constant (ϵ').

$$\tan \delta = \epsilon'' / \epsilon'$$

The lower the loss factor, the lower the absorption capacity of the substance. Materials with low absorption capacity can be used as neutral components, e.g as vessel material. Some substances, e.g water, have a relatively high loss factor at room temperature but this decrease once a certain temperature has been reached. The dielectric factor depends on substance, frequency and temperature (Anton-Paar, 2006).

To heat a substance, the substance must absorb electromagnetic energy. There are two mechanisms available for the absorption of microwave energy namely:

- (i) Dipole rotation
- (ii) Ionic conduction

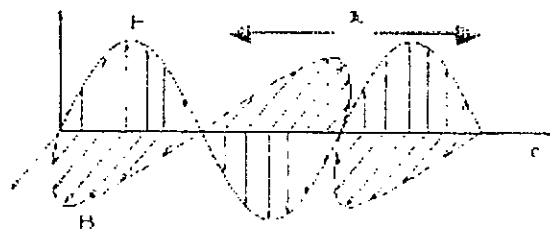


Fig 1.3 Representation of an electromagnetic wave

Table 1.3

The dielectric loss factor of some materials

Materials	$\tan \delta$ at 2.5 GHz
Quartz	2.6 at 25 °C
Borosilicate	12.3 at 25 °C
PTFE, PFA	< 1.5 at 25 °C
PE	3.1 at 25 °C
PVC	56.1 at 20 °C
Ceramic (Al_2O_3)	10.1 at 25 °C
Distilled water	1688.3 at 25 °C
Distilled water	535.7 at 85 °C

PTFE – polytetrafluoroethylene, PFA- perfluoralkoxy

PE –polyethylene, PVC- polyvinylchloride

(Anton-Paar, 2006).

Dipole Rotation

This is the case with materials which have a pronounced dipole (water, acids, solvents). In the rapidly changing electric field, the molecules try to orient themselves in the direction of the field lines. This sets them in rotation-vibration. The closer the resonance frequency of the molecule is to the frequency of microwave, the more intensive the energy absorption from the microwave field.

Ionic Conduction

Heating in the electromagnetic field also occurs when there are free ions (electrolytes, glassy materials and ceramic materials).

Both mechanisms-dipole rotation and ionic conductance are influenced by various factors:

- Wavelengths
- Physical properties of solution (Dielectric constant, polarity, temperature, viscosity, and thermal capacity)
- Ion characteristics (ionic conduction) (size, concentration, charge and mobility)

The use of microwave heating has numerous advantages to conventional thermal convention heating in sample extraction and digestion. In conventional heating, the material is heated from an external source outside the digestion vessel (figure 1.6A), whereas in microwave heating the digesting material absorbs the heat inside the vessel directly (Fig 1.4B). Heating from an external source requires that the vessel be

heated first and a thermal gradient reached before heating of the sample begins, thus increasing the digestion time and also increasing the energy requirement to heat both the material and the vessel. When using microwave heating the reagent will absorb the energy and heating will begin to occur almost immediately.

Generally, microwave digestion instruments are either closed-vessel or open-vessel systems. Open vessel systems mainly use microwave radiation which is focused on the sample. As the digestion vessel is open the heating temperature is equivalent to the boiling point of the digestion reagents used. One potential benefit over the use of closed vessels is that any gasses evolved from any reactions, occur without build up of pressure. However, as the vessel is open, there is an increased chance of external contamination (Anton-Paar, 2006).

In closed –vessel systems, microwave radiation is dispersed into a cavity where sample vessels are placed. As the vessels are closed, high pressures and therefore temperatures can be obtained. The maximum temperature and pressure achieved depends on the thermal and pressure stability of the digestion vessels and the properties of the solvent (Anton-Paar, 2006).

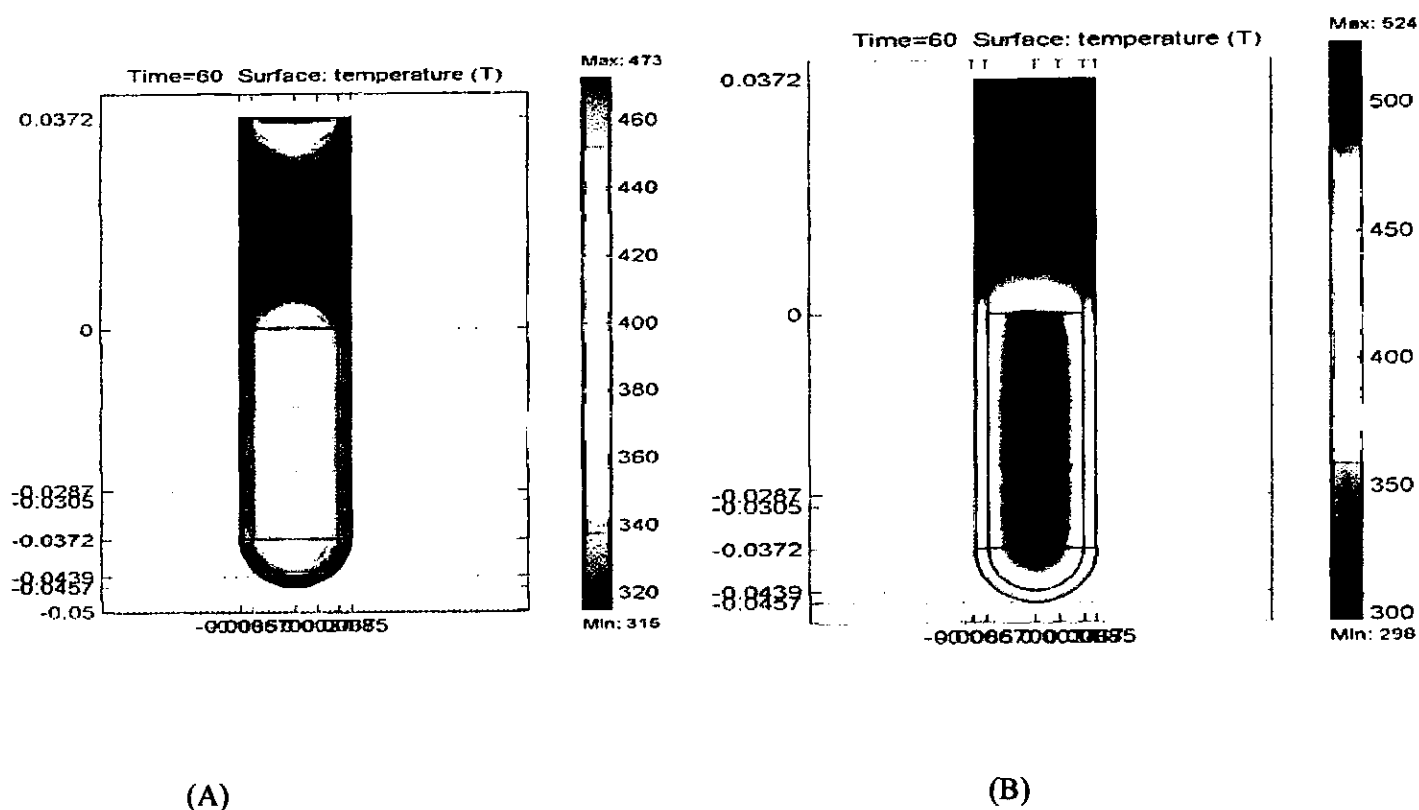


Fig 1.4 – Thermal distribution throughout a digestion vessel (A) heated using an external source and (B) heated using microwave radiation. (Anton-Paar, 2006).

1.13 CHEMOMETRIC/STATISTICAL ANALYSIS

This is the application of mathematical or statistical methods to chemical data. Some critical elements of chemometrics used in this study include:

1.13.1 Principal Component and Factor Analysis (PCA and PFA)

This is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences.

A sample with a large number of variables (e.g 8 metal concentrations) measured can be uniquely defined by the combination of different variable values (concentrations). Where there is correlation between the variables in different samples, the data set can be defined using a smaller number of abstract variables which are given the term “Principal Components” (PCs) i.e. the data is decomposed into PCs, which retain all the information about the data set, and this simplifies data handling. Instead of defining the data on axes corresponding to variable measurements new axes are defined to explain the maximum variation of the data. Principal component one (PC1) always explains the most variation; PC2 is orthogonal to PC1 and explains the next most variation and so on (Vandeginste, 1997).

When there are large differences in magnitude of the variables measured, data must be scaled, or PC1 is likely to relate to only the variable with the highest magnitude. Results can be scaled in many different ways. PCA will produce very different results depending upon how the data is scaled. Data is commonly scaled by subtracting the

mean and dividing by the standard deviation to give a new data distribution with mean = zero and unit variance (autoscaling). This weighs each analyte with equal variation and therefore removes the potential relationship for metal concentrations in soils/sediments, of increased variability and anthropogenic input. Autoscaling allows potentially common sources and relationships between analytes to be investigated (Vandeginste, 1997; Miller and Miller 2005).

PCA produces arrays of scores (sample patterns) and loadings (variable relationships). Eigenvalues are values associated with each PC determined, and are used to calculate the scores matrix from the singular value decomposition of the original (scaled) data matrix. Examinations of loadings provide information about the relationships between the analytes, while examination of the scores provide information about the sample sites (Vandeginste, 1997).

Literature on previous studies of sediments has often used principal factor analysis to study the relationships between the analytes and relate that to anthropogenic input. PFA requires the data to be autoscaled before performing PCA. The desired number of PCs to use in further calculations is then estimated from a plot of eigenvalues. A balance between use of as few PCs as possible and loss of information is required: for example, if four PCs define 95 % of the variation in the data, and five PCs define 98 %, it is not worth it to include the fifth PC. The reduced set of data can then be defined on a new set of axes to meet different criteria. The method used in literature is a varimax rotation. This type of rotation maximises the loadings in any factor with

as few original variables as possible. Mathematically, this is done by maximising the simplicity (variance of the values squared) of the new matrix. This produces new scores and loadings data sets related to new principal factors, instead of PCs. These principal factors no longer capture the most variation possible, but usually capture almost as much as equivalent PC (Vandeginste, 1997; Smith 2002).

The loading matrix produced by PFA can then be studied to give information on possible common sources related to the factors, in terms of real events and situations compared to the mathematical abstract space PCA often works in (Vandeginste, 1997).

1.13.2 Significance Test

One of the most important properties of an analytical method is that it should be free from systematic error, which then means that the value given for the amount of analyte should be the true value. This property of an analytical method may be tested by applying the method to a standard test portion containing a known amount of analyte. In order to decide whether the difference between the measured value and standard amount can be accounted for by only random error, a significance test is employed (Miller and Miller, 2005). A statistical t value is calculated and compared with a tabulated value for the given number of tests at the desired confidence level. If the calculated t exceeds the tabulated t value, then there is a significant difference between the results by the two methods at that confidence level. If it does not exceed the tabulated value, then we can predict that there is no significant difference between

the two methods which then implies that that the two results are identical (Christian, 1994).

The student's t test is used when an accepted value μ is known, while the paired t-test is applied when two methods of analysis are compared by studying tests samples containing different amounts of analyte.

1.14 STUDY AIMS AND OBJECTIVES

The main aim of this research is to undertake a chemometric analysis of some potentially toxic metals in sediments of some selected water bodies of the Lagos Lagoon system, and determine their mobility and bioavailability. The work also seeks to determine optimal remediation strategies/conditions for the polluted sediments (ex-situ) using EDTA.

This study therefore involved:

1. Characterization of the concentration of Cd, Cr, Cu, Pb and Zn in the sediments of selected water bodies of the Lagos Lagoon system.
2. Investigation of significant correlations between the metals in surface sediments and master variables along the water bodies
3. Examination of a common influential link between Cd, Cr, Cu, Pb, Zn, CEC, pH, and % organic carbon in the water bodies.
4. Determination of the fractionation pattern of Cd, Cr, Cu, Pb and Zn in sediments from the Lagos Lagoon and some adjoining water bodies, their mobility and hence, their potential bioavailability.
5. Determination of the efficiency of EDTA as remediating agent/extractant for the removal of metals from the contaminated sediments using batch extraction and column leaching,
6. Comparison of the effects of batch extraction and column leaching on the fractionation pattern of metals in sediments.

CHAPTER TWO

MATERIALS AND METHODS

2.1 STUDY AREA

2.1.1 The Lagos Lagoon

The Lagos Lagoon is a large expanse of shallow water which is about 50 km long and 3 to 13 km wide and separated from the Atlantic Ocean by a narrow strip of barrier bar complex. It is a brackish coastal lagoon on the western part of Nigeria (Fig 1.7). It extends from the Lagos harbour to the Niger Delta in southwest Nigeria, and is in fact the largest lagoon in the Gulf of Guinea (Odiete, 1999). It is located between longitude 3° 23' and 3° 40'E and between latitude 6° 22' and 6° 48'N. It is a highly urbanized brackish ecosystem impacted mainly by municipal and industrial activities that have significantly increased in the past decades. A number of flood plains, network of marshes, swamps, streams, creeks and rivers receive domestic, municipal and industrial waste effluents, and finally empty into the Lagos Lagoon. Being open to the sea all year round, the brackish environment of the lagoon is therefore a consequence of the influence of tidal sea water incursion and freshwater discharge from adjoining creeks and rivers. The west end of the lagoon is highly urbanized and industrialized, consequently, the water at that end receives most of the urban and industrial wastes generated in the area (Okoye, 1989). The Lagos Lagoon is used for fishing, irrigation and recreation, therefore its pollution by potentially toxic metals has adverse effects on the aquatic life as well as human beings whose life and livelihood depend on the Lagos Lagoon (WES, 1997; Isebor et al., 2006).

2.1.2 Odo-Iyaalaro Creek

The Odo-Iyaalaro creek drains Ikeja industrial area. Its source is from a spring in Adekunle village behind Ajowa plastics on Agidingbi road on the Isheri/Agidingbi axis. The creek is bounded by Adekunle suburb in the north, Ogba Industrial estate on the west, Agidingbi in the east and Adeniyi Jones/Aromire in the south. It cuts across Adekunle Village and Awolowo road, passing under Oregon- Opebi link road, and Ikorodu Road near Maryland. The stream passes between Ojota and Mende from where it joins Ogudu Creek and empties into the Lagos lagoon.

The creek is located in an agricultural and residential environment which has industries surrounding it. It is a major drainage channel and receives industrial and domestic wastes from Surulere Industrial Estate road, Lateef Jakande Road, Adeniyi Jones and Awosika Estate through Aromire. The industries located along the course of the creek discharge their effluents directly into it. The colour of the creek changes according to the colour of the effluent being discharged into it, hence the name "Odo-Iyaalaro" which means "the dye stream". Some of the industries which discharge their effluents into the stream include Reliance textiles, Universal steel, Metalum, Cadbury, Guinness, Fototek, Moukafoam, Duraclean, WEMPCO, Chemiron, Daily Times, Nigerian Bottling Company (WES, 1997).

2.1.3 Shasha Creek

The creek starts from the foot of a hill at Water Bus Stop, which is a few metres away from Shagari low cost housing Estate, in Ipaja area of Alimosho Local Government

Area and flows through Dopemu area in the middle of Agege, near Abeokuta Expressway. It flows through International airport road, Osolo way, Oke-Afa bridge, Okota/Isolo Low Cost Housing Estate, Amuwo Odofin, Festac/Mile 2 Canal and finally empties into the Lagos lagoon at Coconut (Ibafo). The creek is used for domestic and agricultural purposes like fishing and irrigation.

2.1.4 Ibeshe Creek

Ibeshe creek starts from Latosi-Abuja community in Ikorodu area of Lagos state. The stream runs directly through the back of a textile industry and drains into the Lagos lagoon at Ofin in Ikorodu.

The textile industry discharges its effluent directly into the creek thereby polluting it. The current colour of the creek is bluish, presumably from contamination from industrial effluents.

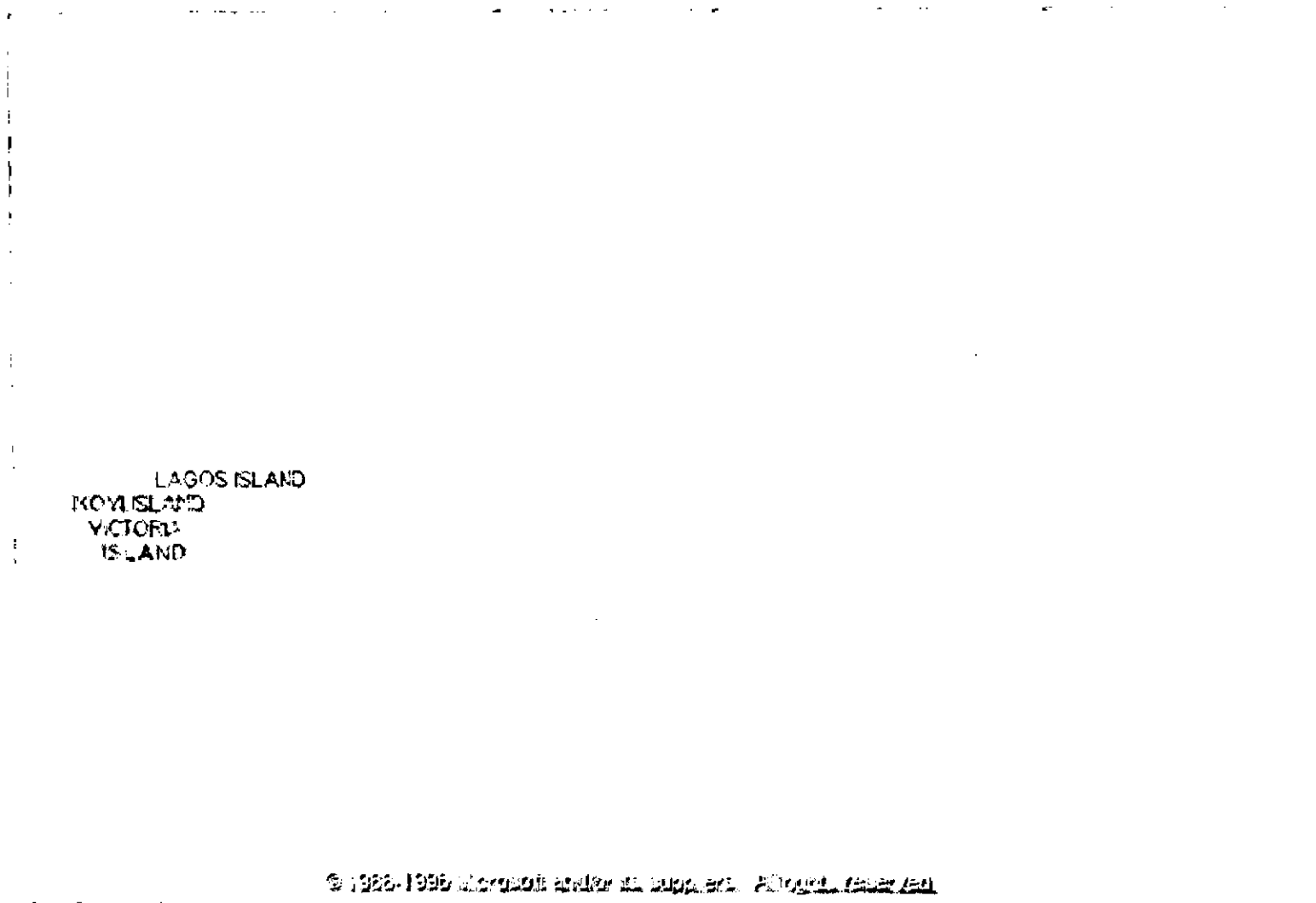


Fig 2.1 Map of the Lagos lagoon showing the tributaries of rivers imputing into it, and its narrow entrance into the sea.

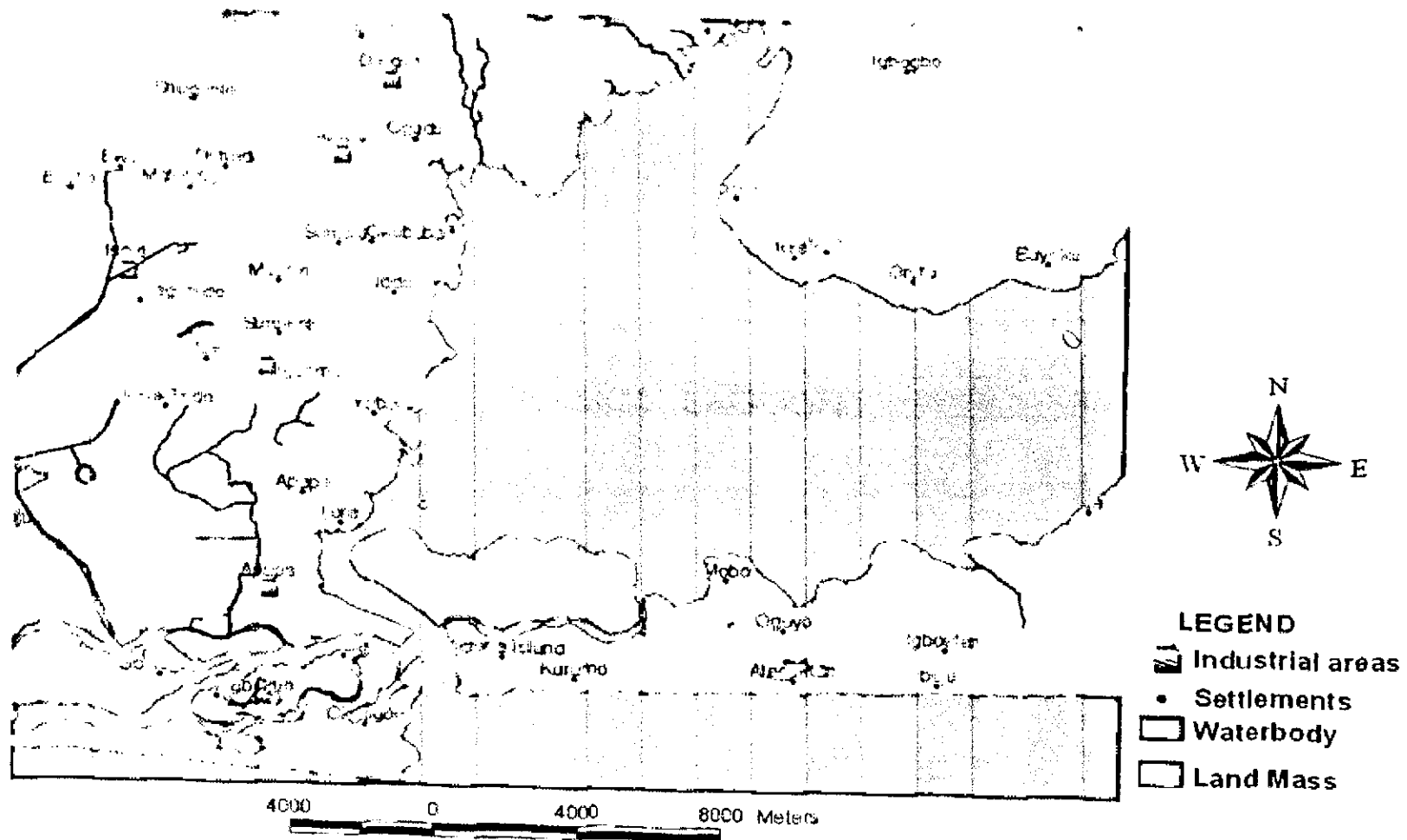


Fig 2.2 Map of Lagos lagoon showing the major industrial zones around Lagos metropolis

2.2 SAMPLING

The Lagos Lagoon and three adjoining water bodies which receive industrial effluents, were the study sites where stations were located. Samples for preliminary studies were collected between 2002 and 2003, while the samples used for the main study were collected between January 2004 and March 2005. Samples were collected from three points along the course of each of the creeks, the point of discharge of the streams into the Lagos Lagoon, and 1km east and west of the point of discharge of the streams into the Lagoon. Samples were also collected from five other points on the Lagos lagoon. Samples from points 1 and 2 could only be collected once, due to the restrictions at those points from the Ministry of Environment. Water samples were collected four times during the year, while sediment samples were picked bimonthly. Apart from the first month in which twenty- three samples were collected, twenty-one samples were collected during the other sampling period and the grab sampling method was adopted. The sample points are shown in the map (Fig. 2.3) and the coordinates are shown in Appendix I

Water samples were collected into plastic bottles which had been thoroughly washed and rinsed with the river water while water samples for dissolved oxygen analysis was collected in DO bottles. Sediment samples were collected by means of a Van Veen grab sampler into a clean polyethylene bag and taken to the laboratory for analysis.

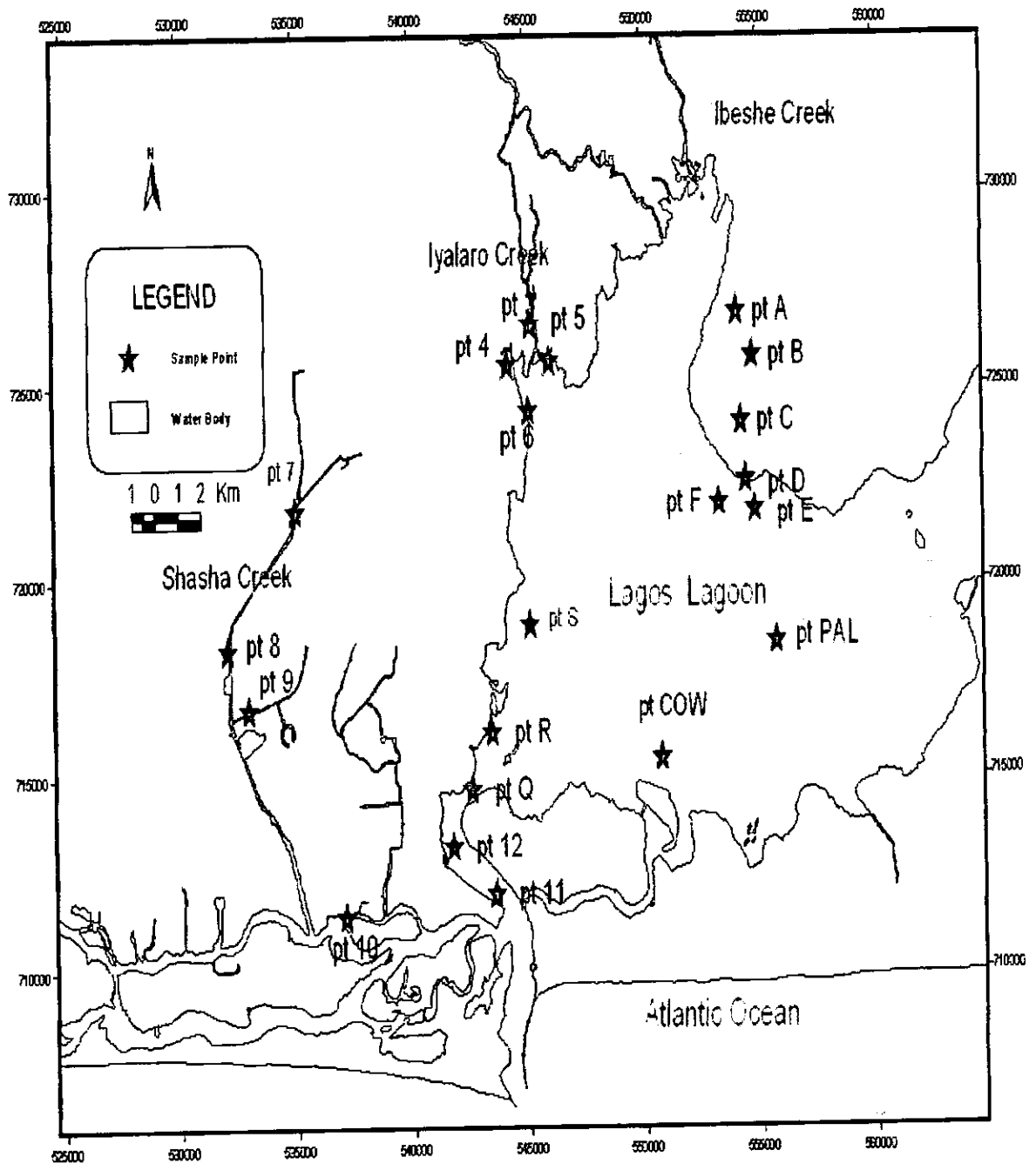


Fig 2.3 Map showing the sampling points within the Lagos Lagoon system

2.3 PHYSICOCHEMICAL ANALYSIS OF WATER SAMPLES

The parameters were determined using the APHA (1999) method, and are outlined below:

2.3.1 Determination of pH

The pH of the water samples were measured electrochemically at room temperature by using a Mettler Toledo pH meter. The pH meter was calibrated with buffers 4.0 and 6.9, and the pH reading for each of the water samples were taken after dipping the rinsed pH meter probe into the container containing the sample.

2.3.2 Determination of Total Solids

20 ml of water sample was pipetted into a pre-cleaned and weighed crucible, and dried at a temperature of 105 °C for 3 hrs, cooled in a dessicator and weighed. Drying, cooling and weighing were continued until a constant weight was obtained.

The amount of total solids was then calculated using the formula:

$$\text{Total solids (mg/l)} = \frac{(A - B) \times 100}{\text{sample volume (ml)}}$$

Where;

A = weight of dried residue + crucible (mg)

B = weight of crucible (mg)

2.3.3 Determination of Total Dissolved solids

20 ml of water sample was filtered (using a glass fibre) into a pre-cleaned and weighed crucible, and dried at a temperature of 105 °C for 3 hrs, cooled in a

dessicator and weighed. The total dissolved solids was then determined as in section 2.3.2

2.3.4 Determination of Conductivity

The conductivity of the water sample was determined using a conductivity meter, whose cell constant had been determined using 0.01 M KCl solution. The probe of the conductivity meter was dipped into the water sample and the conductivity reading taken from the meter.

2.3.5 Determination of Acidity

50ml of water sample was pipetted into a 250 ml conical flask and two drops of phenolphthalein indicator was added. The resulting solution was titrated to a pink coloured end point with standardized 0.01 moldm⁻³ NaOH solution, and the acidity calculated using the formular :

$$\text{Acidity [mg CaCO}_3\text{/l]} = \frac{V \times M \times 50,000}{\text{Vol of sample}}$$

V= titre value

M = Molarity of NaOH used

2.3.6 Determination of Alkalinity

50 ml of water sample was pipetted into a 250 ml conical flask, and two drops of phenolphthalein indicator was added. This was titrated to a courlourless end point with standard 0.1 moldm⁻³ HCl. To determine the total alkalinity, two drops of mixed indicator (bromocresol green and methyl red) was added to the solution, and further

titrated with the HCl solution to a pink colour end point, and the titre value noted. The total alkalinity was deduced using the following formular:

$$\text{Total alkalinity [mg CaCO}_3\text{/l]} = \frac{V \times M \times 50,000}{\text{Vol of sample}}$$

V= titre value

M = Molarity of acid used

2.3.7 Determination of Chloride

This was determined using the mercuric nitrate method. The water samples were diluted using different dilution factors, depending on the chloride concentration of the samples. 50 ml of the diluted water sample was pipetted into a conical flask, seven drops of phenylcarbazone indicator was added, and the resulting green solution was titrated against standard 0.0141 N HgNO₃ solution to a purple colour end point after addition of 1.0 ml of 0.1 moldm⁻³ HNO₃ except in cases where the green colour was obtained. Thereafter, 1.0 ml was added. Blank titration was done by titrating the standard 0.0141 N HgNO₃ with distilled water.

The chloride concentration was calculated using the formular :

$$\text{Chloride [mg/l]} = \frac{(V_1 - V_2) \times 1,000}{\text{Vol of sample}}$$

V₁ is the volume of HgNO₃ used for titrating the sample

V₂ is the volume of HgNO₃ used for the blank titration

1 ml of HgNO₃ = 1 mg of Cl⁻

2.3.8 Determination of Hardness

25 ml of diluted water samples (different dilution factors were used, depending on the hardness) was transferred into 250 ml Erlenmeyer flask, 1 ml of buffer (NH_4Cl in NH_3) was added, followed by two drops of Eriochrome black T. indicator. The resulting violet/purple colour changed to blue on titrating with 0.01 M EDTA.

The total hardness was calculated using the following formular:

$$\text{Total Hardness [mgCaCO}_3\text{ /l]} = \frac{M \times V_1 \times 100,000}{\text{Vol of sample}}$$

M = molarity of EDTA used for titration

V_1 = volume of EDTA used for titration

2.3.9 Determination of Dissolved Oxygen

The dissolved oxygen was determined using the Azide modification method. To fix the dissolved oxygen, 1 ml each of MnSO_4 and alkali-iodide-azide solution was added to the water sample which had been collected in a Winkler bottle. The manganic hydroxide precipitate formed, was then dissolved by adding 2 ml of concentrated H_2SO_4 , and the bottle swirled a few times to ensure complete dissolution. 50 ml of the resulting solution was used in titration against standard 0.0125 M sodium thiosulphate solution.

Calculation: For a 50 ml sample, 1 ml of 0.0125 M thiosulphate = 2 mg D.O/ l

2.3.10 Determination of Biochemical Oxygen Demand (BOD)

The BOD of the water samples was determined by determining the DO of the water sample before and after incubation for 5 days at 20 °C.

The dilution water was prepared by adding 1 ml each of nutrient solutions (phosphate buffer, magnesium sulphate, CaCl_2 , FeCl_3 , Na_2SO_3) per L of freshly distilled water.

The water samples were diluted as appropriate and the dissolved oxygen determined immediately and after incubation for 5 days at 20 °C

$$\text{BOD}_5 (\text{mgO}_2/\text{L}) = \frac{DO_1 - DO_5}{P}$$

Where :

DO_1 = Dissolved oxygen concentration at day 1

DO_5 = Dissolved oxygen concentration at day 5

P = decimal volumetric fraction of sample used

2.3.11 Determination of Phosphate

Phosphate was determined using the colorimetric method for the determination of orthophosphate. Orthophosphates react with ammonium molybdate to form molybdophosphoric acid. This is reduced by ascorbic acid to the intensity coloured complex known as molybdenum blue.

1000 ppm standard stock solution of phosphate was prepared using KH_2PO_4 and serial dilutions were made. Various concentrations ranging from 0.15-1.35 ppm was prepared from 5 ppm in a 50 ml standard flask, and 8 ml of reducing reagent was added and made up to mark with distilled water. This was left for about 10 mins for

colour development to occur, and the absorbance was measured at 880 nm using a Genesys 10 UV – Visible spectrophotometer. The absorbance values were then used to plot a calibration graph.

The reducing agent is a mixture of 5 N H_2SO_4 , ammonium molybdate solution, 0.1 N ascorbic acid and potassium antimonyl tartarate.

25 ml of each of the water sample was measured in a 50 ml standard flask and 8 ml of the reducing reagent was added and made up to mark with distilled water. The solution was left to stand for 10 mins and the absorbance measured.

A blank determination was carried out and the phosphate concentrations in water samples were generated from Beer's plot.

2.3.12 Determination of Sulphate

This was determined using the turbidimetric method. Standard solutions of 2-50 ppm SO_4^{2-} were prepared (using NaSO_4) in 100 ml standard flask. Each of the standard solutions were placed in beakers, and 5.0 ml conditioning reagent was added and placed on a magnetic stirrer for proper mixing. 0.5 g of BaCl_2 was added while stirring at a constant speed. The absorbance was taken at 420 nm using Genesys 10 UV/Visible spectrophotometer.

The same procedure was used to determine the absorbance of the water samples, and correction for sample colour and turbidity was achieved by carrying out a blank determination. The concentration of the sulphate in water samples was determined from the beer's plot.

2.4 SEDIMENT ANALYSIS

2.4.1 Determination of pH

This was determined according to British Standard ISO 10390 (2005). 5 g of the air dried and sieved sediment sample was weighed into a sample bottle, and 25 ml of 0.01 mol l⁻¹ solution of calcium chloride was added. The suspension was shaken and mixed vigorously for 5 mins using a mechanical shaker, and kept for at least 2 hrs before the pH measurement. The pH was measured using a Philips PW 9420 pH meter, which had been calibrated with buffers 4.0 (C₈H₅O₄K) and 9.2 (Na₂B₄O₇·10H₂O) respectively.

2.4.2 Determination of Total Organic Carbon

0.2-0.5 g of air dried sediment samples were weighed into 250 ml conical flasks and 10.0 ml of 1 N K₂Cr₂O₇ was added and the solution gently swirled. 20 ml of concentrated H₂SO₄ was added, and swirling was continued, to ensure proper mixing of the sediments and the reagents. The mixture was allowed to stand for 30 mins after which 100 ml of water was added followed by the addition of 3 drops of ferroin indicator after cooling. The unreacted indicator was then titrated against standard 0.4 N Ferrous Sulphate Solution until colour changed to wine red (Walkley and Black, 1934).

Blank titration was done in the same way without the sediment sample. The percentage organic carbon was then obtained using the expression.

$$\% \text{ Organic Carbon} = \frac{(A - B) \times M \times 0.003 \times F \times 100}{\text{Mass of air - dried sample}}$$

A = Vol. of ferrous sulphate used for blank

B = Vol. of ferrous sulphate used for sample

M = molarity of ferrous sulphate

F = correction factor = 1.33

2.4.3 Determination of Cation Exchange Capacity (CEC)

This was determined by first saturating the soil with sodium ion, the sodium ion was then exchanged for ammonium ion. The amount of sodium exchanged was determined by FAAS (Flame Atomic Absorption Spectrophotometer), using caesium as an ionisation suppressant (British Standard, ISO 13536 1995). 4 g of the air-dried sediment sample was weighed into 50 ml centrifuged tubes and 33 ml of 1 N sodium acetate solution was added and the mixture shaken for 5 mins. This was to saturate the soil with sodium ions. The solution was centrifuged for 5 mins at 3,000 rpm and the supernatant discarded. This was repeated three times, giving a total of four treatments.

33 ml of 95 % ethanol was then added and shaken for 5 mins, centrifuged for 5 min and supernatant discarded. This step was repeated three times. The sodium ion from the sample was replaced by extraction with three 33 ml portions of 1 N ammonium acetate solution. Each of these was shaken for 5 mins, centrifuged for 5 min and supernatant stored in 100 ml volumetric flask. The solution in the standard flask was made up to mark with 1 N ammonium acetate solution. The amount of sodium ion in

the solution was determined using an FAAS. Standards were prepared by serial dilution of 1,000 mg/l sodium metal stock solution in ammonium acetate solution.

2.4.4 Digestion of sediments using different types of acids

To investigate the best acids for the digestion of the sediments collected, four different acids were used. 2 g of sediment samples were digested with 25 ml of each of the acids (nitric acid, *aqua-regia* (3HCl:1HNO₃), nitric/perchloric (1:1) acid, nitric/sulphuric acid (1:1)) on a hotplate for 2 hrs. The mixture of acids were always freshly prepared and used immediately. After digestion, the resulting solution was filtered into a 50 ml standard flask, made up to the mark with distilled water, and analysed for Cd, Cr, Cu, Pb and Zn.

To determine the % recovery of each of the metals using the different acids, the sediment samples test were spiked with different concentrations of the analyte (60 µg, 60 µg, 200 µg, 1,000 µg and 100 µg of Cd, Cr, Cu, Pb and Zn respectively), and the sediments were taken through the same analytical procedure, and recovery calculated. The digestions were carried out in triplicates and the recoveries were thus calculated using the formula:

$$\% \text{ Recovery} = \frac{S - U}{T} \times 100\%$$

Where S = µg of analyte in spiked sample

U = µg of analyte in unspiked sample

T = µg of analyte added as spike

2.4.5 Digestion of sediments using different particle sizes

Sediment samples were sieved using different sieve sizes. The sizes used are <600 µm, >600 µm <1.18 mm, >1.18<2.0 mm and > 2.0 mm. 2 g of each of the fractions were digested with 25 ml *aqua-regia* as in section 2.3.4. The resulting solution was filtered into a 50 ml standard flask, made up to the mark with distilled water, and stored in plastic bottles prior to analysis.

2.4.6 Determination of total heavy metals in sediments

1 g of the dried and sieved sediment sample was weighed into "Advanced Composite Vessels"(ACV), and 20 ml solution of *aqua regia* was added and left overnight. The digestion was performed in an MDS 2000 microwave oven (CEM Corporation, Bucks, UK) (British Standard, ISO 11466 1995). The microwave oven could hold a maximum of 12 ACVs, and the microwave power was adjusted from 0-630 W, depending on the number of vessels used for digestion. The sediment samples were digested using the program shown in Table 2.1

After digestion, the samples were filtered into 100ml standard flasks using Fisherbrand QL 100 filter paper(11 cm), made up to the mark with distilled water and stored in plastic bottles. The extracts were stored in a refrigerator at 4 °C prior to analysis.

The digestions were carried out in triplicates. For each sample and for each batch of digestion there was a procedural blank, and a secondary reference material-

GLAURM (digested in duplicate). For every fifth batch of digestions, a primary reference material (CRM-143R) was used.

Table 2.1 Microwave digestion program for the digestion of sediment samples

	STAGE 1	STAGE 2
Pressure (PSI)	60	120
Time (minutes)	20	30
Time at pressure (minutes)	5	20

2.4.7 Comparative Analysis of Sequential extraction Schemes

Three different sequential extraction schemes were selected to evaluate and compare the results obtained in the speciation of sediment samples from the Lagos lagoon system. The details of the sequential extraction schemes are given below.

Sequential Extraction Procedure by Tessier et al. (1979)

- (i) **Exchangeable.** 1 g of sediment was extracted at room temperature with sodium acetate solution (1 M, pH 8.2) for 1 hour with continuous agitation.
- (ii) **Bound to carbonates.** The residue from (i) was leached at room temperature with 8 ml of 1 M NaOAc (adjusted to pH 5.0 with acetic acid) for 5 hours with continuous agitation
- (iii) **Bound to Fe-Mn oxides.** The residue from (ii) was extracted with 20 ml 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25 % (v/v) HOAC at $96 \pm 3^\circ\text{C}$ for 5 hours with occasional agitation

(iv) **Bound to Organic Matter.** To the residue from (iii) were added 3 ml of 0.02 M HNO_3 and 5 ml of 30 % H_2O_2 adjusted to pH 2 with HNO_3 . The mixture was heated to $85 \pm 2^\circ\text{C}$ for 3 hrs with intermittent agitation. A second 3 ml aliquot of 30 % H_2O_2 was then added, and the mixture heated again to $85 \pm 2^\circ\text{C}$ for 3 hrs with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAC in 20 % (v/v) HNO_3 was added and the sample was diluted to 20 ml and agitated continuously for 30 mins.

(v) **Residual.** In order to be able to calculate the mass balance, this step was modified by using aqua-regia instead of HF-HClO_4 as recommended by Tessier. The residue from step (iv) was digested with aqua-regia for two hours on a hot plate.

Original BCR Sequential Extraction Procedure

Step 1 (Acid soluble). 1 g of air dried sediment was extracted with 40 ml of 0.11 mol l^{-1} CH_3COOH for 16 hr at $22 \pm 5^\circ\text{C}$ (overnight).

Step 2 (Bound to Fe-Mn oxides). Residue from step 1 was extracted with 40 ml of freshly prepared 0.1 mol l^{-1} hydroxylamine hydrochloride at pH 2.0 for 16 hr at $22 \pm 5^\circ\text{C}$ (overnight).

Step 3 (Bound to Organic Matter). 10 ml of 8.8 mol l^{-1} hydrogen peroxide was added carefully in aliquots (to avoid losses due to possible violent reactions) to the residue from step 2, and digested at room temperature for 1h with occasional manual shaking. The digestion was continued for 1h at $85 \pm 2^\circ\text{C}$ with occasional agitation for the first 30 mins in a water bath and then reduced to a volume of $<3 \text{ ml}$. 10 ml of hydrogen peroxide was further added to the digest and concentrated to about 1 ml. 50

ml of 1.0 mol l^{-1} ammonium acetate was then added, extracted and washed as in previous steps.

As an internal check on the procedure, the residue from step 3 was digested in *aqua regia* as in section 2.3.6, and the total amount of metal extracted (i.e, sum of step1+step2 + step 3 + residue) was compared with that obtained by the *aqua regia* digestion of a separate 1 g sample of the sediment.

Modified BCR Sequential Extraction Procedure

This was carried out according to the method of Rauret et al. (1999)

Step 1. 40 ml of 0.11 mol l^{-1} CH_3COOH was added to 1 g of air dried sediment in a 50 ml centrifuge tube, stoppered and extracted by shaking with a mechanical, end-over-end shaker at a speed of 23 rpm for 16 hr at $22 \pm 5 \text{ }^\circ\text{C}$ (overnight). The extract was separated from the solid residue by centrifugation at 3000 g for 20 min and the supernatant liquid decanted into a polyethylene container. The extract was stored in a refrigerator at about 4°C prior to analysis. The residue was washed by adding 20 ml of distilled water, shaken for 15 min on the end-over-end shaker and centrifuged for 20 mins at 3000 g. The supernatant was carefully discarded without discarding any of the solid residues.

Step 2. 40 ml of freshly prepared 0.5 mol l^{-1} hydroxylamine hydrochloride was added to the residue from step 1 in the centrifuge tube, extracted, and the residue washed as in step 1.

Step 3. 10 ml of 8.8 mol l^{-1} hydrogen peroxide was added carefully in aliquots (to avoid losses due to possible violent reactions) to the residue from step 2, and digested at room temperature for 1h with occasional manual shaking. The digestion was continued for 1h at $85 \pm 2 \text{ }^{\circ}\text{C}$ with occasional agitation for the first 30 mins in a water bath and then reduced to a volume of $<3 \text{ ml}$. 10 ml of hydrogen peroxide was further added to the digest and concentrated to about 1 ml. 50 ml of 1.0 mol l^{-1} ammonium acetate was then added, extracted and washed as in previous steps.

As an internal check on the procedure, the residue from step 3 was digested in *aqua regia* as in section 2.3.6, and the total amount of metal extracted (i.e, sum of step1+step2 + step 3 + residue) was compared with that obtained by the *aqua regia* digestion of a separate 1 g sample of the sediment.

2.4.8 Remediation Procedure

For the remediation experiment, four of the most polluted sediment samples (in terms of metal concentration) were used for remediation. The sediment samples used, ranged from very acidic to slightly acidic and the samples were contaminated with different metals in varying concentrations.

Sequential extraction using the modified BCR method was performed on the samples to determine the fractionation pattern of Cd, Cr, Cu, Pb and Zn before remediation and batch extraction was carried out on another portion of the air dried sediment.

Batch Extraction

15 ml of 0.05 mol l^{-1} disodium EDTA was added to 3 g of sediment in a 50 ml polyethylene centrifuge tube and shaken for 2 hrs, the extract was separated from the supernatant by centrifugation at 3000 rpm for 20 mins and stored in plastic bottles at a temperature of 4°C prior to analysis. The residue (sediment) was dried at a temperature of 25°C , and sequential extraction was performed as in section 2.3.7. This was done in order to determine the fraction from which the metals were removed.

Column leaching

This was done in order to compare the effects of batch extraction and column leaching on the fractionation pattern of the metals in sediments, and to also predict the efficiency of remediation. The efficiency of batch extraction and column leaching of the metals from the sediments using EDTA were also compared.

5 g of sediment was packed in a column (10 mm x 16 cm). The sediments were prevented from being washed out by blocking the bottom of the column using glass wool. The sediments were first saturated with distilled water. In order to maintain the same soil: solution ratio as that of the batch extraction, 25 ml of 0.05 mol l^{-1} disodium EDTA was leached through the column and the sediment later washed with 5 ml distilled water. The leachates were stored in plastic bottles at a temperature of 4°C prior to analysis. Just like the batch extraction, the sediments were dried, and sequential extraction performed. The extractions were done in duplicates

2.5 Instrumentation

2.5.1 Optimisation of the instrument

The flame AAS (Perkin Elmer AAnalyst 200) instrument conditions used was optimised for each of the analyte under investigations.

2.5.1a Assessment of the fuel flow rates used

The flame fuel flow was optimised for the analyte of interest using a low, non zero standard solutions for each analyte. The optimisation was achieved by analysing the calibrants at flow rates of between 2.0 and 4.0 L min⁻¹. Results are given in Appendix II

2.5.1b Linearity of analyte calibration

The linear range of each analyte of interest was investigated. Two sets of standard solutions were prepared for each analyte, a set was prepared in 5% HNO₃, and another in 20% aqua regia. Calibration graphs were plotted for each analyte, comparisons of the two sets of standards and linear least squares regression analysis was performed on the results to obtain the lines of best fit. The equations of the best fit lines were used to calculate the detection limits of the instrument.

2.5.2 Analysis of Metals using FAAS

For the analysis of solutions for the Pseudototal metal concentration of sediments, working standards were prepared by serial dilution of 1,000 mg/l of metal stock solutions. Working standards of 0, 0.2, 0.4, 0.6, and 0.8 mg/l were used for Cd, 0, 2.5,

5.0, 7.5 and 10.0 mg/l for Cr, 0, 0.5, 1.0, 1.5 and 2.0 mg/l for Cu, 0, 2.0, 4.0, 6.0 and 8.0 mg/l for Pb and 0, 0.2, 0.4, 0.6 and 0.8 mg/l for Zn. The standards were prepared in 5 % HNO₃. The lamp operating conditions is shown in Appendix III. For the analysis of solutions from the sequential extraction procedures, working standard solutions were also prepared from 1000 mg/l stock solutions and made up to the mark with the solutions used in each stage of the extraction. This was done in order to ensure standard and sample solutions were of similar bulk composition so that matrix effects can be eliminated.

As a quality control measure, for every analysis carried out on each day, freshly prepared working standards were used.

2.5.3 Detection Limits

The detection limits of the instruments (DL_{inst.}) for Cd, Cr, Cu, Fe, Li, Pb and Zn were obtained using 0.1, 2.5, 1.0, 100, 0.2, 2.0, and 0.2 mg l⁻¹ calibrant solution respectively. Ten replicate measurements of the calibrant solutions were obtained and the standard deviation of the mean value was used to determine the DL_{inst.} The detection limits were also calculated to take into consideration the digestion methods to obtain the procedural detection limits (DL_{pro.}) (Vandecasteele and Block, 1997). The equations used for the calculation of DL_{inst.} and DL_{pro.} are given below, while the values are given in Appendix III

$$DL_{inst.} = \frac{3s}{b}$$

Where

s = standard deviation of the ten replicate measurements of the calibrant solution

b = slope of the calibration curve

2.6 QUALITY CONTROL

2.6.1 Determination of Pseudototal Metal Concentration

In order to test the methodology and the analytical performance of the laboratory (the reagents used and the analyst), quality control was carried out. This was done with the use of CRM 143 (a primary reference material) and GLAURM (a secondary reference material) for the pseudototal metal determination. For the pseudototal metal digestion, apart from the reagent blank being carried out, for every set of digestion GLAURM analysis was also carried out in duplicate, while in every fifth set of digestion, the CRM 143 reference material was used, and the analysis carried out in duplicate. The digestion was done using a microwave oven as in section 2.4.6. The result of GLAURM reference material is given as a J chart in Fig. 3.8, while the result of CRM 143 is presented in Table 3.5.

2.6.2 Speciation of Metals in Sediments

Quality control was also carried out on the speciation experiments. For the comparative analysis of speciation schemes, validation of the analytical results was tested by recovery experiments. An important consideration in the reliability of a sequential extraction data is the percentage recovery relative to a single digestion using a mixture of strong mineral acids, i.e aqua-regia at the digestion of the residual phase of the sequential extraction protocol employed. The recovery was calculated by

summing up the concentration of each of the metals in the different fractions, and then comparing with the concentration of the pseudototal metals.

$$\text{Recovery} = \left[\frac{\sum \text{sequential extraction procedure}}{\text{single digestion with strong acids}} \right] \times 100$$

The analytical result is shown in Appendix X.

For the speciation of sediments using the modified BCR procedure, two reference materials were also used (BCR 701 (primary reference material) and GLAURM.

For the sequential extraction, GLAURM reference material was used in every set of extraction (result is shown in Fig 3.23) and BCR 701 reference material was used in every third set of extractions (result is shown in Table 3.20). In addition to these, reagent blanks were carried out and percentage recovery was also calculated.

2.6.3 Remediation Experiments

For the remediation experiments, quality control was also carried out by calculating the % recovery. This was done by comparing the sum of fractions after remediation and the amount in leachate with the sum of fractions before remediation. The recovery was calculated by using the formula:

$$= \frac{-(\text{sum of fractions after remediation} + \text{amount in leachate}) \times 100}{(\text{sum of fractions before remediation})}$$

In determining the concentration of metals present in the leachates, working standards were prepared in 0.05 M EDTA solution.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 PHYSICO-CHEMICAL PARAMETERS OF WATER SAMPLES

The results of physico-chemical parameters of the water samples collected from the different water bodies bimonthly are shown in Appendix V – VIII. The range of results for each of the water bodies is presented in the Tables 3.1- 3.4

Table 3.1 shows the results of the physicochemical analysis of water samples from Odo-Iyaalaro. Throughout the period of sampling, dissolved oxygen was not detected at points 3 and 4. The absence of aquatic life proved that there was no dissolved oxygen to support aquatic organisms. At points 5 and 6 on the Lagoon, DO (Dissolved oxygen) was found to be most times higher than the other points. This higher result could be due to the dilution of the polluted river water with the relatively clean water from the Lagos lagoon, thereby increasing the DO concentration. For most of the times, the DO concentration of the water from Odo-Iyaalaro was found to be very low and this was indicative of being heavily polluted.

The BOD of water from the creek was found to be high, and the value was found to be higher when the tide was low i.e water was flowing from the creek to the Lagos lagoon. The pH value was also found to be outside the range of WHO limit for unpolluted water (6.5 – 8.5). The conductivity, total solids and total dissolved solids results were indicative of the tide of the creek at the time of sampling. The values were found to be at their lowest when the tide was low (water flowing from the creek

Table 3.1 The results (range) of the physico-chemical analysis of water samples from Odo-Iyaaloro creek.

Parameters	Sampling Points				WHO Limit
	3	4	5	6	
Dissolved Oxygen (mg O ₂ /l)	*	*	* - 6.5	* - 4.5	-
BOD (mg O ₂ /l)	54.8 - 245.4	36.0 - 208.4	14 - 32.8	32 - 50.4	0
COD (mg O ₂ /l)	75.6 - 278.9	78.2 - 332.2	282.4 - 708.1	204.6 - 613.2	-
Total Hardness (mg CaCO ₃ /l)	48 - 931.4	40.3 - 986.4	198.8 - 1479.6	453.6 - 1521.9	-
Total Alkalinity (mg CaCO ₃ /l)	26.1 - 344.0	17.4 - 322.2	9.1 - 104.5	9.9 - 123.6	-
Acidity (mg CaCO ₃ /l)	16.4 - 69.6	6.0 - 62.5	7.8 - 13.4	8.4 - 17.3	-
Chloride (mg/l)	34.0 - 489.9	41.5 - 1494	154.6 - 5348	103.1 - 5398	250
Sulphate (mg/l)	16.2 - 70.1	28.5 - 34.0	24.2 - 39.9	35.4 - 37.9	-
Phosphate (mg P/l)	0.3 - 1.0	0.1 - 1.0	0.1 - 1.0	0.1 - 0.3	1.0
Conductivity (μS _{cm} ⁻¹)	625 - 1185	518 - 2240	533 - 3340	465 - 3350	-
pH	6.3 - 7.1	6.2 - 7.1	6.2 - 7.1	6.3 - 7.1	6.5-8.5
Total Solids (mg/l)	220 - 1305	180 - 3515	200 - 9550	180 - 14850	500
Total Dissolved Solids (mg/l)	210 - 1050	165 - 2810	166 - 10550	145 - 11690	500

* = Not detected, 3= a point on the stream, 4= point of discharge of the stream into the lagoon, 5 = a point 1 km east into the lagoon, 6= a point, 1km west into the lagoon.

- Not stated

to the Lagoon) and in the month of September which corresponded to the rainy season. The highest values were found in the month of March (during the dry season), and when the tide was high and the water samples contained a lot of dissolved salts from the Lagos Lagoon. The relatively high level of phosphate in this stream could be responsible for the pronounced eutrophication (as seen by the weeds and plants on the surface of the water. The weeds and plants could serve as a medium of filtration thereby enhancing purification.

The conductivity of the surface water in the creek increased with increasing distance into the Lagos Lagoon. This could be as a result of the presence of dissolved salts in the Lagoon water. The high correlation between the conductivity and the total solids in the water proved it. The average pH of the water was about 6.4 at point 3 whereas from point 4, the pH increased to 6.6 and became constant at points 5 and 6. This probably meant that the effluents discharged into the water-body was slightly acidic thereby lowering the pH of the water. By the time the effluents flowed into the lagoon, it became diluted by the large volume of lagoon water.

Generally, water from Odo- Iyaaloro creek can be said to be in category IV (points 5 and 6) i.e; polluted and category V (points 3 and 4) that is; heavily polluted, using the classification of surface water quality by Prati et al. (1971) when DO, BOD, pH etc are the indices of pollution. (Appendix IX)

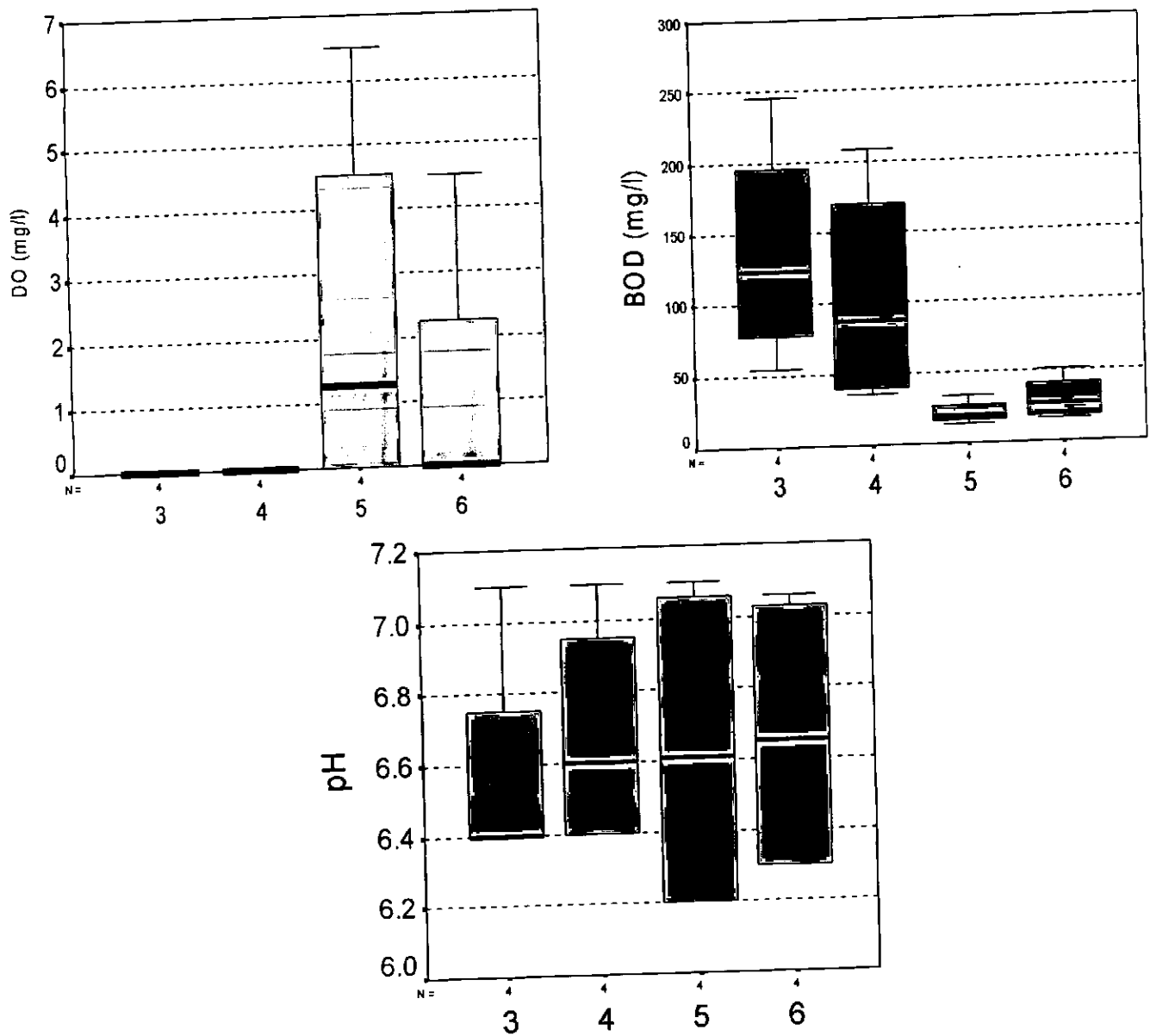


Fig 3.1 Box-and-whisker plots for DO, BOD and pH in Odo-Iyaaloro creek

Table 3.2 shows the results of the physicochemical analysis of water samples collected from Shasha creek. Industrial and domestic effluents rendered the water body lifeless with an alarmingly low DO values at points 7 and 8, while becoming higher as one moved into the Lagos lagoon (Fig 3.2). It was found to decrease again from point 10, which is at Coconut Island and increased to point 11. This result could be because point 11 was close to the point where Ajegunle canal emptied into the Lagos Lagoon thereby polluting the Lagoon and making the DO to be low. The DO at point 11 was found to be non-detectable when the tide was low and slightly higher when the tide was high. This was probably because at high tide, water from the sea which has a high DO content mixed with the water from the Ajegunle Canal thereby diluting the water.

The BOD values were found to generally decrease with decreasing distance from the Lagos lagoon, but from point 10 to 11, it became high for the same reason the DO value became low. The lowest BOD values were observed in the month of March while the highest values were observed in the month of July. The high BOD observed at point 7 indicated that the effluents discharged into the stream could probably be organic. The high organic load at point 7 could also be due to eutrophication. The weeds and plants on the surface of the water could be one of the reasons while the DO was low, while on the other hand, it could serve as a medium of filtration thereby enhancing purification and perhaps precipitation of the organic salts and complexes.

**Table 3.2 The results (range) of the physico-chemical analysis of water samples
from Shasha creek**

Parameters	Sampling points						WHO Limit
	7	-	9	10	11	12	
DO (mg O ₂ /l)	* - 0.7	0	1.3 – 4.8	2.4 – 5.1	* - 3.7	3.0 – 5.9	-
BOD (mg O ₂ /l)	16.9 – 236	-	9.4 - 34.4	8.6 -24.4	28.4-52.8	7.6 – 10	0
Total Hardness (mg CaCO ₃ /l)	38.2 – 384	-	56.7-3617	93 - 4795	115.5- 4795	243 – 5798	-
Total Alkalinity (mg CaCO ₃ /l)	107- 692.4	-	101.7-121.9	56.2-100.2	50.8-234.6	12.2 – 126.3	-
Acidity (mg CaCO ₃ /l)	* - 19.3	-	4.9 – 13.4	2.8 – 5.8	2.3- 7.9	*- 10.5	-
Chloride (mg/l)	30.9 – 200	250	979-10246	2759- 14646	1727- 14720	1985- 13820	250
Sulphate (mg/l)	23.9-52.1	-	94.6-520	510.8- 1600	231.6- 1818	576.2-891	-
Phosphate (mg P/l)	0.1-0.3	1.0	0.2-0.4	0.2-0.3	0.1-0.5	0.1-0.3	1.0
Conductivity (µScm ⁻¹)	138-1,200	-	4,000- 175000	96000 - 230000	57,000 - 275000	210,000- 415000	-
pH	6.9 – 8.9	6.5-8.5	6.7 – 7.3	6.3 – 7.2	6.4 – 7.8	6.3 – 8.2	6.5-8.5
Total Solids (mg/l)	195 -2020	500	2060 - 25040	5,800- 34815	3310- 35190	15,135- 36100	500
Total Dissolved Solids (mg/l)	185-1180	500	1735 - 22120	5730 - 33950	3115 – 32170	13,690- 33100	500

* = Not detected, 7= a point on Oke-Afa canal, 8= point under mile2/festac link bridge, 9 = a point at port –
Novo Creek, 10= Coconut Island, 11= a point on the lagoon, 12= Marina

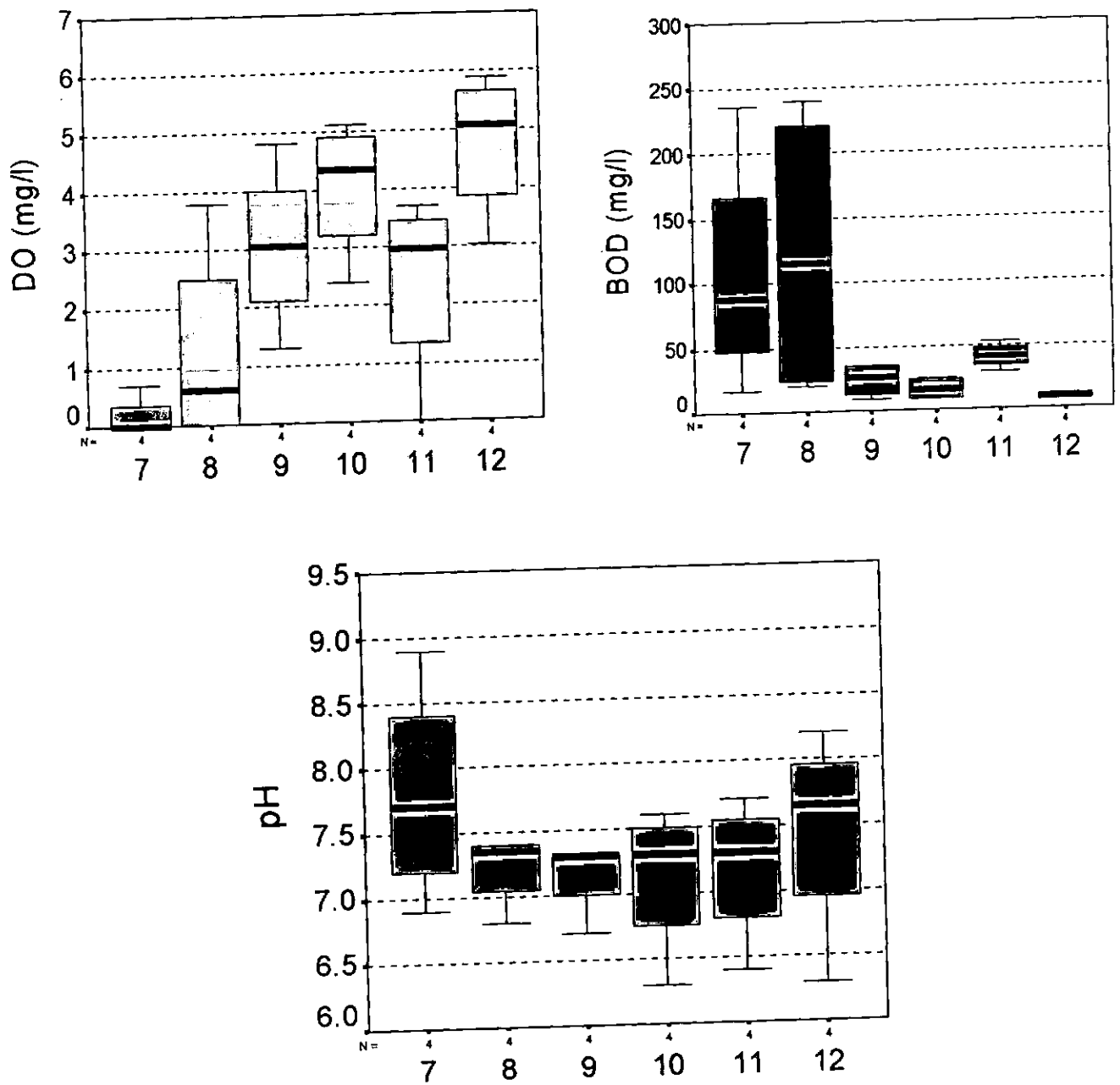


Fig 3.2 Box-and-whisker plots for DO, BOD and pH in Shasha creek

Generally, the phosphate concentrations were observed to be low, while the conductivity values varied with tide and season. At high tide, salt water from the sea which contains a lot of dissolved ions flowed into the creek, thereby increasing the conductivity and the amount of total solids while the opposite is the case when the tide was low.

The pH values for samples collected at point 7 were observed to have a wide range compared to samples from other points. It was observed to be slightly outside the pH range for unpolluted water (WHO limit). This probably indicated that alkaline effluent was being discharged into the creek, thereby making the water alkaline, and by the time the water flowed to point 8, it had been diluted by the stream water.

Table 3.3 gives the range of values for physicochemical analysis of water samples taken from Ibeshe creek. The dissolved oxygen at point A, which is a point just before the river, is polluted by effluents from a textile industry. It had a DO range 3.5- 5.7 mg O₂/L and therefore indicated that the water was just slightly polluted. At point B, which is the point of discharge of the factory effluents into the river, the DO was found to be non-detectable throughout the period sampled. Points C and D had DO which varied between seasons and tide. The highest DO values for these points (C and D) were found to be 3.3 and 5.5 mg O₂/L respectively, and these were observed for samples taken in the month of July when the tide was high. This was because during the rainy season, the rain water diluted the polluted river water, thereby causing the DO to be a slightly higher, and at high tide, there is inflow of the lagoon water into the stream and the relatively high volume of lagoon water with a higher DO mixes with the water from the stream. Points E and F had high DO values because they were samples taken from the Lagos Lagoon. Here the impact of the pollution was not felt because of dilution with the relatively clean Lagoon water. The colour of the stream was observed to be bluish till the point of discharge of the stream into the lagoon. This showed that the creek provided little dilution for the effluent from the textile industry. The low linear velocity of the stream at these points could also account for the little dilution.

As expected, the BOD values for points B and C were found to be the highest throughout the sampling period, and it decreased with decreasing distance into the Lagoon. The high BOD was indicative of the high organic load at this point. This was

**Table 3.3 The results (range) of Physico-chemical analysis of water samples
from Ibeshe creek**

Parameter	A	B	C	D	E	F	WHO Limit
Dissolved Oxygen (mg O ₂ /l)	3.5 – 5.7	*	* - 3.3	* - 5.5	1.7 – 5.9	2.0 – 6.1	-
BOD (mg O ₂ /l)	10.2-22.6	165 - 398	57.3-160	32.4-90	15.6-28.6	12.8– 30	0
Total Hardness (mg CaCO ₃ /l)	* -16.8	* - 358	23.9– 403.2	32.4– 273.4	28.6 – 298.2	16.6– 907.2	-
Total Alkalinity (mg CaCO ₃ /l)	* - 58.4	168.3- 538	49.7- 331.9	45.1– 155.2	42.1 – 69.6	45.9– 77.6	-
Acidity (mg CaCO ₃ /l)	* -6.8	*	0.5 -21.7	4.0-14.9	4.5 – 10.6	4.2 – 7.3	-
Chloride (mg/l)	* - 14.2	37.1– 68.1	24.7- 850.5	232 - 902	607.8- 1804	206- 1726	250
Phosphate (mg P/l)	0.1-0.6	0.1-0.7	0.1-0.3	0.1-1.6	0.1 – 1.8	0.1-3.2	1.0
Conductivity (μScm ⁻¹)	430– 1050	3450-5325	1350- 10,500	1350- 33,500	1950-34,000	2300- 35000	-
pH	6.3 – 6.8	9.2-11.3	6.8 -8.9	6.6 -7.7	6.7 -7.1	6.7- 7.2	6.5-8.5
Total Solids (mg/l)	235-340	1190-2350	715 - 2250	539 - 2450	645 -2050	640- 2160	500
Total Dissolved Solids (mg/l)	160-285	1075-1980	660-2140	525-2350	525-1950	585- 1720	500

* = Not detected, A= a point on the river before the river is being polluted B= point of discharge of the effluents into the stream, C = a point further from the discharge of effluents into the stream, D= point of discharge of the stream into the lagoon, E= a point 1 km east of the point of discharge of the stream into the Lagoon, F= a point 1 km west of the point of discharge of the stream into the Lagoon,

probably because the textile industry discharged a high amount of organics into the stream. This was because textile industries make use of dyes which are organic and the spent dye had intense colour and high BOD values.

The pH of the stream water at point A was observed to be between 6.3 -6.8, while at point B, it was found to be alkaline, indicating that the effluent from the industry was alkaline. The high total solids at point B could also be as a result of effluents from the textile company and also because the stream being already polluted, the villagers living around there dump their rubbish, thereby further polluting the waterbody. The phosphate concentration was found to increase with increasing distance into the Lagoon. The high phosphate concentration could be as a result of the inhabitants in that environment using detergents in their wash solutions.

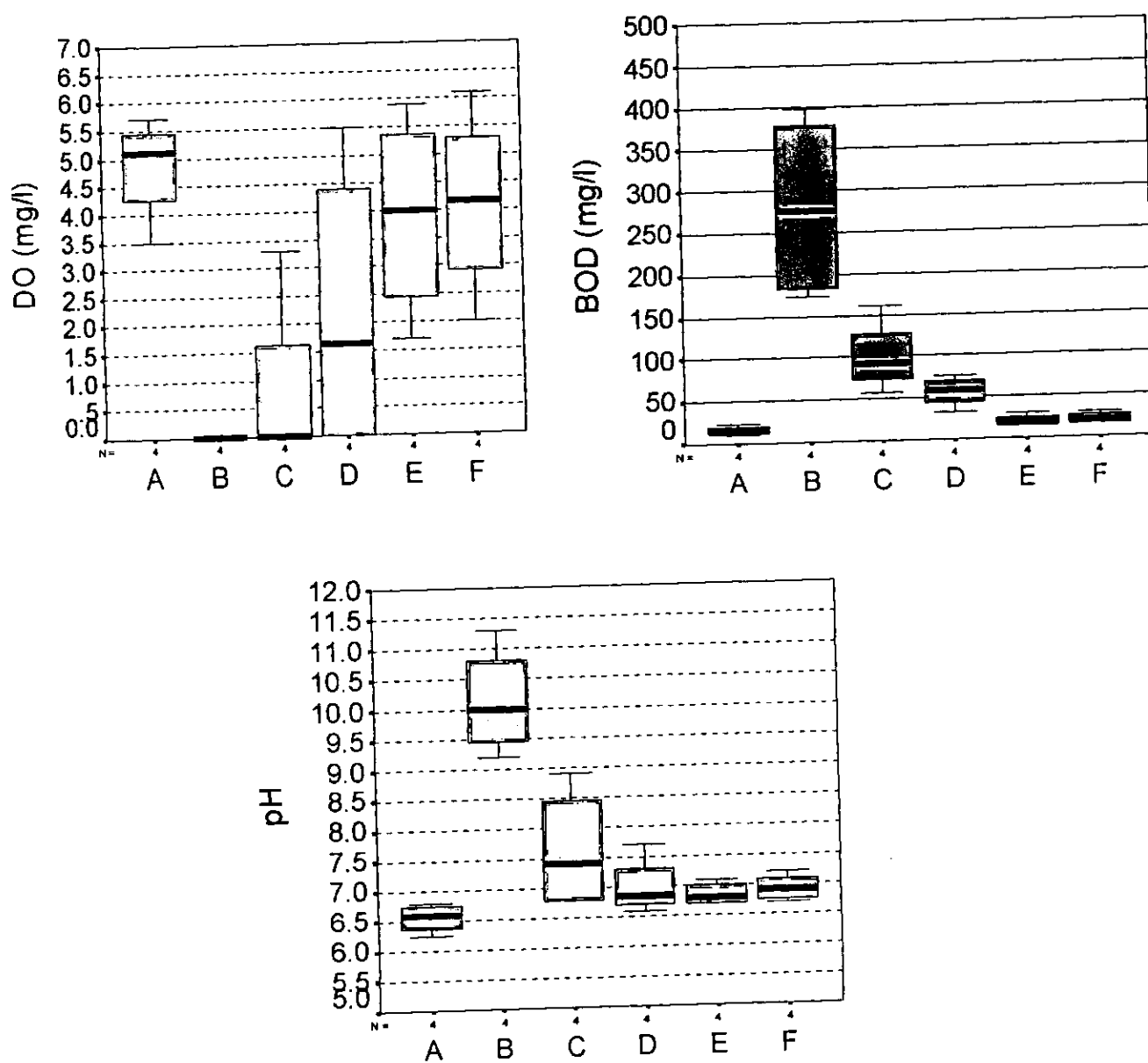


Fig 3.3 Box-and-whisker plots for DO, BOD and pH in Ibeshe creek

Table 3.4 gives the results of physicochemical parameters of water samples collected from different parts of the Lagos lagoon. Points Q, R and S are Iddo, Oko- Baba and Oworonshoki respectively, while Cow (Cowrie Creek) and PAL (Palavar Island) are points on the Lagos Lagoon that are far from industrial or domestic activities.

The DO at points Q, R and S appeared to be independent of tide or seasons and is suitable for aquatic life to survive. This is because inspite of pollution of the water by sewage and other domestic wastes, the impact of the pollution is not so felt because of the relatively large volume of water in the Lagos Lagoon which facilitated dilution of the pollutants. The highest DO values were observed at COW and PAL which are places far from human and industrial activities.

The BOD values for points Q and S were the highest. This was probably because of the untreated sewage discharged into the Lagos Lagoon at point Q and industrial effluents and domestic wastes at point S which may contain high level of organics.

The chloride content of the water is expectedly high. This is due to the presence of chloride salts in the sea water which flows into the Lagos lagoon when the tide is high. The pH range at all the points fall within the WHO limit for unpolluted water (6.5 - 8.5)

Generally, points Q, R and S were more polluted compared to COW and PAL in terms of the DO, BOD, and pH values of the samples collected. This was because domestic wastes are discharged into the Lagos lagoon at these points.

Table 3.4 The results (range) of Physico-chemical analysis of water samples from the Lagos Lagoon

Parameter	Sampling points					WHO Limit
	Q	R	S	COW	PAL	
Dissolved Oxygen (mg O ₂ /l)	4.7- 6.3	3.7 – 5.4	3.4 – 5.0	6.2 – 6.5	6.1 – 6.4	-
BOD (mg O ₂ /l)	11.8 – 30.4	16.8– 24.4	22.2– 34.2	16.2-28.6	14.2 -20.6	0
Total Hardness (mg CaCO ₃ /l)	191.8- 2,057.3	146.8- 1783.8	149.1- 916.3	65.8-102.8	21.5-96.2	-
Total Alkalinity (mg CaCO ₃ /l)	61.5 - 101.7	74.9 -9.0	80.3 -91.0	42.7-60	32.3-40	-
Acidity (mg CaCO ₃ /l)	* - 9.3	3.0- 11.7	2.5-12.8	5.5-7.0	5.1-6.5	-
Chloride (mg/l)	798.9 - 14819	1520.6 - 11752	283.5- 12722.7	587.2- 5541	432.8- 1318.2	250
Sulphate (mg/l)	303.6 – 2432.9	343.4- 22430	32.0 -2343	43.2-1220	87.6 – 93.9	-
Phosphate (mgP/l)	0.2-0.4	0.1-0.3	0.2 -0.3	0.1	0.1	1.0
Conductivity (µScm ⁻¹)	24,000 - 410000	21000 - 315000	3,000 - 330,000	2500- 170000	1300- 60000	-
pH	6.9 – 8.2	6.9 – 7.8	6.9 – 7.5	7.0 – 7.2	7.2 – 7.4	6.5-8.5
Total Solids (mg/l)	3100 – 30870	3910 – 25630	2080 – 23780	1720 – 11080	980 – 3070	500
Total Dissolved Solids (mg/l)	2000 – 28580	3070 – 24060	1500 – 21850	850 – 10840	240 – 1220	500

* = Not detected, Q= Iddo, R= Oko-Baba, S = Oworonshoki, COW=five cowrie, PAL= Palaver Island

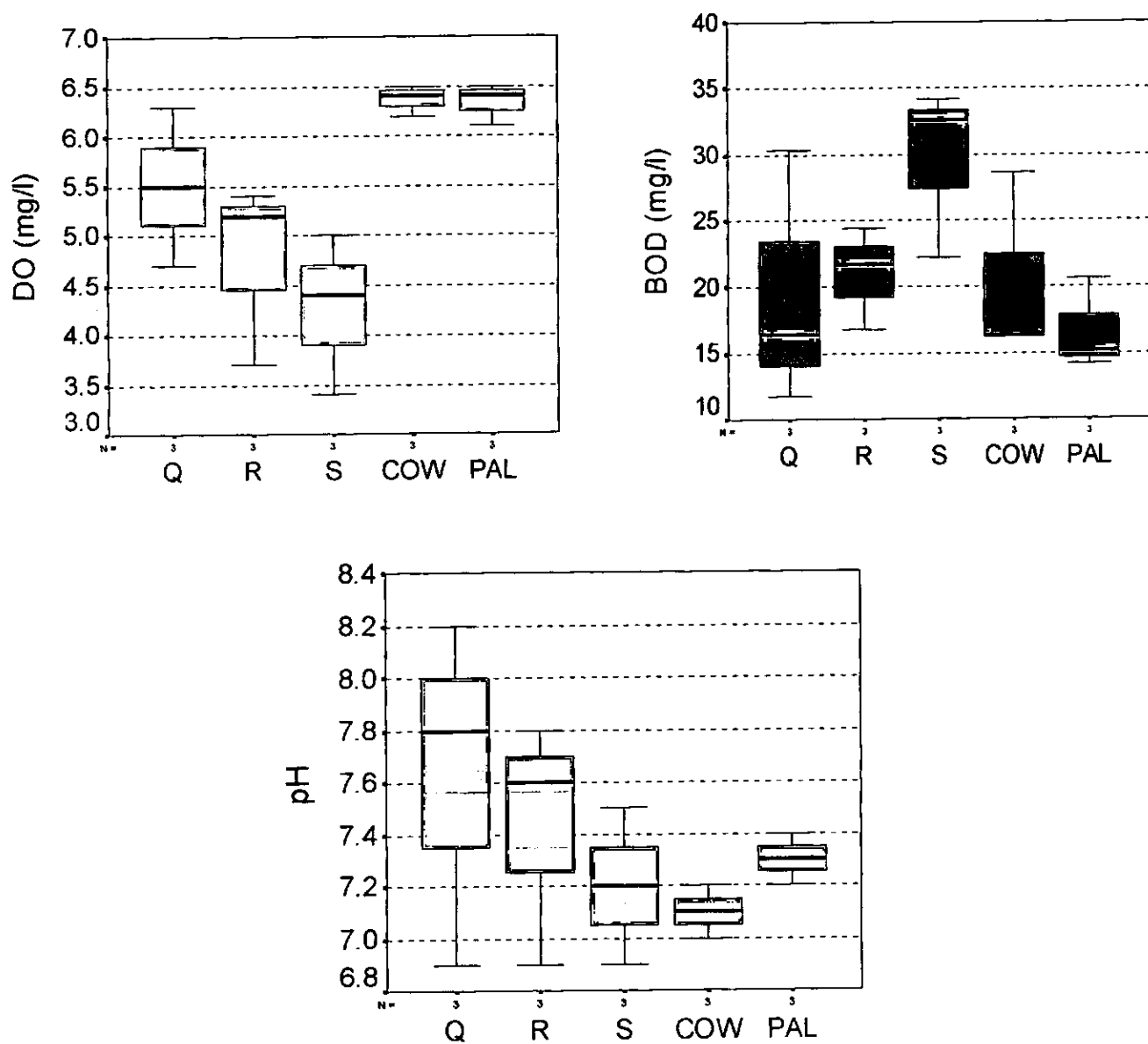


Fig 3.4 Box-and-whisker plots for DO, BOD and pH in the Lagos Lagoon surface water.

3.2 POTENTIALLY TOXIC METALS IN SEDIMENTS

3.2.1 Preliminary analysis

Fig 3.5 shows the mean recovery percentages for the metals as obtained by the four acid digestion procedures. Digestion with nitric acid alone was found to give the lowest recoveries for all the metals (with Zn giving the lowest recovery of 24.3%), except for Pb which had similar recoveries for digestion with nitric acid alone and digestion with nitric/sulphuric acid.

The mean percentage recovery for Cd was found to be generally acceptable, with aqua-regia digestion giving the best recovery of 71.5% followed by nitric acid/sulphuric acid digestion (70.5%). A similar trend was found to occur for Zn, with aqua-regia digestion also giving the best mean percentage recovery (78.4%), followed closely by Nitric/sulphuric acid digestion. This is probably because in addition to the oxidizing nature of nitric acid, the combination with sulphuric acid is able to dissolve many organic materials even though it has the disadvantage of formation of some insoluble sulphates.

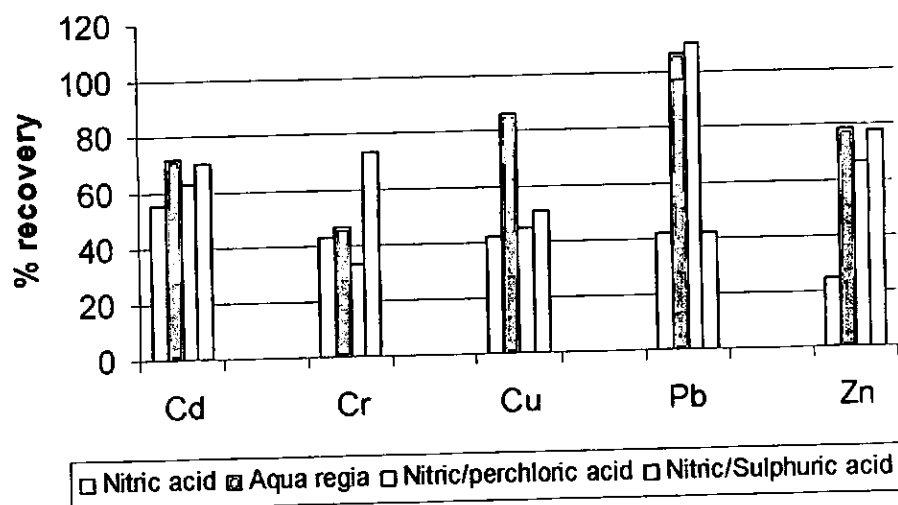


Fig 3.5 Mean recovery percentages for the metals as obtained by the different acid digestion procedures.

The percentage recovery for Pb was found to be inconsistent, with aqua-regia and nitric/perchloric acid digestions giving recoveries of more than 100% (106% and 110% respectively), while nitric acid digestion alone and nitric/sulphuric acid digestion gave mean percentage recoveries below 50% (42.5% and 42.3% respectively). The relatively high recovery for Pb could be due to Pb contamination from the environment.

A low recovery of Cr was observed with digestion with nitric/perchloric acid. A similar result was reported by Agemian and Chau (1976). This was said to be as a result of volatilization losses due to the low boiling point of chromyl chloride (CrO_2Cl_2) of 116 °C formed during the digestion process, compared with the boiling point of perchloric acid which is 200 °C. With nitric acid or aqua-regia, these losses do not occur because the boiling points of nitric and hydrochloric acids are much lower.

Generally, aqua-regia which is a stronger oxidising agent and extracting agent than nitric acid alone (due to the presence of free or nascent chlorine) (Taylor 1931; Maxwell, 1968) gave a consistently good recovery (above 70%) for almost all the metals determined. Aqua-regia which is a mixture of nitric acid and hydrochloric acid (1:3) is better than nitric acid alone because each of the two components carry out different functions. While nitric acid is a powerful oxidizer, hydrochloric acid provides a ready supply of chloride ions which will react with the metals to produce metal –chloride complex. This reaction is an equilibrium reaction which favours the

formation of the anions (metal-chloride complex) and therefore results in the removal of the metal ions from solution. This allows further oxidation of the metal ions to take place, so the metal is dissolved. Aqua-regia therefore provides a high degree of metal extraction, dissolving organic matter, all precipitated and adsorbed metals and also leaches out certain amount of metals from the silicate lattice of the soil/sediment.

The recovery for Cr using aqua regia is however lower compared to the other metals determined, and this could be as a result of the lower temperature of the air-acetylene flame used for the analysis instead of the nitrous oxide-acetylene flame. Since chromium forms a refractory oxide, a hotter flame which is produced by the nitrous oxide-acetylene flame should have been used for the FAAS analysis.

Aqua-regia was therefore chosen as the suitable acid to be used for digestion due to its good recovery and also because it is also a strong oxidizing agent which completely oxidizes all organic matter present, thereby enabling the release of all the anthropogenic metals present in the sediments of study.

3.2.2 Effect of particles size distribution

The sediment is not uniform in size therefore; sediment samples were separated into four size ranges. Figure 3.6 gives the graphical representation of the result of the study on particle size. The four size ranges were $<600\ \mu\text{m}$, $>600\ \mu\text{m} < 1.18\ \text{mm}$, $>1.18 < 2.0\ \text{mm}$ and $>2.0\text{mm}$.

It was observed that in all cases, $<600\ \mu\text{m}$ particle size gave the highest concentration of the metals determined with the exception of Pb. The high amount of metals found in the smaller particle sizes could be as a result of the fact that these fine sediments contain more of clay minerals, organic matter and fine grained quartz, carbonate and feldspar particles. These contain aluminosilicates and also hydroxide groups which can be negatively charged, and therefore able to bind trace metals. A similar result was obtained by Olayinka and Alo (2001) in their analysis of lead in street dust samples from some cities in Nigeria. The concentrations of metals in $<600\ \mu\text{m}$ particle size fractions of the sediments are $4.4\ \text{mgkg}^{-1}$, $38.5\ \text{mgkg}^{-1}$, $27.8\ \text{mgkg}^{-1}$ and $83.7\ \text{mgkg}^{-1}$ for Cd, Cr, Cu and Pb respectively. However Zn had concentrations of $396\ \text{mgkg}^{-1}$, $416\ \text{mgkg}^{-1}$, $374\ \text{mgkg}^{-1}$ and $363\ \text{mgkg}^{-1}$ for particle sizes $<600\ \mu\text{m}$, $>600\ \mu\text{m} < 1.18\ \text{mm}$, $>1.18 < 2.0\ \text{mm}$ and $>2.0\text{mm}$. Generally, the amount of metals extracted decreased with increasing particle size. The loss of extracted amount was in the range 11.5%-46.2% when the extractant process was applied to the largest particle size.

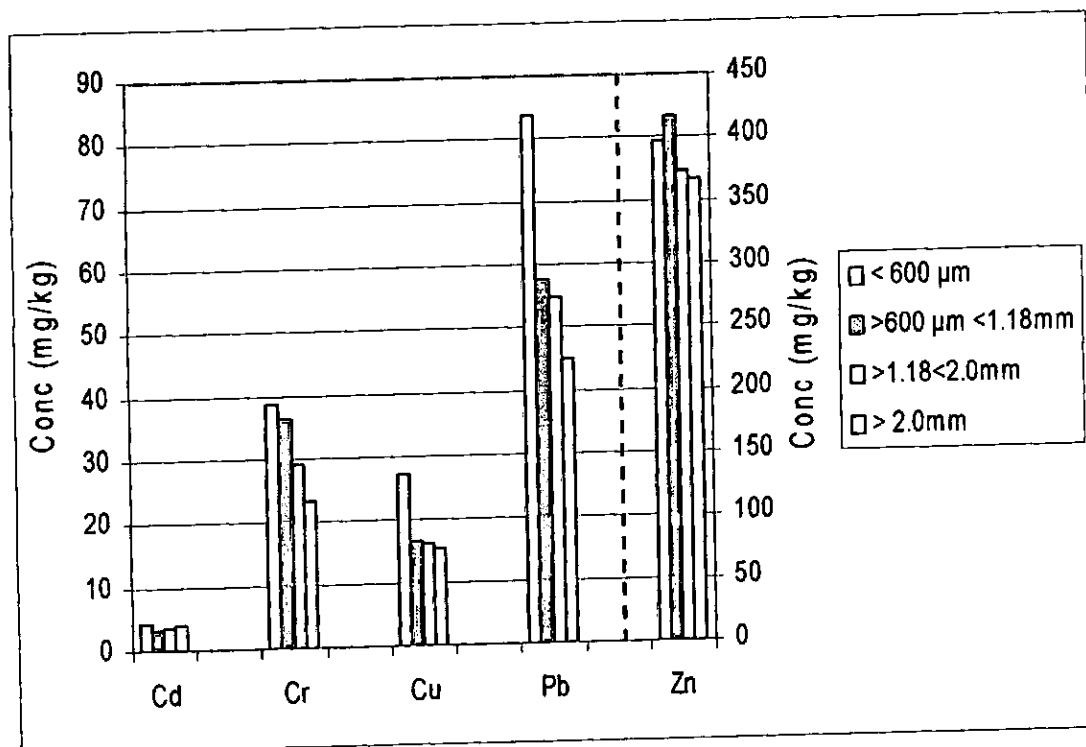


Fig 3.6 Concentration of metals in different fractions of the sediment

From the results obtained, large particle size like > 2.0 mm was therefore discarded and regarded as having less relevance to adverse health effect. For this research, samples < 2.0 mm particle size were used for heavy metal determination since it is deemed suitable.

3.2.3 Linearity of analyte calibration.

The linear range of each set of analyte of interest was investigated and the best calibration solution was determined by preparing two sets of standard solutions for each analyte. A set of standard solution was prepared in 5% HNO_3 and the other was prepared in 20 % aqua-regia, and the graphs obtained are on Fig 3.7a and 3.7b.

The results obtained for the calibrations appear to be generally acceptable. The difference between the two sets of calibration solutions appeared to be less than 10 % except in the case of lithium. The little difference in the slope could be as a result of difference in viscosities, densities, surface tension and volatility of the solvents used. Since the difference is less than 10 %, it then means that 5% HNO_3 which is milder can be used in place of 20 % aqua-regia for Cd, Cr, Cu, Pb and Fe, since 20% aqua-regia which is more concentrated could be corrosive to the components of the instrument used and also hazardous to the analyst.

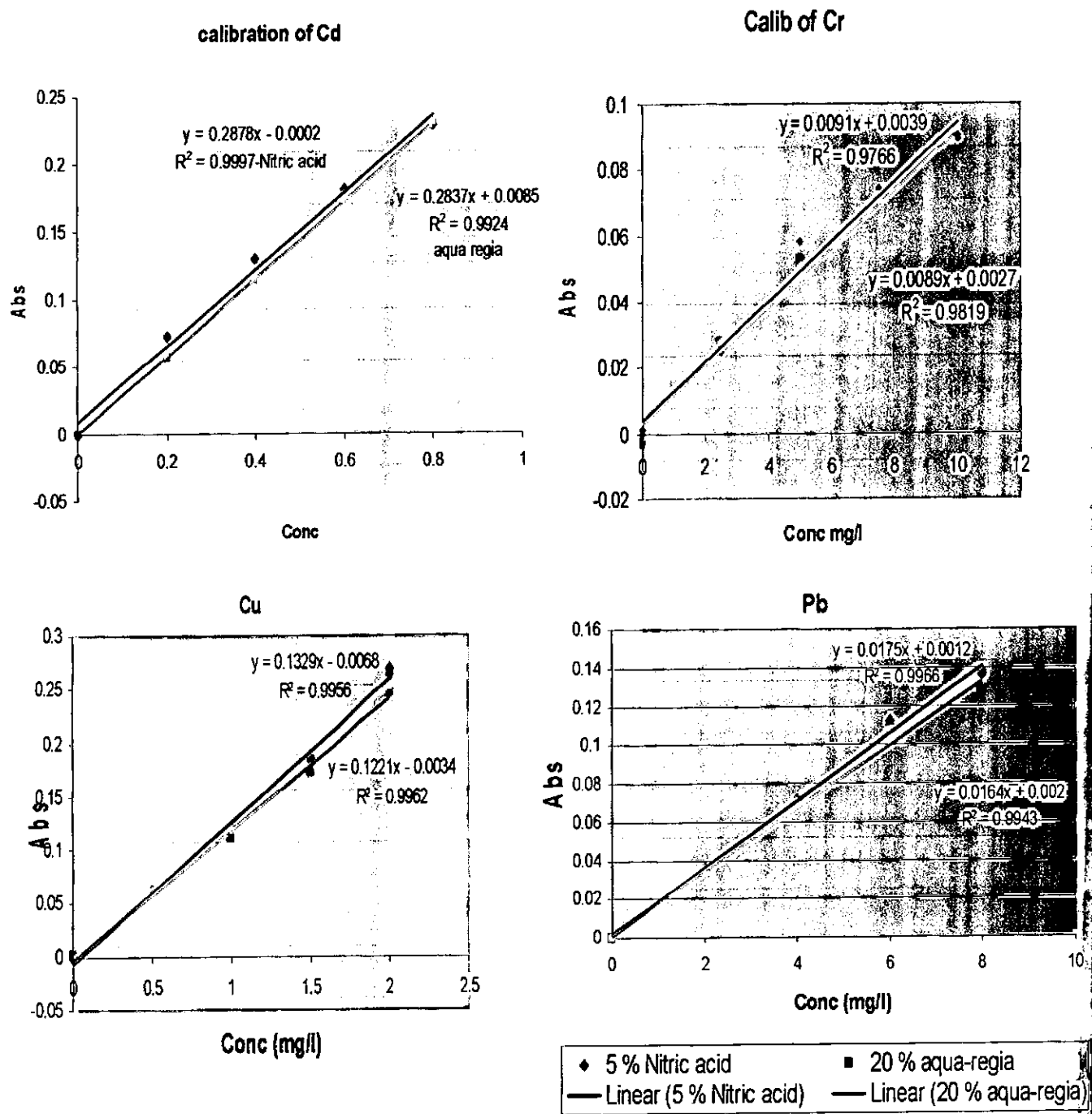


Fig 3.7a Calibration curves for Cd, Cr, Cu and Pb

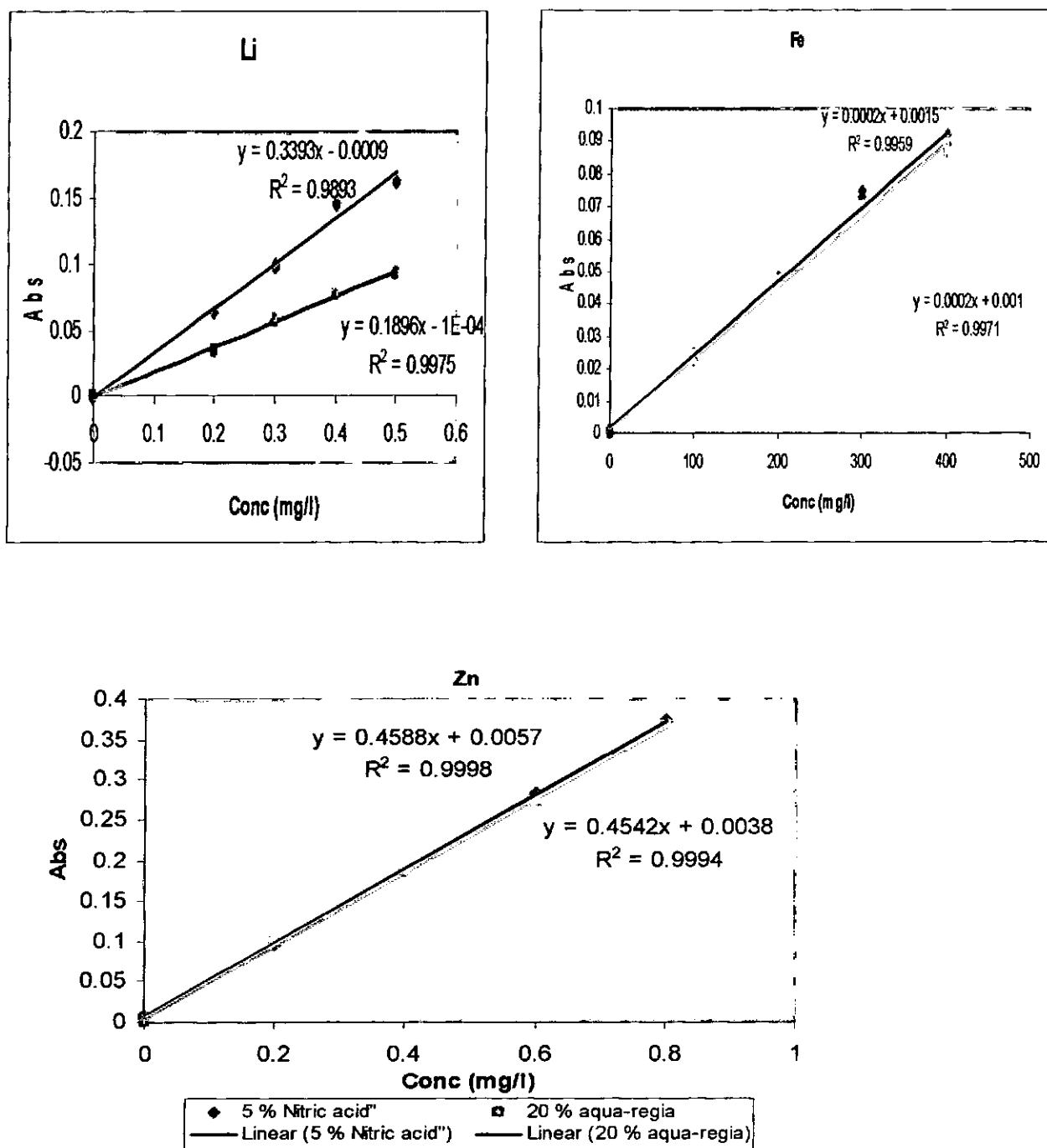


Fig 3.7b Calibration curves for Li, Fe and Zn.

3.2.4 Quality Control of Pseudototal Metal Analysis

To determine the analytical performance of the laboratory and the procedures used, two reference materials were used. The first reference material, BCR CRM 143R is a sewage sludge amended soil which is a certified reference material for aqua-regia soluble metals, while the second reference material- GLAURM is an urban soil secondary material prepared by participants in the EU URBSOIL project for use as internal quality control sample. These were used for the pseudototal metal determination by digesting with aqua regia and making up the digest to appropriate volume with distilled water.

Fig 3.8 shows the representation (J- Chart) of the results obtained from the digestion of each subsample of the secondary reference material. In all, thirty one batches of digestion were carried out for the reference materials. The J-chart showed that almost all the metals determined were within two standard deviations of the target values, and within three standard deviations of the target value in almost all cases. This indicated a good analytical performance of the digestion procedures and the laboratory. The only exceptions occurred in the case of Cr and Zn in some cases. This could probably be as a result of errors that might have occurred during dilutions in the case of Zn and the air-acetylene flame used in the determination of Cr instead of the nitrous-oxide acetylene flame. Dilutions are usually prone to errors. If a little error occurs, because the concentration from the AAS has to be multiplied by the dilution factor the error becomes larger.

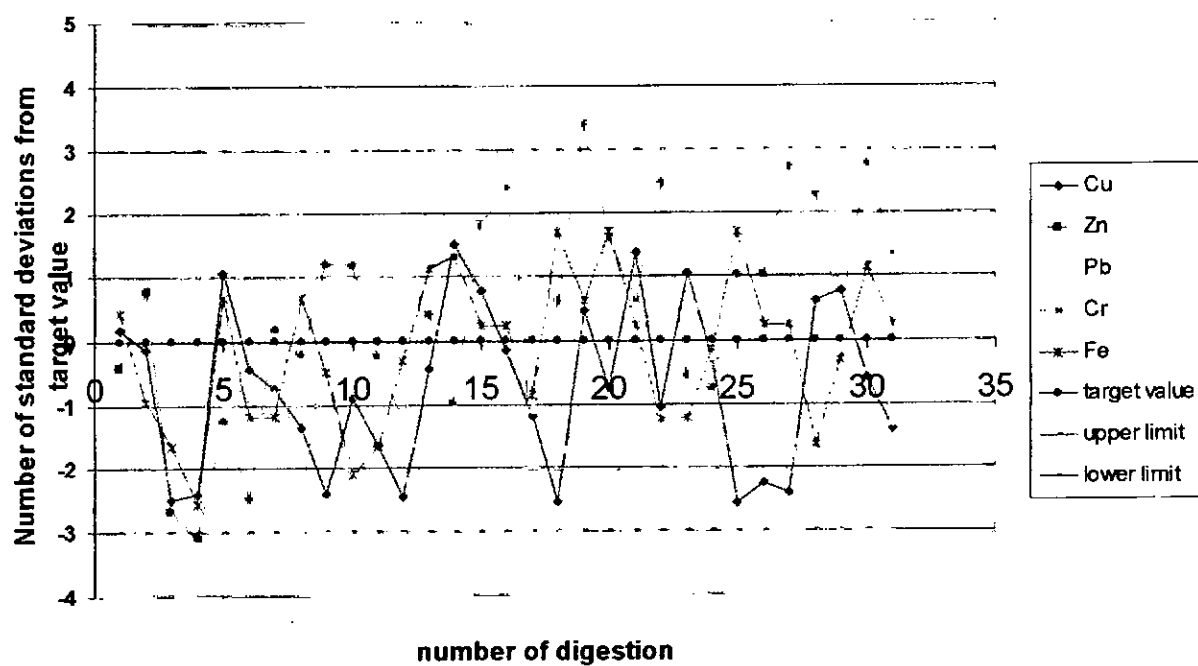


Fig 3.8 Control chart of the results obtained from the digestion of each subsample of the secondary reference material- GLAURM.

**Table 3.5 Result of the analysis of soil properties and total metal concentration
in reference materials- CRM 143R and GLAURM**

CRM 143R	pH	% Organic matter	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Certified	^y	^y	72±1.8	426±12	^y	174±5	1063±16
Found (n = 6)			71.5±3.5	412±8		172±8	1074±12
% Recovery			99.3	96.7		98.8	101
GLA URM							
Target Value	4.2	11.7	<0.74	43.2±3.0	111±5	387±25	177±11
Found (n = 10)	4.2	10.9	<0.9	41.0±6.1	107±7	370±22	179±10
% Recovery	100	93.1		94.9	96.4	95.6	101

^y Not determined

A good agreement was found to occur between the results obtained for the reference materials and the target value, and the recovery obtained was between 93 - 101 %, showing a good analytical performance of the laboratory.

The results of the analysis of pseudototal metal concentration for CRM 143R is shown in Table 3.5. A good agreement was found to exist between the certified/target values and the values found. The recovery for CRM 143R was between 96%-101% for all the metals. They were within two standard deviations of the certified values in most cases and within three standard deviations in all the cases, and a t-test at 95 % confidence level showed no significant difference between the certified values and the found values for CRM 143R. This indicated a good analytical performance of the laboratory, the method used, as well as the analyst.

3.2.5 Heavy Metals in Sediments of the Water-Bodies.

Table 3.6 gives the result of heavy metal concentration, pH, %organic matter and cation exchange capacity of the sediments from Odo-Iyaalero creek.

Table 3.6 Results of physico-chemical analysis of the sediments from Odo-Iyaalero creek.

	pH	%OM	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	CEC (meq/10
J/F pt 1	3.8	6.2	108.3±3.2	42.1±1.8	31±2.4	805±25.1	94.53±5.4	4.0
J/F pt 2	4.2	1.4	41.3±1.9	2.1±0.3	24.8±1.9	100.2±6.2	15.6±2.2	2.0
J/F pt 3	3.8	4.3	43.5±3.2	3.6±0.2	31.5±2.1	109.5±5.8	32.9±1.3	5.8
J/F pt 4	4.6	8.2	36±2.4	2.9±0.2	30.8±2.0	84.5±4.8	25.2±1.2	10.4
J/F pt 5	4.2	11.6	25.5±1.7	1.9±0.1	<22	64.5±3.2	15.9±2.6	7.4
J/F pt 6	3.9	16.4	54.8±3.7	8±0.5	29±1.5	266±8.4	62.2±2.3	7.5
M/A pt 3	3.1	5.1	45.3±3.7	4.8±0.4	102±3.3	157.4±2.6	54.4±2.3	4.2
M/A pt 4	2.8	7.8	<15.4	1.9±0.3	<22	75.2±3.4	38.8±0.8	11.2
M/A pt 5	3.9	10.2	118.6±7.5	21.3±0.6	<22	777±17	138.7±2.4	14.6
M/A pt 6	4.8	21	153.5±2.9	34.4±0.9	30.2±1.9	1044±5	184.8±1.5	12.7
M/J pt 3	4.5	1.4	21.6±3.7	<0.9	<22	18.7±2.8	27.5±2.0	5.2
M/J pt 4	4.2	11.3	52.3±4.2	12.8±1.9	<22	68.3±4.5	40.2±1.9	8.6
M/J pt 5	3.9	12.3	43.8±3.6	6.9±0.3	<22	104.6±9.6	67.8±1.6	12.8
M/J pt 6	4.3	15.7	46.9±2.1	8.6±0.6	<22	224.4±22.3	105.2±3.8	12.6
J/A pt 3	4.9	5.1	98.2±5.8	<0.9	<22	134.2±10.5	15.8±2.2	4.2
J/A pt 4	3.9	7.2	48.5±3.6	<0.9	<22	64.3±3.6	38.2±2.1	10.2
J/A pt 5	4.5	10.9	108.3±2.9	5.5±0.7	25.6±1.7	264.3±7.9	58.9±3.7	11.2
J/A pt 6	4.2	15.3	89.7±4.8	10.2±1.1	28.9±1.6	197.3±12.8	92.4±2.4	12.4
S/O pt 3	5.1	2.9	59.5±2.7	<0.9	<22	64.8±5.9	41.1±2.0	4.6
S/O pt 4	3.6	4.5	48.5±3.6	<0.9	<22	59.9±2.9	43.8±1.9	7.8
S/O pt 5	4.2	8.1	58.2±3.2	2.6±0.4	<22	189.5±6.5	51.1±2.4	14.2
S/O pt 6	3.6	7.5	86.7±4.5	6.1±0.2	<22	376.9±4.7	77.9±1.3	11.8
N/D pt 3	5.6	0.8	19.7±0.5	<0.9	<22	53.1±2.7	29.3±2.2	3.8
N/D pt 4	3.3	5.9	28±3.7	<0.9	<22	82.6±3.7	44.1±0.8	6.8
N/D pt 5	5.0	6.1	60.6±3.6	6.9±0.4	<22	298.1±4.2	67.4±3.4	7.7
N/D pt 6	3.4	4.4	43.1±3.7	2.2±0.1	<22	165±3.4	48.6±1.1	8.9

J/F=January/February, M/A=March/April, M/J= May/June, J/A= July/August, S/O= September/October, N/D= November/December

OM= organic matter

CEC= cation exchange capacity

The sediment pH ranged from 2.8-5.6, indicating that the sediments were acidic. The CEC of the sediments ranged from 2.0 - 14.6 meq/100g, while the %organic matter ranged from 0.8 -16.4 with points 5 and 6 having very high organic matter content for all the months sampled. Pb concentration was found to be quite high, (ranging from 15.4 mg/kg -153.5 mg/kg) with M/A pt 5 and M/A pt 6 having the highest concentrations of 118.6 mg/kg and 153.5 mg/kg respectively. This could be due to the high organic matter content of the sediment since organic matter has been found to influence heavy metal adsorption in soils. This effect is probably due to the high cation exchange capacity of organic material (Maxwell, 1968) The sample collected in J/F pt 1 had very high Pb concentrations (108.3 mg/kg). The high concentration could be because the sample was collected under Maryland Ojota bridge where there is a high traffic density, and Pb could be emitted into the environment, (and into sediments) from the exhausts of vehicles since tetraethyl leaded petrol is used.

Cadmium concentration in Odo-Iyaalero was found to be high. The concentrations ranged from 0.9 mg/kg-42.1 mg/kg. Like in the case of Pb, M/Apt 5 and M/A pt 6 had high concentrations of Cd, 21.3 and 34.4 mg/kg respectively. This can again be due to the high organic matter content of the sediment. It can therefore mean that the source of pollution of these metals (Cd and Pb) is the same. Chromium concentration was found to be low in almost all the points and months sampled, with a range from 22 – 102 mg/kg, indicating that the source is not anthropogenic. High concentration of Cr was found for the sample collected in M/A pt 3, and the reason for the high concentration cannot really be explained. The concentration of zinc in this river was

found to be high, and the source of the metal into the river can be said to be anthropogenic. The concentration ranged from 18.7 mg/kg -1044 mg/kg.

Generally, the concentrations of the metals decreased with decreasing distance from the Lagos Lagoon. This is because accumulation of heavy metals by sediments is linked to local point sources i.e effluents from the different industries will reflect the initial higher levels, whereas the sediments far away from the source will only reflect the overall level of contamination. It was also observed that higher concentrations of heavy metals were found in sediments collected towards the end of the dry season (March/April samples). These could be as a result of accumulation of metals taking place during the dry season, which then gets mobilised and flushed away when the rains come and river flowrate increases.

Generally, there was evidence of high levels of contamination for cadmium, lead and zinc in the sediment samples collected from this water body. These values were all high, compared to levels of heavy metals in unpolluted sediments by researchers (Table 3.7).

Table 3.7 Concentration of heavy metals found in unpolluted sediments

	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Morrison and Brown (2003)	<0.1-0.9	x	x	<1-31	6-208
Salomons and Forstner (1984)	0.4	47	45	30	115
Ruiz (2001)	x	21	13	15	39

x = Not determined

Table 3.8 Results of physico-chemical analysis of sediments from Shasha creek

	pH	%OM	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	CEC (meq/100g)
J/F pt 7	5.3	5.8	188.6±6.8	<0.9	43.1±2.6	432.5±7.3	48.6±3.7	9.8
J/F pt 8	4.9	1.4	24.5±2.4	<0.9	24.2±3.2	87.6±3.2	42.7±1.9	2.2
J/F pt 9	4.3	2.1	32.6±2.1	<0.9	<22	43.6±1.9	33.8±1.6	3.2
J/F pt 10	5.2	0.8	36.8±4.2	<0.9	26.1±1.3	34.2±1.8	26.6±1.6	2.2
J/F pt 11	4.3	8.2	19.4±1.8	<0.9	<22	65.9±2.8	44.8±4.7	6.4
J/F pt 12	7.2	0.6	<15.4	<0.9	<22	40.2±2.5	62.8±3.5	4.8
M/A pt 7	4.9	4.8	93.4±5.5	1.2±0.2	56.7±2.8	467.3±16.7	78.5±4.2	7.6
M/A pt 8	5.2	0.9	54.2±3.8	<0.9	53.2±3.8	93.4±1.3	32.4±2.1	2.4
M/A pt 9	4.3	3.2	56.8±5.6	<0.9	26.7±2.6	74.6±2.9	28.6±1.9	3.4
M/A pt 10	4.6	0.9	<15.4	<0.9	<22	43.2±3.5	15.9±1.9	1.8
M/A pt 11	6.7	7.6	34.2±2.2	<0.9	<22	128.6±3.9	78.2±1.7	3.2
M/A pt 12	7.2	0.6	<15.4	<0.9	<22	20.1±1.2	16.3±1.4	1.6
M/J pt 7	5.9	6.6	201.6±4.8	<0.9	139.7±3.3	641±25	106±1.6	8.2
M/J pt 8	4.4	1.6	44.2±1.9	<0.9	112.3±7.6	111.8±11.5	33.8±2.6	3.4
M/J pt 9	4.5	2.6	67.8±3.5	<0.9	34.2±3.3	40.1±2.1	15.4±2.1	4.4
M/J pt 10	4.4	1	39.2±1.1	<0.9	<22	42.1±1.9	28±0.4	2.3
M/J pt 11	6.8	1.2	<15.4	<0.9	<22	23.8±1.5	15.9±1.1	3.8
M/J pt 12	7.7	0.4	<15.4	<0.9	26.1±3.8	21.4±1.2	23.8±1.3	2.2
J/A pt 7	4.8	7.4	75.2±3.8	1.4±0.2	47.2±3.8	301.2±4.4	98.6±4.3	10.2
J/A pt 8	5.6	0.9	18.6±1.4	<0.9	35.5±3.2	102.3±9.8	<2.8	2.4
J/A pt 9	4.2	3.8	43.2±1.5	<0.9	29.8±2.8	32.1±1.9	<2.8	4.8
J/A pt 10	7.2	0.8	19.9±0.8	<0.9	45.5±3.3	34.7±2.8	26.8±2.0	2.2
J/A pt 11	7.7	3.1	35.6±3.2	<0.9	25.9±2.2	123.6±5.7	54.4±4.1	2.8
J/A pt 12	7.6	0.5	<15.4	<0.9	<22	34.2±2.9	44.2±4.1	2.0
S/O pt 7	5.6	1.4	39±1.2	<0.9	<22	34.6±3.1	27.9±1.9	6.4
S/O pt 8	6.3	0.2	<15.4	<0.9	40.7±2.4	13±1.3	<2.8	3.2
S/O pt 9	5.4	0.3	<15.4	<0.9	25.6±2.1	18.6±1.9	<2.8	3.6
S/O pt 10	7.5	3.5	104±6.5	1.7±0.4	35.5±2.1	189.8±3.6	64±3.1	2.2
S/O pt 11	7.7	1.9	22.4±1.2	<0.9	<22	70.8±4.1	13.6±1.1	3.2
S/O pt 12	7.7	0.4	30.4±2.9	<0.9	<22	38±3.8	11.5±1.0	1.6
N/D pt 7	5.7	1.4	30.4±2.5	<0.9	25.1±1.5	53±2.2	11.9±0.8	7.8
N/D pt 8	6.1	0.3	<15.4	<0.9	<22	1.7±0.3	<2.8	2.4
N/D pt 9	6.4	0.4	<15.4	<0.9	<22	9.7±0.8	3.4±0.5	3.6
N/D pt 10	5	1.6	<15.4	<0.9	<22	82.8±3.3	16±1.6	2.4
N/D pt 11	5.4	2.2	<15.4	<0.9	25.1±1.5	139.1±7.5	17.7±0.9	4.2
N/D pt 12	7.3	0.1	<15.4	<0.9	<22	3.6±0.4	<2.8	2.0

Table 3.8 gives the results of physicochemical analysis and heavy metal concentrations of sediments collected from Shasha creek. The pH ranged from 4.2 – 7.7, indicating acidic to neutral sediments. The %organic matter of the sediments ranged from 0.1 – 8.2 %, while the CEC ranged from 1.6 -10.2 meq/100g.

Pb concentration was found to range from 15.4 mg/kg – 201.6 mg/kg, with points 7 having the highest concentration for all the months sampled. This could be due to the high %organic matter content of the sediment, high CEC and also that the point which is at Oke-Afa canal is very close to a bridge which normally has a high traffic density. Cd in this river was found to be generally low and most times less than the procedural detection limit of the instrument which is 0.9 mg/kg, except in a few cases. This showed that Cd is not a pollutant in this creek. Chromium in this water body ranged from 22-139.7 mg/kg with samples taken from points 7 also having high concentrations. This indicates that the source of chromium at this point is anthropogenic; since levels of chromium found by researchers in their study of other lagoons have been found to be much lower (Morrison et al., 1997; Trocine and Jeffry, 1996). The source of Cr into this waterbody could be from runoffs and effluents from electroplating industries scattered in this region (Isolo).

Cu and Zn were found to range from 2.8-106 mg/kg and 1.7 – 641 mg/kg respectively. Like Odo-Iyaaloro creek, the metal concentrations were found to decrease with decreasing distance from the Lagos Lagoon.

The levels of heavy metals in Shasha creek was found to be lower than that from Odo-Iyaalero creek especially for Pb, Cd and Zn, but the results were still indicative of heavy metal contamination.

Table 3.9 gives the result of heavy metal concentration, pH, %organic matter and cation exchange capacity in the sediments from Ibeshe creek. The pH of the sediments from the waterbody ranged from 3.2 – 7.4 indicating sediments varying from acidic to neutral. The CEC of the sediments ranged from 1.6-5.2 meq/100g, thus indicating sediments with low cation exchange capacity. This correlates with the low organic matter content of the sediments, since sediments with low organic matter have been found to also have low CEC. The % organic matter content of the sediments ranged between 0.2 -7.6 %.

Table 3.9 The results of Physico-chemical analysis of sediments from Ibeshe creek

	pH	%OM	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	CEC (meq/100g)
J/F pt A	6.2	4.1	<15.4	<0.9	<22	20.7±2.2	4.2±0.3	2.0
J/Fpt B	5.8	6.1	<15.4	<0.9	<22	96.9±8.1	332±10.8	3.2
J/F pt C	5.2	1.8	<15.4	<0.9	<22	98.3±2.1	264.8±10.2	2.2
J/F pt D	3.7	0.4	<15.4	<0.9	<22	4.6±0.1	4.2±0.2	2.0
J/F pt E	4.8	0.4	<15.4	<0.9	<22	6±0.5	3.4±0.9	1.8
J/F pt F	6.5	0.3	<15.4	<0.9	<22	8.6±1.1	3.6±0.2	1.8
M/A pt A	6.3	3.8	<15.4	<0.9	<22	11.3±1.7	<2.8	2.6
M/A pt B	4.2	7.2	<15.4	<0.9	32.1±1.3	53.7±0.6	245.6±4.3	3.3
M/A pt C	4.6	2.1	<15.4	<0.9	<22	45.9±2.1	84.6±3.1	3.2
M/A pt D	3.9	1.0	<15.4	<0.9	42.1±1.8	10.3±1.2	24.5±24.5	2.2
M/A pt E	4.6	0.6	<15.4	<0.9	48.3±2.4	7.6±0.4	7.2±1.3	2.0
M/A pt F	4.8	0.4	<15.4	<0.9	41.2±1.6	7.6±0.2	9.3±0.9	1.6
M/J pt A	6.0	0.7	<15.4	<0.9	<22	17.6±2.0	<2.8	2.4
M/J pt B	4.0	7.6	<15.4	<0.9	<22	24.8±1.0	115.3±1.9	4.8
M/J pt C	3.4	1.4	<15.4	<0.9	<22	10.5±1.3	42.2±1.6	3.2
M/J pt D	4.8	5.3	<15.4	<0.9	52.1±2.6	33.1±2.7	10.2±0.4	2.0
M/J pt E	4.7	0.2	<15.4	<0.9	54.5±4.2	6±0.9	5.7±1.1	2.2
M/J pt F	3.8	0.5	<15.4	<0.9	48.8±4.7	11.2±1.4	8±0.4	2.4
J/A pt A	6.9	2.8	<15.4	<0.9	<22	7.8±0.4	3.6±0.5	4.0
J/A pt B	3.6	6.2	<15.4	<0.9	24.3±1.9	18.2±1.2	12.4±1.7	5.2
J/A pt C	3.2	1.3	<15.4	<0.9	<22	12.2±0.7	12.2±1.7	2.2
J/A pt D	3.6	1.0	<15.4	<0.9	<22	11.1±0.8	12.7±0.8	2.6
J/A pt E	4.8	0.4	<15.4	<0.9	<22	9.7±0.4	6.2±0.9	2.4
J/A pt F	4.5	0.3	<15.4	<0.9	<22	7.3±0.3	7.8±0.4	2.8
S/O pt A	7.3	3.0	21.8±2.4	<0.9	45.6±3.9	57.5±0.9	15.2±0.4	4.6
S/O pt B	4.1	5.2	<15.4	<0.9	34.5±2.1	54.2±1.2	13.6±0.4	4.8
S/O pt C	4.3	1.5	<15.4	<0.9	<22	21.8±0.5	6.8±1.2	3.2
S/O pt D	3.8	1.0	<15.4	<0.9	37.2±4.2	18.5±1.2	13.5±1.3	2.0
S/O pt E	4.3	4.7	<15.4	<0.9	35.9±2.1	45.6±2.7	74.7±3.7	2.2
S/O pt F	4.5	0.3	<15.4	<0.9	33.3±1.6	16.8±0.9	56.7±2.7	1.8
N/D pt A	7.4	3.6	26.3±2.2	<0.9	<22	157.5±5.5	15.7±1.5	3.4
N/D pt B	5.7	4.1	18±3.3	<0.9	<22	43.3±1.1	13.7±1.1	4.2
N/D pt C	4.6	1.8	<15.4	<0.9	<22	19.7±1.4	13.8±1.3	3.2
N/D pt D	4.8	0.8	<15.4	<0.9	34.4±1.2	13.5±0.7	14.2±0.7	2.0
N/D pt E	3.6	0.8	<15.4	<0.9	25.7±1.5	27.5±1.5	68.2±2.4	2.0
N/D pt F	4.5	1.2	<15.4	<0.9	<22	13.1±1.2	5.2±0.7	2.2

The heavy metal concentration for the sediments was found to be low except for copper at a few points. This is probably due to the fact that the stream is located in a rural place where there is very little contamination of the sediments by heavy metals from effluents and vehicular emissions. The concentrations of the metals were found to be in the range 15.4 -26.3 mg/kg for Pb, 22-54.5 mg/kg for Cr, 4.6-157.5 mg/kg for Zn, and 2.8 – 332 mg/kg for Cu. The level of Cd in the sediment was found to be lower than the detection limit of 0.9 mg/kg in all the cases. The high concentration of copper in the sediments could be due to the discharge of effluents by a textile company which uses copper as one of the components of its dye. This may account for the high concentration of copper at point B. The concentration of copper was also found to decrease from point B to point F which is a point on the Lagos Lagoon.

Compared to Odo-Iyaalaro and Shasha creeks, the concentration of metals in Ibeshe river sediment is much lower. This could be because there were not many industries discharging their wastes into the waterbody as compared to the other two creeks. Moreover the area is not as thickly populated as the areas where the other two creeks are located; hence anthropogenic sources of pollution are far less there. However, in comparison to the average concentrations of metals found in St. Louis River, Mauritius (Ramessur and Ramjeawon, 2002), the concentrations of Pb and Zn in Odo-Iyaalaro and Shasha creeks have been found to be much higher.

Table 3.10 gives the result of heavy metal concentration, pH, %organic matter and cation exchange capacity of the sediments from the Lagos Lagoon.

The pH of the sediments from the Lagos Lagoon, ranged from 4.1 – 7.0, indicating sediments varying from slightly acidic to near neutral. The CEC of the sediments ranged from 1.8-11.2 meq/100g, with samples collected at points S which is Oworonshoki part of the Lagos Lagoon having the highest cation exchange capacity. This correlates with the high organic matter content of the sediments. The % organic matter content of the sediments ranged between 0.1 -12.6 %.

The concentration of Pb was found to range between 15.4 – 39.2 mg/kg, while Cd was found to be lower than the procedural detection limit of 0.9 mg/kg at most points. Zinc concentration ranged between 1.3 mg/kg and 246.3 mg/kg, while copper concentrations ranged from 2.8 mg/kg -43 mg/kg, with points Q, R and S having the highest concentration of these metals for all the months sampled. The source of metals into these points of the Lagos Lagoon could be said to be anthropogenic, since these points are close to either a bridge, or where human activities take place.

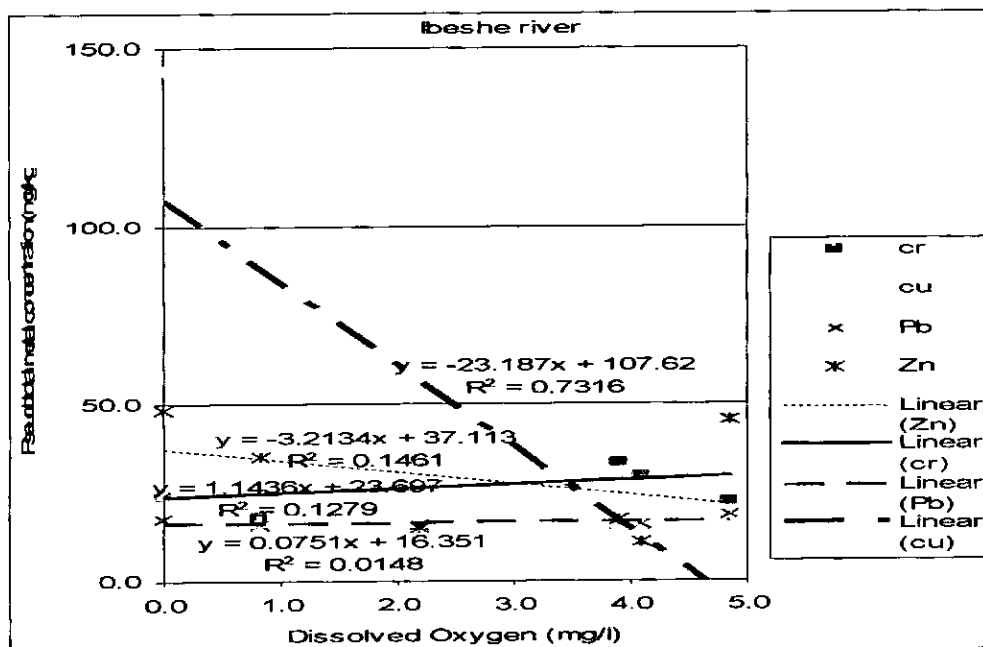
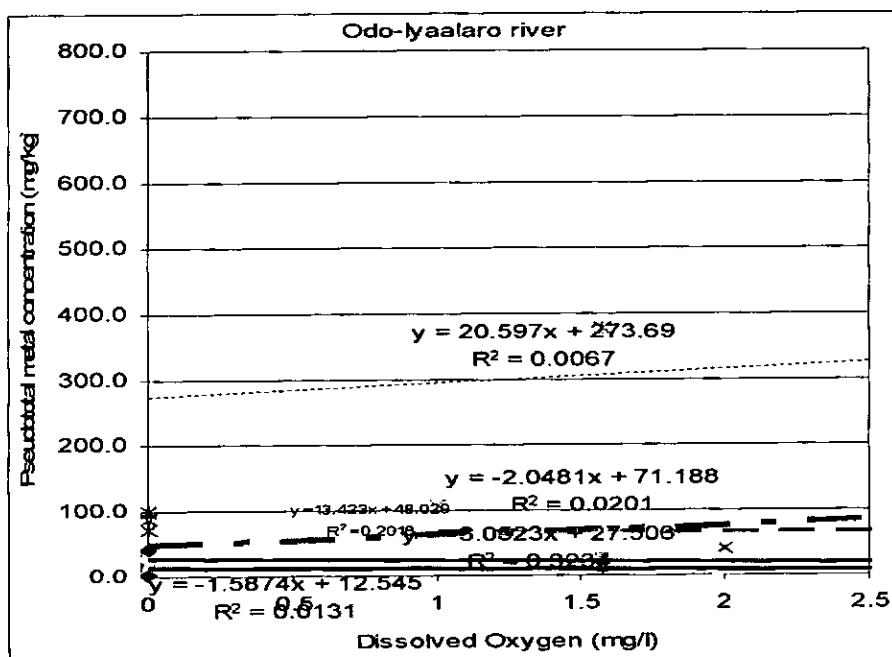
Compared to the streams under investigation, Chromium concentration in the Lagos Lagoon was generally high. It ranged from 23.8-51.7 mg/kg. This probably means that the source of chromium in this water body is lithogenic.

Table 3.10 **Results of physico-chemical analysis of sediments from the
Lagos Lagoon**

	pH	%OM	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	CEC (meq/100g)
S/O pt Q	4.1	3.3	33.2±1.8	<0.9	34.4±1.8	237.6±13.9	35.2±2.8	4.2
S/O pt R	7	4.4	<15.4	<0.9	34.4±1.4	141.7±10.6	19.5±1.6	4.4
S/O pt S	4.1	9.8	39±3.1	<0.9	25.7±0.9	246.3±10.8	43±3.4	8.8
S/O Cowrie	6.6	0.1	<15.4	<0.9	51.7±1.9	1.3±0.3	<2.8	2.2
S/O PAL	6.4	0.2	<15.4	<0.9	36.2±1.3	13.2±0.9	4.2±0.6	2.2
N/D pt Q	4.5	3.5	33.2±0.7	<0.9	34.4±2.1	163.5±8.1	33.7±2.1	5.1
N/D pt R	5.4	4.1	39±2.3	1.3±0.2	51.7±3.2	146±4.8	30±0.8	4.8
N/D pt S	4.3	12.6	39±3.4	2.1±0.2	51.7±4.8	189.6±4.2	33.7±1.5	11.2
N/D Cowrie	6.4	0.1	<15.4	<0.9	42.5±1.3	1.3±0.1	<2.8	2.0
N/D pt PAL	6.6	0.5	<15.4	<0.9	43±3.2	14.8±1.9	<2.8	1.8
J/A pt Q	4.6	3.7	29.8±1.3	<0.9	23.8±0.9	145.6±5.7	31±1.3	5.4
J/A pt R	5.9	4.3	39.2±0.7	<0.9	28.1±2.4	112.1±4.9	16.5±1.6	6.2
J/A pt S	4.4	10.8	34.1±2.8	<0.9	26.5±1.1	223±2.1	29.2±1.9	11.0
J/A Cowrie	6.7	0.2	19.2±1.9	<0.9	45.6±0.8	16.7±0.9	4.2±0.6	2.2
J/A PAL	6.5	0.1	<15.4	<0.9	51.7±2.7	43.3±1.8	<2.8	2.0

1.2.6 Variation of Metal concentration with Dissolved Oxygen.

In Odo- Iyaaloro creek, there was no correlation between the potentially toxic metals in sediments and dissolved oxygen. This could be due to the fact that this stream is generally polluted, while in Shasha creek, Cr, Pb and Zn were significantly negatively correlated. This indicated that the presence of anoxic waters influence the trappings of these metals in the sediments, and these are controlled by scavenging iron sulphide (Skei, 1983). Cu in Ibeshe creek has a significant negative correlation with dissolved oxygen, while in the Lagos lagoon, all the metals examined with the exception of chromium, are negatively correlated (Fig 3.9).



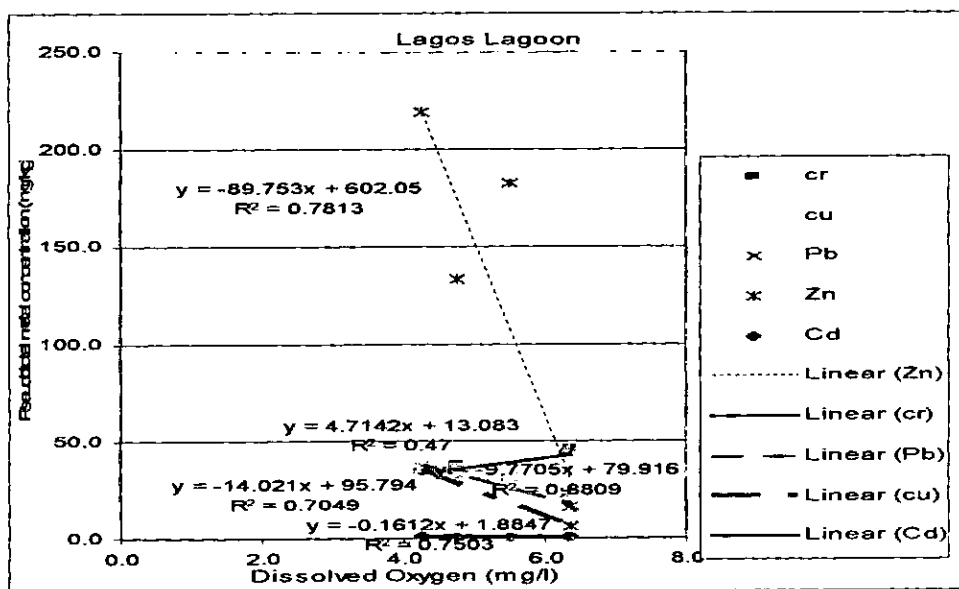
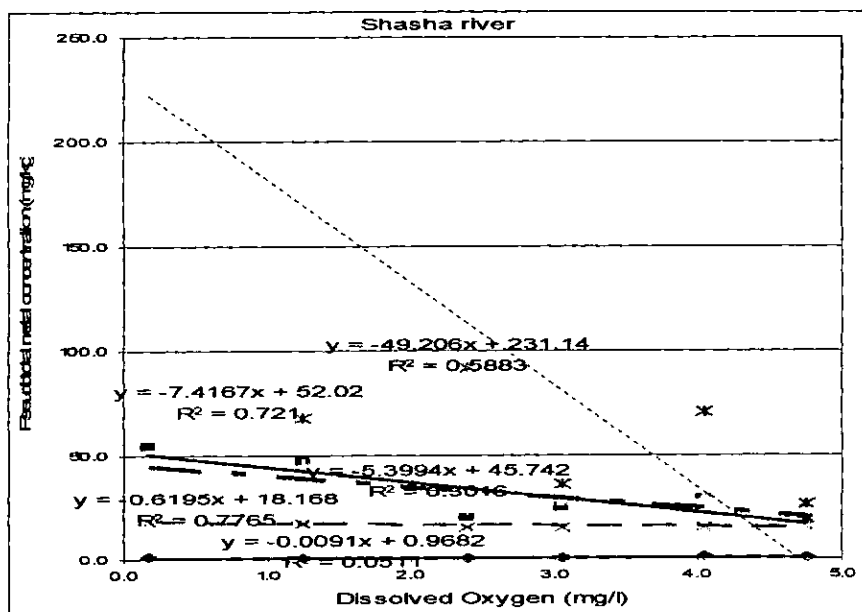


Fig 3.9. Correlation between Dissolved Oxygen and pseudototal metal in sediments of the selected water bodies

3.3 CHEMOMETRIC/STATISTICAL ANALYSIS

3.3.1 Enrichment factor

For a better estimation of anthropogenic input, an enrichment factor was calculated for each metal by dividing its ratio to the normalising element. The normalising elements used were Fe and Li.

Fe vs Li, $r = 0.79$.

This indicates that Fe or Li could be used as reference materials to normalize concentration for most metals in the sediments from the three rivers and the Lagos lagoon.

Since

$$EF = \frac{\left[\text{metallic content} / \text{content of Fe} \right]_{\text{sediment}}}{\left[\text{metallic content} / \text{content of Fe} \right]_{\text{geochemical background noise}}}$$

The values of the concentrations of elements from the earth crust are taken from Riley and Chester (1971). The Enrichment factor was calculated for the average composition of the sediments from each of the points (Tables 3.10 – 3.13). Enrichment factors greater than 1 are generally taken to reflect high levels of anthropogenic pollution.

Pb, Cd, Zn and Cu in sediments of Odo-lyaalaro creek all have enrichment factors greater than 1 for most of the points. This indicated that the source of these metals into this stream is anthropogenic.

Points 5 and 6 showed more enrichment of these metals than the other points. This is probably due to the high cation exchange capacity and high % organic matter of the sediment.

In Shasha creek, point 7 had an enrichment of Pb, Cr, Zn and Cu. This meant that the source of these metals into the waterbody is anthropogenic, and the source could be from the various industries situated around Isolo, and also from vehicular emission from cars and petrol tankers that ply the bridge which is directly under the point of collection. Point 9, which is a point along Shasha stream, called the Port-Novo creek was also found to have a high enrichment factor in the case of Pb. This is probably due to the mechanic workshop very close to the point, and the mechanics probably discharge their spent oil into the river at that point.

Zn and Cu are generally enriched in the sediments from most of the points ($EF > 1$). This could be accounted for by the fact that these metals are generally known as anthropogenic metals (Rodriguez-Martin et al., 2006).

Table 3.11 Average Enrichment factor of metals for sediments from Odo-Iyaalaro creek

Sampling Points	Pb	Cd	Cr	Zn	Cu
3	1.83	0.774366	1.150681	1.343585	1.528514
4	1.3994	1.083835	0.425297	0.702842	1.085248
5	3.342022	3.122914	0.532526	4.02954	2.471967
6	3.445292	4.269452	0.560043	4.758847	3.164468

Table 3.12 Average Enrichment factor of metals for sediments from Shasha creek

Sampling Points	Pb	Cd	Cr	Zn	Cu
7	5.664104	0.750747	2.093138	4.299517	3.045669
8	2.86318	0.861303	0.936198	3.536497	2.022519
9	4.351103	0.865385	0.940635	1.878636	0.888512
10	3.106214	0.723869	0.786814	1.605582	1.748575
11	1.187839	0.40814	0.443631	0.748762	1.471209
12	2.032808	0.751047	0.816356	1.354657	0.694586

Table 3.13 Average Enrichment factor of metals for sediments from Ibeshe creek

Sampling Points	Pb	Cd	Cr	Zn	Cu
A	1.045724	0.423968	0.816056	0.635529	0.280172
B	1.271988	0.572185	1.150569	1.267919	9.288745
C	1.516204	0.694165	1.188269	1.099271	6.350657
D	1.552203	0.710647	1.815426	0.386753	1.778861
E	1.599416	0.732263	2.016363	0.414405	1.712605
F	1.574346	0.720785	1.816678	0.301031	0.93226

Table 3.14 Average Enrichment factor of Metals for sediments from the Lagos**Lagoon**

Sampling Points	Pb	Cd	Cr	Zn	Cu
Q	2.432102	0.68525	1.902459	3.002494	1.50265
R	0.629012	0.167134	0.859164	1.61968	0.682788
S	1.927814	0.494882	0.937159	3.331927	1.377258
COW	1.022826	0.432692	1.568897	0.227506	0.302895
PAL	1.13778	0.520911	1.768443	0.842171	0.303736

The enrichment factor for copper was found to be far greater than 1, especially at points B and C, thus reflecting its anthropogenic origin. It can be seen that from point B to points nearer the Lagos Lagoon, the enrichment factor decreased, indicating that the pollution of point B is from effluents from the textile company situated around that point.

The enrichment factors of the other metals were either less than 1 or just slightly greater than 1 thus indicating that the source might not really be anthropogenic.

Zinc in sediments from the Lagos Lagoon had high enrichment factors at points Q, R and S. This is probably due to the domestic wastes from people living around that part, while COW, and PAL are points which are quite far from either industrial or domestic activities. The high EF of Pb from sediments collected from Iddo area of the Lagos Lagoon (point Q) could be from the tankers which discharge sewage into the Lagos lagoon.

In all, this study has shown that copper is the main metal pollutant in Ibeshe creek, whereas, Cd, Cr, Pb and Zn are the metal pollutants in Odo-lyaalaro and Shasha creeks. This is due to the fact that there are usually more activities taking place around the latter creeks whereas the nearby textile plant may be the major contributor to the high level of copper in the former creek. Of all the water bodies studied, the Lagos lagoon was found to be the least polluted and compared to lagoons in other part of the world (Trocine and Trefry, 1996; Vazquez et al., 1999; Morrison, P.L. Brown, 2003; Maanan et al., 2004; Rigollet et al., 2004; Acevedo-Figueora et al.,

2006; Bernardello et al., 2006), the Lagos lagoon which serves as a source of food basket for the inhabitants of Lagos can be said to be relatively unpolluted

3.3.2 Principal Component Analysis of Sediments

In order to reduce the relatively large number of variables to a smaller number of orthogonal factors, the original data obtained was processed by multivariate statistical methods. The distribution manners of individual associations of elements in sediments were determined by principal components method.

Table 3.15 shows the eigenvalues from the PCA for Odo-Iyaaloro stream. Based on eigen values, the first two factors with the highest values were used. The two factors explained 67.8 % of the total variance. The first factor explaining 50.8 % of the total variance was strongly and positively related to %organic matter, CEC, Pb, Cd, Cu and Zn, while the second factor explaining 19% of the total variance showed a high positive loading on pH and a negative loading on Cr. Fig.3.10

Table 3.15 **Eigenvalues of factor for sediments of Odo-Iyaaloro creek**

Factor	Initial eigenvalues		
	Total	Percent of variance	Cumulative
1	4.081	51.009	51.009
2	1.342	16.771	67.780
3	1.290	16.126	83.906
4	0.600	7.500	91.406
5	0.327	4.094	95.500
6	0.217	2.714	98.213
7	0.101	1.256	99.470
8	0.042	0.530	100.00

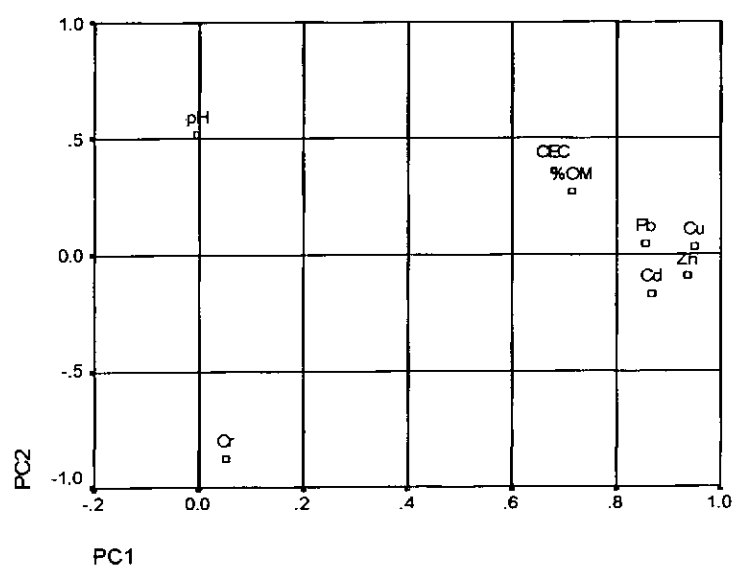


Fig 3.10 Factor loadings of Odo-Iyaalero creek

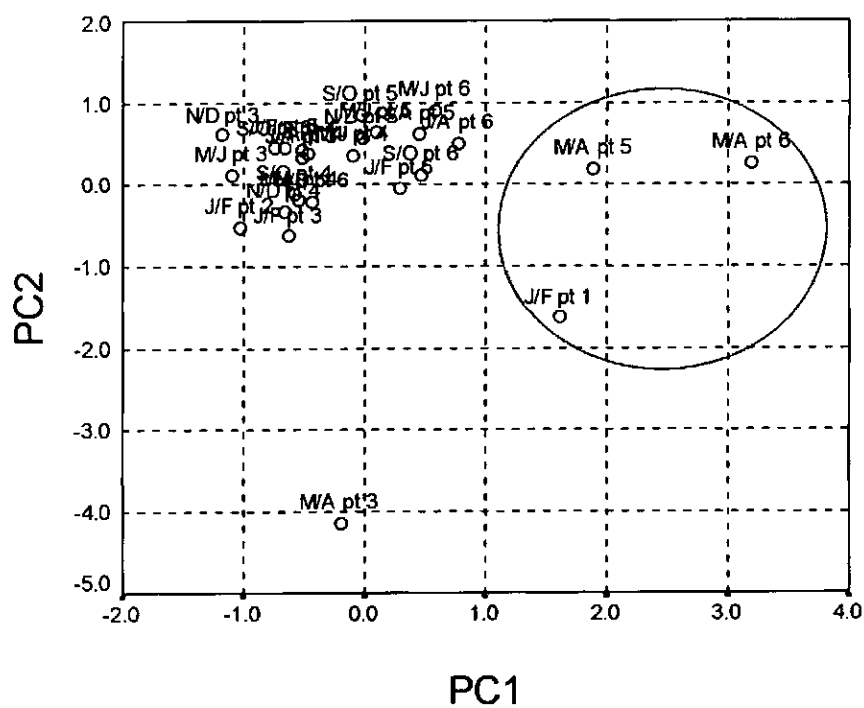


Fig 3.11 Plot of scores for Odo-Iyaalero creek

The plot of factor loadings (Fig 3.10) shows the grouping of the elements in factor 1 (PC1) and factor 2 (PC2). Pb, Cu, Zn and Cd are grouped together and associated with the first principal component which comprises the largest proportion of the total variance, indicating that these metals are from common sources, and according to various studies (Brumelis et al., 2002), the association of these metals with this factor indicate anthropogenic influence. Cr is negatively correlated with pH, and is associated with PC2. The source of Cr in this river can be said to be geogenically influenced (Hanesch et al., 2001).

Fig 3.11 shows the plot of scores for Odo-Iyaalaro creek. Samples collected in March point 5 and 6, and February point 1 were found to be very similar and highly correlated with PC1 which is found to be associated with Cd, Cu, Zn, Pb, % organic matter and CEC Löffler et al., (2002) have previously shown that clay minerals and organic matter build aggregates and flocs which concentrate trace metals and then sink to form a 'fluffy layer'. The element distribution manner here, suggests that this fluffy layer are mainly deposited at points 5 and 6. The environment being of very high organic matter content, could also have generally favoured deposition of these anthropogenic metals. March is the peak of dry season, and when the rains come, it flushes away the adsorbed heavy metals in the sediment.

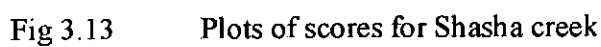
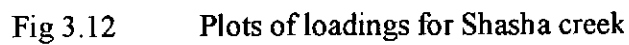
The sample collected in March point 3 was different from the other samples in terms of its chromium concentration. Point 3 is directly under a bridge and when roadside sediments are swept from the bridges, they are dumped into the stream. It is possible

that the point was sampled just after the roads have been cleaned and soils containing chromium from cars have been dumped into the stream. The other samples clustered together are shown to be similar to each other in terms of their heavy metal concentration.

For Shasha stream, two main factors were significant i.e had eigenvalues >1 . The two factors together, explained 69.2 % of the total variance. The first factor (PC1) explained 54.3% of the total variance, while the second factor explained about 15 % of the total variance. Fig 3.12 shows that PC1 is associated with Cu, %organic matter, CEC, Pb, Zn and Cr, while pH and Cd are positively correlated with PC2.

Table 3.16 **Eigenvalues of factor for sediments of Shasha creek**

Factor	Initial eigenvalues		
	Total	Percent of variance	Cumulative
1	4.341	54.268	54.268
2	1.198	14.977	69.245
3	0.923	11.532	80.777
4	0.597	7.466	88.243
5	0.423	5.291	93.533
6	0.257	3.210	96.743
7	0.174	2.180	98.923
8	0.086	1.077	100.000



The plot of scores for Shasha creek (Fig. 3.13) showed that the samples collected at point 7 for almost all the months sampled are highly associated with PC1, and they contain high concentrations of Cu, Pb, Zn and Cr. Their association with PC1 prove their anthropogenic origin. These metals are from vehicular emissions, and also domestic and industrial effluents. The high organic matter content of the sediments at these points could be from the decaying plants, as there were a lot of plants growing at the bank of the creek, and this could be the reason for the concentration at that point being high. The sample collected in September/October at point 10 could be said to be associated with high Cd concentration. This could be from spent oil from the mechanic workshop close to the point of collection.

Table 3.17 **Eigenvalues of factor for sediments of Ibeshe creek**

Factor	Initial eigenvalues		
	Total	Percent of variance	Cumulative
1	2.787	39.813	39.813
2	1.341	19.164	58.977
3	0.968	13.834	72.811
4	0.953	13.610	86.421
5	0.511	7.304	93.725
6	0.242	3.456	97.180
7	0.197	2.820	100.000

For Ibeshe creek, seven variables were used in the PC analysis. Cadmium was excluded since it was found to be below the detection limit throughout the period of sampling. Only the first two factors were significant, with factors 1 and 2 explaining about 59% of the total variance. The first factor explained 39.8 % of the total variance, while the second explained 19.2% of the total variation (Table 3.17).

Figure 3.14 indicates that Cu, % organic matter and CEC are associated with PC1, while pH and Pb are associated with PC2. Fig 3.15 clearly shows that samples collected at point B are the most influenced by the riverine input which is characterised by Cu from the textile factory discharging its untreated effluents into the river at that point. Samples picked in September/October and November/December at point A can be said to be associated with Pb and Zn. This could be due to contamination of the river by zinc from the metallic containers used by the villagers for fetching water from the river, and Pb could come from the few vehicles that pass through the road at that point. The origin of Cr in this stream could be said to be terrigenous, and that samples collected at point E and F which are points into the Lagoon 1 km east and west of the polluting stream are not really affected by the inputs from the creek, and therefore not polluted.

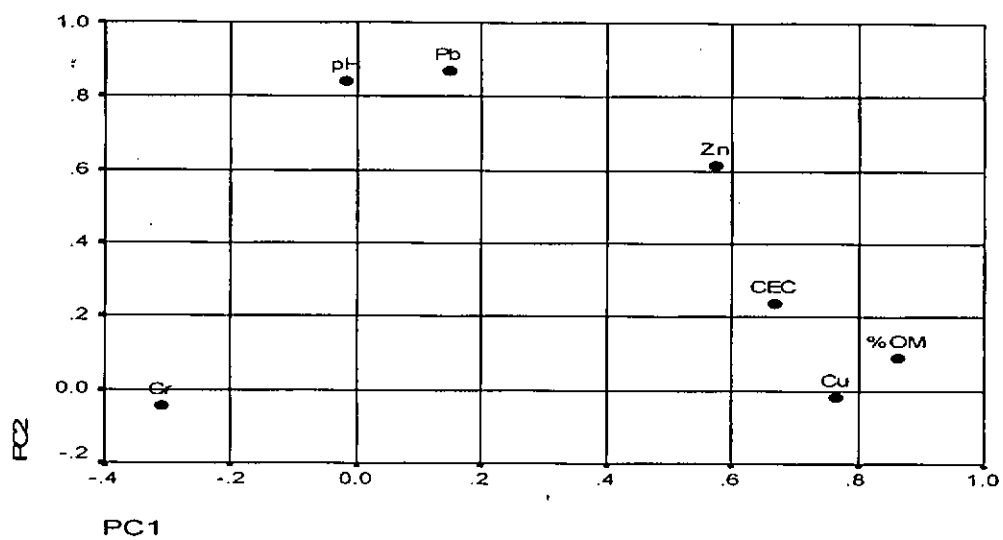


Fig. 3.14 Plots of loadings for Ibeshe creek

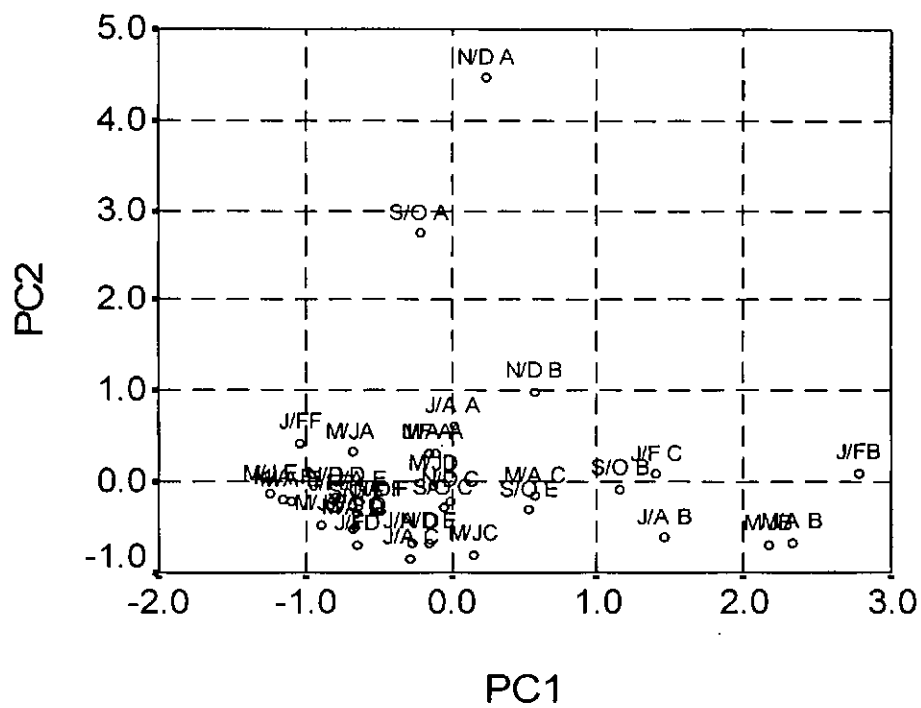


Fig 3.15 Plot of scores for Ibeshe creek

For the Lagos Lagoon sediments, only the first two factors were significant and explained 88.2 % of the total variance.

Percentage organic matter, CEC, Pb, Cu and Zn were found to be positively correlated with PC1, while Cd and Cr are found to be negatively correlated with PC1 (Fig 3.16). Researchers (Brumelis et al., 2002; Loffler et al., 2002) have shown a lithogenic control over the distribution of Cr metal. According to Hanesch et al. (2001), there might also be a geochemical relationship with the parent material, which is well known in basic and ultramafic rock. Samples Q, R and S can be said to be associated with Pb, Cu, and Zn (Fig 3.17) which are known as anthropogenic metals because the points are actually close to areas where there are human and industrial inputs whereas samples from points COW and PAL are almost in the middle of the lagoon and are quite far from human influence.

Table 3.18 **Eigenvalues of factor for sediments of the Lagos Lagoon**

Factor	Initial eigenvalues		
	Total	Percent of variance	Cumulative
1	5.519	68.991	68.991
2	1.537	19.216	88.207
3	0.462	5.770	93.977
4	0.200	2.496	96.472
5	0.143	1.789	98.262
6	0.111	1.386	99.648
7	0.023	0.291	99.939
8	0.048	0.068	100.000

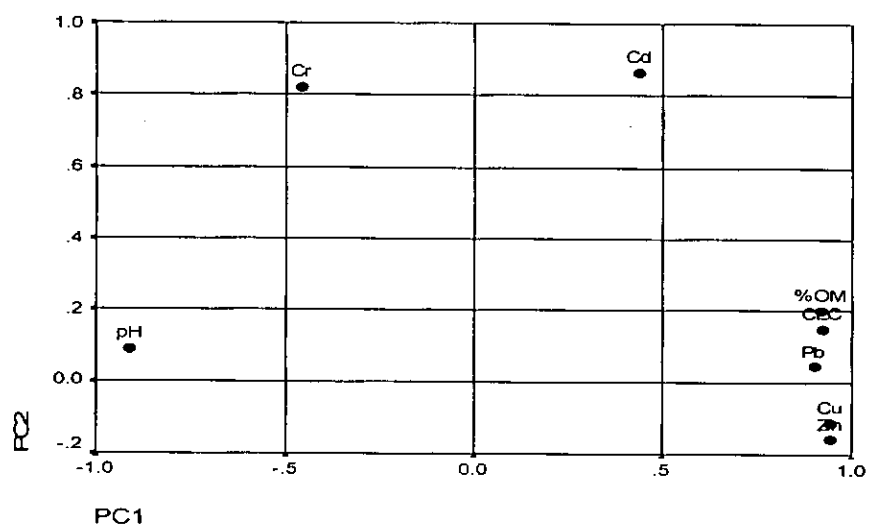


Fig 3.16 Plot of loadings for the Lagos lagoon

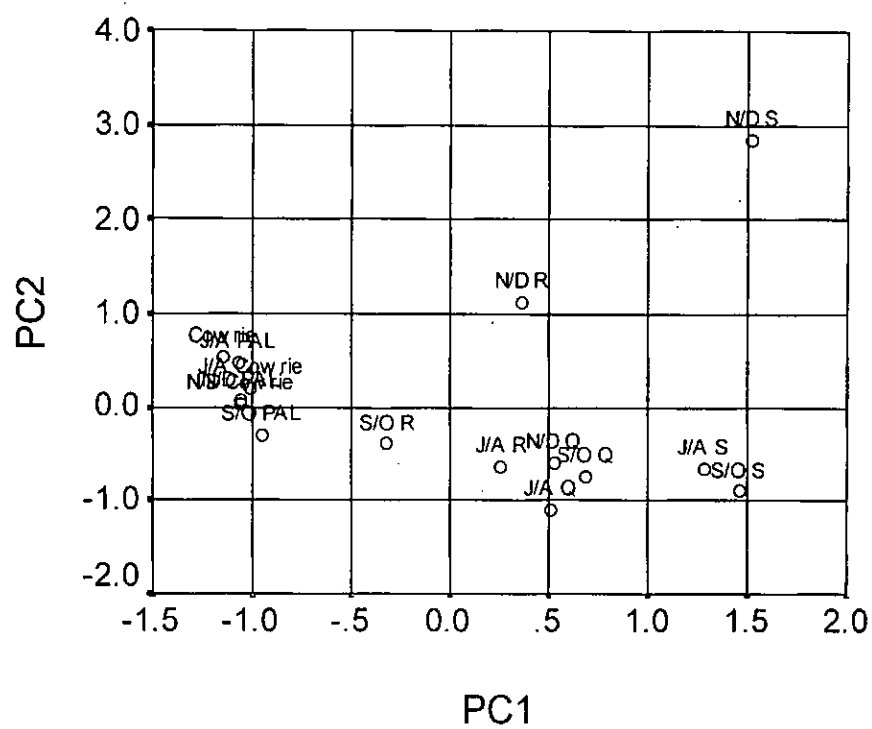


Fig 3.17 Plot of scores for the Lagos Lagoon

3.4 SPECIATION OF METALS IN SEDIMENTS

3.4.1 Comparative Analysis of Sequential Extraction Schemes.

In order to determine the best method for the speciation of metals in the sediment samples from the Lagos Lagoon system, three different sequential extraction schemes were compared.

Table 3.19 Extraction schemes of the different methods

Step	Fraction	Original BCR Extraction method	Tessier	Modified BCR
1	Water Soluble and exchangeable		1M NaOAc, pH 8.2	
1B	Carbonate bound	0.1M CH ₃ COOH	1M NaOAc, pH 5.0 with HOAc	0.1M CH ₃ COOH
2	Fe-Mn oxide bound (reducible)	0.1M NH ₂ OH. HCL, pH 2 with HNO ₃	0.04M NH ₂ OH in 25% HOAc	0.5M NH ₂ OH. HCL, pH 1.5 with HNO ₃
3	Organic matter and sulphide bound (oxidisable)	30% H ₂ O ₂ , 1M NH ₄ OAC (pH 2 with HNO ₃)	0.02M HNO ₃ , 30% H ₂ O ₂ 5ml 3.2M NH ₄ OAC	30% H ₂ O ₂ , 1M NH ₄ OAC (pH 2 with HNO ₃)
4	Residual	Aqua-regia	Aqua-regia	Aqua-regia

Figures 3.18 -- 3.22 show the fractionation pattern of the metals using the Tessier (1979) method, original BCR and modified BCR techniques. The fourth step of the Tessier method was modified by using aqua-regia instead of HF-HClO₄, and the original BCR was also modified by adding a fourth step. These were done to be able to calculate the mass balance. The mass balance (recovery was calculated by summing up the concentrations of metals in steps 1-4, and compared with the total metal concentrations (pseudototal). The mass balance was between 85-110% in most cases. The table showing the recoveries is shown in Appendix X

From the graphs, for all the metals analysed and in all the samples used, there was no significant difference in the sum of the concentrations found in each step of the original BCR and the modified BCR. This is probably due to the similarity in the SES schemes of the two methods.

Comparison between the sequential extraction procedures showed that the Tessier and the modified BCR scheme extracted more Pb, Zn, Cu and Cr in the reducible phase, and consequently a decrease in the oxidisable phase. This might be due to the increase in the concentration of the $\text{NH}_2\text{OH}\cdot\text{HCl}$ and the decrease in the pH for the modified BCR which probably prevented re-adsorption. Readsorption occurs when the metals which had originally been extracted (using hydroxylamine hydrochloride in this case), moves from the solution and adheres to the surface of the sediment matrix. The higher the concentration of the hydroxyl amine hydrochloride present, the more the amount of ions available to break the Fe and Mn oxides bonds. The increase in concentration therefore provided a more effective attack on the more refractory crystalline oxyhydroxides. Furthermore, the decrease in pH probably made the metals more soluble in the extracting solution, preventing readsorption. The same observation was made by Mossop and Davidson (2003) in their comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. In the case of the Tessier, the increase in the amount of Pb, Zn, Cu and Cr extracted could be as a result of the acetic acid used in lowering of pH. Compared to the nitric acid used in both

BCR protocols (original and modified), acetate ions from the acetic acid used has complexing properties (higher stability constant with metals) which prevents readsorption. This also showed that the modified procedure affords a better attack on the iron-based components of the reducible matrix for a range of soils/sediments.

A small difference in the sum of the concentrations found in each step was observed between the BCR methods and the Tessier method. The BCR methods (both original and the modified) removed more Pb compared to the Tessier method. This might be due to differences in the extraction conditions between the schemes. Tessier's method was observed to remove more chromium than the BCR methods. This could be because step 1/1B of the BCR methods (exchangeable and carbonate bound phase) uses 0.1M acetic acid while step 1B of the Tessier method uses 1M sodium acetate adjusted to pH 5 with acetic acid. The reagent in Tessier's method closely resembles the acetic acid used in steps 1/1B of the BCR methods, but with 10 times its concentration, which means that there are more of the anions present in solution to bind with the cation. Furthermore, since the chromium ion is a hard acceptor, it has a higher affinity for the acetate ion which is also a hard donor because it uses the oxygen donor atom. Also, sodium acetate has a higher ionization constant compared to the acetic acid, and this makes the acetate ion in the sodium acetate more readily available for complexation. The higher ionization constant is due to the fact that sodium is a better leaving group than hydrogen ion due to its bigger size. This explains why Tessier's method in step 1B is much more efficient in extracting chromium.

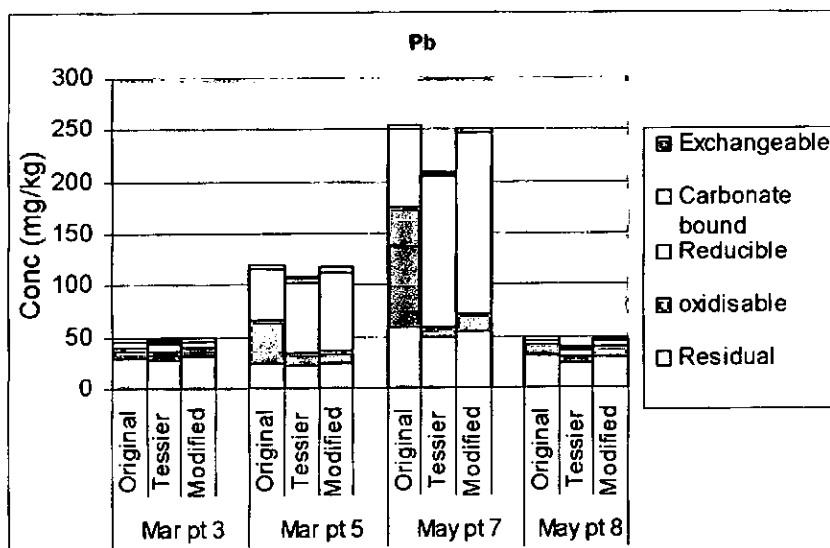


Fig 3.18. Fractionation pattern of lead for the three extraction schemes

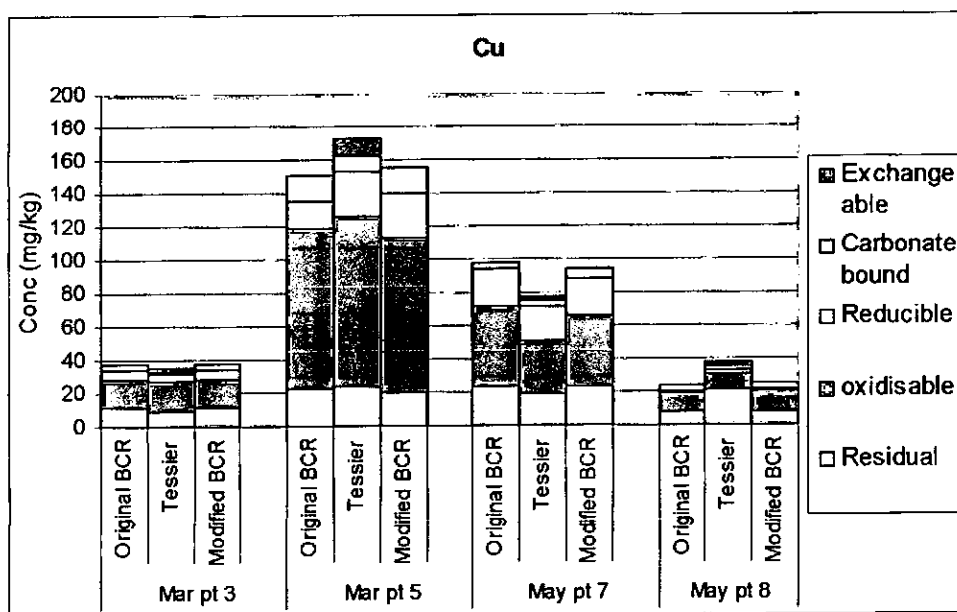


Fig 3.19 Fractionation pattern of copper for the three extraction schemes

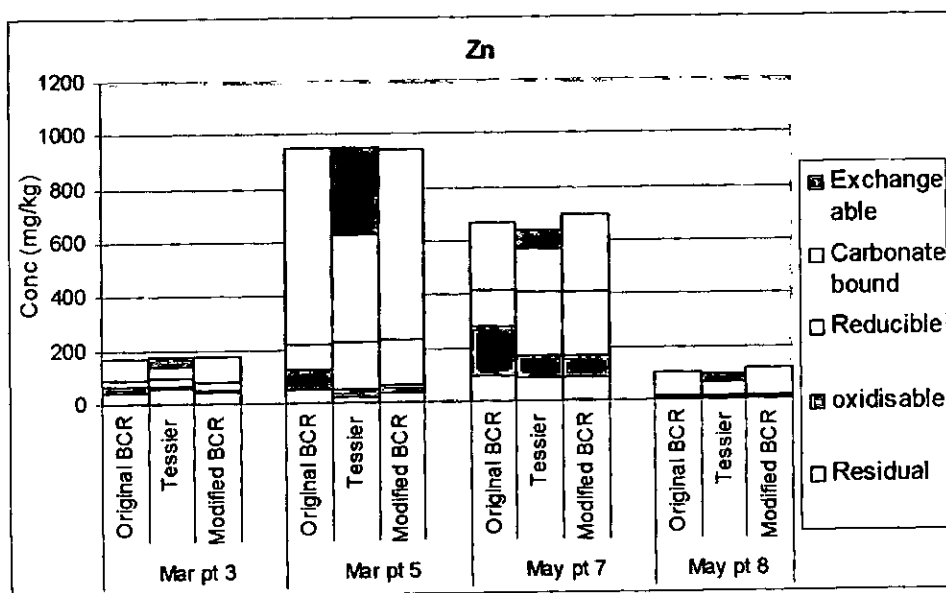


Fig 3.20 Fractionation pattern of zinc for the three extraction schemes

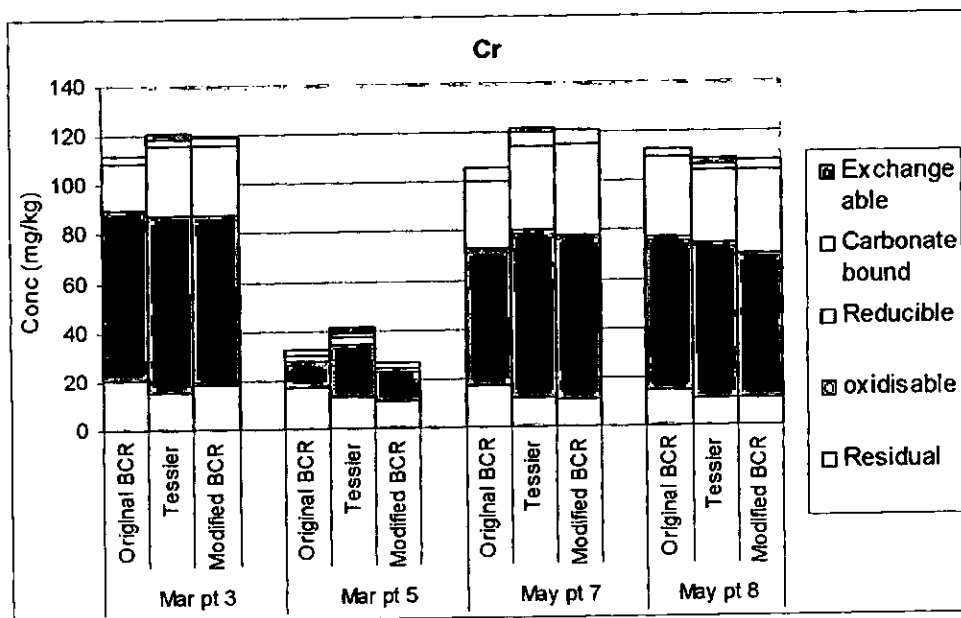


Fig 3.21. Fractionation pattern of chromium for the three extraction schemes

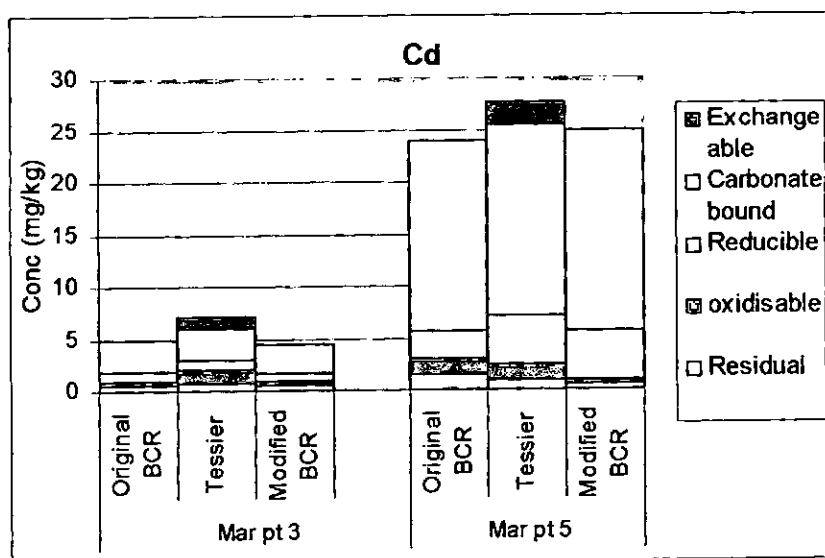


Fig 3.22. Fractionation pattern of cadmium for the three extraction schemes

In the case of zinc, no significant difference was observed both in the sums of the steps and the distribution of the metals along the steps [except for the original BCR (step2) for May pt 7 sample].

Generally, the differences between the sequential extraction schemes could be explained by (i) a large analytical variability of the methods, (ii) differences in the extraction conditions between the two schemes, and (iii) differences in the inorganic and organometallic chemistry of each metal.

Since the aim of the experiment was to quantify the fraction of the metal characterized by the highest mobility and bioavailability, the 3-step procedure, applied on samples for which the total concentration is high enough, was therefore recommended for speciation instead of the long and more tedious procedures which gives more information about the fraction of metals bound to different phases of the sample.

3.4.2 Speciation of Metals in Sediment Samples

From the results from the Principal Component Analysis, the following samples were chosen for speciation. February (FEB) pts B, D and E, March (MAR) pts 3, 5 and 6, May (MAY) pts 7, 8 and 10, September (SEPT) pts Q, R and S, October (OCT) pts 7, 8 and 10, November (NOV) pts 3, 5 and 6, and December pts B, D, E, Q, R, S, COW and PAL (making a total of 26 samples).

3.4.2.1 Quality control

Two reference materials were used to determine the analytical performance of the laboratory and the procedures used. The first reference material - BCR 701 is a lake sediment for determination of extractable trace elements. The second reference material GLAURM -an urban soil secondary material prepared by participants in the EU URBISOIL project for use as internal quality control samples (Davidson et al., 2006).

3.4.2.2 Fractionation of metals in reference materials

The results of the fractionation of the reference material BCR 701 is presented in Table 3.20 in the form of the mean values and standard deviations. Agreement found between the found and certified values was generally acceptable. They were within two standard deviations of the certified values in most steps and within three standard deviations, with the exception of Cd in steps 3 and 4, and Pb in step 1. This is because the certified values were below the detection limit of the FAAS. The precision of the results was good (<10%), except for Zn in steps 3 and 4.

Table 3.20 Evaluation of the analytical performance of the laboratory on the analysis of BCR 701 (reference material)

mg/kg	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Step 1					
Certified value	7.34 ± 0.35	2.26 ± 0.16	49.3 ± 1.7	3.18 ± 0.21	205 ± 6
Found ^a	7.3 ± 0.5	<2.21	48.2 ± 2.0	< 6.6	215 ± 15
Step 2					
Certified value	3.77 ± 0.28	45.7 ± 2.0	124 ± 3	126 ± 3	114 ± 5
Found ^a	3.98 ± 0.2	45.6 ± 3.5	139 ± 9	123 ± 7	122 ± 7
Step 3					
Certified value	0.27 ± 0.06	143 ± 7	55.2 ± 4.0	9.3 ± 2.0	45.7 ± 4.0
Found ^a	< 0.31	146 ± 2	54.4 ± 5.3	8.3 ± 0.7	38.2 ± 4.0
Step 4					
Indicative value	0.13 ± 0.08	62.5 ± 7.4	38.5 ± 11.2	11.0 ± 5.2	95 ± 13
Found ^a	< 0.55	50.0 ± 1.4	32.4 ± 6.1	16.2 ± 2.4	99 ± 12

^a n = 5

The result of fractionation of the GLAURM was also compared to the target values (figure 3.23). There was no significant difference between the values of the sums of steps 1 to step 4, whereas, higher concentrations were found in the step 3 for all the metals. This could be due to the slightly different extraction procedures used. Generally, a good recovery was found for all the metals in all the steps (80-116%), except for Cr in all the steps and Zn in step 4, showing a good analytical performance of the laboratory.

For a further validation of the method, metal recoveries by means of the BCR procedure were also determined. This was done by summing up the concentrations of the metals in steps 1-4, and compared with the total metal concentrations (pseudototal). The mass balance was between 85-115% in most cases.

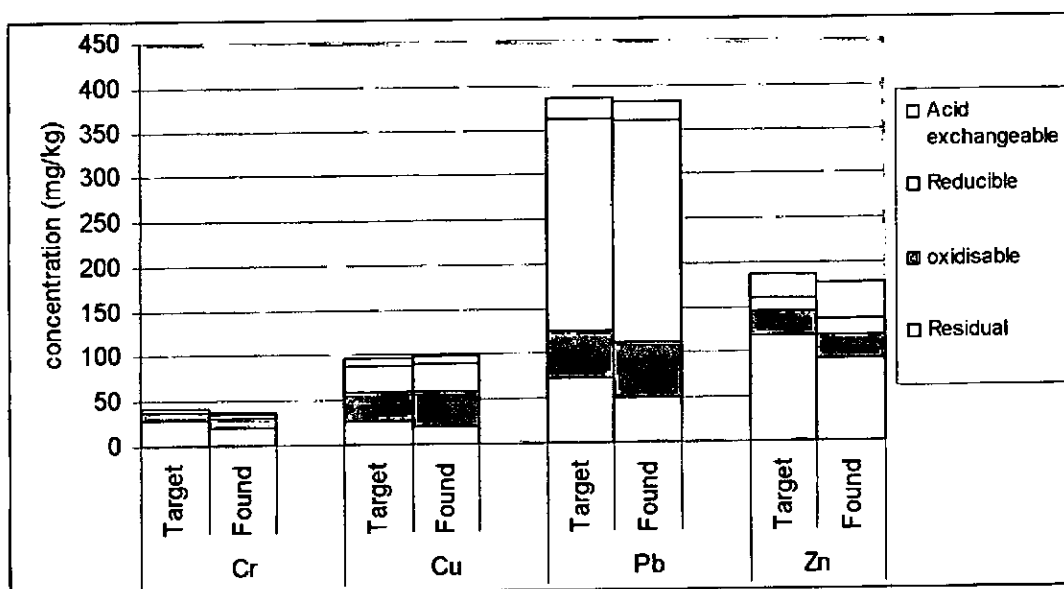


Fig. 3.23 Fractionation pattern of Cr, Cu, Pb and Zn in GLAURM, with respect to the target fractionation pattern. (n =10)

3.4.2.3 Fractionation of Metals in Sediments of the Selected Water bodies.

The average fractionation pattern (average of triplicates) of the potentially toxic elements in sediments of the three water bodies and the Lagos Lagoon are shown in Figures 3.24 – 3.28

Odo-Iyaalaro was the only water body with concentration of Cd high enough to be fractionated and quantified with an FAAS. The concentration of Cd in the other water bodies and in the Lagos Lagoon could not be quantified because it was either too close or below the detection limit of the FAAS. The graph in Fig. 3.27 shows that Cd is mostly associated with the exchangeable phase. The percentage of Cd in the exchangeable phase varied between 40-77%, indicating that it was very mobile, and therefore potentially bioavailable. The sum of steps 1 and 2 (acid exchangeable and reducible phase), accounts for greater than 75% of the Cd present in the sediments for all the samples, showing that Cd in these samples, is potentially bioavailable. This meant that if there was a slight decrease in the pH of the water, or if the condition of the sediment became more anoxic, the metal could be released into the water column, and can be taken up by aquatic organisms. Samples for MAR PT 5 and MAR PT 6 gave the highest concentration of Cd for the easily soluble fraction and also gave the highest total Cd concentration. This indicated severe pollution of the aquatic environment.

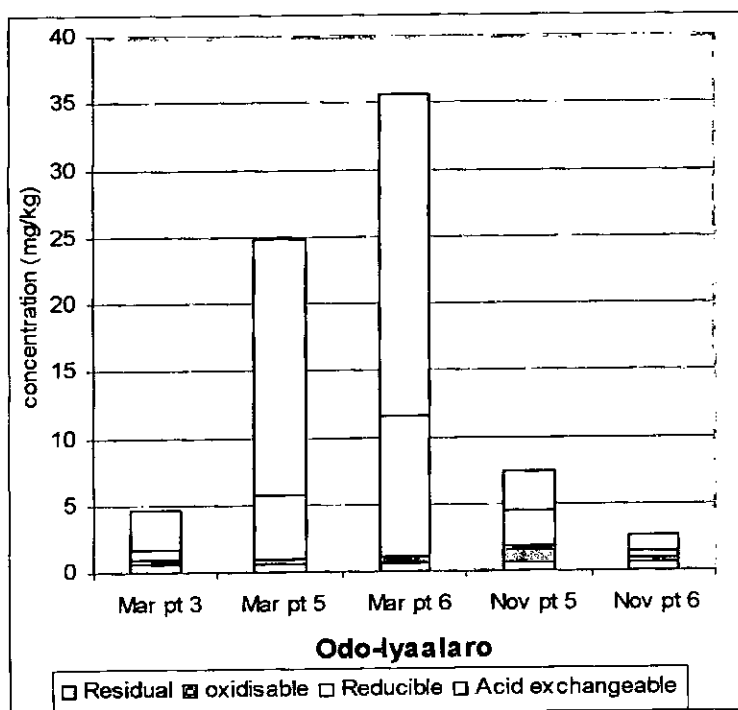


Fig 3.24 Fractionation pattern of cadmium in sediments

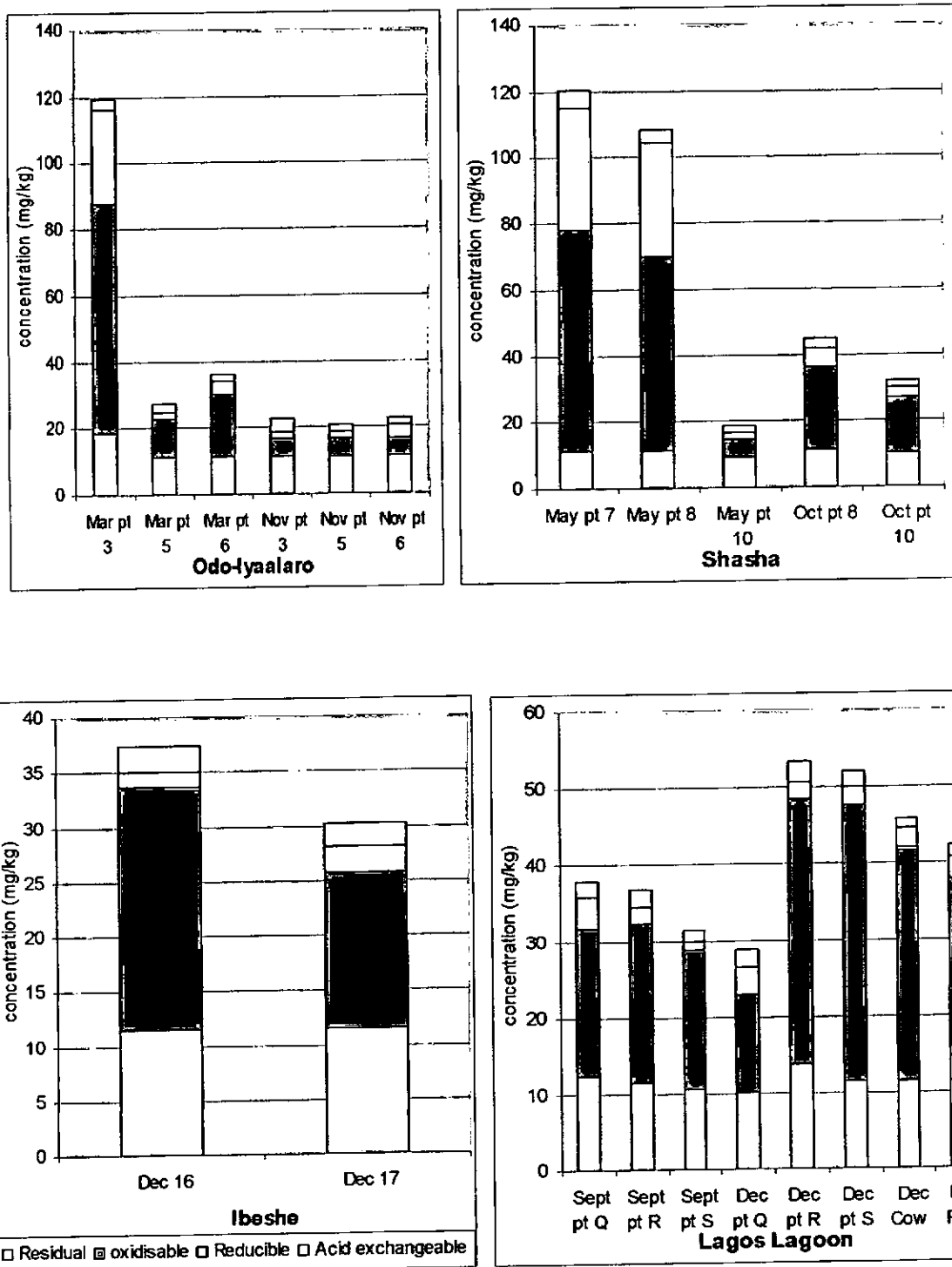


Fig 3.25 Fractionation of chromium in sediments

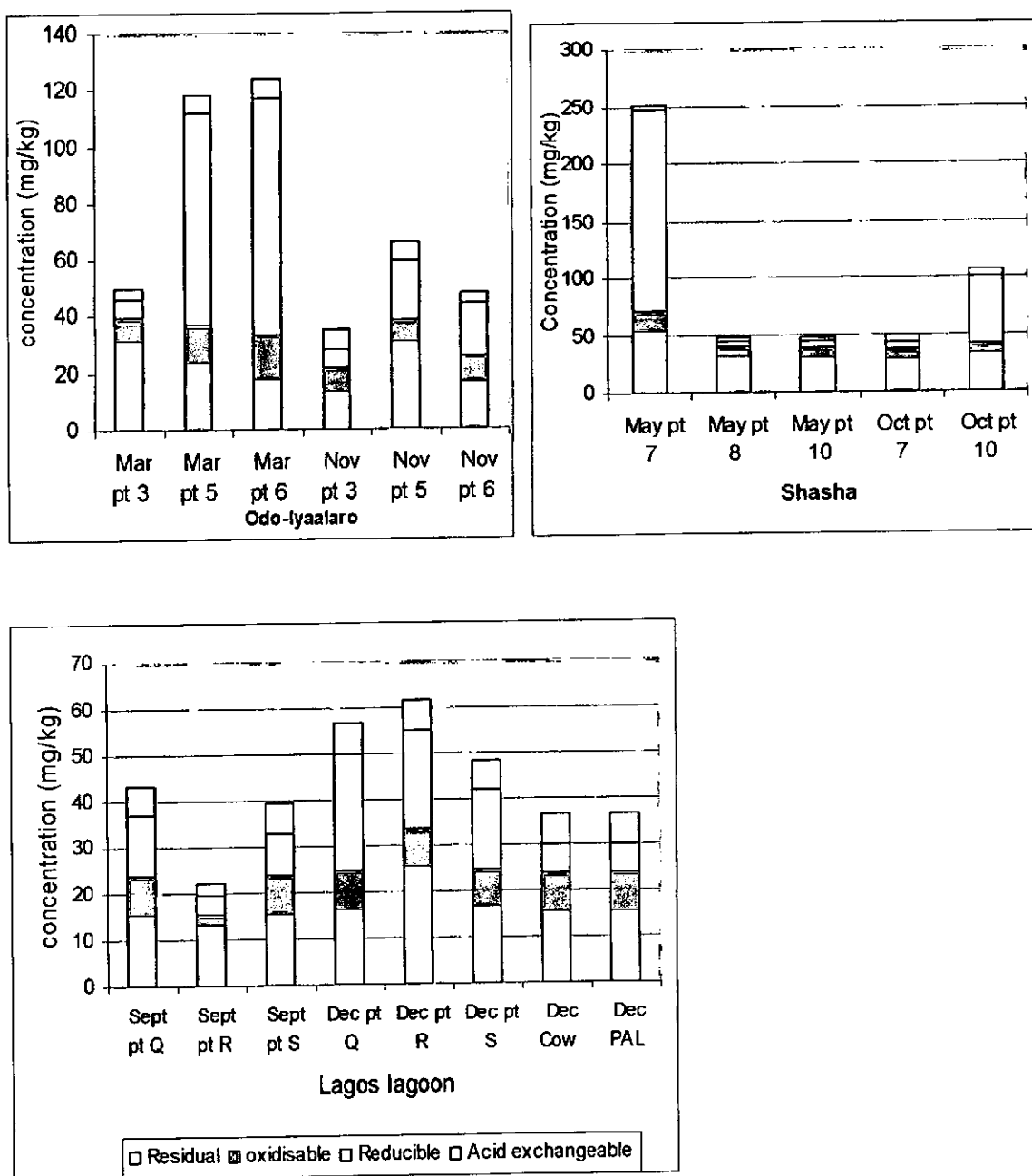


Fig 3.26 Fractionation pattern of lead in sediments

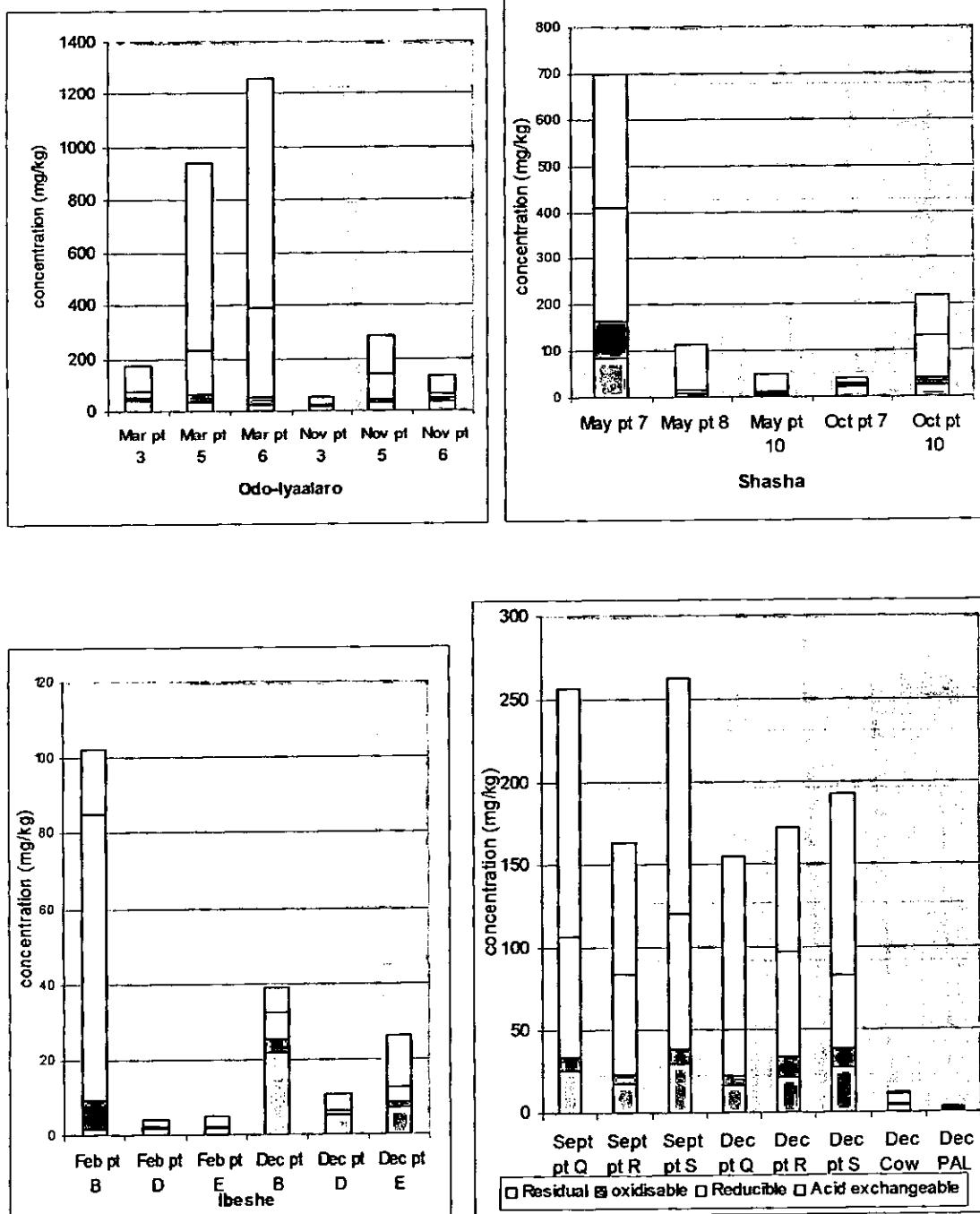


Fig 3.27 Fractionation pattern of zinc in sediments

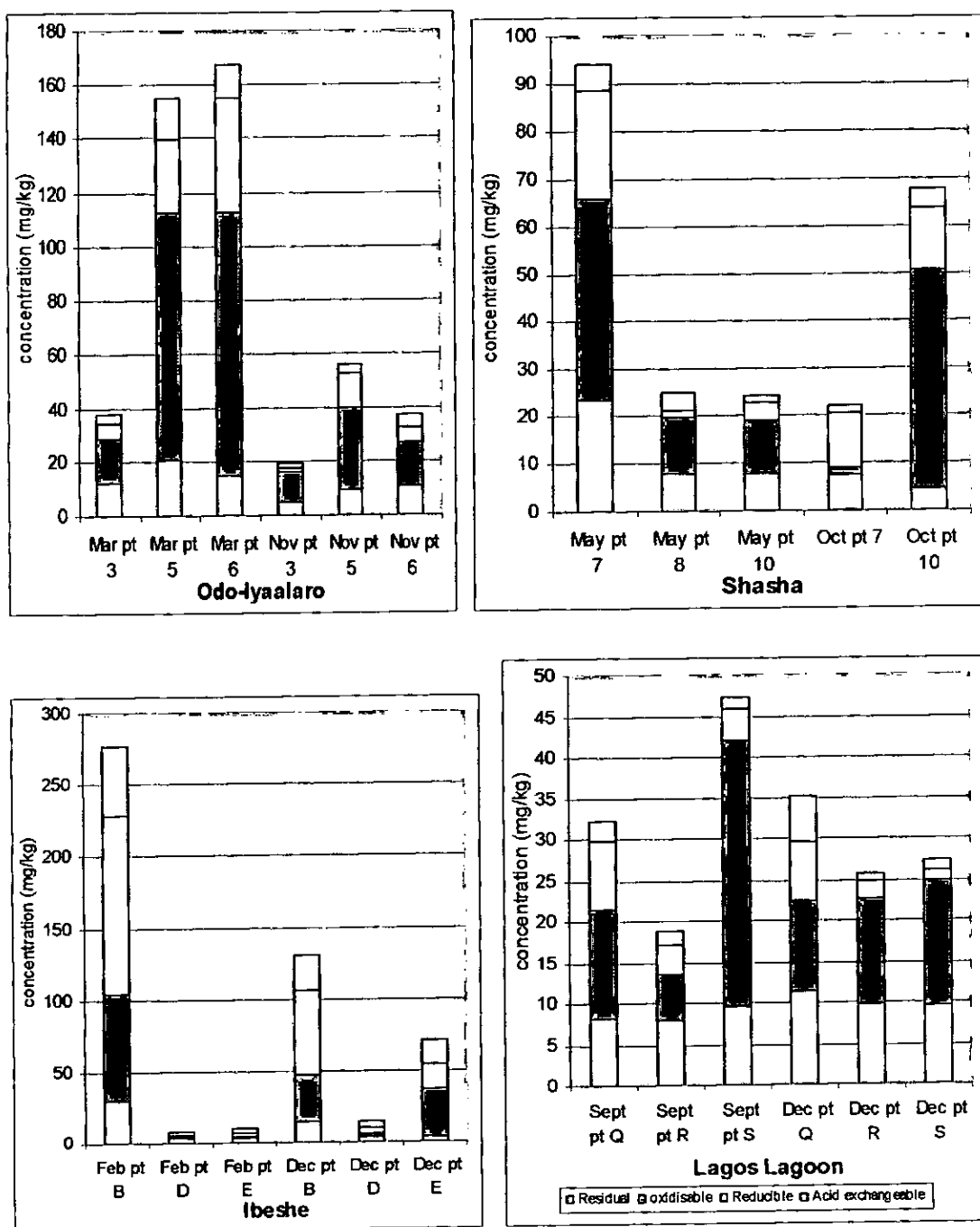


Fig 3.28 Fractionation pattern of copper in sediments

Chromium (Fig.3.25) was shown to be mainly associated with the residual fraction in Odo-Iyaaloro (42-55%), with the exception of MAR PT 3 and MAR PT 6 with 15% and 32% respectively in the residual phase. Cr in samples MAR PT 3 and MAR PT 6 is mostly associated with the oxidisable phase, which is the fraction in which metals are bound to the organic matter and sulphides. MAR PT 3 has the highest total concentration of Cr in Odo-Iyaaloro, and the sum of the first three fractions accounts for greater than 84% of the chromium in that sample. MAR PT 3 could therefore be said to be a hot spot for chromium pollution, and the pollution could be said to be anthropogenic.

In Shasha, Ibeshe and the Lagos lagoon sediments, chromium was mainly associated with organic matter and sulphides (25-70%), and was also significantly present in the residual fraction. This indicated that any oxidising condition such as dredging of the waterways, could release the chromium present into the aquatic environment and this could pose a threat to the aquatic life.

In Odo-Iyaaloro, Shasha and the Lagos lagoon, Cu was mainly distributed between the organic matter and sulphide bound fraction. This agreed with the findings of Mulligan et al. (2001) that copper binds strongly with organic matter and clay minerals. Cu being found with organic complexes is probably because Cu has a high stability constant with humic complexes. This fraction is not considered to be very mobile, since it is thought to be associated with stable high molecular weight humic substances that release small amount of substance in a small manner. This fraction

could be released into the environment if there is an oxidising condition such as dredging of the waterways. In Ibeshe sediments, Cu is distributed among the different phases. The sums of steps 1 and 2, account for the highest percentage of Cu in the sediments (42-62%). Since this element is often associated with the oxidisable fraction, the Cu in the acid soluble phase may possibly result from the overloading of the organic binding sites, which is characteristic of anthropogenic surface pollution. This displays less adsorption and is preferably linked by weak interactions of Cu with the sediments. This actually proves that the source of Cu pollution in the sediment is anthropogenic. The pollution by Cu may be due to the discharge of effluents into the aquatic environment by the textile industry located near the stream. Therefore for this stream, Cu could be said to be potentially bioavailable.

Pb was found to be associated with the four fractions, but the proportion varied between the different water bodies and the samples. The highest percentage of lead was found to be mostly present in the reducible phase for Odo-Iyaaloro, though there was a significant percentage present in the residual fraction. The presence of a high amount of this metal in the reducible phase indicated that a reducing condition such as an anoxic condition could cause the release of this metal into the water column. An anoxic condition could be caused by the presence of microorganisms competing for oxygen.

In Shasha stream, Pb was found to be mostly associated with the residual fraction with the exceptions of samples from MAY PT 7 and OCT PT 10, which had 70 and

55% associated with Fe and Mn oxides and hydroxides (reducible phase). In the Lagos Lagoon, the highest proportion of lead was found in both the residual and reducible phases for almost all the samples, just like the samples from Ibeshe creek. The highest total concentration of Pb was found in samples MAR PT 5, MAR PT 6, and MAY PT 7, and these samples also had the highest percentages in the sum of the first two fractions. The percentage of lead in the sum of the first two fractions was found to be 69%, 72% and 71% respectively, indicating its potential bioavailability and also indicating that the pollution is anthropogenic.

Just like Cd, Zinc was found to be mostly associated with the acid exchangeable phase. This result is consistent with our earlier findings (Oyeyiola et al., 2007) in the determination of the fractionation pattern of Zn in Odo-Iyaalaro using the original BCR sequential extraction scheme. The high mobility of these metals facilitate their being taken up by benthic invertebrates living in sediments. Benthic invertebrates represent an important link in the transfer of metals to higher trophic levels because of their close association with sediments and their ability to accumulate metals. They are also often a major component in the diet of many fish. It has been observed that there is a general order of replacement where it was found that those ions in soil solution, which are mostly attracted replace other cations in the zone of attraction. According to Bittel and Miller (1974), the order of replacement have been found to be $Mg > Cd > Zn > Cu > Pb$. This explains why Cd easily replaces Ca in soil/ sediment solution.

The percentage of zinc in the sediment samples ranged from 37-87% with the exception of samples OCT PT 7, FEB PT B, DEC PT B and DEC Cow. In Odo-Iyaaloro creek, zinc and cadmium were found to show a similar pattern of fractionation. They were both found to be mostly present in the acid exchangeable phase. Pearson's correlation was performed on the amount of Cd in the acid exchangeable phase versus the amount of Zn in the same phase (Fig. 3.29). A very strong correlation was found to exist between them. This is probably due to the similarity in the ionic size and charge of the metals with calcium, and they are therefore able to replace each other in and can be coprecipitated with carbonates present in many types of sediments. The similarity in pattern also shows that the source of pollution is the same.

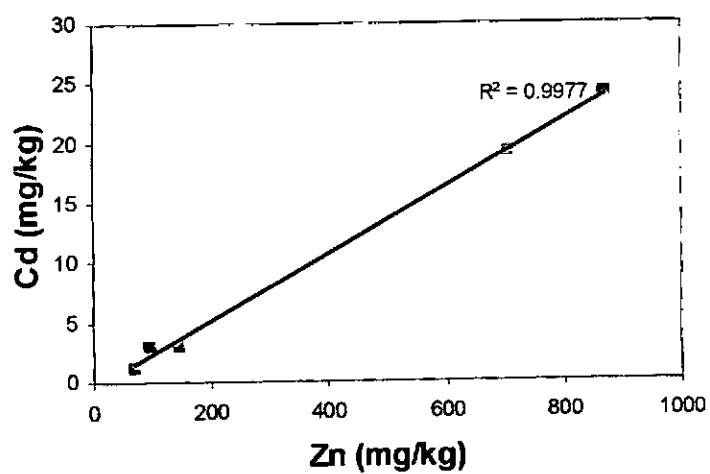


Fig. 3.29 Correlation of Cd and Zn in the acid soluble fraction of sediments in Odo-Iyaaloro creek

3.5 REMEDIATION OF METALS IN SEDIMENTS

Four of the most polluted sediment samples (in terms of metal concentration) were used for remediation experiments. Table 3.21 shows the physicochemical parameters of the sediments selected. The sediment samples used, ranged from very acidic to slightly acidic and the samples were contaminated with different metals in varying concentrations.

Sequential extraction (SE) using the modified BCR method was performed on the samples to determine the fractionation pattern of Cd, Cr, Cu, Pb and Zn before and after remediation. SE was used to compare the effects of batch extraction and column leaching on the fractionation pattern of the metals in sediments, and to also predict the efficiency of remediation. The efficiency of batch extraction and column leaching of the metals from the sediments using EDTA were also compared.

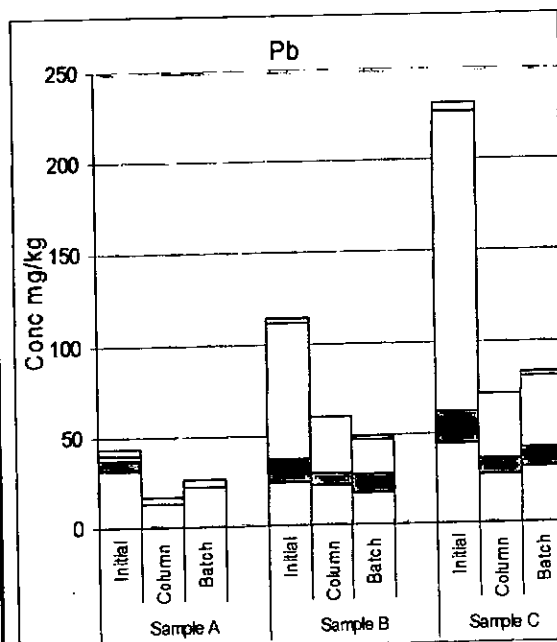
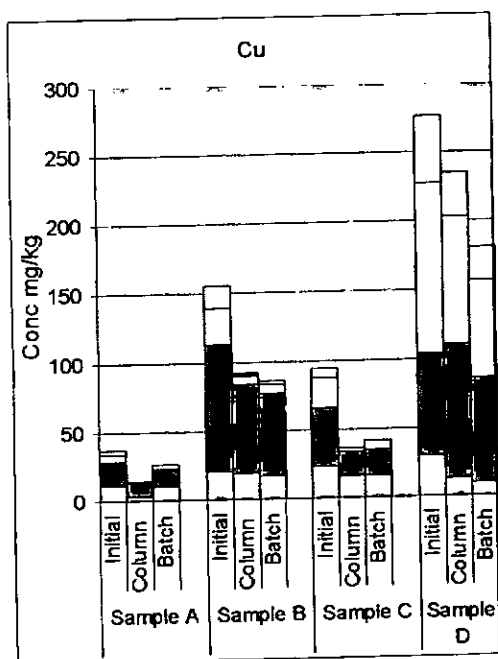
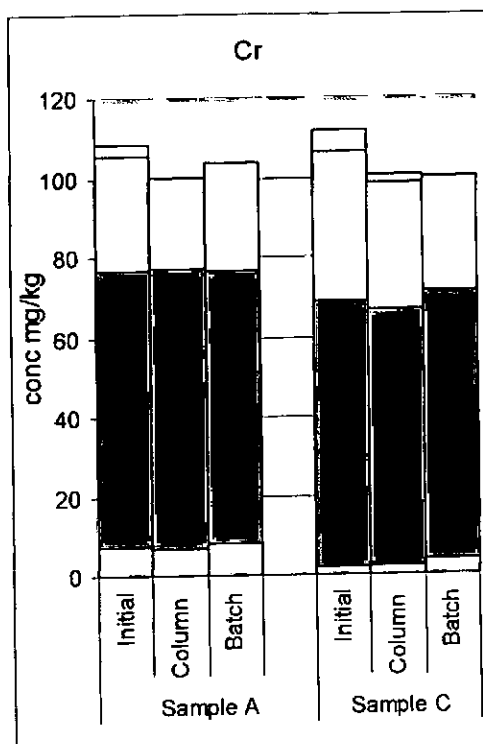
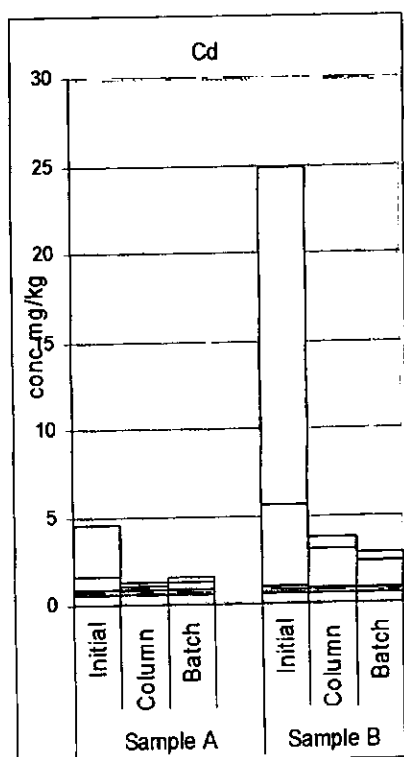
The samples used for remediation are MAR PT 3, MAR PT 5, MAY PT 7 and FEB PT B, and they were re-labelled as samples A, B, C and D respectively.

Table 3.21 Physicochemical properties of the sediment samples for remediation

	pH (CaCl ₂)	% Organic matter	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	CEC (meq/100g)
A	3.1	5.1	4.8 ± 0.4	102 ± 3	54.4 ± 2.3	43.5±3.7	157 ±3	4.2
B	3.9	10.2	21.3 ± 0.6	< 22	139 ± 3.0	119 ±8	777 ±17	14.6
C	5.9	6.6	< 0.9	140 ± 3	106 ± 2	202 ±5	641 ±25	8.2
D	5.8	6.1	< 0.9	< 22	332 ±11	<15.4	96.9±8.1	3.2

3.5.1 Fractionation pattern of metals in the sediments after treatment with EDTA

The fractionation patterns of metals in the sediments before and after remediation with EDTA are shown in Figs 3.30. For both the batch extraction and column leaching, the amount of Cd in the acid soluble and reducible fraction reduced significantly while the oxidisable and residual phases remained unchanged. In sample A, the acid soluble reduced by 91% for both the batch extraction and the column leaching while the reducible fraction reduced by 53% and 74% for the batch extraction and column leaching respectively. For sample B, in the batch extraction, 97% and 68% was removed from the acid soluble and reducible fraction respectively, while 96% and 52% was removed from the acid soluble and reducible fraction respectively in the column leaching. The fractionation pattern of samples A and B were very similar both for the batch extraction and column leaching, and the amount of Cd in the samples was much lower after remediation, and no longer as potentially biavailable compared to the fractions before treatment with EDTA.



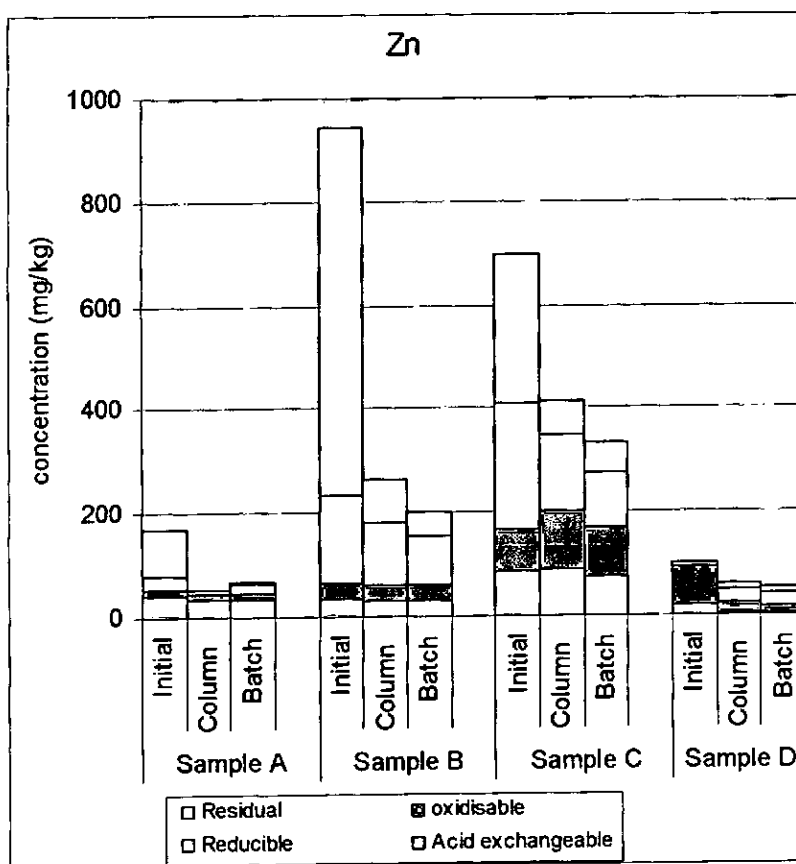


Fig. 3.30 Effect of EDTA on the fractionation pattern of metals in sediments of the Lagos lagoon system

The fractionation pattern of Cr for both samples A and C after EDTA treatment was very similar. There was little or no effect of the EDTA treatment on Cr as only about 3 - 7% of Cr was removed from the samples for both the batch extraction and the column leaching. This probably meant that Cr was present in the sediments as Cr (VI), which is anionic and could not be removed by the chelating agent used. There was a slight increase in the residual fraction for samples A and C for the batch extractions, indicating a shift in the fractions.

In sample A, Cu was removed from all the four fractions, especially in the column leaching. There was an increase in the oxidisable fraction of sample D in the column leaching, thus indicating a shift in the fractionation pattern. Generally, the increase in removal efficiency in the fraction for both the batch extraction and column leaching was generally in the order acid exchangeable > reducible > oxidisable > residual fractions.

The amount of Pb in the reducible fraction, which initially had the highest concentration, reduced from 75mg/kg to 18.8mg/kg and 30.8mg/kg for the batch extraction and column leaching respectively for sample B, while it reduced from 165.5mg/kg to 39.4mg/kg and 35.8mg/kg in the batch extraction and column leaching respectively in sample C. Pb was also removed from the oxidisable fraction, indicating that Pb bound to the organic matter was removed as there was a break down of the organic matter. This was observed in the coffee colour of the leachate obtained from both the column and the batch extractions. Fig 3.30 also showed that the higher the amount of reducible Pb present, the higher the amount removed.

Just like Cd, a very high percentage of Zn was removed from the acid exchangeable and reducible phase. This indicates that EDTA was mainly able to remove the metals that were weakly adsorbed onto the sediments, metals that were bound to carbonates, and some of the metals bound to iron and manganese oxides. This is because of the chelating effect of the EDTA, since chelates have been known to have a high stability constant with metals. Samples A-C had between 80% - 92% of Zn in the exchangeable fraction removed in the batch extraction, while between 78%-92% was removed in the column leaching. The amount of Zn present in the exchangeable fraction decreased to 56%, 12%, 22.5% and 8% for samples A, B, C and D respectively, in the column leaching, while it decreased to 50%, 14%, 23% and 8% for samples A, B, C and D respectively in the batch extraction.

3.5.2 Comparison of batch extraction and column leaching, and % recovery studies for remediation

Fig. 3.31 shows the sum of the fractions before treatment with EDTA (Total Pre), the sum of the fractions after EDTA treatment using column leaching+ the amount in leachate on top of it (Total Post Column), and the sum of the fractions after EDTA using batch extractions and the amount in leachate on top of it (Total Post batch) for the samples.

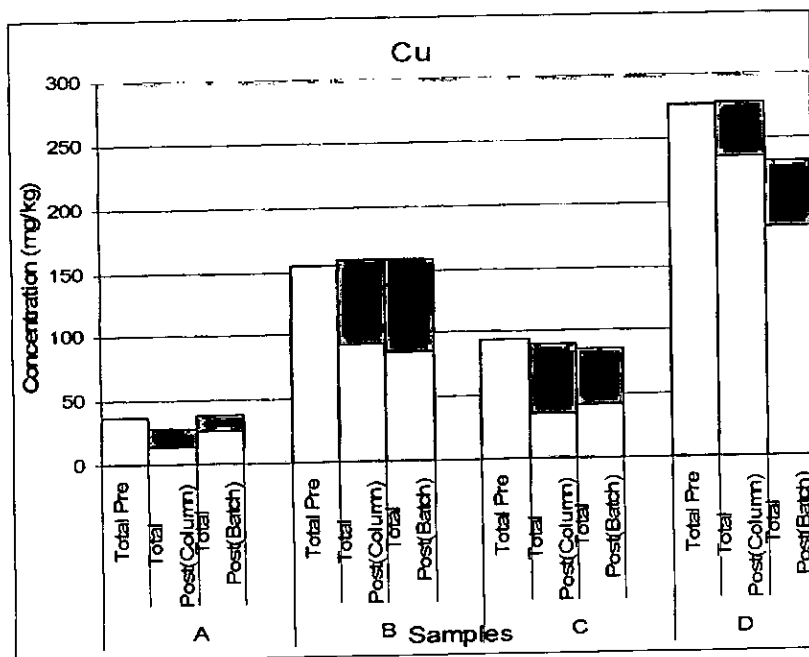
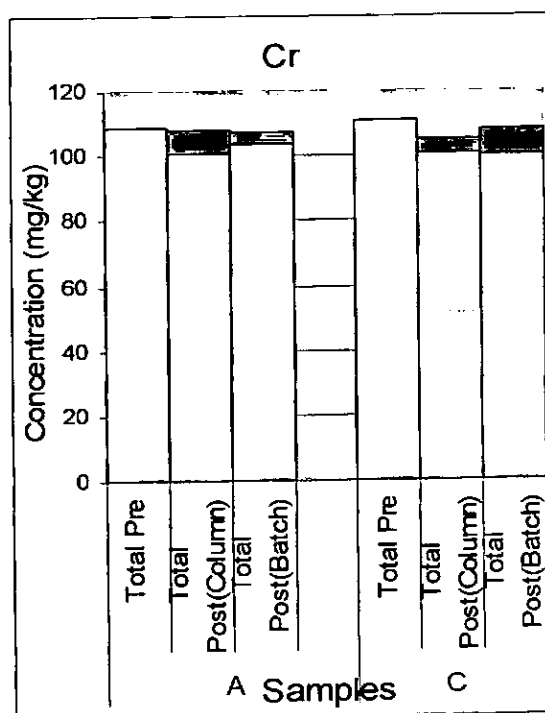
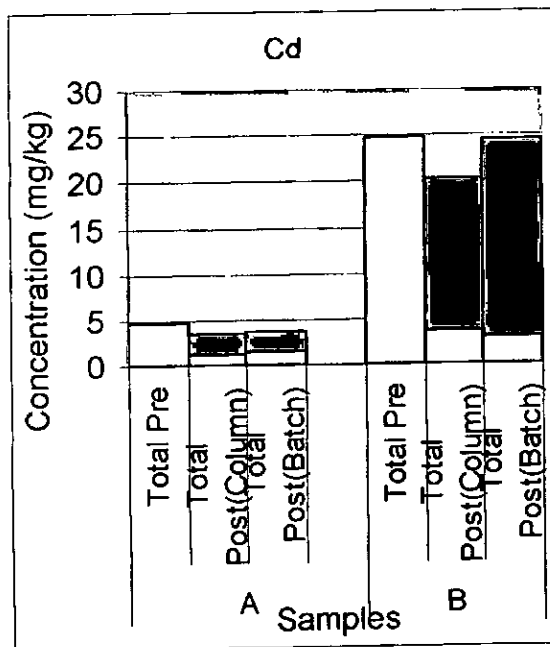
The amount of metals extracted ranged from 48-87%, 3-7%, 18-48%, 8-73% and 8-80% for Cd, Cr, Cu, Pb, and Zn respectively for the batch extraction depending on the sample used, while it ranged from 46-66%, 4-7%, 15-57%, 10-59%, and 9-50% for

Cd, Cr, Cu, Pb and Zn respectively in the column extraction. Sample D had the lowest percentage removal of Cu which is 18% and 15% from batch and column respectively. This is probably because of the nature of the sediment. The sediment had high levels of organics, and the Cu might be tightly bonded to it. This could be because Cu has a very high stability constant with humic complexes, so organic ligands render Cu relatively immobile. This could also account for the low removal of Zn from sample D (8 and 9% for the batch and column leaching). A t-test showed that there was no significant difference between the results from the batch extraction and the column leaching.

Generally, the batch extraction removed a higher % of total Pb probably because there was more contact between the sediment and the extractant solution as compared to the column leaching. The lowest % of total Pb was extracted from sample A. This could be because Pb was mostly present in the residual phase, which is the least mobile, and can therefore not be easily leached by EDTA.

The recovery was calculated by summing up the fractions after remediation and adding the amount in the leachate and dividing by the sum of the fractions before treatment with EDTA. For the batch extraction, the recovery ranged between 81 and 116%, with the exception of Pb in sample A, and Zn in sample D (60 and 67% respectively). For the column leaching, the recovery ranged between 74 and 111% with the exception of Pb in sample A and Zn in sample D (58% and 70% respectively). The low recovery of these samples could be as a result of the shift in

the fractions (redistribution effect), and some of the metals might be trapped in the fraction which is even less mobile than the residual phase. This phase can not be determined using aqua-regia, but could probably be determined by a stronger oxidizing agent (HF).



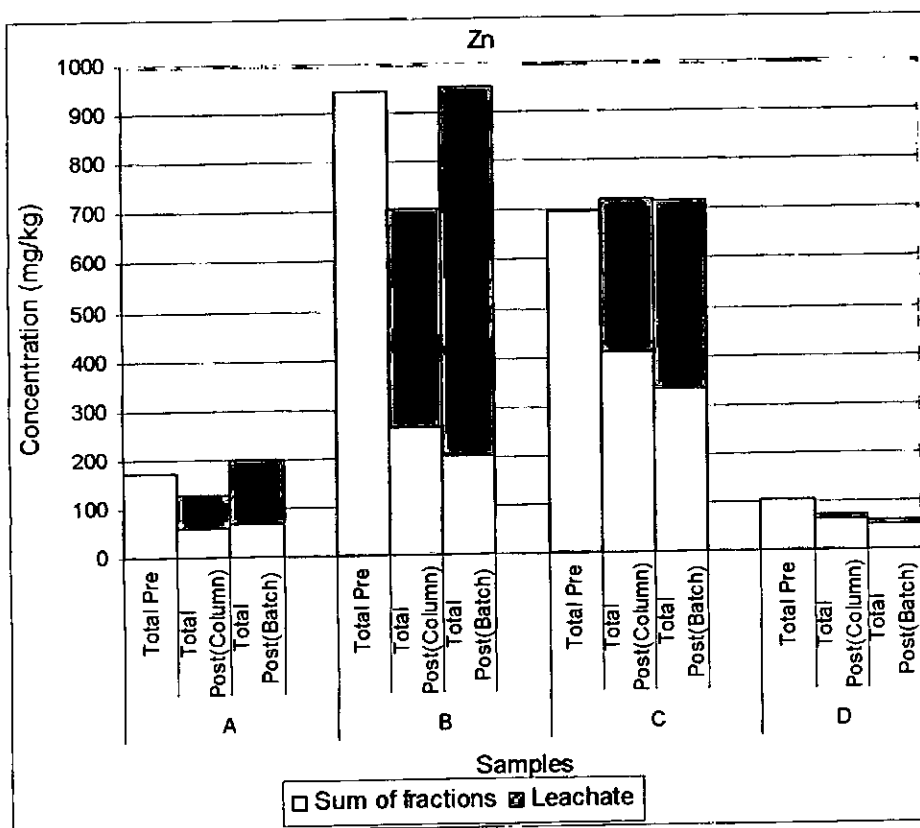
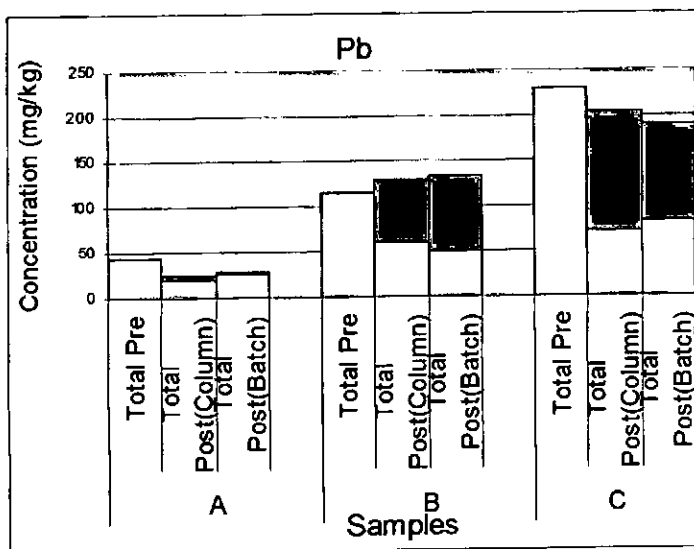


Fig. 3.31. Graph showing recoveries with respect to the total concentration of metals

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

This study has examined the speciation (mobility and bioavailability) and remediation of PTMs in the Lagos Lagoon system (including some adjoining rivers/ creeks). Water and sediment samples collected from Odo-Iyaaloro creek were more polluted with PTMs than those from Shasha and Ibeshe creeks. It was observed that the extent of pollution decreased as we moved into the Lagos lagoon. The relatively low levels of metals in the Lagos lagoon is probably because of the larger amount of sediments involved as compared to the creeks studied. This is due to dilution effect as the creeks empty into the bigger water body. The high amounts of Pb found in samples collected from points under the bridges show the effect of vehicular emissions due to the presence of Pb in our petrol. In Shasha creek Cr, Pb and Zn were significantly negatively correlated with dissolved oxygen in water, and this indicated that the presence of anoxic waters influence the trappings of these metals in the sediments. The generally high concentration of chromium in the Lagos Lagoon indicates that chromium was of terrigenous origin. As chromium can strongly attach to soil/sediment, only a little amount can dissolve in water, the fish also do not accumulate much chromium in their bodies from water, this metal might therefore not be a threat to humans and therefore consumption of fish from the lagoon is safe.

The Enrichment factors determined showed high values for Cd, Cu, Pb and Zn, thus indicating that the source of these metals were anthropogenic. Point 7 along Shasha stream was the most polluted in terms of Pb, Cr and Zn and this may be attributed to vehicular emissions from the high traffic density on the overlying bridge. Of concern also is the extent to which contamination had spread in the streams. For Cu in Ibeshe creek, Enrichment factors were greater than 1 even till the point of discharge into the Lagos lagoon. This was an indication of a wide spread of the contaminant. In Odo-Iyaaloro creek, the distribution of enrichment factors for Pb, Cd, Zn and Cu indicate that contamination may be spreading further out into the coastal environment. Based on the distribution patterns of factor scores, it could be concluded that clay minerals and organic material aggregate to form flocs which effectively concentrate heavy metals in Odo-Iyaaloro stream.

The fractionation pattern of the metals allowed the investigation of their potential mobility in the sediments, that is, their ability to enter the water when there were changes in the environmental conditions of the Lagos lagoon system. Generally for most of the samples, Cd and Zn were found to be associated with the acid exchangeable fraction, while Cr and Cu were found to be distributed between the oxidisable and residual fraction. Pb was found to be mainly associated with the reducible fraction. This was of environmental concern especially for samples MAR PT 5, MAR PT 6, and MAY PT 7, which had high concentrations of lead, which can be released into the aquatic environment under reducing conditions and taken up by the aquatic organisms thereby entering the food chain since the rivers and lagoon are

used for fishing. It was observed from the fractionation pattern of metals in Odo-Iyaalero creek that higher overall concentrations almost always corresponded to higher proportions of metals released in non-residual steps of the BCR. So, the potential environmental impact is greater for two reasons: high concentrations and high lability.

Since the acid soluble and reducible fractions are said to be the most mobile and potentially available fractions, the bioavailability of the potentially toxic elements is in the order $Zn > Cd > Pb > Cu > Cr$.

The washing efficiency of EDTA has been found to be strongly dependent on the source of metal contamination and on metal distribution among the fraction. In the remediation of metals in the sediment samples, up to 80% of Cd and 87% of Zn were extracted in the batch extraction. Generally Zn and Cd had the highest percentage removal, while Cr had the lowest. This was probably because they are mostly present in the acid-soluble/exchangeable phase and reducible phase. These results are consistent with that of Elliot and Shastri (1999) that leaching with EDTA removes HMs mainly from the non-detrital components (exchangeable and reducible fractions), and is ineffective in removing metals from the detrital fractions (oxidisable and residual phase). The amount of metals extracted in the column leaching was comparable to that of batch extraction, as a t-test showed no significant difference in the methods of extraction. Since the column leaching has the advantage of keeping the soil structure intact, it may be more practical and economical to leach polluted soil/sediment by heap leaching after dredging.

4.2 RECOMMENDATIONS

It is recommended that in order to quantitatively evaluate the impact of untreated effluents on the receiving waterbodies, chemical analysis of biota is important. The levels of heavy metals in the diversity of living organisms of the Lagos lagoon system should be examined. Other adjoining creeks and rivers of the Lagos lagoon system should be studied in order to assess their level of pollution, and mathematical models generated for predicting the level of pollutants in the streams/rivers. The levels of metals in living organisms in the streams and the Lagos Lagoon should be correlated with the determined fraction of metals in the non-residual fractions, and bioaccessibility studies should also be carried out.

The kinetics of EDTA as a remediating agent should be studied, and other methods of remediation such as immobilisation of the metals in the sediments should be studied and their fractionation pattern after remediation also studied.

Agencies for environmental Legislation at the Federal/State or LGA level should live up to their responsibilities in ensuring that industries treat their effluents to meet the set standards before they are discharged into the water bodies. The existing Federal and State regulations for limiting pollution of waterbodies need to be strictly enforced. Furthermore, proper Environmental Impact Assessment (EIAs) should be carried out before companies are granted approval for operation. National Standards for sediment quality are urgently needed. This study has also highlighted that a phasedown of Pb in petrol in Nigeria is necessary and vehicles equipped with catalytic converters should be introduced.

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APPENDICES

APPENDIX I: Co-ordinates of sampling points

Odo-Iyaalarostream

Sampling point	Coordinates
3	6° 34' 02.5" N 003° 23' 45.6"E
4	6° 33' 56.0" N 003° 24' 08.9"E
5	6° 33' 54.3" N 003° 24' 25.9"E
6	6° 33' 43.1" N 003° 24' 11.4"E

Shasha Stream

Sampling point	Coordinates
7	6° 31' 46.5" N 003° 18' 57.1"E
8	6° 29' 53.4" N 003° 17' 25.9"E
9	6° 29' 05.6" N 003° 17' 55.7"E
10	6° 26' 15.7" N 003° 20' 17.1"E
11	6° 26' 20.1" N 003° 23' 36.5"E
12	6° 26' 45.1" N 003° 22' 25.9"E

Ibeshe Stream

Sampling point	Coordinates
A	6° 34' 32.8" N 003° 29' 22.9"E
B	6° 33' 56.1" N 003° 29' 44.8"E
C	6° 33' 01.8" N 003° 29' 28.7"E
D	6° 32' 18.5" N 003° 29' 38.1"E
E	6° 32' 52.9" N 003° 29' 40.2"E
F	6° 32' 01.8" N 003° 29' 13.1"E

Lagos Lagoon

Sampling point	Coordinates
Q	6° 28' 10.3" N 003° 23' 04.0"E
R	6° 28' 48.0" N 003° 23' 27.1"E
S	6° 30' 14.1" N 003° 24' 30.5"E
COW	6° 26' 14.2" N 003° 26' 37.3"E
PAL	6° 29' 58.4" N 003° 30' 15.5"E

APPENDIX II : Operating conditions for the FAAS lamp

	Current (mA)	Fuel flow (L/Min)	Air flow	Wavelength (nm)	Slit width (mm)	Lamp energy
Cd	8	2.0	10	228.80	2.7/1.35	64
Pb	10	2.5	10	283.31	2.7/1.05	34
Cu	5	2.5	10	324.75	2.7/0.8	26
Zn	10	2.5	10	213.86	2.7/1.35	44
Cr	12	3.0	10	257.87	2.7/0.8	67

APPENDIX III : FAAS detection limits for standard solutions in 5 % HNO₃

	3s	Slope	DL _{inst} (mg L ⁻¹)	DL _{pro.} (mg kg ⁻¹)
Cd	0.0014	0.2633	0.0055	0.55
Pb	0.0020	0.0131	0.1545	15.4
Cu	0.00298	0.106	0.0281	2.8
Zn	0.0032	0.356	0.0091	0.9
Cr	0.0020	0.0091	0.22	22

APPENDIX IV : FAAS detection limits for standard solutions in solution for speciation

	Step 1 (CH ₃ COOH)		Step 2 (NH ₂ OH.HCL)		Step 3 (NH ₄ OAC)	
	DL _{inst.} (mg L ⁻¹)	DL _{pro.} (mg kg ⁻¹)	DL _{inst.} (mg L ⁻¹)	DL _{pro.} (mg kg ⁻¹)	DL _{inst.} (mg L ⁻¹)	DL _{pro.} (mg kg ⁻¹)
Cd	0.0068	0.27	0.0048	0.19	0.0061	0.31
Pb	0.1667	6.67	0.1640	6.55	0.1627	8.1
Cu	0.0382	1.53	0.0235	0.94	0.0235	1.2
Zn	0.0060	0.24	0.0098	0.39	0.0071	0.35
Cr	0.0552	2.21	0.0583	2.33	0.0963	4.81

APPENDIX V : Physico-chemical parameters of Odo-Iyaalero creek water samples

Jan/ Feb

Parameter	3	4	5	6
Dissolved Oxygen (mgO ₂ /l)	-	-	3.8	1.8
BOD (mgO ₂ /l)	245.4	208.4	14	32
COD (mgO ₂ /l)	278.9	332.2	708.1	613.2
Total Hardness (mgCaCO ₃ /l)	931.4	986.4	1479.6	1521.9
Total Alkalinity (mgCaCO ₃ /l)	344.0	322.3	104.5	123.6
Acidity (mgCaCO ₃ /l)	47.1	38.3	12.1	8.4
Chloride (mg/l)	489.9	1494	5348	5398
Sulphate (mg/l)	17.9	38.5	29.9	37.9
Phosphate (mgP/l)	1.0	1.0	1.0	0.5
Conductivity (μScm ⁻¹)	1050	2240	3,340	3350
pH	6.4	6.8	7.0	7.1
Total Solid ((mg/l)	960	1420	9550	10,340
Total Dissolved Solid ((mg/l)	720	1150	8930	8310

March/April

Parameter	3	4	5	6
Dissolved Oxygen (mgO ₂ /l)	-	-	6.5	4.5
BOD (mgO ₂ /l)	100.8	130.4	32.8	50.4
COD (mgO ₂ /l)	125.4	142.6	365.4	575.6
Total Hardness (mgCaCO ₃ /l)	48	40.3	825	325
Total Alkalinity (mgCaCO ₃ /l)	26.1	17.4	9.1	9.9
Acidity (mgCaCO ₃ /l)	69.6	62.5	7.77	16.4
Chloride (mg/l)	44.0	41.5	178.3	115.2
Sulphate (mg/l)	70.1	34.0	25.8	37.2
Phosphate (mgP/l)	0.3	0.1	0.1	0.1
Conductivity (μScm ⁻¹)	1185	1210	2280	2320
PH	7.1	7.1	7.1	7.0
Total Solid ((mg/l)	1305	3515	13,475	14,850
Total Dissolved Solid ((mg/l)	1050	2810	10,550	11,690

September/October

Parameter	3	4	5	6
Dissolved Oxygen (mgO ₂ /l)	-	-	-	-
BOD (mgO ₂ /l)	54.8	36.0	19.2	16.8
COD (mgO ₂ /l)	75.6	78.2	282.4	288.6
Total Hardness (mgCaCO ₃ /l)	66.6	40.8	198.8	521.9
Total Alkalinity (mgCaCO ₃ /l)	133.8	53.5	53.5	56.2
Acidity (mgCaCO ₃ /l)	16.4	6.0	9.0	9.4
Chloride (mg/l)	34.0	51.5	154.6	103.1
Sulphate (mg/l)	16.2	28.5	24.2	35.4
Phosphate (mgP/l)	0.4	0.2	0.2	0.2
Conductivity (μScm ⁻¹)	625	518	533	465
pH	6.4	6.4	6.2	6.3
Total Solid ((mg/l)	220	180	200	180
Total Dissolved Solid ((mg/l)	210	165	166	145

Nov/Dec

Parameter	3	4	5	6
Dissolved Oxygen (mgO ₂ /l)	-	-	-	-
BOD (mgO ₂ /l)	147	44	20	20
COD (mgO ₂ /l)	162.4	132.2	296.4	204.6
Total Hardness (mgCaCO ₃ /l)	50.4	151.2	201.6	453.6
Total Alkalinity (mgCaCO ₃ /l)	206.1	128.5	96.4	109.7
Acidity (mgCaCO ₃ /l)	71.8	29.2	13.4	17.3
Chloride (mg/l)	36.94	77.8	194.5	194.5
Sulphate (mg/l)	19.9	28.5	39.9	37.2
Phosphate (mgP/l)	1.1	0.5	0.2	0.3
Conductivity (μScm ⁻¹)	1150	1100	700	1150
pH	6.5	6.7	6.7	6.8
Total Solid ((mg/l)	470	390	275	345
Total Dissolved Solid ((mg/l)	360	310	200	310

APPENDIX VI :Physico-chemical parameters of shasha creek water samples

Jan/Feb

Parameter	7	8	9	10	11	12
Dissolved Oxygen (mgO ₂ /l)	-	-	2.9	4.0	3.7	3.0
BOD (mgO ₂ /l)	97.2	239.8	34.4	22.6	41.6	10
COD (mgO ₂ /l)	146	266.5	204	330.2	682.8	690.2
Total Hardness (mgCaCO ₃ /l)	383.6	895	3616.8	4795	4795	4904.6
Total Alkalinity (mgCaCO ₃ /l)	692.4	352.8	121.9	100.2	108.9	126.3
Acidity (mgCaCO ₃ /l)	-	7.5	7.9	2.8	2.3	4.2
Chloride (mg/l)	199.9	110	10246	14646	14720	13820
Sulphate (mg/l)	40.8	82.4	94.6	510.8	310.6	790
Phosphate (mgP/l)	0.2	0.3	0.2	0.3	0.3	0.3
Conductivity (μScm ⁻¹)	940	5,400	140,000	180,000	180,000	210,000
pH	8.9	7.4	7.3	7.6	7.7	7.6
Total Solid ((mg/l)	2020	925	25040	34815	35190	34030
Total Dissolved Solid ((mg/l)	1180	750	22120	33950	32170	32190

September/October

Parameter	7	8	9	10	11	12
Dissolved Oxygen (mgO ₂ /l)	0.7	-	1.3	5.1	3.2	5.4
BOD (mgO ₂ /l)	16.9	19.8	9.4	9.3	39.8	9.0
Total Hardness (mgCaCO ₃ /l)	65.6	178.9	397.6	944.3	546.7	2,584.4
Total Alkalinity (mgCaCO ₃ /l)	107	168.5	101.7	56.2	50.8	72.2
Acidity (mgCaCO ₃ /l)	13.4	15.6	13.4	4.5	4.0	4.0
Chloride (mg/l)	30.9	391.7	979.3	2758.9	1726.7	1984.5
Sulphate (mg/l)	23.93	68.8	161.2	589.2	332.6	788.6
Phosphate (mgP/l)	0.3	1.0	0.4	0.2	0.2	0.1
Conductivity (μScm ⁻¹)	800	6,300	4000	96000	57000	230,000
pH	6.9	7.3	7.3	7.4	7.4	7.7
Total Solid ((mg/l)	195	950	2060	5,800	3,310	15,135
Total Dissolved Solid ((mg/l)	185	900	1925	5730	3115	13690

July/August

Parameter	7	8	9	10	11	12
Dissolved Oxygen (mgO ₂ /l)	-	1.2	3.2	4.7	2.7	5.9
BOD (mgO ₂ /l)	235.6	201.5	34.4	24.4	28.4	7.6
Total Hardness (mgCaCO ₃ /l)	38.2	54.3	56.7	93	115.5	242.7
Total Alkalinity (mgCaCO ₃ /l)	572.4	154.8	120	80	80	100
Acidity (mgCaCO ₃ /l)	-	4.3	4.9	5.8	7.0	10.5
Chloride (mg/l)	70.5	121.4	4523.9	6571	9097.6	14200
Sulphate (mg/l)	52.1	70.2	520.6	1600.8	1817.6	890.7
Phosphate (mgP/l)	0.1	0.1	0.1	0.2	0.1	0.2
Conductivity (μScm ⁻¹)	1200	65,000	175,000	230,000	275,000	415,000
pH	7.9	7.4	7.3	6.3	6.4	6.3
Total Solid ((mg/l)	650	1635	9560	13620	17720	31750
Total Dissolved Solid ((mg/l)	560	1459	1735	11880	16150	30,420

November/December

Parameter	7	8	9	10	11	12
Dissolved Oxygen (mgO ₂ /l)	-	3.8	4.8	2.4	-	4.7
BOD (mgO ₂ /l)	78.8	28	16.6	8.6	52.8	8.4
Total Hardness (mgCaCO ₃ /l)	68.8	2,398.3	2,346.2	3,962.5	2,554.7	5,797.9
Total Alkalinity (mgCaCO ₃ /l)	208.8	123.1	112.4	96.4	234.6	112.4
Acidity (mgCaCO ₃ /l)	19.3	8.9	6.4	3.5	7.9	-
Chloride (mg/l)	39.9	6660.9	6879.7	11911.9	7633	16482
Sulphate (mg/l)	26.8	79.8	112.4	567.9	231.6	576.2
Phosphate (mgP/l)	0.3	1.0	0.4	0.2	0.5	0.1
Conductivity (μScm ⁻¹)	137.5	124500	120,000	195,000	108,000	230,000
pH	7.5	6.8	6.7	7.2	7.8	8.2
Total Solid ((mg/l)	400	14500	14510	14930	15410	36100
Total Dissolved Solid ((mg/l)	340	13100	13180	12580	14080	33100

APPENDIX VII :Physico-chemical parameters of Ibeshe creek water samples
May/June

Parameter	A	B	C	D	E	F
Dissolved Oxygen (mgO ₂ /l)	5.0	-	-	-	3.2	3.8
BOD (mgO ₂ /l)	10.2	165	142	90	15.6	12.8
Total Hardness (mgCaCO ₃ /l)	13.8	122.6	142	201	214.6	322.4
Total Alkalinity (mgCaCO ₃ /l)	15.3	168.3	49.7	45.1	42.1	45.9
Acidity (mgCaCO ₃ /l)	6.6	-	17.2	7.94	10.6	7.3
Chloride (mg/l)	-	42.5	6702.2	528.6	709	830
Phosphate (mgP/l)	0.6	0.3	0.3	1.6	1.8	3.2
Conductivity (μScm ⁻¹)	1050	3900	1350	1350	3750	3000
pH	6.25	9.7	6.8	6.6	6.7	6.7
Total Solid ((mg/l)	320	1240	730	780	1120	1450
Total Dissolved Solid ((mg/l)	160	1980	690	560	840	760

September /October

Parameter	A	B	C	D	E	F
Dissolved Oxygen (mgO ₂ /l)	5.7	-	-	3.3	4.8	4.5
BOD (mgO ₂ /l)	15.8	174	160	62	19.2	30
Total Hardness (mgCaCO ₃ /l)	-	-	23.9	273.4	298.2	447
Total Alkalinity (mgCaCO ₃ /l)	38.2	577.8	267.5	58.9	45.5	48.2
Acidity (mgCaCO ₃ /l)	6.8	-	0.5	4.0	4.5	4.2
Chloride (mg/l)	14.2	37.1	24.7	232	180.4	206.2
Sulphate (mg/l)	38.5	125	158.5	50.8	45.5	47.0
Phosphate (mgP/l)	0.1	0.1	0.1	0.1	0.1	0.1
Conductivity (μScm ⁻¹)	520	5325	2850	2425	1950	2300
pH	6.5	11.3	8.9	6.8	6.7	6.8
Total Solid ((mg/l)	235	1190	800	535	645	640
Total Dissolved Solid ((mg/l)	180	1075	680	525	525	585

July/August

Parameter	A	B	C	D	E	F
Dissolved Oxygen (mgO ₂ /l)	5.2	-	3.3	5.5	5.9	6.1
BOD (mgO ₂ /l)	22.6	358	57.3	32.4	28.6	16.6
Total Hardness (mgCaCO ₃ /l)	15.2	353	18.6	19.6	19.6	19.6
Total Alkalinity (mgCaCO ₃ /l)	58.4	695.9	50	55	45	50
Acidity (mgCaCO ₃ /l)	4.5	-	5.8	7.6	5.8	5.3
Chloride (mg/l)	-	68.1	850.5	902	902	1726
Sulphate (mg/l)	42.4	16.40	43.4	42.2	38.6	43.4
Phosphate (mgP/l)	0.1	0.6	0.1	0.1	0.1	0.1
Conductivity (μScm ⁻¹)	430	4125	10500	33500	34,000	35,000
pH	6.7	9.2	6.8	6.9	6.9	7.0
Total Solid ((mg/l)	340	2530	2250	2400	2050	2160
Total Dissolved Solid ((mg/l)	285	1490	2140	2350	1950	1140

Nov/Dec

Parameter	A	B	C	D	E	F
Dissolved Oxygen (mgO ₂ /l)	3.5	-	-	-	1.7	2.0
BOD (mgO ₂ /l)	14.2	398	97	77	16	21.6
Total Hardness (mgCaCO ₃ /l)	16.8	252	403.2	252.0	151.2	907.2
Total Alkalinity (mgCaCO ₃ /l)	24.2	538	331.9	155.2	69.6	77.6
Acidity (mgCaCO ₃ /l)	6.4	-	21.7	14.9	8.4	4.9
Chloride (mg/l)		53.5	87.5	549.4	607.8	850.9
Phosphate (mgP/l)	0.1	0.7	0.1	0.1	0.1	0.1
Conductivity (μScm ⁻¹)	550	3450	2250	4875	6150	5550
pH	6.8	10.3	8.0	7.7	7.1	7.2
Total Solid ((mg/l)	260	1565	715	1135	1820	1885
Total Dissolved Solid ((mg/l)	180	1420	660	920	1730	1720

**APPENDIX VIII :Physico-chemical parameters of Lagos Lagoon water samples
July/August**

Parameter	Q	R	S	COW	PAL
Dissolved Oxygen (mgO ₂ /l)	6.3	5.2	3.4	6.5	6.1
BOD (mgO ₂ /l)	30.4	24.4	32.6	28.6	20.6
Total Hardness (mgCaCO ₃ /l)	191.8	146.8	156.2	78.3	21.5
Total Alkalinity (mgCaCO ₃ /l)	100	90	90	60	40
Acidity (mgCaCO ₃ /l)	9.3	11.7	12.8	7.0	5.3
Chloride (mg/l)	14,819	11,752	12,453	5,541	721.6
Sulphate (mg/l)	2432.9	2243.0	2343	1,220	93.9
Phosphate (mgP/l)	0.4	0.1	0.2	0.1	0.1
Conductivity (μScm ⁻¹)	410,000	315,000	330,000	170,000	60,000
pH	6.9	6.9	6.9	7.0	7.2
Total Solid ((mg/l)	30870	24270	23780	11080	3,070
Total Dissolved Solid ((mg/l)	28580	23,320	21850	10,840	1,220

September/October

Parameter	Q	R	S	COW	PAL
Dissolved Oxygen (mgO ₂ /l)	5.5	5.4	4.4	6.4	6.5
BOD (mgO ₂ /l)	11.8	21.7	22.2	16.3	15.2
Total Hardness (mgCaCO ₃ /l)	447.3	596.4	149.1	65.8	32.2
Total Alkalinity (mgCaCO ₃ /l)	61.5	74.9	80.3	42.7	32.3
Acidity (mgCaCO ₃ /l)	3.0	3.0	2.5	5.5	6.5
Chloride (mg/l)	798.9	1520.6	283.5	587.2	432.8
Sulphate (mg/l)	303.6	343.4	32.0	43.2	87.6
Phosphate (mgP/l)	0.2	0.3	0.3	0.1	0.1
Conductivity (μScm ⁻¹)	29,000	51,000	3,000	2500	1300
pH	7.8	7.8	7.2	7.2	7.4
Total Solid ((mg/l)	3100	2910	2080	1720	980
Total Dissolved Solid ((mg/l)	2,000	3,070	1500	850	240

November /December

Parameter	Q	R	S	COW	PAL
Dissolved Oxygen (mgO ₂ /l)	4.7	3.7	5.0	6.2	6.4
BOD (mgO ₂ /l)	16.4	16.8	34.2	16.2	14.2
Total Hardness (mgCaCO ₃ /l)	2,057.3	1,783.8	916.3	102.8	96.2
Total Alkalinity (mgCaCO ₃ /l)	101.7	99.0	91.0	56.4	38.2
Acidity (mgCaCO ₃ /l)	-	3.5	4.0	6.1	6.3
Chloride (mg/l)	13,430	12,730	2,722.7	1627.5	1318.2
Sulphate (mg/l)	1528.2	1344.1	936	540	892
Phosphate (mgP/l)	0.2	0.2	0.2	0.1	0.1
Conductivity (μScm ⁻¹)	24,000	21,000	8,000	4800	2100
pH	8.2	7.6	7.5	7.1	7.3
Total Solid ((mg/l)	29,850	25,630	7,820	4250	1280
Total Dissolved Solid ((mg/l)	27730	24060	6900	3890	960

APPENDIX IX: Some parameters (indicative of Gross Organic Pollution) used in the classification of surface water quality

Parameter	Class I	Class II	Class III	Class IV	Class V
pH	6.5-8.0	6.0-8.4	5.0-9.0	3.9-10.1	< 3.9-10.1
Dissolved Oxygen (mgO ₂ /L)	7.8	6.2	4.6	1.8	<1.8
BOD (mgO ₂ /L)	1.5	3.0	6.0	12.0	>12.0
NH ₃ (mg/L)	0.1	0.3	0.9	2.7	>2.7
COD (mgO ₂ /L)	10	20	40	80	>80
Suspended Solids (mgO ₂ /L)	20	40	100	278	>278

NB: Class I Excellent Quality
 Class II Acceptable Quality
 Class III Slightly polluted
 Class IV Polluted
 Class V Heavily Polluted

Source: Prati et al., (1971)

APPENDIX X: The percentage recoveries obtained from the three different SES

Metal	Original BCR	Tessier method	Modified BCR
Cd	107 ± 7	130 ± 2	106 ± 15
Cr	98 ± 16	110 ± 22	98 ± 14
Cu	85 ± 19	94 ± 29	86 ± 19
Pb	111 ± 10	98 ± 9	110 ± 10
Zn	99 ± 9	97 ± 13	103 ± 9