IMPACT OF ANTHROPOGENIC ACTIVITIES ON THE WATER QUALITY OF SONGOR LAGOON, ADA, GREATER ACCRA REGION

By

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DECLARATION

This thesis is the original research work undertaken by Justice Sackey in the Department of Nuclear Sciences and Applications, University of Ghana, under the supervision of Dr. Dennis Adotey and Prof. Samuel Dampare.

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DEDICATION

I dedicate this work to the almighty God for his grace, guidance and protection and to my mother, Madam Regina Aryeetey, siblings and my beloved Ms. Ellen Akofa Terkper for their support and encouragement throughout my studies.

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ABBREVIATIONS

µg/g	Microgram per Gram
AAS	Atomic Absorption Spectrophotometry
ALK	Alkalinity
As	Arsenic
BDL	Below Detection Limit
BOD	Biological Oxygen Demand
Ca	Calcium
CA	Cluster Analysis
Cd	Cadmium
Cl	Chloride
Cr	Chromium
Cu	Copper
CV-AAS	Cold Vapour Atomic Absorption Spectrophotometry
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
ECD	Electron Capture Detector
EF	Enrichment Factor
EPA	Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectrophotometry
Fe	Iron

ABBREVIATIONS (CONT)

GC	Gas Chromatography
H_2SO_4	Sulphuric Acid
HCH	Hexachlorocyclohexane
HCl	Hydrochloric Acid
$HClO_4$	Perchloric Acid
HCO_3^-	Bicarbonate
Hg	Mercury
HG-AAS	Hydride Generation Atomic Absorption Spectrophotometry
HNO_3	Nitric Acid
HPLC	High Performance Liquid Chromatography
IAEA	International Atomic Energy Agency
K	Potassium
LOD	Limit of Detection
LOQ	Limit of Quantification
MAE	Microwave Accelerated Extraction
MCL	Maximum Contamination Limit
MDL	Minimum Detection Limit
Mg	Magnesium
mg/Kg	Milligram per Kilogram
mg/L	Milligram per Litre
MOFA	Ministry of Food and Agriculture
Na	Sodium

ABBREVIATIONS (CONT)

ND	Not Detected
Ni	Nickel
NO_3^-	Nitrate
^oC	Degrees Celsius
OCPs	Organochlorine Pesticides
Ops	Organophosphorus Pesticides
Pb	Lead
PC	Principal Component
PCA	Principal Component Analysis
PCBs	Polychlorinated Biphenyl
PFPD	Pulse Flame Photometric Detector
PO_4^{3-}	Phosphate
SAL	Salinity
SO_4^{2-}	Sulphate
SPE	Solid Phase Extraction
SPs	Synthetic Pyrethroids
TDS	Total Dissolved Solids
TEMP	Temperature
TH	Total Hardnes
UNEP	United Nations Environmental Program
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
Zn	Zinc

ABSTRACT

Wetlands are vital ecosystems with important social, economic and environmental functions. The Ada Songor lagoon (located in the Dangbe East district, Greater Accra Region), is an internationally designated wetland (Ramsar site). Intense anthropogenic activities have impacted negatively on the quality of water and sediment in the lagoon. The study assessed the extent of heavy metal, pesticide residues and nutrients contamination of surface water and sediment in the Ada Songor Lagoon. The objective of the study was achieved through the determination of physico-chemical parameters [pH, temperature, electrical conductivity (EC), salinity, total dissolved solids (TDS), alkalinity, turbidity, biological oxygen demand (BOD), total hardness)]; the nutrients load (SO_4^{2-}, PO_4^{3-}, NO_3^-) using UV-Visible Spectrophotometry; major ions (Na^+, K^+, Ca^{2+}, HCO_3^-); trace metals (Cd, Cr, Ni, Pb, Co, Zn, Cu, As and Hg) using Atomic Absorption Spectrometry (AAS); and, pesticides residues [organochlorines (OC's), and synthetic pyrethroids by gas chromatography-electron capture detection (GC-ECD) and organophosphorus (OP's) by gas chromatography-pulse flame photometric detection (GC-PFPD)]. Na and K contents were determined by Flame Emission Photometry. The water temperature (25.7 to 26.6 ^oC), fall in the range of 25 to 30 ^oC suitable for sustainability fish and aquatic organisms. The pH range (8.18 to 9.70) which is typical of coastal waters in Ghana is ideal for aquatic organisms. The TDS range (591 to 1,046 mg/L) is not ideal for water birds spawning since it make it harder for them to find food. BOD ranges from 1.19 to 5.35 mg/L. The pattern of ionic dominance in the lagoon during the present study was $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The cationic dominance pattern was similar to that of seawater as observed by other works. Nitrate levels ranges from 0.83 to

0.92 mg/L. PO_4^{3-} in this study varied from 0.05 to 2.92 mg/L which exceeds the levels in most natural waters. The hydrogen sulphide like smell of the sediment in the lagoon may be due to the levels of the sulphate levels (65.8 to 190 mg/L). The concentration (in ranges, mg/L) of trace metals in water samples were: Cd (<0.001 to 0.09 mg/L); Pb (<0.001 to 0.42 mg/L); Ni (<0.001 to 0.18 mg/L); Cr (<0.001 to 0.03 mg/L); Mn (<0.001 to 0.14 mg/L). The concentration (in ranges, mg/Kg) of trace metals in sediment samples were: Cd (<0.001 to 0.44 mg/Kg); Pb (<0.001 to 3.83 mg/ Kg); Ni (<0.001 to 1.60 mg/Kg); Cu (<0.001 to to 0.21 mg/Kg); Cr (<0.001 to 0.17 mg/Kg); Mn (<0.001 to 0.14 mg/L); Zn, (<0.001 to 1.19 mg/Kg); Fe (134 to 1429 mg/Kg). The following elemental associations were obtained from Principal Component and Hierarchical Cluster Analyses (PCA and HCA): Mg-Mn-As-Pb, Cd-Ni and K. This could be linked to usage of agrochemicals by farmers and dumping of domestic waste. Cd and Ni occur as important anthropogenic markers in the lagoon. Enrichment Factor indicated high enrichment of the metals (especially Cd and Pb). Six (6) different types of organochlorine pesticide residues and metabolites (β-HCH, γ-HCH, σ-HCH, heptachlor, aldrin and β-endosulfan) were detected in the sediment (0.001-0.101 μg/g). 12 different types of organophosphorous [0.004 and 7.494 μg/g] (diazinon, fonofos, dimethoate, pirimiphos, chlorpyrifos, malathion, fenitrothion, parathion, chlorfenvinphos, profenofos, phorate, ethoprophos) were identified in the sediment. Six (6) synthetic pyrethroids residues and metabolites (cypermethrin, bifenthrin, permethrin, fenvalerate, deltametrin, cyfluthrin and alethrin) were detected in the sediment [0.001-0.014 μg/g]. The Principal Component Analysis, supported by Custer Analysis identified anthropogenic and natural/geogenic sources as responsible for controlling the variability of pollutants in surface water and sediment.

CHAPTER ONE

INTRODUCTION

1.1 Background to the study

The United Nations Convention on Wetlands of International Significance [Ramsar Convention (1971)], defines wetlands as areas of lands whose soil is saturated with moisture permanently or seasonally and are covered partially or completely with shallow pools of water which may be fresh, salt or brackish (Ramsar Convention Secretariat, 2013; Ghana National Commission on UNESCO, 2010). Wetlands are vital ecosystems with significant social, economic and environmental functions, such as, control of storm surges, regulation of river flow, filtration of pollutants, provision of nesting sites and nursery sites for important biodiversity. In addition, wetlands also play an important global role in regulating atmospheric carbon dioxide (Russi *et al*., 2013; Ramsar Handbook 7, 2007; Barbier *et al*., 1997; Ghana National Commission on UNESCO, 2010).

As a party to the United Nations Convention on Biological Diversity and the Ramsar Convention, the African Convention on the Conservation of Nature and Natural Resources (1968), and also as a member of the World Network for Biosphere Reserves, Ghana has the responsibility to ensure the sustainable utilization of wetlands for human benefit, in a way compatible with the maintenance of the natural properties of the ecosystem (Abdul-Razak, 2012).

Ghana has numerous wetlands (Muni-Pomadze, Densu Delta, Sakumo, Songor, Keta Lagoon Complex and Owabi) by virtue of drainage by several rivers. The coastal area is particularly noted for this due to the presences of four major rivers, over 90 lagoons, as well as marshes, estuaries and swamps (Finlayson *et al*., 2000; Ghana National Commission on UNESCO, 2010). However, increasing population has led to tremendous pressure on the resources of all wetlands in Ghana. High rural-urban migration coupled with high anthropogenic activities, have underscored the need for the protection of the wetlands from impacts of land-based activities (Gyasi *et al*., 1995; Yeboah *et al*., 2013). In view of the international importance of Ramsar sites, there is a need for constant monitoring of the quality of water and sediment at Ramsar sites in order to ascertain threats to the life of such sites due to continuing anthropogenic activities within the catchment areas of the sites.

The Songor wetland (located at Ada in the Dangbe East district of the Greater Accra region of Ghana) is one of the largest Ramsar sites in Ghana. It is associated with the Volta estuary. The Songor wetland is important for migratory birds en route the East Atlantic fly way and other animal species listed in the International Union for Conservation of Nature (IUCN) Red Data List which are wholly protected in Ghana (Finlayson *et al*., 2000). The site also has the highest total tern count on the Ghana coast and supports naturally important bird populations (over 10% of the total coastal count). The most significant species groups identified for conservation included 3 species of marine turtle (leather back, olive ridley and green turtle), the West African manatee, the red and white mangroves, the mona and green monkeys, the Nile and west African Crocodiles, the African python, genet cat, fifteen (15) fish species and forty two (42)

species of water birds (Ntiamoa-Baidu and Gordon, 1991; Piersma and Ntiamoa-Baidu, 1995; Ntiamoa-Baidu *et al*., 1998).

1.2 The impact of anthropogenic activities on the quality of water and sediment in the Songor lagoon

Disturbances and threats, including changes in land use and major development projects (factors which may have a negative impact on the water and sediments quality of the Songor lagoon) include; over-fishing, over exploitation of mangroves, blocked creek channels, refuse dumping in lagoon to reclaim lands, over population, conversion of ecological habitats into salt pans and farms, over-grazing, use of pesticides/herbicides for farming, building across river channels and damming of freshwater channels (Ramsar Wetland Information Sheet, 1998).

Despite the international importance of wetlands and the need to conserve them, there is scarce or no data on the quality of water and sediment in the Songor Lagoon. Lagoons have limited water circulation to compensate for changes in water quality and are susceptible to anthropogenic pollution (Johnson *et al*., 2007). In lagoon systems, water quality assessment is of vast importance in sustaining ecological characteristics. Coastal lagoons are favorable habitats for primary producers (phytoplankton and aquatic plants) because of their relatively low flushing rates (Anthony *et al*., 2009). Nitrogen and phosphorus are dissolved nutrients that occur in limited quantities in natural aquatic environments (Brooks *et al*., 1997). Increased amounts of nitrogen and phosphorus can increase the eutrophication of water bodies, which in turn reduces dissolved oxygen

content and adversely affects aquatic life (Brooks *et al*., 1997). Toxic pesticides can contaminate waterways and wells, harming wildlife and making drinking water unfit for consumption (U.S. EPA, 2000).

Bioaccumulations of contaminants and toxicological effects on wildlife have been documented for wetlands receiving non-point source runoff (Ohlendorf *et al*., 1989; Schuler *et al*., 1990; Welsh and Maughan, 1994; Glenn *et al*., 1999; Garcia-Hernandez *et al*., 2001). Impacts can include direct toxicity to algae and aquatic plants, wetland fauna including wetland invertebrates, amphibians, reptiles, fish, and birds, resulting in the loss of biodiversity and simplification of the food chain (Wren *et al*., 1997; Adamus *et al*., 2001). These impacts have been demonstrated for organophosphorus and pyrethroid pesticides, polyaromatic hydrocarbons, PAHs (Maltby *et al*., 1995), polychlorinated biphenyls, PCBs (Dunier and Siwicki, 1993; Wren *et al*., 1997; Adamus *et al*., 2001), and heavy and trace metals such as mercury (Hg), lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd) [Yousef *et al*., 1990; Campbell, 1994].

1.3 Statement of the Problem

Anthropogenic activities around the Songor lagoon are farming, fishing, salt mining, and tourism. Degradation of the ecosystem is inevitably visible and manifested by changing vegetation and land uses, prevalence of invasive aquatic weeds, coastal erosion and siltation (Ramsar Wetland Information Sheet, 1998).

The Songor Lagoon and its associated ecosystems are highly valued by the communities surrounding it. Social and economic values of the lagoons range from commercial,

recreational, to tourism. Some social and economic values also include ecosystem services that indirectly support human uses (Yeboah *et al*., 2013). The lagoon and surrounding floodplains support large numbers of people through fishing, salt extraction, reed cutting and water supply for agriculture, and also protect developed shorelines by reducing the impact of severe storms (Finlayson *et al*., 2000).

Accordingly, monitoring of the Songor wetlands to ascertain the quality of water and sediment has become imperative in order to acquire baseline data which will serve as reference for further and future monitoring.

1.4 Objectives of the study

The study endeavours to assess the extent of heavy metals, pesticides and nutrients contamination of surface water and sediment in the Ada Songor Lagoon due to anthropogenic activities around the catchment area of the lagoon. The study will also assess unanticipated threats to the ecosystem.

1.4.1 Specific Objectives of the Study

The specific objectives of the study are:

(a) To identify the impact of each anthropogenic activity on the quality of water and sediment in the lagoon;

(b) To assess the degree of anthropogenic contamination using geo-accumulation index and enrichment factor;

(c) To identify the threat posed by anthropogenic activities to the total tern count contribution of Ghana;

(d) To assess the contribution of anthropogenic activities to loss of biodiversity; and,

(e) To recommend appropriate and sustainable mitigation measures to help curb contamination of the Ada Songor Ramsar Site.

1.5 Justification for the study

Contaminated sediments can threaten aquatic creatures in the benthic environment, exposing worms, crustaceans and insects to hazardous concentrations of toxic chemicals. Some polluted sediment can kill benthic organisms, thereby reducing the food available to larger animals such as fish (Pan and Brugam, 1997). Pollutants in aquatic ecosystems precipitate on sediments surface as deposited pollutants. Sediments are well known sinks for metal contaminants (Li and Thornton, 2001). Contaminated sediments do not always

remain at the bottom of a water body. When the water stirs up due to activities such as dredging, sediments can re-suspend. Re-suspension may mean that all of the animals in the water and not just the bottom-dwelling organisms will be directly exposed to toxic contaminants (Pan and Brugam, 1997).

Water and sediment quality characteristics are important factors in maintaining healthy lagoon habitats. In an attempt to maintain lagoon sustainability and assess the societal value of lagoon ecosystems, which are strongly impacted by anthropogenic activities (Lotze *et al*., 2006; Nixon *et al*., 2007), it is important to monitor the watershed with appropriate descriptors of both the water and the benthic (sediment) components of lagoon ecosystems (Souchu *et al*., 2000).

The present study assesses the impact of anthropogenic activities on the quality of surface water and bottom sediments in the Ada Songor Lagoon.

CHAPTER TWO

LITERATURE REVIEW

Wetlands are receiving increasing attention due to population pressure, developmental activities related to manufacturing, trade and transport, agriculture, extraction of natural resources, presence of vital and critical habitats. The loss of habitats, deteriorating water quality, sedimentation, and municipal and industrial pollution are of major concern to wetland zone managers.

This chapter focuses on the most relevant work done in the area from available literature in a manner that will give a comprehensive picture of the current state of research in the field. This chapter also discusses lagoon ecosystem, as well as environmental impact caused by human activities. Water and sediment quality parameters and pollution indices are also discussed. Analytical methods are also discussed.

2.1 Review of previous studies on anthropogenic impact on water and sediment quality of lagoons

Lagoons and estuaries are among Ghana's most critical habitats providing fish and other wildlife resources in support of the country's economy. In the context of climate change, it is feared that these ecosystems are faced with enormous threat. Possible impacts relate to sea level rise (SLR) that may result in widespread loss of these habitats. Land use changes around wetlands could magnify the impacts of climate change on these

ecosystems and may be disastrous for the welfare of coastal communities due to its potential impacts on property, water and food security (Aheto *et al*., 2011).

Apau *et al*., (2012) carried out on a study the Kpeshi Lagoon to identify the chemical and physical characteristics of the water. The study revealed that a lot of industrial activities are carried out around the Lagoon and it is being gradually turned into a place of refuse damp. Nutrient and organic matter were found to be the most frequent cause of pollution of the lagoon with mean sulphate, nitrate and phosphate concentrations of 11,852 mg/L ± 2,915.08, 2,905.71 mg/L ± 616.52 and 487.14 mg/L ± 257.02 respectively. Iron (Fe) and aluminum (Al) recorded the highest concentration of 13.2 mg/L ± 3.47 and 13.6 mg/L ± 4.29 respectively in water sample. Fish sample revealed calcium and potassium as having the highest concentration of 15,709 mg/Kg ± 75.35 and 5,999.94 mg/Kg ± 87.30 respectively with sodium and aluminium recording 3,775.70 mg/Kg ± 24.80 and 708.47mg/Kg ± 4.95 respectively. The results as compared to the WHO guidelines indicate that the Lagoon is highly contaminated.

The heavy metal burdens in the sediments of the Fosu lagoon of Cape Coast revealed significant variations in the distribution of the metals, with Pb showing the greatest variation and Fe the least. Enrichment level of Fe was minimal; Cu and Zn were significantly enriched and Pb showed very high to extremely high enrichment. The average geo-accumulation values and pollution load index calculated for the five studied sites indicated that the lagoon is practically unpolluted with Fe, Cu and Zn, but moderately polluted with Pb (Bentum *et al*., 2011).

The Keta Lagoon and its catchment areas in Ghana are influenced by intensive agriculture and the use of agro-chemicals. The Water Quality Index of the Keta lagoon and its floodplains showed various degrees of poor water quality and therefore considered unsuitable for drinking and recreation. By WHO standards, this calls for intensive physical and chemical treatment of the water for human consumption (Lamptey *et al*., 2013).

The Densu River is a typical river used for drinking water source, flowing through agricultural areas in Southern Ghana. Fianko *et al*., (2011) detected organochlorines pesticide residues and metabolites in water and sediment samples (dieldrin, DDT, DDE, endosulfan sulphate, α - endosulfan, γ - HCH, δ - HCH, aldrin, γ - chlordane ,endrin, endrin ketone, endrin aldehyde, methoxychlor and heptachlor). From the research, in an average of 13.69% of sediment and 3.30 % of water samples, at least one pesticide residue was detected per sample. A total of 8 different pesticides residues were detected in water samples with concentrations ranging between 0.1 µg/L and 48.6 µg/L whiles in sediment samples 14 different types were detected with concentrations ranging between 0.10 µg/L and 163 µg/L. Endosulfan, endrin and chlordane registering levels above their recommended limits of 20.0 µg/L, 0.600 µg/L and 0.200 µg/L respectively for drinking water. The results revealed that improper land use in the basin has led to poor water quality.

Water samples were collected from the Sakumo lagoon for NO_2-N, PO_4-P, NO_3-N and NH_4-N, analysis showed that, of all the nutrients studied, phosphates were the highest in the Sakumo lagoon. And the nutrient levels in the lagoon have also shown significant increase over the years (Nartey *et al*., 2011).

Laar *et al.*, (2011) in the study of the pollution status of the Sakumo Ramsar using Hydrochemistry and Isotopic Composition indicated both higher enrichment of heavier isotopes and higher chloride concentration in water samples from the lagoon than in water samples from other sources (industries and feeder streams).

Nutrient and organic matter were among the frequent source of pollution in the Kpeshi lagoon with mean sulphate, phosphate and nitrate concentrations of 190 ± 109, 1.62 ± 0.49 and 0.89 ± 0.26 mg/L, respectively. Fish samples however revealed very high concentrations of calcium and potassium measuring 15,709 ± 75.35 and 5,949.49 ± 87.30 mg/Kg, respectively. Sites closer to settlement community and the hospitality industries appeared to be relatively more contaminated (Fianko *et al*., 2013).

Addo *et al*., (2012) studied the levels of metal contamination and distribution in the sediment samples in the Mokwé Lagoon were assessed using geoaccumulation index, enrichment factor, contamination factor and pollution load factor. The metal index analysis indicated high enrichment of the metals (especially Cr and Ni) which reflected anthropogenic effects of contamination attributable to several sources. The study calls for constant environmental monitoring to forestall any heavy metal hazard which could be detrimental to the aquatic ecosystem of the lagoon.

2.2 Lagoon Ecosystems

2.2.1 Physical Characteristics of Lagoons

A coastal lagoon is a "shallow coastal water body separated from the ocean by a barrier, connected at least intermittently to the ocean by one or more restricted inlets" (Kjerfve, 1994). With a geographic range stretching from the arctic to the tropics (Nichols and Boon 1994), coastal lagoons are typically found along low-lying coastlines that have a tidal range of < 4 m (Martin and Dominguez 1994). Lagoons constitute 13% of coastal regions globally, range in area from < 0.01 km² to > 10,000 km², and are typically < 5 m deep (Bird, 1994; Kjerfve, 1994).

Coastal lagoons are formed and maintained through sediment transport processes. Sediment carried by rivers, waves, currents, wind, and tides accumulates in river and tidal deltas, on marshes and flats where submerged aquatic vegetation slows currents, and on wash-over fans (Anthony *et al*., 2009; Nichols and Boon, 1994). The process of sedimentation can eventually fill in lagoons. Lagoon barriers are constantly eroded by waves and wind, requiring continuous sediment deposition to maintain them (Bird, 1994; Nichols and Boon, 1994).

Water quantity and quality in a lagoon is influenced by the rate at which the lagoon loses or gains water from evaporation, precipitation, groundwater input, surface runoff, and exchange with the ocean (Allen *et al*., 1981). Lagoon-ocean exchange is driven by tides and wave action and is often the largest component of lagoon water balance. Heat is also lost and gained through exchange with the atmosphere, sediment, and ocean (Smith, 1994; Zimmerman, 1981).

The flushing rate, i.e., the rate at which water enters, circulates through, and exits the lagoon, is a fundamental physical property and controls the retention time of waterborne constituents. Lagoons tend to have low flushing rates because of restricted exchange with the ocean, contributing to high primary productivity and potentially high pollutant concentrations (Spaulding 1994). Determinants of the flushing rate include the size and shape of the lagoon, the level of connectivity with the ocean, tidal range, and freshwater flow (Phleger 1981).

2.2.2 Ecological Characteristics of Lagoons

Coastal lagoons are highly productive ecosystems. They contribute to the overall productivity of coastal waters by supporting a variety of habitats, including salt marshes, seagrasses, and mangroves. They also provide essential habitat for many fish and shellfish species. For example, seagrass beds are a common feature of soft-substrate lagoons on the Atlantic coast. Where seagrass beds occur, *Zostera marina* (eelgrass) is the most dominant species from Maine to the Carolinas, whereas *Thalassia testudinalinum* (turtle grass) is the most dominant species south of the Carolinas (Bertness, 2007). Such beds play an important role in influencing the shape and stability of the shoreline, regulating dissolved oxygen (Nixon and Oviatt, 1972), and filtering suspended matter (Bertness, 2007). They can enhance the biodiversity of a lagoon by providing a physical refuge from predation and also serve as nursery and feeding habitats for a variety of organisms (Heck and Thoman 1984; Harris *et al*., 2004). On the Atlantic coast, salt marshes are one of the most prevalent habitats in lagoons (Bertness, 2007) and

are one of the most productive natural vascular plant communities in the world (Whittaker, 1975).

Because of their relatively low flushing rates, coastal lagoons are favorable habitats for primary producers (phytoplankton and aquatic plants). Nutrients are transported to lagoons from surface water and groundwater flows and through exchange with the ocean. Because nutrient availability often limits primary productivity, coastal lagoons can foster high rates of primary production, thereby supporting high rates of secondary production compared to other aquatic ecosystems (Nixon, 1982, 1995). However, primary production that exceeds the demands of consumers can lead to eutrophication (Valiela *et al*., 1992). Eutrophication is characterized by excessive phytoplankton and macroalgal blooms and subsequent hypoxia, reduced light penetration (McGlathery, 2001; Anderson *et al*., 2002), stress and die-offs of marine organisms, loss of seagrass beds, changes in food web interactions and community structure, and loss of biodiversity (National Research Council, 2000).

2.2.3 Social and Economic Value of Lagoons

Lagoons and their associated ecosystems are highly valued by society. Social and economic values of coastal lagoons range from commercial, recreational, to tourism. Some social and economic values also include ecosystem services that indirectly support human uses. For example, salt marshes provide nursery habitat for juvenile fish that support commercial fisheries and also protect developed shorelines by reducing the impact of severe storms.

Coastal lagoons provide productive activities that include photography and landscape painting, as well as settings for films, literature, songs, and other artistic expressions. These artistic creations encompass both personal aesthetic response to natural systems and profit from the sale of resulting artworks. Coastal lagoons also provide enjoyment of scenery, sounds of waves and shorebirds, and other sensory landscape features.

Small seaside cottages on stilts, for example, sit alongside lagoons or barrier islands and command million dollar price tags. Such prices reflect the powerful effect of values on coastal waterfront property. The strength of coastal lagoon values is clearly evident when people choose to live in areas of high environmental risk such as low-lying coastal landscapes to benefit from aesthetic amenities or the cultural sense of place that these landscapes provide (Couzin, 2008).

2.3 Economic importance of the lagoon to the people of Dangbe East District

The Songor Lagoon is of particular cultural and utilitarian value to the local people living in and around Ada. Reeds, fuel wood, tilapia, crab, and other game are harvested from the site on a mainly subsistence basis (Finlayson *et al*., 2000), while salt is extracted for widespread distribution in Ghana and across West Africa. In addition to harvesting the natural products of the lagoon, the local people use the land around the lagoon for cattle grazing, road development, and farming cassava, maize, tomatoes, okra, pepper, beans, onions and watermelons. The lagoon is also viewed as a sacred cultural site for some (Yeboah *et al*., 2013). Additionally, several community leaders of Ada have indicated

that the natural habitat surrounding the town has been traditionally protected for generations. Aside from granting the lagoon and Volta estuary recognition as some of the few places left on earth where sea turtles still nest, the people of Ada believe that these sites are powerful places where human, animal, and other spirits meet. (Ntiamoa-Baidu and Gordon 1991)

Songor Lagoon's complement of rare and diverse species makes it a popular tourist attraction. Birders are probably the lagoon's most avid ecotourists, attracted to the thousands of birds that migrate to the site in the European winter. The area's two bird watching platforms, one in Pute and one in Lolanya, host the birders while they observe and photograph varieties such as sandwich, black, royal, roseate, and little terns, black-winged stilts, ringed plovers, curlew sandpipers, spotted redshanks, and greenshanks. The lagoon's second most popular ecotourist attraction is its guided sea turtle walk program. The walks are managed by the Ghana Wildlife Division, with the best months to see turtles being August through March.

2.4 Threats to the life of the lagoon

The main threats to the site exist as varied forms of excessive utilization. Some common cases are over-fishing, extreme harvesting of mangroves, extensive drainage and cultivation for farmland, heavy grazing by cattle and livestock, and an unsustainable level of salt winning (Ntiamoa-Baidu, 1991, Yeboah *et al*., 2013). These threats are difficult to neutralize because the human communities surrounding the lagoon are largely poor and over-populated. In effect, the local people are dependent upon their harvesting of the lagoon for survival. Although ecotourism provides an ecologically friendly source of

income, the practice is not extensive enough to sustain the local communities (Yeboah *et al.*, 2013).

Additional threats originate from the use of pesticides and herbicides, the damming of creeks and channels for the purpose of expanding infrastructure, and rubbish dumping. These threats can and, in some instances, have had dire consequences. The breeding cycles of nesting species, like the several sea turtle species hosted by the lagoon, can be disturbed by exaggerated human activity. Furthermore, the eggs of such species are often trampled by grazing cattle and livestock. Another realized effect of human exploitation is the apparent shrinking of the lagoon, which can be easily observed in the satellite photo comparison shown at the opening of this article. Further disturbance of the lagoon could result in not only the loss of species that inhabit the site, but also the loss of nutritive and moderating benefits provided by the site. Aside from purifying ground water, acting as a reservoir for nutrients, and supporting the local food chain, the lagoon regulates water flow, staggers and lessens the effects of flooding, and disperses the extreme erosive forces exerted on the shore by the Atlantic Ocean (Ghana National Commission on UNESCO, 2010).

2.5 Water and Sediment Quality

The total chemical composition of surfacial sediments is a valuable index of environmental contamination. They are a poor means of assessing the pathways by which the contaminants have accumulated in the bottom sediments. Therefore, chemical availability of contaminants on sediments had been used to deduce the sources and

pathways by which major and trace contaminants had entered the aquatic environment (Wren *et al*. 1997).

Variations among the sediments worldwide may, however, be large, due to regional differences in climate, topography, geology, and vegetation. Moreover the contribution from human activity to the chemistry of the aquatic system is in many cases significant. The geochemical characteristics of the sediments can be used to infer the weathering trends and the sources of pollution (Glenn *et al*., 1999; Garcia-Hernandez *et al*., 2001). The sediment history broadly reflects the contamination history of an area. Currently, environmental pollution because of urbanization and industrial development is a major concern (Lotze *et al*., 2006; Nixon *et al*., 2007).

Sediments provide useful information about the water quality from a past period and about the events that occurred in pre-cultural time. The pollution history of aquatic ecosystem had been studied by sediments (Oyewale and Musa, 2006). Many researchers had used sediment to study the behavior of metals (Berke, 2006).

2.6 Water and Sediment Pollutants

2.6.1 Heavy metal

Metals enter the environment by two means: natural processes (including erosion of ore-bearing rocks, wind-blown dust, volcanic activity and forest fires); and processes derived from human activities by means of atmospheric deposition, rivers, and direct discharges or dumping (Clark, 2001). Over the past three decades, metals had been discharged into

the world's rivers and estuaries as a result of rapid development (Sin *et al*., 2001). Unlike organic contaminants, natural processes of decomposition do not remove heavy metals; instead heavy metals can be enriched by aquatic organisms and can therefore be converted to organic complexes that may even be more toxic (Kishe and Machwa, 2003).

Anthropogenically introduced metals were ultimately transferred to the bed sediments (Ahmed, 2005). Although sediment analysis do not represent the extent of toxicity, they are useful to assess the burden of anthropogenic component over and above lithogenic background and also in some instances, trace the sources of pollution long after input has taken place (Kishe and Machwa, 2003).

A variety of processes lead to the association of heavy metals with solid phases, such as direct adsorption by fine-grained inorganic particles of clays, adsorption of hydrous ferric and manganic oxides which may in turn be associated with clays, adsorption on, or complexation with natural organic substances which may also be associated with inorganic particles, and direct precipitation as new solid phases (Ochieng, 2007). All metals are toxic above some threshold bioavailability levels, although Hg, Cu, Cd and Pb are particularly toxic (Ahmed, 2005). These metals, normally occur at low concentrations, function in combination with organic molecules, usually proteins.

Incidents of heavy metal pollution of coastal lagoons by anthropogenic input today are common even in the less industrialized countries. Impacts of environmental degradation were being experienced both on land and sea probably at more or less equal magnitudes (An, 2006; Wu *et al*., 2007). Heavy metals are present in lagoon waters in both dissolved and solid forms and play a role in many biogeochemical cycles. These metals are rapidly

and efficiently removed to the sediment via adsorption onto surface particles, precipitation, and incorporation into biogenic material (Ahmed, 2005).

Even at low levels, heavy metals are capable of exerting considerable biological effects (Farkas *et al*., 2007). Comparison of levels of heavy metal pollution in aquatic environments was undertaken by analysis of water, sediments and members of indigenous biota, i.e. bio-monitors (Phillips and Rainbow, 1993). The study of metals in the aquatic environment has received considerable attention because of their biological significance as well as the possibility of their transfer to man through food chains that can be harmful (GESAMP, 2001).

2.6.2 Nutrients

Urbanization generally leads to higher nutrient concentration in storm runoff (Roussiez *et al*., 2006). Nutrients such as phosphorous and nitrogen are essential for the growth of algae and other plants. Aquatic life is dependent upon these photo synthesizers, which usually occur in low levels in surface water. Excessive concentrations of nutrients, however, can over stimulate aquatic plant and algae growth. Bacterial respiration and organic decomposition can use up dissolved oxygen, depriving fish and invertebrates of available oxygen in the water (eutrophication).

Phosphorus: Phosphorus occurs naturally in low concentrations and is essential for all forms of life. It comes from processes such as weathering of rock and the decomposition of organic matter. Phosphorus indicates nutrient status, organic enrichment and the consequent health of the water body. Increased levels may result from erosion, discharge

of sewage or detergents, urban runoff, and rural runoff containing fertilizers, animal and plant matter. When concentrations are too high problems such as algal blooms, excessive weed growth and the loss of species diversity can occur. Abundant plant growth such as algal blooms leads to increased pH and turbidity and sometimes to the production of toxins and odor (Wild 1995; Gopalkrusna, 2011).

Nitrogen: Nitrogen in urban runoff/streams occurs in three forms:

• Gaseous form (Nitrogen and Ammonia)

• Inorganic form (Nitrates, nitrites and Ammonium)

• Organic form (biological material e.g. protein)

Natural breakdown of vegetation, run-off from lawn and crop fertilizers and effluent can contain nitrates. Run-off from feedlots can have concentrated ammonia and nitrates. Inadequately treated sewage, poor septic tank systems and streams fed by nitrate rich groundwater can all increase nitrogen in waterways. Ecosystems can be affected when nitrogen concentrations become too high. This may result in algal blooms and an overabundance of oxygen-dependant bacteria that deplete the water of oxygen. Nitrate in high concentrations may be harmful to stock. Excessive nitrates in drinking water can cause methaemoglobinaemia (blue baby) in bottle-fed infants (Tank, 2013; Gopalkrushna, 2011). High concentrations of ammonia are also very toxic to aquatic animals.

2.6.3 Pesticides

Pesticides used in agriculture, public health and agricultural pest control programmes can enter the environment in a number of ways depending upon the method and proficiency of application, as a result of accidents or through the unauthorized dumping of unwanted pesticide products or their containers (Amaraneni, 2002). Pesticide residues are the deposits of pesticide active ingredient (a.i.), its metabolites or breakdown products present in some component of the environment after its application, spillage or dumping. Residue analysis provides a measure of the nature and level of any chemical contamination within the environment and of its persistence. It is often difficult to correlate pesticide residues in the environment with effects on fauna and/or ecological processes. They can, however, show whether an animal or site has been exposed to chemicals and identify the potential for future problems (Amaraneni, 2002; Arnold, 1996; Awasthi, 2000)

All pesticides are subject to degradation and/or metabolism once released into the environment. The rates of degradation and dissipation vary greatly from pesticide to pesticide and situation to situation. The object of residue analysis is to indicate the residues present at the time of sampling and every precaution must be taken to ensure that the sample arriving at the laboratory has not been allowed to deteriorate in such a way that the results are meaningless. Some losses of and/or changes in the chemicals are inevitable and these will vary depending upon the conditions and the nature of the pesticides present. When sampling for residue analysis, the aim is to minimize these losses and thus maximize the correlation between the result obtained from the sample taken and the residue level actually present at the sample site.

It is difficult to make any general statements on interpretation of this data as the individual compounds are so markedly different. However, increased water solubility indicates the potential for greater movement/leaching from the soil (although the type of soil in the treatment area is important in such considerations, e.g. clay soils are more retentive than sandy soils). Soils with high organic matter content are also more retentive to certain residues. The half-life data (i.e. the times taken for half of the active ingredient to have been lost through degradation or dissipation) is a useful indicator of likely persistence and will help shape, particularly with regard to time scales, any proposed sampling programme. The significance of known metabolites/breakdown products should also be taken into account.

2.6.3.1 Organochlorines

Mobility of organochlorines in soil is generally limited, although it is greater in sandy soil. They tend to be bound in clay soils with limited leaching. Residues of the parent compound or metabolites can be found in soil, sediment, vegetable samples and in vertebrates/invertebrates for extended periods. Their solubility in water is low, although residues can be detected in water where there is extreme contamination and, particularly, on suspended matter in water (Amaraneni, 2002). Examples of water solubility, persistence in soil and mammalian excretion of some OCs are given below.

Lindane (hexachlorocyclohexane)

Lindane is the gamma isomer of benzene hexachloride.

Water solubility: 7.3 mg/L (25 ºC), 12 mg/L (35 ºC). Half-life of 15 months (temperate) when incorporated into the soil and much shorter if sprayed on the soil surface. Shows a low soil affinity and may be mobile in certain soil types. Fairly readily metabolized by animals to pentachlorocyclohexane, 1,2,4 trichlorobenzene and isomeric trichlorophenols and excreted as glucuronic acid derivatives. Other isomers of benzene hexachloride can be more persistent.

Dieldrin

Water solubility: 0.19 mg/L (25 ºC). Persistent in soil under temperate conditions; at average application rates (3.1–5.6 kg/ha), it is estimated that roughly 95% will disappear in 12.8 years on average. In bright sunlight, photo-dieldrin can be formed, which is a more toxic product. Some accumulation of dieldrin occurs in animal tissue, particularly fat; dieldrin is very slowly metabolized to water-soluble products which are excreted from the body.

DDT (p-p' isomer)

Practically insoluble in water. Reported half-lives are 28 days (river water) and 56 days (lake water). Residues are lost by volatilization, photodegradation, adsorption on particulate matter and sedimentation. In soil, DDT is chemically and microbially degraded. In temperate climates, a half-life of 2–15 years is reported; under tropical conditions, the half-life is 5–12 months. In the tropics, initial dissipation is rapid, through

volatilization. Metabolized (very slowly) to a range of saturated and unsaturated products by progressive dechlorination. Residues accumulate in fatty tissues and are excreted in milk.

Heptachlor

Water solubility is low: 0.056 mg/L (25–29 ºC). Heptachlor is rapidly hydrolyzed in water with the product then converted to the epoxide. Loss from water by volatilization, photodegradation and sedimentation. Persistent in soil with a reported half-life of 250 days; substantial variation reported depending on soil type. In soil, it undergoes hydrolysis and then microbial epoxidation. Half-life in soil (Temperate climate) is 9–10 months at agricultural rates of application. In animals, heptachlor metabolizes to the epoxide which can be found in most body organs but it particularly accumulates in body fat.

Endosulfan

Water solubility: 0.32–0.33 mg/L (22 ºC). In neutral river water, residues will disappear in approximately 4 weeks; persistence extended under acidic conditions and substantially so (5 months) under basic conditions. Half-life in soil is 30–70 days and the main metabolite is endosulfan sulphate which is degraded more slowly and is thus an important metabolite. The soil half-life for total endosulfan (both isomers plus sulphate metabolite) is 5–8 months. Endosulfan sulphate again is the primary metabolite on plants; plant half-life is 3–7 days (varies with species). Rapidly metabolized and excreted by mammals.

2.6.3.2 Organophosphates

Organophosphates have a fairly limited environmental persistence.

Water solubility is variable but higher than with the organochlorines; residues generally break down quite quickly in water (hydrolysis) and are not generally detected except where the contamination is quite recent. Soil residues are similarly short-lived. Residues are probably only of interest for 5–15 days after spraying unless in shaded areas or where the concentrations applied are high (Bergmam, 1997).

Examples of water solubility, persistence in soil and mammalian excretion of some OPs are given below.

Fenitrothion

Water solubility: 21 mg/L at 20 ºC. Half-life in soil is 12–28 days, less in submerged conditions (4–20 days). Rapid mammalian metabolism and excretion.The most important metabolites are dimethylfenitrooxon and 3-methyl-4-nitrophenol. Plant metabolism to similar products (and their decomposition products) with a half-life of the parent compound of about 4 days (Bergmam, 1997).

Fenthion

Water solubility: 4.2 mg/L at 20 ºC. Rapid degradation in soil and water (half-life is approximately 1 day). Elimination of residues in mammals by excretion of hydrolysis products. Major metabolites are fenthion sulfoxide and sulfone and their oxygen

analogues. Further degradation of these metabolites to the corresponding phenols can occur. Similar degradation pattern occurs on plants.

2.6.3.3 Pyrethroids

Pyrethroid insecticides are generally non-persistent in the environment, being rapidly degraded in the presence of strong sunlight. Residues are probably only of interest for 5–7 days after spraying, unless in shaded areas and where the concentrations applied are particularly high. Proper and accurate detection of residues requires a specialist laboratory (Awasthi, 2003).

Examples of water solubility, persistence in soil and mammalian excretion data of some Pyrethroid are given below.

Cypermethrin

Water solubility: 0.004 mg/L at 20 ºC. In river water, rapid degradation is reported (a half-life of approximately 5 days). In soil, it is fairly persistent; degrades by hydrolysis (approximately 16 weeks). Mammalian metabolism/excretion is similar to that for deltamethrin (Awasthi, 2003).

Permethrin

Water solubility: 0.2 mg/L at 20 ºC. Rapidly degraded in soil and water. In mammals, elimination is by hydrolysis, hydroxylation and elimination as glucoside conjugate. In the rat, an orally administered dose is completely eliminated within 12 days.The metabolism of the trans isomer is more rapid than that of the cis-isomer (Awasthi, 2003).

Deltamethrin

Water solubility: <0.2 µg/L at 25 ºC. In soil, it is microbially degraded in 1–2 weeks. Residues strongly bound in the soil with little risk of leaching. In rats, it is virtually eliminated from the body within 8 days with extensive metabolism occurring.

2.6.4 Eco-toxicological Impact of Pesticides

In the 1960s, organochlorine insecticides and fungicides became very common in agriculture, such as aldrin, dieldrin, chlordane, heptachlor and toxaphene. These pesticides caused extensive wildlife mortality, especially when they were used for budworm control and Dutch Elm disease in forests, grasshopper, mosquitoes and fire ant control (Peterle, 1991; Dustman *et al*., 1969).

Field studies demonstrated that in addition to direct toxicity, insecticides, herbicides and agricultural practices were exerting changes and ecological effects to wildlife by altering habitat, vegetation, insect prey base and other parameters (Katagi, 2010; Daam *et a.l*, 2010; Mineau, 2005). Studies for residues in bird tissues and field trials demonstrated that DDT was more toxic to aquatic species than to terrestrial vertebrates (Robbins *et al*., 1949; Mitchell *et al*., 1953).

Aquatic pollution by pesticide, their metabolites and decomposition byproducts, is considered as the most important. When aquatic habitats receive pesticides through agricultural drain waters and runoffs, there can be substantial perturbation to the function and processes of the biotic components of the ecosystem (Weis *et al*., 2001; Relyea, 2005). In aquatic communities pesticide pollution can affect the way that species interact

with each other. Pesticides can cause direct and indirect effects on aquatic communities, such as changes in species; such as species density and species' traits in certain sensitive ecosystems.

However, there is a growing appreciation that pesticides at sub-lethal concentrations can alter a wide range of individual traits including changes in neurotransmitters, hormones, immune response, reproduction, physiology, morphology and behaviour [e.g. swimming ability, predator detection] (Weis *et al*., 2001).

Pesticide pollution can lead to changes in community structure of an ecosystem. Species that are more sensitive to the pesticide are eliminated and those that are more tolerant come to dominate the ecosystem (Relyea, 2005**)**. Importantly, these changes in community structure are a function of the pesticide concentration applied to the ecosystem (Kreutzweiser *et al*., 2002).

Herbicides eliminate wild vegetables and herbs thus reducing the amount of food for organisms and changing physicochemical parameters. Reductions in producer biomass can lead to lower dissolved oxygen, reduced pH, increased alkalinity and increased conductivity (Downing *et al*., 2004).

There is ecological evidence that pesticides can have long-lasting effects on ecosystems. For example, a study demonstrated that two years after the application of the insecticide *fenvalerate* an invertebrate pond community was significantly different in species diversity and abundance compared to control sites (Woin, 1998).

2.6.5 Physico-chemical parameters influencing water and sediment pollution

The distribution and concentration of pollutants in aquatic environments depend on a number of factors (e.g. chemical composition, size of the deposited particulate matter, biological activity occurring at the bottom), and are strongly influenced by a variety of physical and chemical parameters (e.g. salinity, temperature, Eh and pH) which control their stability (Coccioni, 2009).

pH

pH is the negative logarithm of the hydrogen ion concentration ($pH = -Log_{10}[H^+]$).

Metals such as copper, cadmium, lead, and zinc can be mobilized during oxidation of anoxic or at low pH sediments through oxidation of sulphide phases (Kerner and Wallmann 1992) and oxidation of organic matter (Forstner and Patchineelam 1980). Metals released from sediments at the sediment-water interface are largely controlled by Eh and pH of a sediment system (Peters *et al.*, 1997). Factors such as Total Organic Carbon and pH should also be mentioned to document the release of metals from the sediment to solution and vice versa (Charkhabi 2008).

pH as one of the vital environmental characteristics decides the survival, physiology and metabolic activities of aquatic animals' metabolism, physiology and growth of aquatic organisms. Ramanathan *et al*. (2005) recommended optimum range of pH 6.8-8.7 for maximum growth and production of shrimp carp. pH is influenced by acidity of the bottom sediment an indirect measure of the concentration of anions in and biological

activities. High pH may result from high rate of photosynthesis by dense phytoplankton blooms. pH higher than 7 but lower than 8.5 is ideal for biological productivity, but pH at <4 is detrimental to aquatic life (Abowei, 2010). pH may be affected by total alkalinity and acidity, run off from surrounding rocks and water discharges. The pH of a water body influences the concentration of many metals by altering their availability and toxicity. Metals such as zinc (Zn) and cadmium (Cd) are most likely to have increased detrimental environmental effects as a result of lowered pH (DWAF, 1996).

Calcium Carbonate

The sediment samples analyzed for $CaCO_3$ content in the near shore environments of Goa indicated high carbonate content (60–90%), attributable to the rich benthic fauna and shell fragments in the area (Murthy 1994). An accurate interpretation of lagoon sediment record requires an understanding of the processes controlling the preservation of $CaCO_3$ (Milliman *et al.,* 1999).

According to Rifaat and Al-Washmi (2001), the sediments off Jeddah City were characterized by high carbonate contents due to their biogenic origin containing coral debris, molluscan shells, coralline algae, bryozoans and foraminifera. Sediments of Muthupet mangroves indicated the association of trace metals with Fe oxyhydroxides rather than Mn, Calcium carbonate also plays a much more significant role in trace metal absorption than organic carbon (Raman *et al.,* 2007). The major sources of carbonate materials in the sediments are the shells and broken shell fragments of organisms,

calcareous tests of organisms, and dilution of biogenic calcite by detrital material in the sediments (Hussain *et al.*, 2007).

Temperature

Temperature is a limiting factor in the aquatic environment (Odum, 1971; Boyd, 1979). Water temperature is probably the most important environmental variable. It affects metabolic activities, growth, feeding, reproduction, distribution and migratory behaviours of aquatic organisms (Crillet *et al*., 2006). It affects solubility of gasses in water, gas solubility decreases with increased temperature. Temperature is affected by time of the day; high temperatures may be recorded in daytime and become low at night. Temperatures at which environmental samples are collected measurements are important. For instance, high temperatures may increase the toxicity of many substances such as trace metals in water. In addition to microbial activities within an aquatic medium, temperature and pH are two important factors that govern the methylation of elements such as lead (Pb) and mercury (Hg) [APHA, 1980].

Salinity

Salinity is a dynamic indicator of the nature exchange system. It is expressed as the total concentration of electrically charged ions (cations) in water in part per thousand (‰). The cations include CO_3^-, SO_4^{2-} , Cl^-, HCO_3^-, NO_3^- , NH_4^{2-} and PO_4^{2-} . It is expressed either as a mass of these ions per unit volume or milli-equivalent of the ions per volume of water (Edokpayi, 2005).

It determines distribution of organisms in aquatic environments (Crillet *et al*., 2006). The salinity of the water within the estuary tells us how much fresh water has mixed with sea water. Oxygen solubility decreases slightly as salinity increases, but oxygen solubility decreases more as temperature goes up regardless of salinity (Abowei and George, 2009). The solubility of oxygen in important factor in seawater is 21% less than that of freshwater at 32 degrees Fahrenheit and 17 % less than that of freshwater at 100 degrees Fahrenheit. Oxygen solubility in freshwater decreases from 14.6 to 8.24 mg/L as temperature rises from 32 to 100 degrees. This is a 46.3% decrease (Abowei and George, 2009). On the other hand, oxygen solubility in seawater decreases from 11.5 to 6.75 mg/L for this same temperature increase, a decreased oxygen solubility of 41.3%. The salt concentration directly affects the salinity which impacts circulation with estuaries and coastal high concentrations regions can derive from or be strongly influenced by density variation associated with salinity (Crillet *et al*., 2006; Edokpayi, 2005).

Alkalinity

Alkalinity of a water body is a measure of its capacity to neutralize acids to a designated pH (APHA, 1980; Edokpayi, 2005). Alkalinity is an indirect measure of the concentration of anions in water. The dissolved anions according to McNeely *et al*., (1979) may be sourced from bicarbonates, carbonates, hydroxides, phosphates borates or silicates which may be derived from industrial wastes, dissolved rocks, salts, soils or bottom sediments. Alkalinity between 30 and 500 mg/L is generally acceptable to fish and shrimp (Abowei and George, 2009), between 20 and 50 mg/L according to Boyd

(1982) will permit plankton production for fish culture. High alkalinity results in physiological stress on aquatic organisms and may lead to loss of biodiversity.

Total Dissolved Solids

Total suspended and dissolved solids affect metabolism and physiology of fish and other aquatic organisms. They are products of run offs. They increase with increased rainfall and have adverse effects on dissolved oxygen and carbon dioxide. Dissolved solids could directly influence water

Oxygen solubility decreases slightly as salinity increases, conductivity, the higher dissolved solids the higher the conductivity.

2.7 Anthropogenic Activities Influencing Pollution of Lagoon Environment

The catchment areas of coastal lagoons basin are very densely populated. The functions of the wetlands are being adversely affected by the high population and associated increase in human activities including farming, over-fishing, over exploitation of mangroves, blocked creek channels, refuse dumping in lagoon to reclaim lands, conversion of ecological habitats into salt pans and farms, over-grazing, use of pesticides/herbicides for farming, building across river channels and damming of freshwater channels (Ramsar Wetland Information Sheet, 1998). These human activities

around lagoons are likely to impact on the water and sediment quality and the quality of wetland resources. Impacts can include direct toxicity to algae and aquatic plants, wetland fauna including wetland invertebrates, amphibians, reptiles, fish, and birds, resulting in the loss of biodiversity and simplification of the food chain (Wren *et al*. 1997; Adamus *et al*., 2001).

Review of literature done by deGraft-Johnson *et al.* (2010) documents the following as the major threats to the survival and management of coastal water bodies in the Western Region of Ghana includes:

1. Overexploitation of marine fisheries resources due to overcapitalization of the fishing industry, use of small mesh nets in the beach seine fishery and other illegal fishing methods

2. Loss of coastal habitat through establishment of monocrop plantations, destruction of wetlands for infrastructure development, solid waste disposal, harvest of mangrove forests, beach sand mining and tourism development

3. Pollution of the marine and coastal environment from domestic and industrial solid waste, siltation, sewage disposal, mining waste, pesticides and fertilizers

4. By-catch of endangered species like seabirds, sea turtles, sharks, dolphins and manatees from the use of non-selective gears in the fishing industry

5. Accelerated coastal erosion from deforestation, sand and stone winning, and infrastructure development as the Takoradi Port and the nearby fishing harbor

6. Increasing population density which could bring about an increase in the rate of exploitation of resources of fragile ecosystems

7. Weak governance, legislation and institutional framework due to the fragmented nature of environmental legislation and lack of political will to enforce legislation

8. Development of oil and gas resources which has the potential to increase conflicts with the fishing industry over the use of marine space, and its potential negative impacts on coastal and marine habitats

2.8 Pollution Indices

Various formulations and methods as given below are available to distinguish between geogenic input and anthropogenic inputs.

2.8.1 Geoaccumalation Index

The Geoaccumalation Index (Igeo) was originally defined by Muller (1979) in order to determine and define metal contamination in sediments, by comparing current concentrations with pre-industrial levels. Muller (1969) had distinguished seven classes of geoaccumulation index, the highest class (class six) reflected 100-fold enrichment above the background values. It had been widely utilized in marine sediments (Farkas *et al*., 2007) to assess the process.

2.8.2 Enrichment Factor

Al is one of the most abundant elements on the earth and usually has no contamination concern and had been widely used by many researchers to study the sources and contamination of trace metals in riverine, estuarine and coastal environment (Farkas *et al*., 2007). Normalizing elements relative to Al is widely used to compensate for variations in both grain size and composition, since it represents the quantity of aluminosilicates which is a predominant carrier phase for adsorbed metals in coastal sediments (Taylor *et al*., 1985). According to Hakanson *et al* (1980), Normalizing method is also a powerful tool for the regional comparison of trace metals content in sediments and can also be applied to determine enrichment factors (EF). Apart from Al, Fe and Si were also used.

Enrichment Factor can indicate whether the metals are from natural weathering processes of rocks or from anthropogenic sources and reflect the status of environmental contamination. The assessment criteria are generally based on the EF values. If an EF value lies between 0.5 and 1.5, it suggests that the trace metals may be entirely from crustal materials or natural weathering processes (McDonald *et al*., 2000).

CHAPTER THREE

MATERIALS AND METHODS

This chapter consists of five parts, sections 3.1 to 3.6. Part 1 (Section 3.1) describes the study area. Part 2 (Section 3.2) describes reconnaissance study, sampling and sample collection protocols. Physico-chemical parameters [pH, conductivity, alkalinity, salinity, biological oxygen demand (BOD), total hardness and chloride measurements are described in Part 3 (Section 3.3). Determination of major ions (Na and K) , and the nutrients load (SO_4^{2-}, PO_4^{3-} and NO_3^-) are described in Part 4 (Section 3.4). Part 5 (Section 3.5) describes the sample preparation protocol, analytical procedures for the determination of heavy metals (Fe, Mg, Mn, Zn, Ni, Cu, Co, Cr, Cd, As Hg and Pb). Pesticide residues measurements (organochlorines, pyrethroid and organophophorus) in sediment samples are described in Part 6 (Section 3.6)

3.1 The Study Area

3.1.1 The Songor Lagoon

The Songor Lagoon is located in the Dangme East District of the Greater Accra Region of Ghana. The geographical coordinates of the Songor Lagoon are between 05°45'N, -06°00’N and between 000° 20’E and 000° 35’E. The Songor lagoon has a high salinity filled by seepage, runoff, creeks and streams. It is 75 m above sea level in the north, and 15 m near the Gulf of Guinea (Ramsar Wetlands Information Sheet, 1998).

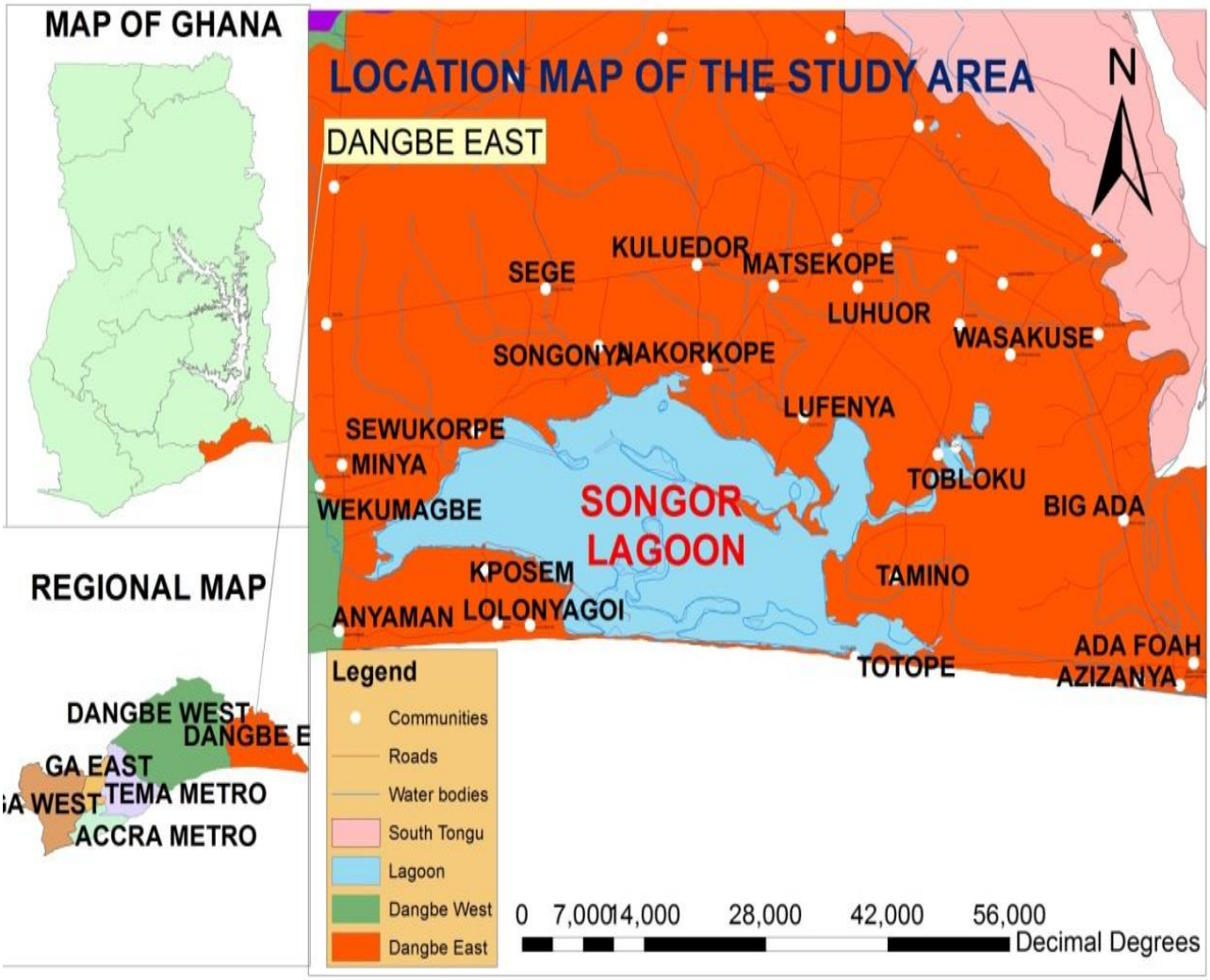

Fig 3.1: Map of the Dangme East District showing the location of the Songoor lagoon

3.1.2 International designation

The Songor lagoon is an internationally important wetland designated as Ramsar site on the basis of their total waterbird populations and the occurrence of internationally

important numbers of several species of birds (Ntiamoa-Baidu and Gordon 1991; Piersma and Ntiamoa-Baidu 1995; Ntiamoa-Baidu *et al*., 1998). The lagoon and surrounding floodplains support large numbers of people through fishing, salt extraction, reed cutting and water supply (Finlayson *et al*., 2000)

The Songor lagoon is the biggest lagoon in the Songor Ramsar site. The water body covers an area of 115 km^2 and it extends for about 20 km along the coast and 8 km inland behind the narrow sand dune. The lagoon, together with the surrounding floodplain, has extensive shallow water mudflats and islands suitable for feeding and roosting of seashore birds. (Finlayson *et al*., 2000)

3.1.3 Climate, Geology and Vegetation

Climate

The climate of the study area lies within the dry Equatorial climatic region of Ghana, which also covers the entire coastal belt of the country. The coastal lands of Ghana have two clearly defined seasons, the Dry season and the Rainy season. The Rainy season exhibits double maxima, the main one occurring between April and June and the minor one between September and October. June is normally the wettest month in the area. The prevailing wind direction is from the southwest (the southwest monsoons). This is a characteristic feature for the entire coastal belt of the country. Mean monthly averages of daily wind speed range between 21.1 and 29.0 km h^{-1}. However, high velocity winds (110

km h^{-1}) of short duration have been recorded in Accra (Ntiamoa-Baidu *et al*., 1998; Finlayson *et al*., 2000). The north east trade winds rarely reach the coast.

Generally, relative humidity is high in the mornings and at night, but is at a minimum in the afternoon. The relative humidity is about 60% due to the proximity of the sea, the volta river and other water bodies.

The minimum average temperatures between is 23ºC and 26ºC whereas the maximum lies between 27ºC and 32ºC. August is normally the coldest month in the area. (Ramsar Wetlands Information Sheet, 1998; Finlayson *et al.*, 2000)

Geology

Unconsolidated sand, clay and gravel occur in the deltaic and lagoon areas. The area has a very smooth coast without cliff and 15 m below seas level. The landscape is generally flat with the creeks supplying freshwater from the Volta River to the lagoon during high water tides. Typical soils found around the lagoon are tropical grey earth. The water is generally clear to the bottom with maximum depth of 80 cm. A small section of the northern and eastern parts fall under the dahomeyan complex rocks of Precambrian age. The dahomeyan rocks consist predominantly of gneisses, schists and migmatities. The rocks weather into dark grey calcareous clay and silt which are only slightly permeable. (Ntiamoa-Baidu *et al*., 1998; Finlayson *et al*., 2000)

Vegetation

The vegetation is basically coastal savannah characterized by short savannah grasses interspersed with shrubs and short trees. Along the coast, are stretches of coconut trees

and patches of coconut groves. The closed lagoon and the inundated mudlfats form the main habitats. The vegetation composition is made up of *Paspalum vaginatum, Cyperus articulatus, Sesuvium portulacastrum* and *Elocharis mutata* that dominate the floodplains. The catchment areas are dominated by *Adropogon guyanus*, *Heteropogon contortus* and *Azadirachta indica* (neem tree). *Rhizophora racemosa* and *Avicennia africana* are found along the creeks. (Ntiamoa-Baidu *et al*., 1998; Finlayson *et al*., 2000)

3.2 Field Reconnaissance Study, Sampling of Water and Sampling of Sediment

3.2.1 Field reconnaissance study

Prior to collection of water and sediment samples from the study area, a five-day reconnaissance study was undertaken. The essence of this study was to familiarize with the Dangbe East district, in general, the Songor lagoon. The reconnaissance study was undertaken in order to assess the extent of anthropogenic activities (farming, salt mining, fishing, to mention a few) taking place within the catchment area of the Songor lagoon. The study also gave an idea of the equipment required for sampling. A sampling strategy was also mapped up for the study (with the aid of the map of the district, the map of the Songor Ramsar site).

3.2.2 Sample containers

All polyethylene containers (500 mL polyethylene bottles, polyethylene scoops) for sampling were immersed in a 10% HNO_3 solution for 48 hours and thoroughly rinsed with double-distilled water before use (Mahapatra *et al*., 2001; Bohrer *et al*., 2007; Momen *et al*., 2006).

3.2.3 Sample collection

Collection of water and sediment samples was done between October, 2013 and January 2014. The lagoon was divided into three sections (upstream, midstream and downstream) to account for all the major activities hosted by the lagoon. At each section, two replicate 10 water samples [(ten samples for nutrients load and physico-chemical parameters determination), and (ten samples for heavy metal content determination)]. For the sediments, two different samples were collected; [a] ten (10) bottom sediments samples were collected for heavy metal content determination, [b] five (5) bottom sediments samples were collected for pesticide residue analysis. All the samples were collected from the main Songor lagoon and along the stretch of the lagoon.

A vivid description of the three sections, sampling points and sample collection points are presented in Table 3.1 (A, B and C). The sampling map is also presented in Fig 3.2.

During the sampling campaign, disposable nitrile gloves were used to prevent potential contamination from dermal contact. The gloves were replaced for each sampling grid to prevent potential cross contamination of samples. The National Grid Reference of each sampling location was recorded using a geographical positioning system (GPS)

(GARMIN eTrex Vista HCx). Each section (upstream, midstream and downstream) and point of sampling were given unique reference numbers and the sampling containers were labeled accordingly.

Table 3.1A: Description of sampling sites and sampling points [**Upstream**]

Sampling Section	Sampling towns	Location	Sampling codes			Anthropogenic activities around sampling location
			Water	Sediment 1	Sediment 2	
	Kpotitsekope to Kablevu	Kpotitsekope town	UW 1	US 1A		Farming, Salt winning, Reed harvesting, Cattle grazing
		5 m from Kpotitsekope	UW 2	US 2A	US 2B	
		10 m from Salt Pans	UW 3	US 3A		
		20 m east of Salt Pans	UW 4	US 4A	US 4B	
		30 m from Kpotitsekope	UW 5	US 5A		
		30 m from Kablevu	UW 6	US 6A	US 6B	
		20 m from Kablevu	UW 7	US 7A		
		10 m from Salt Pans	UW 8	US 8A	US 8B	
		5m from Kablevu	UW 9	US 9A		
		Kablevu town	UW 10	US 10A	US 10B	

Table 3.1B: Description of sampling sites and sampling points [**Midstream**]

Sampling Section	Sampling towns	Location	Sampling codes			Anthropogenic activities around sampling location
			Water	Sediment 1	Sediment 2	
	Ayonukope	Ayonukope town	MW 1	MS 1A		Farming, Salt winning, Reed harvesting, Cattle grazing
		5 m from Ayonukope	MW 2	MS 2A	MS 2B	
		10 m from Salt Pans	MW 3	MS 3A		
		20 m from Salt Pans	MW 4	MS 4A	MS 4B	
		30 m from Ayonukope	MW 5	MS 5A		
		50 m from Ayonukope	MW 6	MS 6A	MS 6B	
		20 m west of SW 16	MW 7	MS 7A		
		10 m from SW 17	MW 8	MS 8A	MS 8B	
		5m down of SW 17	MW 9	MS 9A		
		20m to totope town	MW 10	MS 10A	MS 10B	

Table 3.1C: Description of sampling sites and sampling points [**Downstream**]

Sampling Section	Sampling towns	Location	Sampling codes			Anthropogenic activities around sampling location
			Water	Sediment 1	Sediment 2	
	Totope to Pute	Totope town	DW 1	DS 1A		Farming, Salt winning, Reed harvesting, Cattle grazing
		5 m down from SW 21	DW 2	DS 2A	DS 2B	
		10 m east of SW 21	DW 3	DS 3A		
		20 m from SW 23	DW 4	DS 4A	DS 4B	
		30 m from Totope town	DW 5	DS 5A		
		30 m from Pute	DW 6	DS 6A	DS 6B	
		20 m from the creek	DW 7	DS 7A		
		10 m from GWL Post	DW 8	DS 8A	DS 8B	
		5m from Pute	DW 9	DS 9A		
		Pute town	DW 10	DS 10A	DS 10B	

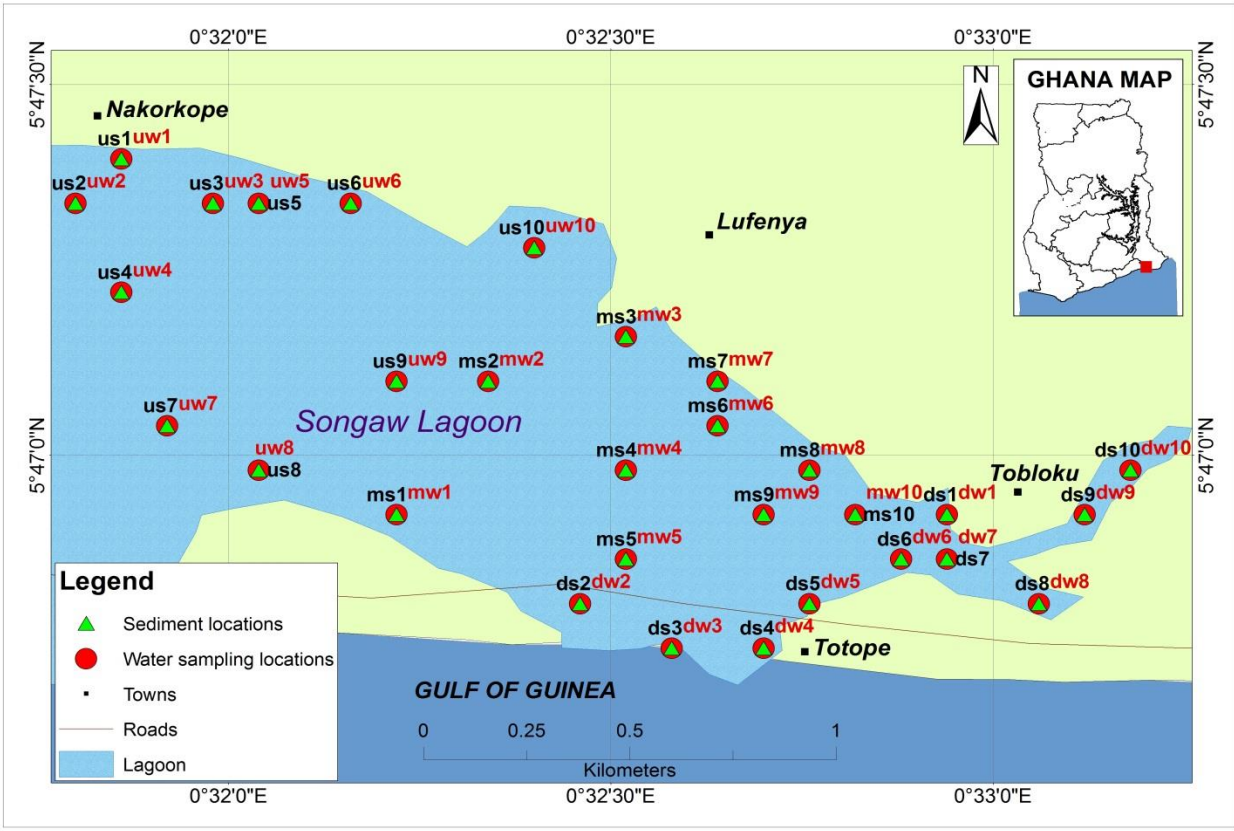

Fig 3.2: Sampling map showing the sampling points

3.2.4 Sampling of water

Samples for physicochemical parameters and heavy metals

Samples for chemical analysis were collected in pre-cleaned, high-density 500 mL polyethylene bottles. Prior to sample collection, the appropriate sampling bottles were rinsed three times with lagoon water. The sampling container was placed under the water (~ 5-10 cm) and filled completely with water. The bottle was immediately capped and labeled.

This was followed by the determination of some physic-chemical parameters (electrical conductivity, total dissolved solids, pH and temperature). Electrical conductivity and total dissolved solids (TDS) were measured using a portable HACH Sension 5 Conductivity meter.

pH and temperature were measured using the HANNA Combo HI 98129-pH meter and mercury-in-glass thermometer respectively.

The pH meter and conductivity meter were both calibrated before usage. The pH meter was calibrated using standard acetic acid-sodium acetate buffer of pH 4.01 and standard borax-sodium hydroxide buffer pH 10.01. Each time the pH of a sample was read, the electrode was rinsed with distilled water and a small portion of the next sample to be determined.

The conductivity meter was standardized using the standard reference solution of 0.01 M KCl solution at approximately 25^{o}C. The conductivity of this solution was 1413 μScm^{-1}.

Water Samples that were used for the determination of sodium, potassium, nutrients load and heavy metal contents were filtered through 0.45 µm membrane filters using positive pressure, just after sampling. This was followed by the addition of 5 mL of 6 M HNO_3 to keep the samples at pH < 2.

The samples were acidified because some cations (Cd, Cr, Co, Fe, Pb, Mn, Zn) are subject to loss by adsorption on, or ion exchange with, the walls of the containing vessel. Acidification with nitric acid to a pH below 2.0 minimizes precipitation and adsorption on container walls (APHA, 2005).

To minimize the potential for volatilization or biodegradation between sampling and analysis, the samples were kept as cool as possible without freezing. All samples were placed in thermo-insulated containers with ice packs and transported to the laboratory at the Ghana Atomic Energy Commission for processing and analysis. At the laboratory, samples trace metal analyses were kept in a refrigerator at 4 $^{\circ}$C.

Samples for DO

Two separate water samples for BOD determination were collected in 300 mL BOD bottles. The BOD bottle was placed below the surface of the water and filled completely with water till the point of the water overflowing. The bottled was capped below the surface of the lagoon water. This was followed immediately by the fixation of oxygen in one of the water samples (sample used for DO_1 analysis). The procedure for oxygen fixation is as follows:

About 1 mL $MnSO_4$ followed by 1mL of alkali-iodide-azide reagent were added to the sample using a pipette. The tip of the pipette was placed below the water level. The bottles were immediately stoppered.

The BOD bottles were then stored in a thermo insulated container, transported to the laboratory. The DO_1 analysis was done immediately the samples were taken to the lab.

The samples for the analysis of DO_5 were stored in the dark cool place for five (5) days. At the end of the five day period, the bottles were removed and further analysis was done. The additional analysis performed is described:

The content of the BOD bottle were mixed by inverting the bottle 2-3 times. On addition of the $MnSO_4$ and alkali-iodide-azide solution, a white precipitate of manganese (II) hydroxide [$Mn(OH)_2$] is formed.

$$MnSO_4 + 2NaOH \rightarrow Mn(OH)_2\downarrow + Na_2SO_4$$

The $Mn(OH)_2$ formed combines with dissolved oxygen in the sample to form a brown precipitate of manganese (III) hydroxide [$MnO(OH)_2$ (Brown ppt)]

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2\downarrow$$

1 mL conc. H_2SO_4 was added to the content of the bottle. The bottle was re-capped tightly and inverting 2-3 times for thorough mixing and complete dissolution of the precipitate. On acidification, the brown precipitate dissolves and oxidizes iodide ions to free iodine.

$$MnO(OH)_2\downarrow + 2H_2SO_4 \rightarrow Mn(SO_4)_2 + 3H_2O$$

$$Mn(SO_4)_2 + 2KI \rightarrow MnSO_4 + K_2SO_4 + I_2$$

The iodine liberated was then titrated with sodium thiosulphate using starch indicator.

$$S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Calculation

Assumption

When 1 mL $MnSO_4$ followed by 1mL alkali-iodide-azide reagent is added to the samples after collection, 2 mL of original sample is lost. Therefore 201 mL is taken for titration which will correspond to 200 mL of original sample.

200 x 300/ (300-1) = 201 mL

Therefore, 1 mL of 0.025 M $Na_2S_2O_3$ = 0.2 mg of O_2

Equation for calculation:

$$DO\left[DO_1 \ \& \ DO_5\right](mg/L) \ = \ \frac{(0.2 \ \cdot \ 1000) \ \cdot \ V_{0.25\,M\ Na_2S_2O_3}}{V_{sam}}$$

$$BOD = DO_1 - DO_5$$

3.2.5 Sampling of Sediment

At each sampling point, two different sediment samples were collected. One sediment sample was used for heavy metal content determination and the other sediment sample for pesticide residue analysis.

3.2.5.1 Sediment samples for heavy metals analysis

Sediment samples for heavy metals analysis were collected with a polypropylene spoon. The spoon was used to scoop soil sample from the lagoon bed at about 30cm and placed in an air tight polyethylene bags. The samples were then placed in thermo-insulated containers with ice packs for transportation to the Ghana Atomic Energy Commission laboratories at Kwabenya, Accra.

3.2.5.2 Sediment samples for pesticide residue analysis

Sediments samples for organic (pesticides) analysis were collected separately into borosilicate jars lined with aluminum foil. Samples were placed in a thermo-insulated container with ice packs to maintain a low temperature during transportation and transported to the laboratories of the Ghana Standards Authority in Accra (Fianko et al., 2011).

3.3 Sample Preparation

Samples for heavy metal analysis

At the laboratory, organic debris and other unwanted materials were gloved-handpicked from the samples for heavy metal analysis, followed by lyophilization in a Christ Gamma 1-16 lyophilizator (Donkor et al., 2006). After lyophilization, the dried sediment samples were ground and sieved using 2 mm sieve. Samples were stored in double-bagged polyethylene bags with hermetic seals. The samples were kept in refrigerators at 4^{o} C. Aliquots of these samples were taken and used for the analysis.

3.4 Physico-chemical parameters analysis

3.4.1 Determination of alkalinity and bicarbonate contents

The alkalinity of water is attributed to the presence of: caustic alkalinity (due to OH^- and CO_3^{2-}) and temporary hardness (due to HCO_3^-). Alkalinity of water means the total content of the substances (OH^-, CO_3^{2-} and HCO_3) in it which causes an increased in the OH^- ion concentration due to dissociation or hydrolysis. Alkalinity is therefore a measure of ability of water to neutralize acids.

In the determination of total alkalinity, the contents of OH^-, CO_3^{2-} and HCO_3^- were estimated together by titration against a standard acid (HCl) potentiometrically to a pH 4.5.The determination is based on the following reactions:

$$OH^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(l)}$$

$$CO_3^{2-}{}_{(aq)} + H^+_{(aq)} \rightarrow HCO_3^-{}_{(aq)}$$

$$HCO_3^-{}_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(aq)}$$

The pH of the water samples from the study area were all above 4.5, hence the Alkalinity was determined by the potentiometric method.

Potentiometric determination of total alkalinity

For water samples with pH > 4.5, the potentiometric method was used to determine the alkalinity. The detailed experimental procedure for alkalinity determination is as follows:

About 50 mL aliquot of the water sample was transferred into a 250 mL conical flask and titrated with 0.02 M HCl solution till pH of 4.5. Three replicate titrations were done and the mean titre value calculated. The volume of water sample used for the titration, the volume of acid used (average titre) and molarity of acid were substituted into the equation (3.2) to calculate the alkalinity.

$$Alkalinity\ \left(mg\ CaCO_3 / L\right) = \frac{A \cdot M \cdot \left(50000\right)}{V_{sam}}$$

Where: A is the titre value (mean volume of standard acid used) in mL; M is the molarity of the titrant (standard HCl solution) and V_{sam} is the volume of sample to be analyzed.

The bicarbonate HCO_3^- concentration was calculated from the equation (APHA, 1995):

$$\left[HCO_3^-\right] = \left(1.2191817\right) \times Alkalinity$$

3.4.2 Determination of Cl^-, Total Hardness (TH), and Ca

Chloride (Cl^-), total hardness (TH) and calcium (Ca) were determined by titrimetry using the colour comparator method. For Cl^- determination, a mixed $AgNO_3$ and $K_2Cr_2O_4$ solution was used as comparator colour standard. Eriochrome black T indicator was used for determination of total hardness. Murexide indicator was used for the determination of Ca.

3.4.2.1 Chloride (Cl^-)

The chloride content was determined by titrimetry using the Argentometric method (APHA 1992, 4500-Cl-B). The method is based on the titration of the water sample with silver nitrate ($AgNO_3$) using potassium chromate (K_2CrO_4) as indicator. As the silver nitrate solution is slowly added, a precipitate of silver chloride forms.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

The end point of the titration occurs when all the chloride ions are precipitated. Then additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

$$2Ag^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow Ag_2CrO_{4(s)}$$

The chloride content of the water samples was determined as follows:

About 0.6 mL of K_2CrO_4 was added to about 25 mL aliquot of the water sample, and titrated with 0.0141 M $AgNO_3$ solution till the greenish yellow colour of the solution changed to brick-red. Three replicate titrations were done and the mean titer was calculated. In cases where there was dilution of the water sample, the concentration calculated was multiplied by the dilution factor to give the actual concentration of the analyte in the sample. The chloride content was calculated from the equation (3.4):

$$Cl^- = \frac{(A - B) \cdot N \cdot M \cdot (1000)}{V_{sam}}$$

A is the mean titer value (volume of $AgNO_3$ solution used) in mL; N is the molarity of the titrant ($AgNO_3$ solution); M is the atomic molar mass of Cl, (M = 35.34 g mol^{-1}); B is the titer value of blank solution in mL, and V_{sam} is the volume of sample.

3.4.2.2 Total Hardness (TH)

Total hardness was determined as follows: about 1 mL of NH_3 buffer and 0.8 mL of Eriochrome black T indicator were respectively added to 25 mL aliquot of the sample. The solution was titrated with a 0.01 M EDTA (Ethylene diamine tetra-acetate $C_{10}H_{16}N_2O_8$) solution until the purple colour of the sample solution changed to blue-black (Fig 3a and 3b). In cases where there was dilution of the water sample, the concentration calculated was multiplied by the dilution factor to give the actual concentration of the analyte in the sample. The hardness of water was calculated using the equation below:

$$Hardness\,(EDTA)\ as\ mg\ CaCO_3/L \quad = \quad \frac{A \cdot B \cdot (1000)}{V_{sam}}$$

Were A is the mean titer value (volume of EDTA solution used) in mL; B is the mass of $CaCO_3$ in mg equivalent to 1.000 mL EDTA titrant and V_{sam} is the volume of sample used for titration.

Fig. 3.3a: Mixture of sample solution, NH_3 buffer and Eriochrome black T indicator

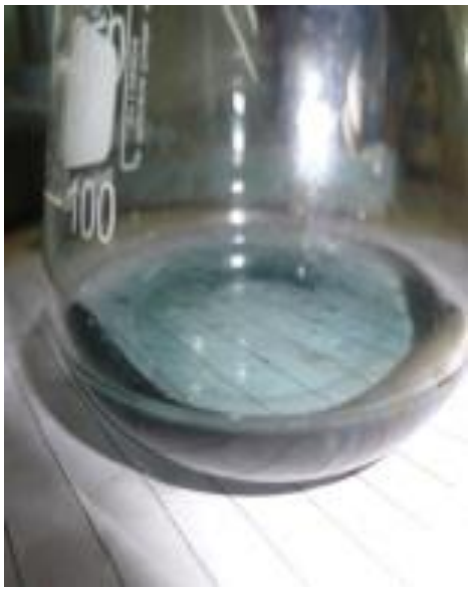

Fig 3.3b: Colour of solution at the end of the titration

3.4.2.3 Calcium (Ca)

The Ca content of the water samples was determined as follows: 1 mL of 1 M NaOH and 100 µL murezide indicator were added to about 25 mL aliquot of the water sample. The sample solution was titrated against 0.01 M EDTA until the pinkish colour of the sample solution changed to purple (Fig 3.5a and Fig 3.5b). Three replicate titrations were done and the mean titre value calculated. In cases where there was dilution of the water sample, the concentration calculated was multiplied by the dilution factor to give the actual concentration of the analyte in the sample. The calcium content (mg L^{-}) was calculated using the equation (3.6):

$$Ca = \frac{A \cdot B \cdot (400.8)}{V_{sam}}$$

Where: A is the volume of titrant used (mean titre value); B is the mass of $CaCO_3$ in mg equivalent to 1.00 mL EDTA titrant at the calcium indicator end point, and V_{sam} is the volume of sample used for titration.

Fig. 3.4a: Mixture of NaOH, murexide indicator and aliquot of water sample

Fig 3.4b: Purple colour developed at the end of titration

3.5 Determination of major ions (Na and K) and the nutrients load (SO_4^{2-}, PO_4^{3-} and NO_3^-)

3.5.1 Determination of K and Na Contents

The levels of Na and K in the water samples were determined by the flame photometric method, using the Sherwood 420 Flame Photometer (Sherwood, UK)

Reagents

Masking agent

A 100 mg L^{-1} Li solution was prepared by dissolving 6.941 g $Li_2SO_4 \cdot H_2O$ in double-distilled water and diluting to the mark in a 1000 mL volumetric flask.

The suppressor solution is important because Na, K and Li are Group one elements. The addition of Li is to mask other Group one elements [Rubidium (Rb), Cesium (Cs) and Francium (Fr)] present in the water samples with the exception of Na and K.

Standards

Mixed Na/K calibration standard

A 100 mg L^{-1} mixed Na and K calibration standard was prepared by pipetting 1 mL of commercially-available stock Na standard and 1 mL of commercially-available stock K standard into a 10 mL volumetric flask and diluting to mark.

Calibration of flame photometer

A 2 mL volume of the masking agent was added to 5 mL of the mixed Na and K standard and thoroughly mixed by swirling. The combined solution was aspirated into the liquefied petroleum gas (LPG)-fed flame of the Sherwood 420 Flame Photometer. The concentrations of Na and K were respectively read. This was followed by analysis of the blank solution and subsequently the water samples.

Analysis of water samples

A blank solution made up of thoroughly mixed double distilled water-masking agent (5:2) was aspirated into the liquefied petroleum gas (LPG)-fed flame of the Sherwood 420 Flame Photometer. After analysis of the blank, the Na and K contents in the water samples were determined. The procedure for the analysis of the water samples is as follows:

A 5 mL volume of the water sample was transferred into 10 mL test tube followed by addition of 2 mL of masking agent. The mixture was homogenized by shaking for about 1 minute. The homogenized solution was aspirated into the flame of the photometer. The contents of Na and K were read at 589 nm and 768 nm respectively for sodium, Na and Potassium, K. the values were recorded. In cases where there was dilution of the water sample, the concentration recorded was multiplied by the dilution factor to give the actual concentration of the analyte in the sample.

3.5.2 Determination of PO_4^{3-}, SO_4^{2-} and NO_3^-

The phosphate, sulphate and nitrate concentrations in the water samples were determined according to the official methods in the Association of Official Analytical Chemists manual (AOAC International, 2007). Phosphate was determined by Official method 4500-P E (Ascorbic acid method). Official method 4500-SO_4^{2-} E (Turbidimetric method) was used for the determination of sulphate. Nitrate was determined using AOAC Official method 973.50.

3.5.2.1 Determination of Phosphate (PO_4^{3-})

Principle

Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form an antimonyl-phosphomolybdate complex, which is reduced to intensely coloured molybdenum blue by ascorbic acid. The absorbance of the molyddenum blue is measured at a wavelength of 880 nm on a UV-visible spectrophotometer.

Instrumentation

A Shimadzu UV-1201 UV-visible Spectrophotometer (Japan) with 1 cm matching quartz cells was used for absorbance measurements.

Chemicals

Ammonium heptamolybdate, $[(NH4)_6Mo_7O_{24}\cdot 4H_2O]$, Potassium antimonyl tartrate $[K(SbO)C_4H_4O_6.5H_2O]$, Sulphuric acid (96% H_2SO_4), Ascorbic acid.

Reagents

Potassium antimony tartrate [$K(SbO)C_4H_4O_6 \cdot ½H_2O$]

A 500 mL volume of potassium antimony tartrate solution was prepared by dissolving 1.375 g $K(SbO)C_4H_4O_6$ $½H_2O$ in about 400 cm^3 double-distilled water and diluting to 500 cm^3. The solution was stored in a glass-stoppered bottle.

Ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] solution

A 500 mL ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] solution was prepared by dissolving 20 g ammonium molybdate with double-distilled water and diluting to the 500 mL mark.

Ascorbic acid

A 0.1 M solution of ascorbic acid was prepared by dissolving 1.76 g ascorbic acid in double-distilled water and diluting to the 100 mL mark. Since ascorbic acid solutions are not stable for long periods of time at room temperature, they are always prepared fresh.

Combined Reagent

The combined reagent is an acidic (H_2SO_4) solution of potassium antimony tartrate, ammonium molybdate and ascorbic acid.

A 100 mL combined reagent was prepared by adding 50 mL of 5 M H_2SO_4 to a mixture of 5 mL potassium antimony tartrate, 15 mL ammonium molybdate and 30 mL ascorbic acid. After the addition of the reagents, it was allowed to attain room temperature,

followed by thorough mixing. The combined reagent was stored in a plastic bottle. The reagent is always prepared fresh because it is stable for only four hours.

Phosphate standard

A stock standard phosphate solution (50 $mg \cdot L^{-1}$) was prepared by dissolving 219.5 g of oven-dried potassium dihydrogen phosphate, KH_2PO_4, in double distilled water to make 1000 mL of solution. Working solutions of concentrations 0.2, 0.4, 0.6, 0.8, and 1.0 mg L^{-1} were prepared daily by appropriate dilution of the stock.

Calibration of UV-Visible spectrophotometer

In order to construct a calibration curve, 10 mL aliquot of the calibrant solutions were transferred into separate 20 mL test tubes. To each test tube, 2 mL of the combined reagent was added to each test tube, and left for about 5 minutes. During this period, the blue colour of antimonyl-phosphomolybdate complex was developed in each test tube. Appropriate aliquot of each blue-coloured calibrant solution was transferred into a 1 mL cuvette; the cuvette was inserted into the spectrophotometer and the absorbance measured at a wavelength of 880 nm against a reagent blank.

A calibration graph of absorbance against concentration of PO_4^{3-} in each calibrant solution was plotted. The concentration of PO_4^{3-} in the water samples were deduced from the calibration graph (Appendix 10A).

Determination of phosphate in water samples

A 10 mL aliquot of the water sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was followed to obtain

the absorbance of each water sample at a wavelength of 880 nm on the UV-visible spectrophotometer. The concentration of PO_4^{3-} in each water sample was obtained from the calibration graph.

3.5.2.2 Determination of sulphate (SO_4^{2-})

Principle

The method is based on the reaction of sulphate ion (SO_4^{2-}) with barium chloride ($BaCl_2$) under acidic conditions to precipitate barium sulphate ($BaSO_4$). The absorbance of the white $BaSO_4$ suspension is measured at a wavelength of 420 nm on a UV-visible spectrophotometer.

Instrumentation

A Shimadzu UV-1201 UV-visible Spectrophotometer (Japan) with 1 cm matching quartz cells was used for absorbance measurements.

Chemicals

Barium chloride ($BaCl_2$, 99.999%), Sodium chloride (NaCl), Hydrochloric acid (HCl), Sodium sulphate (Na_2SO_4), glycerol

Reagents

Acid salt solution

60 g NaCl was dissolved in 5 mL of 37% HCl and diluted to the mark with double-distilled water in a 250 mL volumetric flask.

Sulphate standards

A stock standard sulphate solution (100 mg L^{-1}) was prepared by dissolving 0.1479 g of anhydrous Na_2SO_4 in double distilled water to make 1000 mL of solution. Working solutions of concentrations 15, 20, 25, 30 and 35 mg L^{-1} were prepared daily by appropriate dilution of the stock.

Calibration

10 mL volume of the standard SO_4^{2-} calibrants solutions were quantitatively transferred into separate test tubes. To each test tube, 1 mL of the acid salt solution, 0.5 mL of glycerol solution (conc.) and 0.5 g $BaCl_2$ were added. The resulting cloudy solution was shaken for 60 sec and left for 5 min. Appropriate aliquot of the cloudy solution was transferred into 1 cm cell and the absorbance of the coloured solution measured at a wavelength of 420 nm on the UV-visible spectrophotometer. The absorbance of each calibrant solution was plotted against the concentration of the calibrants (Appendix 10B). A straight line graph was obtained. The concentration of the water samples were deduced from the graph after measurement of the absorbance of each water sample at a wavelength of 420 nm on the UV-visible spectrophotometer

Measurement of SO_4^{2-} in water samples

A 10 mL aliquot of the water sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was followed to obtain the absorbance of each water sample at a wavelength of 420 nm on the UV-visible spectrophotometer. The concentration of SO_4^{2-} in each water sample was obtained from the calibration graph. In cases where there was dilution of the water sample, the concentration deduced from the calibration graph was multiplied by the dilution factor to give the actual concentration of the analyte in the sample.

3.5.2.3 Determination of Nitrate (NO_3^-)

Principle

The method is based on the reaction of the nitrate ion with brucine sulfate in a H_2SO_4 solution at a temperature of 100°C. The yellow colour of the resulting complex is measured at a wavelength of 410 nm.

Standards

A stock standard nitrate solution of concentration 100 mg L^{-1} was prepared by dissolving 0.7218g of KNO_3 (pre-oven dried at 105 ºC for 24 hours) in double distilled water to make 1000 mL of solution. The stock solution was preserved with 2 mL $CHCl_3$ .Working calibrant solutions of concentrations 0.2, 0.4, 0.6, 0.8, and 1.0 mg L^{-1} were prepared daily by appropriate dilution of the stock.

Reagents

Brucine-sulfanilic acid reagent

1 g of brucine sulfate [$(C_{23}H_{26}N_2O_4)_2$ $H_2SO_4 \cdot 7H_2O$] and 0.1 g sulfanilic acid ($NH_2C_6H_4SO_3H \cdot H_2O$) were dissolved in 70 mL hot double-distilled water. 3 mL conc. HCl was added; the resulting solution was cooled and diluted to the 100 mL mark with double-distilled water. The reagent was stored in a dark bottle at 5°C.

Calibration

5 mL of each calibrant solution was pipetted into separate 20 mL test tube. To each test tube, 1 mL of 30% NaCl solution was added, followed by the addition of 5 mL of 6.5 M H_2SO_4. The test tubes were swirled to ensure thorough mixing of the reagents. A 0.5 mL volume of the brucine-sulfanilic acid reagent was added to the content of each tube (except blank). The test tubes were then placed on a rack and lowered into a water bath at 95 ºC for 25 minutes. At the end of the 25 minutes, the rack of test tubes was removed from the bath and immersed in ice. An appropriate aliquot of the yellow coloured calibrant solution was transferred into a 1 cm cell. The cell was placed into the spectrophotometer and the absorbance of the solution measured at a wavelength of 410 nm.

A standard graph of absorbance of standards against concentration of standards was plotted (Appendix 10C).

Measurement of nitrate in water samples

A 5 mL aliquot of each water samples were transferred into separate 20 mL test tube and the same procedure as used for the establishment of the calibration curve was followed to

obtain the absorbance of each sample at a wavelength of 410 nm on the UV-visible spectrophotometer. The concentration of NO_3^- in each water sample was deduced from the calibration graph. The concentration was calculated from the relation:

$$C_{NO_3^-} = C_{Calib.} \cdot D_f$$

Where; $C_{NO_3^-}$ is the nitrate concentration,

$C_{Calib.}$ is the concentration from the calibration curve and

D_f is the dilution factor.

$$D_f = \frac{Initial\ volume}{Volume\ taken} * \frac{Final\ volume}{100}$$

3.6 Determination of Heavy Metals

Determination of the levels of As, Hg, Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, and Pb in water and sediment samples was achieved by atomic absorption spectrometry. Hydride generation atomic absorption spectrometry (HG-AAS) was used for the determination of As, cold vapour atomic absorption spectrometry (CVAAS) using sodium borohydride as reducing agent was used for the determination of Hg. Flame atomic absorption spectrometry (FAAS) was used for the determination of Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, and Pb. Prior to the determination, the samples were mineralized using microwave digestion.

Instrumentation

Varian AA 240FS fast sequential atomic absorption spectrometer equipped with a deuterium background corrector (VARIAN, Australia).

A VGA-77 vapour generator (Varian, Australia) equipped with a peristaltic pump to provide continuous flow vapor generation.

ETHOS 900 microwave digester (Milestone, USA) was used for digestion of water samples.

Chemicals

Commercially available stock standard solutions of Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, As and Pb used were purchased from Fluka, Chemie, Switzerland, Commercially available stock standard solution [(999 ± 4 µg Hg mL in 1.4% (w/w) HNO_3], was purchased from Spectrascan, Teknolab AB, Sweden. Sodium borohydride ($NaBH_4$), Sodium hydroxide (NaOH), Nitric acid (65% HNO_3), Hydrochloric acid (37 % HCl), and Hydrogen peroxide (30%, H_2O_2) were purchased from Sigma-Aldrich, Germany.

The water used throughout the study was de-ionised distilled water (DDW) obtained by passing distilled water through a mixed bed ion-exchange column (Barnstead 9-034-3, Fischer Scientific Company).

3.6.1 Digestion

Water

Digestion of water samples was done according to the procedure described by Hoenig et al., (1998). The procedure is as follows:

6 mL of HNO_3 (65%), 3 mL of HCl (37%) and 0.25 mL of H_2O_2 (30%) were added to 5 mL of water sample in Teflon digestion tubes, the tubes were covered tightly and placed in the ETHOS 900 microwave digester. The water samples were digested using a four-step digestion procedure (Table 3.2). At the end of the digetion, the digest was cooled, transferred into clean 25 mL volumetric flask and diluted to 20 mL with double-distilled water. This was followed by atomic absorption measurement.

Table 3.2: Microwave digestion programme used for digestion of samples

Digestion Step	Digestion Time (min)	Microwave			
		Power (W)	Pressure (bar)	Temperature 1 (^oC)	Temperature 2 (^oC)
1	5	250	100	400	500
2	1	0	100	400	500
3	10	250	100	400	500
4	5	450	100	400	500

Temperature 1 and temperature 2 represent the initial and final digestion temperatures

Sediment

About 1.5 g of the lyophilized sediment sample was weighed and placed into the digestion bombs. This was followed by the addition of 10 mL of HNO_3-HCl (1:3 v/v). The samples were digested in the microwave system for 26 minute (the detailed digestion programme is described above). After digestion the samples were left overnight to cool. This was followed by atomic absorption measurement.

3.6.2 Measurement of total Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, and Pb using the Flame Atomic Absorption Spectrometer

The instrumental conditions used for flame atomic absorption spectrometric determination of As, Hg, Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, and Pb were the following: the air-acetylene flame atomizer was made up of air as oxidant (flow rate: 13.50 L/min) and acetylene as fuel (flow rate: 2 L/min). The lamp current and wavelength of the hollow cathode lamps and the spectral slit width used for Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, and Pb determinations are presented on Table 3.3.

Table 3.3: FAAS conditions used for determination of Fe, Mg, Mn, Zn, Cd, Co, Ni, Cr, Cu, Pb

Element	Hollow cathode lamp		
	Current (mA)	Wavelength (nm)	Slit width (nm)
Fe	5.0	248.3	0.2
Mg	4.0	285.2	0.5
Mn	5.0	279.5	0.2
Zn	5.0	213.9	1.0
Cd	4.0	288.8	0.5
Co	7.0	240.7	0.2
Ni	4.0	232.0	0.2
Cr	7.0	357.9	0.2
Cu	4.0	324.7	0.5
Pb	5.0	217.0	1.0

Calibration of atomic absorption spectrometer

The atomic absorption spectrometer was calibrated with the calibration standards for the element being determined. The absorbances obtained were used to plot calibration graphs for each element. After the calibration, each element was determined by measurement of the absorbances of the samples aspirated into the absorption cell.

Calculation of concentration

The concentration of each analyte in the water and sediment samples was calculated from the calibration curve for the analyte. In cases where there was dilution of the water sample, the concentration deduced from the calibration graph was multiplied by the dilution factor to give the actual concentration of the analyte in the sample.

Concentration of each analyte was calculated from their respective calibration regression lines. The actual concentration of the analyte in the sample was calculated using the relation:

$$C_{Sample}\,(\mu g\ g^{-1}) \quad = \quad \frac{C_{AAS} \cdot \ D_f \cdot \ V_N}{m_{Sample}}$$

Where: C_{AAS} = Concentration of analyte obtained from calibration regression line (mg L^{-1}), D_f = Dilution factor, V_N = Nominal volume or sample volume (mL), C_{sam} = Actual concentration of analyte in sample (µg g^{-1}) and m_{sam} = Mass of homogenized sample measured for digestion (g).

3.6.3 Determination of As by HG-AAS

Hollow cathode lamp

The radiation sources were the hollow cathode lamp of As (wavelength 193.7 nm; spectral slit width 0.5 nm; lamp current 10 mA).

Reagents

Hydride generation was performed with a 0.6% (w/v) $NaBH_4$ in 0.5% (w/v) NaOH as the reductive solution with 6 M HCl as the carrier solution.

Standard

Calibration standards for As (0.2, 0.4, 0.6 mg L^{-1}) were prepared daily by appropriate dilution of the commercial stock standard solutions for As.

Reduction of As^V to As^{III}

To reduce all As^V to As^{III}, 4 mL of freshly prepared 5 M KI was added to the digest solution.

$$As^{5+} + 2I^- \rightarrow As^{3+} + I_2 \quad \text{..... (3.7)}$$

This was followed by hydride generation and subsequently by atomic absorption measurement.

Calibration

The HG-AAS system was calibrated with As standard calibrants (0.2, 0.4, 0.6 mg As L^{-1}) and the absorbance obtained were used for linear regression analysis (plot of absorbance against the concentration of the calibrants). The concentration of As was deduced from the equation of the regression line.

Hydride generation and atomic absorption measurement

The continuous flow approach of an HG-AAS system was used to merge sample solution and reagents. The sample solution (flow rate 5 mL/45 sec) was mixed in a PEEK (polyetheretherketone) cross connector with both HCl (flow rate 5 mL/45 sec) and $NaBH_4$ (flow rate 5 mL/45 sec) solutions (both solutions pumped and added with the peristaltic pump) and pumped into the reaction coil. During the mixing, the tetrahydroborate ion, BH_4^- converts As(III) into the hydride (AsH_3). Furthermore, the tetraborohydrate is hydrolyzed in the presence of HCl producing considerable hydrogen.

$$3BH_4^- + 3H^+ + 4H_3AsO_3 \rightarrow 3H_3BO_3 + 4AsH_3 + 3H_2O$$

$$BH_4^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 4H_2$$

The gaseous hydride formed together with the hydrogen gas generated were separated from the liquid in the A-shaped gas-liquid separator component of the vapour generator, and transferred with a flow of argon gas into the Perma-pure dryer and dried by a stream of nitrogen gas. The liquid goes to waste and the gaseous hydride and excess hydrogen formed were swept out of the vapour generation vessel by the argon gas (flow rate 13.5 mL min^{-1}) into the AAS detection system. In the detection system, AsH_3 was atomized in the air-acetylene flame (also fed by the excess hydrogen generated) aligned in the light path of a As lamp in an atomic absorption spectrometer. Absorbance measurements were recorded and the concentration deduced from the regression line.

Calculation of concentration

The concentration of As in each water sample was obtained from the equation of the regression line. The concentration of As in the sample (mg L^{-1}) was done using the relation:

$$C_{Sample}\,(\mu g\ g^{-1}) \;=\; \frac{C_{AAS}\cdot\ D_f\cdot\ V_N}{m_{Sample}}$$

Where: C_{AAS} = Concentration of analyte obtained from calibration regression line (mg L^{-1}), D_f = Dilution factor, V_N = Nominal volume or sample volume (mL), C_{sam} = Actual concentration of analyte in sample (µg g^{-1}) and m_{sam} = Mass of homogenized sample measured for digestion (g).

Where: D_f is dilution factor, and $Conc_{calib}$ is the concentration from calibration curve

3.6.4 Determination of Hg by CV-AAS using sodium borohydride as reducing agent

Hollow cathode lamp

The radiation sources were the hollow cathode lamp of Hg (wavelength 253.7 nm; spectral slit width 0.5 nm; lamp current 4 mA) (Varian, Australia).

Standard

Calibration standards for Hg (0.1, 0.25, 0.5 mg L^{-1}) were prepared daily by appropriate dilution of the commercial stock standard solutions of Hg.

Reagents

Cold vapour generation for Hg determination was performed using 0.3% (w/v) $NaBH_4$ in 5% (w/v) NaOH as the reductive solution and 5 M HCl as carrier solution.

Calibration

The CVAAS system was calibrated with Hg standard calibrants (0.1, 0.25, 0.5 mg L^{-1}) and the absorbances obtained were used for linear regression analysis (plot of absorbance against the concentration of the calibrants). The concentration of Hg was deduced from the equation of the regression line.

Cold vapour generation and atomic absorption measurement

Cold vapor atomic absorption spectrometry (CVAAS) using sodium borohydride ($NaBH_4$) as the reducing agent, was employed to determine mercury concentrations. A brief description of the determination of Hg is as follows:

A peristaltic pump was used to merge sample solution and reagents. The sample solution (flow rate 5 mL/45 sec) was mixed in a PEEK (polyetheretherketone) cross connector with both HCl (flow rate 5 mL/45 sec) and $NaBH_4$ (flow rate 5 mL/45 sec) solutions (both solutions pumped and added with the peristaltic pump) and pumped into the reaction coil.

During the mixing, the tetrahydroborate ion, BH_4^- converts (reduction) Hg into the elemental state (Hg^0).

$$BH_4^- + 4Hg^{2+} + 3H_2O \rightarrow 4Hg^0 + H_3BO_3 + 7H^+$$

The elemental Hg formed was separated from the liquid in the gas-liquid separator component of the vapour generator, by a stream of the carrier gas, argon, (flow rate 13.5 mL min^{-1}) into the Perma-pure dryer and dried by a stream of nitrogen gas. The Hg^0 then enters the atomic absorption cell. In the absorption cell, Hg^0 aligned in the light path of the Hg lamp. Hg^0 absorbs 253.7 nm light in proportion to the concentration of mercury in the sample. Absorbance measurements were recorded and the concentration deduced from the regression line.

Calculation of concentration

The concentration of Hg in the sample was obtained from the equation of the regression line. The concentration of Hg in the sample was done using the relation:

$$C_{Sample}\,(\mu g\ g^{-1}) = \frac{C_{AAS} \cdot D_f \cdot V_N}{m_{Sample}}$$

Where: C_{AAS} = Concentration of analyte obtained from calibration regression line (mg L^{-1}); D_f = Dilution factor, V_N = Nominal volume or sample volume (mL); C_{sam} = Actual concentration of analyte in sample (µg g^{-1}) and m_{sam} = Mass of homogenized sample measured for digestion (g).

3.7 Determination of Pesticide Residues (OCs, OPs and Synthetic Pyrethroids)

The determination of OC's, pyrethoids and OPs in sediments was done according to the scheme presented in Fig 3.1. The detailed experimental procedure is also described.

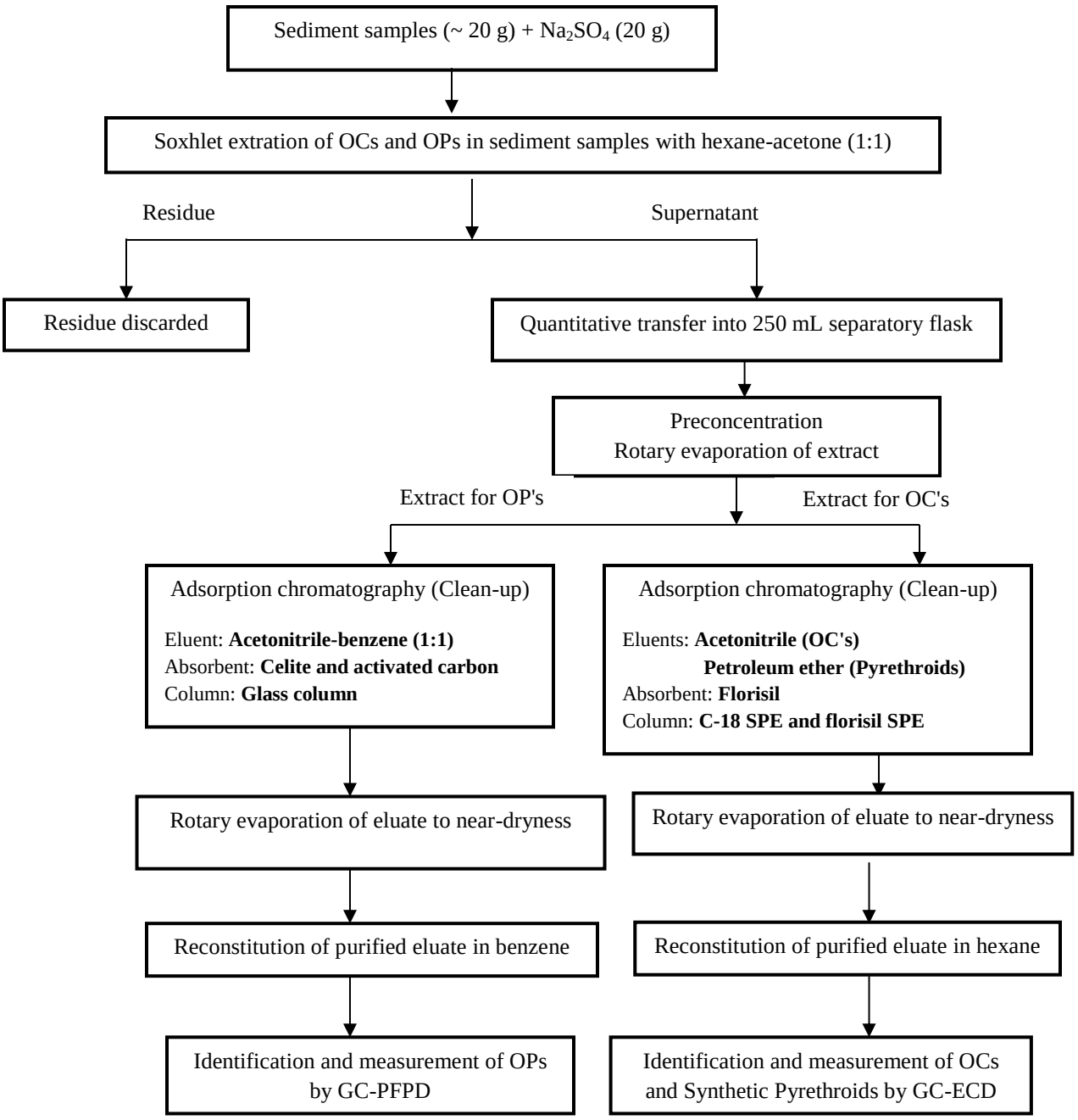

Fig 3.5: Scheme for extraction, clean-up and chromatographic analysis of OCs, Pyrethroids, and OPs in sediment

3.7.1 Determination of Organochlorine and Synthetic Pyrethroid Pesticides

Instrumentation

Varian CP-3800 Gas Chromatography System equipped with Ni-63 Electron Capture Detector (ECD) and a CombiPAL Autosampler from Varian Inc., Australia.

30m + 10m EZ Guard x 0.25mm Internal Diameter Fused with silica capillary coated with VF-5ms (0.25µm film) Analytical Columns from Varian Inc., Australia.

Rotary film evaporator (Bibby, RE 200B and Buchi Ratovapor R-210) equipped with Water bath (Bibby, RE 200B and Buchi, B-491), Recirculating chiller (Buchi, B-740) was used for the concenetration. Horizontal shaker (IKA-Werke HS 501 Digital) was used for shaking. Vortex mixer (thermolyne [Maxi Mix-Pus]) and ultrasonic baths (Clifton SW 3H and Grant XUB 18UK) were also used.

Chemicals

All chemicals used in the determination were HPLC grade and were purchased from BDH, England: Acetone, Acetonitrile, Ethyl Acetate, Diethyl ether, Petroleum ether, n-hexane, Methanol, Methylene chloride, Benzene, Dichloromethane.

Certified reference standards were purchased from Dr. Ehrenstorfer GmbH, Germany.

Sodium sulfate (anhydrous), Sodium chloride and Ethylene glycol were purchased from BDH, England.

Reagents

Stock solution of organochlorine pesticides [1mg/mL]

50 mg of the organochlorine pesticides reference standard was weighed and transferred into 50 mL individual volumetric flasks. It was dissolved in hexane and filled to the 50 mL mark.

Intermediate solution, 10µg/mL

1 mL of each stock solution was pipetted into individual 100 mL volumetric flasks. It was dilute to volume with hexane.

Working solution 1 µg/mL

1 mL of each intermediate solution was pipetted into a 100 mL volumetric flask and diluted to volume with hexane.

Stock solution of pyrethiods pesticides [1mg/mL]

50 mg of the pyrethiods pesticides reference standard was weighed and transferred into 50 mL individual volumetric flasks. It was dissolved in hexane and filled to the 50 mL mark.

Intermediate solution, 10µg/mL

1 mL of each stock solution was pipetted into individual 100 mL volumetric flasks. It was dilute to volume with hexane.

Working solution 1 µg/mL

1 mL of each intermediate solution was pipetted into a 100 mL volumetric flask and diluted to volume with hexane.

Extraction

Sediment samples (~ 20 g, wet) were mixed with anhydrous Na_2SO_4 (~20 g) and ground to form free flowing powder. The powdered sample was extracted for 6 hrs with a soxhlet extractor using a 50 mL mixture of hexane and acetone [1:1 (v/v)].

Pre-concentration

After extraction, they were centrifuged for 20 minutes at 3000 rpm and the sample extract decanted. The remaining water phase was liquid – liquid extracted with acetonitrile-methylene chloride [(75:25 (v/v)]. The extraction was repeated three times with 25 mL of the extraction mixture on each occasion. The combined organic phase extracts were then dried with anhydrous sodium sulphate (15 g) and concentrated to 5 mL using rotary evaporator at 35 ^{0}C (Solution A).

Sample Clean-up

Column for separation of OC's (C-18 SPE)

C-18 solid phase extraction (SPE) cartridges were used for the sample clean-up. The C-18 cartridges were conditioned twice with 5 mL petroleum ether, 5mL acetone and 5mL methanol. Each sediment extract (solution A) was percolated through the cartridges at a flow rate of approximately 5 mL/min under vacuum pump. The pesticides trapped in the

cartridges were eluted two times, each with 3 mL acetonitrile. The sample eluate was concentrated using the rotary evaporator aided with a water chiller to 2 mL at 35^0C and then diluted in 5mL n-hexane. (Solution B)

Column for separation of pyrethiods (Florisil SPE)

Florisil cartridges were conditioned with 10 mL n-hexane. Solution B was loaded and eluted three times, each with 4ml petroleum ether-diethyl ether [85:15 (v/v)]. The sample extract was concentrated using the rotary evaporator aided with a water chiller to 2 mL and dissolved in n-hexane for GC analysis.

Gas chromatograph-Electron capture detector (GC-ECD)

The GC analysis was performed on Varian CP-3800 gas chromatograph equipped with Electron Capture Detector (ECD). The column, which consist of 30 m + 10 mm EZ Guard x 0.25 mm internal diameter fused silica capillary coated with VF-5 ms (0.25 µm Film) from Varian, Australia was used for the analysis. The detection and determination of the residues were performed by injecting 1 µL of the 2 mL purified extract into the injection port of a gas chromatograph system.

The column temperature was programmed from 70 ^{0}C, held for 2 mins at a rate of 25 ^{0}C/min to 180 ^{0}C, held for 1 min, and then at a rate of 5 ^{0}C/min to 300 ^{0}C. The temperatures of the injector and detector were 270 ^{0}C and 300 ^{0}C, respectively. The injection was carried out on a splitless injector at 270 ^{0}C. The carrier gas was nitrogen while helium gas was used for the makeup flow. The run time was 31 mins. The detailed gas chromatographic conditions are presented in Table 3.4.

Calibrations and estimation

Identification of pesticide residues was accomplished using reference standards and relative retention time techniques, while the concentration of the residues was determined by comparing the peak heights of the samples with the corresponding peak heights of the reference standards of known concentrations. The Residual Level (µg/g) of the analyte is given by the formular below;

$$Residual\ level_{[Sample]}\ (\mu g\ g^{-1}) = \frac{Peak\ Area_{(Sam)} \cdot V_{Std} \cdot V_{Extract}}{Peak\ Area_{(Std)} \cdot V_{Sam} \cdot M_{Sam}} \cdot C_{Std}$$

Where:

Peak Area $_{(sam)}$ = peak Area of sample injected (mv),

Peak Area $_{(std)}$ = peak Area of standard injected (mv),

V_{std} = volume of sample injected (µL/mL),

V_{sam} = volume of standard injected (µL/mL),

C_{std} = concentration of standard (µg/mL), and

M_{sam} = weight of sample taken (g)

3.7.2 Determination of Organophosphorous Pesticides

Instrumentation

Varian CP-3800 Gas Chromatography System equipped with Pulse Flame Photometric Detector (PFPD) and a CombiPAL Autosampler from Varian, Australia.

30 m x 0.25 mm Internal Diameter Fused with silica capillary coated with VF-1701ms (0.25 µm film) Analytical Columns from Varian, Australia.

Rotary film evaporator (Bibby, RE 200B and Büchi Rotavapor R-210) equipped with Water bath (Bibby, RE 200B and Büchi, B-491), Recirculating chiller (Büchi, B-740) was used for the concenetration. Horizontal shaker (IKA-Werke HS 501 Digital) was used for shaking. Vortex mixer (thermolyne [Maxi Mix-Pus]) and ultrasonic baths (Clifton SW 3H and Grant XUB 18UK) were also used.

Chemicals

All chemicals used in the determination were of HPLC grade: Acetone, Acetonitrile, n-hexane, Benzene and Dichloromethane were purchased from BDH, England. Certified reference standards were from Dr. Ehrenstorfer GmbH, Germany.

Sodium sulphate (anhydrous), Sodium chloride and Ethylene glycol were purchased from BDH, England.

Reagents

Stock solution of organophosphorous pesticide, 1mg/mL

100 mg of each organophosphorus pesticide reference standards was weighed and transferred into 100 mL individual volumetric flasks.it was dissolved in benzene and filled to the 100 mL mark.

Intermediate solution, 10µg/mL

1 mL of each stock solution was pipetted into individual 100 mL volumetric flasks. It was dilute to volume with benzene.

Working solution 0.5 µg/mL

5 mL of each intermediate solution was pipetted into a 100 mL volumetric flask and diluted to volume with benzene.

Extraction

Sediment samples (~ 20 g, wet) were mixed with anhydrous Na_2SO_4 (~ 20 g) and ground to form free flowing powder. The powdered sample was extracted for 6 hrs with a 50 mL mixture of hexane and acetone (1:1 v/v) using soxhlet extractor.

Pre-concentration

After extraction, they were centrifuged for 20 minutes at 3000 rpm and the sample extract decanted. The remaining water phase was liquid – liquid extracted with dichloromethane-acetone (1:1 v/v) three times, each with 25mL. The combined organic phase extracts were then dried with anhydrous sodium sulphate (15 g) and concentrated to 5 mL with rotary evaporator at 40 ^{0}C.

Cleanup

The glass column was filled with 2 g celite adsorbent followed by 4 g of activated carbon-celite (1:4 w/w) and topped with glass wool. The column was conditioned with 10 mL benzene. The sample was transferred to the column with 2 mL of benzene and eluted with two times, each with 3mL acetonitrile-benzene (1:1 v/v).

The sample extract was concentrated using the rotary evaporator aided with a water chiller to 2 mL at 40 ^{0}C and dissolved in benzene for GC analysis.

Gas chromatograph

The GC analysis was performed on Varian CP-3800 gas chromatograph equipped with PFPD (Pulse Flame Photometric Detector). The column, which consists of 30 m x 0.25 mm internal diameter fused silica capillary coated with VF-1701ms (0.25 µm Film) from Varian, Australia, was used for the analysis. The detection and determination of the residues were performed by injecting 1 µL of the 2 mL purified extract into the injection port of a gas chromatograph system.

The column temperature was programmed from 70 ^{0}C, held for 2 mins at a rate of 25 ^{0}C/min to 200 ^{0}C, held for 1 min, and then at a rate of 20 ^{0}C/min to 250 ^{0}C. The temperatures of the injector and detector were 270 ^{0}C and 280 ^{0}C, respectively. The injection was carried out on a splitless injector at 270 ^{0}C. The carrier gas was nitrogen while air and hydrogen gas was used for the makeup flow. The run time was 15 mins. The detailed gas chromatographic conditions are presented in Table 3.4 above.

Calibrations and estimation

Identification of pesticide residues was accomplished using reference standards and relative retention time techniques, while the concentration of the residues was determined by comparing the peak heights of the samples with the corresponding peak heights of the reference standards of known concentrations. The Residual Level (µg/g) of the analyte is given by the formulae below;

$$C_{Sample}\,(\mu g\ g^{-1}) \;=\; \frac{peak\ Area_{(Sam)} \cdot \ V_{Std} \cdot \ V_{Extract}}{peak\ Area_{(Std)} \cdot V_{Sam} \cdot W_{Sam}} \cdot C_{Std}$$

Where:

Peak Area $_{(sam)}$ = peak Area of sample injected (mv),

Peak Area $_{(std)}$ = peak Area of standard injected (mv),

V_{std} = volume of sample injected (µl/ml),

V_{sam} = volume of standard injected (µL/mL),

C_{std} = concentration of standard (µg/ml), and

W_{sam} = weight of sample taken (g)

Table 3.4: Chromatographic Conditions for the Determination of Organochlorines and Synthetic Pyrethroids, and Organophosphorus

Parameters	Conditions	
	Organochlorines and Synthetic Pyrethroids	Organophosphorus
Column	30 m + 10 mm EZ Guard X 0.25 mm internal diameter fused silica capillary coated with VF-5 ms (0.25 µm Film) [Varian, Australia]	30 m x 0.25 mm internal diameter fused silica capillary coated with VF-1701 ms (0.25 µm Film) [Varian, Australia]
Injector		
-Mode of injection	Splitless	Splitless
-Temperature	270 ^{o}C	270 ^{o}C
Oven	70 ^{o}C /2 min $\xrightarrow{25\,^{o}C/min}$ 180 ^{o}C /1 min $\xrightarrow{5\,^{o}C/min}$ 300 ^{o}C	70 ^{o}C /2min $\xrightarrow{25\,^{o}C/min}$ 200 ^{o}C /1min $\xrightarrow{20\,^{o}C/min}$ 250 ^{o}C
Detector		
-Type	Electron capture (ECD)	Pulse flame photometric (PFPD)
-Temperature	300 ^{o}C	280 ^{o}C
Carrier gas	Nitrogen (Flow rate: 1 mL/min)	2 mL/min
Supporting gas	Helium (Flow rate: 29 mL/min)	Air (Flow rate: 17 mL/min)
		H_2 (Flow rate: 14 mL/min)
		Air 2 (Flow rate: 10 mL/min)

3.7.3 Quality Control and Quality Assurance

Before analysis was performed, standards were run to check for the column performance, peak height, resolution and the detection limit. The correlation coefficients of calibration curves were all higher than 0.998. The quality assurance measures included strict cleaning procedures, procedural blank, recovery of spiked standards and monitoring of detector response.

3.7.3.1 Recovery study

Recovery studies were undertaken to evaluate the efficiency of the extraction procedure used. The recovery of the pesticides was done in replicate and was determined by spiking the previously analysed samples with the pesticide standard at concentrations of 0.5 mg/Kg. The pesticides in the sediment were then extracted. The extract obtained, was then cleaned and reduced to near dryness using a rotary evaporator. Solvent exchanged was carried out by dissolving and collected the cleaned extract into a 2 mL vial for subsequent analysis.

The recovery values expressed in percentages were calculated from the chromatograms.

$$\%\ recovery = \frac{CS_2 - CS_1}{CS} \cdot 100\%$$

Where:

CS_1 = concentration of pesticide residues in the sample,

CS_2 = concentration of pesticide residues in the spiked sample,

CS = initial concentration of pesticide

3.7.4 Determination of method detection limits (MDLs)

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. A solution of the analyte that is 3 times the estimated detection was prepared. The method detection limit was determined according to the formula:

$$MDL = t\,value_{(Student's)} \cdot \sigma_{replicate}$$

3.7.5 Determination of limit of detection (LOD)

The limit of detection (LOD) is the lowest quantity of a substance that can be distinguished from the absence of that substance (blank value) within a stated confidence limit. It is taken as the concentration of an analyte in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The limits of detection of the pesticide residues were determined by replicate chromatographic runs (6 times) of the least concentration of the pesticide reference standards (10 ng/mL) and then multiplying the standard deviation obtained by 3.

3.7.6 Determination of limit of quantification (LOQ)

The limit of quantification (LOQ) is the level above which quantitative results may be obtained with a specified degree of confidence. It is mathematically defined as being equal to 10 times the standard deviation of the results for a series of replicates used to

determine the limit of detection. The limits of quantitation of the pesticide residues were determined by replicate chromatographic runs (6 times) of the least concentration of the pesticide reference standards (10 ng/mL) and then multiplying the standard deviation by 10.

3.8 Statistical Analysis

The measured parameters were subjected to hierarchical cluster analysis (HCA) and principal component analysis/factor analysis using SPSS 16.0 statistical package. Prior to such analyses, the raw data were normalized to avoid misclassifications due to the different order of magnitude and range of variation of the analytical parameters (Aruga *et al*. 1995).

Principal component analysis transforms the original variables of a data set into new, uncorrelated variables or axes, known as the principal components, which are linear combinations of the original variables (Shrestha and Kazama 2007). Exploratory factor analysis is used for reducing the complex set of variables to smaller number of factors (Howitt and Cramer 2005). The physicochemical and metal data were subjected to principal component analysis for exploration of the extent of metal pollution and source identification. Varimax rotation was used to maximize the sum of the variance of the factor coefficients which better explained the possible groups/sources that influenced the water systems (Gotelli and Ellison 2004).

The correlation coefficient matrix measures how well the variance of each constituent can be explained by its relationship with others (Liu *et al*. 2003). The factor scores from the

R-mode PCA were used with ArcGIS to determine the spatial variations of the dominant processes influencing the surface water hydrochemistry in the area. Discussions on the interpolation techniques, such as kriging, and integrated use of factor analysis and kriging methods in the analysis of hydrochemical data have been provided in literature (Boamponsem *et al*. 2010; Yidana and Yidana 2010).

Cluster analysis is an exploratory unsupervised data analysis tool for solving classification problems for variables and objects. The main objective is to sort cases (monitoring points) into groups or clusters so that the degree of association is strong between members of the same cluster and weak between members of different clusters. Each cluster describes, in terms of the data collected, the class to which its members belong (Einax *et al*., 1997). The squared Euclidean distance was used to measure similarity among clusters while Ward's method was used as an agglomeration technique (Einax *et al*. 1997). It has been suggested in literature that the use of either Euclidean or squared Euclidean distance as a similarity measure in combination with Ward's linkage algorithm often yields optimal classification results (e.g., Güler *et al*. 2002; Banoeng-Yakubo *et al*. 2009; Bhuiyan *et al*. 2010a, b; Boamponsem *et al*. 2010; Yidana and Yidana 2010).

The hydrochemical data were examined by both R-mode and Q-mode HCA. The R-mode HCA was used to establish relationships between the variables (analyzed parameters), whereas the Q-mode HCA was used to classify the cases (samples), measured by the variables, into statistically defined groups. Dendrograms were generated for the R-mode and Q-mode HCA, with the phenon lines set to a rescaled linkage distance of about 15 to show statistical similarity. The so-called phenon line is a horizontal line drawn across a

dendrogram at a certain similarity level to delimit groups of the same rank, and it is thus useful in determining groups or clusters.

The subjective selection of the partitioning level, where the phenon line can be moved up or down on the dendrogram to decrease or increase the number of clusters, makes HCA a semi-objective method (Guler *et al*., 2002).

CHAPTER FOUR

RESULTS AND DISCUSSION

The study endeavours to assess the extent of heavy metals, pesticides and nutrients contamination of surface water and sediment in the Ada Songor Lagoon due to anthropogenic activities around the catchment area of the lagoon. The quality of water and sediments in the Songor Lagoon was assessed by the determination of the following parameters; Pesticides residues (OCs, OPs and synthetic pyrethroids), trace metals (Cd, Cr, Ni, Pb, Co, Zn, Cu, As and Hg), the nutrients (SO_4^{2-}, PO_4^{3-}, NO_3^-) load, as well as physic-chemical parameters (pH, Temperature, EC, Salinity, TDS, Alkalinity, BOD, Total Hardness). The degree of anthropogenic contamination was assessed using geo-accumulation index, pollution load index and enrichment factor.

Results for physico-chemical parameters and nutrient loads of water are presented and discussed. Concentrations of heavy metals in water and sediment, and contamination status of bottom sediments are discussed. The levels of pesticides residue and metabolites in the sediment are also presented and discussed.

4.1 Physico-chemical characteristics, Major inorganic ions and Nutrient load of water

4.1.1 Physico-chemical characteristics

The results for the determined physico-chemical parameters of water from the Songor lagoon are presented in Table 4.1.

Table 4.1: Levels of physico-chemical parameters in water

Sampling Location	Physico-chemical parameters						
	pH	Temp., ^{0}C	EC, mS/cm	TDS, mg/L	BOD, mg/L	Alkalinity., mg/L	Salinity,‰
UW1	8.41	26.20	1640.00	817.00	2.45	144.00	960.00
UW2	8.42	26.20	1452.00	727.00	4.13	128.00	840.00
UW3	8.40	26.10	1676.00	837.00	5.35	124.00	980.00
UW4	8.41	26.20	1443.00	721.00	1.19	92.00	830.00
UW5	8.26	26.20	1181.00	591.00	2.04	92.00	670.00
UW6	8.26	26.10	1505.00	752.00	3.11	92.00	870.00
UW7	4.40	26.20	1709.00	854.00	1.87	152.00	1000.00
UW8	8.44	26.60	1810.00	905.00	5.14	148.00	1070.00
UW9	8.18	26.60	1370.00	685.00	2.12	88.00	780.00
UW10	8.44	26.50	1951.00	975.00	1.89	132.00	1160.00
MW1	8.40	26.50	1383.00	691.00	4.45	104.00	800.00
MW2	8.24	26.30	1299.00	649.00	5.11	92.00	750.00
MW3	8.48	26.30	2000.00	1001.00	4.71	140.00	1190.00
MW4	8.41	26.20	1839.00	919.00	3.87	140.00	1090.00
MW5	8.47	26.30	1913.00	956.00	4.58	64.00	1130.00
MW6	9.70	26.20	1771.00	885.00	3.91	60.00	1040.00
MW7	8.26	26.00	1770.00	885.00	4.12	72.00	1040.00
MW8	8.31	25.90	1847.00	923.00	3.95	52.00	1090.00
MW9	8.34	26.00	1753.00	877.00	3.41	76.00	1030.00
MW10	8.39	26.20	1862.00	931.00	5.01	64.00	1100.00
DW1	8.32	26.20	1901.00	948.00	4.54	20.00	1130.00
DW2	8.39	26.20	1874.00	936.00	4.08	104.00	1170.00
DW3	8.41	26.20	2090.00	1046.00	3.79	56.00	1250.00
DW4	8.47	26.00	1928.00	963.00	4.23	56.00	1140.00
DW5	8.45	26.00	1860.00	929.00	3.94	60.00	1100.00
DW6	8.46	25.90	1754.00	876.00	4.11	64.00	1030.00
DW7	8.47	25.90	1930.00	965.00	5.21	60.00	1180.00
DW8	8.46	25.80	1877.00	939.00	4.83	60.00	1170.00
DW9	8.47	25.90	1968.00	984.00	3.67	68.00	1170.00
DW10	8.40	25.70	2000.00	1002.00	3.71	64.00	1190.00

Temperature

Temperature is one of the essential physical parameter of water quality to measure because it influences the aquatic life by alter the dissolve oxygen (DO) concentration in the water making oxygen less available for respiration and metabolic activity of aquatic organisms (Tank and Chippa, 2013; Jalal and Sanalkumar, 2012). Water temperature is an affective factor to control the chemical reactions and its rate within the water body that determines the usefulness of the water (Metcalf and Eddy, 2003). Temperature of the studied water bodies were measured by digital thermometer during sample collection and average temperature is range between 25.70 ^{o}C to 26.60 ^{o}C. The standard temperature for sustaining aquatic life varies between 25.00 ^{o}C to 30.00 ^{o}C (Weldermeriam, 2013; Abulude *et al.*, 2006). The highest water temperature is found (26.60 ^{o}C) in UW8 whereas lowest temperature (25.70 ^{o}C) is recorded in DW10.

pH

pH that maintain the acidic or basic property, is a vital characteristic of any aquatic ecosystem since all the biochemical activities and retention of physico-chemical attributes of the water are greatly depend on pH of the surrounding water (Jalal and Sanal Kumar, 2013) . Most of the similar study suggested that water samples are slightly alkaline due to presence of carbonates and bicarbonates (Tank and Chippa, 2013; Gopalkrushna, 2011; Verma *et al*., 2012). Higher range of pH indicates higher productivity of water because availability of carbonates and bicarbonates in water enhance dissolve carbon dioxide level by dissociation and acts as a raw material for photosynthesis (Gopalkrushna, 2011). The pH value of all the studied water samples

varied from 8.18 to 9.70. The alkaline nature of the pH's obtained in the study is in agreement with the observation that most coastal waters in Ghana are slightly alkaline in nature (Biney, 1982; 1990). A pH range of 6.50 to 9.00 is ideal for the life of aquatic organisms like fish (Alabaster and Lloyd, 1980; Abulude, 2006). Therefore, the general measured pH range (8.18 and 9.70) is good for the health of the lagoon and will support the life of aquatic organisms. The highest and lowest pH is found in MW6 (8.66) and UW9 (8.12) respectively.

Total Dissolved Solids (TDS)

Type and quantity of TDS define the electrical conductivity of the water body (Tank and Chippa, 2013). The amount of total dissolved solids (TDS) in water indicates salinity of water and may also be used as an indicator for rapid plankton growth and sewage contamination. In this study, TDS value ranged from 591 to 1046 mg/L. The highest TDS value was found in DW3. The TDS values of the Songor lagoon indicate that, the lagoon is a brackish lagoon (Ella, 2007). High levels of dissolved solids will not be suitable for fish and water birds spawning since this will make it harder for them to find food (Peirce *et al*. 1997). Turbid and particle-laden waters that enter the Songor lagoon, as well as evaporation of the lagoon water as a result of salt mining activities may be reasons for the high TDS.

Electrical Conductivity (EC)

EC is the measure of the ability of an aqueous solution to transmit an electric current. Conductivity depends upon the presence of cations and anions, their total concentration, mobility, valence and temperature of water which is a good measure of total amount of salt present in water (Fianko *et al*., 2013).

Conductivity of the water samples varied from 1181 to 2090 mS/cm along the lagoon in general, and that reflect the amount of charged substances in the water samples. Sample water DW3 has the highest EC value. There is currently no official guideline as to what is considered safe level for conductivity (Karikari *et al*., 2007). However, the conductivity of most freshwaters ranged from 10 to 1000 µS/cm, but many exceed 1000 µS/cm, especially in polluted waters or those receiving large quantities of land run-off (Chapman, 1992). The high conductivity values may be attributed to the presence of dissolved solids in the waters. However, the high conductivity values may be attributed to high ionic exchange between the sea and the lagoon as a result of the human activities in the area such as the fishing and salt mining (Fianko *et al*., 2013).

Alkalinity

Alkalinity express the buffering capacity of the water which appreciably maintain the pH by absorbing access H^+ ions and protects the water body from pH fluctuation. The main species responsible for alkalinity are carbonates, bicarbonates, hydroxide ions, ammonia, organic acid etc. Alkalinity acts as a buffer against rapid pH change (Chapman, 1992).

Levels of alkalinity in the water samples during the study period ranges from 20.0 to 152.0 mg/L for the sampling sites with UW7 recorded the highest (152.0 mg/L) and DW1 having lowest (20.0 mg/L). High alkalinity values in the lagoon indicated that the water had a higher capacity to neutralize a change in pH (Chapman, 1992). The alkalinity could be attributed to the continuous removal of vegetation by the farmers, fishermen and salt miners within the catchment area of the Songor lagoon for farming and fuel wood, space for parking of canoes and space for packing salt. Land use impacts (farming practices) which expose the soil and underlying rocks through the process of weathering could also have contributed to the alkalinity levels in the water (Fianko *et al*., 2013).

Salinity

Generally, the salinity of the water ranges from 670 to 1250 ‰. Salinity is a primary factor affecting the distribution of benthic organisms in estuary (Markmann 1986, Hymanson *et al*. 1994). The salinity in the lagoon water could be due to the mixing of sea water and blocked creek channels (anthropogenic activity); reduction in freshwater inflow to the lagoon. Reduction in freshwater inflow can result in saline water extending further and displacing brackish habitats at the expense of saline habitats (Adams *et al*., 1992; Wortmann *et al*., 1998). Closure of the creek channels also prevents recruitment of invertebrates and fish to the Songor lagoon from the Volta River. Freshwater inflow thus influences the ‘connectivity’ of nursery habitats for certain species within estuaries. Species may inhabit a variety of freshwater and estuarine habitats at different stages of their life cycle and the loss of connectivity between these habitats due to reduced

freshwater supply can influence the survival of juvenile organisms reliant on those habitats to complete their life cycle.

Biochemical oxygen demand (BOD)

Biochemical oxygen demand is a measure of the amount of biologically degradable organic material that is present in the water. It indicates the amount of oxygen that aerobic aquatic organisms could potentially consume in the process of metabolizing all the organic matter available to them. The consequence of high BOD is low levels of dissolved oxygen in affected waterways resulting in aquatic organisms becoming stressed and in extreme cases, suffocating and dying (Ameka *et al*., 2000). With the exception of some collection points (UW1, UW4, UW5, UW7, UW9 and UW10), all other samples recorded biological oxygen demand values higher than the WHO limit of <3.0 mg/L. The BOD levels in general ranges from 1.19 to 5.35 mg/L. The high BOD values recorded may be due to the dumping of refuse in to the lagoon.

4.1.2 Major inorganic ions of water

Sodium

Sodium concentrations in general ranged from 1,216.0 to 14,560.0 mg/L. The highest values were measured in UW2 (12,260.00 mg/L), MW8 (14,560.00 mg/L) and DW10 (14,262.00 mg/L). Concentrations of sodium in natural surface waters may vary considering local geological conditions and wastewater discharges. Values can range

from 1 mg/L or less to 105 mg/L or more in natural brines (Chapman 1992). The WHO guideline limit for sodium in surface water is 200 mg/L and for ground-water levels frequently exceed 50 mg/L (Chapman 1992). Sodium concentrations ranged from 11,700 to 19,640 mg/L with a mean concentration of 15,166 mg/L was measured in the kpeshi lagoon (Fianko *et al*., 2013). Gordon (1995) also measured a mean sodium concentration of 52,725 mg/L at the Kpeshi lagoon in the dry season. The very high sodium concentrations measured may be due to seawater intrusion.

Potassium

Concentrations of potassium ranged between 1326.0 and 2434.0 mg/L with the highest concentration recorded at MW7. The high potassium levels recorded were indication of the influence from domestic discharge and agricultural effluents especially fertilizers containing potassium through soil run off into the lagoon. The high mean level of potassium recorded at MW7 indicated the discharge of domestic waste and agricultural effluents especially fertilizers containing high levels of potassium through soil run off into the lagoon.

Magnesium and Calcium

Concentrations of magnesium ranged from 14.0 to 109 mg/L with the lowest concentration at UW5. The levels of magnesium in the lagoon can be attributed to the use of fertilizers by vegetable crop farmers which may contain high levels of the element.

The pattern of ionic dominance in the lagoon during the present study was $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The cationic dominance pattern was similar to that of seawater as observed by Karikari *et al.* (2005).

Chloride (Cl^-):

Chloride is present in all natural surface and ground water from as low concentration to high concentration. Chlorides are mainly come from inorganic salts like NaCl, KCl and $CaCl_2$ etc. which are generally provided by soil, natural layers of chloride salts, domestic sewage and animal wastes (Gopalkrushna, 2011; Chapman, 1992). Chloride is not harmful to humans but high concentration of chloride increase the corrosive property of water. The chloride content of studied water samples varied from 41,987 to 104,768 mg/L. Sample water UW10 have the highest chloride (104,768 mg/L).

Sea water intrusion could best be used to explain the relatively high values recorded for chloride levels during the study, given the proximity of the lagoon to the sea. The people around the catchment also block fresh water inflow from the Volta lake and introduce sea water to enable them mine salt.

4.1.3 Nutrient load of the water

Nitrates, Phosphorous and Sulphate were the nutrients measured in the water samples. Nitrates are veritable indication of biological pollution in natural waters. They are considered to be non-cumulative toxins (Dallas and Day, 1993).

Nitrate (NO_3^-)

Inorganic nitrogen present in water as Nitrate (NO_3^-) is the main nutrient that accelerates the growth of hydrophytes and algae. Nitrate occurs in water from various natural sources and due to human activities like food production, agriculture and manure disposal of domestic and industrial sewage. High level of nitrates is found in rural areas because of extensive application of nitrogenous fertilizers in agriculture. In urban areas sewage water rich in nitrates contaminate surface water thus increases the nitrate amount. (Tank, 2013; Gopalkrushna, 2011). A small amount of nitrate is common in all kinds of surface water. All water samples had nitrate levels below 1.0 mg/L. Nitrate levels ranges from 0.83 to 0.92 mg/L. The concentrations of NO_3^-, according to McCutcheon *et al*. (1989), were not alarming and that the lagoon was free from organic waste contamination. Nitrate stimulates the growth of hydrophytes and phytoplankton that consequently increase the nutrient in water body leading to eutrophication.

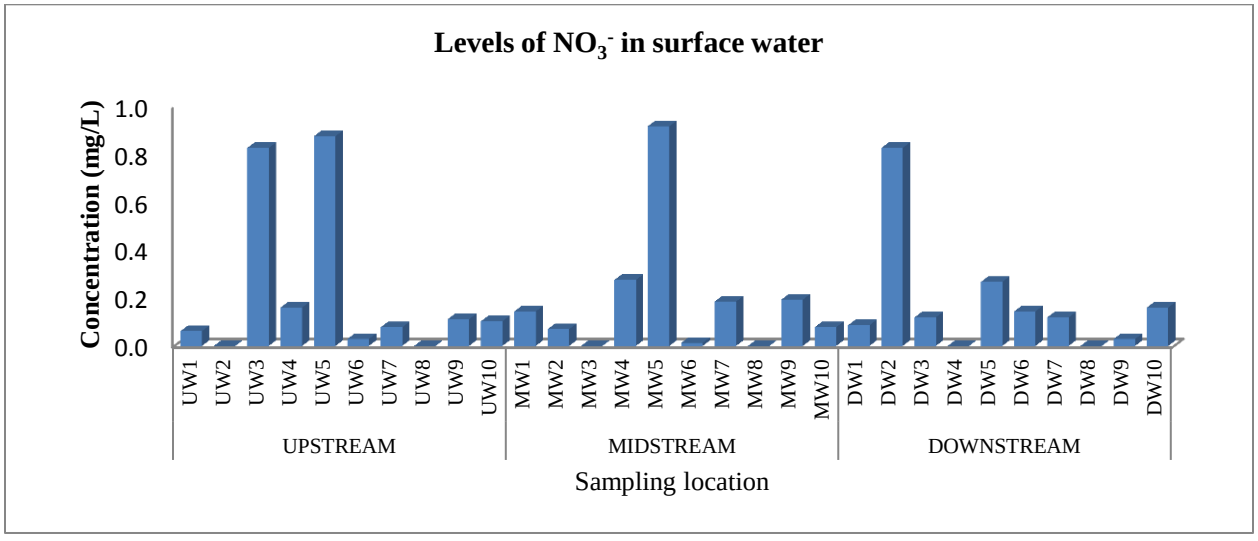

Fig 4.1: levels of NO_3^- in water

Phosphate (PO_4^{3-}):

Phosphorus is rarely found in high concentrations in surface waters as it is taken up by plants. Phosphate may occur in surface water as result of domestic wastes, detergent and agricultural run-off containing fertilizer. In most natural surface waters phosphorus ranges from 0.005 to 0.060 mg/L (Wild 1995; Gopalkrusna, 2011). Phosphorous is a limiting nutrient for algal growth and therefore controls the primary productivity of a water body (Karikari *et al*., 2007). It is also an essential nutrient and another indicator of anthropogenic biological pollution. In most natural waters, PO_4^{3-} concentrations range from 0.005 to 0.020 mg/L (Chapman, 1992). In pristine waters, PO_4^{3-} concentrations may be as low as 0.001 mg/L (Karikari *et al*., 2007). Levels of PO_4^{3-} in this study varied from 0.05 to 2.92 mg/L which exceeds the levels in most natural waters (Chapman, 1992; Wild 1995). The relatively high phosphate concentrations in the lagoon may have the potential of causing eutrophication thereby reducing the level of oxygen in the lagoon needed by aquatic organisms especially fish for respiration (Fianko *et al*., 2013).

High concentrations of phosphate are largely responsible for eutrophic conditions in a water body. The comparatively high amount of phosphate might be due to discharge of domestic sewage and dumping of domestic waste into the lagoon (Benjamin *et al*, 1996).

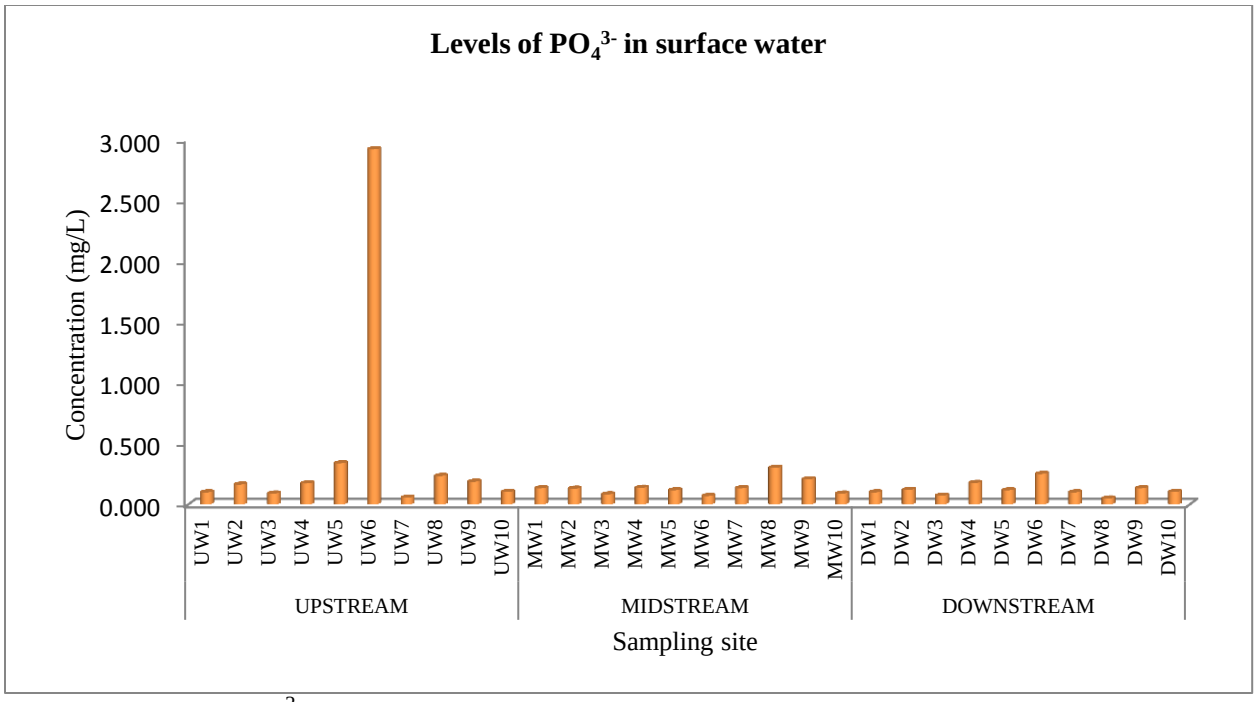

Fig 4.2: levels of PO_4^{3-} in water

SO_4^{2-}

Sulphate values were generally high at almost all the sampling sites. The sulphate levels varied from 65.8 to 190 mg/L. The highest values were recorded at MW7 (190 mg/L). The high sulphate values may be due to the influx of domestic wastes and sulphate containing fertilizers from agricultural farms. Sulphates cause scaling in water supplies, and problem of odour due to its reduction to H_2S. The hydrogen sulphide like smell of the sediment in the lagoon may be due to the levels of the sulphate.

Sulphate is one of the nutrients that accelerate the growth of hydrophytes and algae. The high concentrations of sulpate in the lagoon may have the potential of causing eutrophication (Fianko *et al.*, 2013). High concentrations of sulphate are largely responsible for eutrophic conditions in a water body

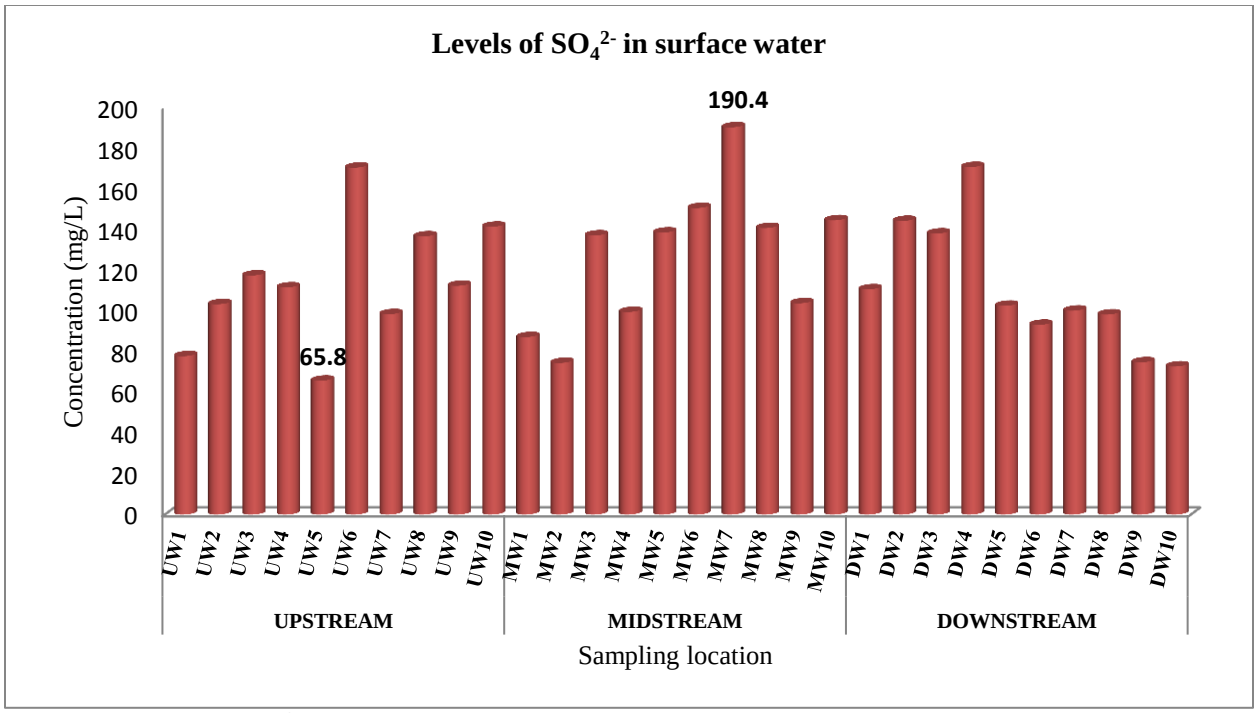

Fig 4.3: levels of SO_4^{2-} in water

4.2 Concentrations of heavy metals in water and sediment, and contamination status of bottom sediments

4.2.1 Validation of atomic absorption spectroscopy method

The validity of the atomic absorption spectroscopy method used for the determination of the heavy metals in water and sediment was checked by analysis of appropriate reference material. SRM 1643e (trace metals in water) and SRM 1646a (estuarine sediment), obtained from the National Institute of Standards and Technology (NIST), Technology Administration, US Department of Commerce was used for the water and sediment analysis respectively. Comparison of the results obtained in this study with the NIST recommended and information values are presented in Table 4.2. The results obtained in the present study are in good agreement with the NIST recommended values. This

confirms the reliability of the atomic absorption spectroscopy method for the determination of Fe, Mg, Mn, Zn, Ni, Cu, Co, Cr, Cd, As Hg and Pb.

Table 4.2: Validation of AAS methods using NIST SRM 1643e and NIST SRM 1646a

	NIST SRM 1643e (Fresh Water)		NIST SRM 1646a (Estuarine Sediment)	
Element	Concentration (µg/kg)		Concentration (mg/kg)	
	Present study	Certified	Present study	Certified
Mn	35.88 ± 2.90	38.02	231.31 ± 4.26	234.5
Zn	75.07 ± 1.95	76.5	46.72 ± 1.91	48.9
Cd	5.42 ± 1.55	6.408	0.11 ± 0.05	0.148
Cr	17.80 ± 1.99	19.90	38.95 ± 1.02	40.9
Cu	23.02 ± 0.92	22.20	7.52 ± 4.11	10.01
Pb	18.10 ± 1.09	19.15	10.23 ± 1.01	11.7
As	57.31 ± 1.81	58.98	5.21 ± 2.91	6.23

Data for present study are presented as mean ± standard deviation [$\bar{x} \pm \sigma$] of three replicate measurements

4.2.2 Concentration of heavy metals in water and sediments

Concentrations of Fe, Mg, Mn, Zn, Ni, Cu, Co,Cr, Cd, As Hg and Pb in the water samples are presented in Table. 4.2. The concentrations of heavy metals, Cu, Hg and Zn concentration levels were all below the detection limit in the water samples. The concentrations of heavy metals (As, Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb and Zn) measured in sediment samples, were generally higher than water samples. The high level of heavy metals in the sediment relative to levels in water is expected as sediments have been

described as a sink or reservoir for pollutants in water (Onyari *et al*., 2003; Samir *et al*., 2006). The low concentrations of the heavy metals in the surface water could be due to dilution, adsorption, and precipitation.

The Levels of trace metals measured in the lagoon sediments may be from the discharge of domestic waste and residues from agrochemicals used in the catchment by farmers due to the absence of chemical and manufacturing industries. These may be carried to the lagoon as runoff or through neglect or by eroding soil or percolating or leaching through the soil (Fianko *et al*., 2013). Trace and heavy metals in the agrochemicals will cause widespread damage to biota. Widespread application of the agrochemicals may eliminate food sources that certain types of animals need, causing the animals to relocate, change their diet or starve to death (Fianko *et al*., 2013). The levels of trace metals in the lagoon sediments may bioaccumulate to enhance toxic levels in the bodies of organisms that consume them over time and they eventually die (Palmateer 1992). The geology of the area could also influence the heavy metals levels.

Table 4.3: Levels of heavy metals in water

Sampling Location	Metals (mg/L)										
	As	Cd	Cr	Co	Cu	Fe	Mn	Ni	Pb	Zn	Hg
UW1	BDL	0.040	0.028	BDL	BDL	BDL	0.024	0.164	0.012	BDL	BDL
UW2	BDL	0.056	0.024	BDL	BDL	BDL	BDL	0.176	BDL	BDL	BDL
UW3	BDL	0.060	0.012	BDL	BDL	BDL	BDL	0.080	BDL	BDL	BDL
UW4	0.020	0.076	0.016	0.048	BDL	BDL	BDL	0.036	0.064	BDL	BDL
UW5	0.024	0.072	BDL	0.068	BDL	BDL	BDL	0.112	0.064	BDL	BDL
UW6	0.032	0.080	0.012	0.060	BDL	BDL	BDL	0.104	0.092	BDL	BDL
UW7	0.044	0.080	BDL	0.116	BDL	BDL	0.080	0.096	0.248	BDL	BDL
UW8	0.040	0.084	BDL	0.100	BDL	BDL	0.044	0.108	0.256	BDL	BDL
UW9	0.064	0.092	BDL	0.060	BDL	BDL	0.072	0.104	0.328	BDL	BDL
UW10	0.076	0.088	BDL	0.132	BDL	BDL	0.124	0.184	0.420	BDL	BDL
MW1	0.056	0.084	BDL	0.196	BDL	BDL	0.136	0.004	0.296	BDL	BDL
MW2	0.060	0.060	BDL	0.116	BDL	BDL	0.064	BDL	0.308	BDL	BDL
MW3	0.020	0.040	BDL	0.208	BDL	BDL	BDL	0.140	0.196	BDL	BDL
MW4	0.028	0.036	BDL	0.212	BDL	BDL	0.036	0.060	0.224	BDL	BDL
MW5	0.056	0.016	BDL	0.180	BDL	0.044	0.024	0.032	0.228	BDL	BDL
MW6	0.036	0.020	BDL	0.268	BDL	BDL	0.040	BDL	0.236	BDL	BDL
MW7	BDL	0.020	BDL	0.288	BDL	BDL	0.052	BDL	0.184	BDL	BDL
MW8	0.036	BDL	BDL	0.268	BDL	BDL	0.040	BDL	0.256	BDL	BDL
MW9	BDL	BDL	BDL	0.184	BDL	BDL	BDL	BDL	0.184	BDL	BDL
MW10	BDL	BDL	BDL	0.128	BDL	BDL	0.016	BDL	0.224	BDL	BDL
DW1	0.016	0.008	BDL	0.116	BDL	0.544	0.012	0.028	0.184	BDL	BDL
DW2	0.024	0.016	BDL	0.072	BDL	0.148	0.020	0.032	0.196	BDL	BDL
DW3	0.024	0.016	BDL	BDL	BDL	0.252	0.032	0.096	0.208	BDL	BDL
DW4	BDL	0.028	BDL	BDL	BDL	0.008	0.008	BDL	0.128	BDL	BDL
DW5	0.012	0.040	BDL	BDL	BDL	BDL	BDL	BDL	0.236	BDL	BDL
DW6	0.068	0.056	BDL	BDL	BDL	BDL	0.016	BDL	0.312	BDL	BDL
DW7	0.048	0.060	BDL	BDL	BDL	BDL	0.012	BDL	0.276	BDL	BDL
DW8	0.060	0.076	BDL	BDL	BDL	0.108	0.044	0.100	0.320	BDL	BDL
DW9	0.068	0.076	BDL	BDL	BDL	BDL	0.024	BDL	0.400	BDL	BDL
DW10	0.080	0.068	BDL	BDL	BDL	BDL	0.008	0.044	0.420	BDL	BDL

BDL: Below Detection Limit

Cadmium

The concentration of Cd in water and sediment ranged from below detection limit to 0.09 mg/L and below detection limit to 0.44 mg/Kg respectively. Water samples from MW8, MW9 and MW10 had Cd concentrations below detection limits. For sediments, US1 to US6, MS8 to MS10 and DS1 to DS5, cadmium was not detected. Cd is an important factor in aquatic monitoring studies, because it has been found to be toxic to fish and other aquatic organisms (Pascod, 1992). Cadmium is more toxic in freshwater than in saltwater because cadmium combines with chlorides in saltwater to form a molecule that is less available from solution (Bradl, 2005; Wright and Welbourn, 2002). Skeletal deformities in fish can result in impaired ability of the fish to find food and to avoid predators. Cadmium impairs aquatic plant growth. This affects the entire ecosystem because green plants are at the base of all food chains. When aquatic plants that are exposed to cadmium do not grow normally, there will be less food available for aquatic animals (Bradl, 2005; Landis and Yu, 2003; Wright and Welbourn, 2002).

Sources may include leaching from Ni-Cd based batteries (Hutton *et al*., 1987). Thus, the indiscriminate dumping of refuse into the lagoon in the catchment area could pose a potential danger for Cd toxicity.

Lead

Lead level in the lagoon water varied between below detection limit and 0.42 mg/L. UW2 and UW3 lead levels were below detection limit. Lead level in the lagoon sediment sample varied from below detection limit to 3.83 mg/ Kg in. sample locations US1 and US2 Pb level were below detection limit. The highest level of Pb was in DS10 (3.83

mg/Kg). The level of Pb obtained in the sediment were higher than those in the lagoon water, hence the sediment could be an influencing factor on the level of Pb in the lagoon water with other enhancing factors like pH, since water acidity is known to influence the solubility and availability of metals (Addo *et al*., 2011).

The permissible limit for Pb in surface water according to the USEPA (1986) is 0.05 mg/L. This means that apart from sampling sites UW2 and UW3 for water, all the sampling sites are contaminated with lead.

Lead bioconcentrates in the skin, bones, kidneys, and liver of fish rather than in muscle and does not biomagnify up the food chain. This makes lead less problematic via this route of exposure. However, people who eat the whole fish and wildlife, who, of course, eat the whole fish, can potentially be exposed to high concentrations of lead (Wright and Welbourn, 2002). When lead concentrations in algae exceed 500 µg/Kg, enzymes needed for photosynthesis are inhibited (Taub, 2004). When less photosynthesis takes place, the algae will produce less food and therefore will not grow as much. Decreased algal growth means less food for animals; this has repercussions for the entire ecosystem. Fish are more sensitive than algae to lead. When lead concentrations exceed 100 µg/L, gill function is affected. Embryos and fry are more sensitive to the toxic effects of lead than are adults. Lead is more toxic at lower pH and in soft water (Taub, 2004; Wright and Welbourn, 2002). As is the case with other metals, the toxicity of lead to fish depends in part on the species. Goldfish are relatively resistant because they can excrete lead via their gills (Landis and Yu, 2003).

Copper and Zinc

The results of the analyses indicate that concentration of the Copper (Cu) varied from below detection limit to 0.21 mg/Kg; for Zn it ranged from below detection limit to 1.19 mg/Kg in the sediment samples. However, none of these metals were detected in the water samples from the lagoon. Cu and Zn permissible limit in surface water according to USEPA (1986) are 1.00 mg/L and 1.00 mg/L respectively. Extensive literature on aquatic toxicity of Zn and especially its toxicity to fish has been reviewed by Alabaster and Lloyd (1980) and by Spear (1981). Zn is unusual in that it has low toxicity to man, but relatively high toxicity to fish (Alabaster and Lloyd, 1980).

Nickel

Levels of Ni in the lagoon water ranged from below detection limit to 0.18 mg/L. The Ni levels in the sediment samples ranges from below detection limit to 1.60 mg/Kg. The ranges obtained in the sediments were much higher than the water, indicating that the sediment is more contaminated. Water sample locations DW4 to DW9 and MW6 to MW10 were all below detection limit, while sediment sample location DS4 to DS7 were also below detection limit. The typical concentration of Ni in unpolluted waters is given as 0.015 to 0.020 mg/L (Salnikow and Denkhaus, 2002). Possible contamination of the metal in some traditional fishes cannot be ruled out, since Pane *et al.* (2003) has reported Ni toxicity in rainbow trout. Although, Ni is considered an essential element to plants and some animals (e.g. Ni is present in the enzyme urease), its essentiality to man is yet to be demonstrated (Teo and Chen, 2001). Nickel also is a naturally occurring element found in a number of mineral ores including Ni sulphides, oxides and silicates. Possible sources of

Ni in surface water include anthropogenic sources, combustion of fossil fuels (Merian, 1984), old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Ni alloys (Addo *et al*., 2011; Fianko *et al*., 2013).

Chromium

Chromium concentration in lagoon water varied from below detection limit to 0.03 mg/L. Cr concentration levels in sampling sites UW7 to DW10 were below detection limit.

Chromium concentration in lagoon sediment varied from below detection limit to 0.17 mg/Kg. Sampling sites US3 to MS3 and MS8 to DS6 were below detection limit. The biological effects of Cr depend on its valency. In the trivalent form, Cr is essential element but in the hexevalent form it is carcinogenic (Chiba and Masironi, 1992). Low concentrations of hexavalent chromium cause sublethal toxic effects in aquatic plants and animals. For example, 62 µg/L inhibits growth in algae and 16 µg/L inhibits growth in chinook salmon (Taub, 2004). Chinook salmon are more sensitive than algae. This is consistent with the overall finding that aquatic animals are more sensitive to metals than are aquatic plants (Wright and Welbourn, 2002). Although reducing the growth of a plant or animal is not directly lethal, the smaller size increases the vulnerability of the organism to predators. As is the case with other metals, chromium toxicity to aquatic organisms increases as water temperature increases and as pH and salinity decrease. Additionally, chromium is more toxic in soft water than in hard water and there are species differences in sensitivity. For example, fathead minnows are more sensitive than goldfish. The concentration of chromium that caused death in 50% of the exposed population was 3 mg/L in soft water and 72 mg/L in hard water for fathead minnows and

18 mg/L in soft water and 133 mg/L in hard water for goldfish (Puget Sound Water Quality Authority, 1988; Taub, 2004).

In this area, Cr may have originated from weathering or rock, wet precipitation and dry fallout from the atmosphere and run off from the terrestrial systems since there are no tanning activities in the area.

Iron

Iron, Fe concentrations in the sediment ranges from 134 to 1429 mg/Kg. Sampling site US2 recorded the highest (1429 mg/Kg) whilst the water varied between below detection limit to 0.54 mg/L. Fe was present in only water sample DW1 to DW4 and DW8. The concentrations of Fe in the lagoon may arise from land-use practices in the catchment such as agricultural activities (the use of agrochemicals and fertilizers by farmers). Iron at very high levels is toxic and may inhibit enzymatic functions (WRC, 2003) in aquatic organisms. Elevated levels of iron in coastal waters will also increase the susceptibility of the fishes in the lagoon to infectious diseases (Fianko *et al*., 2013). Fe is an important metal in both plant and animals, especially in cellular processes but above 0.3 mg/L, it discolours aerobic waters (WHO, 2004).

Manganese

Manganese occurs naturally in most surface waters and in soils that may erode into waters. However, human activities are also responsible for much of the manganese contamination in water in most areas (Fianko *et al*., 2013). The manganese concentration in the lagoon sediment ranged from 11.3 to 41.9 mg/L. the Mn concentrations varied between below detection limit to 0.14 mg/L. Samples UW2 to UW7, MW3, MW9 and DW5 were below detection limit.

The recommended MCL for Mn in water is 0.05 mg/l (USEP, 2010). Mn in nature is found in form of oxides, silicates and carbonates. It functions as co-factor in the synthesis of urea from ammonia, amino acid and fatty acid metabolism and glucose oxidation. Mn is an element of low toxicity having considerable biological significance and one of the more biogeochemical and active transition metals in aquatic environment (Evans *et al*., 1977). It occurs in surface waters that are low in oxygen and often does so with Fe. It accumulates in certain species of fish (Uthe and Blish, 1971).

4.2.3 Contamination status of bottom sediments

Urban runoff and anthropogenic activities is recognized as a major source of contaminants (Characklis and Wiesner 1997, Paul and Meyer 2001). Wetlands can accumulate contaminants over time, so there is concern that the risk to wildlife from contaminant toxicity may outweigh the benefits that these urban wetlands provide as habitat (Helfield and Diamond 1997, Wren *et al*. 1997). Bioaccumulation of contaminants and toxicological effects on wildlife have been documented for wetlands

receiving nonpoint source runoff (Ohlendorf *et al*. 1989, Schuler *et al*. 1990, Welsh and Maughan 1994, Glenn *et al*. 1999, Garcia-Hernandez *et al*. 2001). Impacts can include direct toxicity to algae and aquatic plants, wetland fauna including wetland invertebrates, amphibians, reptiles, fish, and birds, resulting in the loss of biodiversity and simplification of the food chain (Wren *et al*. 1997, Adamus *et al*. 2001). These impacts have been demonstrated for heavy and trace metals such as Hg, Pb, Zn, Cu, and Cd (Galli 1988, Yousef *et al*. 1990, Campbell 1994, Brown and Bay 2006). The presence and relative severity of effects depends on many site-specific factors, such as the wetland type, contaminant loading rates and concentrations, landscape position, hydrology, nature of sediment storage and transport, and structure of the biotic communities (Schueler 2000).

Sediments represent one of the ultimate sinks for heavy metal discharge into the environment (Gibbs, 1977; Luoma and Bryan, 1981). In order to protect the aquatic life community comprehensive methods for identifying and assessing the severity and soil contamination have been introduced over the past decades (Loska *et al*., 1997; Chapman, 2000: Ghrefat and Yusuf, 2006). In this study, the index of geoaccumulation (Igeo), Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI) have been applied to assess heavy metals (Cd, Cr, Ni, Pb and Zn) distribution and contamination in the sediment samples of the Songor Lagoon.

4.2.3.1 Enrichment factor

The enrichment factor is the relative abundance of a chemical element in a soil compared to the bedrock (Hernandez *et al*., 2003). Enrichment factor is a convenient measure of geochemical trends and is used for comparison between areas. It is applied widely in mangrove geochemical studies (Ramanathan *et al*., 1999; Abraham, 1998; Soto-Jime´nez *et al*,, 2001; Kamau, 2002; Qu *et al*., 1993; Kehrig *et al*,, 2003).

As proposed by Simex and Helz (1981), the Enrichment Factor (EF) was employed to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin from sites by individual elements in sediments. Fe was chosen as the normalizing element while determining EF-values, since in wetlands it is mainly supplied from sediments and is one of the widely used reference element (Loska *et al*., 2003; Kothai *et al*., 2009; Chakravarty and Patgiri, 2009; Seshan *et al.*, 2010). Seshan *et al.*, (2010) have indicated that several researchers have also employed Al and Si as reference elements in the calculation of EF. An element also qualifies as a reference one, if it is of low occurrence variability and is present in the environment in trace amounts (Loska *et al.*, 2003). In this study, iron was also used as a conservative tracer to differentiate natural from anthropogenic components. According to Ergin *et al.* (1991), the metal EF is defined as follows:

$$EF_{metal} = \frac{\left(M/Fe\right)_{sample}}{\left(M/Fe\right)_{background}}$$

Where:

M is the metal of interest

EF values were interpreted as suggested by Birch (2003) where EF<1 indicates no enrichment, <3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe; and >50 is extremely severe. The background value is that of average shale (Turekian and Wedepohl, 1961). Elements which are naturally derived have an EF value of nearly unity, while elements of anthropogenic origin have EF values of several orders of magnitude.

The values for the enrichment factors of Cd, Mn, Ni, Cr, Cu, and Pb are presented in the Appendix 7. From the table, there was no enrichment in Cd for samples US1 to US6 and MS8 to DS5. Sediment samples US1 and US2 show no enrichment of any of the metals. However, sediment samples DS6 to DS10 are very severely enriched with Cd and Pb. There was no enrichment of chromium in any of the sediment samples. Only sediment sample MS1 show minor enrichment with Cu.

EF Status	Cd	Mn	Ni	Cr
No Enrichment	US1 - US6 MS8 - DS5	US2	US2, MS1 - MS3 MS6, MS8, MS9, DS1 - DS8	US1 -DS10
Minor			US4	
Moderate		MS1 - MS3; MS5, MS7, MS8	US1, US3, US5, MS10, DS9 DS10	
Moderately Severe		US1, US3 - US6, US10 MS4, MS9 - DS10	US6 -US10, MS4, MS5 MS7	
Severe		US3, US7 - US9, MS6		
Very Severe	US7 -MS7 DS6 - DS10			

4.2.3.2 Geo-accumulation index

Geo-accumulation index was used to assess heavy metal accumulation in sediments as introduced by Muller (1969) to measure the degree of metal pollution in aquatic sediments studies (Praveena *et al*., 2007, 2008; Chakravarty and Patgiri, 2009).

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

where, C_n is the measured concentration of a heavy metal in stream sediments, B_n is the geochemical background value in average shale of element n and 1.5 is the background matrix correction due to Terrigenous effects.

The index of geo-accumulation includes seven grades (0 to 6) ranging from unpolluted to very highly polluted. The grades are as follows:

I-geo was classified into seven grades:

I-geo ≤ 0 (grade 0), unpolluted;

0< I-geo ≤1 (grade 1), slightly polluted;

1 < I-geo ≤ 2 (grade 2), moderately polluted;

2< I-geo ≤3 (grade 3), moderately severely polluted;

3< I-geo ≤4 (grade 4), severely polluted;

4< I-geo ≤5 (grade 5), severely extremely polluted;

I-geo > 5 (grade 6), extremely polluted contaminated

The calculated Igeo values for each metal in the sediment samples among the sampling locations are presented in Fig. 4.4. It is evident from Fig. 4.4 that all the sites of sediments sample collection from the Songor lagoon under the current study are

unpolluted (I-geo<0) according to the I-geo calculations based on the use of average shale as background material for the elements.

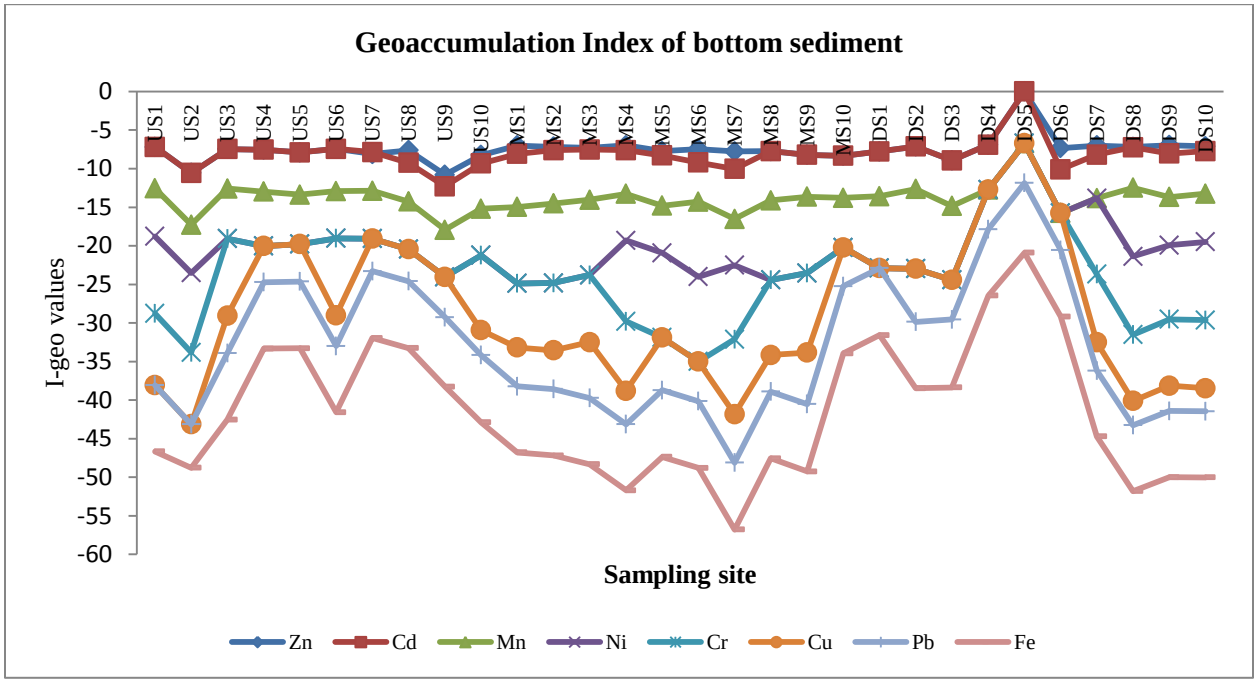

Fig 4.4: Geo-accumulation Index of metals in sediment

4.3 Concentration of Pesticide residues and metabolites in sediment

Bioaccumulation of contaminants and toxicological effects on wildlife have been documented for wetlands receiving nonpoint source runoff (Ohlendorf *et al*. 1989, Schuler *et al*. 1990, Welsh and Maughan 1994, Glenn *et al*. 1999, Garcia-Hernandez *et al*. 2001). Impacts can include direct toxicity to algae and aquatic plants, wetland fauna including wetland invertebrates, amphibians, reptiles, fish, and birds, resulting in the loss of biodiversity and simplification of the food chain (Wren *et al*. 1997, Adamus *et al*. 2001). These impacts have been demonstrated for organophosphorus and pyrethroid pesticides (Katznelson *et al*. 1995, Harris *et al*. 1998), polyaromatic hydrocarbons

(PAHs; Maltby *et al*. 1995), polychlorinated biphenyls (PCBs; Dunier and Siwicki 1993, Wren *et al*. 1997, Adamus *et al*. 2001).

The study detected residues and metabolites of organochlorines (OCs), pyrethroids and organophosphorus (OPs) in sediment samples from the Songor lagoon. These pesticides were extensively used in the past in the pineapple, vegetable and food crop farms (*MOFA, 2003*). The occurrence and concentration of pesticides and metabolites varied widely between samples of different collection points. A total of 6 different types of organochlorine pesticide residues and metabolites were detected in varying concentrations ranging between 0.001 µg/g and 0.101 µg/g in the samples whiles 12 different types of organophosphorous with concentrations between 0.004 µg/g and 7.494 µg/g were detected in sediment samples. A total of 6 different types of synthetic pyrethroids residues and metabolites were detected in varying concentrations ranging between 0.001 µg/g and 0.014 µg/g. Of the numerous pesticides evaluated, Dimethoate (7.494 µg/g at DS2B), recorded the highest concentration while in β-HCH (0.001 µg/g at MS10B and DS4B), δ-HCH (0.001 µg/g at DS4B and DS6B), Aldrin (0.001 µg/g at MS10B) and Heptachlor (0.001 µg/g at DS6B) registered the lowest concentrations.

The concentrations of individual pesticides measured in sediment samples from majority of sampling sites were below detection limit. Out of the 15 sediment samples analysed, synthetic pyrethroids and organophophorous pesticide residues were the most detected. The samples did not record significant levels of organochlorine pesticide residues as most of them were below detection limit.

4.3.1 Levels of Synthetic Pyrethroid pesticides in sediment

The primary mode of action of pyrethroids in vertebrates and invertebrates is the disruption of voltage sensitive sodium channels in the neurons (Naharashi, 1996). Due to their cost-effectiveness, they gained rapid and widespread adoption by the agricultural community, and soon were used globally on a broad range of crops (Maund *et al*., 2009). High levels of toxicity of synthetic pyrethroids were observed in laboratory acute and chronic studies to a range of aquatic arthropods, particularly crustaceans and certain aquatic insects (Hill, 1989). Although of relatively low toxicity to terrestrial vertebrates for insecticides (due to their rapid metabolism by birds and mammals), fish were also found to be relatively sensitive most probably because of a less pronounced ability to metabolise the compounds (Haya, 1989). Based on their inherent toxicity in laboratory studies, pyrethroids are still among the most aquatic ecotoxicologically active of all pesticides, with effect concentrations in standard acute and chronic studies with fish and arthropods ranging from the microgram to nanogram per litre level (Solomon *et al*., 2001). Surveys of sediments have now established significant pyrethroid residues in urban areas, and the potential effects of these on aquatic ecosystems is currently being investigated (Weston *et al*., 2004).

Almost all the sampling locations recorded appreciable levels of synthetic pyrethroid pesticide residues in sediment samples. The levels generally ranged from 0.001 µg/g to 0.014 µg/g. The highest synthetic pyrethroid pesticide concentration was found for allethrin at sampling Site US 2B. Significant levels of cypermethrin, permethrin, and cyfluthrin were detected at sites US 2B to DS 10B (Table 4.3). Concentration of cypermethrin varied between 0.001 µg/g and 0.007 µg/g, permethrin 0.001µg/g to 0.013

µg/g; deltamethrin ranging from 0.002 µg/g; cyfluthrin between 0.001 µg/g and 0.002 µg/g and bifenthrin was between 0.001 µg/g and 0.003 µg/g.

The discharge of agro-chemicals from flood plains, agricultural fields through agricultural runn off might have contributed to the elevated pesticides concentration.

The USEPA has assembled a working group to evaluate the potential for sediment toxicity from synthetic pyrethroids (USEPA, 1999b). The working group investigated the environmental fate, bioavailability and toxicity of cypermethrin in three sediment types. Ten-day acute toxicity tests on sediment containing cypermethrin were performed using the midge *Chironomus tenfuns* and the amphipod *Hyullelu uzfecu.* Ten-day LC_{50} values ranged from 14.2 to 37.4 µg/Kg cypermethrin for C. *fentuns* and 3.1 to 21.1 µg/Kg cypermethrin for ***H.*** *uztecu.* These studies indicate that, although cypermethrin binds rapidly to sediment and suspended particulate matter, it remains biologically available (USEPA, 1999b).

Bifenthrin tends to bioconcentrate in fish. Whole-body bioconcentration factor (BCF) values for fathead minnow *Pimephales promelas* in water were 21,000 and 28,000X in 0.0037µg/L for 127 and 254 days, respectively (McAllister 1988).

The synthetic pyrethroids in the sediment samples indicate that farmers around the lagoon do use synthetic pyrethroids base pesticides in their farming activities. The discharge of agro-chemicals from flood plains, agricultural fields through agricultural runoff might have contributed to the elevated pesticides concentration.

4.3.2 Levels of Organochlorine pesticides in sediment

Organochlorine pesticide residues; Methoxychlor, Dieldrin, Endrin, Endosulfan, α - Endosulfan, β - Endosulfan, γ - Chlordane, p,p'- DDD, p,p'- DDE, p,p'- DDT were not detected in all the samples. β –HCH was detected in only MS10B and DS4B (0.001 µg/g). γ - HCH ranged from 0.001 to 0.043 µg/g. US6B, US8B, US10B, MS4B, MS8B and US2B were all below detection limit, and DS8B were not detected.

The absence of DDT and its metabolites in the soil samples indicates that farmers around the lagoon do not use these pesticides in their farming activities due to the ban on its use.

Organochlorine peasticides are extremely toxic to fish and aquatic invertebrates (Sunderam *et al*., 1992) and it has been implicated increasingly in gonadal toxicity (Sinha *et al*., 1997), genotixicity (Chaudhuri *et al*., 1999) and neurotixicity (Paul and Balasubramanian, 1997; Siddique *et al*., 2003. Persistence of organochlorines in soil and water environments had been widely reported by different researchers under different conditions (Rao and Murty, 1980; Guerin and Kennedy, 1992 and Sethunathan *et al*., 2002). Because of its abundant usage and potential transport, organochlorine pesticides contamination is frequently found in the environment at considerable distances from the point of its original applications (Man singh and Wilson, 1995 and Miles and Pfeuffer, 1997). DeLorenzo et al., (2002) reported on the bioconcentration factors (BCF) for freshwater green algae (Pseudokirchnereilla subcapitatum) and freshwater water flea (Daphnia magna) as 2682 and 3278, respectively, with little evidence on bioaccumulation in phytoplankton and zooplankton.

The discharge of agro-chemicals from flood plains, agricultural fields through agricultural runoff might have contributed to the elevated pesticides concentration. The presence organochlorine pesticides in the sediment samples indicate that farmers around the lagoon use organochlorine pesticides in their farming activities.

4.3.3 Levels of Orgnophosphorus pesticides in sediment

In the UK, the volume of seeds eaten by many bird species is large enough to pose a potential risk if the seeds are treated with one of the more toxic fungicides (Prosser & Hart, 2005).

Organophosphate insecticides, including disulfoton, fenthion, and parathion are highly toxic to birds. These have frequently poisonined raptors foraging in fields (Mineau, 1999). Field studies have led to the conclusion that given the usual amounts of insecticide used, "direct mortality of exposed birds is both inevitable and relatively frequent with a large number of insecticides currently registered" (Mineau, 2005). In the USA, some 50 pesticides have killed songbirds, gamebirds, raptors, seabirds and shorebirds (BLI 2004). ln a small area of the Argentine pampas, monocrotophos, an organophosphate, has killed 6,000 Swainson's hawks. Worldwide, over 100,000 bird deaths caused by this chemical have been documented (Hooper, 2002).

Methamidophos was not detected in all the sediment all the sediment samples. Pirimiphos was detected in many of the sample with the exception of US2B, US4B, US10B, MS8B, DS8B and DS10B. Pirimiphos varied from 0.012 to 0.251 µg/g. Pirimiphos was detected in many of the sediment samples from Kpotitsekope and Totope. The discharge of agro-

chemicals from flood plains, agricultural fields through agricultural runoff might have contributed to the elevated pesticides concentration. The presence organphosphorus pesticides in the sediment samples indicate that farmers around the lagoon use organophosphorus pesticides in their farming activities.

4.4 Pollution Source Identification

The calculated factor loadings, cumulative percent and percentages of variance explained by each factor in R-mode PCA are listed in Tables 4.3, and 4.4,. Four factors with eigenvalues >1 were extracted from the varimax-rotated factor analysis of all parameters in the data set. The retained factors which led to a reduction of the initial dimension of the data set and explained about 76% and 64% of the total variance are mentioned as PC in Tables 4.3 and 4.4 respectively. The communalities shown by the variables, considering six (6) factors, varied from 19% for pH to 97% for TDS and EC (Table 4.3). Ca, EC, Salinity, TDS and Total Hardness were significantly loaded on one factor. They were, however, retained in the final factor model due to their high communalities values (about 90% and above) which showed how well the variances of these parameters were explained by the set of factors. Therefore, their high loadings on one factor could probably be explained by their derivation from one source.

Table 4.4: Varimax rotated factor loadings and communalities of water quality parameters (significant values are in bold type face)

	R-mode						
PARAMETER	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	COMMUNALITIES
ALK	-0.202	0.176	**0.69**	-0.307	-0.059	0.024	0.647
As	-0.051	0.173	0.152	**0.869**	-0.113	-0.098	0.833
BOD	0.163	-0.02	-0.375	-0.092	**0.514**	0.189	0.476
Ca^{2+}	**0.881**	-0.241	0.11	-0.138	-0.177	0.052	0.899
Cd	-0.103	0.139	**0.66**	0.239	-0.112	-0.305	0.628
Cl^{-}	0.086	**0.962**	-0.006	0.023	0.137	0.006	0.951
EC	**0.885**	0.121	-0.193	0.133	0.258	0.229	0.972
HCO_3^{-}	0.017	**0.955**	0.138	0.109	-0.098	-0.027	0.954
K^{+}	0.189	0.203	-0.356	-0.211	**0.608**	0.083	0.625
Mg^{2+}	0.017	**0.955**	0.138	0.109	-0.099	-0.027	0.954
Mn	-0.041	**0.813**	-0.015	0.359	0.171	0.146	0.842
Na^{+}	-0.211	0.044	-0.112	-0.213	***-0.858***	0.161	0.867
Ni	0.117	-0.095	**0.867**	-0.075	-0.11	0.054	0.795
NO_3^{-}	-0.124	0.072	0.028	0.06	0.183	***-0.679***	0.52
Pb	0.086	0.183	-0.255	**0.845**	0.129	0.074	0.842
pH	0.141	0.153	-0.166	0.125	-0.016	0.333	0.198
PO_4^{3-}	-0.412	***-0.506***	0.074	0.099	-0.053	0.145	0.464
SAL	**0.886**	0.125	-0.193	0.145	0.254	0.217	0.969
SO_4^{2-}	0.158	-0.078	0.017	-0.067	0.321	**0.77**	0.733
TDS	**0.886**	0.118	-0.194	0.133	0.254	0.23	0.972
TEMP	-0.468	0.226	**0.598**	0.066	0.074	0.332	0.748
TH	**0.923**	0.164	0.02	-0.112	0.156	0.068	0.92
Eigen Value	5.814	4.291	2.295	1.703	1.427	1.281	
% of Variance	26.428	19.506	10.431	7.739	6.489	5.824	
Commulative %	26.428	45.933	56.364	64.103	70.592	76.415	

Table 4.5: Varimax rotated factor loadings and communalities of metals in water (significant values are in bold type face)

	R-mode			
PARAMETER	PC 1	PC 2	PC 3	COMMUNALITIES
As	**0.713**	0.328	-0.024	0.617
Ca^{2+}	-0.445	0.239	0.320	0.358
Cd	0.254	**0.826**	-0.097	0.757
K^{+}	0.028	-0.443	**0.676**	0.654
Mg^{2+}	**0.727**	0.128	-0.098	0.554
Mn	**0.851**	-0.052	0.185	0.761
Na^{+}	-0.099	-0.096	***-0.852***	0.745
Ni	-0.178	**0.830**	0.023	0.722
Pb	**0.709**	-0.226	0.233	0.608
Eigen Value	2.569	1.812	1.395	
% of Variance	28.544	20.137	15.497	
Commulative %	28.544	48.68	64.177	

Table 4.6: Factor scores for R-mode factor analysis of water quality parameters

	PC1	PC2	PC3	PC4	PC5	PC6
UW1	0.323	**1.065**	**0.888**	-1.952	0.093	-1.010
UW2	-0.574	-0.298	0.515	-2.687	-1.766	**0.819**
UW3	0.307	-0.218	**0.837**	-2.756	**1.092**	-1.037
UW4	-0.580	-0.858	0.526	0.071	-1.939	-0.342
UW5	-1.495	-2.334	0.538	0.479	-1.893	-1.537
UW6	-0.952	-2.169	**1.119**	0.640	**0.942**	0.755
UW7	0.287	**1.634**	**0.969**	-0.086	-0.147	-0.677
UW8	0.050	-0.075	**1.797**	0.677	0.756	**1.815**
UW9	-1.841	0.353	**1.264**	**1.020**	0.548	-0.078
UW10	**0.926**	**1.865**	**1.458**	0.617	-1.831	**0.959**
MW1	-1.797	**2.022**	-0.060	0.291	-0.812	-0.074
MW2	-2.880	0.966	-0.886	0.379	**1.151**	-0.849
MW3	0.686	-1.679	1.091	0.235	0.708	**1.396**
MW4	0.615	0.357	0.797	0.056	0.580	-0.517
MW5	0.355	0.000	0.244	0.659	**1.009**	0.060
MW6	-0.495	0.581	-1.018	0.738	0.229	**1.714**
MW7	-0.234	0.389	-0.744	-1.003	**1.790**	0.201
MW8	-0.023	0.294	-2.278	-0.214	-1.341	**1.812**
MW9	-0.234	-0.956	-1.530	-1.075	0.438	-0.344
MW10	0.193	-0.515	-1.344	-0.852	0.420	**0.815**
DW1	0.610	-0.583	-0.832	0.585	0.271	-0.270
DW2	0.160	0.202	0.355	0.333	0.352	0.139
DW3	**1.000**	0.408	0.267	0.246	**1.187**	0.025
DW4	0.587	-0.150	-0.619	-0.418	-0.521	**1.488**
DW5	0.830	-0.465	-0.626	0.272	-0.699	-0.789
DW6	-0.211	0.077	-1.040	0.710	0.104	-0.769
DW7	0.748	0.038	-0.777	0.639	0.386	-0.871
DW8	**1.240**	0.006	-0.021	0.623	-0.398	-0.052
DW9	0.798	0.169	-0.749	**0.943**	-0.358	-0.965
DW10	**1.601**	-0.125	-0.141	**0.831**	-0.350	-1.818

The factor scores for all samples and their distributions are shown in Tables 4.5. Factor scores represent cumulate contribution of all parameters loaded on a particular factor/principal component. Positive and negative scores in PCA indicate that most water samples were either essentially affected or unaffected by the presence of the extracted loads on a specific factor/component, respectively.

The first principal component (PC1) in the lagoon water data sets explained more than 26% of total variance, and is heavily loaded on Ca, EC, Salinity, TDS and Total Hardness. These parameters retain high scores in UW10, DW3, DW8 and DW10 (Table 4.5), and may be considered as most important parameters in these samples. Components in PC1 are derived from mixed sources such as seawater intrusion and for salt mining and using of agrochemicals for farming. PC2, explaining about 20% of total variance, has high loadings for Cl^-, HCO_3^-, Mg, Mn and PO_4^{3-} (decreasing) which may be derived from domestic waste and agrochemicals (fertilizers). The factor scores of the R-mode PCA show that these parameters are importantly distributed in samples UW1, UW7, UW10 and MW1 (Tables 4.3). PC2 could be explained in lesser extent as anthropogenic (domestic waste and farming) sources. PC3, accounting for 10% of total variance, is loaded on Alkalinity, Cd, Ni and Temperature. These parameters may have emanated from domestic waste (e.g., electronic devices and batteries). Cd and Ni are major components of electronic devices.The effect of these components is significant in UW1, UW2, UW6 to UW10. PC3 can be explained as domestic discharge (anthropogenic) from communities around the catchment of Ayorkope. PC4 accounts for 7.74% of the total variance and is mostly contributed by As and Pb, which are derived from automobile waste. PC4 may be considered as anthropogenic source component (automobile waste).

High scores of PC4 are observed in samples UW9, DW9 and DW10, suggesting that As and Pb are important parameters in these samples. PC 5 accounts for 6.5% of the total variances and is mostly contributed by BOD, K^+ and decreasing Na^+ which are derived from fertilizers. Na decrease as BOD and K^+ increase in PC 5. High scores of PC 5 are observed in samples UW3, UW6, MW2, MW5, MW7 and DW3. PC 6 which accounts for 6% of the total variances and is contributed by SO_4^{2-} as NO_3^- decreases. These parameters are derived from fertilizers. High scores of PC 6 are observed in samples UW2, UW8, UW8, UW10, MW2, MW6, MW8, MW10 and DW4 indicating that SO_4^{2-} is important parameter in these samples.

In order to further investigate elemental distribution, PCA was performed on the metal data set only. Here, three factors are retained again accounting for 64% of the total variance. Three factors, PC1, PC2, and PC3, were extracted, which explained more than 28%, 20%, and 15% of total variance, respectively (Tables 4.4). The elemental loadings on PC1, PC2, and PC3 in the metal data set were As, Mg, Mn, and Pb; Cd, and Ni; and K^+ and Na^+, respectively, and elemental patterns were similar to that obtained for all parameters data set (the physicochemical parameters and metals).

To investigate elemental distribution in the sediment samples, PCA was performed on the metal data set. Here, three factors are retained again accounting for 73% of the total variance. Three factors, PC1, PC2, and PC3, were extracted, which explained more than 29%, 25%, and 19% of total variance, respectively (Appendix 9). The elemental loadings on PC1, PC2, and PC3 in the metal data set were As and Mg; Pb, and Fe; and Mn, Ni and Zn, respectively, and elemental patterns were similar to that obtained for water samples.

The relationships among the analyzed parameters are also visualized in the factor loadings plots of PC1 vs. PC2, PC1 vs. PC3, PC1 vs. PC4, PC1 vs. PC5, PC1 vs. PC6 (Fig. 4.5 to Fig 4.9).

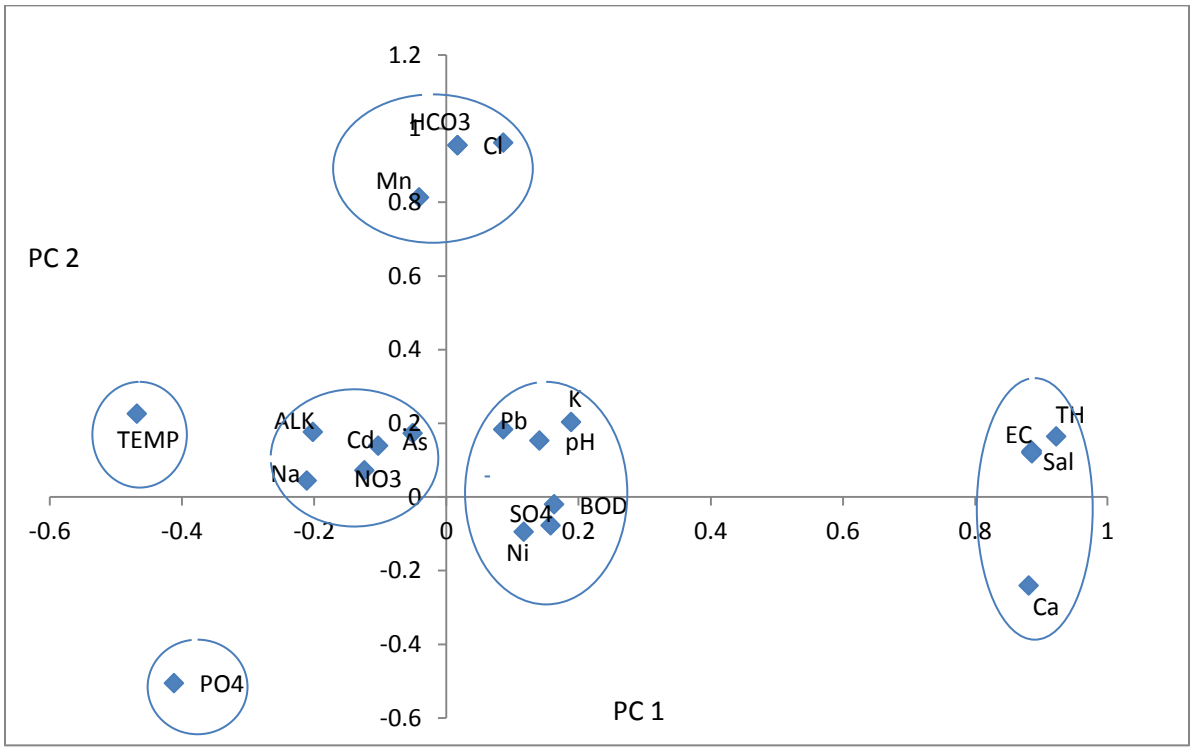

Fig 4.5: Plot of first two principal component loadings, PC 1 vs. PC 2

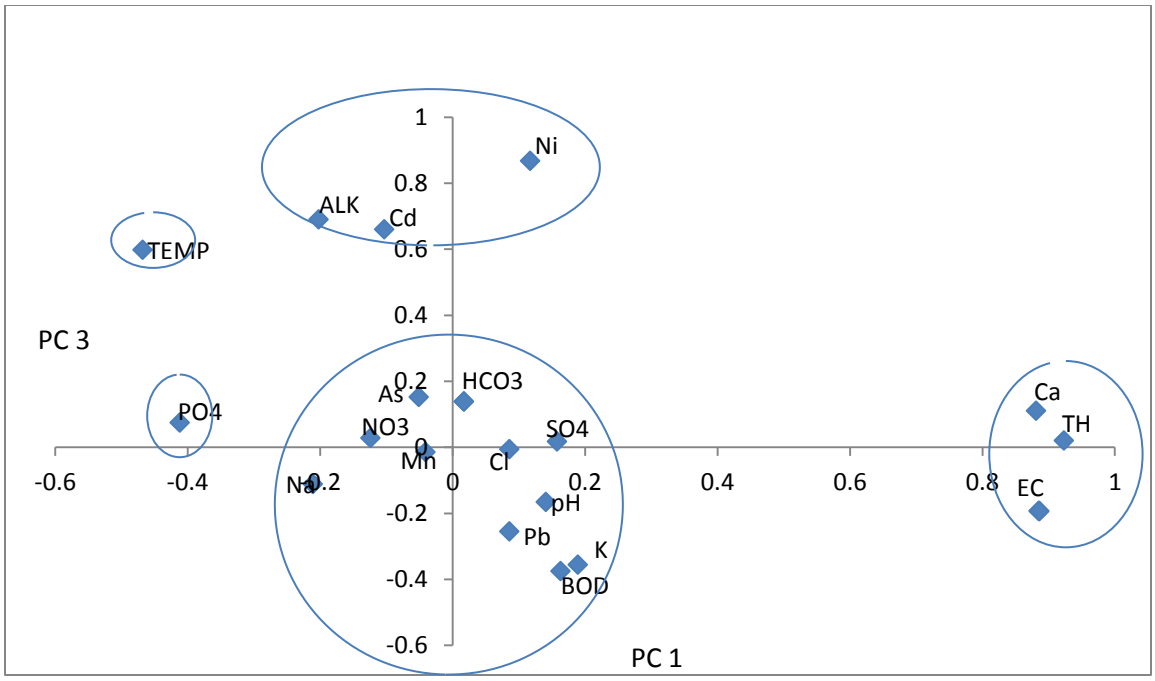

Fig 4.6: Plot of two principal component loadings, PC 1 vs. PC 3

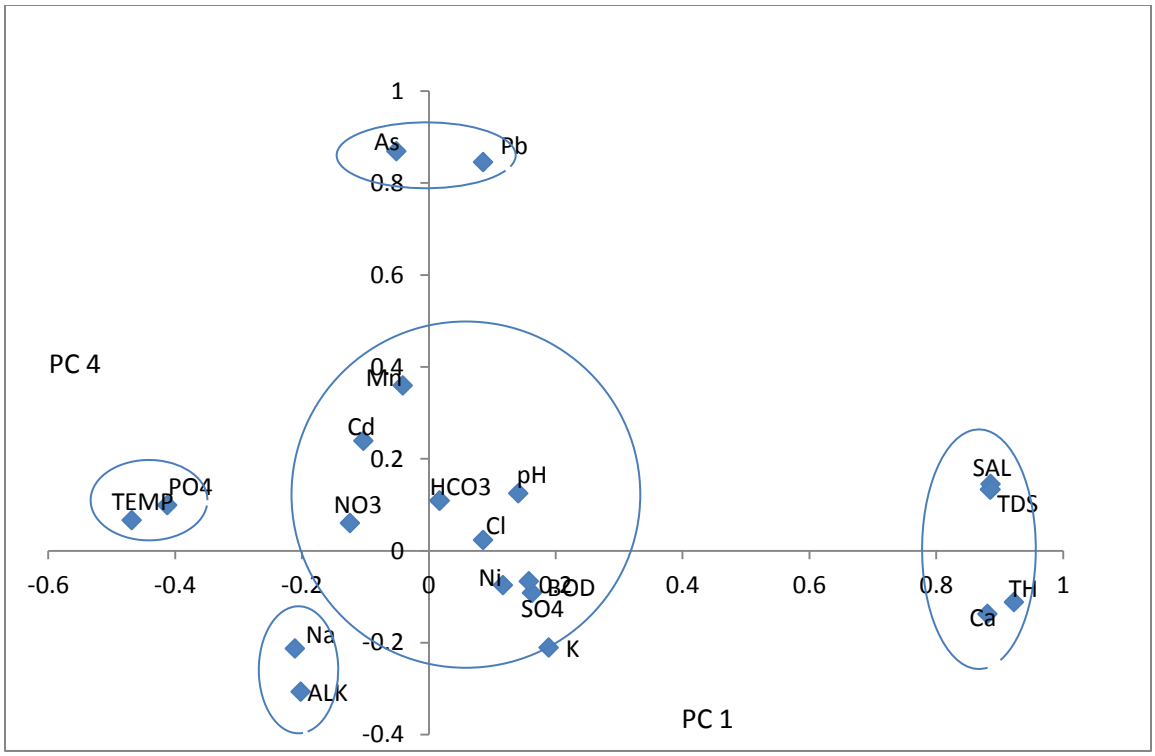

Fig 4.7: Plot of two principal component loadings, PC 1 vs. PC 4

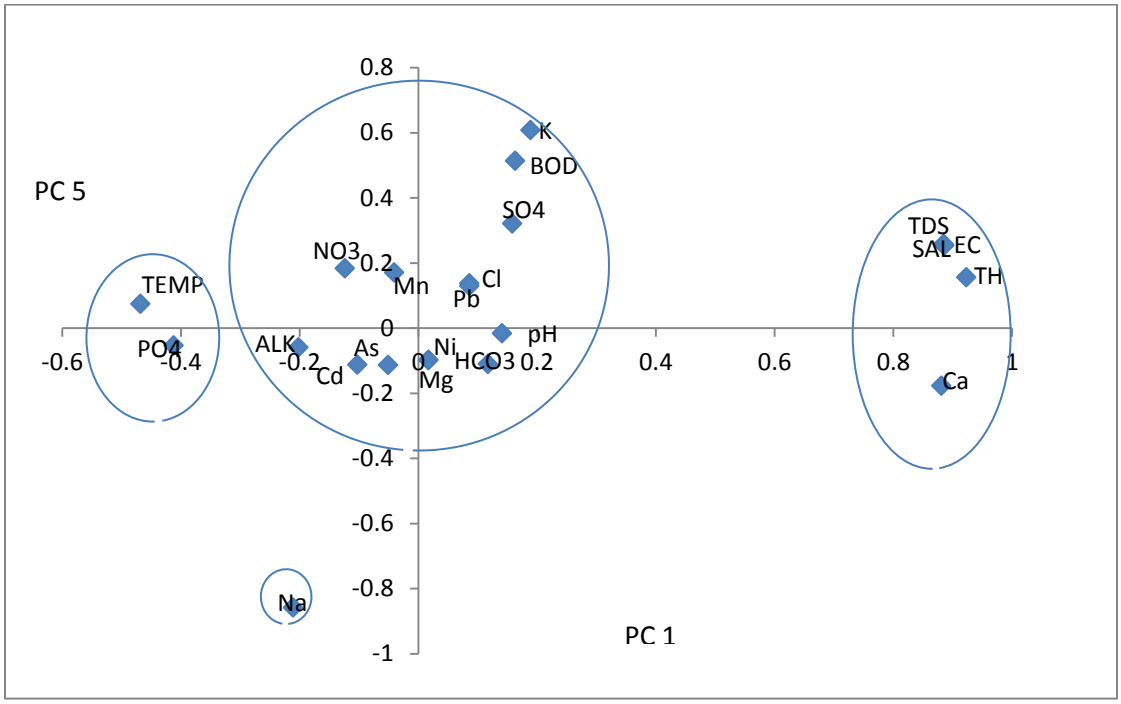

Fig 4.8: Plot of two principal component loadings, PC 1 vs. PC5

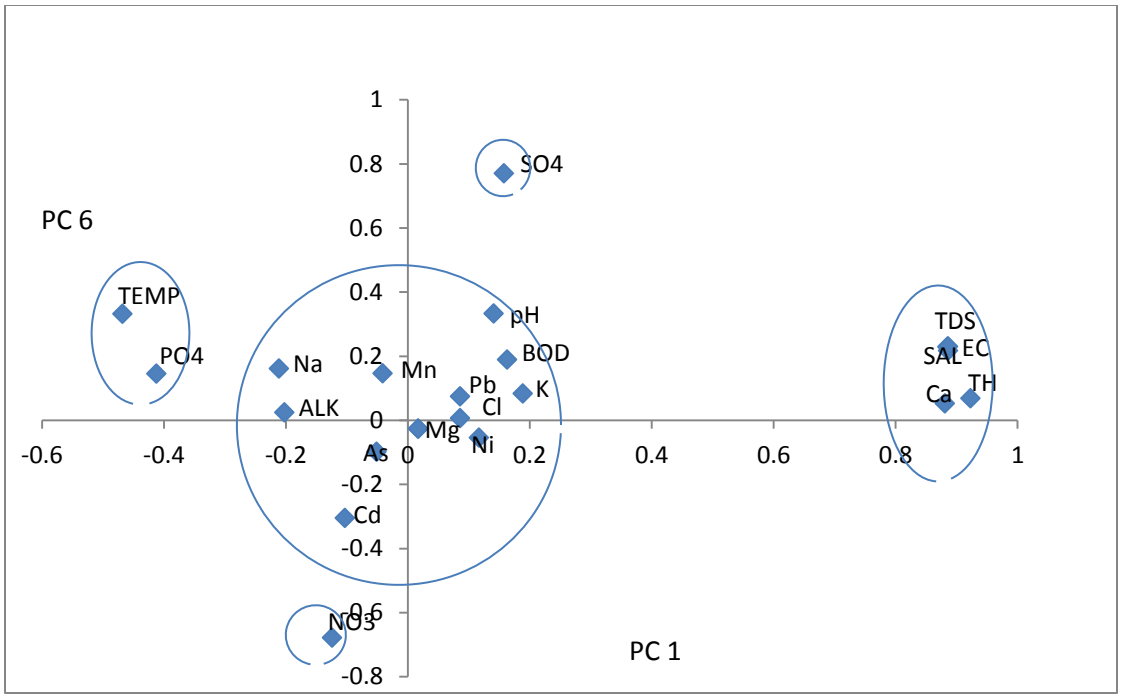

Fig 4.9: Plot of two principal component loadings, PC 1 vs. PC 6

For a better understanding of the sources of metals in the water courses, R-mode cluster analysis was also performed to visualize the relationships between physicochemical–metal and metal–metal groupings in data sets. The results are graphically presented in Fig. 4.9 to Fig 4.11. Elements/parameters belonging to the same cluster/group are likely to have originated from a common source.

The CA results largely agree with the PCA results. The R-mode CA retains three (3) main clusters for data sets of all parameters and metal samples separately, with the phenon line set to a rescaled linkage distance of about 15. For all parameters, cluster 1 consists of Alkalinity, Ni, Temperature, Cd, Na^{+} and PO_4^{3-} (Fig. 4.9). This cluster is almost similar to PC3 in PCA analysis. Cluster 2 contains HCO_3^{-}, Mg, Mn, Cl^{-}, As, Pb, and NO_3^{-} similar to PC2 in PCA and cluster 3 consists of EC, TDS, Salinity, Ca^{2+}, TH,

BOD, K^+, SO_4^{2-} and pH. The metal–metal CA presented in Fig. 4.11 shows similar clustering, where cluster 1 contains Cd, Na^+, and Ni; cluster 2 is made up of Mg, Mn, As and Pb; and cluster 3 contains Ca^+ and K^+. The R-mode PCA and CA have yielded the following elemental associations in the water data set: Mg-Mn-As-Pb and Cd-Ni, which are mainly derived from anthropogenic sources. These anthropogenic sources are linked to the usage of agrochemicals and domestic waste dumping.

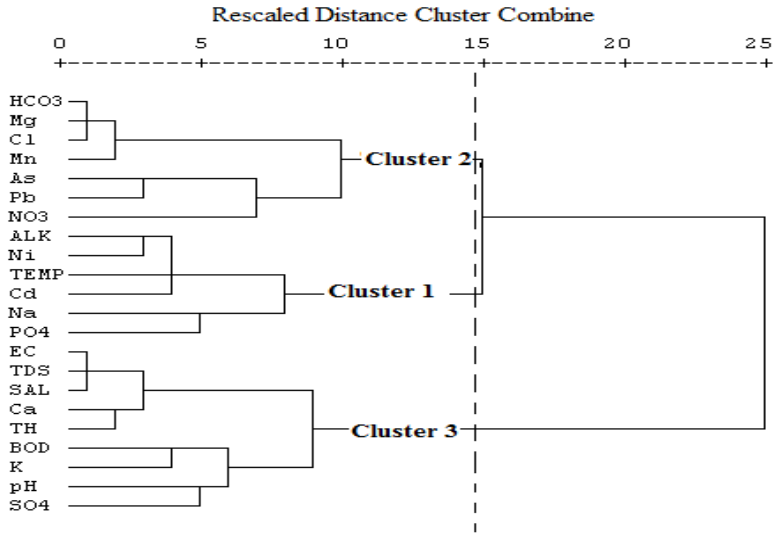

Fig 4.10: Dendrogram showing the hierarchical clusters of parameters in water

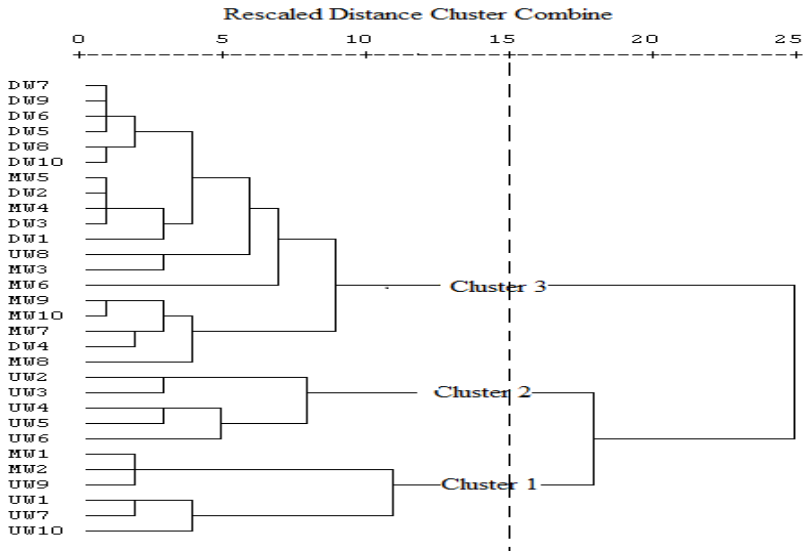

Fig 4.11: Dendrogram showing the hierarchical clusters of sampling sites of water

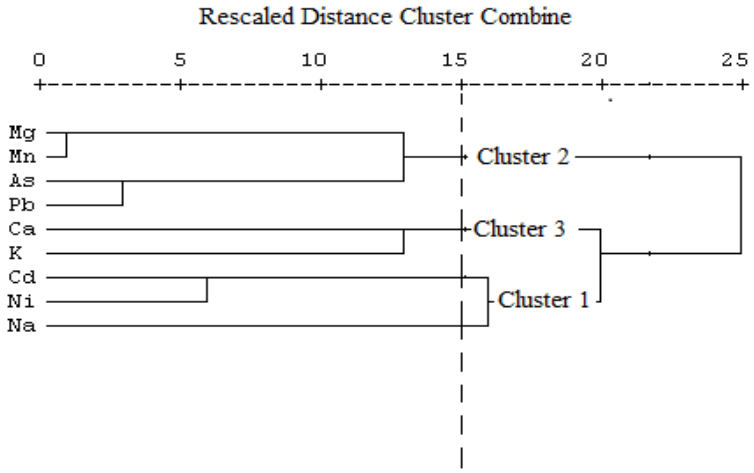

Fig 4.12: Dendrogram showing the hierarchical clusters of metals in water

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The objective of the study was to assess the extent of heavy metals, pesticides and nutrients contamination of surface water and sediment in the Ada Songor Lagoon due to anthropogenic activities around the catchment area of the lagoon. The study also identified sources of pollution and unanticipated threats to the ecosystem.

The study of Songor lagoon water quality properties in terms of its physico-chemical parameters was assessed. Values obtained for temperature (25.7 to 26.6 ^{o}C) fall in the range of 25 to 30 ^{o}C for fish and aquatic organisms. The pH range (8.18 to 9.70) which is typical of coastal waters in Ghana is ideal for aquatic organisms. The total dissolved solids in the lagoon water varied between 591 to 1,046 mg/L which is not ideal for water birds spawning since it make it harder for them to find food. The Electrical Conductivity values (1,181 to 2,090 mS/cm) are typical of coastal lagoons in Ghana. The alkalinity varied from 20 to 152 mg/L. These values are good for the lagoon since alkalinity maintain the pH of water. The salinity values (670 to 1250 ‰) of the lagoon indicate that the lagoon is brackish type and confirms the reason for the salt mining. With the exception of some collection points (UW1, UW4, UW5, UW7, UW9 and UW10,), all other samples recorded biological oxygen demand values higher than the WHO limit of <3.0 mg/L. The BOD levels in general ranges from 1.19 to 5.35 mg/L. The high BOD values recorded may be due to the dumping of refuse in to the lagoon.

The pattern of ionic dominance in the lagoon during the present study was $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The cationic dominance pattern was similar to that of seawater as observed by other works. The sodium values ranged between 1,216 to 14,560 mg/L. These values were above WHO guideline limit of 200 mg/L but were typical of coastal lagoons in Ghana. The chloride values (41,987 to 104,768 mg/L) indicate high salt content and confirm the salt mining activities in the study area.

All water samples had nitrate levels below 1.0 mg/L. Nitrate levels ranges from 0.83 to 0.92 mg/L. The concentrations of NO_3^- were not alarming and that the lagoon was free from organic waste contamination. PO_4^{3-} in this study varied from 0.05 to 2.92 mg/L which exceeds the levels in most natural waters. Sulphates cause problem of odour due to its reduction to H_2S. The hydrogen sulphide like smell of the sediment in the lagoon may be due to the levels of the sulphate.

Chromium concentration in lagoon water varied from below detection limit to 0.03 mg/L. Cr concentration levels in sampling sites UW7 to DW10 were below detection limit. Chromium concentration in lagoon sediment varied from below detection limit to 0.17 mg/Kg. Sampling sites US3 to MS3 and MS8 to DS6 were below detection limit.

Lead level in the lagoon water varied between below detection limit and 0.42 mg/L. UW2 and UW3 lead levels were below detection limit. Lead level in the lagoon sediment sample varied from below detection limit to 3.83 mg/ Kg in. sample locations US1 and US2 Pb level were below detection limit. The highest level of Pb was in DS10 (3.83 mg/Kg). The level of Pb obtained in the sediment were higher than those in the lagoon water, hence the sediment could be an influencing factor on the level of Pb in the lagoon

water with other enhancing factors like pH, since water acidity is known to influence the solubility and availability of metals

The concentration of Cd in water and sediment ranged from below detection limit to 0.09 mg/L and below detection limit to 0.44 mg/Kg respectively. Water samples MW8, MW9 and MW10 Cd concentrations were below detection limits. For sediments, US1 to US6, MS8 to MS10 and DS1 to DS5 were below detection limit. The range obtained for the water is not in good agreement with US EPA tolerance level of <0.01 mg/L for wastewater USEPA as well as 0.05 mg/L Maximum Contaminant level (MCL) for natural waters USEPA.

Levels of Ni in the lagoon water ranged from below detection limit to 0.18 mg/L. The Ni levels in the sediment samples ranges from below detection limit to 1.60 mg/Kg. The ranges obtained in the sediments were much higher than the water, indicating that the sediment is more contaminated. Water sample locations DW4 to DW9 and MW6 to MW10 were all below detection limit, while sediment sample location DS4 to DS7 were also below detection limit. The typical concentration of Ni in unpolluted waters is given as 0.015 to 0.020 mg/L.

The concentrations of heavy metals, Cu, Hg and Zn concentration levels were all below the detection limit in the water samples. The concentrations of heavy metals (As, Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb and Zn) measured in sediment samples, were generally higher than water samples. The high level of heavy metals in the sediment relative to levels in water is expected as sediments have been described as a sink or reservoir for pollutants in water. The low concentrations of the heavy metals in the surface water could be due to dilution, adsorption, and precipitation. The Levels of trace metals measured in the lagoon

sediments may be from the discharge of domestic waste and residues from agrochemicals used in the catchment by farmers due to the absence of chemical and manufacturing industries. These may be carried to the lagoon as runoff or through neglect or by eroding soil or percolating or leaching through the soil. Trace and heavy metals in the agrochemicals will cause widespread damage to biota. Widespread application of the agrochemicals may eliminate food sources that certain types of animals need, causing the animals to relocate, change their diet or starve to death. The levels of trace metals in the lagoon sediments may bioaccumulate to enhance toxic levels in the bodies of organisms that consume them over time and they eventually die.

There was no enrichment in Cd for samples US1 to US6 and MS8 to DS5. Sediment samples US1 and US2 show no enrichment of any of the metals. However, sediment samples DS6 to DS10 are very severely enriched with Cd and Pb. There was no enrichment of chromium in any of the sediment samples. Only sediment sample MS1 show minor enrichment with Cu. There was no geo-accumulation of the metals in any of the sediment samples.

The study detected residues and metabolites of organochlorines (OCs), pyrethroids and oranophosphorus (OPs) in sediment samples from the Songor lagoon. These pesticides are extensively used in on pineapple, vegetable and food crop farms. The occurrence and concentration of pesticides and metabolites varied widely between samples of different collection points. A total of 6 different types of organochlorine pesticide residues and metabolites were detected in varying concentrations ranging between 0.001 µg/g and 0.101 µg/g in the samples whiles 12 different types of organophosphorous with concentrations between 0.004 µg/g and 7.494 µg/g were detected in sediment samples. A

total of 6 different types of synthetic pyrethroids residues and metabolites were detected in varying concentrations ranging between 0.001 µg/g and 0.014 µg/g. Of the numerous pesticides evaluated, Dimethoate (7.494 µg/g), recorded the highest concentration while in β-HCH (0.001 µg/g), δ-HCH (0.001 µg/g), Aldrin (0.001 µg/g) and Heptachlor (0.001 µg/g) registered the lowest concentrations.

The concentrations of individual pesticides measured in sediment samples from majority of sampling sites were below detection limit. Out of the 15 sediment samples analysed, synthetic pyrethroids and organophophorous pesticide residues were recorded more detectable levels. The samples did not record significant levels of organochlorine pesticide residues as most of them were below detection limit.

Almost all the sampling locations recorded appreciable levels of synthetic pyrethroid pesticide residues in sediment samples. The levels generally ranged from 0.001 µg/g to 0.014 µg/g. The highest synthetic pyrethroid pesticide concentration was found for allethrin at sampling Site US 2B. Significant levels of cypermethrin, permethrin, and cyfluthrin were detected at sites US 2B to DS 10B (Table 4.3). Concentration of cypermethrin varied between 0.001 µg/g and 0.007 µg/g, permethrin 0.001µg/g to 0.013 µg/g; deltamethrin ranging from 0.002 µg/g; cyfluthrin between 0.001 µg/g and 0.002 µg/g and bifenthrin was between 0.001 µg/g and 0.003 µg/g.

Organochlorine pesticide residues; Methoxychlor, Dieldrin, Endrin, Endosulfan, α - Endosulfan, β - Endosulfan, γ - Chlordane, p,p'- DDD, p,p'- DDE, p,p'- DDT were not detected in all the samples. β –HCH was detected in only MS10B and DS4B (0.001 µg/g). γ - HCH ranged from 0.001 to 0.043 µg/g. US6B, US8B, US10B, MS4B, MS8B and US2B were all below detection limit, and DS8B were not detected.

The principal component analysis, supported by cluster analysis identified anthropogenic (i.e., Salt mining, farming, reed cutting, refuse dumping and blocking of fresh water inflow) and natural/geogenic sources (weathering of parent materials) as responsible for controlling the variability of physicochemical parameters, metal contents and pesticides in the surface water and sediment in the Songor lagoon.

The Q-mode CA and PCA methods suggest that the proximal sampling stations of UW1, UW3, UW6, UW7, UW8, UW9, UW10, DW3, DW8 and DW10, bear similar geochemical characteristics and are mostly contaminated by anthropogenic inputs.

5.2 Recommendations

a) To preserve the ecological and biodiversity of the Songor lagoon, it remains important that anthropogenic inputs from the catchment area are devoid of heavy metals and pesticides.

b) Regulatory mechanism should be enforced to ensure that current trends are not exacerbated.

c) Furthermore, this study proposes the use of bio indicators such as fish, birds and other wildlife for monitoring and ecological risk assessment.

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APPENDIX 1

Levels of major inorganic ions in water samples.

Levels of major inorganic ions in water

Sampling Location	Major Inorganic ions (mg/L)								
	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
UW1	1906.00	1490.00	2917.82	54.40	87572.80	175.562	77.905	0.062	0.100
UW2	1490.00	12260.00	2949.89	32.00	65579.70	156.055	103.460	BDL	0.164
UW3	1870.00	1364.00	2949.89	30.80	82774.30	151.179	117.587	0.827	0.090
UW4	1340.00	6920.00	2725.44	27.20	67978.90	112.165	111.714	0.160	0.174
UW5	1054.00	6260.00	2853.70	14.00	50384.40	112.165	65.841	0.877	0.338
UW6	1752.00	1064.00	2821.63	18.80	76776.20	112.165	170.603	0.029	2.920
UW7	1964.00	1722.00	2821.63	74.00	75576.60	185.319	98.540	0.078	0.056
UW8	1506.00	940.00	2981.95	40.40	101569.00	180.439	136.794	BDL	0.234
UW9	1400.00	1000.00	2276.54	48.80	71977.70	107.288	112.508	0.111	0.187
UW10	1326.00	7620.00	3142.27	108.80	104768.00	160.932	141.556	0.103	0.103
MW1	1366.00	5640.00	2308.61	102.80	59181.60	126.795	87.270	0.144	0.133
MW2	1912.00	1574.00	1891.78	48.00	64779.90	112.165	74.571	0.070	0.130
MW3	1814.00	1604.00	2885.76	14.80	84773.70	170.685	137.270	BDL	0.083
MW4	1864.00	1366.00	3110.21	42.40	95170.50	170.685	99.651	0.276	0.137
MW5	1800.00	1216.00	2917.82	37.20	52983.60	78.028	138.698	0.981	0.117
MW6	1836.00	1268.00	2565.12	40.00	46985.40	73.151	150.762	0.012	0.070
MW7	2434.00	930.00	2853.70	36.00	48984.80	87.781	190.444	0.185	0.133
MW8	2336.00	14560.00	2885.76	34.80	48984.80	63.397	140.921	BDL	0.302
MW9	1884.00	1636.00	2725.44	22.40	51983.90	92.658	103.937	0.193	0.207
MW10	1686.00	2062.00	2981.95	23.60	51983.90	78.028	144.730	0.078	0.090
DW1	1722.00	1538.00	2981.95	28.80	56982.30	24.384	110.762	0.086	0.100
DW2	1440.00	1840.00	2693.38	44.40	41987.00	126.795	144.413	0.827	0.120
DW3	2138.00	830.00	3046.08	43.20	45985.70	68.274	138.222	0.119	0.070
DW4	1342.00	1644.00	3046.08	41.20	54983.00	68.274	170.921	BDL	0.177
DW5	1358.00	2126.00	3110.21	36.00	46985.40	73.151	102.667	0.267	0.117
DW6	1902.00	2106.00	2661.31	38.00	47985.40	78.028	93.302	0.144	0.251
DW7	1720.00	1086.00	2981.95	38.00	48984.80	73.151	100.286	0.119	0.100
DW8	1738.00	1630.00	3174.34	35.20	49984.50	73.151	98.381	BDL	0.049
DW9	1680.00	1520.00	2949.89	40.40	47985.10	82.904	74.889	0.029	0.133
DW10	1680.00	14262.00	3238.46	40.40	44986.10	78.028	72.825	0.160	0.103

APPENDIX 2

Levels of heavy metals in sediment samples

	Metal (mg/Kg)										
ID	Fe	Zn	Pb	Cd	Co	Mn	Ni	Cr	Cu	As	Mg
US1	186.016	0.973	BDL	BDL	BDL	32.453	1.373	0.133	0.107	2.773	38.132
US2	1428.942	0.093	BDL	BDL	BDL	12.960	1.347	0.107	0.107	2.813	36.266
US3	180.779	0.813	1.040	BDL	BDL	38.586	1.133	BDL	0.067	2.747	34.532
US4	180.472	0.760	1.173	BDL	0.240	31.599	0.760	BDL	BDL	2.667	31.999
US5	176.303	0.600	1.040	BDL	0.307	30.439	1.200	BDL	BDL	2.667	29.466
US6	183.704	0.827	1.920	BDL	0.667	30.173	1.467	BDL	0.067	3.147	31.599
US7	174.994	0.520	1.627	0.533	0.493	41.866	1.373	BDL	BDL	3.373	40.532
US8	173.410	0.720	1.707	0.147	0.613	41.426	1.413	BDL	BDL	3.213	38.666
US9	138.857	0.080	0.800	0.160	0.533	27.066	1.480	BDL	BDL	3.200	38.132
US10	168.836	0.467	3.213	0.213	0.707	23.066	1.573	BDL	0.080	3.213	37.332
MS1	185.127	1.107	0.920	0.213	0.747	11.400	0.107	BDL	0.213	2.827	35.466
MS2	182.347	0.987	0.920	0.333	0.667	11.293	0.080	BDL	0.160	2.613	32.533
MS3	182.993	0.907	0.200	0.387	0.400	14.613	0.120	BDL	0.160	2.533	31.999
MS4	185.999	1.120	1.480	0.293	0.440	26.813	1.547	0.093	0.133	2.440	31.333
MS5	175.171	0.667	0.267	0.307	0.400	14.800	1.480	0.067	BDL	2.360	30.666
MS6	178.290	0.813	0.840	0.133	BDL	40.092	0.120	0.067	BDL	2.680	33.333
MS7	174.299	0.653	0.387	0.093	BDL	15.160	1.600	0.173	0.080	3.280	41.466
MS8	176.513	0.667	1.120	BDL	BDL	16.280	0.080	BDL	0.080	3.213	40.799
MS9	167.317	0.480	0.293	BDL	BDL	31.346	0.107	BDL	0.053	2.360	32.266
MS10	167.867	0.440	0.933	BDL	0.520	31.133	1.173	BDL	BDL	2.240	29.999
DS1	171.874	0.653	0.000	BDL	BDL	24.173	0.160	BDL	BDL	2.400	31.066
DS2	179.697	1.013	0.253	BDL	BDL	29.546	0.080	BDL	BDL	2.427	31.866
DS3	155.439	0.293	0.867	BDL	BDL	22.266	0.133	BDL	BDL	2.400	31.466
DS4	181.684	1.187	0.853	BDL	1.200	24.266	BDL	BDL	BDL	2.547	30.666
DS5	133.863	0.000	0.853	BDL	1.200	12.880	BDL	BDL	BDL	3.333	37.599
DS6	179.842	0.880	1.080	0.067	0.133	26.746	BDL	BDL	BDL	3.400	38.132
DS7	192.221	1.107	2.360	0.200	0.213	26.919	BDL	0.141	0.147	3.333	38.399
DS8	190.945	0.973	3.387	0.440	0.147	35.612	0.213	0.120	0.173	3.160	35.866
DS9	184.141	1.147	3.093	0.213	BDL	26.813	1.347	0.173	0.173	3.107	38.532
DS10	185.434	1.027	3.827	0.293	BDL	29.533	1.347	0.120	0.147	3.147	37.732

BDL (Below Detection Limit)

APPENDIX 3

Synthetic pyrethroids of sediment samples from the Songor Lagoon.

PYRETHROID	SAMPLE ID														
(µg/g)	US2B	US4B	US6B	US8B	US10B	MS2B	MS4B	MS6B	MS8B	MS10B	DS2B	DS4B	DS6B	DS8B	DS10B
Allethrin	0.014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bifenthrin	ND	ND	BDL	BDL	BDL	BDL	BDL	ND	0.03	BDL	ND	0.001	BDL	BDL	BDL
Fenpropathrin	ND	ND	ND	BDL	ND	ND	BDL	ND	ND	BDL	ND	BDL	BDL	BDL	ND
Permethrin	0.002	0.003	ND	0.001	0.002	0.005	0.007	0.002	0.002	0.006	0.005	0.007	0.003	0.013	0.009
Cyfluthrin	0.002	0.002	0.003	0.003	0.004	0.004	0.003	0.001	0.002	0.002	0.002	0.003	BDL	0.001	0.001
Cypermethrin	0.001	0.002	0.005	0.003	0.007	0.006	0.003	0.001	0.006	0.004	0.002	0.003	0.005	0.004	0.002
Fenvalerate	0.001	0.002	0.001	0.002	0.001	0.002	0.001	0.001	0.001	0.003	0.004	0.003	0.002	0.005	0.005
Deltamethrin	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	BDL	BDL	BDL	BDL	BDL	BDL
λ-Cyhalothrin	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	BDL	BDL	BDL	BDL	BDL

ND: (Not Detected), BDL: (Below Detection Limit)

APPENDIX 4

OCPs of sediment samples from the Songor Lagoon.

OCP	SAMPLE ID														
(µg/g)	US2B	US4B	US6B	US8B	US10B	MS2B	MS4B	MS6B	MS8B	MS10B	DS2B	DS4B	DS6B	DS8B	DS10B
α-HCH	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	BDL	0.001	0.001	ND	BDL
β-HCH	ND	BDL	ND	BDL	ND	BDL	BDL	BDL	BDL	0.001	BDL	0.001	BDL	BDL	BDL
γ-HCH	ND	0.001	BDL	BDL	BDL	0.003	BDL	0.004	BDL	0.012	0.043	0.043	0.011	ND	BDL
heptachlor	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	BDL	BDL	0.001	ND	BDL
γ-Chlordane	ND	ND	ND	BDL	ND	BDL	ND	ND	BDL	BDL	BDL	BDL	BDL	ND	BDL
α-Endosulfan	ND	BDL	BDL	BDL	BDL	BDL	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
β-Endosulfan	ND	ND	0.004	0.004	ND	0.003	ND	0.004	ND	ND	0.001	BDL	ND	BDL	BDL
Endosulfan sulphate	BDL	BDL	BDL	BDL	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Aldrin	ND	BDL	ND	ND	ND	BDL	BDL	BDL	BDL	0.001	ND	0.001	BDL	ND	BDL
Dieldrin ND	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
Endrin	ND	ND	ND	BDL	BDL	ND	BDL	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p'-DDE	ND	ND	BDL	BDL	ND	ND	BDL	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p'-DDT	ND	BDL	ND	BDL	BDL	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL
p,p'-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	BDL	ND	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	BDL	ND	BDL	BDL	BDL

p,p'-DDE (para, para-dichlorodiphenyl dichloroethylene) p,p'-DDD (para, para-dichlorodiphenyl trichloroethylene)

APPENDIX 5

OPPs of sediment from the Songor Lagoon.

OPP	SAMPLE ID														
(µg/g)	US2B	US4B	US6B	US8B	US10B	MS2B	MS4B	MS6B	MS8B	MS10B	DS2B	DS4B	DS6B	DS8B	DS10B
Methamidophos	BDL	BDL	ND	BDL	ND	ND	ND	ND	ND	BDL	ND	ND	ND	BDL	ND
Ethoprophos	0.004	0.004	ND	0.003	0.003	0.007	ND	0.004	ND	ND	ND	ND	ND	ND	ND
Phorate	0.012	0.013	ND	0.012	0.011	ND	ND	ND	ND	ND	ND	ND	0.029	ND	ND
Diazinon	ND	0.017	0.015	ND	ND	ND	ND	0.018	0.015	ND	ND	ND	ND	ND	ND
Fonofos	0.013	0.007	0.006	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethoate	ND	0.287	ND	ND	ND	1.138	ND	ND	0.133	ND	7.494	ND	ND	ND	ND
Pirimiphos-methyl	ND	ND	0.012	0.013	ND	0.021	0.023	0.019	ND	0.029	0.216	0.251	0.224	ND	ND
Chlorpyrifos	0.010	ND	ND	ND	ND	ND	ND	ND	ND	2.249	ND	0.616	ND	ND	0.613
Malathion	0.029	ND	ND	ND	0.031	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fenitrothion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.575	ND
Parathion	ND	0.009	ND	ND	0.010	ND	ND	ND	ND	ND	ND	ND	0.082	ND	ND
Chlorfenvinphos	ND	ND	ND	ND	0.056	0.187	0.064	ND	ND	ND	ND	ND	ND	ND	ND
Profenofos	0.072	ND	ND	ND	0.065	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: (Not Detected), BDL: (Below Detection Limit)

APPENDIX 6

Geo-accummulation (I-geo) values of metals.

Sample ID	Zn	Cd	Mn	Ni	Cr	Cu	Pb	Fe
US1	-7.194	0.000	-5.378	-6.215	-9.984	-9.306	0.000	-8.572
US2	-10.576	0.000	-6.703	-6.243	-10.306	-9.306	0.000	-5.631
US3	-7.453	0.000	-5.129	-6.492	0.000	-9.984	-4.850	-8.613
US4	-7.551	0.000	-5.417	-7.068	0.000	0.000	-4.676	-8.616
US5	-7.892	0.000	-5.471	-6.409	0.000	0.000	-4.850	-8.650
US6	-7.429	0.000	-5.484	-6.120	0.000	-9.984	-3.966	-8.590
US7	-8.098	0.245	-5.011	-6.215	0.000	0.000	-4.205	-8.660
US8	-7.629	-1.617	-5.026	-6.173	0.000	0.000	-4.136	-8.673
US9	-10.799	-1.492	-5.640	-6.107	0.000	0.000	-5.229	-8.994
US10	-8.254	-1.077	-5.871	-6.019	0.000	-9.721	-3.223	-8.712
MS1	-7.009	-1.077	-6.888	-9.901	0.000	-8.306	-5.027	-8.579
MS2	-7.174	-0.433	-6.901	-10.316	0.000	-8.721	-5.027	-8.601
MS3	-7.296	-0.219	-6.530	-9.731	0.000	-8.721	-7.229	-8.596
MS4	-6.991	-0.617	-5.654	-6.043	-10.498	-8.984	-4.341	-8.572
MS5	-7.740	-0.553	-6.511	-6.107	-10.984	0.000	-6.814	-8.659
MS6	-7.453	-1.755	-5.073	-9.731	-10.984	0.000	-5.158	-8.633
MS7	-7.769	-2.269	-6.477	-5.994	-9.605	-9.721	-6.278	-8.666
MS8	-7.740	0.000	-6.374	-10.316	0.000	-9.721	-4.743	-8.648
MS9	-8.214	0.000	-5.429	-9.901	0.000	-10.306	-6.676	-8.725
MS10	-8.339	0.000	-5.438	-6.442	0.000	0.000	-5.006	-8.720
DS1	-7.769	0.000	-5.803	-9.316	0.000	0.000	0.000	-8.686
DS2	-7.136	0.000	-5.514	-10.316	0.000	0.000	-6.888	-8.622
DS3	-8.924	0.000	-5.922	-9.579	0.000	0.000	-5.113	-8.831
DS4	-6.908	0.000	-5.798	0.000	0.000	0.000	-5.136	-8.606
DS5	0.000	0.000	-6.712	0.000	0.000	0.000	-5.136	-9.047
DS6	-7.339	-2.755	-5.657	0.000	0.000	0.000	-4.796	-8.621
DS7	-7.009	-1.170	-5.648	0.000	-9.846	-8.846	-3.668	-8.525
DS8	-7.194	-0.032	-5.244	-8.901	-10.136	-8.605	-3.147	-8.534
DS9	-6.957	-1.077	-5.654	-6.243	-9.605	-8.605	-3.278	-8.587
DS10	-7.117	-0.617	-5.515	-6.243	-10.136	-8.846	-2.971	-8.577

APPENDIX 7

Enrichment factor (EF) values of metals

	Cd	Mn	Ni	Cr	Cu	Pb
US1	0	9.150	5.124	0.376	0.601	0
US2	0	0.476	0.654	0.039	0.078	0
US3	0	11.194	4.351	0	0.387	13.576
US4	0	9.183	2.923	0	0	15.343
US5	0	9.055	4.724	0	0	13.921
US6	0	8.614	5.542	0	0.381	24.665
US7	479.498	12.547	5.447	0	0	21.937
US8	133.066	12.528	5.657	0	0	23.226
US9	181.285	10.222	7.398	0	0	13.596
US10	198.794	7.165	6.468	0	0.497	44.915
MS1	181.301	3.229	0.400	0	1.209	11.728
MS2	287.601	3.248	0.305	0	0.920	11.907
MS3	332.438	4.188	0.455	0	0.917	2.579
MS4	248.119	7.560	5.772	0.263	0.752	18.778
MS5	275.431	4.431	5.864	0.200	0.000	3.593
MS6	117.658	11.793	0.467	0.196	0.000	11.119
MS7	84.247	4.561	6.372	0.522	0.481	5.235
MS8	0	4.837	0.315	0	0.475	14.974
MS9	0	9.825	0.442	0	0.334	4.137
MS10	0	9.726	4.852	0	0	13.121
DS1	0	7.376	0.646	0	0	0
DS2	0	8.623	0.309	0	0	3.327
DS3	0	7.513	0.595	0	0	13.158
DS4	0	7.005	0	0	0	11.084
DS5	0	5.046	0	0	0	15.044
DS6	58.321	7.800	0	0	0	14.172
DS7	163.696	7.344	0	0.400	0.800	28.974
DS8	362.539	9.781	0.775	0.330	0.952	41.857
DS9	182.271	7.636	5.076	0.494	0.987	39.644
DS10	248.876	8.352	5.041	0.339	0.830	48.700

APPENDIX 8A

Varimax rotated factor loadings and communalities of sediment metals (significant values are in bold type face)

	PC 1	PC 2	PC 3	Communalities
As	**0.954**	0.163	-0.093	0.945
Fe	0.095	**-0.86**	-0.01	0.748
Mg	**0.952**	-0.05	-0.044	0.911
Mn	0.062	0.364	**0.691**	0.614
Ni	0.016	-0.338	**0.723**	0.638
Pb	0.209	**0.816**	0.07	0.714
Zn	-0.21	0.095	**0.721**	0.572
Eigen value	2.063	1.753	1.326	
% of Variance	29.472	25.041	18.944	
Cumulative %	29.472	54.513	73.457	

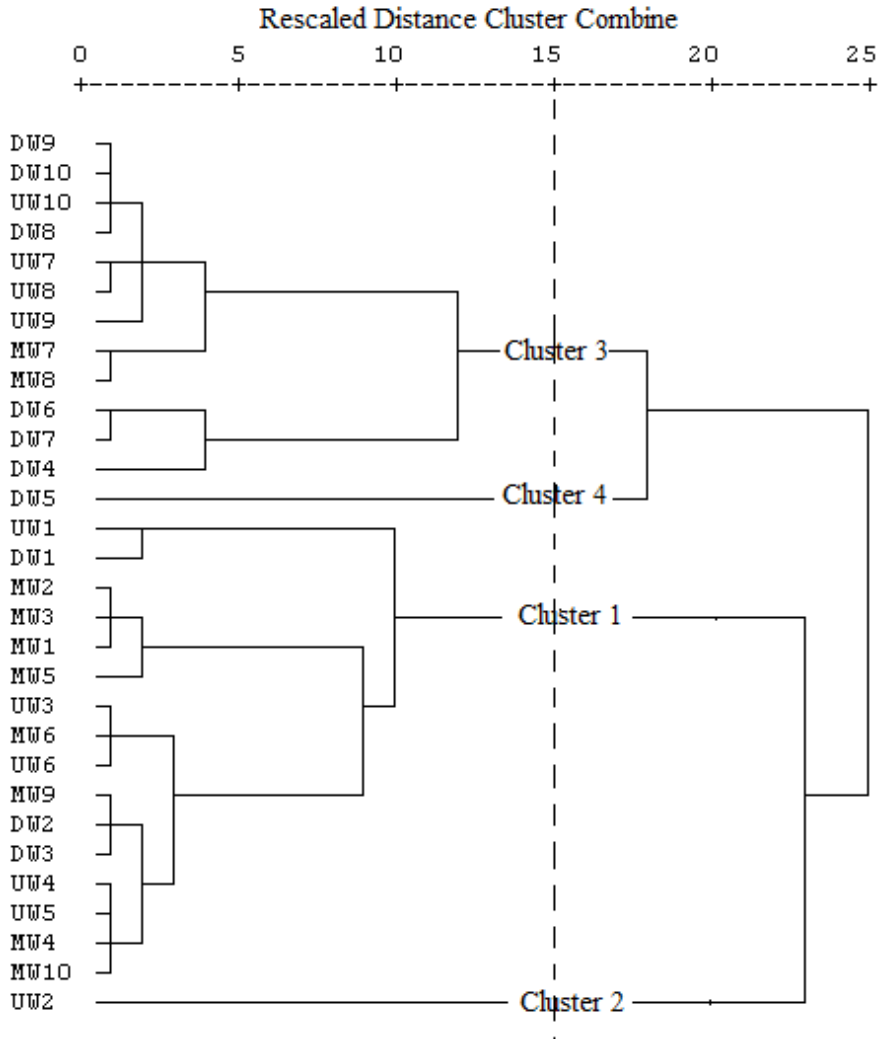
APPENDIX 8B

Factor scores for the R-mode factor analysis of metals in sediment samples (significant values are in bold type face)

	PC 1	PC 2	PC 3
US1	0.289	-1.446	**0.884**
US2	0.606	-4.577	-0.637
US3	-0.017	0.252	**0.978**
US4	-0.543	0.285	0.622
US5	-0.938	0.302	0.546
US6	0.043	0.337	0.726
US7	**1.576**	0.311	**1.052**
US8	**1.148**	0.358	**1.120**
US9	**1.006**	0.284	-0.080
US10	**0.911**	0.273	0.332
MS1	-0.070	-0.128	-0.724
MS2	-0.796	-0.036	-0.871
MS3	-0.968	-0.255	-0.550
MS4	-0.985	0.147	0.683
MS5	-1.348	-0.360	-0.185
MS6	-0.363	0.480	0.576
MS7	**1.377**	-0.448	0.013
MS8	**1.161**	0.060	-0.468
MS9	-1.061	0.242	0.076
MS10	-1.503	0.284	0.465
DS1	-1.385	-1.136	-0.095
DS2	-1.054	0.153	0.193
DS3	-1.144	0.398	-0.434
DS4	-1.238	**0.815**	-0.947
DS5	**0.906**	0.693	-4.028
DS6	**0.937**	**0.802**	-0.816
DS7	**0.932**	**0.860**	-0.719
DS8	0.662	0.540	0.669
DS9	**0.942**	0.208	0.777
DS10	**0.918**	0.303	**0.844**

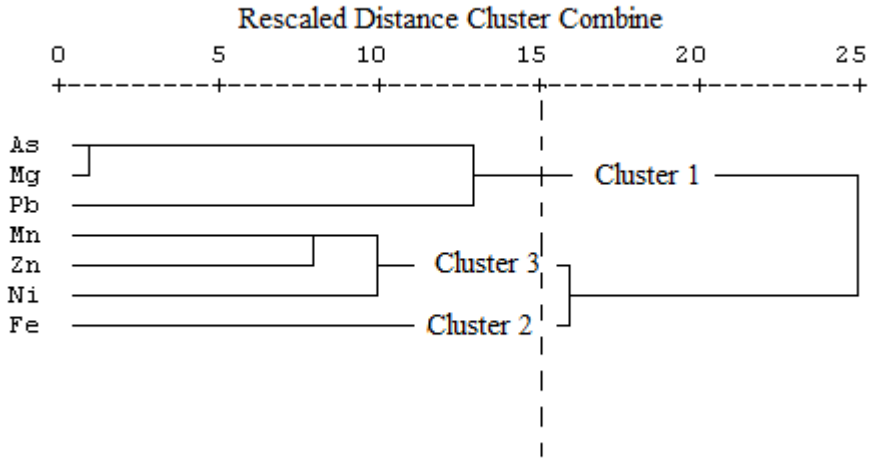
APPENDIX 9A

Dendrogram showing hierarchical clusters of sampling sites of sediments



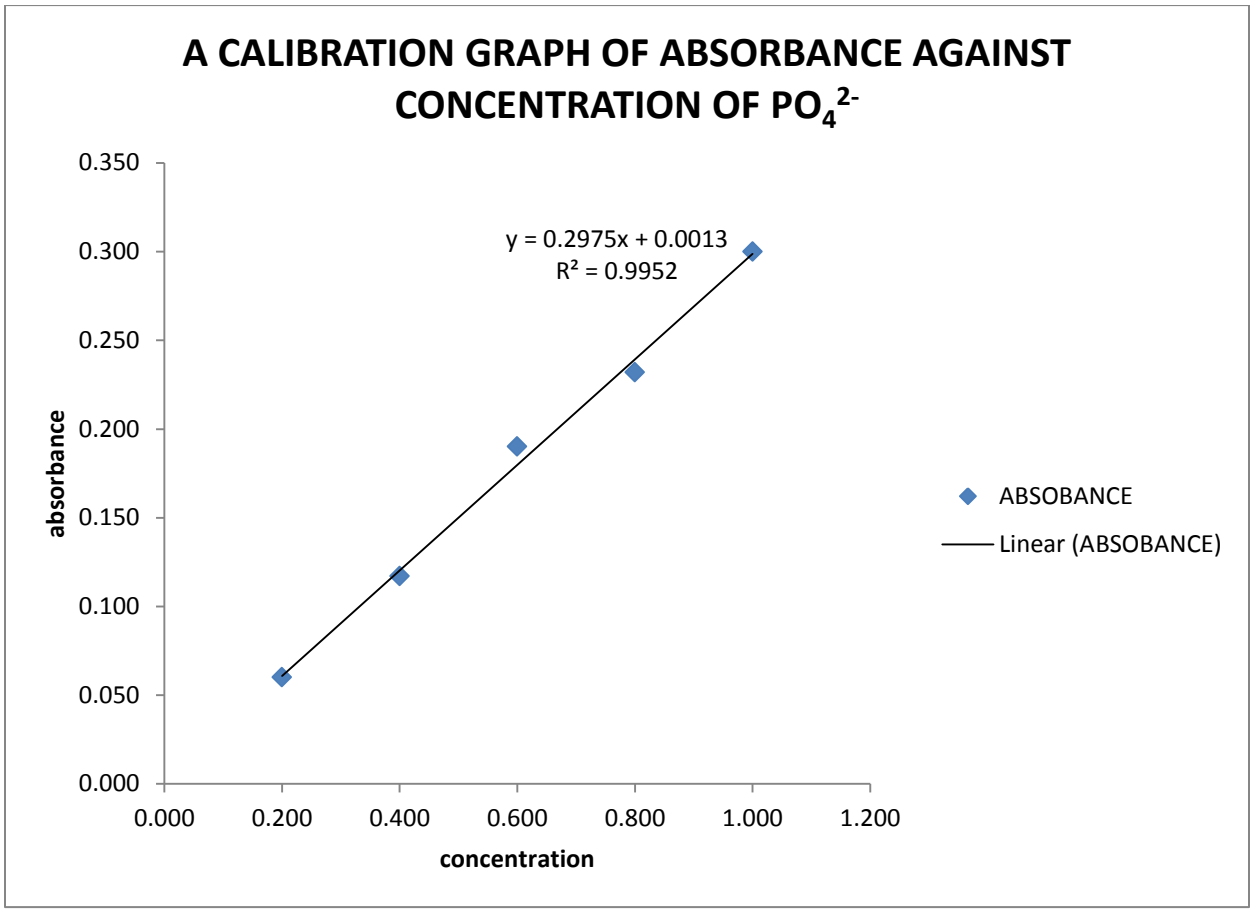
APPENDIX 9B

Dendrogram showing hierarchical clusters of metals in sediment samples



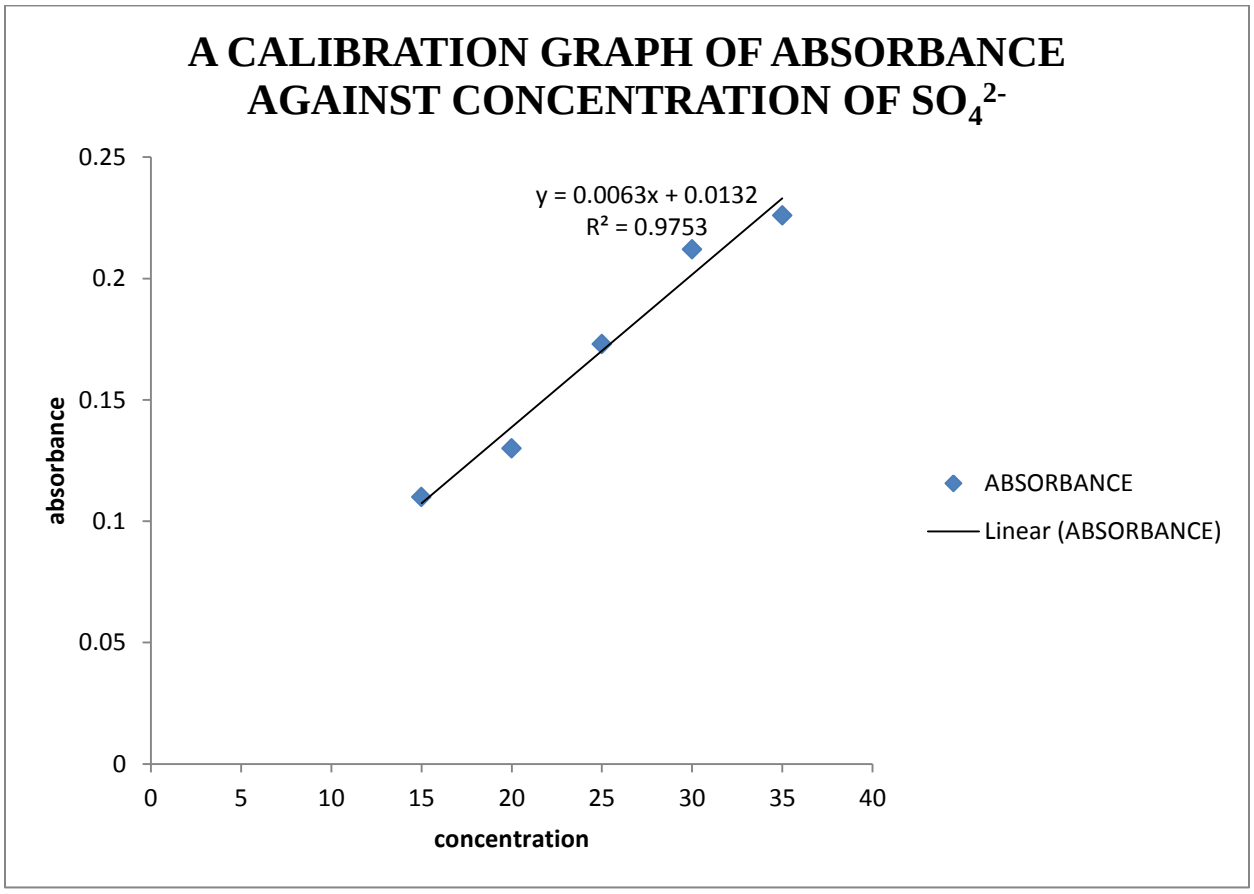
APPENDIX 10A

Calibration curve for analysis of PO_4^{2-} using UV-VIS spectrophotometer



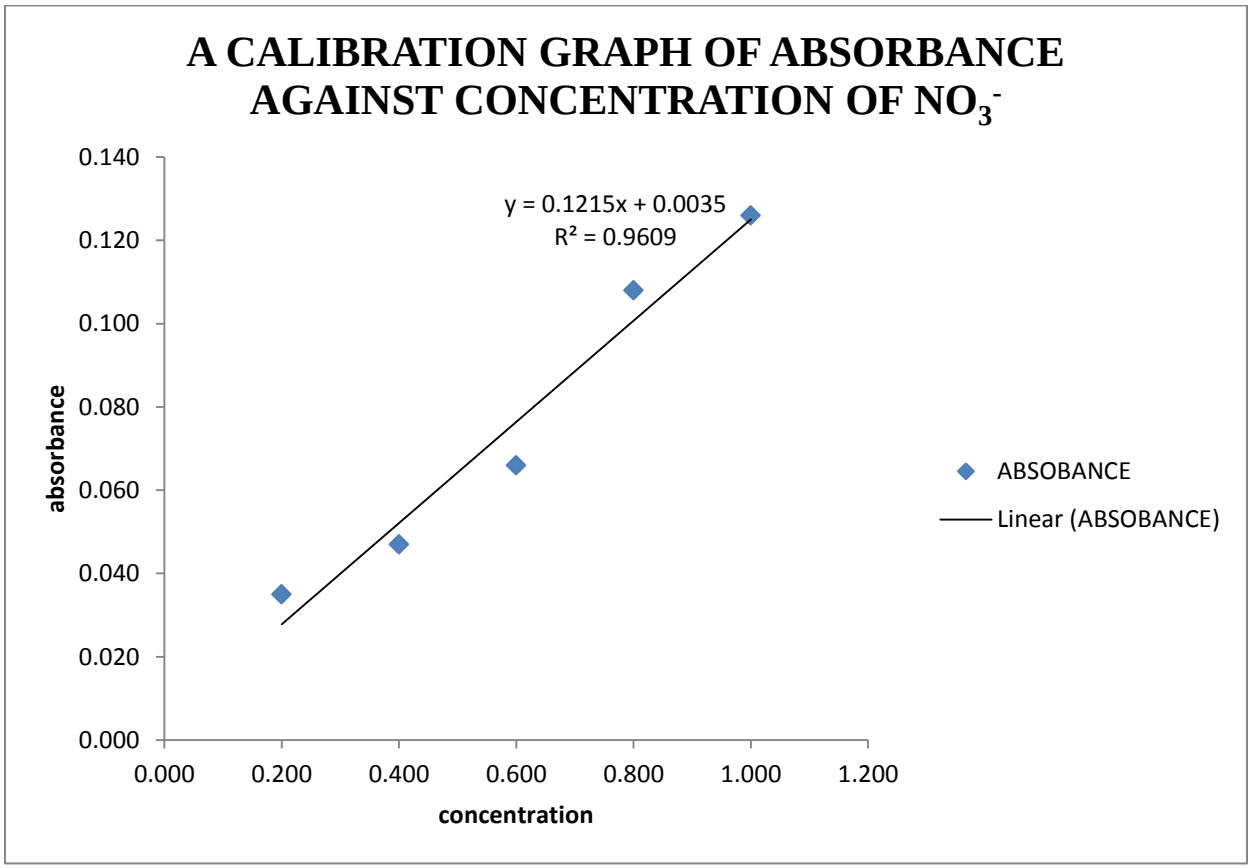
APPENDIX 10B

Calibration curve for analysis of SO_4^{2-} using UV-VIS spectrophotometer



APPENDIX 10C

Calibration curve for analysis of NO_3^- using UV-VIS spectrophotometer



APPENDIX 10D

Calibration curve for analysis of Fe using AAS