MODELLING OF HEAVY METAL BIOACCUMULATION OF *Eichhornia crassipes* [MART.] SOLMS AND *Pistia stratiotes* L. IN OLOGE LAGOON, LAGOS, NIGERIA

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CERTIFICATION

I certify that this work was carried out by **Chinatu Charity NDIMELE** of the Department of Botany, Faculty of Science, University of Ibadan, Oyo State, Nigeria under my supervision.

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Date

DEDICATION

This project is dedicated to GOD Almighty for his immesurable blessings and unmerited favour that has culminated in the successful completion of this project.

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ABSTRACT

Macrophytes such as *Eichhornia crassipes* and *Pistia stratiotes* are known bioaccumulators found in the Ologe Lagoon which receives effluents mainly from Agbara Industrial Estate. However, the mechanism of heavy metal bioaccumulation by these macrophytes has not been fully understood. This study was designed to determine the mechanism of heavy metal bioaccumulation and model the phytoremediation capabilities of the macrophytes.

Five sampling stations: Owo (before the point of discharge of effluent as control), Agbara, Otto Jetty, Morogbo and Etegbin (after the point of effluent discharge) were selected for the study. Water samples, sediments, *E. crassipes* and *P. stratiotes* were collected using standard procedures in these stations from July, 2013 to December, 2014 from the lagoon and analysed for heavy metals using standard methods. Temperature, pH, Conductivity, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Dissolved Oxygen (DO) were determined according to APHA methods. Selected heavy metals: Zn, Fe, Cu, Pb and Cd in water, sediments and the two macrophytes were determined in accordance with FAO/SIDA method. *Eichhornia crassipes* and *P. stratiotes* were grown in three different concentrations (10, 15 and 20 mg/L) of $CuSO_4.5H_2O$; $ZnSO_4$; $FeSO_4.7H_2O$ and $Pb(NO_3)_2$ in three replicates for six weeks. Thereafter, plant leaves, stems and roots were harvested and analysed for metal bioaccumulation and translocation. Time evolution of pollution was determined using first and second-order kinetic models. Data were analysed using descriptive statistics, ANOVA and Fisher's LSD test ($\alpha_{0.05}$).

Water temperature ranged from 28.7±0.37-29.4±0.69°C, pH (6.7±0.1-6.9±0.1), Conductivity (1565±784.7-3088±1478.6 µS/cm), TSS (10.4±0.5-20.6±1.2 mg/L), TDS (89.2±1.8-1739±872.2 mg/L), BOD (2.9±0.7-3.7±0.2 mg/L), COD (13.8±0.8-23.9±1.0 mg/L) and DO (4.2±0.2-4.9±0.2 mg/L).

The concentration of Zn (30±2.0 µg/L) in water sample was higher than the USEPA limit (6 µg/L at 45 mg/L hardness) for the protection of aquatic ecosystems. The highest {Fe (2310±613 mg/kg) and Cu (38.20±10.21 mg/kg)} and lowest {Fe (1305±848 mg/kg) and Cu (2.92±0.37 mg/kg)} concentrations in sediment were recorded in Agbara and Etegbin respectively. The concentration (mg/kg) of heavy metals in *E. crassipes* and *P. stratiotes* from Agbara was significantly higher (Fe=1368±236.12; Zn=42.60±5.62) than values obtained from other sampling stations (Fe=470±55.96-642.58±303.26; Zn=11.14±1.83-20.41±4.31). In the laboratory experiment, metals were accumulated through the roots to the shoot (phytoextraction) via a concentration gradient (for *E. crassipes* pots spiked with 10, 15 and 20 mg/L of Zn, the average quantity of the metal absorbed were 5.56±0.09, 8.89±0.60 and 15.58±0.15 mg/L respectively). The bioaccumulation factor in *E. crassipes* varied from 10 (Pb) to 9000 (Fe) while in *P. stratiotes*, it varied from 9 (Pb) to 8500 (Cu). Translocation factors were higher in root/stem (7.06±1.09 for Pb) than stem/leaf (5.42±1.12 for Pb). Iron accumulation in different parts of *E. crassipes* {(mg/kg) was: {leaf (0.45±0.06-15.58±0.15); stem (0.33±0.05-16.48±0.44); root (0.40±0.07-18.50±3.16)} and *P. stratiotes* was: {leaf (0.36±0.06-6.67±1.17) and root (0.45±0.08-7.49±1.78)}. Pots seeded with Fe maintained green colouration for a longer time than those seeded with Cu, Zn and Pb. The time evolution of pollution was best described by first-order kinetic model.

Eichhornia crassipes and *Pistia stratiotes* bioaccumulated heavy metals and the mechanism of bioaccumulation is a function of time and level of concentration of the heavy metals.

Keywords: Bioconcentration factors, Translocation factors, First-order kinetic model

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CHAPTER ONE

INTRODUCTION

Nigeria has a population estimated at about 183.5 million people with an average annual growth rate of about 2.75% {United Nations Environment Programme (UNEP, 2012). In order to adequately cater for this population, there is the need to diversify the economy from its perennial mono-economic status depending mostly on crude oil to multi-economic structure with the development of more sectors especially the industrial and agricultural sectors. Industrial revolution in Nigeria has been gradual with the establishment of industrial estates in major cities like Lagos and Port Harcourt. These industries are intended among other things to provide opportunities for the population especially the young ones to meet their basic necessities of life and live meaningfully.

Industrialization also meant that the country no longer depend on crude agricultural practices but has embraced modern and sophisticated methods of agricultural operations, which involves the use of machineries, chemicals, etc. This has ensured greater food security and created job opportunities in the parts of the country where this has been practised. This industrialization has come with a prize and it is particularly disheartening because the country was not pro-active enough to envisage the problems and put strategies in place to tackle them as they arise. One of these problems is industrial waste management. Industries in Nigeria generate enormous wastes but there are often times no proper waste disposal mechanisms incorporated in the design of the companies and in their scheme of activities. Where they exist at all,

they are either non-functional or operating below their installed capacities. This attitude has resulted in the discharge of industrial waste directly into water bodies often times untreated. Some of the constituents of industrial wastes in Nigeria include dyes, cyanide, ammonia, phenol etc. However, one of the most commonly encountered is heavy metal. The indiscriminate discharge of these harmful wastes into the water bodies is gradually becoming worrisome because of the health hazards of these wastes on man. The hazardous effects on man and his environment are due to the fact that some of these metals are non-biodegradable (Kumolu-Johnson *et al.*, 2010). They persist and accumulate in aquatic flora and fauna and when these organisms are consumed by man overtime, these harmful substances or pollutants bioaccumulate and bio-magnify within the system of man and other living organisms that consume them causing teratogenicity, mutagenicity, etc (Oyewo, 1998).

One of the most cost-effective and environmentally friendly ways of removing heavy metals from the aquatic environment is by phytoremediation. This process involves the *in situ* use of plants and their associated micro-organism to degrade, contain or render harmless contaminants in soil or groundwater (Cunningham *et al.*, 1996). In essence, phytoremediation employs human initiative to enhance the natural attenuation of contaminated sites and, as such, is a process that is intermediate between engineering and natural attenuation. Few of the aquatic plants that has been tested and found effective in phytoremediation are water hyacinth (*Eichhornia crassipes*) and water lettuce (*Pistia stratiotes*) (Lin and Mendelssohn, 1999).

Water hyacinth and water lettuce have constituted menace to fishing and navigation in Nigerian aquatic ecosystems since they entered our waters some decades ago (Edewor, 1988). All efforts to eradicate them have not yielded impressive results.

Thus, current efforts which is geared towards their utilization rather than eradication is in line with global trend and policy on resource use, which is sustainable resource exploitation. In the light of the fore-going, it becomes pertinent to investigate the efficacy of these invasive plant species as phytoremediative plants for heavy metal-polluted natural aquatic bodies because other methods are expensive and environmentally unfriendly. This shift in research focus could change the status of these aquatic plant species from menace to beneficial and greatly sought flora.

1.1 Water Resources

Nigeria is blessed with abundant inland water resources (Fig. 1). There are 149.919 km^2 of inland waters made up of major lakes, rivers, ponds, floodplains, mining and stagnant pools (Ita *et al*., 1985). In the 1980s, there were 347 reservoirs and lakes, 839 floodplains and rivers, 5000 fish ponds, 89 cattle drinking ports, and many earth wells and boreholes (Satia, 1990). There are several abandoned mine pits particularly in Plateau, Anambra, and Enugu States that hold considerable amount of water all year round, ranging from 0.2 - 0.7 hectares. Also excavation ponds of abandoned sand and stone quarries associated with road construction sites are common along major highways. The determination to solve the problems of drought resulted in the development of lakes and reservoirs, which are now abundant in the northern parts of the country most, affected by drought, such as Kano, Jigawa and Katsina States.

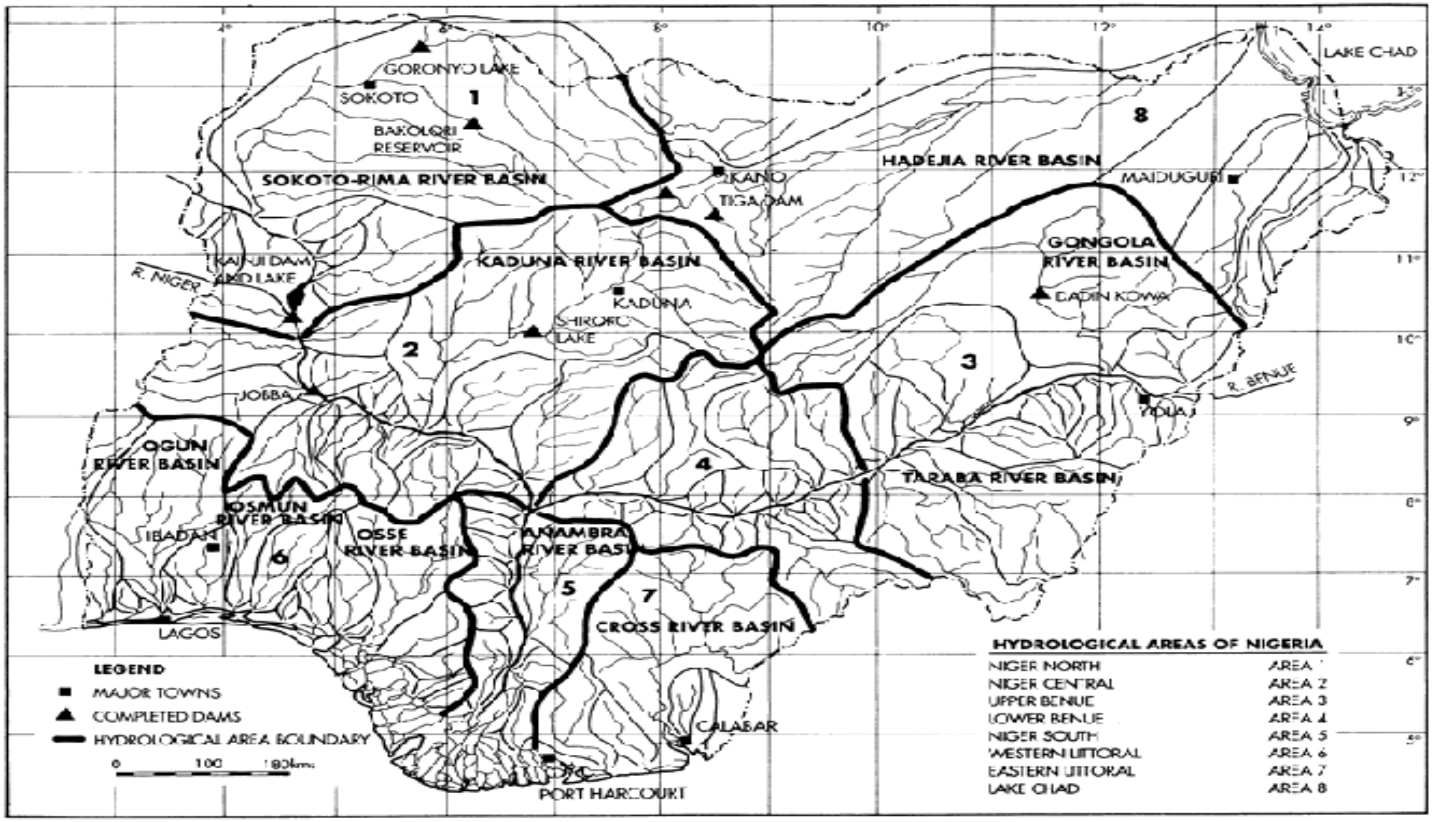


Fig. 1.1: Hydrological Map of Nigeria

Source: Ita *et al.*, 1985

1.2: The Nigeria Aquatic Environment

One of the indices that can be used to classify aquatic environment is the degree of salinity. This index places the hydrosphere into three distinct categories: freshwater, marine water and brackish water. A water body with salinity level below 5 ppt is described as a freshwater body (e.g. rivers, stream), those with salinity level above 35 ppt are called marine water or ocean (e.g. Atlantic ocean, Pacific ocean, Indian ocean etc) while those whose salinity level that fluctuates between these two extremes are referred to as brackish water e.g. Lagos lagoon (Ajao, 1990).

Nigeria has a coastline of 853 km bordering the Atlantic Ocean in the gulf of Guinea. She has a maritime area of about 46, 500 km^2 between 0 - 20m depth and an exclusive economic zone (EEZ) of 210, 900 km^2 (World Resources, 1990). The Atlantic Ocean coastline is interrupted by a series of estuaries, which form the Niger Delta swamps in the middle where the lower Niger River drains the waters of the Rivers Niger and Benue into the ocean. The total brackish area is estimated as 12, 940 km^2 with mangrove comprising 9, 700 km^2 and the saline swamps of the Niger Delta occupying 750,000 hectares (Ajao *et al*., 1996). The Nigerian inshore water is rich with both living and non-living resources. The living resources include pelagic fish (Bonga, Ilisha, Sardine, etc) and demersal fin and shellfishes such as crayfish, prawn, etc. The inshore water is characterized by turbulent and surf beaten coast and lots of nutrients brought in by river effluents and mangrove swamp drainage.

1.3 Pollution

Pollution is defined as the introduction by man into the environment of harmful substances or energy which is liable to cause hazards to human health, harm to biological resources and ecological systems, damage to structures or interfere with the

legitimate use of the environment (Holdgate, 1979). Edward (1992) defined pollution as the release of substances or energy into the environment by man in quantities that can damage his health or his resources. Pollution is not only caused by man but could also result from such natural processes or events like weathering of geological structures, volcanic eruption, wild fire, surface water run-off etc (Kumolu-Johnson *et al.*, 2010). Pollutants are substances in the wrong amount at the wrong place and at the wrong time.

1.3.1 Causes of Water Pollution

Anthropogenic water pollution occurs when one or more of the following pollutants are introduced into the water body intentionally or accidentally. These pollutants are: sewage and waste water, industrial effluents, crude oil spillage, marine dumping, radioactive waste, agricultural waste runoffs, mining activities and thermal effluent.

Sewage and waste water: Sewage is a turbid liquid consisting of 90% water containing a complex of organic and inorganic matters in the form of visible suspended solids, colloidal particles and microorganisms such as bacteria, protozoa, viruses, etc. In most developing countries, this sewage and waste water is not treated before dumping into water bodies. This is very unhealthy because they contaminate the water bodies and the environment, thus causes various health problems.

Industrial effluents: Industries produce about 90% of waste water (Osibanjo, 1986). These waste water contains toxic chemicals and heavy metals which cause harm to man and his environment. Most of these industries do not have proper waste management practice before their waste is pumped through drains and canals into river and streams and later into seas, lagoons and oceans. These toxic chemicals alter

the properties of these water bodies such as colour change, increase the temperature of the water, increase in nutrient content (eutrophication) etc, and this poses serious threat to living organisms.

Crude oil spillage: Crude oil is a complex mixture of hydrocarbons with small amount of sulphur, oxygen, nitrogen, inorganic and organic metallic compounds. Crude oil spillage is one of the major causes of water pollution and this poses a great threat to aquatic organisms because large quantity of crude oil enter into the water body and does not dissolve with water, thus blocking light penetration into the underwater.

Marine dumping: Garbages such as plastic, nylon, glass, aluminum, rubber, tin, that are disposed into water body are not biodegradable as such they can remain in the water for years. Although, these debris are not poisonous to aquatic organisms but they can smother or choke aquatic organisms such as fish, water snails, periwinkles etc.

Radioactive waste: Nuclear energy is produced using nuclear fission or fusion in nuclear power plants. Some radioactive substances or wastes are produced during this process, and thus need to be disposed properly to prevent serious environmental hazards such as cancer.

Agricultural wastes and runoffs: The use of agrochemicals to enhance agricultural productivity is of considerable antiquity (Adesiyan, 1992). Fertilizers and chemicals (pesticides, insecticides etc.) are used by farmers to increase crop production and protect crops of pests and diseases respectively. However, these chemicals are poisonous when washed by rain through runoffs into streams and rivers and later seas,

oceans and lagoons. Most of these chemicals pose serious health hazards to man and his environment.

Mining activities: Mining activities also contribute to water pollution. Mining is the process of breaking the rock and extracting coal and other mineral resources from the underground. This process involves the release of toxic chemicals and emission of large amount of metal waste which when carried away through erosion into our water body results to fish kill and other environmental hazards.

Thermal effluent: Many industrial processes use water as a coolant. This is often discharged clean but much warm. Thermal pollution may not be toxic but affects aquatic organisms because of the sudden rise in temperature. Increase in the temperature of a water body decreases oxygen levels and this can cause fish kill, reduce species biodiversity etc.

1.3.2 Effects of Pollution in Aquatic Ecosystems

Industrial waste often contains many toxic substances that damage the health of aquatic animals and those that feed on them. Their effect might be either mild or fatal. They can cause immune suppression, reproductive failure, acute poisoning etc. Heavy metals from industrial waste water can accumulate in the waterbody, fish, flora and other aquatic organisms and subsequently humans that feed on them. Heavy metals can cause slow development of cells and tissues, result in birth defects and some are carcinogenic to humans. Microbial pollutants from sewage often result in infectious diseases that affects both aquatic and terrestrial life through water. This results or causes diseases such as cholera, diarrhea and typhoid fever. Organic matter and nutrients (eutrophication) cause depletion of oxygen when aquatic plants die and

decay but photosynthesis adds oxygen to water. This increases oxygen in the water column. Oil spillage and suspended particles in freshwater reduce light penetration into the underwater and the quality of drinking water for humans. This disrupts the growth of photosynthetic plants and micro-organisms. Sulphate particles from acid rain can cause harm to the health of marine life in the rivers and the lakes it contaminates and it can result in mortality.

1.4 Heavy Metals

Heavy metal is a metal of relatively high density (3.5 g/cm^3 – 7 g/cm^3) or of high relative atomic weight (22.98 g - > 40 g) (Kumolu-Johnson *et al*., 2010). Heavy metal is also of environmental concern. This is however subject to harmful effects of some heavy metals such as Cadmium (Cd), Mercury (Hg), Lead (Pb), Arsenic (As) etc. Heavy metals are naturally found in the environment but they often become concentrated due to human activities such as domestic and industrial sewage disposal, mining, fertilizer and chemical application, vehicular emissions etc. and naturally by weathering, volcanic emissions and forest fire. Heavy metals such as copper, iron, zinc, vanadium and manganese are essential for human in trace quantities (Banfalvi, 2011), however, lead, cadmium, mercury and arsenic are poisonous even at low concentrations and have no known dietary importance.

1.4.1 Copper (Cu)

Copper (Cu) has an atomic number of 29 and atomic mass of 63.55 g/mol. It belongs to group l1 on the periodic table. Cu is reddish with a bright metallic lustre. It is malleable, ductile and a good conductor of heat and electricity. Cu is one of the most important trace elements that is essential to the human body although at low

concentrations. Cu is used as an effective algaecide and molluscicide (Abou-zaid *et al.*, 1988). It is also important in preventing premature ageing and increasing energy production. Cu is essential for regulated health rhythm, balanced thyroid glands, and reduced symptoms of arthritis, quick wound healing and increased red blood cell formation (Getachew, 1988).

Prolonged exposure to copper can cause irritation of the nose, mouth and eyes. It causes headaches, dizziness, stomach ache, vomiting and diarrhea. High intake of Cu may cause liver and kidney damage and even death. (Kumolu-Johnson *et al.*, 2010)

1.4.2 Iron (Fe)

Iron (Fe) is derived from Latin name ferrum. It has atomic number of 26 and atomic mass of 55.85 g/mol. It belongs to group 8 on the periodic table. Fe is a lustrous, ductile, malleable, silver-grey metal. It is known to exist in a distinct crystalline forms. By mass, it is the most common element on the earth. Fe is essential to almost all the living things. It can be found in meat, whole meal products, potatoes, vegetables etc. Fe is an essential part of haemoglobin, the red colouring agent of the blood that transports oxygen in the body. When Fe is absorbed and remains in the tissues, it may cause conjunctivitis, choroiditis and retinitis (Gulani, 1998). Chronic inhalation of excessive concentrations of iron oxide fumes or dust may result in development of siderosis and the risk of lung cancer development (Scheid *et al.*, 2009). Fe deficiency in humans can cause anaemia.

1.4.3 Lead (Pb)

Lead has an atomic number of 82 and atomic mass of 207.2 g/mol. Pb is a bluish-white lustrous, soft, highly malleable and ductile metal. It is a relatively poor

conductor of heat and electricity. Pb is one of the most poisonous metals that cause various health hazards. It can enter into the human body through the food chain and uptake of food (65%), water (20%) and air (15%) (Ndimele *et al.*, 2009). It enters the drinking water through corrosion of galvanised pipes especially when the water is slightly acidic. Pb is not useful to humans even at low concentration and can cause series of health problems such as disruption of the biosynthesis of haemoglobin and anaemia, an increase in blood pressure, kidney damage, miscarriage and subtle abortions, disruption of nervous system, brain damage, declined fertility in men through sperm damage, diminished learning abilities in children, behavioural disruption of children such as aggression, impulsive behavior and hyperactivity (US Center for Disease Control, 2005) and can also cause serious damage to the nervous systems and the brains of unborn children (Bank *et al.*, 1997).

1.4.4 Zinc (Zn)

Zinc has an atomic number of 30 and atomic mass of 65.4 g/mol. It belongs to group 12 on the periodic table. Zinc is a lustrous bluish-white metal. It is brittle and crystalline at ordinary temperature but becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals. It occurs naturally. Drinking water and many foods contain certain concentration of zinc. Some soils are heavily contaminated with Zinc and these are usually found in areas where zinc has to be mined or refined or where sewage sludge from industrial areas has been used as fertilizer. Zinc is the 23rd most abundant element in the earth's crust (Authman, 1998). Zn plays a role in the synthesis of nucleic acid and it is also a component of many enzymes. Zn and its compounds are used in medicine, paint and plumbing works. Zinc is essential for

human health but when its consumption exceeds threshold level, it can cause loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores, stomach cramps, skin irritations, vomiting, nausea and anaemia, retard growth, delayed sexual maturation etc (Clarke *et al*., 1981). Zinc is an essential trace element for living things. It is found in almost 100 specific enzymes (Prasad, 2008).

1.4.5 Cadmium (Cd)

Cadmium has atomic number of 48 and atomic mass of 112.4 g/mol. Cd is lustrous, silver-while, ductile and very malleable metal. Its surface has a bluish-tinge and the metal is soft enough to be cut with a knife but it tarnishes in air. Cd is one of the numerous metals that is not useful to human body even at relatively low concentration (Law *et al*., 2005). Cd is a toxic metal that is used in electroplating, plastic and battery industries. Human intake and accumulation of Cd through the food chain and prolong inhalation of Cd in air can cause various health hazards such as damage to the lungs, damage to the filtering mechanism of kidney, diarrhea, stomach pain and severe vomiting, bone fracture, reproductive failure and infertility, damage to the immune system and the central nervous system, psychological disorders, DNA damage or cancer development and even death (Clarke *et al*., 1981). Cd is responsible for several causes of food poisoning and it replaces Zn biochemically to cause high blood pressure, kidney damage etc (Fishar and Ali, 2005).

1.5 Water hyacinth (*Eichhornia crassipes*)

Eichhornia crassipes commonly known as water hyacinth belongs to the family Pontederiaceae. Water hyacinth is a free-floating, monocotyledonous, perennial aquatic plant with broad, thick, glossy round leaves, inflated leaf stems and showy

lavender purple flower. Its fruit is a dehiscent capsule containing up to 200 small seeds (Pieterse, 1997). *E. crassipes* may be up to l metre high above water surface. They have long, spongy and bulbous stalks which supports a single spike of 8 - 15 conspicuously attractive flowers. Water hyacinth grows in fresh waters. Its temperature tolerance is 12°C (minimum), 25° - 30°C (optimum) and 33^{o} - 35^{o} C (maximum) (Kasselmann, 1995). It tolerates an estimated pH of 5.0 – 7.0 (Chetta and Madsen, 1995, Delgado *et al*., 1994). However, it does not grow in brackish water because of its salt content. Water hyacinth reproduces both sexually by seeds and asexually by runners or stolons which forms the daughter plants. Each plant can produce thousands of seeds yearly and these seeds can remain viable for more than 28 years (Sullivan and Wood, 2012). *E. crassipes* is a fast growing plant; its population can double in as little as 6 days (Mitchell, 1976). They can be controlled biologically, chemically and mechanically.

1.5.1 Uses of *Eichhornia crassipes*

They are used in biogas production (Wolverton *et al*., 1975); paper production (Nolan and Kirrnse, 1974); animal feed production (Kusemiju and Akingboju, 1988), and production of compost manure {Chukwuka and Omotayo (2008); Omotayo and Chukwuka (2009)}. The plant is used as a carotene–rich table vegetable in Taiwan. Japanese sometimes cook and eat the green parts and inflorescence (Duke, 1983). The flowers are used for treating the skin of horses and they can also be used in the manufacturing of furnitures, handbags, ropes as well as in phytoremediation of polluted aquatic environment (Ndimele and Jimoh, 2011).

1.6 Water Lettuce (*Pistia stratiotes*)

Pistia stratiotes commonly known as water lettuce belongs to the family, Araceae. Water lettuce is a free floating perennial monocotyledonous plant with a spongy thick dusty green leaves. The leaves are simple and are covered with fine hairs which form basket-like structures that traps air bubbles. The leaves are arranged spirally from the centre of the plant forming a rosette. The leaves are 2.54 – 15.24 cm wide and up to 14 cm long with a large parallel veins running through out its length. They have wavy margin and no stem.

The flowers are dioecious and are hidden in the middle of the plant amongst the leaves. Water lettuce is one of the world's most productive freshwater aquatic plants. It grows in water with high nutrient content particularly those that have been contaminated with human loading of sewage and fertilizer. Its temperature tolerance for growth is in the range 22^0 - 30^oC (optimum), 15°C (minimum) and 35°C (maximum), (Kasselmann, 1995).

Water lettuce often exhibit weedy growth behavior and can be found growing also in canals and reservoirs (Kasulo, 2000). Water lettuce reproduce sexually through fertilization forming small green berries and asexually through short stolon forming a dense mat. *P. stratiotes* can be controlled biologically, chemically and mechanically.

1.6.1 Uses of water lettuce

They are used in tropical aquarium to provide cover for fry and small fishes. They out-competes algae for nutrients thereby preventing massive algal bloom.

1.7 Problems of Water Hyacenth and Water Lettuce

Water hyacinth and water lettuce are not new in the ecological history of man (Uka and Chukwuka, 2007; Gruptal *et al*., 2012). Water hyacinth has been described as the most

troublesome weed in the world (Gopal and Sharma, 1981) because of its rapid rate of multiplication. Water hyacinth and water lettuce form thick mats creating the following problems: Theft mats clog waterways making navigation, fishing and almost all other water activities impossible; their mats block sunlight penetration and at water interface. This greatly reduces oxygen level in the water subsequently affecting aquatic organisms. Mats have greatly reduced aquatic biodiversity, that is, it eliminates other submersed plants by blocking sunlight penetration, altered emerged plant communities by pushing away and crushing them and also animal communities by blocking access to the water and/or eliminating plants and animals that depend on them for shelter and nesting. It degrades water quality which makes the water unsafe for drinking and not useful for most domestic activities (Uka and Chukwuka, 2007). Various eradication and/or control measures that have been used have not yielded any good results, therefore their utilization has been embraced such as in their uses mentioned above including phytoremediation.

1.8 Distribution of *E. crassipes* and *P. stratiotes* Globally and in Nigerian Aquatic Ecosystem

Water hyacinth and water lettuce are found almost in every part of the world. They are present in freshwater bodies in Africa, Asia, Australia and North America (Dagno *et al.*, 2012). Africa has particularly been affected by the introduction and spread of water hyacinth, facilitated in part due to a lack of naturally occurring enemies. In a review of water hyacinth infestation in eastern, southern and central Africa, Mujingni (2012) reports that the weed was first recorded in Zimbabwe in 1937. Water hyacinth has also spread to West Africa. It was first reported in Cameroon between 1997 and 2000 and since then the country's wetlands have become "home" for the weed (Forpah, 2009). In Nigeria, almost all river bodies have been dominated by water hyacinth (Borokini and Babalola, 2012).

1.9 Phytoremediation

Phytoremediation is the use of plant to remove pollutants from the environment (Raskin, 1996). This concept is relatively new, cost effective and environment friendly compared to other methods of remediation. Aquatic macrophytes such as *Ipomoea aquatica* Forsk, *Typha angustata* Bory and Chaub, *Echinochloa colonum* (L.) Link, *Pistia stratiotes* L, *Eichhornia crassipes* (Mart.) Solms among others have been used for phytoremediation. These plants have the ability to hyperaccumulate toxic metals in their tissues and convert the pollutants to less toxic compounds and volatilize them (Terry and Zayed, 1994). Some aquatic plants can filter pollutants from water (Brooks and Robinson, 1998) and therefore can be used for phytoremediation of polluted environment.

1.10 Justification

Lagos and Ogun States are the two major industrial hubs in Nigeria. Ogun State has the highest number of industries in the country and one of its towns, Ota has the third largest concentration of industries in Nigeria. Lagos is a metropolitan city with large number and concentration of industries. These industries discharge their wastes into inland water bodies in the state and the neighbouring states often times untreated. Cases of fish kill resulting from pollution of Ologe Lagoon have been reported (Kumolu-Johnson *et al.,* 2010). These industrial effluents contains pollutants like heavy metals, which are non-biodegradable and consequently, can persist in the aquatic ecosystems for years until the threshold is reached at which point their deleterious effects become obvious. Federal Ministry of Housing and Environment (FMHE, 1983) reported that Cu, Zn, Mn, Pb and Fe were the most common heavy metals found in all the effluents analysed from various industries in Nigeria while Cr was found consistently in textile effluents. Water hyacinth and water lettuce are the principal aquatic weeds in Africa and have been described as noxious weeds in more than 50

countries and 5 continents of the world {Global Invasive Species Database (GISD, 2005)}. They have literally taken over our water bodies and have exerted enormous socio-economic hardship on the riverine population that depend on these water bodies and the services they provide for subsistence. Efforts to eradicate these aquatic macrophytes have not produced encouraging results. Therefore, the need to utilize them becomes imperative. These plants have the ability to absorb heavy metals and thus, rid the environment of these pollutants and their adverse consequences. This phenomenon called phytoremediation is what this study examined.

1.11 Aims and Objectives of the Research

1.11.1 Aim

To assess the ability of water hyacinth and water lettuce in phytoremediation of heavy metal polluted aquatic environment (Ologe Lagoon).

1.11.2 Specific Objectives of the Research

(i) To study the temporal and spatial variation of some physico-chemical parameters of Ologe Lagoon and their effects on the heavy metal status of the lagoon.

(ii) To investigate the heavy metal content of water, water hyacinth and water lettuce from Ologe lagoon.

(iii) To investigate the phytoremediation of heavy metal by water hyacinth and water lettuce in natural environment.

(iv) To investigate the phytoremediation of heavy metal by water hyacinth and water lettuce in the laboratory.

(v) To determine the bioconcentration factors (BCF) of heavy metals in water hyacinth and water lettuce.

(vi) To determine the translocation factors (TF) of heavy metals in water hyacinth and water lettuce.

(vi) To examine the model that best fits the description of the removal of metals from the aquatic plants.

1.12 Statement of Problem

(i) Ologe Lagoon is polluted with heavy metals and other pollutants from Agbara Industrial Estate.

(ii) Water hyacinth and water lettuce are aquatic menaces that needs to be eradicated and/or controlled or utilised.

CHAPTER TWO

LITERATURE REVIEW

The presence of heavy metal in the aquatic environment is of great concern not just because they are toxic at relatively high concentration but also because of their persistence in the environment long after the sources of pollution have been controlled or prevented (Kumolu- Johnson *et al.*, 2010). Some heavy metals such as zinc, iron and selenium are present in small quantities, and are essential nutrient in diet of most animals. However, when they occur slightly in greater concentration, they become toxic to wildlife as it occurred in San Jacquin in California,, USA among other places (O'Toole and Raisbeck, 1998). Other heavy metals like lead, mercury and cadmium have no dietary roles and should not be consumed by living organisms.

2.1 Sources of Heavy Metal in the Aquatic Environment

Heavy metals enter into the aquatic environment from both natural and anthropogenic sources. Important natural sources include weathering, volcanic eruption and forest fire while the anthropogenic sources include mining effluents, domestic effluent, industrial effluent, petroleum industry activity, burning of fossil fuel, leaching of metals from garbage and solid waste dump, incineration of domestic waste, shipping activities including those of motorized boats and canoes, agricultural farmland run-off e.g. fertilizers, pesticides (Calamari and Maeve, 1994; Ajao *et al.*, 1996). However, Ayodele *et al.*, (1991) and Kumolu-Johnson *et al.*, (2010) pointed out that industrial and domestic effluent constitute the largest sources of heavy metal in the environment. Oyewo (1998) stated that industrial activities result in the release of

huge amount of heavy metal into the environment along with industrial waste water, solid waste and the flue gases. Carmody *et al.,* (1992) reported that the level of chromium, copper, lead, nickel and zinc increased by ten to hundred fold in natural water immediately around solid waste dumps in New York bight when compared with areas further away from the dump sites. Davidson *et al.,* (2004) reported that Mistsui mining and smelting company in Japan in the early 19th century discharged cadmium (a by-product) into Jinzu Gawa River and when the populace around consumed rice grown with this contaminated river water, they suffered softening of bones and kidney failure. O'Toole and Raisbeck (1998) reported the outbreak of mercury poisoning in Minamata and Nigata, Japan in 1950 which caused a disease known as Minamata disease that killed more than 600 people. WHO (2008) estimated 143,000 death and 600,000 new cases of children with intellectual disabilities each year as a result of lead poisoning. Proireschi (1998) and Gilbert and Weisis (2006) opined that water from earthen ware pipes are better than water from lead pipes. This is because white lead are produced, this mixes up with water hence making the water harmful for consumption.

Ajao *et al* (1996) reported the following as the anthropogenic sources of heavy metals into the environment.

- Mining effluents.
- Domestic effluents and urban storm water run-off.
- Petroleum industry activities.
- Industrial effluents.
- Logging and timber transportation by water.
- Shipping activities including those of motorized boats and canoes.
- Agricultural / farmland run-off e.g. fertilizers, pesticides.

❖ Atmospheric sources e.g. gas-flaring, incineration of domestic waste.

In Nigeria, a few chemical surveys of industrial effluents by Federal Ministry of Housing and Environment have revealed that effluents from local industries like their counterparts in other parts of the world contain varying types and amounts of heavy metals which enter the aquatic and terrestrial environments via effluent discharges. In 1983, the Environment Planning and Protection Division of the Federal Ministry of Housing and Environment (FMHE, 1983), having analyzed effluents from various industries located all over Nigeria, produced a monograph describing the types and concentrations of heavy metals in these effluents.

The FMHE (1983) report showed that Cu, Zn, Mn, Pb and Fe were the most common heavy metals in all the effluents while Cr was found consistently in textile effluents. In this report (FMHE, 1983), divergent ranges of occurrence for different heavy metals in the investigated industrial effluents were as follows: Cu (0.01-0.05 mg/L), Fe (nd-3.20 mg/L), Zn (0.03-0.26 mg/L) and Cr (nd-0.25 mg/L). Towards the end of the twentieth century in Nigeria, Ajao *et al.,* (1996) showed that effluents from textile mills in Kaduna, Katsina and Sokoto States all contained heavy metals with the following range of concentration: Fe (115.20-127.50 mg/L), Mn (nd-9.00 mg/L), and Zn (4.00-43.80 mg/L). Ayodele *et al.,* (1991) detected several heavy metals including Pb, Cr, Cd, Cu, Ni and Mn in effluents from Sharada industrial Estate in Kano. More recently, studies by Kumolu-Johnson *et al.,* (2010), Ndimele *et al.,* (2009), Agboola *et al.,* (2008) have also revealed the presence of heavy metals in Nigeria's inland water bodies especially those that receive effluents from industries. Thus, several reports have established the fact that local industries contribute to the increasing levels of heavy metals in drainages, streams, estuaries and the sea. However, Oyewo (1998)

reported that these earlier reports have not included any simultaneous effort to estimate the quantities of heavy metals that were discharged by the evaluated industries into the receiving aquatic ecosystems over unit time periods. He further opined that such estimates will be useful in assessing the rate of build-up of heavy metals (which are persistent once in the environment) and will be invaluable in the control and management of heavy metal pollution in the recipient environment. Kumolu-Johnson *et al.,* (2010) opined that the observation by Oyewo (1998) is valid and important but accomplishing that task is difficult because the industries will give researchers the correct information and would also prevent access to their waste treatment facility if it exist in order to estimate these values.

Oyewo (1998) reported that apart from liquid effluents, industrial solid wastes have also been shown to be sources of heavy metal pollution in aquatic and terrestrial environments including ground water. For instance, Anake *et al.*, (2009) reported that the ranges of Cd, Cr, Ni and Pb levels for all the dumpsites in Kaduna and Kano were 0.30–49.8, 5.76–139, 0.39–19.1 and 42.6–9662 mg/kg, respectively. Fodeke (1985) through a survey of natural waters near solid waste dump sites demonstrated heavy metal contamination of these waters as a result of leachates from such dump sites. Usman *et al.*, (2012) sampled soil sediments from three decomposed municipal solid waste dump sites located in Esso, Gbangbara and Eyagi areas of Bida town and analyzed them for some heavy metals (Cu, Fe, Pb, Mn and Cr). The results showed that average mean concentration of Cu (342.22±7.6 mg/kg), Mn (570.00±1.0 mg/kg) and Fe (371.11±1.2 mg/kg) in the three dump sites were exceptionally high. Akinola *et al.*, (1981) in their chemical survey of crop from the Nigerian agricultural industry found that wastes contained various types of heavy metallic compounds like Zn, Cu, Fe and Mn. These authors reported the presence of 15.36, 4.16, 6.56 and 8.32 mg/kg

of Zn, Cu, Fe and Mn respectively in crop wastes like maize and cocoa husks, weed stalk and plantain peels. It is therefore important to avoid dumping such crop wastes in bodies of water to avoid the release of heavy metallic compounds into such waters as the metal-contaminated plant parts decay.

Industrial activities also result in the emission of combustion products, which contain heavy metals (Oyewo, 1998). According to Merlini (1980), modern industry is responsible for heavy metals in the atmosphere, for it has been shown that air samples from industrialized cities have more than five times amounts of suspended metals, than in samples of air from sub-urban areas. Law (1981) reported that the burning of fossil fuels in industries and elsewhere is an established source of heavy metal pollution since fuels contain a variety of heavy metallic compounds. However, Oyewo (1998) observed that not much information is available in Nigeria on the status of heavy metal pollutants in the air due to the very limited and recent air quality monitoring activities.

2.2 Occurrence, Distribution, Pathway and Fate of Heavy Metals in Aquatic Environment

Heavy metals occur naturally as trace elements whereas man-made additions sometimes increase their load in the ecosystem leading to environmental pollution (Oyewo, 1998). Oyewo (1998) also reported that the industrial and agricultural activities of man result in the concentration and redistribution of heavy metals in various segments of the biosphere. He therefore opined that knowledge of the distribution of heavy metals and their rates of concentration or accumulation in various compartments of the environment is a major endeavour in environmental monitoring programmes of several nations. In Nigeria, most efforts so far have been concentrated on determining the types and amounts of heavy metals in industrial

effluents and some segments of the environment of interest to the scientific evaluators. For instance, in a study of heavy metals and microbial contamination of Tilapia species in Lagos Lagoon, Fodeke (1979) determined the concentrations of heavy metals in whole as well as different parts of Tilapia species collected from the Lagos Lagoon and concluded that the measured values were high: the gut contained 0.03-0.19 ppm Hg, 0.03-3.72 ppm Pb, 0.04-0.19 ppm Cu and 0.64-2.23 ppm Ni. In the whole minced fish, the author measured 0.10-0.40 ppm Hg, 0.16-0.90 ppm Pb, 7.50-17.27 ppm Fe, 0.19-2.53 ppm Cu and 0.46-0.89 ppm Ni. More significant is the paucity of records in sustained measurements of levels of heavy metals generated by local industries and the level of presence of such metals in recipient ecosystems (aquatic and terrestrial) (Oyewo, 1998). He further opined that as long as man-induced generation of heavy metals continue in industrial and domestic activities in Nigeria and elsewhere, such sustained measurements will be needed to facilitate the identification and quantification of the state of environmental degradation attributable to heavy metal emission. Results from such regular monitoring exercises will be invaluable in the proper management and control of heavy metal pollution in the environment.

According to Calamari and Naeve (1994), Ajao *et al.*, (1996) and Oyewo (1998), industrial activities are not the only source of heavy metal into the environment, other sources include, untreated wastes, discharge from sewage treatment works, agricultural wastes, urban run-off and storm waters. Oyewo (1998) also reported that in order to establish and quantify the contribution of man to heavy metal content via industrial and domestic activities, it is useful to know background or natural levels of metals before the establishment of modern industry. In an area where such baseline data are not available, adjacent uncontaminated areas within similar geographical

region could provide background levels of metals that may be useful in making deductions on the extent of man-made heavy metal contamination.

Calamari and Naeve (1994) reported that in an aquatic environment, metals are partitioned among the various environmental compartments (Water, suspended solids, sediment and biota). They also opined that the metals in the aquatic environment may occur in dissolved, particulate and complexed form. They equally reported that the main processes governing distribution and partition are dilution, advection, dispersion, sedimentation and adsorption / desorption. Nonetheless, some chemical processes could also occur. Thus, speciation under the various soluble forms is regulated by the instability constants of the various complexes and by the physico-chemical properties of the water (pH, dissolved ions and temperature).

Adsorption could be the first in the ultimate removal of metals from water. In the course of distribution, permanent or temporary storage of metals take place in the sediments of both freshwater and marine environments. Microbial activity and redox processes may change the properties of sediments and affect the composition of interstitial water. As a result, iron and manganese oxides may be converted to carbonates or sulphides, leading to a decrease in the adsorption capacity of the sediments. Reworking of the sediments by organisms will also bring sediments to the surface, where a significant fraction of the metal will be released (Calamari and Naeve, 1994).

Many transformations of heavy metals in aquatic environment occur as biochemically mediated reduction, methylation, demethylation and oxidation of single metals. Redox reactions may also facilitate some transformations. The biochemical processes are carried out by microorganisms and alga (Calamari and Naeve, 1994). According to

Jernelov (1975), methylation of mercury takes place when microorganisms while consuming organic substances, happen to come in contact with mercury ions. This may also be true for As, Sn and Pb.

Earlier workers have made several measurements of increasing levels of heavy metals in soil, water and air due to anthropogenic activities. For instance, Modamio (1986) investigated the distribution of heavy metals in some estuarine sediments from the Catalonian coast, which is highly industrialized region of Spain. The author found that sediments from Besos estuary contained relatively high concentrations of Hg (17 µg/g), these values being several folds higher than the amounts of Cu (48 ppm) and Pb (20 ppm) occurring in uncontaminated near shore sediments far removed from such estuaries that receive effluents from several industries (Riley and Chester, 1977). A Nigerian study on heavy metal distribution in Lagos lagoon by Okoye (1989) also showed that sediments from the highly industrialized region in his study site had relatively higher levels of Cd (8.97 µg/g) and Zn (198 µg/g), which were two to three times higher than the values from the relatively uncontaminated region of the lagoon. Most studies on the distribution of heavy metals in water bodies reveal that levels of heavy metals in the bottom sediments are usually higher than in the water column: Ndimele (1999) reported that in one of his sampling stations in Agbara, the range of values of Fe in water were 0.010-0.70 mg/L whereas the sediment contained about 8.00 - 40.00 mg/L. He made a similar observation in the other sampling stations and for other heavy metals he worked on. Other studies that have affirmed this assertion are Okoye (1989) on the Lagos Lagoon, Chukwu (1991) on Sasa River and Chye-Eng Seng *et al.*, (1987) in the State of Penang in Malaysian coastal waters. Oyewo (1998) opined that the cause of this observation is due to the fact that sediments act as sink for heavy metals derived from weathering as well as those anthropogenic inputs. He

further stated that the heavy metals that are suspended in the water column and those associated with suspended particulates ultimately sink to the bottom and become incorporated in the sediments and concluded by asserting that the biological significance of this differential distribution and concentration of heavy metals is that benthic organisms which live on and forage in bottom sediments will be exposed to greater risks of damage and or bioaccumulation. Evaluation of the risk of damage by heavy metal pollution must therefore involve benthic species to be comprehensive and useful for ecological management.

Pollution studies on 26 rivers in some southern and northern states of Nigeria (Ajayi and Osibanjo, 1981), on rivers in the Niger Delta (Kakulu and Osibanjo, 1992), on the cocoa growing area of Ondo State in south-west Nigeria (Ogunlowo, 1991) and the Lagos waters (Okoye, 1991) showed that, with the exception of iron, the concentrations of most trace metals in the surface waters were generally lower than global average levels for surface waters and the international drinking water standards.

Statistical treatment of the results of metal analyses of 176 stream sediment samples from the Ife- Ilesha area (1800 km^2) of southern Nigeria (Ajayi, 1981) showed that all the elements have density distribution close to natural background levels. Ojo (1988) also used various statistical methods for the interpretation of the geochemical data obtained from analyses of Cu, Pb, Zn, Co, Fe, Mg, Mn and Ca in 373 stream sediment samples collected over an area of 700 km^2 within the upper Benue Trough (Nigeria) and concluded that these elements exhibit various patterns of association depending on their nature and prevailing environmental conditions. Other studies in the area (Kakulu and Osibanjo, 1988, 1992) revealed higher levels of Pb, Cr, Ni, V and Zn in

Port Harcourt and Warri sediments which suggest that effluents from petroleum refineries located in those cities have contributed significantly to the heavy metal pollution of the respective aquatic ecosystems.

Studies in sediments, water and biota of the second largest natural lake in the world, Lake Victoria (Alala, 1998, Ochieng, 1987) showed no significant heavy metal pollution. However, more recent studies in the same lake revealed increase Lead (Pb) levels largely due to increased stopping traffic and associated problems, car washing and discharges from local industries (Wandiga and Onyari, 1987, Onyari and Wandiga, 1989). Ochumba (1987) studied physico-chemical parameters, dissolved oxygen and heavy metal concentrations in Lake Victoria as the possible causes of periodic fish kills. The author attributed the fish kills to dissolved oxygen depletion.

Several reports from workers have confirmed that metals accumulated by biota correspond with the metals in both sediments and the water column of their environment: Ndimele (1999) analysed two resident fish species (*Chrysichthys nigrodigitatus* and *Cynothrissa mante*) in Ologe lagoon located to the west of Lagos State, Nigeria. He discovered that the bodies of these fish species had accumulated the heavy metals (Fe, Zn, Cu and Pb) that were detected in the bottom sediment and water column of the lagoon. Other workers who made similar assertion are Patel *et al.*, (1985) and Oyewo (1988). Such results provide the basis for the assertion now commonly made that the concentrations of contaminants / pollutants in some aquatic plants and animals reflect the concentrations in their environment (Herung *et al.*, 1981, Bryan and Langston, 1982, Miller *et al.*, 1992). Thus, regular measurement of the amounts of accumulated heavy metals in the tissues of benthic organisms could

serve as good indicators of the type and levels of heavy metals in Nigerian water bodies (Oyewo, 1998).

2.3 Biological Effects of Heavy Metals

The biological effects of heavy metals range from beneficial stimulation to harmful retardation and death. Some heavy metals including Cu, Mn, Mo, Fe, V and Zn are essential for good health and normal growth; playing important roles in key metabolic activities in plants and animals. Such essential elements only become toxic when concentration exceeds the trace amounts required for normal metabolism (Law, 1981). Other heavy metals like Pb, Cd and Hg are non-essential to the physiological activities of living organisms.

All biochemical reactions are enzyme-catalysed and more than one quarter of all known enzymes contain metallic ions as structural members or the enzymes require metal ions for their activity (Harper *et al.*, 1977). Plant and animal tissue contain Cr while considerable Cu and Fe are present in the pigments, chlorophylls, xanthophylls, carotenes, phycoerythrin and phytocyanin which are found in chloroplast (West *et al.*, 1966). These pigments absorb solar energy, which is converted to Adenosine triphosphate (ATP); a universal form of metabolic energy employed in cellular activities (Jones, 1976). Thus, essential heavy metals play crucial and beneficial roles in biochemical reactions vital for all life processes.

The harmful effects of heavy metals like other chemicals in the environment could be manifested in a number of ways including; reduction in the number of survivors, undesirable influence on metabolism or breeding efficiency and alteration of behavioural pattern of living organisms (Gerlach, 1981). In a local study on the

influence of domestic and industrial effluents on populations of sessile and benthic organisms in Lagos Lagoon, Ajao (1990) established that the study environment contained measurable levels of heavy metals, hydrocarbons, organochlorides and polychlorinated biphenyls (PCBs). The author subsequently concluded that these pollutants / contaminants which are usually found in effluents from different categories of industries have resulted in ecological disequilibrium manifested as gross changes in community structure of the benthos in his study area. The most obvious effects of these pollutants / contaminants on Lagos lagoon benthos was a decline in number of some individuals and species in some areas of the lagoon as well as the total elimination of all benthic species from some grossly polluted sites for varying periods (Ajao, 1990). Generally, factors influencing heavy metal toxicity include type and form of the metal, presence of other metals or toxins, environmental factors and conditions of the target organism of interest including its state of health and stage in life cycle. In general, the toxicity of heavy metals is nearly attributable to the capacity of the metal ions to form stable complexes with the active sites of proteins (Waldichuk, 1980). Consequently, many heavy metals bind to many enzymes, which mediate vital life processes, resulting in the disruption of cellular activities, which, the enzyme catalyse.

2.4 The Ecological Importance of Bioaccumulation and Biomagnification of Heavy Metals.

It is well known that heavy metals are non-degradable substances and many of their compounds are not easily broken down or metabolized and subsequently excreted by living organisms (Unsal, 1984). A consequence of this situation is that on many occasions, the rate of absorption of heavy metals exceeds the rate of metabolic conversion into water-soluble state and its subsequent excretion leading to a resultant

accumulation in organs and tissues (Oyewo, 1998). Some animals that are highly tolerant to heavy metals can store substantial amounts in their organs and body tissues, which can then transfer such metallic load to carnivores that feed on such infested tissues (Kim *et al.*, 1996). Thus, heavy metals can be transferred across links in the food web by animals (that cannot efficiently excrete these compounds but store them in their tissues), which become food for animals at a higher trophic level in the food chain. When an animal continuously feeds on metals-infested prey and cannot itself metabolize and excrete the metals, it eventually accumulate a higher amount than in its individual prey leading to the phenomenon of bioaccumulation and biomagnification (Oyewo, 1998). A compulsory route through which biomagnification of heavy metals can occur is via steady and direct absorption of the metals from contaminated media that holds minute but constant amounts of these persistent heavy metals in ecosystems.

The ecological survey carried out by Oyewo (1998) has shown that the levels of mercury in the bodies of resident lagoon animal species such as *Tilapia* sp, hermit crab (*Clibanarius africanus*) and periwinkle (*Tympanotonous fuscatus*) were significantly higher than the concentrations prevailing in the lagoon waters to which they were exposed under natural conditions. The possibility that the mercury content in the bodies of these lagoon animals arose from bioaccumulation of this heavy metal from the environment was given confirmation by experiment carried out by Oyewo (1998). These laboratory experiments showed that when live *Clibanarius africanus* or *Tympanotonous fuscatus* were exposed to sub-lethal concentrations of measurable levels of this heavy metal, the amounts accumulated increased with exposure period and dosage.

According to Baron (1995), bioaccumulation can be viewed simply as a result of the competing rates of chemical uptake and elimination, the latter comprising biotransformation and excretory processes. Oyewo (1998) also reported differential bioaccumulation in Lagos lagoon species with *C. africanus* accumulating more mercury than *T. fuscatus* probably due to the greater exposure of the body of the former and acquisition of shell without operculum, which increased mercury absorption. This observed differential toxicity of mercury and other heavy metals against different aquatic species have been observed by earlier workers in different countries (Bryan, 1976, Mackie, 1989, Chen *et al.*, 1991), and have always been attributed to differences in the chemistry and mechanisms of actions of the different metals. For instance, heavy metals based on their chemical nature are known to have differences in penetrability of living tissues. Other processes and factors, which influence their toxicity such as formation of complexes with proteins, their metabolism and excretability, sequestration in lipids and other tissues differ considerably between metallic species (Oyewo, 1998). Mercury has been reported by several authors to be one of the most toxic heavy metals in nature. Infact, Gerlach (1981), Baron (1995) and Oyewo (1998) opined that mercury was the most toxic of all the heavy metals they studied in their different works. According to Dufus (1980), the high electronegativity of Hg and the resultant high affinity for sulphydryl groups are two biochemical reasons for the high toxicity of the heavy metal. Furthermore, the lipids solubility of Hg (especially in the alkylated form) gives it an affinity for nervous tissue which accounts for many of its primary harmful effects including abnormalities in cell division, increased chromosomal damage and enzyme inhibition (Dufus, 1980, Baron, 1995).

2.5 Phytoremediation of Trace Metals

Remediation is a programme of activities designed to rehabilitate an impacted ecosystem. Phytoremediation is a form of bioremediation, which is the use of biological processes to detoxify polluted sites. Bioremediation can also be defined as the enhancing of rehabilitation of an impacted ecosystem by micro - organisms which have been described by Ekundayo (1978) as our unseen allies in fight against pollution". Phytoremediation specifically is the use of plants to remove pollutants from the environment or render them harmless (Raskin, 1996). Several species of plants have been shown to have the ability to grow in contaminated soils and actually extract the pollutant from the growth medium. These plants function in several different ways. Some plants can hyperaccumulate toxic heavy metals in their tissues. Others can convert the pollutants to less toxic compounds and volatilize them (Terry and Zayed, 1994; Brooks, 1998.). Some aquatic plants roots can filter contaminants/pollutants from water (Brooks and Robinson, 1998). Phytoremediators have been studied for use in cleaning up heavy metals like aluminium (Al), cadmium (Cd), chromium (Cr^{3+} and Cr^{6+}), copper (Cu), mercury(Hg), nickel (Ni), lead (Pb) and zinc (Zn). Phytoremediation has also been tested for clean - up of explosives like 2,4,6 - trinitrotoluene (TNT), trichloroethylene (TCE) and other volatile organic chemicals, and organic compounds such as petroleum compounds (Cunningham and Ow, 1996; Thompson *et al.*, 1998). If effective, phytoremediation can be an *attractive alternative to current remediation methods because the treatment can be done in* situ, the cost of plants is lower than most other current technologies and it is relatively environmentally safe. Using this technology lowers the total cost of the clean - up project and minimizes the disturbance the remediation will cause in the environment. There are limitations, however. One of the problems associated with

phytoremediation is that the technology is still very new and is not completely understood. The use of chelators to mobilize the metal ions is necessary in some instances for uptake by plant roots, and the results can be unpredictable. If the plants do not take up the metals rapidly enough, the pollutants could move off site (Cunningham and Ow, 1996). The plants that are best hyperaccumulators are very small plants and do not produce high biomass (Banuelos *et al.*, 1997). A phytoremediation project may take several years to show results (Cunningham and Ow, 1996).

2.6 The Aquatic Macrophytes: Water Hyacinth (*Eichhornia crassipes*) and Water Lettuce *(Pistia stratiotes*)

Aquatic weeds such as water hyacinth, water lettuce and fern have been reported to be present in Africa since the nineteenth century (Tackholm and Drar, 1950). Mitchell *et al.*, (1990) reported that these weeds have massively invaded African freshwater bodies during the early 1950. These weeds grow and multiply rapidly clogging water ways and consequently disrupting all water activities such as transportation, fishing, recreation, construction of dams etc. Water hyacinth and water lettuce are the principal aquatic weeds in Africa. They have been described as noxious weeds in more than 50 countries and five continent of the world (GISD, 2005).

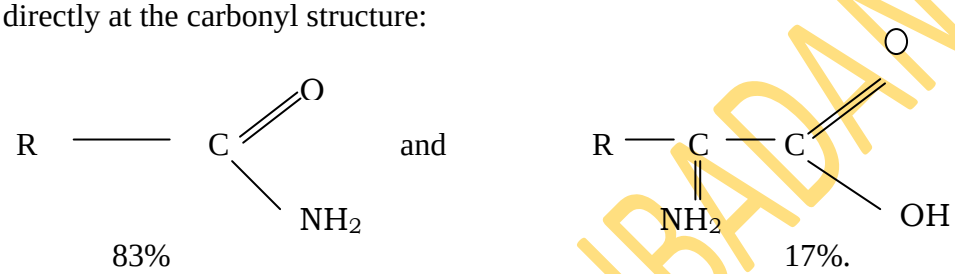
2.6.1 Water Hyacinth

2.6.1.1 Elemental Constituent of Water Hyacinth

Fresh water hyacinth contains about 90% water and about 15-20% solid materials (Kumolu-Johnson *et al.*, 2010). Dry weight of the weed contains about 25-30% of protein-related matter specifically amino-acid, about 17% of total protein matter and

50-60% amides. Amides are toxics matter and this is why water hyacinth are not eaten fresh like other vegetables. Edewor (1988) reported that there are about 36-40% carbon content in dry water hyacinth.

Direct carbonylation reaction reveal that the carbonates and nitrates obtained were in the order of 40% to 60% in yield ratio (Kumolu-Johnson *et al.*, 2010). Thus, water hyacinth has a predominantly cellulosic structure highly impregnated by the amino group directly at the carbonyl structure:



83% 17%.

Where R could be CH_2 or long chain CH_2-CH_2

Abdel-Sabour and Abo El-Seoud (1996) reported that elemental content varies in water hyacinth shoots and roots. Concentrations of K, Na and Ca levels were highest whereas Rb and Cs were the lowest. Shoots/roots concentration ratios was always 3 for Na, K and Ca, however it was 0.3 for other elements, with the exception of samples collected from Abo -Zabal drain which was around 0.3 for all elements due to high accumulation of these metals in roots. This might indicate that the water hyacinth nutrient balance is affected significantly by ambient element levels in the growing media (water body). Caesium apparently is not an essential component of plant tissues, and there are few data on its occurrence in plants. Caesium is relatively easily taken up by plants, although its absorption by roots appeared not to be parallel to K absorption. Abdel-Sabour and Abo El-Seoud (1996) reported that Cs contents in water hyacinth ranged from 0.09 to 0.87 mg/kg. They also found that different crops accumulated Cs in roots (highest value, 0.32 mg/kg). Their data showed a higher

accumulation in root samples from both the drain and Ismailia canal which may suggest a potential accumulation of this metal in those water bodies. As expected, most major elements are concentrated in aerial parts, while trace elements are concentrated in roots. While trace elements levels were significantly higher in samples collected from Abo-Zabal drain compared to Nile and canal samples. Iron contents ranged from 334 to 1554 mg/kg. Where Fe is easily soluble, plants may take up a very large amount of Fe. The natural Fe content of fodder plants ranges from 18 to about 1000 mg/kg.

2.6.1.2 Scientific Classification of Water Hyacinth

Kingdom:	Plantae
Division:	Magnoliphyta
Class:	Liliopsida
Order:	Liliales
Family:	Pontederiaceae
Genus:	*Eichhornia*

Species

E.	*crassipes*	-	Common water Hyacinth
E.	*azurea*	-	Anchored Water Hyacinth
E.	*diversifolia*	-	Variable leaf Water Hyacinth
E.	*paniculata*	-	Brazilian Water Hyacinth
E.	*natans*	-	

2.6.1.3 History of Spread of Water Hyacinth

Barrett (1989) reported that water hyacinth is a native to the Northern neotropics of South America while Hickman (1993) has a different opinion. He reported that water hyacinth originated from Amazonia and spread naturally throughout South America. According to Barrett and Forno (1982), water hyacinth was introduced to USA, South East Asia and South Africa as ornamental in the late 19th century and its now

naturalized in most tropical and sub-tropical areas. It was introduced to the US in 1880, Egypt in 1879, Asia in 1888, Australia in 1895 and Congo, the Nile and Late Victoria in 1950s (Edewor, 1988). Water hyacinth currently occur along the coast of Australia from Kiama in new South Wales to Southern Cape York peninsula in Queensland **(**Hassan and Chakrabarti, 2009)**.**

Water hyacinth entered into Africa freshwater bodies during the early 1950s (Mitchell *et al.*, 1990). Edewor (1988) reported that water hyacinth entered into Lagos Lagoon, Nigeria through Republic of Benin in 1985 and since then, it has spread throughout the country freshwater body impinging all water activities such as navigation, fishing, recreation etc.

2.6.1.4 Problem Caused by Water Hyacinth Infestation

Water hyacinth is a major environmental concern in many countries of the world (Ndimele, 2003). It rapidly invades vast or huge water areas due to its high rate of vegetable reproduction which forms dense mats and cover water ways. It affects all water based economic activities such as navigation, fishing, recreation, water quality, hydraulic and hydroelectric infrastructure among other (Hassan *et al.*, 2009). In the early 19th century in Vietnam, Laos and Cambodia, water hyacinth constituted a great nuisance in their water bodies (Pieterse, 1997). Ding *et al.*, (2001) and Chu *et al.*, (2006) reported that water hyacinth became problematic in the 80s after it was introduced as a folder in the 50s to solve shortage of feeds. They further opined that water hyacinth is responsible for most of the economic damage caused by foreign invasive species. Invasion of water hyacinth in any water body causes a change or affect biodiversity because it smothers native plant species and also other micro-organism in symbiotic and parasitic relationship with the plant. It increases water

evaporation and obstruct light penetration into the under water. Reduction in water oxygen and increase in the acidity of the water endangers aquatic life. Water hyacinth also provides breeding habitat for undesirable vector of human and animal disease such as mosquitoes and bilharzias-carrying snail (Pieterse, 1997).

2.6.1.5 Examples of threats posed by water hyacinth infestation

2.6.1.5.1 Destruction of biodiversity

Today, biological alien invasions are a major driver of biodiversity loss worldwide, (Pyšek and Richardson 2010). Water hyacinth is challenging the ecological stability of freshwater bodies (Gichuki *et al.*, 2012), out-competing all other species growing in the vicinity and posing a threat to aquatic biodiversity (Patel, 2012). Besides suppressing the growth of native plants and negatively affecting microbes, water hyacinth prevents the growth and abundance of phytoplankton under large mats, ultimately affecting fisheries (Gichuki *et al*., 2012).

2.6.1.5.2 Oxygen depletion and reduced water quality

Large water hyacinth mats prevent the transfer of oxygen from the air to the water surface, or decrease oxygen production by other plants and algae (Vila *et al.*, 2011, Villamagna and Murphy, 2010). When the plant dies and sinks to the bottom, the decomposing biomass depletes oxygen content in the water body (EEA, 2012). Dissolved oxygen levels can reach dangerously low concentrations for fish and other aquatic organisms that are sensitive to such changes. Furthermore, low dissolved oxygen conditions catalyse the release of phosphorus from the sediment which in turn accelerates eutrophication and can lead to a subsequent increase in water hyacinth or algal blooms (Bicudo *et al.*, 2007). Death and decay of water hyacinth vegetation in

large masses deteriorates water quality and the quantity of potable water, and increases treatment costs for drinking water (Patel, 2012; Mironga *et al.,* 2011; Ndimele *et al.,* 2011).

2.6.1.5.3 Breeding ground for pests and vectors

Floating mats of water hyacinth support organisms that are detrimental to human health. The ability of its mass of fibrous, free-floating roots and semi-submerged leaves and stems to decrease water currents increases breeding habitat for the malaria-causing anopheles mosquito as evidenced in Lake Victoria (Minakawa *et al.,* 2008). Mansonioides mosquitoes, the vectors of human lymphatic filariasis causing nematode Brugia, breed on this weed (Chandra *et al.*, 2006, Varshney *et al.,* 2008). Snails serving as vector for the parasite of *Schistosomiasis* (Bilharzia) reside in the tangled weed mat (Borokini and Babalola, 2012). Water hyacinth has also been implicated in harbouring the causative agent for cholera (Fong, 2013). For example, from 1994 to 2008, Nyanza Province in Kenya, which borders Lake Victoria accounted for a larger proportion of cholera cases than expected given its population size (38.7% of cholera cases versus 15.3% of national population) (Fong, 2013). Yearly water hyacinth coverage on the Kenyan section of the lake was positively associated with the number of cholera cases reported in the Province (Feikin *et al.,* 2010). At the local level, increased incidences of crocodile attacks have been attributed to the heavy infestation of the weed which provides cover to the reptiles and poisonous snakes (Patel, 2012; Ndimele *et al.,* 2011).

2.6.1.5.4 Blockage of waterways, hampering agriculture, recreation and hydropower

Water hyacinth often clogs waterways due to its rapid reproduction and propagation rate. The dense mats disrupt socioeconomic and subsistence activities (ship and boat navigation, restricted access to water for recreation, fisheries, and tourism) if waterways are blocked or water pipes clogged (Ndimele *et al.*, 2011, Patel, 2012). The floating mats may limit access to breeding, nursery and feeding grounds for some economically important fish species (Villamagna and Murphy, 2010). In Lake Victoria, fish catch rates on the Kenyan section decreased by 45% because water hyacinth mats blocked access to fishing grounds, delayed access to markets and increased costs (effort and materials) of fishing (Kateregga and Sterner, 2009). In the Wouri River Basin in Cameroon, the livelihood of close to 900,000 inhabitants was distorted; the entire Abo and Moundja Moussadi Creeks were rendered impassable by the weed leading to a complete halt in all the socioeconomic activities with consequent rural exodus (Mujingni, 2012). The weed made navigation and fishing almost impossible task in Nigeria (Ndimele *et al*., 2011).

While navigation in the Brahmaputra River in India was affected by the weed, it also blocked irrigation channels and obstructed the flow of water to crop fields (Patel, 2012). For example, in West Bengal, it causes an annual loss of paddy rice (Patel, 2012) by directly suppressing the crop, inhibiting rice germination and interfering with harvesting (European Environmental Agency (EEA), 2012). The dense growth entangles with boat propellers, hampering fishing. Water hyacinth slows water flow by 40 to 95% in irrigation channels (Jones, 2009), which may cause severe flooding. The communities of Bwene and Bonjo in the Wouri River Basin in Cameroon

regularly suffer from floods during the rainy season due to blockage of waterways around the villages by the weed (Mujingni, 2012).

It is estimated that the flow of water in the Nile could be reduced by up to one tenth due to increased losses from evapotranspiration by water hyacinth in Lake Victoria (Ndimele *et al.,* 2011). Water loss by the same process and blocking of turbines on Kafue Gorge in Zambia translates into lost water for power generation and eventually into lost of revenue of about US$15 million every year for the power company (Zambia Environment Outlook (ZEO), 2008). Many large hydropower schemes are also suffering the effects of water hyacinth (Shanab *et al.*, 2010). For example, cleaning intake screens at the Owen Falls hydroelectric power plant at Jinja in Uganda were calculated to be US$1 million per annum (Mailu, 2001).

2.6.1.6 Method of Controlling Water Hyacinth Infestation

The spread of invasive alien species (Fig 2.1) is neither easy to manage nor easy to reverse, threatening not only biodiversity but also economic development and human wellbeing (UNEP, 2012). Native to the Amazon Basin in South America, water hyacinth has emerged as a major weed in more than 50 countries in the tropical and subtropical regions of the world with profuse and permanent impacts (Ndimele *et al.*, 2011). Worryingly, climate change may allow the spread of water hyacinth to higher latitudes (Patel, 2012). Intensified monitoring, mitigation and management measures are needed to keep water hyacinth at unproblematic levels. There are 3 commonly used control measures to suppress water hyacinth infestation. These are physical, chemical and biological methods.

2.6.1.6.1 Manual and Mechanical Control

Physical methods for control of water hyacinth involve drainage of water body, manual removal of the weeds (Fig 2.2) or pulling through nets (Patel, 2012). Employing machines like weed harvesters, crusher boats, and destruction boats prove expensive, approximately US$600 - 1,200 per hectare (Villamagna and Murphy, 2010) as well as unpractical for areas larger than a hectare given the rapid rate of increase of the weed. There may also be additional fees for disposal of plant material. The costs of water hyacinth management in China were estimated to amount around EUR 1 billion annually (EEA, 2012). In Europe, management costs to remove 200,000 tonnes of the plant along 75 km in the Guadiana River basin on the Portuguese-Spanish border amounted to EUR 14,680,000 between 2005 and 2008 (EEA, 2012). Dagno *et al*. (2007) reported that mechanical management of the weed in Mali cost around US$ 80,000–100,000 per year. Maintaining a clear passage for ships to dock at Port Bell in Uganda was estimated to cost US$ 3-5 million per year (Mailu, 2001). Yet, while mechanical removal has been effective to a considerable extent, the infestations soon return because shredded bunches of the weed were carried by waves to other unaffected areas where they establish and start proliferating (Shanab *et al*., 2010).

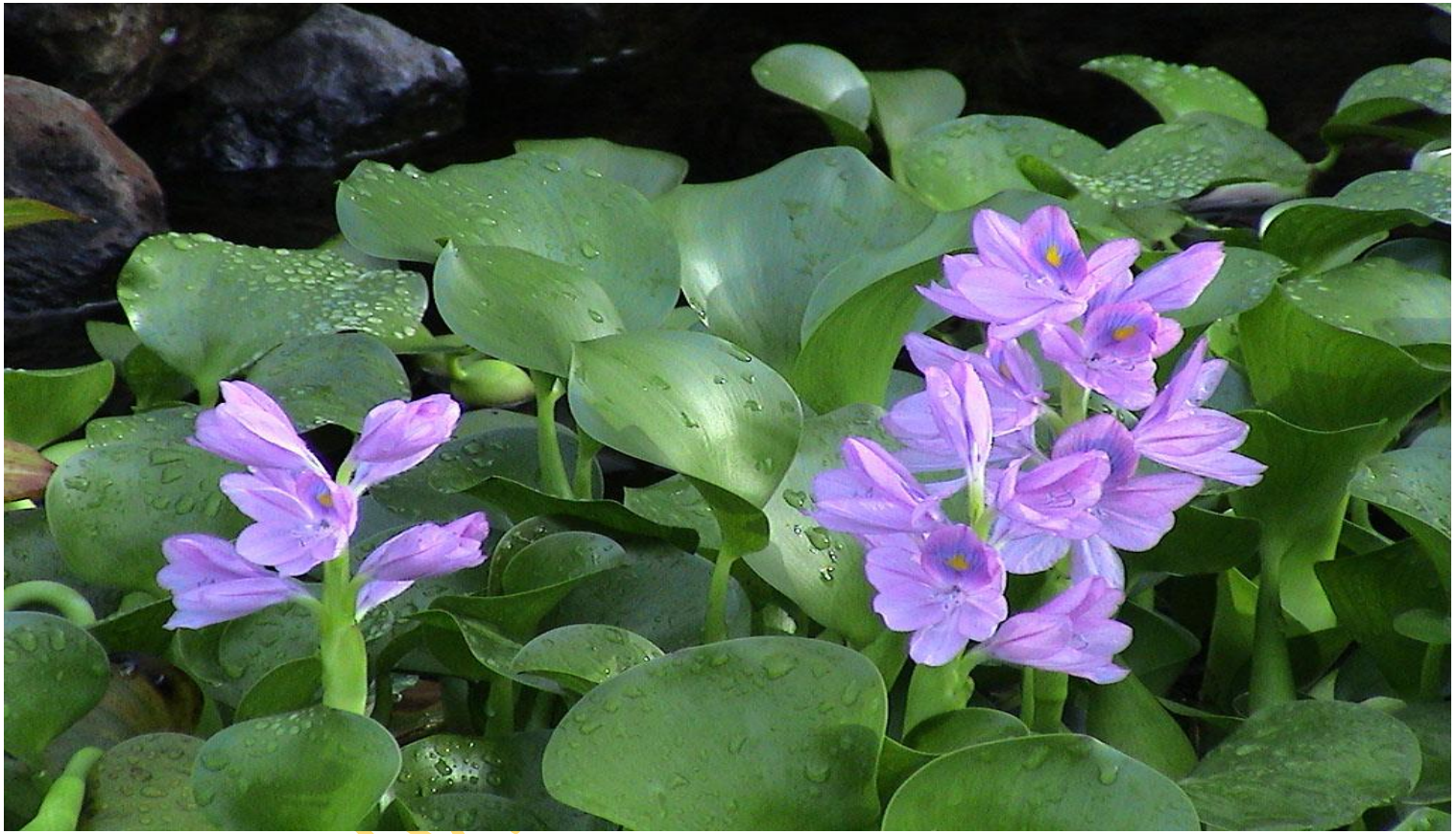


Fig. 2.1: Water Hyacinth {*Eichhornia crassipes* (Mart.) Solm-Laubach: Pontedericeae}

Source: Julien, (2000)

Fig. 2.2: Manual Removal of Water Hyacinth in Ologe Lagoon, Lagos, Nigeria

Source: Ndimele, (2003)

2.6.1.6.2 Chemical control

A generally cheaper method has been used worldwide to reduce water hyacinth populations through the use of chemical herbicides (such as Paraquat, Diquat, Glyphosate, Amitrole, 2, 4-D acid) (Villamagna and Murphy, 2010). However, their use directly interferes with the biocontrol agents currently deployed against this weed. Long term use may degrade water quality and put aquatic life at risk (Malik, 2007) with significant socio-economic impacts if beneficial or designated uses of the water body such as drinking and preparing food are affected (Dagno *et al.*, 2012). Considering that hundreds of thousands of hectares have been invaded by the weed, it is unlikely that it will be controlled by chemical means alone (Borokini and Babalola, 2012).

2.6.1.6.3 Biological control

In recent years, focus has shifted to natural enemies of water hyacinth including plant pathogens (Dagno *et al.*, 2012, Villamagna and Murphy, 2010). The aim of any biological control is not to eradicate the weed, but to reduce its abundance to a level where it is no longer problematic. While there exists several native enemies of water hyacinth, two South American weevil beetles (*Neochetina eichhorniae* and *Neochetina bruchi*) (Fig 2.3) and two water hyacinth moth species (*Niphograpta albiguttalis* and *Xubida infusella*) have had effective long-term control of water hyacinth in many countries, notably at Lake Chivero (Zimbabwe), Lake Victoria (Kenya), Louisiana (USA), Mexico, Papua New Guinea and Benin (Gichuki *et al.*, 2012, Dagno *et al.*, 2012, Williams *et al.*, 2007). Researchers have identified another tiny insect, *Megamelus scutellaris*, from South America which is highly host-specific

to water hyacinth and does not pose a threat to native or economically important species (Coetzee *et al.*, 2009).

The weevils reduce water hyacinth vigour by decreasing plant size, vegetative reproduction, flowering and seed production (Fig 2.4). They also facilitate the transfer and ingress of deleterious microorganisms associated with the weevils (both fungi and bacteria) into the plant tissues (Venter *et al.*, 2012, Wilgen and Lange, 2011). Control of water hyacinth using fungal pathogens has greatly stimulated interest in the management of the weed. Several fungal species such as *Cercospora rodmanii*, *Alternaria alternata* and *Alternaria eichhorniae* are recognized as potential mycoherbicide agents although no commercial mycoherbicide is available for water hyacinth (Dagno *et al.*, 2012).

Fig. 2.3: Water hyacinth Weevil (*Neochetina eichhorniae*)

Source: Julien, (2000)

Fig. 2.4: Water hyacinth plants stressed by weevils tend to be of small stature and lose buoyancy

Source: Julien, (2000)

Invasive alien species are a major global challenge requiring urgent action (Xu *et al.*, 2012). They are considered one of the key pressures on world's biodiversity: altering ecosystem services and processes, reducing native species abundance and richness, and decreasing genetic diversity of ecosystems (Rands *et al.*, 2010). They cause substantial economic losses estimated by one study to total US$120 billion annually in the USA (Pimentel *et al.*, 2005). In South Africa, estimated economic costs due to invasive alien species are currently above US$ 700 million (Rands 6.5 billion) per annum or 0.3% of South Africa's GDP, (Wilgen and Lange, 2011) and could rise to over 5% of GDP if invasive plants are allowed to reach their full potential (Wilgene and Lange, 2011).

Water hyacinth has been identified by the International Union for Conservation of Nature (IUCN) as one of the 100 most aggressive invasive species (Téllez *et al.*, 2008) and recognized as one of the top 10 worst weeds in the world (Shanab *et al.*, 2010, Gichuki *et al.*, 2012, Patel, 2012). It is characterised by rapid growth rates, extensive dispersal capabilities, large and rapid reproductive output and broad environmental tolerance (Zhang *et al.*, 2010). In Africa, for example, where water hyacinth is listed by law as a noxious weed in several countries, it is the most widespread and damaging aquatic plant species. The economic impacts of the weed in seven African countries (Ethiopia, Ghana, Uganda, Zambia, South Africa, Rwanda and Nigeria) have been estimated at between US$20-50 million every year (Borokini and Babalola, 2012). Across Africa costs may be as much as US$100 million annually (UNEP, 2006).

The success of this invasive alien species is largely due to its reproductive output. Water hyacinth can flower throughout the year and releases more than 3,000 seeds per

year (Gopal, 1987; EEA, 2012). The seeds are long-lived, up to 20 years (Gopal, 1987). While seeds may not be viable at all sites, water hyacinth commonly colonises new areas through vegetative reproduction and propagation of horizontally growing stolons. In the early stages of infestation, the weed takes foothold on the shoreline in the areas where native aquatic plants thrive (Gichuki *et al*., 2012). However, it is not restricted to shallow water, unlike many submersed and emergent macrophytes, because its roots are free-floating near the surface (Villamagna and Murphy, 2010).

2.6.1.7 Geographical distribution and pathways of introduction

Water hyacinth is found across the tropical and subtropical regions (Figure 2.5). Originally from the Amazon Basin, its entry into Africa, Asia, Australia, and North America was facilitated by human activities (Dagno *et al.*, 2012).

Africa has particularly been affected by the introduction and spread of water hyacinth, facilitated in part due to a lack of naturally occurring enemies. In a review of water hyacinth infestation in eastern, southern and central Africa, Mujingni (2012) reports that the weed was first recorded in Zimbabwe in 1937. It colonized important water bodies, such as the Incomati River in Mozambique in 1946, the Zambezi River and some important rivers in Ethiopia in 1956. Rivers in Rwanda and Burundi were colonised in the late 1950s while the Rivers Sigi and Pangani in Tanzania were infested in 1955 and 1959. The plant colonised Kafue River in Zambia in the 1960s, the Shire River in Malawi in 1968 and Lake Naivasha in Kenya in 1986 (Mironga *et al*., 2012). The plant was recorded from Lakes Kyoga in Uganda in 1988-89, Victoria in 1989–1990, Malawi/Nyasa in 1996 and Tanganyika in 1997. Lake Victoria in Africa is the second largest freshwater lake in the world and currently supports approximately 30 million people. Infestation of water hyacinth in the lake has been a

serious nuisance, generating public outcry (Gichuki *et al.,* 2012). At its peak, it was estimated that the weed was growing at 3 hectares (12 acres) per day on the lake. The plant also spread fast throughout Uganda's lakes and rivers in just 10 years.

In Nigeria, water hyacinth was first noticed in 1985 in Lagos Lagoon (Edewor, 1988). The water hyacinth present in Nigerian waters today is of the South American species - *Eichhornia crassipes*. It is believed to have found its way into the Nigerian waters from neighbouring Republic of Benin (Edewor, 1988). Since then, it has spread to a lot of water bodies in the country, making navigation and fishing an almost impossible task.

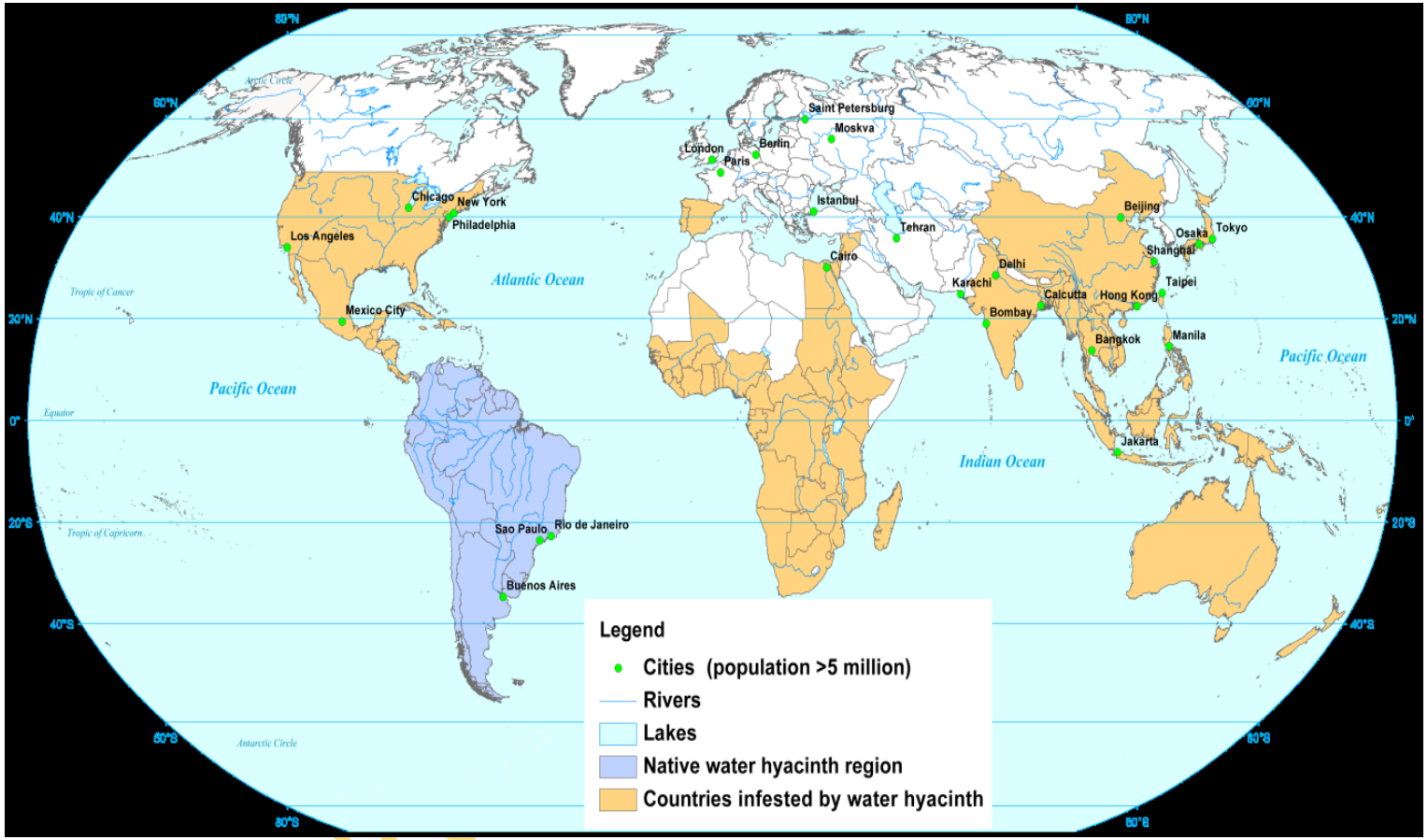


Figure 2.5: Global distribution of water hyacinth

Source: Téllez *et al.*, (2008)

Water hyacinth has also spread to West Africa. It was first reported in Cameroon between 1997 and 2000 and since then the country's wetlands have become "home" for the weed (Forpah, 2009). In Nigeria, almost all river bodies have been dominated by water hyacinth (Borokini and Babalola, 2012). The water hyacinth problem is especially severe on the River Niger in Mali where human activities and livelihoods are closely linked to the water systems (Dagno *et al.*, 2012). It occurs throughout the Nile Delta in Egypt and is believed to be spreading southwards, due to the construction of the Aswan Dam which has slowed down the river flow, enabling the weed to invade. Infestation of water hyacinth in Ethiopia has also been manifested on a large scale in many water bodies of the Gambella area, Lake Ellen in the Rift Valley and Lake Tana (Fessehaie, 2012).

In Europe, water hyacinth was established locally in the Azores (France) and in Corsica (Italy), and casual records are known from Belgium, the Czech Republic, Hungary, the Netherlands and Romania (EEA, 2012). In particular, it is a threat in Spain and Portugal.

In Asia, water hyacinth is widespread on freshwater wetlands of the Mekong Delta, especially in standing water (Fig 2.6). It has been detected in the Sundarbans mangrove forest of Bangladesh (Biswas *et al.*, 2007) and has caused heavy siltation in the wetlands of the Kaziranga National Park, India. Deepor Beel, a freshwater lake formed by the Brahmaputra River is heavily infested with this weed (Patel, 2012). The lake is considered one of the large and important riverine wetlands in the Brahmaputra valley of lower Assam, India. As in many other countries, water hyacinth has caused many economic, social and environmental problems in southern China.

In Mexico, more than 40,000 hectares of reservoirs, lakes, canals and drains are infested with water hyacinth (Jimenez and Balandra, 2007). In California, USA, this weed has caused severe ecological impacts in the Sacramento-San Joaquin River Delta (Khanna *et al.*, 2011).

Fig. 2.6: Water hyacinth covering a waterway in south of India

Source: Patel, (2012)

2.6.1.8 Reduction of Water Hyacinth Infestation by utilization

Research into the utilization and related technologies for the control of water hyacinth have been tested over the last few decades (Chukwuka Omotayo, 2008; Omotayo and Chukwuka, 2009; Ndimele *et al.*, 2011). It has been reported that the biomass can be used in waste water treatment, heavy metal and dye remediation, as substrate for bioethanol and biogas production, electricity generation, industrial uses, medicines, animal feed, agriculture and sustainable development (Patel, 2012). However, seldom does utilization provide a sustained solution to the spread and impact of water hyacinth, and in fact could provide a perverse incentive to maintain the invasive plant to the detriment of the environment and production systems at high economic and social costs. There is no one example from anywhere in the world where utilization alone has contributed to the management of any invasive plant (EEA, 2012).

2.6.1.9 Waste water treatment and clean-up of polluted environment

Water hyacinth has the potential to clean up various contaminated waters (Mahamadi and Nharingo, 2010). It can be used to treat wastewater from dairies, tanneries, sugar factories, pulp and paper industries, palm oil mills, distilleries etc. (Jafari, 2010). The plant can absorb into its tissues large quantities of heavy metals from water column and grows very well in water polluted with organic contaminants and high concentrations of plant nutrients (Ndimele, 2012). In the Ologe Lagoon, Nigeria, water hyacinth that was not deliberately introduced into the lagoon to absorb heavy metals did so, even when the concentration of the heavy metals in the water column was very small

2.6.1.10 Ecological Impart of Water Hyacinth Infestation

Between 1991 and 1993, a biological control programme of water hyacinth was undertaken in Southern Benin. It consisted of the release of three natural enemies, two weevil species (*Neochetina eichhorniae* and *Neochetina Bruchi*) and one moth (*Sameodes albiguttalis*) that feed exclusively on water hyacinth. In 1999, a survey of 365 men and women from 192 households in 24 villages in the target area revealed that water hyacinth, although not eliminated, was perceived by the villagers as having been reduced from a serious pest to one of minor or moderate importance. At the peak of the infestation, water hyacinth had reduced the yearly income of this population of about 200,000 people by approximately US$84 million (UNEP, 2006). Lost revenues for men were mostly in fishing, while women experienced lost revenues in trade, primarily food crops and fish. The reduction of water hyacinth cover through biological control was credited with an increase in income of US$30.5 million per year (UNEP, 2006). The total cost of the control programme is estimated at a present value of US$2.09 million. The benefits therefore appear to outweigh the costs by a ratio of 124:1 (De Groote *et al.*, 2003).

In California, water hyacinth leaf tissue was found to have the same mercury concentration as the sediment beneath, suggesting that plant harvesting could help mediate mercury contamination (Greenfield *et al.*, 2007). While water hyacinth's capacity to absorb nutrients makes it a potential biological alternative for treatment of agro-industrial wastewater, one of the major challenges is how to properly dispose the vast amount of the plant materials which may have to be considered as toxic waste (Zhang *et al.*, 2010).

2.6.1.11 Alternative fuel and energy source

Water hyacinth fulfills all the criteria deemed necessary for bioenergy production – it is perennial, abundantly available, non-crop plant, biodegradable and has high cellulose content. However, its strong disadvantage is that it has over 90% water content which complicates harvesting and processing. The biomass can be subjected to biogas production to generate energy for household uses in rural areas. Experiments in China show that mixing biomass of water hyacinth with pig manure leads to a much higher biogas production than by using pig manure alone (Lu *et al*., 2010). It can also be used for producing ethanol, but technical and logistical challenges need to be overcome before the commercial scale ethanol production becomes a reality because of the high tissue water content (Ndimele *et al*., 2011).

2.6.1.12 Semi-industrial uses and household articles

As a readily available resource, water hyacinth has been used in several small cottage industries in the Philippines, Indonesia and India for paper, rope, basket, mats, shoes, sandals, bags, wallets, vases, etc (Ndimele *et al*., 2011; Patel, 2012). Yet, these are rarely successful to reduce infestations and the market for these products is far too small to have any impact on water hyacinth populations. In addition, income generation may facilitate its spread to new and uninvaded water bodies.

2.6.1.13 Animal feedstock and agricultural use

When sun-dried, water hyacinth has been found to be rich in protein, vitamins and minerals and serves as a high quality feedstock for some non-ruminant animals, poultry and fishery in Indonesia, China, the Philippines and Thailand (Lu *et al.*, 2010). However, it is not recommended for use if primarily used for removal of heavy

metals and toxic substances from wastewater (Chunkao *et al*., 2012). Decomposed and dried water hyacinth can also be used as green manure or as compost that improves poor quality soils decades (Chukwuka Omotayo, 2008; Omotayo and Chukwuka, 2009; Ndimele *et al.*, 2011). However, its high alkalinity (pH>9) and potentially toxic heavy metals contents would restrict its use to flowering-plants, with no allowable application to horticulture for edible vegetables (Chunkao *et al*., 2012).

2.6.2 Water Lettuce

2.6.2.1 Elemental Constituent of Water Lettuce

Water lettuce (Fig 2.7) contain 4.3% moisture content and 35.2 - 44.5% ash content (Wasagu *et al*, 2013). The low moisture content allow the plant long shelf-life and decrease in microbial activities especially during storage (Abdullahi, 2002). High ash content indicates that water lettuce is rich in mineral content (Oyeleke, 1984). The plant crude fibre is in the range of 17.5 - 20.5% (Wasagu *et al.*, 2013). Carbohydrate content of water lettuce ranges from 30 - 38%, crude protein content is between 3.18 - 6.96%, while it crude lipid content range between 1.33 - 2.17% (Wasagu *et al.*, 2013). Senna *et al.* (1998) reported that water lettuce is a poor sources of fat (lipid) compared to some vegetable consumed in Nigeria and Republic of Niger.

Fig. 2.7: Water Lettuce (*Pistia stratiotes*)

Source: Patel, (2012)

2.6.2.2 Scientific Classification of Water Lettuce

Kingdom: Plantae

(unranked): Angiosperms

(unranked): Monocots

Order: Alismatales

Family: Araceae

Subfamily: Aroideae

Tribe: Pistieae

Genus: *Pistia*

Species: *Pistia stratiotes*

2.6.2.3 History of Spread of Water Lettuce

Water lettuce is a free-floating plant which is found globally in the tropics and sub-tropic although its spread is limited by severe cold regions (Holm *et al*., 1977). Water lettuce was first discovered in New Zealand water-ways in 1973. It was introduced in the aquarium trade, though it could have been present long before its discovery in 1973 (Holm *et al*., 1977). Water lettuce, one of the most widely distributed hydrophytes occur in all continents except in Antarctica (Holm *et al*., 1977), In Europe, it is used as a summer plant in garden pond (Holm *et al*., 1977) but in the tropics, it is a serious weed.

Water lettuce was first reported in Florida in 1765, which led many to believe it was native to North America. However, Cordo *et al*., (1981) reported that water lettuce is probably from South America because of the abundance of regionally native insect associated with water lettuce. According to Subbarao and Koike (2007), water lettuce was first brought to America from Europe by Christopher Columbus in the late 15th

century. Between the late 16th and the early 18th century, many varieties were developed in Europe particularly Holland (Cordo *et al*., 1981).

In Ontario Canada, it was found in ponds connected to the Rideau Canal near Ottawa and in the well and canal in the Niagara region, Lake Saint Clair and its tributaries, Bronte Creek and beaches east of Toronto (Dray *et al.*, 1990). According to Vandiver (1999), an explorer in the 18th century was the first person to record the presence of water lettuce in North America, some expert believe it came from Africa, southern Asia or south America.

Water lettuce was first discovered from the Nile near Lake Victoria in Africa {Global Invasive Species Database (GISD, 2005)}. It is now present either naturally or through human activities in nearly all tropical and sub-tropical water-ways. It was cultivated in ancient Egypt for the production of oil from it seed. Thin plant was probably selectively bred by the Egyptians into a plant grown for its edible leaves.

2.6.2.4 Problems Caused by Water Lettuce Invasions

Water lettuce, a free-floating plant has been described as a noxious weed in South Africa (GISD, 2005). This plant reproduces and spreads rapidly often times forming thick or dense mats and covering water bodies in the tropics and sub-tropics. The ability of the plant to reproduce rapidly coupled with lack of any control measures enables them to proliferate at the expense of beneficial native plant communities. Infestation of the plant negatively disrupts all life on the water body. Its mat clog waterways preventing navigation, recreation, fishing, irrigation canals and flood control. It affects hydroelectricity production, destroys rice paddies etc.

Dense mats reduces dissolved oxygen level and light penetration into the under waters-thereby increasing the potentials for death of aquatic organisms. It also damages fish and

wildlife habitats thus significantly hindering fish management and restoration efforts. Rivers (2002) reported the negative impacts of water lettuce invasion in 16 states of the USA.

2.6.2.5 Methods of Controlling Water Lettuce Infestation

There are 3 methods mainly used to control water lettuce infestation. They are physical, chemical and biological. Although, the best form of invasive species management is prevention. Since high nutrient content in any water body enhances the growth of invasive species, the flow of nutrients from surrounding catchments such as sewage disposal, inflow of agricultural runoffs should be minimized as much as possible but when or if prevention is no longer visible, it is best to control invasion when mat is still small.

2.6.2.5.1 Physical Method

This involves the use of machine such as aquatic weed harvesters to remove or collect water lettuce from water surface. Physical method in usually effective for small infestation. This is done by raking or pulling with an encircling rope to the bank of the river. Aquatic weed harvesting craft is often used for dense infestation. Since water lettuce can survive for a long time out of water, the plant is allowed to dry out and break down. All plant removed must be placed away from flood line to avoid regrowth. This method is laborious and cost effective.

2.6.2.5.2 Chemical Method

This involves the use of herbicides such as 2,4 -D; disquat e.t.c. to control the infestation of water lettuce .This method has been widely used and can be effective and cost effective. When 2, 4-D herbicides is sprayed on the leaves of the plant, it inhibits the growth of new tissues and cellular apoptosis (Jimenez, 2005)

2.6.2.5.3 Biological Method

This also involves the use of biological agents such as *Neohydronomus affirius* to control water lettuce invasion. This method has been used in Australia. The larvae of moth, *Spodoptera pectinicornis* has been reported to control *P. stratiotes* in Thailand (GISD, 2005).

CHAPTER THREE

MATERIALS AND METHODS

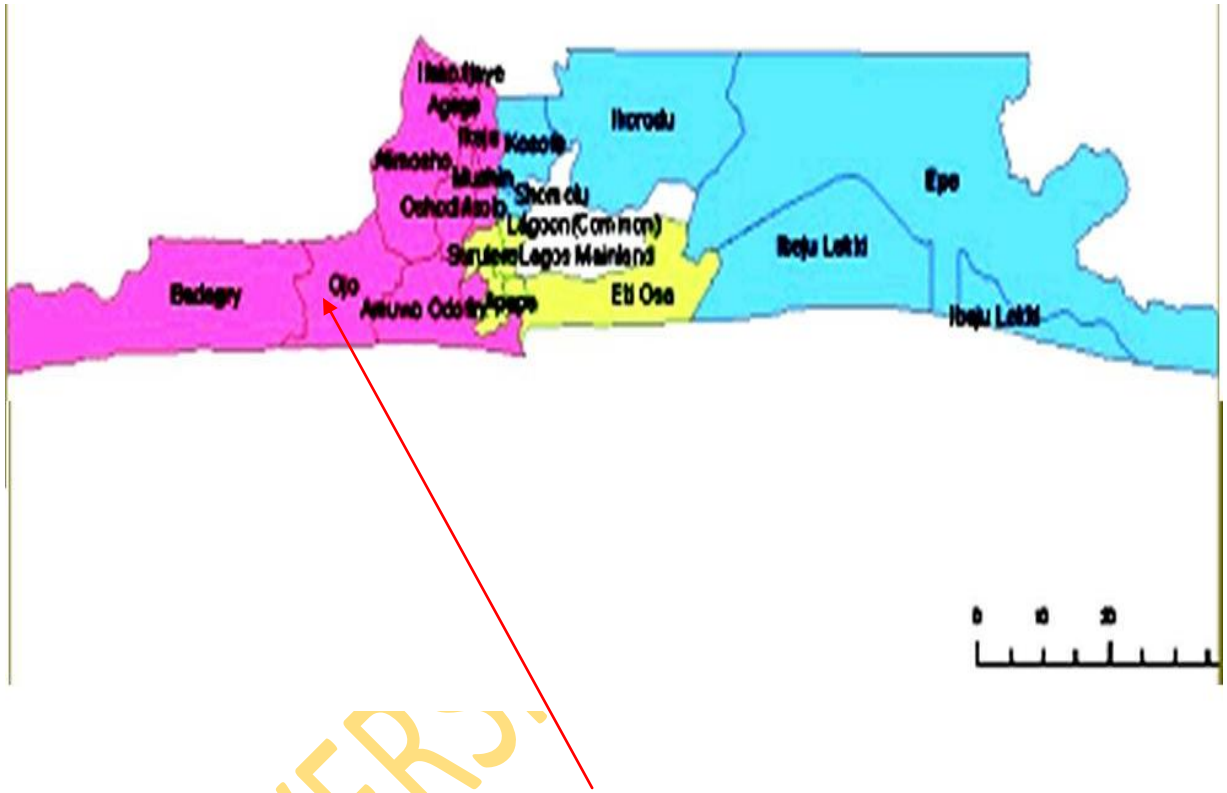
3.1 The Location and Climate of Lagos State

Lagos State is situated in the Western part of Nigeria (Fig. 3.1). Lagos State lies between longitudes 2°45' East to 4°20' East and latitudes 6°2' North to 6°4' North. The state is bounded on the west by Republic of Benin, on the east and north by Ogun State while on the south, it is bounded by the Atlantic Ocean (Fig. 3.2) (Kumolu-Johnson *et al*., 2010).

Lagos State has a high temperature range (23 - 30°C) and the highest occurs around January and March, which are the peaks of dry season (Clarke *et al.,* 2013). The lowest temperature is recorded in the peak of the rainy season(Clarke *et al.,* 2013). The climate is characterized by a double maxima types of rainfall which normally last from April to November. Sometimes, the rain could start early, around March or even February and could also end late, encroaching into November and occasionally December. During this time, the rainfall is always heavy, with some occasional flooding especially in coastal areas(Kumolu-Johnson *et al.,* 2010). The intensity of the rainfall is as a result of coastal location, low elevation and the prevailing rain bearing south-westerlies. The rainfall is at its peak around May - July and September - October with a short break in August (mean: 1600 mm; range: 1007 – 2000 mm) (Kumolu-Johnson *et al*., 2010). The relative humidity is high throughout the year and it ranges between 65% - 80%. Lagos State has the west equatorial type of climate due to its position to the equator and the Gulf of Guinea.

Fig. 3.1: Map of Nigeria Showing the 36 States and the Federal Capital Territory

Source: UNEP, (2012)



Location of the Study site

Fig. 3.2: Map of Lagos State Showing the Local Government Areas

Source: UNEP, (2012)

3.2 Description of Agbara Industrial Estate

Agbara Industrial Estate is a model integrated town developed on 454.1 hectares of land. It is situated at about 31 kilometre west of Lagos on the Lagos – Badagry expressway on high ground above Owo River. It derived its name from the neighboring Agbara village. The estate is on a laterite outcrop in an area of lowland behind the swamp forest of Ologe Lagoon (Eniola, 1999). Eniola (1999) also reported that there are 16 industries operating in the estate while Kumolu-Johnson *et al*. (2010) reported about 20 industries in the estate. Most of these industries belong to the food and beverages, and pharmaceutical groups. These industries includes Beta Glass Nig Plc, Vita Malt Plc, Pharma Deko, Nestle Nig Plc, Evans Medical Nig. Plc, Unilever Nig. Plc, Glaxo SmithKline Nig. Plc among others.

Presently, there are about 23 industries operating in the estate. The location and accessibility of Agbara Industrial Estate makes it an advantageous place to site an industry since raw material and finished goods can easily be transported in and out of the industry. Waste water from residential quarter and the industries are channeled to the treatment zone where it is treated before it is discharged into the swamp leading to Ologe Lagoon. The sewage treatment plant is like an aerated Lagoon system called "simplex cone" turbine aeration system. The plant carries out primary treatment through oxidation process before discharging the treated effluent into Ologe Lagoon via the nearby creek.

3.3 Study Areas

Three water bodies (Owo River, Ologe Lagoon and Etegbin) (Fig. 3.3) were studied while sample were collected from five sites (Owo River, Agbara, Otto Jetty, Morogbo and Etegbin). One site from study area A (Owo River - control), three sites (Agbara,

Otto Jetty and Morogbo) from study area B (Ologe Lagoon) and one site from study area C (Etegbin)

3.3.1 Study Area A (Owo River)

Owo River is a tributary of River Ogun in Ogun State which opens into Ologe Lagoon, a form of freshwater at Oto-Awori town in Ojo Local Government Area of Lagos State. It lies between latitudes 6° 12'N and 6° 33'N and longitudes 3° 12'E and 3° 48'E (Anektehai *et al.*, 1997). Owo River link Ijon/Ayobo to Ayetoro/Itele to Ota, Igbesa, Agbara and then finally opens to Ologe Lagoon. The course of River Owo and Illo marks Lagos boundary with Ogun State through Agbara town and drain into Ologe Lagoon, a lagoon of ecological importance to the west African coast because it open to the Atlantic ocean via Lagos habour and Badagry Creek. The vegetation around Owo River is characterized by stilt rooted trees with a dense undergrowth of shrubs and sward of floating plant water hyacinth, water lettuce and other aquatic macrophytes such as *Ipomea aquatica* which cover the edges of the river. This river also has some human activities taking place in and around it such as washing of cloth and automobiles, fishing, buying and selling of snail and fishes and transportation. This river is up stream occurring before the discharge point from Agbara Industrial Estate and therefore serve as a positive control site.

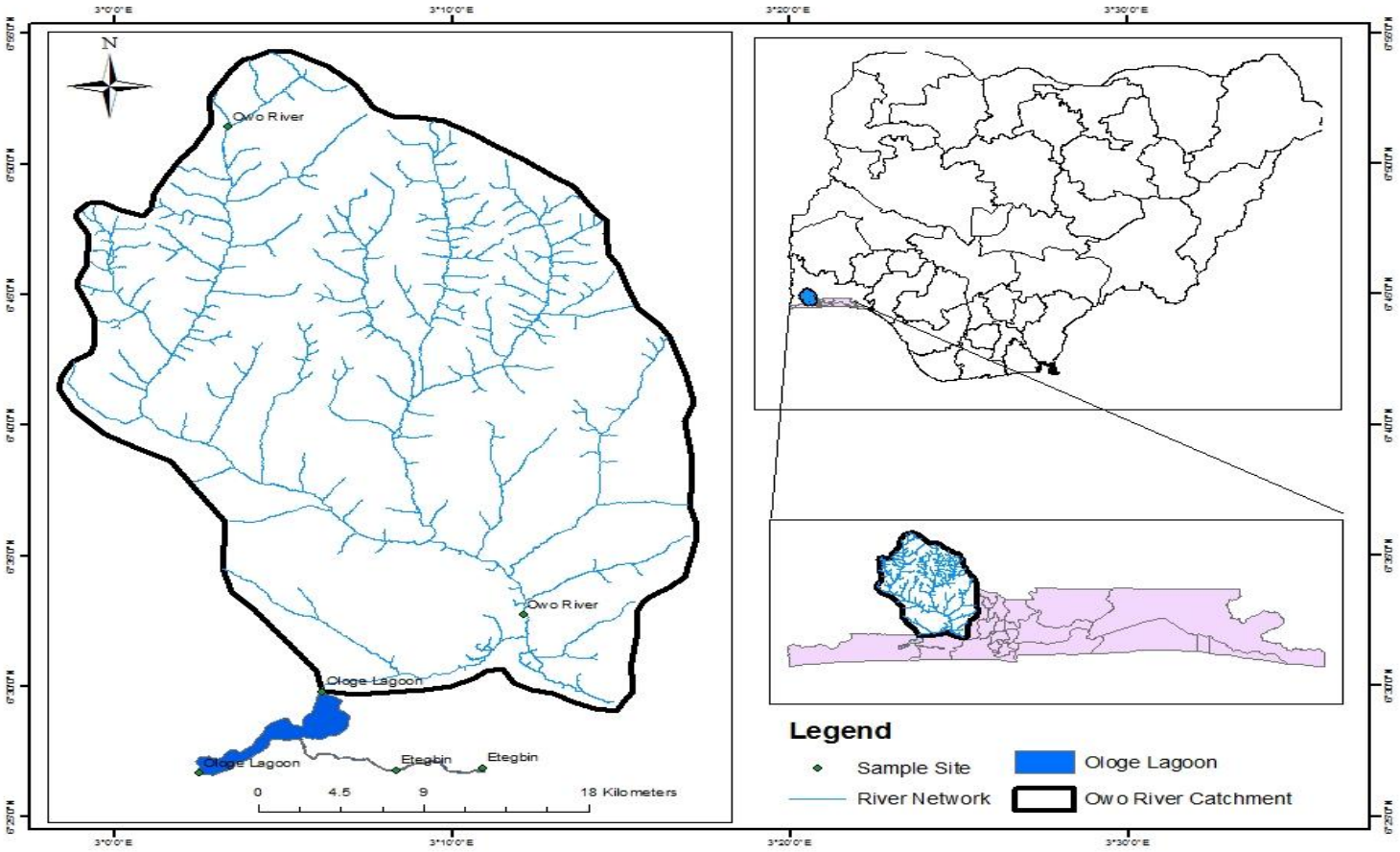


Fig. 3.3: Map of Sampling Stations

Source: Field Survey, (2013)

3.3.2 Study Area B (Ologe Lagoon)

Ologe Lagoon is a freshwater lagoon system located in the eastern part of Lagos State (Fig. 3.4). Its main body lies in Badagry Local Government Area of Lagos State with a surface area of about 9.4 km (Anetakihai *et al*., 1997). It lies between latitudes 6° 27' N and 6° 30' N and longitudes 3° 02' E and 3° 07' E. The lagoon is connected to the Atlantic Ocean via the Lagos harbour and Badagry Creek. Its major sources of water is Owo River in Toto-Owu town where Rivers Ore and Illo form a confluent with River Oponu in Ogun State (Anetekhai *et al*., 1997). Ologe Lagoon is bounded on the north by Igbesa and Agbara (Ogun State) and Oto/Ijanikin in Lagos State, on the west by Esepe-Mushim and Ale, on the south by Gbanko and Badagry Creek and on the east by villages and towns such as Ikotun, Egan, Idoluwo, Illemba, Ibese and Ojo town. Most of these are fishing villages and towns with factories which produces different product ranging from Agro-allied chemical and pharmaceuticals; and this lagoon serve as sink for their effluent discharge. The vegetation around Ologe Lagoon is characterized by stilt rooted trees with a dense under growth of shrubs, palm trees and sward of floating grass. Major ecosystem services provided by the lagoon includes transportation, fetching of firewood, netting of basket, dumping of refuse, sewage disposal, digging etc. This lagoon is the first recipient of the discharges from Agbara Industrial Estate before flowing to other rivers downstream.

3.3.3 Study Area C (Etegbin River)

Etegbin River is a freshwater body (Fig. 3.3). It is located in Shibiri, Ojo Local Government Area of Lagos State. It lies between latitudes 6° 27' N and 6° 45' N and longitudes 3° 15' E and 3° 90' E. The vegetation around this river is characterized by stilt rooted trees such as palm trees, e t c. Water hyacinth and water lettuce cover the

edges of the water body while some float further into the river. Etegbin River has a wide navigable mouth that makes it possible to be put in use for transportation and recreation. Other human activities include buying and selling of fishes, crabs, and prawn, dumping of refuse and sewage, construction work such as building of canoes and boats, digging, relaxation spots e.t.c. Etegbin River is downstream and it receives its water from Ologe Lagoon.

3.4 Method

This study was conducted over a period of 24 month while samples were collected for 18 months from July, 2013- December, 2014 spanning through the wet and dry seasons. Five sampling stations were used namely Owo river, Agbara closest to discharge, Otto jetty, Morogbo in Ologe lagoon and Etegbin river. The sampling stations were chosen based on their nearness to effluent discharge point from Agbara industrial estate and the presence of water hyacinth and water lettuce. Samples were collected once monthly and analysed for physico-chemical parameters and heavy metals.

3.4.1 Sample Collection

3.4.1.1 Collection of Water Sample for Physico-Chemical Parameter Measurement

One litre plastic bottles were used to collect water sample from each sampling station for the determination of physico-chemical parameters which include conductivity, total dissolved solids (TDS), total suspended solids (TSS), salinity, acidity, alkalinity, dissolved oxygen, biological oxygen demand (BOD), chemical oxygen demand (COD) and nutrients (nitrate, sulphate, phosphate, calcium and magnesium). Two

hundred and fifty milimitre reagent and opaque bottle each was used to collect sample for dissolved oxygen demand (OD) and biological oxygen demand (BOD) measurement.

3.4.1.2 Collection of Water Sample for Heavy Metal Analysis

Water samples were collected at the sampling stations at 20 cm depth below water surface in 250 ml plastic bottles with screw caps. The bottles were soaked in 10% nitric acid (reagent grade, Spectrosol, England) for 24 hours prior to sampling and then rinsed six times with Milli-Q deionized water (Millipore, USA) before use (Laxen and Harrison, 1981) to avoid contamination. The water samples were acidified immediately after collection by adding 5 ml nitric acid (Analar grade, Merck, Darmstadt, Germany) to minimize adsorption of metals onto the walls of the bottles (APHA 1985). Samples were then taken for heavy metal analysis using Atomic Absorption Spectrophotometer (AAS).

3.4.1.3 Collection of Sediment Sample for Heavy Metal Analysis

Grab samples of sediment were collected using a 5 cm diameter steel pipe pressed through the water column to obtain a sediment core of about 30 cm (Ali and Fishar 2005) and placed into clean polythene bags previously treated with 10% nitric acid (Analar grade, Merck, Darmstadt, Germany) and sealed. The samples collected from each site consisted of 4–5 composite samples. All sediment samples were stored in a cooler containing ice pack and transported to the laboratory immediately for further analysis.

3.4.1.4 Collection of Water Hyacinth and Water Lettuce for Heavy Metal Analysis

Water hyacinth and water lettuce were collected from each sampling station by hand. Plant samples were rinsed with the lagoon water, packed in a polythene bag and then transportation to the laboratory.

3.4.2 Determination of Physico-Chemical Parameter

3.4.2.1 Temperature, pH, Conductivity, TSS, TDS, Acidity and Nutrients

Temperature and pH were determined *in situ* by mercury-in-glass thermometer and pH meter (Exec 407227) respectively. Conductivity, TSS, TDS, acidity and nutrients (nitrate, sulphate, phosphate, calcium and magnesium) were determined according to the methods described by APHA (1985).

3.4.2.1.1 Conductivity

Procedure:

Conductivity was determined using a conductivity meter (***Hach CO150).*** The meter was calibrated using NaCl calibration solution. Measurements were then carried out by immersing the conductivity probe (cell) in the samples. Conductivity values were read off the display screen.

3.4.2.1.2 Acidity

Titration Method

Procedure

Fifty millilitres of the water sample was titrated against standard base (0.050M) with methyl orange indicator.

Calculation

Acidity (as mg $CaCO_3$/l) (mg/L) = $\frac{Titre(ml)\ x\ molarity}{volumetitrated(ml)}\ x\ \frac{50{,}000}{1}$

3.4.2.1.3 ***Total Dissolved Solids (TDS):*** **Dried at 180^{0}C;** ***Gravimetric Method (APHA 2540C)***

Procedure

A clean evaporating dish (porcelain is preferred) was dried at (180 ± 2) ^{0}C for 1 hour and cooled in a desiccator before being weighed.

One hundred millilitres of a well mixed sample was filtered into a pre-weighed dish and then dried for at least 1 hour at (180 ± 2) ^{0}C, cooled in a desiccator and then weighed.

Calculation

Total Dissolved Solids (TDS) (mg/L) = $\frac{\textbf{(A – B) (1,000,000)}}{\textbf{C}}$

Where A = weight of dish + solids (g)

B = weight of dish (g)

C = volume of sample evaporated (ml).

3.4.2.1.4 Total Suspended Solids (TSS): Dried at 103 – 105^{0}C; Gravimetric Method (APHA 2540D)

Procedure

One hundred millilitres of a well mixed sample was the filtered through a tarred filter. The filter was dried at 103 – 105 ^{0}C for 1 hour, cooled in a desiccator and weighed.

Calculation

Total Suspended Solids (TSS)mg/L = $\frac{\textbf{\textit{(A – B) x 10}}^{\textbf{6}}}{\textbf{\textit{C}}}$

Where A = Weight of filter plus solids (g)

B = Weight of filter (g)

C = Volume of sample filtered (ml).

Nitrate (NO^-_3)

Colorimetric Method (Hach method 8039 HR)

Ten millilitres sample was mixed in a sample vial with Nitraver-5 powder. The mixture was allowed to stand 5 minutes for reaction to complete. Programme **(**#320**)** was **s**elected on HachDR 2500 spectrophotometer. The instrument was zero with the blank and nitrate was determined in prepared samples.

Phosphorus; Molybdenum-blue method

Ten millilitres sample was mixed in a sample vial with potassium persulphate powder. Two millilitres 5.25 N H_2SO_4 was added to the mixture. The mixture was heated for 30 minutes on a hot plate after which it was cooled to room temperature. Two millilitres 5N NaOH was added to the mixture and the volume was adjusted to 10 ml. The content of 1 Hach***phosVer 3*** reagent powder was added to the mixture and allowed to stand for 5 minutes. Programme (#540) was selected on HachDR 2500 spectrophotometer. The instrument was zero with the blank and phosphate was determine in prepared samples.

3.4.2.1.5 Sulphate

Turbidimetric Methods (HACH 8051)

Method

Twenty five millilitres sample was added to a sample vial. The content of 1 *sulfaVer 4* powder was added to the sample vial, mixed and allowed to stand for 5 minutes. Programme **(**#680**)** was selected on HachDR 2500 spectrophotometer. The instrument was zero with sample blank and sulphate was determined in prepared samples.

2.4.2.1.6 Calcium and Magnesium; EDTA Titrimetric Methods

Twenty millilitres sample was titrated with 0.01 M standard EDTA solution, using eriochrome black T indicator. Titre values (A) were recorded. Another 20 ml sample was titrated with 0.01 M standard EDTA solution, using murexide indicator. Titre values (B) were also recorded.

Calculations:

a. Total Hardness (mg/L) = A x 2.5 x 0.4007 x1000 / 20

b. Calcium (mg/L) = B x 0.4007 x 1000 / 20

c. Magnesium (mg/L) = (Total hardness - [Ca x 2.5]) / 4.1

3.4.2.2 Dissolved Oxygen (DO)

Two millilitres of manganous sulphate (Winkler A) solution and 2 ml of potassium iodide (Winkler B) solution was added to the sample to fix the oxygen. The bottle were carefully closed with a stopper and mixed thoroughly by shaking. Two mil[ilitres of concentrated tetraoxosulphate VI acid (H_2SO_4) was added to the precipitate and the bottle shaken thoroughly to de-fix the oxygen. One hundred millilitres of the solution was placed in a conical flask and titrated against 0.0250 N sodium thiosulphate solution ($Na_2S_2O_3.5H_2O$) using two drops of starch station as indicator. Dissolved oxygen (mg/L) was calculated as follows:

DO = Vol. of $Na_2S_2O_3.5H_2O$ (ml) X 0.025N X 8 X 100 / Vol. of water sample (ml)

3.4.2.3 Biological Oxygen Demand (BOD)

The dissolved oxygen of water sample of the opaque bottles were determined after 5 days of incubation in dark cupboard. The difference between the dissolved oxygen of

the incubated sample and the dissolved oxygen of the initial sample equals the biological oxygen demand.

3.4.2.4 Chemical Oxygen Demand (COD)

Twenty millilitres of water sample were transferred into 125 ml Erlenmeyer flask. Ten millilitres of 0.025 N $K_2Cr_2O_7$, 0.4 g of $AgSO_4$ crystals, 0.4 g of $HgSO_4$ crystal and 3 ml of concentrated H_2SO_4 were added to the sample flask. The content in flask were thoroughly mixed and the flask was attached to a condenser and then heated. After 2 hours, the condensates were washed into the flask with 20 ml of distilled water. The content of the flask were then diluted to 80 ml with distilled water. Two to 3 drops of ferroin indicator was added to 80 ml of the digested sample and was titrated with ferrous ammonium sulphate. Chemical oxygen demand was calculated as follows:

$$\text{COD (mg/L)} = \frac{\text{Vol. of } Fe(NH_4)_2(SO_4)_2\,6H_2O \text{ (ml)} \times 0.025\text{ N} \times 8 \times 100}{\text{Vol. of water sample (ml)}}$$

3.4.2.5 Total Alkalinity

Four drops of methyl orange indicator were added to 100 ml of each water sample, which turned yellow. This was then titrated with standard tetraoxosulphate (VI) acid until the yellow colour of the sample changed to faint orange. Total alkalinity was calculated as follows:

$$\text{Total Alkalinity (mg/L)} = \frac{\text{Vol of standard } H_2SO_4 \text{ (ml)} \times 0.02\text{N} \times 50 \times 100}{\text{Vol. of water sample (ml)}}$$

3.4.2.6 Salinity

Ten millilitres of the sample was measured into conical flask and 15 ml of potassium chromate was added to the samples. The content in the conical flask was titrated with silver nitrate until the initial yellow colour turned to a brick red precipitate.

Salinity (Parts per thousand) = Vol. of silver nitrate (ml) x 1.8065

3.4.3 Sample Treatment (Digestion)

3.4.3.1 Digestion of Sediment Samples

Sediment samples were oven-dried at temperature of 105±14°C for 24 hours. Stones and plant fragments were removed by passing the dried sample through a 2 mm mesh. The samples were then grinded using an agate mortar, sieved through a 500 µm stainless steel mesh in order to obtain fine particle-size fractions and stored in glass bottles pre-washed in acid and rinsed in Milli-Q deionized water (Millipore, USA). For determination of heavy metal content in sediment, 0.25 g sediment sample was digested in teflon vessels with 12 ml HNO_3 (65% Suprapur, Merck, Darmstadt, Germany) : HCl (37% Suprapur, Merck, Darmstadt, Germany) (3:1) mixture in a microwave oven (MARSX-Press, CEM) (USEPA, 2007; FAO/SIDA, 1986). After microwave digestion, the sample solution was filtered, adjusted to appropriate volumes with Milli-Q deionized water (Millipore, USA) and set aside for heavy metal analysis.

3.4.3.2 Digestion of Plant Samples

In the laboratory, plant samples were washed using a sequence of tap water, distilled water and deionizer water, then plant samples were oven-dried at 450-500 °C for 24 hours. Thereafter 2g of the ash were poured into a beaker and 10 ml nitric acid were added and the content were filtered into a conical flask. Then twenty five millimitres of deionizing water was added to it, and transferred to dispensing bottle for heavy metal analysis.

3.4.4 Determination of Heavy Metal in Samples

Before analysis, the samples were filtered through a 0.45 µm nitrocellulose membrane filter. Sample blanks were prepared by adding 10 ml of nitric acid to 100 ml of deionised water (Alam *et al*., 2002). All samples were analyzed for the five heavy metals (Cu, Fe, Pb Zn and Cd) by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) Varian Liberty Series II (Operating conditions: RF Power, 1000W; Plasma gas flow, 12L/min; Torch configuration, Radial; Nebulizer, V-groove; Spray chamber, Double-pass cylindrical; Detector, Photomultiplier). The absorption wavelengths for Cu, Fe, Pb and Zn were 324.8, 259.9, 220.4, and 213.9 nm respectively. Standard solutions for system calibration and control of analytical accuracy were prepared by dilution of stock solutions (Merck, multi element standard). All specimens were ran in batches that included blanks, a standard calibration curve, two spiked specimens, and one duplicate. In order to validate the method for accuracy and precision, dogfish muscle (DORM-2, National Research Council, Canada) was analyzed (n=6) as a certified reference material and the recovery (% mean recovery ± S.E.) was analyzed (n=6). All analyses were carried out in duplicate, and the results were expressed as the mean.

3.5 Phytoremediation Experiment in the Laboratory

The experiment was conducted in the Laboratory of the Department of Fisheries, Faculty of Science, Lagos State University, Ojo, Lagos State, Nigeria. To ensure that the phytoremediative plant (water hyacinth and water lettuce) continues to photosynthesize, the experimental units were kept in an open space but under

transparent roof/shade to prevent dilution by rain water. The water in the experimental units was checked regularly and made up to the appropriate mark when it falls below the required level due to evaporation and transpiration from the surface of the leaves of the plants. The initial concentrations of the metals (Zn, Fe, Cu and Pb) in the laboratory water and in the two aquatic plants were determined prior to exposure to the metals and were found to be very negligible.

3.5.1 Acclimatization of the aquatic macrophytes (water hyacinth and water lettuce)

The water hyacinth (*Eichhornia crassipes*) and water lettuce (*Pistia stratiotes*) used for this study were collected from Badagry Lagoon, Lagos, Nigeria and brought to the laboratory of the Department of Fisheries, Faculty of Science, Lagos State University, Ojo, Lagos, Nigeria. The choice of Badagry Lagoon was because there are no industries discharging effluents into the water body. The plants were rinsed three times in tap water to remove epiphytes and insect larvae growning on it. Thereafter, 250±20 g of the water hyacinth and 50±8 g of water lettuce were put in plastic tanks containing 15 liters of water. Then, the plants were acclimatized for 21 days so that it can adapt to the laboratory condition.

3.5.2 Heavy metal application rate

In this study, the following compounds: Zn, Fe, Cu and Pb were used to separately spike the experimental units containing water hyacinth and water lettuce; zinc sulphate [$ZnSO_4$] iron sulphate heptahydrate [Fe (SO_4).7H_2O], copper sulphate pentahydrate [Cu (SO_4).5H_2O] and Lead (II) nitrate [$Pb(NO3)_2$] were the salts of the heavy metals that were used in spiking the water. Experimental bowls were prepared

to separately contain these compounds of the heavy metals at different concentrations of the two plants.

The weight of the metals were determined from their compounds: [$ZnSO_4$], [Fe (SO_4).7H_2O], [Cu (SO_4).5H_2O] and [$Pb(NO3)_2$]. The concentrations of the metals used in this experiment were 10, 15, 20 mg/L.

3.5.3 Calculation of concentration of copper (Cu) administered to the experimental units

In order to get the concentration of Cu (10 mg/L, 15 mg/L and 20 mg/L) administered to each experimental unit, the relationship between the molar masses of the copper-containing compound ($CuSO_4.5H_2O$) and elemental copper was explored using the method described by Wei *et al*. (2010).

Molar mass of $CuSO_4.5H_2O$ = 249.5 g

Molar mass of Cu = 63.5 g

3.93 g of $CuSO_4.5H_2O$ contains 1 g of Cu. (249.5 g/63.5 g)

To convert the masses of the compound and element to milligram (mg) since the concentration of the metal is in mg/L, each of the masses was divided by 1000

Therefore, 0.00393 mg of $CuSO_4.5H_2O$ contains 0.001 mg of Cu

That is, if 0.00393 mg of $CuSO_4.5H_2O$ is added to 1 L of water, it gives 0.001 mg Cu/L of water

To get 10 mg Cu/L of water, the mass of Cu (0.001 mg) is multiplied by 10000.

Since copper sulphate ($CuSO_4.5H_2O$) would be administered, its mass is also multiplied by 10000 to get 10 mg Cu/L of water.

That is, 39.3 mg of ($CuSO_4.5H_2O$) in 1 Litre of water would yield 10 mg Cu/L of water

Volume of water in experimental bowl = 15 Litres

To maintain the concentration of copper at 10 mg/L, the mass (39.3 mg) of $CuSO_4.5H_2O$ is multiplied by 15 to 589.5 mg (0.590 g) of $CuSO_4.5H_2O$

For 15 mg/L Cu, 884.25 mg (0.884 g) of $CuSO_4.5H_2O$ was added

For 20 mg/L Cu, 1179 mg (1.179 g) of $CuSO_4.5H_2O$ was added

A similar procedure was used to arrive at the masses of [$ZnSO_4$], [Fe (SO_4).$7H_2O$] and [$Pb(NO3)_2$] administered to the experimental units to get the appropriate concentrations of Zn, Fe and Pb.

3.5.4 Experimental procedure

Ninety-six (96) experimental units were used for this experiment. Forty-eight (48) of the experimental units had water hyacinth grown in them while the other forty-eight (48) had water lettuce grown in them. The initial mean weight of water hyacinth and water lettuce in each of the experimental units was 250±20 g and 50±8 g respectively. Each experimental unit was a rectangular plastic tank of dimension 60 by 35 by 25 cm containing 15 litres of water.

Three copper concentrations (10, 15 and 20mg/L) were randomly assigned to three (3) experimental units. After 24 hours, water hyacinth with initial mean weight of 250±20 g was grown separately on each copper experiment. The average biomass of water hyacinth per litre of water in each experimental unit was approximately 17 g. A control experiment containing water hyacinth and water lettuce but no salts of the heavy metals was also set up simultaneously. The experimental units replicated thrice

to give a total of 12 experimental units to monitor Cu accumulation by water hyacinth. The experiment lasted for six (6) weeks.

A similar experiment was set up for Zn, Fe and Pb in order to examine the ability of water hyacinth to absorb these metals.

A similar experiment using water lettuce was also set up to examine the phytoremediative ability of water lettuce.

3.5.5 Experimental Design

The experiment was a completely randomized design. A weekly measurement of metal concentration in water, water hyacinth (leaf, stem and root) and water lettuce (leaf and root) was done using the method earlier described in sections 3.4.3 and .3.4.4.

3.5.6 Bioconcentration Factor

The bioconcentration factor (BCF) gives an index for measuring the capacity of biota to accumulate metals from their environment. The bioconcentration factor was calculated as follows;

The ratio of the concentration of the trace element in the plant tissues at harvest to the initial concentration of the element in the external environment (water) (Zayed *et al*., 1998). Using this formula:

$BCF = (P / E)i$

Where,

P represents the concentration of the trace element in plant tissues (mg/kg dry weight); E represents the trace element initial concentration in the water (mg/L), i

denotes the heavy metal, and BCF is the bioconcentration factor and it is dimensionless. The higher the BCF, the better or higher the accumulation capacity of the plant.

3.5.7 Translocation Factor (TF)

The Translocation Factor was calculated to determine the relative translocation of metals from the water to the various plant components (root, stem, and leaf) (Barman *et al*. 2000; Gupta *et al*. 2008).

TF = Concentration of metal in plant tissue / shoot (stem, or leaf)/Concentration of metal in corresponding root.

3.5.8 Determination of Order of Removal of Metals

Kinetic modeling was done in order to estimate the rates of metal removal in each of the experimental units. A scatter diagram was used to determine the order of the removel of the metals in each of the experimental units. For first-order reactions, a plot of ln[Metal] versus time would be linear while a plot of 1/[Metal] versus time would give a straight line for a second-order reaction (Snoeyink and Jenkins, 1980).

For first-order kinetic models, the rate of loss of metal is proportional to its concentration.

$d[Metal]/dt = -k[Metal]$

where [Metal] is the concentration of Metal and t is the time.

Integrating the equation above yields:

$\ln[Metal]_t = -kt + \ln[Metals]_0$

and $[Metal]_t = [Metal]_0 e^{-kt}$

where $[Metal]_t$ is the Metal concentration at time t, $[Metal]_0$ is the initial Metal concentration in the experimental units and *k* is the first-order reaction constant.

The first-order reaction constant, *k*, is the gradient of the line from the plot of the natural logarithm of [Metal] versus time.

3.5.9 Statistical Analysis

Monthly and spatial variations were tested using two-way analysis of variance (ANOVA) and where there was significant variation, Fisher's Least Significant Difference (LSD) was used to separate the means. The seasonal dynamics was tested using the independent sample test (t-test). The chi-square test was used to compare heavy metal levels in water to the standards set by the Food and Agricultural Organisation/World Health Organisation (FAO/WHO 1992, WHO 2008). In all cases, the level of significance was set at $\alpha = 0.05$. All the statistical tests were performed using computer Statistical Package for Social Sciences (SPSS version 20.0).

CHAPTER FOUR

RESULTS

4.1 Spatial Variation of Physico-chemical Parameters

The results of the spatial variation of the physico-chemical parameters of water in the five sampling stations of are shown in Table 4.1. Conductivity, total dissolved solids, salinity, alkalinity and chemical oxygen demand varied significantly ($p<0.05$) among the sampling stations. The highest value (3088±1478.60 µS/cm) of conductivity was recorded in Owo River while the lowest value (168.99±1.55 µS/cm) was recorded in Agbara. Total dissolved solids was observed to be highest (1739±872.17 mg/L) in Morogbo while the least value (87.19±1.78 mg/L) was recorded in Agbara. The value of salinity observed in Agbara (0.12±0.01 ppt) was significantly different ($p<0.05$) from the values recorded in the other sampling stations. The highest value (41.91±6.07 mg/L) of alkalinity observed in Owo River was significantly different ($p<0.05$) from the lowest value (29.29±1.08 mg/L) recorded in Agbara. The highest value (23.89±0.97 mg/L) observed in Etegbin River varied significantly from the least value (13.78±0.83 mg/L) recorded in Owo River.

4.2 Spatial Variation of Nutrients Concentrations

Table 4.2 shows the variation of nutrient concentration of water among the five sampling stations. All the nutrients investigated showed significant ($p<0.05$) spatial variation in concentration except nitrate. For all the nutrients that varied significantly, their lowest and highest values occurred in Agbara and Owo River respectively. The least values for sulphate, phosphate, calcium and magnesium were 1.53±0.09,

0.66±0.10, 5.40±0.22 and 2.24±0.52 mg/L respectively. Their respective highest values were 25.16±12.21, 2.15±0.24, 33.29±12.73 and 37.14±17.73 mg/L.

4.3 Spatial Variation of Heavy metals in the Water Columns

The variation of the heavy metal content in water columns among the sampling stations is shown in Table 4.3. The concentrations of all the heavy metals measured in water columns of the five sampling sites were not significantly different ($p>0.05$). The values of zinc, iron and cadmium varies from 0.03±0.002 – 0.05±0.004, 0.22±0.001 – 0.29±0.02 and 0.003±0.006 - 0.004±0.005 mg/L respectively. The values recorded for copper and lead were 0.01mg/L in most cases.

4.4 Spatial Variation of Heavy metal Concentrations in Sediment

Table 4.4 shows the variation of heavy metal concentration in sediment of the sampling stations. The concentration of zinc, iron and copper were significantly different ($p<0.05$) among the sampling stations. The value of zinc (10.50±1.58 mg/kg) measured in Agbara was the highest and it was significantly different ($p<0.05$) from the values obtained in the other sampling stations. The highest value (2310±613 mg/kg) of iron was observed in Agbara, while the lowest value (1305±848mg/kg) was obtained in Etegbin. Cu was highest (38.20±10.21 mg/kg) in Agbara while it was lowest (2.92±0.37 mg/kg) in Etegbin and the value obtained in Agbara was significantly ($p<0.05$) higher than those measured in the other sampling stations.

Table 4.1: Spatial Variation of Physico-chemical Parameters

Physical stations	Temp. (°C)	pH	Conductivity (µS/cm)	TSS (mg/L)	TDS (mg/L)	Salinity (ppt)	Acidity (mg/L)	Alkalinity (mg/L)	BOD (mg/L)	COD (mg/L)	DO (mg/L)
OWO R	28.7±0.37^{a}	6.96±0.10^{a}	3088±1478.60^{a}	10.44±0.50^{a}	1730±897.01^{a}	1.66±0.78^{a}	19.97±7.06^{a}	41.91±6.07^{a}	2.94±0.71^{a}	13.78±0.83^{a}	4.93±0.19^{a}
AGBARA	29.7±0.54^{a}	6.75±0.03^{a}	168.99±1.55^{b}	16.72±1.07^{a}	89.19±1.78^{a}	0.12±0.01^{b}	15.93±4.19^{a}	29.29±1.08^{b}	3.28±0.16^{a}	14.56±0.76^{a}	4.66±0.38^{a}
OTTO J	29.8±0.67^{a}	6.71±0.02^{a}	1565±784.66^{c}	16.44±1.07^{a}	1220±612.35^{b}	0.94±0.38^{a}	18.56±4.25^{a}	32.34±4.96^{ab}	3.67±0.16^{a}	18.78±0.64^{ab}	4.22±0.19^{a}
MOROGBO	28.8±0.87^{a}	6.75±0.02^{a}	1602±678.87^{c}	18.72±1.30^{a}	1739±872.17^{b}	0.98±0.41^{a}	16.48±4.40^{a}	33.94±5.03^{ab}	3.17±0.15^{a}	20.28±1.01^{b}	4.52±0.20^{a}
ETEGBIN	29.4±0.69^{a}	6.94±0.11^{a}	3052±1432.80^{a}	20.61±1.21^{a}	1203±308.69^{ab}	1.64±0.75^{b}	21.77±7.57^{a}	38.03±6.96^{a}	3.44±0.17^{a}	23.89±0.97^{b}	4.63±0.31^{a}

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

OWO R = Owo River
OTTO J = Otto Jetty
Temp. = Temperature
TSS = Total Dissolved Solids
TDS = Total Suspended Solids
BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand
DO = Dissolved Oxygen

Table 4.2: Spatial Variation of Nutrient Concentrations in the Sampling Stations

SAMPLING STATIONS	Nitrate (mg/L)	Sulphate (mg/L)	Phosphate (mg/L)	Calcium (mg/L)	Magnesium (mg/L)
OWO RIVER	3.89±0.34[a]	25.16±12.21[a]	2.15±0.24[a]	33.29±12.73[a]	37.14±17.73[a]
AGBARA	2.74±0.32[a]	1.53±0.09[b]	0.66±0.10[b]	5.40±0.22[b]	2.24±0.52[b]
OTTO JETTY	3.15±0.25[a]	12.37±5.30[c]	0.79±0.17[b]	22.19±8.30[c]	20.78±8.54[c]
MOROGBO	3.18±0.26[a]	13.68±5.98[c]	0.85±0.19[b]	24.67±9.37[c]	22.39±9.27[c]
ETEGBIN	3.91±0.38[a]	21.94±11.30[a]	1.61±0.31[a]	33.23±13.26[a]	36.66±18.40[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

Table 4.3: Variation of Heavy Metal in Water Column of the Sampling Stations

SAMPLING STATION	Zn (mg/L)	Fe (mg/L)	Cu (mg/L)	Pb (mg/L)	Cd (mg/L)
OWO RIVER	0.04±0.002[a]	0.22±0.01[a]	0.01±0.001[a]	0.01±0.001[a]	0.003±0.006[a]
AGBARA	0.03±0.002[a]	0.23±0.03[a]	0.01±0.001[a]	0.01±0.001[a]	0.03±0.009[a]
OTTO JETTY	0.04±0.003[a]	0.29±0.02[a]	0.01±0.001[a]	0.01±0.001[a]	0.004±0.005[a]
MOROGBO	0.05±0.004[a]	0.29±0.02[a]	0.01±0.001[a]	0.01±0.001[a]	0.004±0.005[a]
ETEGBIN	0.04±0.002[a]	0.22±0.01[a]	0.01±0.001[a]	0.01±0.001[a]	0.003±0.004[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

Table 4.4: Variation of Heavy Metal Concentrations in Sediment of the Sampling Stations

SAMPLING STATION	Zn (mg/Kg)	Fe (mg/Kg)	Cu (mg/Kg)	Pb (mg/Kg)	Cd (mg/Kg)
OWO RIVER	5.70±0.58[a]	2608±154[a]	3.07±1.16[a]	0.56±0.10[a]	0.02±0.001[a]
AGBARA	10.50±1.58[b]	2310±613[a]	38.20±10.21[b]	0.89±0.12[a]	0.10±0.003[a]
OTTO JETTY	5.63±0.79[a]	1492±628[b]	6.92±2.39[a]	0.29±0.05[a]	0.02±0.001[a]
MOROGBO	5.88±3.57[a]	1559±855[b]	3.10±0.42[a]	0.26±0.04[a]	0.03±0.02[a]
ETEGBIN	6.42±1.05[a]	2305±848[a]	2.92±0.37[a]	0.25±0.04[a]	0.02±0.002[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

4.5 Spatial Variation of Heavy metal Concentrations in Water Hyacinth (*Eichhornia crassipes*)

Table 4.5 shows the variation of heavy metal concentration in water hyacinth from the sampling stations. Spatial variation of all the heavy metals in water hyacinth (*Eichhornia crassipes*) was significant ($p<0.05$) except cadmium. The highest value (42.60±5.62 mg/kg) of Zn obtained in Agbara was significantly different ($p<0.05$) from the values measured in the other sampling stations. Agbara had the highest value (1368±236.12 mg/kg) of Fe while the lowest value (464.31±180.12 mg/kg) was obtained in Etegbin. The value of Cu in Agbara (6.34±4.13 mg/kg) was significantly higher ($p<0.05$) than the values measured in the other sampling stations. The highest value (1.69±0.53 mg/kg) of Pb was observed in Agbara and it varied significantly from values measured in Owo River, Otto Jetty, Morogbo and Etegbin.

4.6 Spatial Variation of Heavy metal Concentrations in Water Lettuce (*Pistia stratiotes*)

The variation of heavy metal content in water lettuce among the sampling stations is presented in Table 4.6. The concentration of zinc, iron, copper and lead varied significantly ($p<0.05$) among the sampling stations. The concentration of zinc was highest in Agbara (37.78±5.20 mg/kg) while Owo River (10.97±2.00 mg/kg) had the least concentration. Iron (Fe) occurred highest (1205±214.77 mg/kg) in Agbara and lowest (352±55.98 mg/kg) in Owo River. The concentrations of Cu in Agbara (6.46±1.13 mg/kg) was significantly different ($p<0.05$) from the values obtained in Owo River (1.64±2.00 mg/kg), Otto Jetty (1.71±020 mg1kg), Morogbo (1.71±0.24 mg/kg) and Etegbin (1.62±0.16 mg1kg). The highest value (1.47±0.40 mg/kg) of Pb obtained in Agbara significantly higher ($p<0.05$) from the values obtained in the other sampling stations.

Table 4.5: Variation of Heavy Metal Concentration in Water Hyacinth (*Eichhornia crassipes*) from the Sampling Stations

SAMPLING STATION	Zn (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
OWO RIVER	11.14±1.83[a]	470±554.96[a]	8.18±1.63[a]	0.54±0.79[a]	0.001±0.01[a]
AGBARA	42.60±5.62[b]	1368±236.12[b]	6.34±4.13[b]	1.69±0.53[b]	0.003±0.02[a]
OTTO JETTY	18.30±4.91[a]	642.58±303.26[a]	1.92±0.19[a]	0.40±0.07[a]	0.001±0.01[a]
MOROGBO	16.67±4.19[a]	542.43±239.73[a]	1.78±0.19[a]	0.36±0.06[a]	0.001±0.01[a]
ETEGBIN	20.41±4.31[a]	464.31±180.12[a]	1.72±0.19[a]	0.34±0.06[a]	0.002±0.02[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

Table 4.6: Variation of Heavy Metal in Water Lettuce (*Pistia stratiotes*) from the Sampling Stations

SAMPLING STATION	Zn (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
OWO RIVER	10.97±2.00[a]	1352±554.98[a]	1.64±2.00[a]	0.47±0.06[a]	0.001±0.01[a]
AGBARA	37.78±5.20[b]	1205±214.77[b]	6.46±1.13[b]	1.47±0.40[a]	0.003±0.02[a]
OTTO JETTY	18.20±5.05[a]	581.26±276.81[a]	1.71±0.20[a]	0.38±0.06[a]	0.001±0.01[a]
MOROGBO	15.26±4.19[a]	521.63±233.88[a]	1.71±0.24[a]	0.34±0.05[a]	0.001±0.01[a]
ETEGBIN	17.72±4.02[a]	420.52±168.06[a]	1.62±0.16[a]	0.36±0.06[a]	0.001±0.02[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

4.7 Monthly Variation of Physico-chemical Parameters

The results of the monthly variation of the physico-chemical parameters in the sampling stations is shown in Table 4.7. Conductivity, total suspended solids, total dissolved solids, salinity, acidity, alkalinity, chemical oxygen demand and dissolved oxygen varied significantly ($p<0.05$) within the months. The highest value (8847±5339 µS/cm) of conductivity was obtained in January, 2014, while the lowest value (119.48±13.67 µS/cm) occurred in August, 2013. The value (22.40±3.54 mg/L) of total suspended solids obtained in July, 2013 was the highest while the lowest value (11.20±0.58 mg/L) was observed in February, 2014. The highest value of total dissolved solids recorded in January 2014 was 10042±2643 which was significantly different ($p<0.05$) from the least value (52.26±7.68 mg/L) recorded in August, 2014. The salinity values measured from July, 2013 - December, 2013 and May, 2014 - December, 2014 varied significantly ($p<0.05$) from the values observed between January, 2014 and April, 2014.

The highest value (64.26±26.02 mg/L) of acidity was got in October, 2013 while the lowest value (5.34±0.47 mg/L) was recorded in February, 2014. The alkalinity value (78.34±11.09 mg/L) measured in January, 2014 was the highest and it also varied significantly ($p<0.05$) from the lowest value (19.02±1.20 mg/L) got in September, 2014. The highest value (21.00±3.85 mg/L) of COD was observed in July, 2013 while its least value (12.00±2.02 mg/L) was obtained in August, 2014. The value (24.74±0.24 mg/L) of dissolved oxygen measured in October, 2014 varied significantly ($p<0.05$) from the values measured in the other months of study.

Table 4.7: Monthly Variation of Physico-chemical Parameters in Water of all the Sampling Stations

MONTHS	Temp. (°C)	pH	Cond. (µS/cm)	TSS (mg/L))	TDS (mg/L)	Salinity (ppt)	Acidity (mg/L)	Alkalinity (mg/L)	BOD (mg/L)	COD (mg/L)	DO (mg/L)
JUL, 2013	27.8±0.51^{a}	6.76±0.02^{a}	124.28±13.98^{a}	22.40±3.54^{a}	69.44±6.78^{a}	0.12±0.01^{a}	15.60±0.28^{a}	27.40±1.42^{a}	3.60±0.24^{a}	21.00±3.85^{a}	5.32±0.50^{a}
AUG, 2013	28.8±0.67^{a}	6.67±0.04^{a}	119.48±13.67^{a}	15.60±2.87^{a}	67.80±6.55^{a}	0.10±0.01^{a}	16.36±1.73^{a}	22.86±1.20^{a}	2.40±0.24^{a}	14.40±2.20^{ab}	4.82±0.44^{a}
SEP, 2013	27.3±0.56^{a}	6.64±0.02^{a}	121.88±13.36^{a}	14.40±2.58^{a}	66.14±15.44^{a}	0.13±0.01^{a}	21.40±2.20^{a}	19.98±1.18^{a}	3.80±0.20^{a}	17.00±2.88^{a}	4.52±0.19^{a}
OCT, 2013	28.1±0.54^{a}	6.81±0.02^{a}	121.28±14.95^{a}	18.60±2.14^{a}	72.30±7.54^{a}	0.12±0.00^{a}	64.26±26.02^{b}	26.32±4.14^{a}	2.80±0.20^{a}	20.60±1.75^{a}	2.32±0.22^{a}
NOV, 2013	29.1±0.68^{a}	6.79±0.02^{a}	130.36±11.95^{a}	16.40±1.57^{a}	72.82±7.08^{a}	0.12±0.01^{a}	11.24±0.37^{a}	25.12±2.33^{a}	3.40±0.24^{a}	17.00±1.34^{a}	4.32±0.17^{a}
DEC, 2013	28.4±0.87^{a}	6.79±0.01^{a}	133.34±13.32^{a}	14.60±1.33^{a}	72.82±6.52^{a}	0.13±0.01^{a}	12.74±0.79^{a}	25.26±0.86^{a}	3.00±0.32^{a}	18.60±2.20^{a}	4.68±0.80^{a}
JAN, 2014	29.2±0.55^{a}	7.10±0.29^{a}	8847±5339^{b}	14.60±0.97^{a}	10042±2643^{b}	6.96±2.19^{b}	7.16±0.84^{c}	78.34±10.9^{b}	3.60±0.24^{a}	18.60±1.29^{a}	4.74±0.17^{a}
FEB, 2014	27.4±0.59^{a}	7.10±0.28^{a}	7306±1908^{b}	11.20±0.58^{b}	3142±1040^{c}	3.45±0.99^{b}	5.34±0.47^{c}	65.58±10.2^{b}	3.00±0.3 ^{a}	19.00±0.55^{a}	4.66±0.28^{a}
MAR, 2014	28.2±0.64^{a}	7.13±0.26^{a}	7768±1961^{b}	12.60±0.51^{b}	3727±965^{c}	3.48±0.95^{b}	5.82±0.60^{c}	69.92±10.2^{b}	3.00±0.32^{a}	18.40±1.63^{a}	4.78±0.18^{a}
APR, 2014	28.6±0.54^{a}	7.14±0.25^{a}	7680±1940^{b}	11.80±0.58^{b}	3774±972^{c}	3.60±1.00^{b}	5.44±0.42^{c}	69.12±10.0^{b}	3.40±0.24^{a}	18.00±1.10^{a}	4.99±0.12^{a}
MAY, 2014	29.0±0.50^{a}	6.74±0.04^{a}	371.88±247^{a}	22.00±2.93^{a}	69.36±6.49^{a}	0.12±0.01^{a}	15.00±0.17^{a}	28.28±0.99^{a}	3.60±0.24^{a}	19.40±3.09^{a}	5.24±0.48^{a}

Table 4.7 continued

MONTHS	Temp. (°C)	pH	Cond. (µS/cm)	TSS (mg/L))	TDS (mg/L)	Salinity (ppt)	Acidity (mg/L)	Alkalinity (mg/L)	BOD (mg/L)	COD (mg/L)	DO (mg/L)
JUN, 2014	28.9±0.66^{a}	6.74±0.04^{a}	371.88±247^{a}	22.00±2.93^{a}	69.36±6.49^{a}	0.12±0.01^{a}	15.00±0.17^{a}	28.28±0.99^{a}	3.60±0.24^{a}	19.40±3.09^{a}	5.24±0.48^{a}
JUL, 2014	27.6±0.57^{a}	6.74±0.04^{a}	373.28±248^{a}	21.60±3.11^{a}	70.76±6.75^{a}	0.12±0.01^{a}	14.94±0.29^{a}	26.86±1.29^{a}	3.60±0.24^{a}	20.40±3.47^{a}	5.24±0.48^{a}
AUG, 2014	28.3±0.36^{a}	6.67±0.01^{a}	135.66±13.16^{a}	13.80±2.48^{b}	52.26±7.68^{a}	0.10±0.01^{a}	14.30±1.32^{a}	20.68±1.02^{a}	2.60±0.24^{a}	12.00±2.02^{b}	4.84±0.38^{a}
SEP, 2014	29.1±0.48^{a}	6.65±0.02^{a}	124.68±12.44^{a}	14.60±2.62^{a}	66.26±6.85^{a}	0.12±0.01^{a}	22.00±.34^{a}	19.02±1.20^{a}	4.40±0.24^{a}	18.00±2.88^{a}	4.60±0.26^{a}
OCT, 2014	28.6±0.61^{a}	6.81±0.02^{a}	123.20±14.18^{a}	19.20±1.91^{a}	71.64±7.45^{a}	0.12±0.00^{a}	61.80±24.37^{b}	25.82±4.34^{a}	2.60±0.24^{a}	20.80±2.08^{a}	2.74±0.24^{b}
NOV, 2014	28.7±0.45^{a}	6.73±0.03^{a}	125.24±11.28^{a}	16.80±1.39^{a}	70.26±7.86^{a}	0.13±0.01^{a}	12.24±0.60^{a}	28.20±1.49^{a}	3.60±0.24^{a}	17.20±1.32^{a}	4.86±0.13^{a}
DEC, 2014	28.6±0.54^{a}	6.74±0.03^{a}	134.76±12.32^{a}	15.20±1.07^{a}	71.98±4.99^{a}	0.13±0.01^{a}	13.10±0.62^{a}	24.82±1.11^{a}	3.40±0.24^{a}	18.80±1.98^{a}	4.74±0.73^{a}

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

Temp. = Temperature
TSS = Total Dissolved Solids
TDS = Total Suspended Solids
BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand
DO = Dissolved Oxygen

4.8 Monthly Variation of Physico Nutrients Concentration in Water

Table 4.8 shows the monthly variation of nutrients content in water (nitrate, sulphate, phosphate, calcium and magnesium) for the the priod of this study. All the nutrients showed significant ($p<0.05$) monthly variation except nitrate and phosphate. The nutrients that varied significantly (sulphate, calcium and magnesium) showed the same pattern or trend. The values of the nutrients obtained between January, 2014 – April, 2014 were significantly ($p<0.05$) higher than the values obtained in the other months.

4.9: Monthly Variation of Heavy Metal Concentrations in Water Column and Sediment

Table 4.9 shows the monthly variation of heavy metal concentration in the water column. All the heavy metal except Fe was not significantly different ($p>0.05$). The values of Fe observed in Aug, 2013, and Aug, 2014 varied significantly ($p<0.05$) from other month studied except March, 2014. The monthly variations in the concentrations of Zn, Cu, Pb and Cd observed during the course of study range from 0.03 – 0.05, 0.01 – 0.02, 0.001 – 0.002 and 0.006 – 0.009 mg/L respectively.

The monthly dynamics of heavy metal content in the sediment of the sampling stations studied is shown in Table 4.10. Monthly variation in the concentration of Zn, Fe, Cu and Pb with the exemption of those of Cd were significantly different ($p<0.05$). The highest value (104.20±14.79 mg/kg) of Zn was observed in December, 2013 while the lowest value (27.40±9.16 mg/kg) was recorded in September, 2013. The value (24934.60±11237.49 mg/kg) obtained in January, 2014 for Fe is significantly different ($p<0.05$) from values observed in Feb – April, 2014 and other months of study. The highest value (301.20±253.48 mg/kg) of Cu was recorded in May, 2014 while the least value (5.86±0.74 mg/kg) was recorded in March, 2014. The values (1.16±35 and 0.86±0.12 mg/kg) observed for Pb in February and March, 2014 respectively varied significantly ($p<0.05$) from the values obtained in the other months of the study.

Table 4.8: Monthly Variation of Nutrients Concentrations in Water of the Sampling Stations

Month	Nitrate (mg/L)	Sulphate (mg/L)	Phosphate (mg/L)	Calcium (mg/L)	Magnesium (mg/L)
JUL, 2013	3.96±0.40[a]	2.10±0.06[a]	0.32±0.18[a]	4.480±0.18[a]	2.00±0.28[a]
AUG, 2103	2.36±0.63[a]	1.66±0.23[a]	0.77±0.51[a]	4.46±0.62[a]	2.38±0.30[a]
SEPT, 2013	5.24±0.25[a]	1.72±0.21[a]	2.06±0.47[a]	4.62±0.36[a]	1.92±0.30[a]
OCT, 2013	3.24±0.50[a]	1.44±0.13[a]	0.77±0.36[a]	3.48±0.72[a]	1.96±0.25[a]
NOV, 2013	3.14±0.57[a]	1.34±6.14[a]	0.83±0.21[a]	4.04±0.23[a]	2.58±0.22[a]
DEC, 2013	1.76±0.34[a]	1.48±0.12[a]	1.10±0.10[a]	4.80±0.33[a]	2.70±0.28[a]
JAN, 2014	3.52±0.89[a]	114.16±37.31[b]	3.28±0.76[a]	93.04±24.26[b]	162.22±129.78[b]
FEB, 2014	3.52±0.49[a]	40.46±13.07[c]	1.62±0.45[a]	88.88±22.48[b]	74.48±19.39[b]
MAR, 2014	3.84±0.70[a]	45.02±12.55[c]	1.26±0.20[a]	92.10±23.68[b]	78.30±19.81[b]
APR, 2014	3.50±0.57[a]	43.96±11.40[c]	1.38±0.30[a]	90.86±22.91[b]	80.88±20.65[b]
MAY, 2014	3.92±0.33[a]	2.40±0.89[a]	0.35±0.19[a]	4.76±0.15[a]	2.26±0.29[a]
JUN, 2014	3.92±0.33[a]	2.40±0.89[a]	0.35±0.19[a]	4.76±0.15[a]	2.26±0.29[a]
JUL, 2014	3.92±0.33[a]	2.40±0.89[a]	0.35±0.19[a]	4.76±0.15[a]	2.26±0.29[a]
AUG, 2014	2.38±0.53[a]	1.84±0.19[a]	0.79±0.52[a]	4.46±0.52[a]	2.58±0.34[a]
SEPT, 2014	5.18±50[a]	1.82±0.22[a]	1.99±0.45[a]	4.70±0.36[a]	2.08±0.34[a]
OCT, 2014	3.46±6.51[a]	1.50±0.10[a]	0.87±0.38[a]	3.59±0.76[a]	1.96±0.21[a]
NOV, 2014	2.86±6.51[a]	1.50±6.05[a]	1.11±0.19[a]	4.84±0.32[a]	3.36±0.25[a]
DEC, 2014	2.62±6.39[a]	1.62±0.80[a]	1.07±6.18[a]	5.02±0.39[a]	3.00±0.27[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

Table 4.9: Monthly Variation of Heavy Metals in Water Column in all the Sampling Stations

Month	Zn (mg/Kg)	Fe (mg/Kg)	Cu (mg/Kg)	Pb (mg/Kg)	Cd (mg/Kg)
JULY, 2013	0.50±0.00[a]	0.25±0.02[a]	0.01±0.002[a]	0.001±0.001[a]	0.008±0.004[a]
AUG, 2013	0.03±0.01[a]	0.17±0.02[a]	0.01±0.001[a]	0.002±0.001[a]	0.009±0.005[a]
SEP, 2013	0.04±0.01[a]	0.22±0.02[a]	0.01±0.002[a]	0.001±0.001[a]	0.006±0.003[a]
OCT, 2013	0.03±0.01[a]	0.27±0.03[a]	0.02±0.001[a]	0.001±0.001[a]	0.006±0.004[a]
NOV, 2013	0.04±0.01[a]	0.23±0.02[a]	0.02±0.001[a]	0.002±0.001[a]	0.007±0.003[a]
DEC, 2013	0.04±0.01[a]	0.23±0.02[a]	0.02±0.001[a]	0.001±0.001[a]	0.006±0.002[a]
JAN, 2014	0.04±0.01[a]	0.23±0.02[a]	0.01±0.001[a]	0.001±0.001[a]	0.008±0.003[a]
FEB, 2014	0.05±0.01[a]	0.22±0.04[a]	0.02±0.001[a]	0.001±0.001[a]	0.01±0.005[a]
MARCH, 2014	0.05±0.01[a]	0.20±0.04[a]	0.03±0.001[a]	0.002±0.001[a]	0.008±0.006[a]
APRIL, 2014	0.05±0.01[a]	0.21±0.04[a]	0.03±0.001[a]	0.001±0.001[a]	0.008±0.005[a]
MAY, 2014	0.05±0.01[a]	0.31±0.04[a]	0.02±0.001[a]	0.001±0.001[a]	0.006±0.002[a]
JUNE, 2014	0.05±0.02[a]	0.31±0.04[a]	0.03±0.002[a]	0.001±0.002[a]	0.008±0.005[a]
JULY, 2014	0.05±0.02[a]	0.31±0.04[a]	0.02±0.002[a]	0.001±0.001[a]	0.008±0.005[a]
AUG, 2014	0.03±0.01[a]	0.19±0.02[a]	0.03±0.001[a]	0.002±0.001[a]	0.008±0.005[a]
SEPT, 2014	0.05±0.01[a]	0.26±0.02[a]	0.02±0.002[a]	0.001±0.001[a]	0.008±0.006[a]
OCT, 2014	0.03±0.01[a]	0.30±0.04[a]	0.03±0.002[a]	0.001±0.001[a]	0.006±0.004[a]
NOV, 2014	0.04±0.02[a]	0.25±0.02[a]	0.03±0.002[a]	0.001±0.002[a]	0.006±0.004[a]
DEC, 2014	0.05±0.01[a]	0.25±0.04[a]	0.03±0.002[a]	0.001±0.001[a]	0.009±0.005[a]

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

4.10: Monthly Variation of Heavy Metals in Water Hyacinth (*Echhornia crassipes*) and Water Lettuce (*Pistia stratiotes*)

Tables 4.11 and 4.12 shows the monthly variation of the heavy metal concentration in water hyacinth and water lettuce respectively. The highest value (620.60±96.29 mg/kg) of Zn in water hyacinth was observed in October, 2013 while the least value (18.54±2.22 mg/kg) was recorded in March, 2014. The values of Fe observed in February and April, 2014 in water hyacinth varied significantly ($p<0.05$) from value obtained in March, 2014 (44506.20±6635.48 mg/kg) and other months of study. Most of the monthly values recorded for Cu in water hyacinth during the study were significantly different ($p<0.05$) from each other.

All heavy metals except Cd exhibited significant ($p<0.05$) monthly variation in water lettuce. Zinc, Fe and Cu showed similar trend with the values recorded in February – April, 2014 varying significantly ($p<0.05$) than the values reported in the other months.

4.11: Effects of Seasonal Dynamics on Physico-chemical Parameters

Figure 4.1: shows the seasonal variation of the physico-chemical parameters in the five sampling stations. There were no significant difference ($p>0.05$) between the values recorded in both the dry and wet seasons for pH, total suspended solids, salinity, biological oxygen demand, chemical oxygen demand and dissolved oxygen. However, conductivity, total dissolved solids, acidity and alkalinity were significantly ($p<0.05$) affected by seasonal dynamics. In all cases, the dry season values were higher than the wet season.

Table 4.10: Monthly Variation of Heavy Metals in Sediment in all the Sampling Stations

Month	Zn (mg/Kg)	Fe (mg/Kg)	Cu (mg/Kg)	Pb (mg/Kg)	Cd (mg/Kg)
JULY, 2013	61.40±18.68^{a}	2120±1185^{a}	269.40±224.67^{a}	4.14±0.35^{a}	0.18±0.05^{a}
AUG, 2013	64.20±11.29^{a}	3517±1642^{a}	202.20±111.40^{a}	4.80±1.48^{a}	0.31±0.10^{a}
SEP, 2013	27.40±9.16^{b}	9173±1778^{a}	67.60±40.90^{b}	5.50±2.76^{a}	0.16±0.04^{a}
OCT, 2013	86.80±9.55^{c}	10132±2297^{a}	89.80±39.12^{b}	6.92±2.34^{a}	0.23±0.05^{a}
NOV, 2013	95.00±33.41^{c}	13575±2507^{a}	32.00±14.81^{c}	5.04±3.25^{a}	0.19±0.06^{a}
DEC, 2013	104.20±14.79^{c}	8037±1334^{a}	91.20±60.45^{b}	4.18±1.45^{a}	0.21±0.08^{a}
JAN, 2014	89.40±24.79^{c}	24934±11237^{c}	17.00±4.30^{c}	3.06±1.58^{a}	0.13±0.38^{a}
FEB, 2014	17.62±3.90^{d}	58293±18129^{b}	8.40±2.73^{d}	1.16±0.35^{b}	0.33±0.16^{a}
MARCH, 2014	30.56±5.07^{b}	100086±21356^{b}	5.86±0.74^{d}	0.86±0.12^{b}	0.35±0.15^{a}
APRIL, 2014	48.42±13.30^{e}	89188±9353^{b}	7.44±0.74^{d}	2.84±1.13^{a}	0.35±0.16^{a}
MAY, 2014	71.00±21.16^{a}	2285±1257^{a}	301.20±253.48^{a}	5.38±0.16^{a}	0.28±0.15^{a}
JUNE, 2014	69.40±19.74^{a}	222±1239^{a}	288.40±241.42^{a}	4.94±0.24^{a}	0.27±0.15^{a}
JULY, 2014	66.40±19.55^{a}	2153±1205^{a}	85.20±39.65^{b}	4.58±0.30^{a}	0.27±0.15^{a}
AUG, 2014	66.20±13.78^{a}	3521±1654^{a}	197.80±114.25^{a}	4.78±1.78^{a}	0.32±0.17^{a}
SEPT, 2014	30.80±9.73^{b}	9251±1829^{a}	66.60±38.94^{b}	6.18±3.14^{a}	0.32±0.17^{a}
OCT, 2014	90.80±10.58^{c}	10162±2375^{a}	93.20±40.51^{b}	7.28±2.45^{a}	0.30±0.14^{a}
NOV, 2014	101.82±39.80^{c}	13383±2801^{a}	34.80±16.35^{c}	4.58±2.62^{a}	0.40±0.20^{a}
DEC, 2014	107.00±14.46^{c}	7857±1266^{a}	93.20±60.00^{b}	4.76±1.39^{a}	0.68±0.39^{a}

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

Table 4.11: Monthly Variation of Heavy Metal Concentration in Water Hyacinth (*Echhornia crassipes*) from all the Sampling Stations

Months	Zn (mg/Kg)	Fe (mg/Kg)	Cu (mg/Kg)	Pb (mg/Kg)	Cd (mg/Kg)
JULY, 2013	145.00±46.84^{a}	1839.00±1429.38^{a}	70.20±33.41^{a}	7.48±1.22^{a}	0.01±0.01^{a}
AUG, 2013	296.80±74.41^{ae}	2776.00±2139.07^{a}	55.20±19.22^{ab}	9.86±5.67^{a}	0.02±0.01^{a}
SEP, 2013	167.40±43.29^{a}	3265.60±1529.89^{a}	30.00±15.71^{ab}	19.76±13.39^{b}	0.03±0.01^{a}
OCT, 2013	620.60±96.29^{b}	6087.80±3303.80^{a}	35.60±8.64^{ab}	5.88±1.40^{a}	0.002±0.01^{a}
NOV, 2013	150.94±113.23^{a}	6893.60±2913.54^{a}	22.00±4.53^{ab}	4.12±1.42^{a}	0.04±0.01^{a}
DEC, 2013	246.20±35.20^{ae}	5869.40±1167.66^{a}	40.60±11.02^{ab}	1.66±0.27^{a}	0.03±0.02^{a}
JAN, 2014	138.56±75.77^{a}	7109.00±1795.40^{a}	12.14±1.85^{b}	2.60±0.95^{a}	0.01±0.01^{a}
FEB, 2014	75.66±53.54^{c}	24754.60±14080.07^{b}	8.20±1.77^{b}	0.36±0.01^{c}	0.02±0.01^{a}
MARCH, 2014	18.54±2.22^{d}	44506.20±6635.48^{c}	7.66±0.80^{b}	0.18±0.05^{c}	0.02±0.01^{a}
APRIL, 2014	39.52±9.25^{c}	27484.80±6815.72^{b}	6.66±1.82^{b}	0.18±0.05^{c}	0.02±0.01^{a}
MAY, 2014	156.60±51.01^{a}	1999.00±1561.36^{a}	84.60±40.11^{a}	8.30±1.49^{a}	0.01±0.01^{a}
JUNE, 2014	152.20±48.90^{a}	1908.06±1506.53^{a}	76.20±35.86^{a}	8.06±1.39^{a}	0.01±0.01^{a}
JULY, 2014	149.40±48.58^{a}	1905.80±1488.60^{a}	71.00±33.81^{a}	7.72±1.36^{a}	0.01±0.01^{a}
AUG, 2014	325.40±76.09^{e}	2893.60±2225.88^{a}	62.40±20.71^{a}	11.30±6.22^{ab}	0.02±0.01^{a}
SEPT, 2014	170.40±42.99^{a}	3303.60±1558.97^{a}	32.80±18.02^{a}	19.50±12.93^{b}	0.02±0.01^{a}
OCT, 2014	614.00±99.90^{b}	6259.60±3429.99^{a}	37.80±8.72^{a}	6.10±1.32^{a}	0.02±0.01^{a}
NOV, 2014	224.46±122.37^{ae}	6991.00±2974.84^{a}	24.12±4.88^{a}	5.44±1.40^{a}	0.02±0.01^{a}
DEC, 2014	236.40±33.41^{ae}	5712.20±1162.19^{a}	41.00±10.15^{a}	1.70±0.18^{a}	0.02±0.02^{a}

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

4.12: Effects of Seasonal Dynamics on Heavy Metal Content in Water Column and Sediment

Fig.4.2 shows the seasonal dynamics of heavy metal concentrations in the water columns of the sampling stations. There were no clear difference in the dry and wet season values for all the heavy metals studied. The values range from 0.001±0.04 mg/L.

The seasonal variation of heavy metal content in the sediment of the sampling stations of are shown in Fig. 4.3. The values of zinc, iron and copper measured in both seasons varied but they were not significant ($p>0.05$). However, lead and cadmium had similar values in both season. The wet season values of iron and copper were higher than the dry season values. However, zinc recorded higher value in the dry season than wet season.

Table 4.12: Monthly Variation of Heavy Metals in Water Lettuce (*Pistia stratiotes*) from all the Sampling Stations

Month	Zn (mg/Kg)	Fe (mg/Kg)	Cu (mg/Kg)	Pb (mg/Kg)	Cd (mg/Kg)
JULY, 2013	138.0±54.21^{a}	1614.8±1209.4^{a}	73.8±37.5^{a}	7.06±1.69^{a}	0.30±0.01^{a}
AUG, 2013	246.4±38.86^{a}	2261.8±1838.1^{a}	43.2±17.38^{a}	8.52±3.89^{a}	0.02±0.01^{a}
SEP, 2013	139.2±31.47^{a}	2799.0±1343.4^{a}	24.6±15.3^{a}	16.44±10.39^{b}	0.04±0.02^{a}
OCT, 2013	591.2±80.32^{a}	5354.8±2877.8^{a}	38.0±11.04^{a}	5.9±0.75^{a}	0.03±0.01^{a}
NOV, 2013	159.34±126.23^{a}	5984.4±2472.2^{a}	24.80±4.68^{a}	3.80±1.46^{a}	0.03±0.02^{a}
DEC, 2013	252.8±36.33^{a}	5566.0±886.3^{a}	46.2±14.88^{a}	2.48±0.36^{a}	0.04±0.02^{a}
JAN, 2014	97.66±45.77^{a}	5877.0±1375.64^{a}	14.00±3.81^{a}	1.56±0.38^{a}	0.20±0.01^{a}
FEB, 2014	52.90±81.48^{b}	25101.2±15998.13^{b}	6.40±1.29^{b}	0.26±0.24^{c}	0.02±0.01^{a}
MARCH, 2014	17.24±2.19^{b}	40418.6±4909.76^{b}	6.00±2.32^{b}	0.20±0.03^{c}	0.02±0.01^{a}
APRIL, 2014	35.64±8.544^{b}	24604.6±6117.2^{b}	5.00±0.96^{b}	0.20±0.03^{c}	0.18±0.01^{a}
MAY, 2014	148.0±132.28^{a}	1761.8±1296.76^{a}	93.00±46.88^{c}	8.04±1.83^{a}	0.02±0.01^{a}
JUNE, 2014	145.2±56.67^{a}	1682.2±1258.04^{a}	83.00±42.38^{c}	7.78±1.79^{a}	6.14±0.02^{a}
JULY, 2014	142.6±55.83^{a}	165.9.4±1249.57^{a}	80.4±41.27^{c}	7.50±1.81^{a}	0.04±0.02^{a}
AUG, 2014	243.8±40.67^{a}	2339.0±1897.20^{a}	46.00±18.63^{a}	10.10±4.49^{a}	0.14±0.02^{a}
SEPT, 2014	142.0±32.4^{a}	2844.2±1358.7^{a}	26.80±15.59^{a}	15.94±9.52^{b}	0.16±0.02^{a}
OCT, 2014	595.6±83.52^{c}	5560.8±3041.3^{a}	39.6±10.92^{a}	6.02±0.69^{a}	0.02±0.01^{a}
NOV, 2014	203.56±123.31^{a}	5568.0±2651.25^{a}	26.20±5.62^{a}	4.44±1.83^{a}	0.02±0.01^{a}
DEC, 2014	246.2±34.55^{a}	5486.61±884.05^{a}	48.20±16.05^{a}	2.66±0.28^{a}	0.17±0.01^{a}

- Values in the same column and with the same superscript letters are not significantly different ($p>0.05$).
- All the values are expressed as Mean±SE

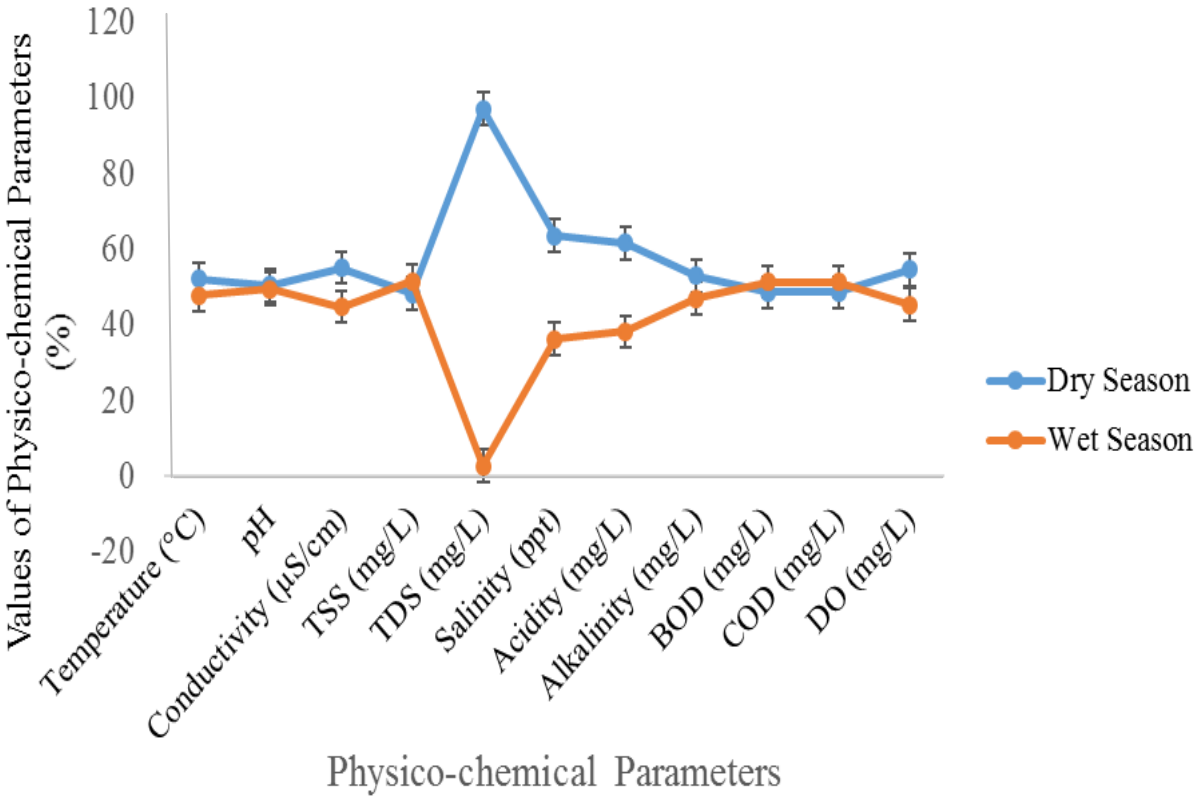


Fig. 4.1: Seasonal Variation in Physico-chemical Parameters in the Sampling Stations

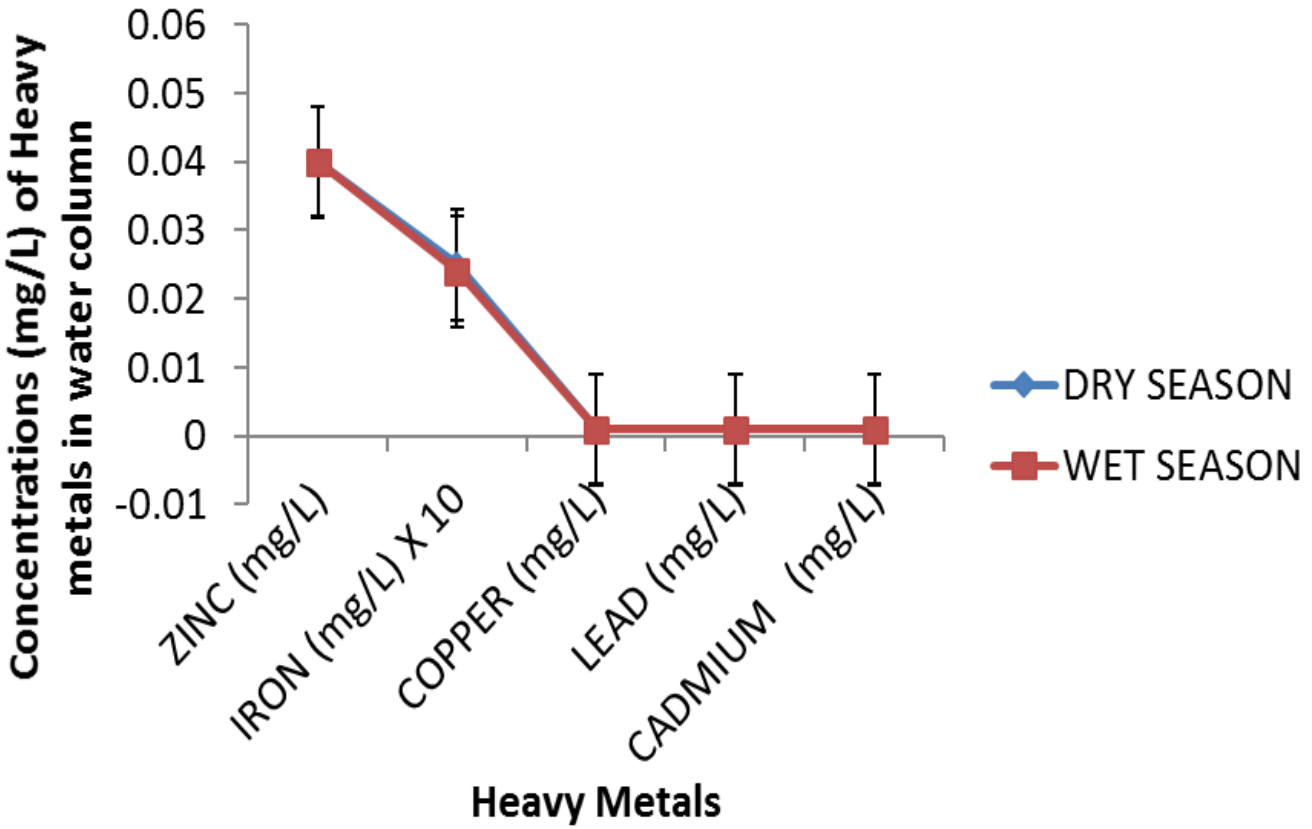


Fig. 4.2: Seasonal dynamics of heavy metal content (mg/L) in Water Column of the sampling stations

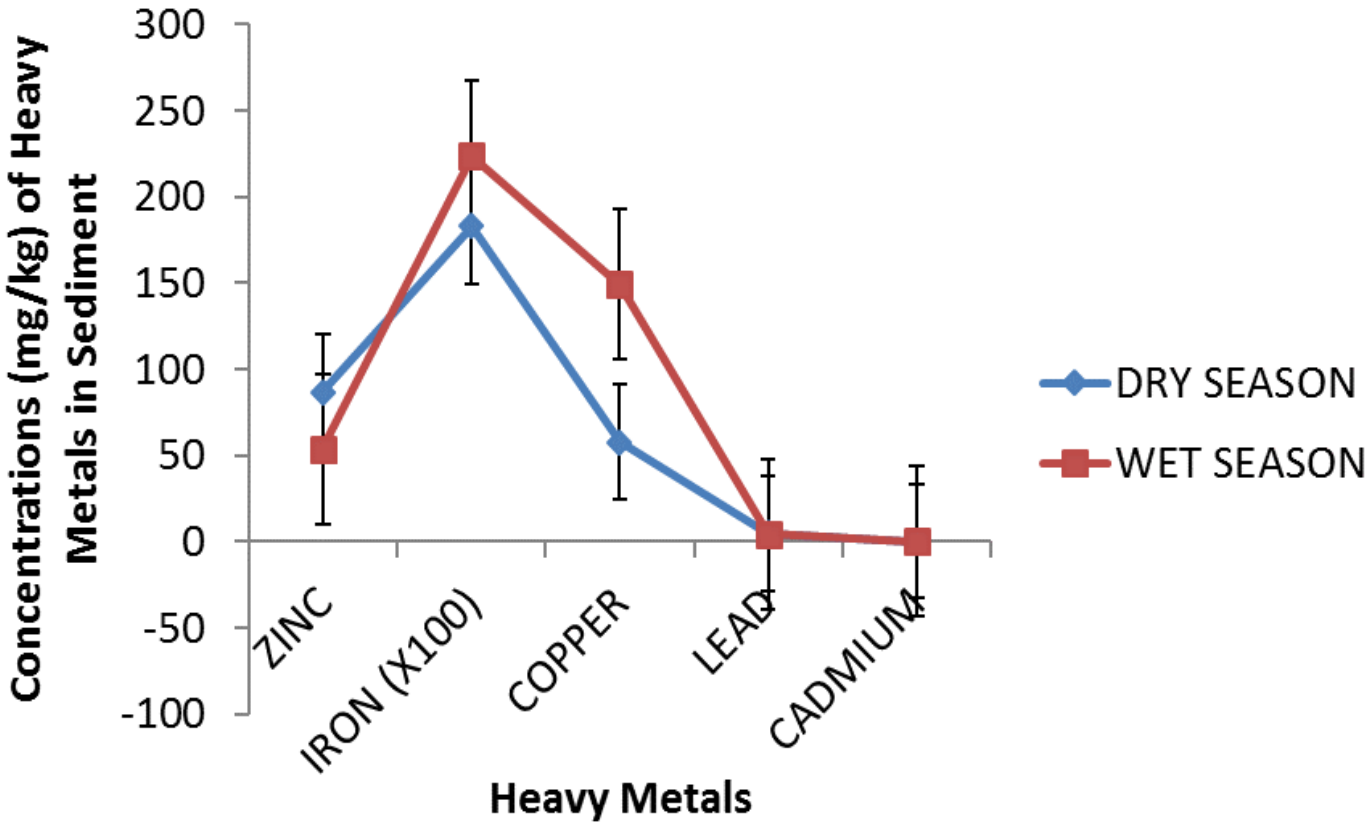


Fig. 4.3: Seasonal dynamics of heavy metal concentration (mg/kg) in Sediment of the sampling stations

4.13: Effects of Seasonal Dynamics on Heavy Metal Content in Water Hyacinth (*Echhornia crassipes*), Water Lettuce (*Pistia stratiotes*) and Nutrients

The seasonal dynamics of heavy metal content in water hyacinth and water lettuce are shown in Fig.4.4 and Fig. 4.5 respectively. In each case, there were no significant differences ($p>0.05$) in the dry and wet season values for all the heavy metals. Dry season value was higher than wet season value for iron while the reverse was the case for copper. The effects of seasonal dynamics on the nutrient content of the sampling stations are shown in Fig. 4.6. There was no significant difference ($p>0.05$) between the wet and dry season values. Dry season values of the metals were constantly higher than the wet season.

4.14 Bioconcentration Factor (BCF) of Heavy Metals in Water Hyacinth and Water Lettuce

The bioconcentration factor of heavy metals in water hyacinth and water lettuce from the sampling stations are shown in Figs. 4.7 and 4.8 respectively. Iron and copper were more absorbed than zinc, lead and cadmium in all the sampling stations. The order of bioaccumulation of the elements were Fe>Cu>Zn>Pb>Cd.

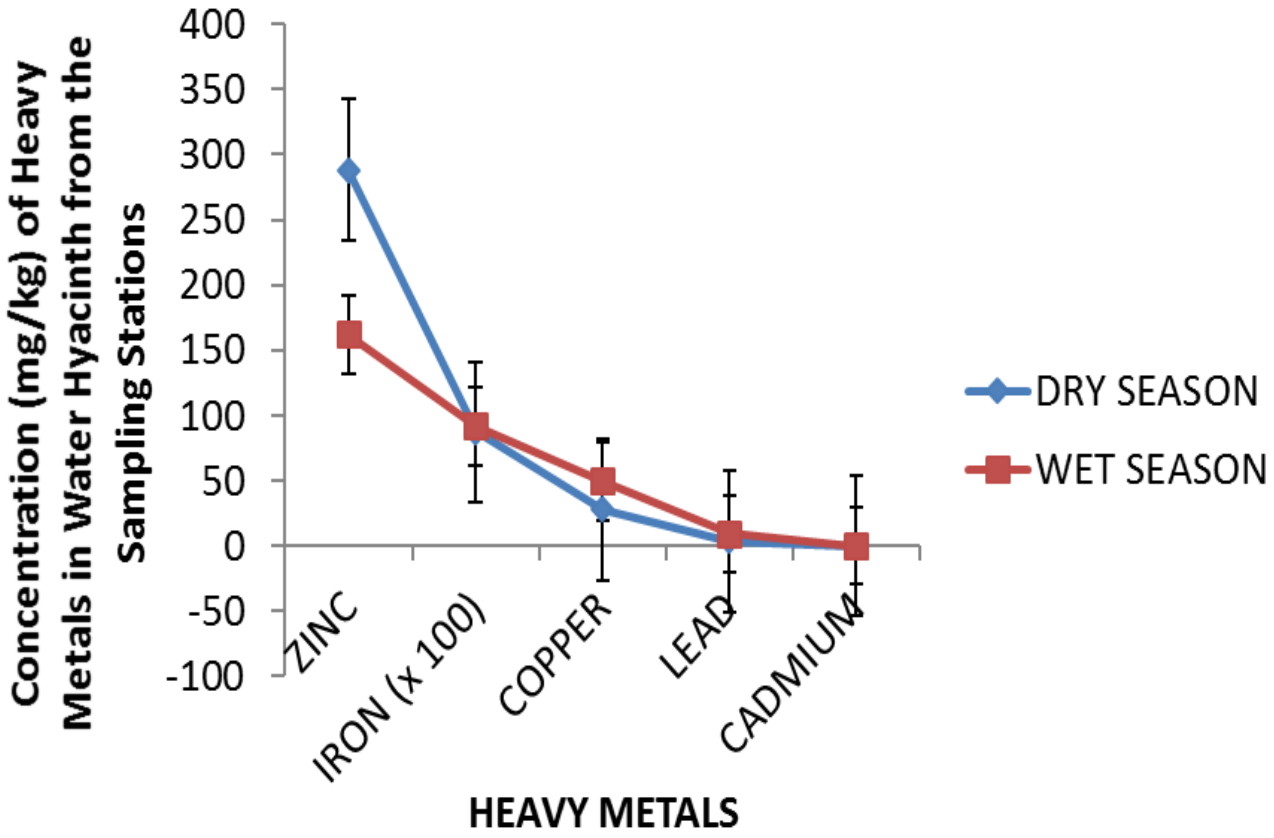


Fig. 4.4: Seasonal dynamics of heavy metal concentration (mg/kg) in Water Hyacinth from the sampling stations

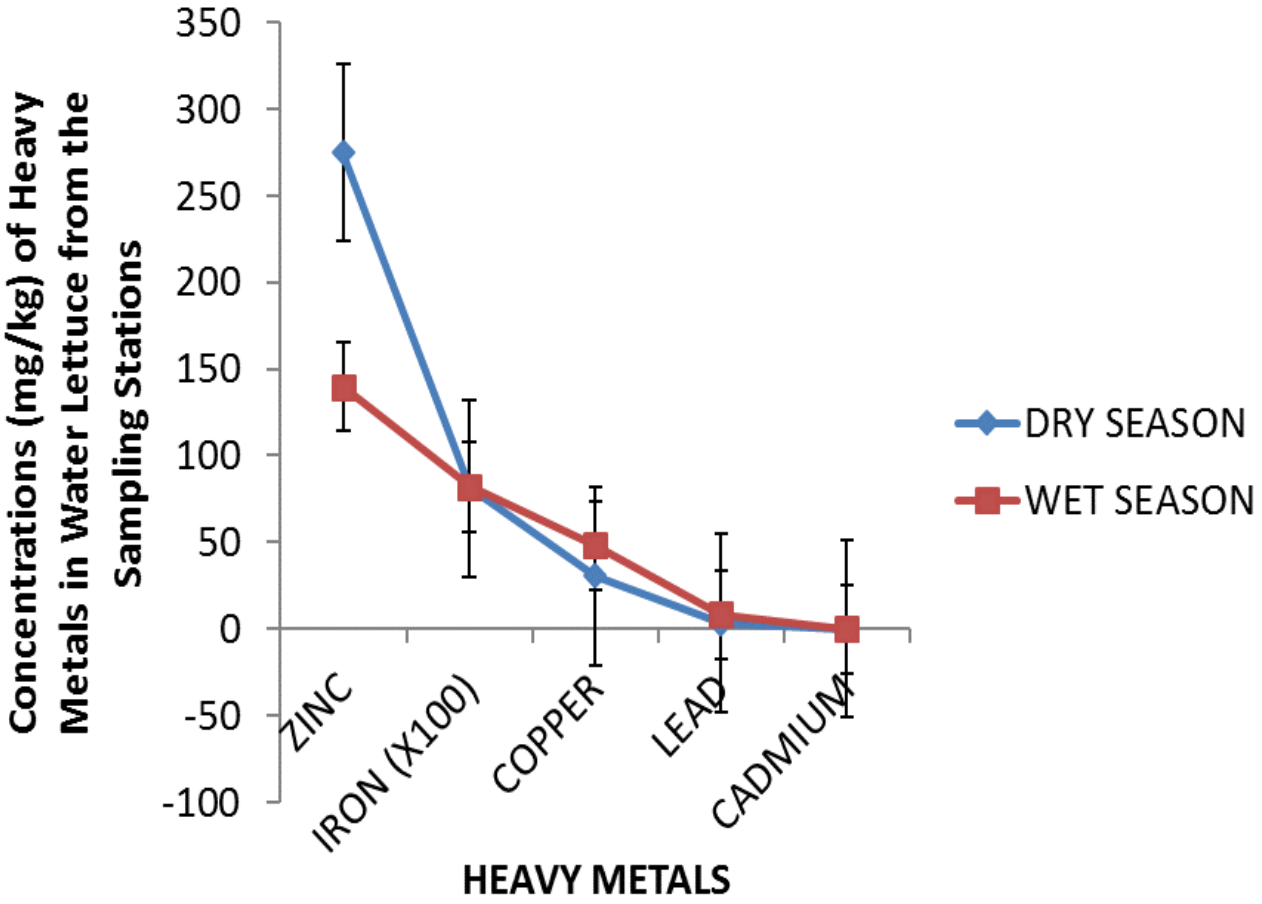


Fig. 4.5: Seasonal dynamics of heavy metal concentration (mg/kg) in Water Lettuce from the sampling stations

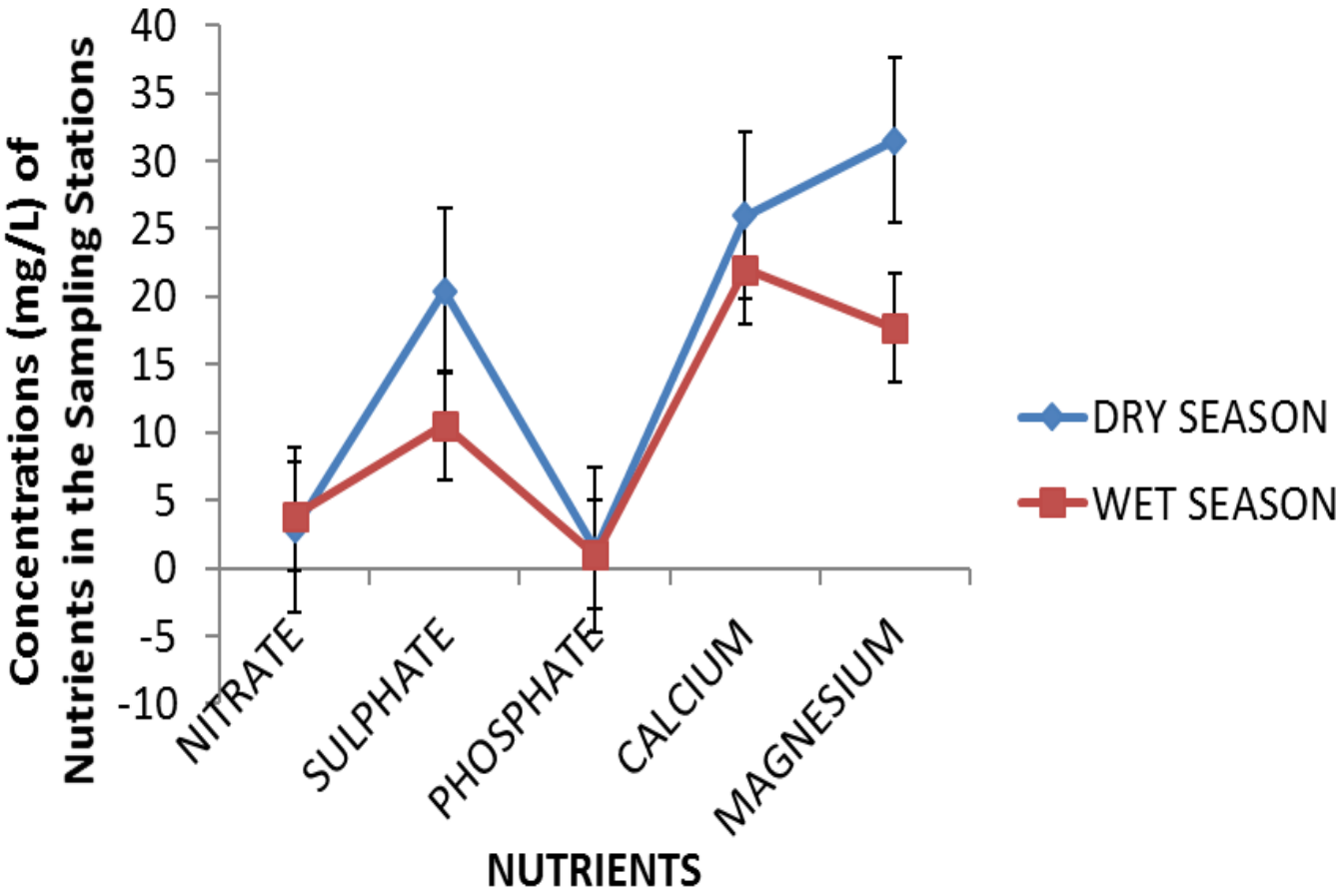


Fig. 4.6: Seasonal dynamics of Nutrients (mg/L) in the sampling stations

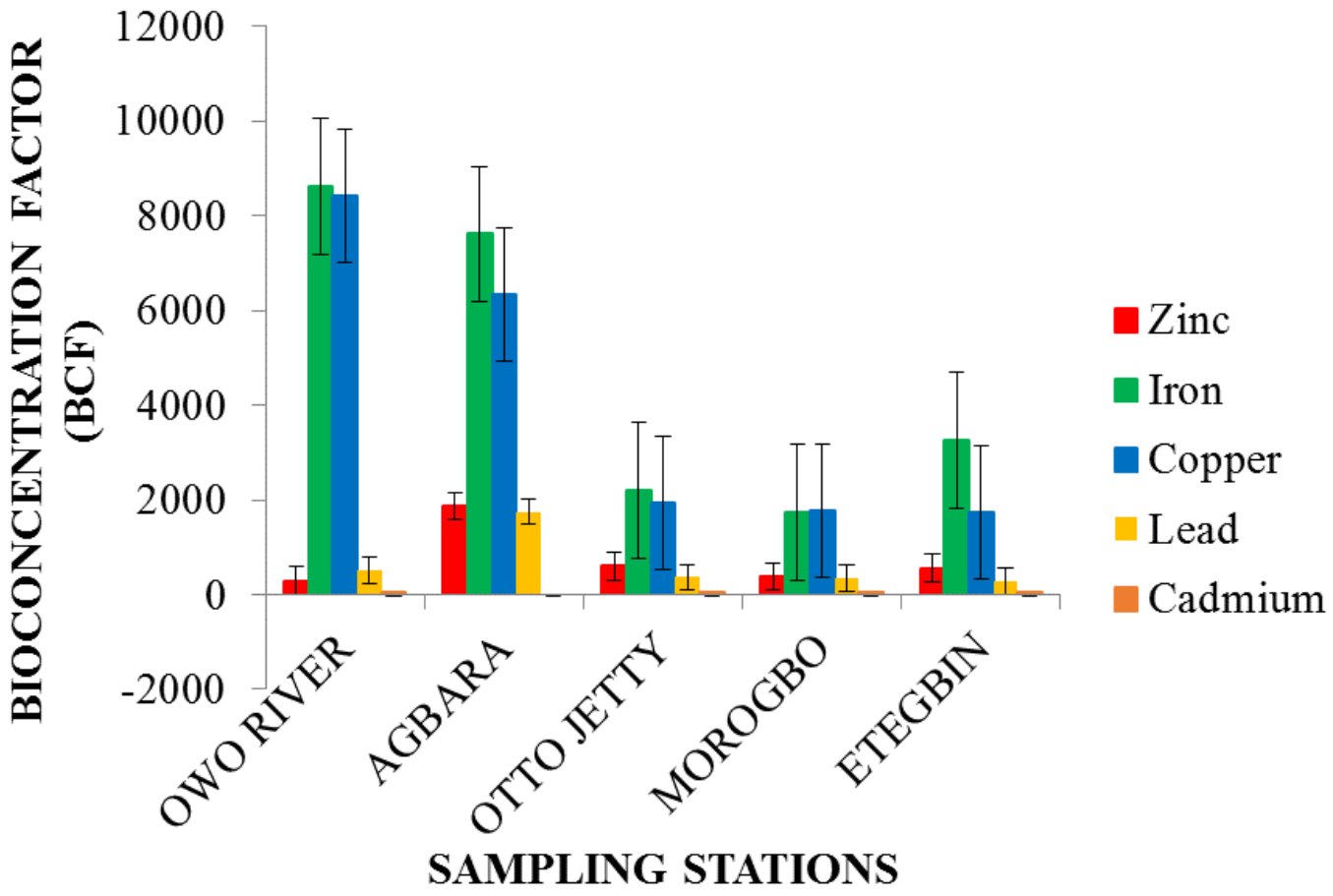


Fig. 4.7: Bioconcentration Factors (BCF) of Heavy Metals in Water Hyacinth from the Sampling Stations

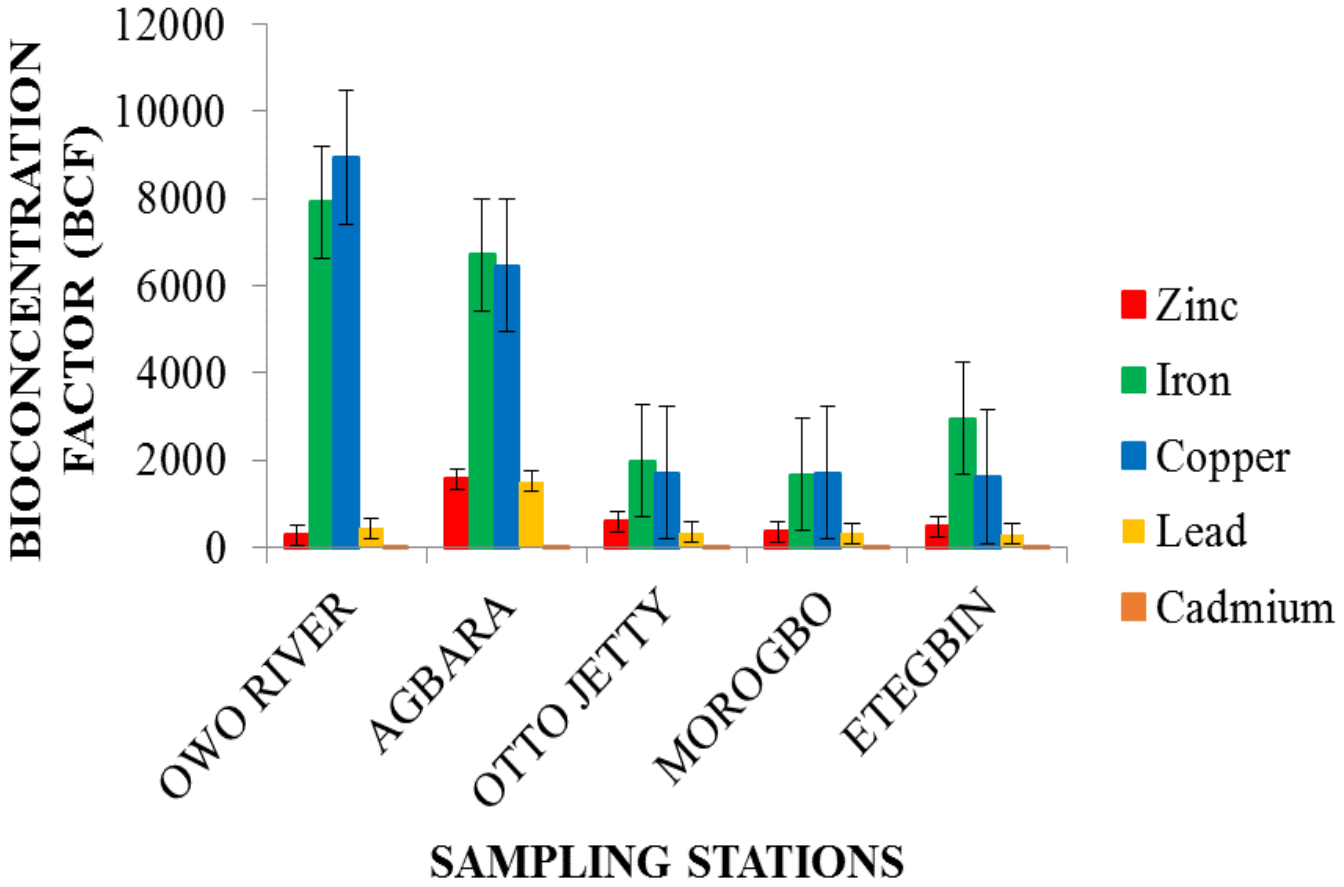


Fig. 4.8: Bioconcentration Factors (BCF) of Heavy Metals in Water Lettuce from the Sampling Stations

4.15 Heavy metal accumulation in Water Hyacinth (*Eichhornia crassipes*) in the Laboratory Experiment

The mean values of the heavy metals (Zn, Fe, Cu and Pb) accumulation at different concentration gradients in phytoremediation tests are shown in Table 4.13. All the metals followed the same general trend; the metal accumulated was proportional to the initial concentration of the metals in water. Water hyacinth accumulated significantly ($p<0.05$) higher concentration of the metals in experimental units spiked with the compounds of those metals than the control except in Cu. Pots seeded with Fe maintained green colouration for a longer time than those seeded with Cu, Zn and Pb. The results also show that the root of water hyacinth accumulated more metals than the stem and leaf regardless of the initial concentration of the metals.

4.16 Heavy metal accumulation in Water Lettuce (*Pistia stratiotes*) in the Laboratory Experiment

The accumulation of the metals (Zn, Fe, Cu and Pb) in Water Lettuce (*Pistia stratiotes*) is presented in Table 4.14. Just like the experiment with water hyacinth, all the experimental units followed the same trend; metal accumulation varied proportionally as the initial concentration of the metals in water. That is, the treatment spiked with the highest concentration of metal accumulated most metal and the experimental unit spiked with the least concentration of metal accumulated least metal. The accumulation of metals by water lettuce in experimental units spiked with metals were significantly higher ($p<0.05$) than the control, which contained only water lettuce and no metal. In all cases, the root of water lettuce accumulated more metals than the leaf.

Table 4.13: Heavy metals Concentration (mg/kg) in shoots and roots of water hyacinth (Phytoremediation)

Plant Parts	Treatment			
Zn				
	Control	10 mg/L	15 mg/L	20 mg/L
Leaf (mg/kg)	0.15±0.04[a]	5.56±0.09[b]	8.89±0.60[b]	15.58±0.15[c]
Stem (mg/kg)	0.13±0.06[a]	6.96±0.16[b]	7.49±0.35[b]	16.48±0.44[c]
Root (mg/kg)	0.14±0.08[a]	14.40±1.09[b]	15.45±2.14[b]	18.50±3.16[b]
Fe				
Leaf (mg/kg)	0.13±0.74[a]	6.88±1.60[b]	10.23±2.42[b]	6.78±1.06[b]
Stem (mg/kg)	0.15±0.74[a]	7.50±0.13[b]	8.88±1.21[b]	9.67±1.33[b]
Root (mg/kg)	0.16±0.79[a]	13.33±1.48[b]	11.03±1.23[b]	15.03±2.66[b]
Cu				
	Control	10 mg/L	15 mg/L	20 mg/L
Leaf (mg/kg)	0.13±0.03[a]	0.45±0.06[a]	0.55±0.10[a]	0.63±0.05[a]
Stem (mg/kg)	0.14±0.04[a]	0.55±0.06[a]	0.33±0.05[a]	0.48±0.14[a]
Root (mg/kg)	0.13±0.05[a]	0.40±0.07[a]	0.45±0.13[a]	0.50±0.16[a]
Pb				
Leaf (mg/kg)	0.13±0.03[a]	3.76±0.90[b]	5.45±0.82[b]	6.69±1.12[b]
Stem (mg/kg)	0.17±0.04[a]	4.61±0.11[b]	7.93±1.32[b]	9.87±1.45[b]
Root (mg/kg)	0.16±0.06[a]	8.49±1.67[b]	10.49±1.58[b]	12.86±1.98[b]

Values with same alphabet on the same row are not significantly different (P<0.05)

Table 4.14: Heavy metals Concentration (mg/kg) in leaves and roots of water lettuce (Phytoremediation)

Plant Parts		**Treatment**		
Zn	Control	10 mg/L	15 mg/L	20 mg/L
Leaf (mg/kg)	0.11±0.02[a]	3.43±0.12[b]	4.45±0.32[b]	5.87±0.57[b]
Root (mg/kg)	0.16±0.07[a]	4.56±0.91[b]	5.86±1.21[b]	7.49±1.78[b]
Fe				
Leaf (mg/kg)	0.12±0.04[a]	3.65±0.81[b]	5.11±1.13[b]	6.67±1.17[b]
Root (mg/kg)	0.15±0.09[a]	4.78±1.23[b]	6.16±1.43[b]	7.45±1.51[b]
Cu				
	Control	10 mg/L	15 mg/L	20 mg/L
Leaf (mg/kg)	0.09±0.03[a]	0.47±0.05[b]	0.61±0.06[b]	0.74±0.08[b]
Root (mg/kg)	0.11±0.05[a]	0.51±0.09[b]	0.68±0.12[b]	0.76±0.14[b]
Pb				
Leaf (mg/kg)	0.03±0.01[a]	0.36±0.06[b]	0.61±0.12[b]	0.78±0.09[b]
Root (mg/kg)	0.06±0.02[a]	0.45±0.08[b]	0.54±0.08[b]	0.81±0.10[b]

Values with same alphabet on the same row are not significantly different ($P<0.05$)

4.17 Translocation of metals (Zn, Fe, Cu and Pb) from Root to stem and leaf of Water Hyacinth in the Laboratory Experiment

The translocation factors of the metals from root to stem and leaf is shown in Table 4.15. All the metals showed measurable translocation from root to stem and leaf. The translocation factors in the experimental units spiked with metals at different concentrations (10mg/L, 15 mg/L and 20 mg/L) were significantly ($p<0.05$) higher than the values obtained in the control. However, there was no significant ($p>0.05$) difference in the translocation factors amo0n0g0 0t0h0e0 0t0r0e0a0t0m0e0n0t0s0 0s0p0i0k0e0d0 0w0i0t0h0 0m0e0t0a0l0s0.0 0T0h0e0 0t0ranslocation factors in stems were generally higher than the values obtained in leaves for the control, 10 mg/L and 20 mg/L but lower in 15 mg/L.

4.18 Translocation of metals (Zn, Fe, Cu and Pb) from Root to Leaf of Water Lettuce in the Laboratory Experiment

The translocation of the metals in water lettuce is presented in Table 4.16. The translocation factor varied proportionally with the initial concentration of metal in water. The translocation factors of metals in treatments spiked with various concentrations of the metals were significantly ($p<0.05$) higher than the values recorded in the control.

From Tables 4.15 and 4.16, it is obvious that water hyacinth has a higher translocation of the metals from water.

Table 4.15: Translocation factor of metals (Zn, Fe, Cu and Pb) in Water Hyacinth shoots

Translocation Factor				
Plant Parts	**Treatment**			
Zn	Control	10 mg/L	15 mg/L	20 mg/L
Leaf	0.14±0.02[a]	10.21±1.69[b]	13.45±2.01[b]	4.24±3.08[b]
Stem	0.15±1.42[a]	10.34±2.85[b]	8.63±2.43[b]	10.31±2.68[b]
Fe				
Leaf	0.25±0.04[a]	5.13±0.95[b]	8.95±1.28[b]	5.03±1.35[b]
Stem	0.63±0.09[a]	5.45±0.45[b]	8.25±1.32[b]	7.13±1.68[b]
Cu				
Leaf	0.13±0.08[a]	12.00±1.78[b]	15.00±5.00[b]	10.00±4.06[b]
Stem	0.25±0.11[a]	14.88±2.33[b]	9.50±3.52[b]	11.00±2.61[b]
Pb				
Leaf	0.34±0.05[a]	4.25±0.93[b]	6.87±1.21[b]	5.42±1.12[b]
Stem	0.74±0.07[a]	5.67±0.78[b]	6.56±1.03[b]	7.06±1.09[b]

Values with same alphabet and on the same row are not significantly different ($P<0.05$)

Table 4.16: Translocation factor of metals (Zn, Fe, Cu and Pb) in Water Lettuce leaves

Translocation factor				
Plant Parts	Treatment			
Zn	Control	10 mg/L	15 mg/L	20 mg/L
Leaf	0.43±0.08[a]	5.12±0.81[b]	6.51±1.03[b]	7.34±1.12[b]
Fe				
Leaf	0.34±0.04[a]	3.89±0.86[b]	5.01±1.02[b]	6.05±1.21[b]
Cu				
Leaf	0.36±0.09[a]	5.80±1.11[b]	7.23±1.34[b]	8.12±1.56[b]
Pb				
Leaf	0.46±0.03[a]	4.57±0.97[b]	5.98±1.01[b]	6.39±1.13[b]

Values with same alphabet and on the same row are not significantly different ($P<0.05$)

4.19 Bioconcentration Factor (BCF) of Metals in Water Hyacinth in the Laboratory Experiment

The bioconcentration factors (BCF) of the investigated metals (Zn, Fe, Cu and Pb) in water hyacinth in the laboratory experiment are shown in Table 4.17. There was no significant variation ($p>0.05$) in BCF values recorded in the different experimental units. However, the values obtained in treatments spiked with 20 mg/L were generally higher than the values recoded in the other treatments.

4.20 Bioconcentration Factor (BCF) of Metals in Water Lettuce in the Laboratory Experiment

Table 4.18 shows the bioconcentration factors (BCF) of the investigated metals (Zn, Fe, Cu and Pb) in water lettuce in the laboratory experiment. The values obtained were not significant ($p>0.05$) and were generally dependent on the initial concentration of the metal in water.

On the average, *E .crassipes* has a higher bioconcentration ability of all the elements that *P. stratiotes* (Table 4.17 and 4.18).

4.21 Removal of Metals by the Aquatic Plants

The coefficient of determination (r^2) for linear plots using the first-order model gave higher values than the values obtained using the second-order model in ten of the twelve experimental units (Table 4.19). Therefore, the first-order model provides a better description of the metal removal rates in the present experiment. However, for higher concentration of 15 mg/L and 20 mg/L Fe, second order kinetics is a better model for the removal of the element (Table 4.19).

Table 4.17: Bioconcentration Factor (BCF) of metals (Zn, Fe, Cu and Pb) in Water Hyacinth

	Bioconcentration Factor		
Plant Parts	**Treatments**		
Zn	10 mg/L	15 mg/L	20 mg/L
Leaf	0.16±0.04[a]	0.15±0.05[a]	0.21±0.07[a]
Stem	0.15±0.04[a]	0.13±0.03[a]	0.16±0.04[a]
Root	0.18±0.04[a]	0.21±0.05[a]	0.23±0.06[a]
Fe			
Leaf	0.69±0.16[a]	0.68±0.16[a]	0.34±0.05[a]
Stem	0.75±0.13[a]	0.59±0.08[a]	0.49±0.07[a]
Root	1.33±0.15[a]	0.74±0.08[b]	0.75±0.13[a]
Cu			
Leaf	0.05±0.01[a]	0.04±0.01[a]	0.02±0.01[a]
Stem	0.06±0.01[a]	0.03±0.01[a]	0.03±0.01[a]
Root	0.08.± 0.03[a]	0.13±0.09[a]	0.21±0.08[a]
Pb			
Leaf	0.51±0.05[a]	0.66±0.08[a]	0.54±0.06[a]
Stem	0.67±0.06[a]	0.61±0.09[a]	0.6.23±0.06[a]
Root	1.43±0.11[a]	0.82±0.09[b]	1.34±0.15[b]

Values with same alphabet on the same row are not significantly different (P<0.05)

Table 4.18: Bioconcentration Factor (BCF) of metals (Zn, Fe, Cu and Pb) in Water Lettuce

Bioconcentration Factor			
plant Part	**Treatment**		
Zn	10 mg/L	15 mg/L	20 mg/L
Leaf	0.05±0.01[a]	0.05±0.01[a]	0.07±0.02[a]
Root	0.07±0.02[a]	0.08±0.02[a]	0.09±0.03[a]
Fe			
Leaf	0.08±0.03[a]	0.10±0.04[a]	0.12±0.05[a]
Root	0.10±0.05[a]	0.14±0.06[b]	0.17±0.04[b]
Cu			
Leaf	0.03±0.01[a]	0.03±0.01[a]	0.04±0.01[a]
Root	0.04.± 0.03[a]	0.05±0.02[a]	0.07±0.03[a]
Pb			
Leaf	0.05±0.01[a]	0.06±0.02[a]	0.08±0.04[a]
Root	0.05±0.01[a]	0.08±0.03[b]	0.09±0.04[b]

Values with same alphabet on the same row are not significantly different (P<0.05)

Table 4.19: Comparison of coefficients of determination (r^2) for first order and second order linear models for the Phytoremediation experiments

Treatment model	First-order linear model r^2	Second-order linear model r^2	Preferred
	Initial Metal Concentration (10 mg/L)		
Zinc	0.95	0.94	First-order
Iron	0.93	0.92	First-order
Copper	0.95	0.81	First-order
Lead	0.89	0.89	First-order
	Initial Metal Concentration (15 mg/L)		
Zinc	0.98	0.96	First-order
Iron	0.90	0.94	Second-order
Copper	0.85	0.70	First-order
Lead	0.86	0.79	First-order
	Initial Metal Concentration (20 mg/L)		
Zinc	0.97	0.96	First-order
Iron	0.97	0.99	Second-order
Copper	0.99	0.97	First-order
Lead	0.87	0.81	First-order

CHAPTER FIVE

DISCUSSION

5.1 Physico-chemistry of the Study Areas

The results of the analysis of the physico-chemical parameters revealed that the following parameters had significant ($p<0.05$) spatio-temporal variation; conductivity, total suspended solids, total dissolved solids, salinity, acidity, alkalinity, chemical oxygen demand and dissolved oxygen in the stations. The values recorded for pH, temperature and alkalinity fall within the range (pH 6.5–9.5, temperature <40 °C and total alkalinity 20 mg/l as $CaCO_3$) recommended by the Federal Environmental Protection Agency (FEPA, 2003) for the survival of aquatic fauna and flora. However, dissolved oxygen concentrations was slightly above the value of 5.0 mg/L recommended by FEPA (2003).

The dissolved oxygen content of the water bodies did not show significant ($p>0.05$) variation. Earlier studies by Uka and Chukwuka (2007) and Ndimele (2012) indicated that water hyacinth infestation has significant ($p<0.05$) effects on the dissolved oxygen content of freshwater bodies. In addition, Frodge *et al.* (1995) reported that dissolved oxygen content was lower in patches of the *Brasinia scherberi* in lake Northwest of United States of America. Ndimele (2012) reported that the mean value of dissolved oxygen recorded in Badagry Creek (4.48±0.19 mg/L) was higher than the value (4.18±0.17 mg/L) in Ojo. He further opined that the relatively high value of dissolved oxygen recorded in Ojo compared to the two other stations that had water

hyacinth might be due to the dredging activities in the site. This could cause frequent mixing of atmospheric oxygen with the water and this could result in increased oxygen content of the water.

Conductivity has a direct correlation with total dissolved solids, salinity (total salt content), mineralization and nutrient status of an aquatic ecosystem (Uka and Chukwuka, 2007; Akan *et al.*, 2008). The range of conductivity (119.48±13.67 - 8847±5339 µS/cm) observed in the sampling stations in the present study is above the range reported by Uka and Chukwuka (2007) and Akan *et al.* (2008). Kumolu-Johnson and Ndimele (2012) studied the physico-chemistry of Ologe Lagoon, Lagos, Nigeria and reported conductivity values ranging from 117±53.33 – 605.00±180.58 µS/cm. The increase in value recorded in the present study might be due to dredging activities in some of the sampling stations including Ologe Lagoon (Agbara, Otto Jetty and Morogbo). Dredging could cause increased mineralization, which might lead to increase in conductivity, total dissolved solids and salinity (Ndimele *et al.,* 2009).

Biological oxygen demand (BOD) is a measure of the biological activities of a water body. It is an indication of the organic load and it is a pollution index especially for water bodies receiving organic effluent. The range of BOD (2.40±0.24 – 4.40±0.24 mg/l) recorded in this study is lower than the values (8.0 – 22.4 mg/L) reported by Nyananyo*et al.* (2007) in River Nun, Bayelsa State, Nigeria. High BOD in water hyacinth-infested aquatic ecosystem have been attributed to the decomposition of dead plant (Nyananyo *et al.*, 2007). Organic matter decomposition requires oxygen from the water. This increases the BOD, which reduces the dissolved oxygen available to aquatic organisms for survival.

5.2 Heavy Metal Content in Water

The heavy metal content in water column gives an indication of the metal load in the aquatic ecosystem. The heavy metal content in water column of the sampling stations were low and did not show any significant ($p>0.05$) spatio-temporal variation. The values of Fe (0.22±0.01 – 0.29±0.02 mg/L) and Pb (0.01±0.001 mg/L) recorded in the present study are lower than the values reported in previous studies by Kumolu-Johnson *et al*. (2010) and Agboola *et al.* (2008) in Ologe Lagoon and Badagry Creek respectively. The reduction of these heavy metals may be due to phytoremediation by water hyacinth and water lettuce over time. However, Zn (0.03±0.002 – 0.05±0.004 mg/L) and Cu (0.01±0.001 mg/L) are higher than previously reported values indicating that increases in the number of industries and industrial activities in Agbara Industrial Estate may have resulted in additional industrial effluents, which are eventually emptied into Ologe Lagoon.

The concentrations of all the heavy metals did not show significant ($p<0.05$) variation among the sampling stations and they are lower than the values obtained in Makera Drain, which receives effluent from textile companies in Kaduna, northern Nigeria (Ali *et al.*, 2005). Although, the complexity of interaction between different compartments of an ecosystem makes it difficult to draw firm conclusions, the concentrations of these metals in water column are within the range of values reported for unpolluted freshwater bodies in Nigeria (Kusemiju*et al.*, 2001, Anetekhai*et al.*, 2007, Obasohan and Eguavoen, 2008). Adefemi*et al.* (2008) did not detect Cu, but reported mean Zn and Fe concentrations of 30 µg/L and 80 µg/L respectively in Ureje Dam in south-western Nigeria. Obasohan and Eguavoen (2008) reported Cu and Zn ranges of 1.0 - 63 µg/L and 1.0 – 110 µg/L respectively in the Ogba River, Benin City, Nigeria.

The mean concentrations of the heavy metals (Zn, Fe, Cu, Pb and Cd) in the water column of the sampling stations are below the World Health Organisation limits for drinking water (Cu = 2.0 mg/L; Fe = 2.0 mg/L; Zn = 3.0 mg/L; Pb = 0.015 mg/L; Cd = 0.005 mg/L) (WHO, 2008). The range of concentrations of Cu and Fe in this study are below the limits (Cu, 4.7 µg/L for a 4-day average at 45 mg/L hardness; Fe, 1000 µg/L) recommended by United States Environmental Protection Agency (USEPA, 1996) for the protection of aquatic ecosystems. However, the value of Zn is higher than the USEPA (1996) limit for Zn (6 µg/L at 45 mg/L hardness) for the protection of aquatic ecosystems. Although, the results of the metal content in water column indicate reduction when compared with previous studies and the values are still lower than the recommended limits set by World Health Organisation, it is important to monitor these water bodies regularly in order to detect sudden changes and take appropriate steps to avert dangers to aquatic organisms and man.

5.3 Heavy Metal Content in Sediment

Two of the investigated heavy metals (Fe and Cu) have increased from the values reported in previous studies in Ologe Lagoon and Badagry Lagoon by Kumolu-Johnson *et al* (2010) and Agboola *et al* (2008) respectively. This indicates that these heavy metals discharged into Ologe Lagoon from Agbara Industrial Estate have been on the increase. However, the values of Zn and Pb have decreased compared to previously reported values. A possible reason for this decline might be the massive invasion of sampling stations by water hyacinth and water lettuce from neighbouring Republic of Benin (Edewor, 1988). Water hyacinth and water lettuce have been reported to absorb metals (Wolverton and McDonald, 1978) and have been used as a phytoremediation species especially water hyacinth. Clearing and harvesting of this

plants for easy navigation by fishermen could reduce the metal load in the sampling stations. The values of Cu (Table 4.4) recorded in this study is higher than the WHO recommended limit of 2 mg/kg (WHO, 2008) and Fe (Table 4.4) is also higher than the USEPA limit of <0.3 mg/kg (USEPA, 2008). The higher concentrations of Fe in the sediment obtained in this study have also been reported in previous studies in Ondo State coastal region (Asaolu and Olaofe, 2005). They opined that the high level of Fe may be due to anthropogenic activities and the fact that Fe occurs in high concentrations naturally in Nigerian soils.

5.4 Heavy Metal Content in Water Hyacinth (*Eichhornia crassipes*) and Water Lettuce (*Pistia stratiotes*)

The concentrations of the heavy metals in water hyacinth and water lettuce showed significant variation among the sampling stations (Tables 4.5 and 4.6). The values of the metals in Agbara (sampling site closest to effluent discharge point from Agbara Industrial Estate) were significantly ($p<0.05$) higher than the values obtained from other stations, indicating that effluents from this estate contains heavy metals, which are absorbed by the biota in this environment including water hyacinth and water lettuce. The values of Zn and Fe recorded in this study are higher than the values reported in previous study in Ologe Lagoon (Zn, 1.73±0.68 ppm; Fe, 4.90±1.69 ppm) (Ndimele and Jimoh, 2011). In addition, the metal concentrations in water hyacinth and water lettuce from the sampling stations are also lower than the background range (Zn, 0.03 – 0.05ppm; Fe, 0.87 – 1.48; Pb, 0.03 – 0.05) found in plants (Kabata-Pendias and Pendias, 1992). The increase in some of the metal concentrations in the aquatic plants is because of the values recorded in the water columns and sediments. Oyewo (1998) reported that the concentration of heavy metals found in biota (plants

and animals) of an ecosystem is a function of the values of these heavy metals in the abiotic components (water and sediment) of the same ecosystem.

5.5 Bioconcentration Factors of Heavy Metals in Water Hyacinth and Water Lettuce from the Sampling Stations

The bioconcentration factors (BCF) recorded in this study (Figs. 4.7 and 4.8) are higher than the values (Zn, 53.88; Pb, 6.33) reported by Nirmal-Kumar *et al.* (2008). The ability of water hyacinth and water lettuce to absorb and concentrate these heavy metals even when their values in water are low clearly shows that these aquatic plants could be good phytoremediants.

5.6 Heavy metal uptake

In the Phytoremediation experiment, the accumulation of heavy metal in the plant tissues varies with the concentration gradient. The analysed result shows that water hyacinth and water lettuce absorbed the highest concentration of the metals at 20mg/L. This shows that the aquatic plants can tolerate the metals at a high concentration. According to Srivastava *et al.*,(2006), copper does display a toxic effect at high concentrations, impairing the permeability of the membrane, chromatin structure, enzyme activity, the process of photosynthesis and respiration.

5.7 Translocation factor

The translocation Factor (TF) of the heavy metals (Zn, Fe, Cu and Pb) under investigation at each concentration gradient (10, 15 and 20 mg/L) shows that water hyacinth (*E. crassipies*) and water lettuce (*P. stratiotes*)accumulates all the heavy metals and translocate them to the shoots, but the highest translocation value for Zn,

Fe and Cu was in the treatment spiked with metals at concentration of 15mg/L. However, the highest translocation factor in Pb was recorded in experimental unit spiked with 20mg/L.

5.8 Bio-concentration Factor in Phytoremediation Experiment

BCF is defined as the ratio of metal concentration in the plant to the initial concentration of metal in the substrate. Higher values of BCF indicate the ability of plants to concentrate metals in their tissues (Ndimele, 2012). Water hyacinth (Table 4.17) and water lettuce (Table 4.18) concentrated/accumulated more metals in the root than in other parts of the plants. According to Lu *et al*. (2010), accumulation of heavy metal by macrophytes can be influenced by the concentration of the heavy metals present in the water medium. In general, a plant with a BCF of more than 1000 is considered a hyper-accumulator. A plant with a BCF of 1 to less than 1000 is considered an accumulator, and with a BCF of less than 1 as an excluder. Since the BCF values obtained in this study are less than 1, water hyacinth and water lettuce can be considered excluder. From the point of view of phytoremediation, a good accumulator has been defined as having the ability to concentrate the heavy metal in its tissues (Zayed*et al*., 1998).

5.9 Kinetic Modelling of the Removal of Metals by the Aquatic Plants

The time evolution of contamination/pollution in this study is best described by the simple first-order kinetic model because the coefficient of determination (r^2) for the first-order kinetic model was higher than the values obtained for the second-order kinetic model for Zn, Cu, Pb for all concentrations and 10m mg/L for Fe but second order for Fe in 15 mg/L and 20 mg/L concentrations. Previous studies (Namkoong*et*

al, 2002; Nocentini*et al.*, 2000) have reported that heavy metal absorption from contaminated media is suitably described by first-order kinetics. The first-order kinetic model implies an exponential decay of substrate concentration with an asymptote to zero (Namkoong*et al.*, 2002).

CONCLUSION

The wind of industrialisation currently blowing in Nigeria should take all aspects of the environment into consideration so that these efforts will result in sustainable development. Although, the results of this study showed that heavy metal values in Ologe Lagoon are still lower than the recommended limits set by World Health Organisation, it is important to monitor these water bodies regularly in order to detect sudden changes and take appropriate steps to avert dangers to aquatic organisms and man. Effluents generated by industries should be treated and rendered harmless before they are discharged into inland water bodies, so that these aquatic ecosystems can continue to provide their services to man and his environment.

Although, water hyacinth and water lettuce have been described as noxious weeds but their abilities to absorb heavy metals from the aquatic environment can be harnessed. This potential of the plants is capable of changing their status from nuisance to economic plants. The results of the metal content in water column in this study indicated reduction in concentration when compared with previous studies. This suggests that water hyacinth and water lettuce, which are present in these water bodies may be accumulating the metals. However, the rate of bioaccumulation is low indicating that these aquatic plants are excluders.

The time evolution of contamination/pollution in this study is best described by the simple first-order kinetic model.

RECOMMENDATIONS

Under the guise of industrial revolution, various discomforting demands are being made on the environment. From what have been revealed in recent time, strategies to solve the global food, energy and economic problems must not be developed in isolation, but in full consideration of the web of interdependence that exist with other major problems facing mankind today. In view of the importance of industrialization to man, their attendant ecological effects must always be kept in mind. It is for this reason that the following suggestions are made:

- Government at Federal and State levels should increase the budgetary allocation to their Ministries of Environment.
- Government and International donor agencies should fund inter-disciplinary research programmes in phytoremediationaimed aimed at restoring Nigeria's heavy metal-polluted ecosystems to its initial status before pollution.
- Finally, the effects of heavy metal absorption on the physiology of water hyacinth and water lettuce should be studied.

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