SPATIAL AND TEMPORAL VARIATIONS OF PHYSICOCHEMICAL CHARACTERISTICS OF SURFACE WATER AND SEDIMENT OF OSUN RIVER IN SOUTHWESTERN NIGERIA

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DEDICATION

I dedicate this research work to:

- Almighty ALLAH. The Most Gracious, Most Merciful, Originator of Heavens and Earth, Full of Majesty and Honour,
- My loving husband, Engineer Rahman Tunde,
- My children of destiny: Aishat, Waliyat, Aminat and Rilwanulahi for their persevearance, endurance, cooperation and encouragement, and
- My parents, late Engineer Alade Oladipo and Mrs Olalonpe Oladipo, for making me what I am today.

ABSTRACT

Osun River is important for domestic, recreational and other activities. It flows along a channel that may be polluted by inputs from industrial, agricultural and other anthropogenic activities thereby limiting its normal use for drinking, fishing, recreation and other purposes. Available literature on the river quality is limited in scope, frequency of sampling and duration of studies. Therefore, a study of the river and its tributaries was carried out to determine the spatial and temporal variations of physicochemical characteristics of its water and sediment.

Surface water and sediments were sampled bimonthly from July 2006 to May 2008 at upstream and downstream points of the main river course and 31 tributaries. Sampling was by compositing at each point of 90 locations for surface water and 63 identified locations for sediment, where possible. Water samples were analysed for alkalinity, hardness, ammonia, anions, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), heavy metals and turbidity. Sediment samples were analysed for organic carbon, particle size and selected heavy metals using APHA methods. Location-based and overall data obtained were fitted into a time series model using a number cruncher statistical system, and applied to predict contaminant concentrations up to year 2018. The Pratti model was applied to determine locational pollution classes (Class 1-5) based on gross organic pollutants and ammonia. Statistical evaluation of data involved use of principal component analysis, analysis of variance and Student's t-test at $p = 0.05$.

The concentrations (mg/L) of alkalinity, hardness, ammonia, nitrate, phosphate and chloride were 93±130, 116±120, 4.2±6.6, 1.8±1.5, 0.15±0.23 and 54±110 respectively. Those of DO, BOD, COD, lead, copper, cadmium and zinc were 7.9±3.0, 6.9±7.5, 135±120, 0.003±0.004, 0.003±0.004, 0.002±0.003, 0.07±0.10 mg/L respectively and turbidity, 34±43 FTU. Values of parameters for upstream locations did not differ significantly from downstream points, indicating randomness of contaminant inputs. Turbidity, sulphate and DO were higher during the wet seasons while phosphate, nitrate and BOD were higher in the dry seasons. Metal levels correlated positively between water and sediment, with coefficients ranging between 0.75 for Cu and 0.99 for Co. Highest concentration factors in sediment were 233 (Pb) and 171 (Zn). Inter-element association in sediment was high only for Pb/Cu ($r = +0.72$). Two locations fitted into Class 4 (grossly polluted) of the Pratti scale, while thirty-one were Class 3 (slightly polluted) which was indicative of pollution derived from mild industrial and agricultural impacts. Fifty-three locations were acceptable (Class 2), and four excellent (Class 1). Time series modelling fitted well for nitrate (R^2= 0.79), phosphate (R^2= 0.84) and BOD (R^2= 0.71) data and gave their 2018 predicted values of 19.2, 18.1 and 21.9 mg/L respectively. Comparison with WHO guidelines indicated that 37.0% of sampling points for surface water were unfit for drinking mostly due to high turbidities, but suitable for irrigation. Metal levels in sediment were within international limits.

Osun River and its tributaries have been adversely impacted upon by non-point pollutant inputs. Further deterioration in the near future was predicted, and heavy metal pollution is not yet a significant problem in the river basin.

Keywords: Osun River, Gross organic pollution, Modelling, Spatial variation, Water quality.

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CERTIFICATION

I certify that this research work was carried out under my supervision by OLAJUMOKE ABIDEMI **OLAYIWOLA,** in the Department of Chemistry, University of Ibadan, Ibadan Nigeria.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 ENVIRONMENTAL POLLUTION

Virtually all types of pollution are harmful to the health of humans and animals. Pollution may not damage ones health immediately but can be harmful after long term exposure. Pollution is the introduction of contaminants into an environment, of whatever predetermined or agreed upon proportions or frame of reference. These contaminants cause instability, disorder, harm, and discomfort to the physical systems or living organisms therein. Pollutants, the elements of pollution, can be foreign substances or energies, or naturally occurring. When naturally occurring, they are considered contaminants when they exceed natural threshold levels. Pollution in general is the activity of disturbing the natural system and balance of an environment.

The increase in pollution over the years by man has caused severe damage to the earth's ecosystem. It is responsible for global warming which is leading to the end of all lives on earth. Over the years has been extreme increase in the rate of human diseases, death rate and extinction of various animals and plants on earth, and that is all because of the pollution caused by man himself.

Until relatively recently in humanity's history, where ever pollution had existed, it has been primarily a local problem. The industrialization of society, the introduction of motorized vehicles, and the explosion of human population, however, have caused an exponential growth in the production of goods and services. Coupled with this growth has been a tremendous increase in waste by-products. The indiscriminate discharge of untreated industrial and domestic wastes into water ways, the spewing of thousands of tons of particulates and airborne gases into the atmosphere, the "throwaway" attitude toward solid wastes, and the use of newly developed chemicals without considering potential consequences have resulted in major environmental disasters. Technology has begun to solve some pollution problems, and public awareness of the extent of pollution will eventually force governments to undertake more effective environmental planning and adopt more effective antipollution measures.

1.1.1 Types of Pollution of Environmental Media

(a) Water pollution

About 75% of the earth's surface is covered with water and more than half of the total population of earth's species resides in water. Moreover, our life greatly depends on water and life without water is impossible. Water is essential for the development and maintenance of the dynamics of every ramification of society (Herschy, 1999; UNSCD, 2000). According to Gore (1993), human beings are made up of water, in roughly the same percentage as water is in the surface of the Earth. Our tissues and membranes, brains, and hearts, our sweat and tears- all reflect the same recipe for life, in which efficient use is made of those ingredients available on the surface of the earth.

Water pollution not only affects the fish and animals living in the water but also affects the whole food chain by also transferring the contaminants to the consumers depending on these animals. Water used from a polluted lake directly contaminates its user. Many water creatures are on the verge of extinction due to the dramatic increase in water pollution.

Conventional pollutants: Conventional or classical pollutants are generally associated with the direct input (mainly by human) of waste products. Rapid urbanization and rapid population increases have produced sewage problems because treatment facilities have not kept pace with need. Untreated and partially treated sewage from municipal wastewater systems and septic tanks in unsewered areas contribute significant quantities of nutrients, suspended solids, dissolved solids, oil, metals (arsenic, mercury, chromium, lead, iron and manganese), and biodegradable organic carbon to the water environment. Conventional pollutants may cause a myriad of water pollution problems. Excess suspended solids block out energy from the sun and thus affect the carbon dioxide-oxygen conversion process, which is vital to the maintenance of the biological food chain. Also, high concentration of suspended solids silt up rivers and navigational channels, necessitating frequent dredging. Excess dissolved solids make the water undesirable for drinking and for crop irrigation.

The Rhine River of Europe, once the most scenic river, is now called the longest sewer line in Europe (Shaheen and Chantarason, 1971). Although essential to the aquatic habitat, nutrients such as nitrogen and phosphorus may also cause over fertilization and accelerate the natural aging process (eutrophication) of lakes. This acceleration in turn produces an overgrowth of aquatic vegetation, massive algal blooms and an overall shift in the biologic community- from low productivity with large numbers of a few species of a less desirable nature.

Nonconventional pollutants: The nonconventional pollutants include dissolved and particulate forms of metals, both toxic and nontoxic and degradable and persistent organic carbon compounds discharged into water as a by-product of industry or as an integral part of marketable products. Nonconventional pollutants vary from biologically inert materials such as clay and iron residues to the most toxic and insidious materials such as halogenated hydrocarbons (DDT, kepone, mirex and polychlorinated biphenyls-PCB). The latter group may produce damage ranging from acute biological effects to chronic sub lethal effects that may go undetected for years. The chronic low-level pollutants are proving to be the most difficult to correct and abate because of their ubiquitous nature and chemical stability.

(b) Soil pollution

Land pollution is the degradation of the Earth’s land surface through misuse of the soil by poor agricultural practices, mineral exploitation, industrial waste dumping, and indiscriminate disposal of urban wastes (EPA, 1998).

The most common and convenient method of disposing of municipal solid wastes is in the sanitary landfill continuous urban development and large solid waste pose as major environmental risks because of the difficulties in disposal. Landfills and other solid wastes disposal sites are major targets of pollution because rainfall and groundwater leach these highly contaminated substances into rivers, streams and waterways (surface water) which are inadvertently used by people residing in such areas. The open dump, once a common eyesore in towns across the United States, that attracted populations of rodents and other pests and often emitted hideous odours is now illegal. Recycling of materials is practical to some extent for much municipal and some industrial wastes, and a small but growing proportion of solid wastes are being recycled. When wastes are commingled, however, recovery becomes difficult and expensive. Crucial issues in recycling are devising better processing methods, inventing new products for the recycled materials and finding new markets for them.

Incineration is another method for disposing solid wastes. Advanced incinerations use solid wastes as fuel, burning quantities of refuse and utilizing the resultant heat to make steam for electricity generation. Wastes must be burned at very high temperatures, and incinerator exhausts must be equipped with sophisticated scrubbers and other devices for removing dioxins and other pollutants. Problems remain, however: that since incinerator ash contains high ratios of heavy metals thus, becoming a hazardous waste itself; the high-efficiency incinerators may discourage the use of recycling and other waste-reduction methods. Compositing is increasingly used to treat some agricultural wastes, as well as such municipal wastes as leaves and bush. Compositing systems can produce usable soil conditioners, or humus, within a few months.

(c) Air pollution

Air pollution is the accumulation in the atmosphere of substances that, in sufficient concentrations, endanger human health or produce other measured effects on living matter and other measured effects on living matter and other materials. Among the major sources of pollution are power and heat generation, the burning of solid wastes, industrial process, and, especially, transportation. The six major types of pollutants are carbon monoxide, hydrocarbon, nitrogen oxides, particulates, sulfur dioxide, and photochemical oxidants.

Smog has seriously affected more persons than any other type of air pollution. It can be loosely defined as multisource, widespread air pollution that occurs in the air of cities. Smog, a concentration of the world's smoke and fog, has been caused throughout recorded history by water condensing on smoke particles, usually from burning coal. As a coal economy has gradually been replaced by a petroleum economy, photochemical smog has become predominant in many cities. Its unpleasant properties result from the irradiation by sunlight of hydrocarbons and other pollutants in the air. Air pollution on a regional scale is in part the result of local air pollution including that produced by individual sources, such as automobiles- that have spread out to encompass areas of many thousands of square kilometers. Oxides of sulfur and nitrogen carried long distances by the atmosphere and then precipitated in solution as acid rain, can cause serious damage to vegetation, waterways and buildings.

Humans also pollute the atmosphere on a global scale, although until the early 1970s little attention was paid to the possible deleterious effects of such pollution. Global warming is the biggest threat towards mankind since the Black Death, claiming millions of lives in the process. The effects of global warming are playing havoc everywhere-like higher temperatures, hurricanes, heavy rains, rise in the sea level; flooding and droughts have now become more frequent and severe in intensity. Certain pollutants decrease the concentration of ozone layer occurring naturally in the stratosphere, which in turn increases the amount of ultraviolet radiation reaching the Earth's surface. Such radiation may damage vegetation and increase the incidence of skin cancer. Examples of stratospheric contaminants include nitrogen oxides emitted by supersonic aircraft and chlorofluorocarbons used as refrigerants and aerosol-can propellants. The chlorofluorocarbons reach the stratosphere by upward mixing from the lower parts of the atmosphere. It is believed that these chemicals are responsible for the noticeable loss of ozone over the Polar Regions that have occurred in the 1980s.

1.2 WATER POLLUTION

Water Pollution is defined as the degradation of the natural quality of water due to the addition of harmful wastes in excessive concentrations (Knapp, 1970).

The causes of water pollution may be due to direct and indirect contaminant sources. The former are effluent outputs from refineries, factories and waste treatment plants. Fluids of differing qualities are emitted to the urban water supplies. In the United States and some other countries, these methods are controlled (Abhay, 2007). Still, pollutants can be found in the water bodies. Indirect contaminant sources are the water supply from soils and ground water systems that have fertilizers, pesticides and industrial wastes. Also, they include those from atmosphere such as factory emissions and automobile discharge. Continuous urban development and large solid waste pose major environmental risks because of the difficulties in disposal. Landfills and other solid wastes disposal sites are major sources of pollution because rainfall and groundwater leach these highly contaminated substances into rivers, streams and waterways (surface water) which are inadvertently used by people residing in such areas. Stranberg (1971) include sewage and other oxygen demanding wastes, infectious agents, organic chemicals, other chemicals and mineral substances, sediments (turbidity), radioactive substances and thermal pollution. Human activities that may result to water pollution include the following, agriculture, irrigation, urbanization, mining, fire and industrialization (Goudie, 1990). These activities have been documented to have impacted negatively on some specified Nigerian surface water (Olajire *et al*., 2003). Of particular interests are the heavy metals because of their very toxic nature. The modern era of industrialization has increased the spread of environmental contamination by heavy metals. Heavy metals toxicity dates back to ancient period. The heavy metals of interest include lead, chromium, cadmium, iron, zinc, manganese, mercury, arsenic, copper etc. According to Freedman (1989) the chemical form of toxic elements dissolved in water is generally relatively available to biota and even seemingly small aqueous concentrations may exert a powerful toxic effect. Though these trace elements are usually present in the environment, they are potentially extremely toxic and not only would they affect the biota at a water soluble concentration, at less than 1ppm, humans can be grossly affected.

The supply of water in several cities is limited, and in many cases, water supply is chronically insufficient for the inhabitants. Despite the inadequacy of water supply, the management and conservation of the available water bodies is generally poor. Industrial growth is fast increasing globally, and so is the water demand for industrial productions or processes. This has put more pressure on the limited available water resources. Water bodies are also constantly used as receptacles for untreated waste water. Poorly treated effluents accruing from industrial activities have rendered many water bodies unsuitable for both primary and secondary usage.

River water quality is often a useful indicator of the state of community health in underdeveloped countries, where, because of inadequate supply of treated tap water, river water serves as a direct source of drinking water, in addition to its normal uses for irrigation, recreation and fishing. The impairment of river in urban settlements of such communities has been shown to be the primary source of health hazards in some cases (Adesina, 1986). Besides the modifying influence on river water quality by natural processes such as weathering of bedrock minerals, leaching of soil nutrients and evapotranspiration, anthropogenic activities which significantly impact on urban river water quality in under-developed communities include the discharge of industrial and domestic wastes into river courses.

1.3 CLASSIFICATION OF THE CAUSES OF WATER POLLUTION

The major sources of water pollution can be classified as municipal, industrial, agricultural and oil spills.

(a) Municipal Water Pollution

Municipal waste is a source of water pollution especially where combined sewers are used to empty both storm water and sanitary wastes into the same water body, usually without being treated. This consists of wastewater from homes and commercial establishments. The contents of municipal water include suspended solids, oxygen-demanding materials, dissolved inorganic compounds and harmful bacteria. Detergent waste containing alkylbenzene sulfonate for instance is not biodegradable and causes foaming problems. This can get into water body from homes and it is at times retained in filtered municipal water supplies, causing odour and taste problems.

(b) Industrial Water Pollution: The characteristics of industrial wastewaters can differ considerably both within and among industries. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic and organic substances. Waste from industries cover the wide gamut of pollutants which come from huge number of chemicals that are made in the world today. When these chemicals are dumped into water bodies, they cause serious harm due to their chemical toxicity. The chemicals from industrial wastes cover a wide spectrum including sulfuric acid waste, hydrocarbons, pulp and paper sulfates, nitric acid, etc. Industries contribute a lot to the pollution of the environment. Most industries in Nigeria do not treat their wastes before disposal.

(c) Agricultural Water Pollution

These are derived from commercial livestock and poultry farming, and are the sources of many organic and inorganic pollutants in surface waters (David and Brad, 2006). Agricultural crops are prevented from being attacked by pest and insects through application of chemicals such as DDT, and a series of chlorinated hydrocarbons have been used in varying degrees. These chlorinated hydrocarbons enter the river from treated areas through water runoff or by natural percolation through the soil. Chlorinated hydrocarbons are biologically non-degradable and are persistent, and this affects organisms in water and humans that eat these organisms. Aquatic ecosystem has the ability to assimilate certain amount of waste and maintain near normal function. However, when these wastes are discharged excessively, the natural cleaning process of a river ceases to exist and this causes damage and death to organisms. Drainage from feed lots (cattle pens constructed for the purpose of fattening up the cattle before slaughter) for example has an extremely high pollution strength (Vesilind and Pierce, 1982).

(d) Oil Spills

Oil is the life-line of the modern industrial revolution. The industrialized nations have developed a great thirst for oil which is shipped from foreign sources under proper controls. Oil is a good source of energy.

Oil spills and contribution from routine operations are another source of water pollution. Sources of oil pollution include losses which arise from careless handling at small factories. Oil pollution of water bodies may arise from spillage of damaged pipeline, leakage at drilling rigs, disposal of used oil or lubricant, gas flaring and usage of chemicals. Any of these situations may lead to the destruction or extinction of wildlife habitat, plants birds and marine life and contamination of drinking water (Smith, 1968). Major oil disasters are Exxon oil spill, in 2010, Ogbodo oil spill, 2001 in Nigeria (Vidal, 2010), Torrey Canyon, in 1967, the Ocean Eagle, in 1968, Puerto Rico URS Research Company, 1970 and Santa Barbara, in 1969 (California University, 1971).

1.4 WATER QUALITY INDICATORS

1.4.1 Biological Indicators

Biological indicators are numerical values derived from actual measurements, have known statistical properties, and convey useful information for environmental decision making. They can be measures, indices of measures, or model that characterize ecosystems or one of their critical components. The primary uses of indicators are to characterize current status and to track or predict significant change. Biological attributes of waterway can be important indicators of water quality. Biological attributes refer to the number and types of organisms that inhabit a waterway. The poorer the quality of water the fewer the number and types of organisms that can live in it (Chris and Edward, 1998). When assessing water quality, it is important to look at the quality of organisms that live in a waterway. Some species are more sensitive to chemical and physical changes in their habitat than other species. If species that tend to be sensitive to pollution are present in a water way, then that water may mostly likely have good water quality.

Examples of biological indicators are fish, algae or protozoas and benthic macro invertebrates like crustaceans, mollusks, worms, and many species of insect larva such as mayflies, caddis flies and beetles (Vannote, *et al.*, 1980). For example, Ayas *et al.* (2007) described the accumulation of some heavy metals Pb, Cd, Cu and Ni in fish samples (*Albumus escherichil, Cuprinus carplo and Silurus glaniso*) and were biologically magnified in the tissues. Chris and Edward (1998) described biological criteria as the broader concept of water resource integrity which supplements the roles of chemical and toxicological approaches and reduces the weelhood of making overly optimistic estimates of aquatic life conditions.

1.4.2 Chemical Assessment

Chemical attributes of waterway are important indicators of water quality. Chemical attributes can affect aesthetic qualities such as how water looks, smells, and tastes. It can also affect its toxicity and whether or not it is safe to use. Chemical quality of water is important to the health of humans as well as the plants and animals that live in and around rivers (Schlesinger, 1991). Assessment of water quality by its chemistry includes measures of many elements and molecules dissolved or suspended in the water. Chemical measures can be used to directly detect pollutants such as lead or mercury. Inbalances within the ecosystem may indicate the presence of certain pollutants. Commonly measured chemical parameters include pH, alkalinity, hardness, nitrates, nitrites and ammonia, ortho and total phosphates, and dissolved oxygen and biochemical oxygen demand. Some chemical measurements actually indicate the physical presence of pollutants in water. Examples are conductivity and density. The use of chemical assessment by many workers abounds Chemical properties of water such as BOD, DO, COD, pH nitrate, and phosphate were used to examine the water quality of rivers. (Onianwa *et al*., 2001; Adeniyi and Imevbore, 2008; Ajibade *et al*., 2008).

1.4.3 Physical Assessment

Physical assessments are important indicators of water quality. The most basic physical attribute of a river or stream is the path along which it flows. Most streams classified as “meandering’’ streams have many bends. The bends are characterized by deep pools of cold water along the outside banks where faster-moving water scours the bank. Meandering streams also have riffles (i.e. portion of a stream characterized by fast-moving turbulent water) along the straight stretches between pools. The S-shaped path of meandering streams prevents water from moving too quickly and flooding downstream ecosystems. The deep, cold pools of water provide ideal habitat for many species of fish even when overall stream flow is reduced. The riffles help to hold water upstream during times of low stream flow. Also, turbulence in the riffles mixes oxygen into the water. Natural stream channel patterns, with their bends, pools and riffles, are essential to decreasing flooding as well as providing a suitable habitat for certain plants and animals.

This makes it important to assess the physical attributes of a stream when examining its water quality. Measurements of a streams physical attributes are used to describe the structure of a sampling site. This allows for the comparison of the biota and chemistry of similarly-structured streams at different locations. Measurements of a stream physical attributes can also serve to indicate the presence of certain effluents, while changes in stream width, depth, and velocity, turbidity, and rock size may indicate dredging in the area. Other physical characteristics measured in a stream include elevation and catchment area, stream order, forest canopy and total solids (Vannote, 1980).

1.5 WATER QUALITY AND ITS BENEFICIAL USES

Water is essential to human life and the health of the environment. As a valuable natural resource, it comprises marine, estuarine, freshwater (river and lakes) and groundwater environment that stretch across coastal and inland areas. Water quality in a body of water influences the way in which communities use the water for activities such as drinking, swimming or commercial purposes. Most people believe good water quality means the water is pure and clean. However, fish and wildlife have lots of other requirements. Fish must get all of their oxygen and food from water, and therefore need water that has enough oxygen and nutrients. Thus, good water quality implies that harmful substances (pollutants) are absent from the water, and needed substances (oxygen, nutrients) are present.

Generally, the water quality of rivers is best in the headwaters, where rainfall is often abundant. Water quality frequently declines as rivers flow through regions where land and water use are intense and pollution from intensive agriculture, large towns, and industry and recreation areas increases. There are exceptions to the rule and water quality may improve downstream, behind dams and weirs, at points where tributaries enter the main stream, and in wetlands. Rivers frequently act as conduits for pollutants by collecting and carrying wastewater from catchments and, ultimately, discharging it into the ocean. Storm water which can also carry heavy loads of nutrients, organic matter and pollutants finds its way into rivers and oceans, mostly via the storm water drain network.

Water quality is the ability of a water body to support all appropriate beneficial uses. Beneficial uses are the ways in which water is used by humans and wildlife; drinking water and fish habitat are two good examples. Beneficial use designations describe existing or potential uses of water body. If water supports a beneficial use, water quality is said to be good or unimpaired. If water does not support a beneficial use, water quality is said to be poor or impaired (Carlson, 1977). Different beneficial uses have different needs. The following beneficial uses have been recognized:

- Water supply for domestic, industrial, agricultural, and stock watering.
- Fishing.
- Wildlife habitat.
- Recreation-primary contact (swimming) and secondary contact.
- Navigation

All rivers, streams, estuaries, and lakes are assigned to a class based on the beneficial uses they could support if they had good water quality. Based on these beneficial uses, they following classes have been defined:

Class AA:	Has all beneficial uses to a high degree.
Class A:	Has all beneficial uses, but not as well as Class AA.
Class B:	Has all beneficial uses except domestic water supply, salmon spawning, fish harvesting, and primary contact recreation.
Class C:	Has only a set of beneficial uses, including industrial water supply, fish migration, wildlife habitat, secondary contact recreation, and navigation.
Lake:	Lake has all beneficial uses, but has hydraulic and water quality characteristics that are different from those of rivers, streams, and estuaries.

Class AA waters have the highest water quality, and Class C waters have the lowest. It is important that a waters' class defines water quality goals and standard, not actual water quality. Class AA water does not necessarily have quality than class B water; it just has higher standards to meet because it could support more beneficial uses. There are many global water quality issues, and a number of priority issues of concern. One of these is safeguarding human drinking water supplies. The protection of source water quality for domestic use (drinking water, abstraction, etc) was identified by the experts' group as a priority for assessment. It was selected because of its significance to human health; could be conducted on a global scale; and the approach for assessment would be user-based and involve application of common guidelines such as those from the World Health Organization across multiple water quality monitoring stations (WHO, 2004).

1.6 THE OSUN RIVER CHANNEL

The Osun River lies within latitude 08°20′N and 6°30′N and longitude 05°10′E and 03°25′E in the forest zone of Nigeria (Figure 1). It flows southwards through central Yoruba-land in South western Nigeria into the Lagos Lagoon and the Atlantic Gulf of Guinea. Osun River is perennial and its volume fluctuates with seasons. It flows through a narrow valley throughout its course across basement complex rocks and incised to the bedrock along many reaches (Tahal, 1976).

The river originates from Igede Ekiti (Ekiti State) and flows through many agricultural plains and cities of about 267 km. The drainage system of Osun River rises in Oke-Mesi ridge, about 5 km North of Effon Alaiye on the border between Oyo and Ondo States of Nigeria. It flows North through the Itawure gap to latitude 7°53′ before winding its way Westwards through Osogbo and Ede and Southwards to enter Lagos Lagoon about 8 km east of Epe. It is underlain by metamorphic rocks of the basement complex, which outcrop over many parts. Rocks of the basement complex found here are schists, associated with quartzite ridges of the type found in Ilesha area. The metamorphic rocks are largely undifferentiated, but specific rock groups are identified. The first group consists of the migmatite complex, including bandid magmatic and auguen gnesses and pegmatites which outcrop in Ilesha and Ife areas. Metasediments consisting of sciests and quartzites, calsilicates, metaconglomerates, amphibolites and metamorphic iron beds make up the second group. They are found in two Ikire areas (Tahal, 1976). The major occupation of the people living along the drainage area of the river is farming, but there are also some industries located near the river and its tributaries. More than 75% of those living along the river course are farmers; consequently crops such as cocoa and palm produce that are produced in commercial quantities serve as raw materials for those industries that

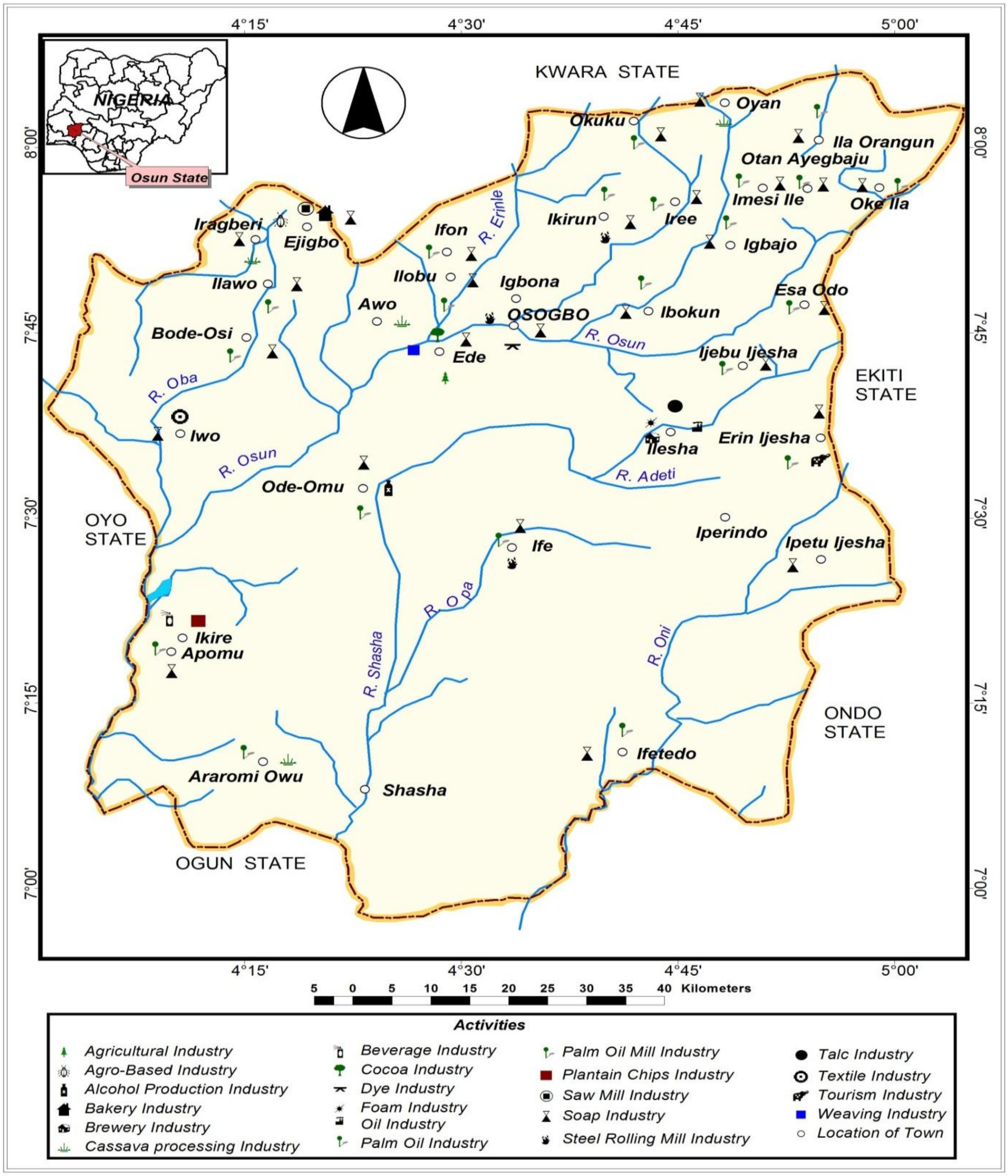

Figure 1: Map of Osun River showing various industrial activities

manufacture cocoa and chocolate-based products. Due to the large concentration of palm trees along the banks of some of the tributaries, it makes it a viable zone for vegetable oil processing industry. River Osun flows through the forest zone in Nigeria, with the abundance of forest; it makes it a haven for any wood- based industry. The farmers living along the bank of the river and its tributaries produces commercial quantities of food crops such as yam, cassava, millet, rice as well as a variety of fruits. In this vein, these foods serve as raw materials for fruit and rice processing industries. Cocoa and kolanut are produced in large quantities. There are many poultry farms, fish ponds located along the banks of this river and its tributaries. Wastes from these farms are used as manure for crops, feed for fish or dumped into the bush and when it rains these get carried away into Osun River and its tributaries and impair the water quality.

With regards to mineral resources, there have been discoveries of various mineral deposits at different locations along the course of the river and its tributaries. The most prominent of these is gold found in commercial quantities around Ilesha. This mineral is already being exploited. Other important minerals found along the bank of the river and its tributaries include nickel, found mostly in various parts of Ile-Ife and Ilesha. Talc, a raw material in the manufacture of fillers in paints, ceramics, cosmetics, paper, textile, plastic and rubber is also found in Ife. Potash occurs in Osogbo. The river also flows through tributaries that have dolomite, limestone and clay. Various industrial activities along Osun River are as shown in Figure 1. The presence of steel rolling mills and machine tools industry at Osogbo and Ikirun facilitated the establishment of many industries such as the International Breweries and Supreme oil at Ilesha, Adeniran Steel and Wire Flexible Packages in Ilesha, Adeyera Industrial Company (metal fabrication) at Ejigbo, They discharge their effluents into the popular Adeti and Aro rivers, which are tributaries of River Osun.

Cottage industries are scattered all over the drainage area of the river in Osun State. There are more than fifty soap making units (including black native soap) operated by rural women in places such as Ede, Osogbo, Okuku and Awo; seven textile units, thirteen tie and dye units, more than 200,111 weaving industries, fifty-three raffia works units, seven cane works, twelve foundry works, 157 goldsmith and brick moulding, several cream making units, leather work units and processing of local gin (Osun State, 2003).

Domestic human wastes such as human excreta, urine and associated sludge (collectively known as black water) and waste generated through bathing and kitchen (collectively known as grey water) are not left out in this pollution saga. Sewage from large and small towns is discharged either into a water body or discharged on land for irrigation. Wastes entering these water bodies are both solid and liquid forms. They are mostly derived from industrial, agricultural and domestic activities. Contributing to the menace of indiscriminate discharges of industrial effluents in some banks of River Osun and its tributaries is the improper disposal of domestic wastes particularly in urban areas. This practice contributes significantly to environmental degradation caused by incessant flooding. Most domestic wastes now contain modern environmental health hazard substances thus posing additional risk to public health. The contributions of various industrial activities in the Osun River area are as shown in Figure 1.

The control site for the study was Egun River, in Iperindo. This site was chosen because it has the same geology as the studied river, Osun and it is less exposed to environmental pollution compared to the Osun River.

Periodical monitoring of chemical and physical water quality indicators is therefore essential for assessing and/or protecting the integrity of River Osun and its tributaries. It has the advantages of identifying changes in water quality, early discovery of emerging water quality problems, the evaluation of pollution control measures, the effectiveness of compliance and how to respond in an emergency situation and the ability to project the future concentrations of these indicators to guide against or reduce future pollution of the water body.

1.7 PREVIOUS STUDIES ON OSUN RIVER

Very little research work has been carried out on the physicochemical characteristics of the river water, sediments and vegetation. For example, Olajire *et al*. (2001) carried out water quality assessment of Osun River by studying inorganic nutrients of surface water and ground water for Na^+, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, CN^-, PO_4^{3-}, pH, temperature, EC, TDS, total hardness and total carbon (IV) oxide at five tributaries of River Osun namely River Asoba, River Ogboagba, River Okoko, River Ajibu, and River Elekunkun. The study was conducted in May, June and August, 1998. Their investigation revealed impairment of the water body by these ions. Adeboye and Alatise (2009) investigated the annual maximum discharges at Apoje station in order to estimate the flood of River Osun at Apoje sub-basin. The stream flow gauge height data for 18 years (1982-1999) were used for the study. Joshua *et al*. (2010) looked into the grain sizes of sediments, types of minerals present in the sediment of River Osun. A total of 106 samples were collected between February and March, 2006 across South Western Nigeria at Ekiti, Osun, Oyo, Lagos and Ogun States. Their investigation revealed that heavy mineral assemblages indicated the presence of opaque and non-opaque mineral. Their investigation showed that heavy mineral in Osun River sediment is mineralogically immature.

Tijani and Onodera (2009) assessed the contamination of thirty-eight bottom sediment samples and corresponding water samples in Osogbo for levels of Mn, Cu, Pb, Zn, Ni, As, Cr and Co in clay fractions using ICP-AES method and X-ray fluorescence. The study highlighted the influence of anthropogenic activities due to lack of proper waste disposal and management practices. Impact of market effluent on chemical quality of BOD, alkalinity, heavy metals and anions of receiving Opa reservoir in Ile-Ife, Osun State was investigated by Eludoyin *et al*. (2004). They observed seasonal variation in most of these variables with high values in dry seasons and low values in the rainy seasons. Comparison of the reservoir water with international limitation standards for drinking water supply showed that it was high and needs treatments, implying that the effluent from the markets and other tributaries of River Osun significantly impacts the chemical quality of the reservoir water.

1.7.1 The Limitation of Previous Studies

The researchers in the previous studies failed to carry out sufficiently detailed work on the physicochemical characteristics of River Osun with regards to the types of parameters studied, duration of the study and the number of sampling points used. For example, Olajire *et al.* (2001) in their study did not investigate levels of heavy metals in surface water at the five tributaries studied. No data was obtained on the level of gross organic pollutants. The investigation was only carried out in the rainy season and for only three consecutive months of only one year. Adeboye and Alatise (2009) carried out their investigation on the estimate of flooding at Apoje station alone for only two consecutive months using data previously collected. The study did not carry out comparison with other sub-stations to know where flooding will occur later. Joshua *et al.* (2010) investigated opaque and non-opaque minerals in sediments of River Osun. They did not investigate these minerals at various tributaries of River Osun and did not discuss the impact these minerals will have on the quality of the river. The duration of the study also did not allow for comparison of these mineral types in rainy season and dry season periods. Tijani and Onodera (2009) did not study other physical properties of sediments such as CEC, organic carbon content and particle size of those sediment samples analyzed. The duration and frequency of sample collection were short and did not create avenue to study how frequently this river sediments were being impaired by anthropogenic activities occurring along the river bank. No detailed investigations on the pollution of plants found along the river bank of River Osun and its tributaries were found in the literature.

The reports obtained from the literature show that the following information are not yet available:

1) Detailed physicochemical properties of surface water, sediment and vegetation.
2) Data for many of the tributaries of Osun River.
3) Data for a longer duration.
4) Comparison of physicochemical properties of surface water in the wet and dry seasons.
5) Predicted water qualities for future dates.

1.8 AIM/SCOPE

The goal of this study was to carry out a more detailed investigation of the quality of the Osun River and its tributaries, taking into account the knowledge gaps in the literature on the subject. The specific objectives in this regards were as follows:

1) To determine physicochemical characteristics and heavy metals contents of the surface water of Osun River and its tributaries bimonthly, over a period of twenty four months.
2) To determine physicochemical characteristics and heavy metals contents of the sediment of Osun River and its tributaries.
3) To determine heavy metals contents of plants along the banks of the river.
4) To classify the river water quality according to standard indices, using the analysis results.
5) To apply the current water/sediment quality data to a predictive model, for the purpose of determining future water/sediment qualities of the river.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 SURFACE WATER QUALITIES

2.1.1 Assessment of Water Quality and Toxicity of Polluted Rivers

The quality of river water is a key issue in water management. In the world today, relatively few rivers remain in an un-impacted or pristine state. Most rivers are affected by a number of in-stream, riparian and catchment medications or practices. This often results in their being less biologically functional and of lower ecological value than their original states. Important river stresses include nutrient enrichment, increasing salinity, pesticides, water extraction, flow controls, loss of riparian vegetation and effluent discharge. The water quality of rivers varies greatly with different waters and their uses as well as with geography, climate, populations and living standards. From the physical point of view, rivers are essentially agents of erosion and of transportation, they remove water and ground sediments from the land surface and carry it to the sea. The hydrological regime, together with the quality and the quantity of sediments, are determined by basin physiography, the climate, the geology and the land use (Knighton, 1998). From a biological point of view, rivers are a typical example of open ecosystems. This is because their metabolism is characterized by continuous energy exchanges (in the shape of biological stuff), between the ground areas and the low stream waters.

Assessment of the physicochemical characteristics of rivers is necessary in order to determine the water quality status of a river. For example, Ajibade *et al*. (2008) examined the physical and chemical properties of the major rivers in Kainji Lake National Park for gross pollutants, anions and metals. The presence of these pollutants greatly affected the water quality of the studied rivers. Mahmood *et al*. (2000) assessed the River Ravi (Pakistan) for the physic-chemistry and heavy metals toxicity and discovered that electrical conductivity of the water was elevated due to the input of large amount of salts and other nutrients in the tributary.

Different parameters have been used to assess the state of water quality of rivers. These parameters include sulphate, phosphate, nitrate, chloride, ammonia, turbidity, alkalinity, hardness, parameters of gross organic pollutants such as DO, BOD and COD, solids, temperature, pH, etc. Onianwa *et al*. (2001) studied the water quality of urban rivers of Ibadan, Nigeria using all the above mentioned parameters and assessed the rivers to be of fairly poor quality. Several other studies on Nigerian surface waters have been conducted (Imevbore, 1967; Adebisi, 1981; Oyeike *et al*., 2002). The characteristics investigated by these authors included plankton, physicochemical properties such as transparency, pH, conductivity, inorganic ions, heavy metals, petroleum hydrocarbons, etc.

Heavy metals are among the very toxic elements. The modern era of industrialization has increased the spread of environmental contamination by heavy metals. Heavy metal toxicity dates back to the ancient period. According to Freedman (1989), the chemical form of toxic elements dissolved in water, generally relatively available to biota even in seemingly small aqueous concentrations, may exert a powerful toxic effect. Asonye *et al*. (2007) examined heavy metals profiles of seventy two rivers, streams and waterways in southwestern Nigeria and found out that most of the metals studied were above the WHO and EEC guide limit, implying that some of the rivers are toxic and might pose serious risks to the health of communities residing around and using these surface waters for domestic, commercial and socio-cultural purposes.

Heavy metals cannot be destroyed biologically but may be transformed from one oxidation state or organic complex to another (Gisbert *et al*., 2003; Garbisu and Alkorla, 2009). Heavy metals therefore poss a potential threat to the environment and human health. Among the major disasters caused by heavy metals are the Minamata Syndrome in 1952 and the ltai-itai Byo in 1955 in Japan (Friedman, 1972).

2.1.2 Significance of Oxygen-Demanding Substances and Nutrients to Surface Water Quality.

Oxygen is one of several dissolved gases important to aquatic life. It is a primary and comprehensive indicator of water quality in surface water. Dissolved oxygen declines have serious implications for the health of aquatic systems. These declines are often attributed to changes in organic or nutrient loading but are generally attributed to species invasions (Caraco *et al*., 2000). The concentration of DO in natural water reduces as a result of biodegradation of carbonaceous and nitrogenous wastes discharged into water bodies and deposited in sediment, and from the point or non-point input of plant limiting nutrients which leads to eutrophication.

Oxygen buck can be induced through over fertilization of water plants by run-off from fields and sewage containing phosphates and nitrates. Under this condition, the number and size of plants increase a great deal. When plants die they become food for bacteria, which in turn multiply and use large amounts of oxygen. An example is the study carried out by Sridhar and Sharma (1985) where low levels of dissolved oxygen was attributed to the incoming organically rich water, coverage of the surface by Pistia plants, and to the decomposition of these plants which resulted in the formation of sludge at the bottom of a lake.

An increase in water temperature can have a number of effects on physical and biological processes that take place in receiving waters. As the temperature increases the solubility of oxygen decreases, which invariably increases the metabolic rate of organisms, resulting in increasing consumption of oxygen (Buren *et al*., 2000). Ecological integrity of aquatic ecosystems is threatened when significant organic pollution exists that exceed self-purification capacity of the water body. For any surface water to sustain aquatic life there should be balanced physicochemical and biological interactions. Abnormally too high or too low of each factor may lead to deleterious ecosystem disturbance such as that discussed by Tesfaye *et al*. (1989) in the discharge of untreated waste into water courses of river systems flowing through Addis Ababa. Freshwater ecosystems have been used for the investigation of factors controlling the distribution and abundance of aquatic organisms (Bagenal, 1978).

Under conditions of nitrate and phosphorus availability, the green algae (chlorophyte) are known to proliferate and form noxious bloom in freshwater environment (Ayoade, 2000).

According to Oputa (2002) hydrobiological changes emanate from adequate solar radiation and nutrient enrichment of a lake, which results in eutrophication. Importantly, blooming of algae species have dentrimental effects on domestic and recreational uses of water, and in many cases have acted as a direct motivation for restoration measures (Bryant, 1994). High phosphate levels could add to the growth of blue-green algae, which could release toxic substances (cyanotoxins) into water. Cyanotoxins are known to have caused the death of farm livestock (Holdworth, 1991). Studies on oxygen demanding substances of rivers in literature abound (Ajayi and Osibanjo, 1981; Fried, 1991; Bich and Anyata, 1999; Izonfuo and Bariweni, 2001; Morrison *et al*., 2002; Islam *et al*., 2007 and Olele and Ekelemu, 2007).

As organic pollution increases, the ecologically stable and complex relationships present in water containing a high diversity of organisms is replaced by a low diversity of pollution-tolerant organisms. The greater the decomposable matter present, the greater the oxygen demand, and the greater the BOD value (Ademoroti, 1996).

2.1.3 Seasonal Dynamics of Physicochemical Properties in Surface Water

Rainfall and solar radiations are the major climatic factors that influence most physicochemical hydrology of water bodies (Odun, 1992; Kadiri, 2000). Seasonal variations in the intensity of rainfall cause both the quality and the quantity of flow of rivers to vary widely. During wet seasons, the storm run-off conveys both suspended and dissolved matter into the rivers. In the dry season, many rivers and streams either dry up completely or have very little flow. Studies have been carried out on some important characteristics of selected rivers and streams in Nigeria. In this region, there are two main seasons, the wet season which is from April to October and the dry seasons from November to March. During the wet season the rains are very heavy, and often the annual rainfall reaches 200cm in several places. The average air temperature is 27^{o}C with a range of less than 2^{o}C (Oluwande, 1978). There is sunlight daily, although its intensity is reduced considerably during a few days in the wet season. In the dry season there is little or no rain. For example Odede and Ekelemu (2007) reported monthly variation in water temperature in dry season, especially in April, compared to the situation in December. The high temperature recorded during March was attributed to the peak of dry season when isolation was at its highest. The minimum and maximum temperatures (25.0℃ – 35.5℃ respectively) are normal for tropical waters and are required for the normal growth of aquatic organisms. The abundant sunlight encourages prolific algae blooms in polluted tropical rivers during the dry season.

As stated by Strahler and Strahler (1973), all rainfall, wherever it occurs, carries with it a variety of ions, some introduced into the atmosphere from the sea surface, some from land surfaces undisturbed by man, and some from man-made sources. The ions and other substances carried into rivers or streams via rainfall may result to pollution. For instance, lower levels of some phyisicochemical parameters like SO_4, Cl^-, PO_4^{3-} , NO_3^- and NH_3 have been reported in the dry season than in the wet season (Devito and Hill, 1998; Izonfuo and Bariweni, 2001), suggesting that runoff water contributes to their levels in rivers.

The characteristics of any water body may indicate its level of pollution. According to Chov (1964), a great deal of information on river water quality may be evaluated from the climatic or geological conditions in the river basin. These two factors generally play a role in the quality of water available for different purposes. In most rivers, the normal dry weather flow is made up primarily of water which seeps from the ground. However, most of the flow of a river is contributed during the high runoff or flood period. During the period of high runoff, most rivers exhibit their most favourable chemical characteristics. Chov (1964), suggests that although the river may contain extremely large amounts of suspended matter, the concentration of dissolved substances are usually low, often only a fraction of that present during dry weather. However, there are some instances where high runoff may cause deterioration in water quality. For instance, if rain falls selectively on the watershed of a tributary which contribute poor-quality water to a comparatively good-quality river system, the water contributed may cause a transitory deterioration of the water quality in the system. For example, Izonfuo and Beriweni (2001) reported higher mean levels of pH, conductivity, TDS, BODS, alkalinity, hardness, Ca, Mg, K, Na, and temperature for the Epie Creek, Niger Delta in the dry season than in the rainy season, and attributed the lower values in the rainy season obtained to run off water which only contributes to dilution of the parameters in the rainy season. They reported a dominance pattern of major cations based on the mean value as $Ca^{++} > K > Na^{+} > Mg^{++}$ in the wet season. This was found to be consistent with the dominance pattern of some African rivers where Ca^{++} was found to be the dominant cation (Imevbore, 1970). DO recorded in wet season was found to be higher than in dry season. The seasonal fluctuation may be due to the effect of temperature on the solubility of oxygen in water. At high temperature, the solubility of oxygen decreases while at lower temperature, it increases (Plimmer, 1978). As DO increases, BOD decreases, and vice versa. Higher BOD in the dry season is perhaps due to the lower volume of water in rivers during the dry season.

2.2 IMPACTS OF HUMAN ACTIVITIES ON SURFACE WATER QUALITY

The industrial revolution of the early 19th century gave great impetus to the factors that brought dramatic changes in the Earth's waters. Ever since then, human impact on Earth's waters has increasingly been detrimental to human survival. Though water pollution is an old phenomenon, the rate of industrialization, and consequently urbanization, has exacerbated its effect on the environment. This is because, the process of urbanization has considerable hydrological impact both in terms of controlling rate of erosion, delivery of pollutants to rivers, and in terms of influencing the nature of runoff and other hydrological characteristics (Goudie, 1990).

Two types of pollutants exist: point source and non-point source. Point source pollution occurs when harmful substances are emitted directly into a body of water. A non-point source delivers pollutants indirectly through environmental changes. The technology exists for point sources of pollution to be monitored and regulated. Non-point sources are much more difficult to control. Pollution arising from non-point sources accounts for a majority of the contaminant in streams, rivers and lakes. Point source pollutants, in contrast to nonpoint pollutants, are associated, as a point location such as toxic-waste spill site. As such, point source pollutants are compared to nonpoint source pollutants, characteristically (i) easier to control, (ii) more readily identifiable and measurable, and (iii) generally more toxic. Nonpoint sources of pollution are the consequences of agricultural activities (e.g. irrigation and drainage, applications of pesticides and fertilizers, runoff and erosion); urban and industrial runoff; erosion associated with construction; mining and forest harvesting activities; pesticides and fertilizer application. Point source includes hazardous spills, underground storage tanks, and storage piles of chemicals, industrial or municipal waste runoff. Compared to point source pollution, nonpoint source pollution is more difficult, related to monitoring and enforcement of mitigating controls due to heterogeneity of soil and water systems at large scales. Characteristically, nonpoint source pollutants (i) are difficult or impossible to trace to a source, (ii) enter the environment over an extensive area and sporadic timeframe, (iii) are related (at least in part) to certain uncontrollable meteorological events and existing geographic/geomorphologic conditions, (iv) have the potential for maintaining a relative long active presence on the global ecosystem, and (v) may result in long-term, chronic (and endocrine) effects on human health and soil-aquatic degradation.

2.2.1 Impact of Industrial Activities on Water Quality of Rivers.

Industrial growth is fast increasing globally, just as the water demand for industrial production processes. This has put more pressure on the limited available water resources. Water bodies are also constantly used as receptacles for untreated waste water or poorly treated effluents accrued from industrial activities. This has rendered many water bodies unsuitable for both primary and secondary usage.

Generally, industrial effluents discharged into water bodies are toxic, and discharge of such untreated or poorly treated effluent could have serious consequences on aquatic organisms (Fisher *et al.*, 1998 and Morseenko, 1999). Different types of industries exist and most of these, especially in Nigeria, do not treat their waste before being disposed. For example, Fakayode (2005) reported that the water qualities of Alaro River in Ibadan, Nigeria were adversely affected and impaired by the discharge of industrial effluent. The quality of the industrial effluent discharged into Alaro River was poor and did not meet the minimum requirement for discharged into surface water. Table 2.1 describes some types of industries, the pollutants they produce and their effect on river water quality.

Table 2.1: Some industrial pollutants and their effect on the environment (FMHE, 1982)

INDUSTRY	POLLUTANTS	EFFECTS
Sugar Refinery	High settleable solids such as bagasse, molasses and press cake biodegradable sugars, Trace metals, Fe, Zn, Cu, Mn, heat from cooling of boilers.	High BOD and COD, low pH, colouration of the water.
Oil and Margarine Factory	Acids, alkalis, fatty materials, glycerol, suspended particles.	High BOD, coating of water surface.
Textile Mills	Biodegradable materials: starch and related compounds, non-biodegradable organics: oils waxes, greases, dyes and pigments.	High pH, BOD and COD, reduction in photosynthetic rate.
	Toxic substances: Trace metals (Cu, Cr), inorganic anions (sulphides, cyanides), organics (phenol, pesticides, used in moth – proofing) acids bases, chlorides and suspended solids.	High colouration of water bodies due to dyes.
Abattoirs	Organic wastes, blood, fats, bones, hair.	Extremely high BOD, high pH, eutrophication of water.
Cement industry	Kiln dust and other particulates. Trace metals: Fe, Cu, Mn.	Indirect effects because most pollutants are airborne. High pH, turbidity.
Breweries	Solid wastes; spent grains and hops, paper labels, rejected crown corks and cartons, broken bottles. Dissolved and suspended solids; sugar, yeast, kieselghur (diatomaceous earth for improving beer colour). Inorganic chemicals: caustic soda, hypochlorites, soaps and detergents, peroxides, silicate oxide.	Turbidity due to high total solids high conductivity and BOD.
Leather and tannery industries	Organic wastes: Flashings, hair, fats Inorganic chemicals: sulphides, carbonates, acids, alkalis, detergent. Tanning agents: phenols, acids, chromium, sulphate, alum, dyes, pigments, oils and waxes.	High BOD, COD, and conductivity of water, possible accumulation of toxic metals in organisms.
Petroleum industries	Oil and grease, organic and inorganic substances, nutrients, heavy metals, organochlorine compounds.	High total solids, total suspended solids, DO, BOD, COD, total nitrogen, total phosphate, lead.

The pollution of rivers and streams with chemical contaminants became one of the most crucial environmental problems within the 20th century. Waterborne chemical pollution entering rivers and streams causes tremendous amounts of destruction. Drinking such water has led to outbreaks of epidemics such as cholera and other water related diseases on several occasions (Adesina, 1986; USFDA, 1993; Frontiers, 1996). Reports of impact of industrial effluent on the physicohemical properties of river abounds (Edltruada, 1996; Adeyeye and Adejuyo, 2002). Unacceptably high levels of the assayed parameters such as pH, temperature, EC, salinity, turbidity, TDS, DO, COD, nitrite and orthophosphate were observed in many, implying that there was an adverse impact on the physicochemical characteristics of the receiving river and stream as a result of the discharge of untreated effluents. This poses health risk to several rural communities which rely on such receiving water bodies as their sources of domestic water.

The petroleum industry impairs the water quality of rivers, especially in the Niger Delta. According to Egborge (1994), rapid urbanization, industrialization and high population gave impetus to the pollution potentials of rivers and streams in the Western and Eastern Niger Delta. The report showed that the petroleum industry is a formidable source of pollutants due to activities such as drilling, production and refining of crude and the production of petrochemicals such as carbon black, marketing, utilization and disposal of spent petroleum products and the events of oil spills. Metals are unique industrial pollutants in that they are found naturally distributed in all the phases of the environment (Ackerfor, 1977). Through industrial processes, metals are concentrated and transformed into various products. These often lead to much higher concentrations of different chemicals than those naturally present in the environment.

Metal wastes are produced by a variety of industries, including mines, tanneries, electroplating, paint, metal pipe and ammunition. These containments are leached into the groundwater through the soil and may finally be transported from there to surface water (Okonkwo and Ablaut, 1999).

Investigation of the effect of brewery industries at different locations in Benin, Ibadan, and Lagos on surface water was reported by Folasegun and Kolawole (2008). They reported that the physicochemical conditions of the streams located at Agidingbi, Alaka, Ona and Ossioma have been adversely influenced by the pollutants. Ipeaiyeda and Onianwa (2009) also reported significant levels of chloride, nitrate, ammonia, dissolved solid, turbidity and BOD and reduced pH and DO downstream the river network of Olosun River in Ibadan, Nigeria as a result of brewery effluents discharged into this river.

2.2.2 Impact of Agricultural Runoff on Surface Water Quality.

Agricultural runoff is excess water from rainfall and other precipitation that runs off agricultural land. When uncontrolled, agricultural runoff removes topsoil, nutrients, fertilizers, pesticides, and organic materials and carries them to water bodies where they become pollutants. Erosion is the detachment of soil particles from clods and the soil surface. Most of this occurs during rain storms which can detach or loosen up to 100 tons of soil per acre in a severe storm. The detached soil can be transported by agricultural runoff which dislodges additional soil particles as it flows across unprotected soil surfaces. Heavier soil particles may settle out in bottomlands and on foot slopes before reaching a body of water.

Nutrients and pesticides that may be present in agricultural runoff also cause serious problems. The direct effect on the producer is the economic losses connected with removing these materials. In addition, nutrients derived from soil, commercial fertilizers or animal manure may cause excessive algal growths in ponds and lakes. These growths filter out and absorb sunlight, and release offensive odours and toxicants. The effects of pesticides on water quality can be dramatic in terms of aquatic life. These substances are as toxic in the water as they are on the field and may affect a wide variety of aquatic organisms. If contacted or ingested in sufficient quantities, pesticides pose a health hazard to all forms of life.

Agriculture involves commercial livestock and poultry farming and it is the source of many organic and inorganic pollutants in surface water. Rain and irrigation water drains off cultivated land that has been fertilized and treated with pesticides. The excess nitrogen and poisons are mixed with it into the water supply. Fertilizers in the absence of natural fertilizer enhance the growth of bacteria that are in water and increase the concentration of bacteria to hazardous levels. Chemical fertilizers contain high levels of nitrogen and phosphorus which are harmful because they flow from crop land to water. Both of these elements are known to cause algal blooms. Algal blooms and erosion present a problem to fish because both contribute to an increase of particles in the water which can occasionally clog the fish's gills, suffocating them (Nanagia *et al*., 2008). For example, Gyles and David (2001) revealed that subsurface tile drainage from row-crop agricultural production has been identified as a major source of nitrate entering surface waters in Mississippi River Basin. Non-controllable factors such as precipitation and mineralization of soil organic matter have a tremendous effect on drainage losses, nitrate concentrations, and nitrate loadings in subsurface drainage water. Cooper (1993) reported agricultural activities to have been identified as major contributors to environmental stress, which affects all ecosystem components. Agricultural contaminants are most noticeable when they produce immediate, dramatic toxic effects on aquatic life, although more subtle, sub lethal chronic effects may be just as damaging over long periods.

2.2.3 Effect of Domestic Sewage Discharge on Quality of Surface Water.

Sewage discharges are major components of water pollution, contributing to oxygen demand and nutrient loading of the water bodies. Organic matter is the important polluting constituent of sewage in respect of its effect on receiving water bodies. Thousands of organic compounds enter water bodies as a result of human activities. Organic matter is mainly composed of proteins, carbohydrates and fats, and measured in terms of BOD and COD. If untreated sewage is discharged into natural water bodies' biological stabilization of organic matter leads to depletion of oxygen in such water bodies. If sufficient oxygen is not available to aquatic life, the ecosystem will be adversely affected. Nitrogen and phosphorus are also very important polluting constituents of sewage because of their role in algal growth and eutrophication of water bodies. Nitrogen is present in fresh domestic sewage in the form of proteinaceous matter urea (i.e. organic nitrogen). The presence of these nutrients, nitrogen and phosphorus, can result in eutrophication which can occur at both microscopic levels in form of algal or macroscopic level in form of larger aquatic weeds.

2.3 SURFACE WATER QUALITY STANDARDS

Water quality standard defines the water quality goals of a water body. Water quality standard regulations establishes the use or uses to be made of a water body, set criteria necessary to protect the uses, and establish policies to maintain and protect water quality. Appropriate uses are identified by taking into consideration the use and values of the water body for public supply, for protection of fish, shellfish, and wildlife, and for recreation, agricultural, industries, and navigational purposes. There are different types of water quality standards that describe guideline values for constituents of water or indicators of water quality. Table 2.2 describes drinking water quality standards for some countries/organization.

Setting water quality standards is a complex task that requires input by experts in water quality and aquatic ecology. The scientific information usually underlying water quality guideline can be used to develop standards, but it is important to understand the difference between guidelines and standards. Guideline is often a benchmark that should be followed, but technically, is not lawfully required to be followed. Standards are a rule dealing with details or procedures, a rule or order issued by an executive authority or regulatory agency of a government (David, 2006). A standard is similar to a guideline, in that, benchmarks are established, but in contrast to a guideline, standards are enforceable by law. Standards, in the context of drinking water, are clearly preferred, because any deviation from the benchmark can result in legal contravention against the negligent body; thus, ensuring safe drinking water. Guidelines are usually based on scientific information about the effects of contaminants on the conditions of a water body, or on the organisms that live in that water body. Standards actually define threshold for the point that is deemed to be acceptable for a given situation. Guidelines for other categories of water usage also exist. These include guidelines for industries such as pulp and paper, iron and steel, petroleum, power generating stations, food and beverage, FAO for trace elements in irrigation water, quality for aquatic life, recreational water quality, and water quality criteria for livestock. These

Table 2.2: Drinking water quality guidelines

Parameter	USEPA (2006)	Canada (1996)	EEC (1980)	Japan NEMAMNR (1997)	WHO (2004)	SON (2007)
Electrical conductivity	-	-	-	-	-	1000
pH	6.5-8.5	6.5-8.5	6.5-9.5	5.8-8.6	6.5-8.5	7.0-8.0
Total dissolved solids	500	500	-	500	1000	500
Turbidity	0.5-5	1	4	1-2	5	5
Hardness	-	-	50	300	-	150
Temperature	-	-	-	-	-	Ambient
Nitrate	10.0	10.0	50	10.0	50	10
Sulphate	250	500	250	-	-	100
Phosphate	-	-	5	-	-	-
Chloride	250	250	250	200	250	250
Ammonia	-	-	-	-	-	0.05
Lead	0.015	0.01	0.01	0.05	0.01	0.01
Copper	1.3	1.0	2.0	1.0	1-2	1.0
Cadmium	0.005	0.005	0.005	0.01	0.003	0.003
Chromium	0.1	0.05	0.05	0.05	0.05	-
Zinc	5.0	5.0	-	1.0	3.0	5.0
Magnesium	-	-	-	-	-	0.20

All units in mg/L except electrical conductivity (µS/cm), Turbidity (FTU), Temperature (^{o}C) and pH with no unit.

EEC (1980), Canada (1996), NEMAMNR (1997), WHO (2004), USEPA (2006), SON (2007).

guidelines are used for comparison purpose to check for compliance. They are as shown in Tables 2.3 – 2.13.

2.4 WATER QUALITY INDICES

The most challenging problem of modern theoretical and applied hydroecology is to understand the fundamental principles of ecology for its application in effective management of water resources for both hydrological availability and water quality. Quantification of water quality aims at describing the condition of a water body with reference to human needs.

The water quality index is a single number that expresses the quality of water by integrating the water quality variables. Its purpose is to provide a simple and concise method for expressing the water quality for different usage. Any number of water quality measurements can serve, and have already been used, as indicators of water quality. However, there is no single measure that can describe overall water quality for any one body of water, let alone at a global level. As such, a composite index that quantifies the extent to which a number of water quality measures deviate from normal, expected of 'ideal' concentrations, may be more appropriate for summarizing water quality conditions across a range of inland water types and over time. Although there is no globally accepted composite index of water quality, some countries and regions have used, or are using, aggregated water quality data in development of water quality indices. Most water quality indices rely on normalizing, or standardizing, data, parameter by parameter, according to expected concentrations and some interpretation of 'good' versus 'bad' concentrations. Parameters are often then weighted according to their perceived importance to overall water quality and the index is calculated as the weighted average of all observations of interest (Stambuk-Giljanovic, 1999; Pesce and Wunderlin, 2000; Sargaonkar and Deshpande, 2003; Liou *et al*., 2004; Tsegaye *et al*., 2006).

Pesce and Wunderlin (2000) compared the performance of three water quality indices on Suquia River in Argentina. All three indices were calculated using observations for twenty different parameters that were normalized to a common scale according to observed

Table 2.3: Water quality tolerance for certain industrial applications (mg/L) except as indicated

Industry General	Turbidity**	Dissolved Oxygen	Hardness	Alkalinity	pH***	Total Solids	Chloride	Indication*
Beverages	2	-	250	125	-	850	250	C
Baking	10	-	D	-	-	-	-	A, B
Food (general)	10	-	10 - 250	30 250	-	850	-	C
Brewing								
Light	10	-	-	75	6.5- 7.0	500	100	C, D, G
Dark	10	-	-	150	7.0^+	1000	100	C, D, H
Laundering	-	-	50	60	6.0 – 6.8	-	-	-
Paper & Pulp								
Ground wood	50	-	200	150	-	500	75	E
Tanning	20	-	50 – 135	135	6.0 – 8.0	100	-	-
Textiles	5	-	20	-	-	-	100	-
General Dyeing	5	-	20	-	-	-	-	-
Boiler feed (0 – 150 pound per square inch)	20	2	50	-	8.0+	1000 - 3000	-	

* A- no corrosiveness, B- no slime formation, C – conformity with federal drinking water standards necessary, D – NaCl, 275 ppm, E – free CO_2 less than 10 mg/L, G- calcium 100 – 200 mg/L, H – calcium 200- 500 mg/L

** FTU

*** No unit

Table 2.4: Water quality guideline for pulp and paper industry

Parameter	Fine Paper	Ground Wood	Kraft		Chemical Pulp & Paper	
			Bleached	Unbleached	Bleached	Unbleached
pH	-	6 - 8	-	-	6 – 8	6 – 8
Turbidity (NTU)	<10	<20	<40	<100	<10	<20
Calcium	<20	<20	-	-	<20	<20
Magnesium	<12	<12	-	-	<12	<12
Chloride	-	25-75	<200	<200	<200	<200
Hardness	<100	<100	<100	<100	<100	<100
Alkalinity	40-75	<150	<75	<159	-	-
Dissolved solids	<200	<250	<300	<500	<200	<250
Suspended solids	<10	-	-	-	<10	<10
Temperature	-	-	-	-	<36	-

Source: Canadian Council of Resource and Environmental Ministers, Canadian Water Quality Guideline (1987)

Table 2.5: Water quality guidelines for the iron and steel industry

Parameter*	Hot-Rolling, Quenching, Gas Cleaning	Rinse Water		Demineralised	Steel Manufacturing
		Cold-Rolling	Softened		
pH	5.0 – 9.0	5.0 – 9.0	6.0 – 9.0	-	6.8 – 7.0
Suspended Solids	<25	<10	ND[a]	ND	-
Dissolved solids	<1000	<1000	ND	ND	-
Dissolved oxygen	--(minimum for aerobic conditions)--------------------				
Temperature	<38	<38	<38	<38	<38
Hardness	NS [b,c]	NS[b]	<100	<0.1	<50
Alkalinity	NS[c]	NS[c]	NS[c]	<0.5	-
Sulphate	<200	<200	<200	-	<175
Chloride	<150	<150	<150	ND	<150

* units in mg/L, except temperature (°C), and pH

Source: Canadian Council of Resource and Environmental Ministers, Canadian Water Quality Guidelines (1987), U.S Environmental Protection Agency (1973)

ND – not detected

b - controlled by other treatment

NS - not specified;

c - the parameter has never been a problem at concentrations encountered

Table 2.6: Water quality guidelines for the petroleum industry

Parameter	Concentration
pH	6.0 – 9.0
Calcium (mg/L)	<75
Magnesium (mg/L)	<25
Sulphate (mg/L)	NS
Chloride (mg/L)	<200
Nitrate (mg/L)	NS
Hardness (as $CaCO_3$) (mg/L)	<350
Dissolved Solids (mg/L)	<750
Suspended Solids	<10

NS- not specified

Source: Canadian Water Quality Guidelines (1987); Ontario Ministry of the Environment (1974) Federal Water Pollution Control Administration (1968).

Table 2.7: Water quality guidelines for power generating stations

Parameters	Cooling Once-Through		Boiler Feedwater (10.35 – 34.48 Mpa)	Miscellaneous Uses
	Fresh	Brackish		
Calcium	<200	<420	<0.01	-
Magnesium	NS	NS	<0.01	-
Ammonia	NS	NS	<0.07	-
Sulphate	<680	<2700	NSc	-
Chloride	<600	<19000	NSc	-
Dissolved Solids	<1000	<35000	<0.5	<1000
Copper	NS	NS	<0.01	-
Hardness	<850	<6250	<0.07	-
Zinc	NS	NS	<0.01	-
Alkalinity ($CaCO_3$)	<500	<115	<1.00	-
pH units	5.0 – 8.3	6.0 - 8.3	8.8 - 9.4	5.0 – 9.0
Chemical Oxygen Demand	<75	<75	<1.00	-
Dissolved Oxygen	-	-	<0.007	-
Suspended Solids	<5000	<2500	<0.05	<5.00

c – controlled by treatment for other constituents

NS- Not specified

Sources: Canadian Council of Resources and Environment Ministers, Canadian Water Quality Guidelines (1987), Krisher (1978)

Chemical Engineering (1978). McGraw-Hill, Inc.

Table 2.8: Water quality guidelines for the food and beverage industry

Parameter*	Baking	Brewing	Carbonate Beverage	Confec-tionary	Diary	Food Canning, Freezing, Dried, Frozen Fruits, Vegetables	Food Process General	Sugar Manufacturing
Turbidity	<10	<10	1 -2	-	-	<5	<5 - 10	-
Suspended Solids	-	-	-	50 – 100	<500	<10	-	ND
Dissolved Solids	-	<800	<850	50 -100	<500	<500	<850	-
Calcium	NS [b, c]	<100	-	-	-	<100	-	<20
Magnesium	-	<30	-	-	-	-	-	<10
Copper	-	-	-	-	ND	-	-	-
Sulphate	-	<100	<200	-	<60	<250	-	<20
Chloride	-	20 – 60	<250	<250	<30	<250	-	<20
Nitrate	-	<10	-	-	<20	<10	-	-
Hardness	NS [b]	<70	200 -250	-	<180	<250	1-250	<100

* all units in mg/L except turbidity (FTU)
ND- Not detected
b – some required for yeast action; excess retards fermentation
c NS- Not specified
Source: Canadian Council of Resource and Environmental Ministers, Canadian Water Quality Guidelines (1987).

Table 2.9: FAO maximum concentrations of trace elements in irrigation water

Element	Recommended Maximum Concentration (mg/L)	Remarks
Cadmium	0.01	Toxic to beans, beets and turnips at concentrations as low as 0.1mg/L in nutrient solution
Cobalt	0.05	Toxic to tomato plants at 0.1mg/L in nutrient solution
Chromium	0.10	Not generally recognized as essential growth element
Copper	0.20	Toxic to a number of plants at 0.1 mg/L in nutrient solutions
Nickel	0.20	Toxic to a number of plants at 0.5 mg/L to 1.0 mg/L
Zinc	2.00	Toxic to many plants at widely varying concentration

The maximum concentration is based on a water application on water is consistent with good irrigation practices (10,000m^3/ha/yr). If the water application rate greatly exceeds this, the maximum concentrations should be adjusted downwards accordingly. The values given are for water used on a continuous basis at one site.

Source: Food and Agricultural Organization of the United Nations (1985).

Table 2.10: Guides for evaluating the quality of water for aquatic life

Determination	Threshold Concentration*	
	Freshwater	Saltwater
Total dissolved solids (TDS) mg/L	2000†	-
Electrical conductivity, µmhos/cm@25°C	3000†	-
Temperature, maximum °C	34	34
Range pH	6.5 – 8.5	6.5 – 9.0
Dissolved oxygen (DO) minimum, mg/L	5.0‡	5.0‡
Ammonia (free) mg/L	0.5†	-
Cadmium, mg/L	0.01†	-
Chromium, hexavalent, mg/L	0.05†	0.05†
Copper, mg/L	0.02†	0.02†
Lead, mg/L	0.1†	0.1†
Nickel, mg/L	0.05†	-
Zinc, mg/L	0.1†	-

* *Threshold concentration is value that normally might not be deleterious to fish life. Waters that do not exceed these values should be suitable habitat for mixed fauna and flora.*

† *Values no to be exceeded more than 20 percent of any 20 consecutive samples, nor in any 3 consecutive samples should other values never be exceeded.*

‡ *Dissolved oxygen concentrations should not fall below 5.0 mg/L data indicate that rate of change of oxygen tension is an important factor.*

Source: California State Water Quality Board (1963).

Table 2.11: Recreational water quality

Parameter	Water Contact		Boating and Aesthetic	
	Noticeable Threshold	Limiting Threshold	Noticeable Threshold	Limiting Threshold
Suspended Solids (mg/L)	20*	100	20*	100
Turbidity (FTU)	10*	50	20*	‡
Range of pH	6.5 – 9.0	6.0 – 10.0	6.5 - 9.0	6.0 – 10.0
Temperature, maximum (^{o}C)	30	50	30	50

***** Value not to be exceeded

† No limiting concentration can be specified in the basis of epidemiological evidence, provided no fecal pollution is evident

‡ No concentration likely to be found in surface waters would immediate use

Source: California State Water Quality Control Board (1963).

Table 2.12: Water quality for livestock

Quality Factor	Threshold Concentration*	Limiting Concentration†
Total dissolved solids (TDS) mg/L	2500	5000
Cadmium mg/L	5	1000
Calcium mg/L	500	500‡
Magnesium, mg/L	1500	3000
Nitrate, mg/L	200	400
Sulphate, mg/L	500	1000‡
Range of pH	6.0 - 8.5	5.6 – 9.0

* Threshold values represent concentrations at which poultry or sensitive animals might show slight effects from prolong use of such water

‡ Total magnesium compounds plus sodium sulphate should not exceed 50 percent of the total dissolved solids.

Source: California State Water Quality Control Board (1963)

Table 2.13: Water quality criteria for livestock (II)

Quality Factor	Limiting Threshold (mg/L)
Cadmium	0.05
Chromium	1
Cobalt	1
Copper	0.5
Lead	0.1
Nickel	1
Zinc	25

Source: Ontario Ministry of the Environment (1984)

Table 2.14: Some parameters (indicative of gross organic pollution) used in the classification of surface water quality

Analytical Parameter	CLASS 1	CLASS 2	CLASS 3	CLASS 4	CLASS 5
pH	6.5 – 8.0	6.0 – 8.4	5.0 -9.0	3.9 – 10.1	3.9 – 10.1
Dissolved Oxygen (mg/L)	7.8	6.2	6.0	1.8	<1.8
BOD (mg O_2/L)	1.5	3.0	6.0	12.0	>12.1
NH_3 (mg/L)	0.1	0.3	0.9	2.7	>2.7
COD (mg O_2/L)	10	20	40	80	80
Suspended Solids (mg/L)	20	40	100	278	>268

N.B Class 1 = Excellent
Class 2 = Acceptable quality
Class 3 = Slightly polluted
Class 4 = Polluted
Class 5 = Heavily Polluted

Source: Pratti *et al.* (1971).

Table 2.15: Sediment quality guidelines values of ERL and ERM for each metal and contamination level ranking (µg/g)

Parameter	Guidelines	
	ERL	ERM
Cadmium	1.2	70
Chromium	81	9.6
Copper	34	270
Lead	46.7	218
Nickel	20.9	51.6
Zinc	150	410

Table 2.16: Canadian and Ontario sediment quality guielines

Heavy metal	Canadian Sediment Quality Guidelines	Ontario Sediment quality Guidelines
Lead (mg/kg)	35.0	31.9
Copper (mg/kg)	35.7	16.0
Cadmium (mg/kg)	0.60	0.60
Chromium (mg/kg)	37.3	26.0
Nickel (mg/kg)	-	16.0
Zinc (mg/kg)	123	120

Table 2.17: Concensus Based Sediment Quality Guidelines of Wisconsin (CBSQG)

Metal	Concensus Based Sediment
Cadmium (µg/g)	0.99
Chromium (µg/g)	43.0
Copper (µg/g)	32.0
Lead (µg/g)	36.0
Nickel (µg/g)	23.0
Zinc (µg/g)	120

Ref: Wisconsin Department of Natural Resources (2003) concentrations and expected ranges. The ‘objective’ and ‘subjective’ indices were then calculated as a function of the normalized values, the relative weight assigned to each parameter, and, in the case of the subjective index, a constant that represented the visual impression of the contamination level of a monitoring station. A third index, ‘the minimal’ index, was calculated as the average of the normalized values for only three parameters (dissolved oxygen, conductivity, and turbidity). The study reported that the minimal index was well correlated to the objective index, and that both water quality indices were generally correlated to the measured concentrations of different parameters. In a study similar to the Argentinean one, Stambul-Giljanov (2003) compared the performance of several water quality indices for Croatian waters. All indices were similar to the objective index used in Argentinan in that field measurements were normalized, or scored, on a parameter by parameter basis according to their observed concentrations, and then a weighted average index was calculated from normalized values. The indices were tested with data for nine water quality parameters collected monthly over one year at 50 sites in Croatia. Examination of the different water quality indices found that two modified arithmetic indices were best suited for discriminating sites according to water quality condition (good versus poor).

Liou *et al*. (2004) developed an index of river water quality in Taiwan that is a multiplicative aggregate function of standardized scores for temperature, pH, toxic substances, organics (dissolved oxygen, BOD, ammonia), particulate (suspended solids, turbidity), and microorganisms (faecal coliforms). The standardized scores for each water quality parameter were based on predetermined rating curves, such that a score of 100 indicates excellent water quality and a score of 0 indicates poor water quality. The index relies on the geometric means of the standardized scores.

The development of various indices based on different parameters in the river has been reported in literature: Tsegaye *et al*. (2006) developed a chemical water quality index on data from 18 streams in one Lake basin in Northern Alabama that summed the concentration of seven water quality parameters (total nitrogen, dissolved lead, dissolved oxygen, pH, and total particulate and dissolved phosphorus) after standardizing each observation to the maximum concentration for each parameter. Pratti *et al*. (1971) suggested an index that included 13 parameters, while the water quality was evaluated by assessing scores from 0 to 14. Sargaonnkar and Deshpande (2003) developed the Overall Index of Pollution (OIP) for Indian rivers based on measurements and subsequent classification of pH, turbidity, dissolved oxygen, BOD, hardness, total dissolved solids, total coliforms, arsenic, and fluoride. Each water quality observation was scored as excellent, acceptable, slightly polluted, polluted, and heavily polluted, according to Indian standards and/or other acceptable guidelines and standards such as World Health Organization and European Community Standards. Once categorized, each observation was assigned a pollution index value and the OIP was calculated as the average of each index value.

Kim and Carone (2005) developed a water quality index that evaluates changes in water quality over time and space. The Scatter Score Index identifies increases or decreases in any water quality parameter over time and/or space. It does not rely on water quality standards or guidelines and can include an unlimited number of parameters. It was developed primarily to detect positive or negative changes in water quality around mining sites in the United States, but could be applied to non-impacted sites as well.

The Well-being Assessment (Prescott-Allen, 2001) calculates a number of indices to assess global human and environmental condition. The indices were developed under two main categories:

(1) Human well-being, including indices for health and population, which assesses both health life expectancy and total fertility rate, and indices for wealth which assesses average household and national wealth; and

(2) Ecosystem well-being, which includes assessment of both air, such as greenhouse gases and ozone depleting substances, and water (such as inland water quality, river conversion and water withdrawal).

To establish an overall Well-being Index, the human and ecosystem indices are combined. The method yields a score for each country, with the top scores translating into a high quality of life for a low environmental price, and the lower scores translating into a low quality of life for a high environmental price. The Environmental Performance Index of Esty *et al*. (2006) is composed of 16 indicators that represent various policy-relevant objectives on a global scale. There are six policy categories: environmental health, air quality, water resources, biodiversity and habitat, productive natural resources and sustainable energy. These six categories are placed into two broad objectives, Environmental Health and Ecosystem Vitality, which are then combined to give the overall Environmental Performance Index (EPI). To calculate the EPI, each of the 16 indicators are converted to a proximity-to-target measure and placed onto 0 to 100 scale (100 is the target and zero is the worst observed value). Principal components analysis is then conducted with all the indicators to distinguish weights for each indicator and groupings into specific objectives and/or policy categories. Those without a clear designation on the PCA are placed into their policy categories after literature review and expert consultation. The EPI score is calculated on a country by country basis that results in a global ranking of countries.

The development of a global index of water quality will not only allow assessment of changes in water quality over time and space but also evaluate successes and shortcomings of domestic policy and international treaties designed to protect aquatic resources. For example, a global index will be one tool for tracking progress towards meeting the Millennium Development Goals and the Plan Implementation of the World Summit on Sustainable Development, as well as other internationally agreed goals and targets.

2.5 RIVER WATER QUALITY MODELS

Water quality concept has been evaluated in the last years owing to greater understanding of water mineralization process and greater concern about its origin. Water quality shows water-rock interaction and indicates residence time and recharge zone confirmation (Cronin *et al*., 2005). Water quality models are very useful in describing the ecological state of a river system and to predict the change in this state when certain boundary or initial conditions are altered. Such changes may be due to morphological modifications of the water body, such as straightening, and discharge regulations using control structures (weirs, dams, etc), changes in the (point or non-point) amount and location of pollutant loading into the system , and changes in meteorological inputs due to changing trends in climate. The degree of complexity in describing the ecological state varies from model to model. Ecological effects of chemical on ecosystems are the results of direct effects of the chemical, determined in single-species toxicity testing and indirect effects due to ecological interaction between species (Laender *et al*., 2007). In order to determine the impacts of a particular discharge in ambient water quality, it is usually necessary to model the diffusion and dispersion of the discharge in the relevant water body. The approach applies both to new discharges and to the upgrading of existing sources.

Models are a set of mathematical expressions (partial or ordinary differential or algebraic equations) describing the physical, biological, chemical, and economic processes which take place in a system (e.g. river). The challenge of using mathematical modeling, as a support tool to evaluate remediation options in developing countries is well documented (Ongley and Booty, 1999). However, modeling is expensive, requires substantial investments in reliable data, development of scientific capacity and a relatively sophisticated management culture that are often not found in developing countries. Nevertheless, new developments in water quality management policies and strategies require prediction of the fate of in stream pollutants, as well as estimates of the likely effects that the resultant water quality may have on recognized water uses. The complex relationships between waste load inputs, and the resulting water quality responses in receiving water bodies are best described with mathematical models. Studying complex hydrologic problems and synthesizing different kinds of information have been made possible using models. The watershed models are of different types and are intended to serve different purposes. Hydrologists classify models into data driven models and mechanistic models. Data-driven models, sometimes called black-box models are usually inferred from the raw or processed data and the formulation may not be conceptually supported by the mechanism of phenomenon under consideration. Regression models, linear time series models, non linear time series analysis and artificial neutral networks have been used for variety of purposes, such as forecasting, rainfall runoff modeling, estimation of missing hydrologic data, and modeling of water quality parameters in streams (Ongley and Booty, 1999).

A modeling approach with at least seven specific characteristics is needed. These characteristics are:

- The watershed or any hydrologic system, are to be described and simulated in a simple fashion.
- The model should start simple, relying on the available data.
- The model should be adequately dynamic to cope with the nature of hydrologic systems.
- The model should have the ability to simulate both linear and nonlinear processes.
- The model needs to provide a way to represent the feedback mechanism in order to handle counter intuitive processes.
- The model should have ability to model human intervention and any shocks that might be encountered in the system and;
- The model should have the ability to test different policy or management scenarios for better decision making.

2.5.1 Model Classification

Water quality models are usually classified according to model complexity, type of receiving water and the water quality parameters (dissolved oxygen, nutrients, etc) that the model can predict. The more complex the model is the more difficult and expensive will be its application to a given situation (Thomann and John, 1987). Model complexity is a function of four factors:

- The number and type of water quality indicators: in general, the more indicators that are included, the more complex, the model will be. Some indicators are more complicated to predict than others.
- The level of spatial detail: as the number of pollution sources and water quality monitoring increase, so do the data required and the size of the model.
- The level of temporal detail: it is much easier to predict long-term static averages than short term. Dynamic changes in water quality point estimates of water quality

parameters are usually simpler than stochastic predictions of the probability distributions of those parameters.

- The complexity of the water body under analysis: small lakes that “mix” completely are less complex than moderate-size Rivers which are less complex than large rivers, estuaries, and coastal zones.

The level of details required can vary tremendously across different management applications. Models can cover only a limited number of pollutants. In selecting parameters for the model, care should be taken to choose pollutants that are a concern in them and are also representative of the broader set of substances which cannot all be modeled in detail.

Simulation models are used to predict a system response to a given design configuration with great accuracy and detail, and to identify the probable costs, benefits and impacts of a project. That is, the simulation model predicts the outcome of a single, specified set of design or policy variables. However, the space of possible design and policy variable values is in general, infinite. Separate simulation model runs are required for each design or policy alternative considered. In many situations the number of alternative designs is sufficiently large to preclude simulating each alternative designs and some other method is normally used to narrow the field of search.

Optimization models provide a means of reducing the number of alternatives which need to be simulated in detail, i.e. screening them. Those models search the space of possible design variable values and identity an optimal design and/or operating policy for a given system design objective and sets of constraints. These models include relationships which describe the state variables and costs or benefits or each alternative as a function of the decision variables.

The assessment of long-term water quality changes is also a challenging problem. During the last decades, there has been an increasing demand for monitoring water quality of many rivers by regular measurements of various water quality variables. The result has been the gradual accumulation of reliable long-term water quality records and the examination of these data for long-term trends (Hirsch *et al*., 1991). Computer systems now offer the possibility of handling and manipulating very large databases in ways which were not previously a practical option. Littlewood *et al*. (1998) have used such databases for estimation of UK river mass loads of pollutants. Miller and Hirst (1998) used the hydrochemical databases from an upland catchment in Scotland for a period of five years to assess the annual variation in amounts and concentration of solutes and to examine the variation in stream water quality due to changes in flow, season and long time trend. Ferrier *et al*. (2001) analyzed in details databases for Scotland and identified temporal changes in water quality over the last 20 years.

2.5.2 Selection Factors for Model Selection

As one might expect the data requirement for different models increase with the complexity and scope of application. Static, deterministic models require point estimates of these data and often use worst case ‘‘design flow” estimates to capture the behavior of pollutants under the worst plausible circumstances.

Selection of an appropriate water quality model depends on the site conditions of the watershed of concern. The selection of appropriate model can be based on the following screening factors:

- Combined point and non point sources: an important screening factor is how the model handles the loadings from point and nonpoint sources. Models based on water quality data implicitly take the point and non point sources into account, whereas models that use continuous simulation of the water quality directly account for the source. Typically, the sources are part of the input parameters.
- Dominant mixing and transport processes: the water body type dictates the dominant mixing and the transport process of a pollutant. In river and streams the dominant processes are advection and dispersion. In estuaries these processes are influenced by tidal cycles and flows. Water body size and net freshwater flow are also important in determining the dominant processes. For discharges in the ocean

surf zone, dominant dispersion processes include mixture due to breaking waves and transport from near shore currents.

- Ability to provide time-relevant analysis, decision making, and guideline establishment. Timely or time-relevant analysis is needed for an effective advisory. Models applied to predict water quality conditions can be used as a basis for decision making and as management tools.
- Ease of use: the level of user experience; simple methods require only a conceptual understanding of the processes and results can be readily obtained.
- Input data requirement: input data requirement are a function of a model's complexity. In general, complex models require more specific and complex input data than simple models. Some of these data might not be readily available and acquiring such data might require expending resources. Therefore, the objective of the model application can be very important in this step.
- Calibration requirements: Decision making and management alternatives based on modeling results require that the model outcome be acceptable and reliable. Not all models can be calibrated. Models that simulate water quality conditions are calibrated against in-stream monitoring stations.

In recent decades, multivariate statistical methods have been employed to extract significant information from hydrochemical datasets in compound systems. Different techniques have been used in attempt to evaluate water quality, essentially based on chemical ions correlation and some ions rapports to predict the origin of the mineralization (Tim *et al*., 1992; Laroche *et al*., 1996; Leon *et al*., 2001; Engelmann *et al*., 2003; Sharma *et al*., 2008; Asien *et al*., 2010). There is the need to provide a cost effective alternative which can help to protect the water quality of lakes. Modeling provides such an alternative to interpret data with prediction for the future. Wang *et al*. (2003a, b) developed a model to study the phosphorus dynamics in aquatic sediment and to conduct dynamics predictions of phosphorus release across a sediment-water interface. The model focuses on the sediment active layer below the sediment-water interface and was based on primary mechanisms regulating phosphorus behavior in sediments.

Petterson (2001) studied the proportions of phosphorus forms as well as total phosphorus content in suspended and settling particles during spring, summer and autumn in order to improve the understanding of particle composition and mineralization process in moderately eutrophic, temperature lakes with summer stratification. However, vast amount of data requirement (rainfall, soil type, land use, etc) places several constraints on the application of these models. Statistical models are developed for estimation of concentration of different water quality constituents using routinely-monitored water quality parameters. The best subset modeling procedure enables comparison between full models (containing all the independent variables). Best subset procedure based on R^2 and F values can be used in model dissemination (Sharma and Jain, 2005). Correlation and regression analysis have been described for the study of land use and non point source impacts on water quality (Rajendra *et al*., 2009).

2.5.3. Diffuse Pollution Modelling

Diffuse pollution refers to the pollution arising from land use activities that are generally dispersed across a catchment, and this form of pollution frequently causes, or contributes towards, water quality problems. Point source pollution input loads are normally determined based on field measured data of flow and water quality indicator. In comparison with point source pollution, diffuse source pollution is more difficult to quantify as it is distributed over large areas and is difficult to measure directly. The modeling of non-point source pollution, however complex is very essential for any water quality management programme (Sekhar and Raj, 1995). Diffuse pollution is hard to analyze, control and manage by its nature. It is usually temporally and spatially uncertain, and thus hard to analyze. In many cases, the discretion diffuse source of pollution into individual point sources can ease diffuse pollution modelling and analysis, and therefore reduce high uncertainty especially, in the spatial distribution of pollution loads (Erturk *et al*., 2007). In recent years GIS (Geographical Information System) software has been increasingly used as a tool in land-use studies for modeling the input of pollution loads from diffuse sources. The use of GIS for water quality modeling abounds in literature (Dimov, 2002; Enrique and Richards, 2005; Yuan *et al*., 2007; Richard *et al*., 2008). For example, Jeuness *et al*. (2002) studied the variation in phosphorus loads of point and non-point sources in the Thau catchment located adjacent to the Mediterranean seas. Wischmeier and Smith (1978), Renard *et al*. (1991), and Silvertum and Prange (2003) developed a land use model based on the widely used universal soil loss equation. The indirect approaches to assess the non point pollution utilize water quality measurements in streams, rivers, or lakes to infer the importance of pollution sources. The alternative approach focuses on the non-point sources and attempts to mathematically describe the transport of pollutants to the water body (Haith and Dougherty, 1976). The indirect approach utilizes water quality data (immission data) from streams, rivers or lakes, and infers the importance of non-point source pollution from these in stream observations. The indirect inference approach can be extended beyond simple loading factors by the use of regression models which have land use characteristics as independent variables, and in-stream water quality parameters as dependent variables.

2.5.4 Trend Analysis

2.5.4.1 Time series analysis

Long-term trend of water quality in natural systems reveal information about chemical and biological changes and variations due to manmade and/or seasonal interventions. The success of such trend analysis depends largely on the initial exploratory analysis of the data and in identifying the appropriate model orders to predict trend (Hipel, 1985). Time series is that collection of quantitative observations that are evenly spaced in time and measured successively. Time series are analyzed in order to understand the underlying structure and function that produce the observations. It is assumed that a time series data set has at least one systematic pattern. The most common patterns are trends and seasonality. Trends are generally linear or quadratic. Seasonality is a trend that repeats itself systematically over-time. A second assumption is that the data exhibits enough of a random process so that it is hard to identify the systematic patterns within the data. Time series anaylysis techniques often employ some type of filter to the data in other to dampen the error. Other potential patterns have to do with lingering effects of earlier observations or earlier random errors.

There are numerous software programs that will analyze time-series; such as NCSS, SPSS, JMP and SAS/ETS. Observations over-time can be either discrete or continous. Both types of observations can be equally spaced, unequally spaced, or have missing data. Discrete measurements can be recorded at any time interval, but are most often taken at evenly spaced intervals. Continous measurements can be spaced randomly in time.

Time series are very complex because each observation is somewhat dependent upon the previous observation, and often is influenced by more than one previous observation. Random error is also influential from one observation to another. These influences are called autocorrelation-dependent relationships between successive observations of the same variable. The challenge of time series analysis is to extract the autocorrelation elements of the data, either to understand the trend itself or to model the underlying mechanisms.

2.5.4.2 Seasonality

Seasonal variation is a component of a time series which is defined as the repetitive and predictive movement around the trend line in one year or less, i.e. the frequency of time-series data to exhibit behavior that repeats itself. Seasonal variation is studied for reasons such as better understanding of the impact the component has upon a particular series and to project the past patterns of the future trends. Seasonality is often the major exogenous effect that must be compensated for to discern trends in water quality. Qian *et al*. (2007) evaluated selected water quality constituents from 1979 to 2004 at three monitoring stations in southern Florida for seasonality. The seasonal patterns of flow-weighted and log-transformed concentrations were identified by applying side-by-side box plots and Wilcoxon signed-rank test ($p< 0.05$). They observed that major water quality indicators (specific conductivity, turbidity, colour and chloride) exhibited significant seasonal patterns. Almost all nutrients species (NO_2-N, NH_4-N, total Kjeldah N, PO_4-P and total P) had an identical seasonal pattern of concentrations significantly greater in the wet than in the dry season. Some water quality constituents were observed to exhibit significant annual or seasonal trends. In some cases, the overall annual trend was insignificant while opposing trends were present in different seasons.

2.5.4.3 Smoothing techniques

Smoothing techniques are used to reduce irregularities (random fluctuations) in time series data. They provide a clearer view of the true underlying behavior of the series. Exponential smoothing is a very popular scheme to produce a smoothed time series. It assigns exponentially decreasing weights as the observation gets older. Exponential smoothing is a widely used method in forecasting based on the time series itself. Unlike regression models, exponential smoothing does not impose any deterministic model to fit the series other than what is inherent in the time series itself.

Types of exponential smoothing

Single exponential smoothing

It is also known as simple exponential smoothing. It is used for short range forecasting, usually just one month into the future. The model assumes that the data fluctuates around a reasonably stable mean (no trend or constituent pattern of growth). The specific formula for simple exponential smoothing is:

$$St = \alpha * Xt + (1-\alpha) * St-1$$

St is exponential smoothing factor

α is alpha value

Xt is observed value at time t

When applied recursively to each successive observation in the series, each new smoothed value (forecast) is computed as the weighted average of the current observation and the previous smoothed observation; the previous smoothed observation was computed in turn from the previous observed value and the smoothed value before the previous observation, and so on.

Double exponential smoothing

This method is used when data shows a trend. Exponential smoothing with a trend works much like simple smoothing except that two components must be updated each period-level and trend. The level is a smoothed estimate of the value of the data at the end of each period. The trend is a smoothed estimate of average growth at the end of each period. The specific formula for simple exponential smoothing is:

$St = \alpha * yt + (1-\alpha) * (St - 1 + bt-1) \qquad 0 < \alpha < 1$

$bt = \gamma * (St - St - 1) + (1 -)bt - 1 \qquad 0 < \gamma < 1$

γ is gamma

St is exponential smoothing factor

Triple exponential smoothing

This method is used when data shows trend and seasonality. To handle seasonality, one has to add a third parameter. A third equation will be introduced to take care of seasonality. The resulting set of equation is called the 'Holt-Winters' (HW) method after the names of the inventors. There are two main HW models, depending on the type of seasonality.

Multiplicative seasonal model

This model is used when the data exhibits multiplicative seasonality.

The time series is represented by the model

$Yt = (b1 + b2t)St + \varepsilon t$

Where,

Yt is the data value observed at time t

b_1 is the base signal also called the permanent component.

b_2 is a linear trend component.

St is a multiplicative seasonal factor.

εt is the random error component

Let the length of the season be L period. The seasonal factors are defined so that they sum up to the length of the season, i.e.

$$\textstyle\sum_{1 \le t \le L} St = L$$

The trend components b2 if deemed unnecessary may be deleted from the model. The multiplicative seasonal models appropriate for a time series in which the amplitude of the seasonal pattern is proportional to the average level of the series, i.e. a time series displaying multiplicative seasonality.

Additive seasonal model

This model is used when the data exhibits additive seasonality. This model assumes that the time series is represented by the model

$Yt = b1 + b2t + St + \varepsilon t$

Where,

b1 is the base signal also called the permanent component

b2 is a linear trend component

St is an additive seasonal factor

εt is the Random error component

Let the length of the season be L periods.

The seasonal factors are defined so that they sum to the length of the season i.e.

$$\sum_{1 \le t \le L} St = 0$$

The trend components b2 if deemed unnecessary may be deleted from the model.

The additive seasonal model is appropriate for a time series in which the amplitude of the seasonal pattern is independent of the average level of the series i.e. a time series displaying additive seasonality.

2.6 SELF-PURIFICATION AND ITS RELATIONSHIP TO POLLUTION ABATEMENT

Running water is capable of purifying itself with distances through a process known as self-purification. This is the ability of rivers to purify itself of sewage or other wastes naturally. It is produced by certain processes which work as rivers move downstream. The mechanisms can be inform of dilution of polluted water with influx of surface water and groundwater or through certain complex hydrological, biological and chemical processes such as sedimentation, coagulation, volatilization, precipitation of colloids and its subsequent settlement at the base of channel or lastly due to biological uptake of pollutants. Certain streams however are capable of adding-up more materials as they flow downstream from riparian inputs (Ongley, 1987; 1991).

Self-purification of rivers primarily involves chemical oxidation, biodegradation of organic material, volatilization of volatile organic compounds, and deposition of solid or particulate materials into the sediment and dilution of the contaminants by water. Self-purification of river involves complex mechanism and depends on several factors such as the flow rate, time, and temperature, presence of microorganisms, pH and dissolved oxygen content of the water. The nature of the contaminants also plays significant roles on the river recovery capacity. Hence, some rivers quickly recover from pollution stress than others depending on the prevailing factors.

Rivers are individualistic and natural purification capacities vary from stream to stream and reach to reach along a river course. A river is not static: it is living, dynamic, constantly responsive to the laws of biologic change and the vagaries that apply to living things. Further, each river is sensitive and/in response to hydrological fluctuations which follow the laws of chance and probability.

The purpose of sewage and waste treatment is to protect the condition of streams consistent with reasonable uses of the water heritage. In sewage and waste disposal it is not economically feasible to provide such a high degree of treatment as to return streams to virgin conditions. On the other hand, neither can our water resources be allowed to degenerate to points where they are useful only as sewers. Approached from either of these extremes, the problem of stream pollution is frequently over simplified, as both ignore completely natural self-purification capacities. If pollution control and stream improvement are to be promoted on a sound and economical basis, it is essential to take into consideration natural self-purification. It is well known that the purifying action of a river-water polluted with sewage is very considerable, as a few miles below the outfall or point of pollution a river may show little or no sign of pollution at all. Purification is effected by sedimentation of the suspended solids, and oxidation of the soluble material. The process of oxidation gives rise to deoxygenation depending on the strength of the sewage, the degree of dilution afforded by admixture with the river water and the velocity of the river. If the concentration of oxidisable material is excessive, the river-water will suffer considerable or complete deoxygenation, and a problem will result owing to the septic condition caused by aerobic decomposition of the organic matter. On the other hand, if there be sufficient dilution the organic matter can be oxidized and thus destroyed without depriving the river-water of oxygen to any appreciable degree.

Recovery from pollution or self purification as it is termed depends on the conditions within the particular river. Ordinarily, towns, situated on the same river are sufficiently separated to give time for the river to recover from the effects of the upper pollution before it is subjected to the next. On the other hand, if towns be close together, a nuisance may result, and the river may become unfit to receive a further volume of sewage lower down, until a considerable length of time and dilution from tributaries enable purification to be effected. Evidence of self- purification of some rivers in literature abounds (Lueck *et al*., 1957; Ifabiyi, 2008; Aisien *et al*., 2010). The mere knowledge that the water is polluted tells little more than the bare fact that the immediate capacity of that body of water for self-purification has been exceeded (Lueck *et al*., 1957). Unfortunately, it is seldom possible to immediately isolate and completely eliminate the sources of overload which may be producing pollution conditions in large rivers and other natural water bodies. Usually it becomes desirable, if not imperative, to learn as much as possible about the working capacity of the water body for self-purification and also of the degree of overload. For example, Cazelles *et al*. (1991) emphasized the role of transport mechanisms (convention and longitudinal dispersion) and the role of benthic bio-film which accounts for 35- 40 % of the organic load removal of a small organically polluted stream of the Albenche River (Savoie, France). Ifabiyi (2008) in his work determined evidence of the process of self purification and identified which of the water chemistry variables were affected by the processes and examined the portability of the water with a view to making recommendations for the purpose of water resources management in Ile-Ife.

Seasonal variation is another factor in the self purification of rivers. Owing to the increased rate of oxidation of organic matter due to greater bacterial activity, and the removal of ammonia due to plant development, the process of purification will operate more rapidly during the warmer months. On the other hand, if the river-water be overcharged with sewage, the nuisance may be greater in the summer months than in the winter, as the increased rate of oxidation may lead to deoxygenation of the water. Bakari (2004) reported that the structure of the bottom substrate mainly influences the degree of self-purification capacity of River Kizinga (Dar es Salaam, Tanzania) in connection with the discharge and flow velocity. He observed that, generally, the river-water purified itself faster during dry season than in rainy season, with turbulence physical state accelerating the purification process. Islam *et al*. (2010) found the treatment efficiency of the Surma River (Bangladesh) by itself purification capacity due to the pollution through discharges of choras (small canal), industrial wastewater discharges and human excreta disposal. Monayari *et al*. (2006) reported the enhancement of self-purification of streams using stepped aeration. He reported that the presence of organic matter in waste affects the amount of oxygen that could be dissolved during cascade aeration which invariable means that the concentration of organic matter should be considered in the equations present in the literature for cascade aeration. Chen *et al*. (2007) reported that seasonal variations of self-purification for the pollutants not only resulted from riverine hydrological and ecological conditions, but was also affected by the pollution loading.

Natural self purification is not a fixed quantity, but rather a range in variability of capacity associated with biological and hydrological changes. Failure to recognize this dynamic character of natural purification results in rigid stream standards which cannot possibly be maintained under a normal pattern of stream variability. Streams cannot be generalized: hence stream standards cannot be applied wholesale to all rivers without regard to their widely varying natural self-purification capacities. River or stream has natural recovery capacity or self purification ability in which the pollutants are removed, redistributed, decomposed or transformed to harmless substances. Self-purification capacity of water is a good indicator to evaluate the ecological status of a water body (Ernewstova and Semenova, 1994).

2.7 SEDIMENT AND NUTRIENT DISCHARGE CHARACTERISTICS OF RIVERS

Water quality impairment is related to flow and sediment from soil erosion. Non-point source pollutants come from a number of sources and are washed into our waterways by surface runoff. When land disturbing activities occur, soil particles are transported by surface water movement, and are often deposited in streams, rivers, lakes and wetlands. This soil material is called sediment, and is the largest single non-point source pollutant and the primary factor in the deterioration of surface water quality. Sediment can also come from the decomposition of plants and animals, while wind, water, and ice can help carry these particles to rivers, lakes and streams. Sediment is the loose sand, clay, silt and other particles that settle at the bottom of bodies of water. The erosion of bedrock and soils leads to accumulation of sediments of past or on-going natural and anthropogenic processes and components. Data from sediments can provide information on the impact of distant human activity on the wider ecosystem.

2.7.1 Characteristics of Eroded Sediments

River bottom sediment plays a role in the study of pollution, and can be used to ascertain the quality of surface waters (Oyeyiola *et al*., 2006). An attempt to understand the dynamics of sediment movement through the river system must take account of the potential contrast between the ultimate and effective particle size distribution of suspended sediment in response to aggregation. Walling and Moorehead (1989) reported that in rivers with relatively low solute concentrations, an order of magnitude difference exists between the medium particle size associated with the ultimate and effective grain size distributions. Cation exchange capacity (CEC) of sediment is a good indicator of water quality. Cation exchange sites are found primarily on clay and organic matter. It is based on surface area of sediment grain particles available for binding cations such as hydrogen (H^+) and free metal ions (e.g. Mn^{2+}). Sediments with a high percentage of grains, such as silt and clay, have high surface-to-volume ratios and can absorb more heavy metals than sediments composed of large grains, such as sand (Liber *et al*., 1992). Organic matter content of sediment can contribute to the total CEC, since it binds sediment particles together into stable aggregates which are necessary for stability and adsorption of cations such as calcium, magnesium, sodium and others. This can significantly influence water holding capacity especially if the sediment is more sandy.

Sediment is the ultimate sink of contaminants in the aquatic systems. Accumulation of contaminated sediment in rivers and lakes is becoming a problem of some concern especially in more industrial and urban environment. Heavy metals in sediments are more dangerous because they bioaccumulate. For example, Kuashik *et al*. (2009) found that sediments of River Yamuna in India showed a significant enrichment with Cd and Al indicating inputs from industrial sources. Accumulation of heavy metals like Pb, Cd, Cu, and Ni have been reported to be very high in sediment samples collected in Nallihan Bird Paradise (Aladag Creek, Kirmir Creek and Sakarya River) in Turkey (Ayas *et al*., 2007) and invariably can affect the existence of organisms in the water body. Toxic chemicals can be attached or adsorbed to sediment particles. These pollutants characteristics can be ascertained by studying the quantity, quality and characteristic of sediment in rivers; this allows one to determine sources and evaluate the impact on aquatic environments. All countries have been affected, though the area and severity of pollution vary enormously. According to government statistics, coal mine has contaminated more than 19,000 km of US streams and rivers with heavy metals, acid mine drainage and polluted sediments.

Studies on heavy metals pollution in sediment abound. Adefemi *et al*. (2007) studied the seasonal variation in heavy metal distribution in the sediment of major dams in Ekiti State, Nigeria. The concentration of most of the metals appeared higher in the dry season than those recorded for the wet season. Adekola *et al*. (2002) determined levels of some heavy metals in urban run-off sediments in Ilorin and Lagos, Nigeria. Zn, Fe and Cd were found in very high concentrations in the urban sediments from the cities while Pb had the lowest level. One of the most distinguishing features of metals from other toxic pollutants is that they are not biodegradable. Sediments can incorporate and accumulate many metals added to a body of natural water. The favourable physicochemical conditions of sediment can remobilize and release the metals to the water column. It has been stated that specific local sources such as discharge from smelters (Cu, Pb, Ni), metal-based industries (e.g. Zn, Cr, and Cd from electroplating), paint and dye formulators (Cd, Cr, Cu, Pb, Hg, Se and Zn), petroleum refineries (As and Pb), as well as effluents from chemical manufacturing plants may lead to metal accumulation in sediments (Bonnevie *et al*., 1994; Al-Masri *et al*., 2002). Thus, there is the need for controlling both point and non-point discharges of heavy metals from industries (Bakan and Ozkoc, 2007). Ying *et al.* 2012 reported that sediment of Honghu Lake (East Central China) showed a decreasing trend while Cd presented an increasing trend. The analysis of ecological risk assessment based on sediment quality guidelines suggested that heavy metals in most sediment from the Honghu Lake had moderate toxicity, with Cr being the highest priority pollutant. Hongbin *et al.* 2011 studied the distribution, sources and ecological risk of heavy metals in surface sediments from Lake Taihu. Their results showed that the measured heavy metals had varied spatial distribution patterns, indicating that they had complex origins and controlling patterns, indicating that they had complex origins and controlling factors.

2.7.2 Sediment Related Problems

2.7.2.1 Fisheries/aquatic habitat

Excess sediment can change a river or stream from one with a clean gravel land to one with a muddy bottom. With this change many of the mature fish and animals will disappear. Stream-born sediment directly affects fish populations in several ways:

- Suspended sediment decreases the penetration of light into the water. This affects fish feeding and can lead to reduced survival.
- Suspended sediment in high concentration irritates the gills of fish, and can cause death.
- Sediment can destroy the protective mucous covering the eyes and scales of fish, making them more susceptible to infection and disease.
- Sediment particles absorb warmth from the sun and thus increase water temperature. This can stress some species of fish.
- Suspended sediments in high concentrations can dislodge plants, invertebrates, and insects in the stream bed. This affects the food source of fish, and can result in smaller and fewer fish.
- Settling sediment can bury and suffocate fish eggs.

- Sediment particles can carry toxic agricultural and industrial compounds. If these are released into the habitat they can cause abnormalities or death in the fish.

2.7.2.2 Bioavailability and toxicity of metals in sediment

Sediments act as a natural sink for many metals moving from the terrestrial environment to the marine environment. Mobilized toxic metals from geogenic or anthropogenic sources can be scavenged from the aqueous environment via sediment/organic matter sorption, or they are biogeochemically cycled by a variety of different microorganisms. When the physicochemical characteristics of the environment such as pH, redox conditions, and dissolved oxygen are changed, metal solubility will increase, resulting in remobilisation. Free toxic metals ions, formerly sequestered in the aforementioned solids, will become more concentrated and bioavailable to both microorganisms alike within that ecosystem. Natural wetlands, salt marshes, estuaries, and inevitably the associated marine ecosystem, will become disrupted.

The bioavailability of heavy metals in sediment in literature abound. Besser *et al*. (2008) studied the bioavailability and toxicity of copper, zinc, arsenic, cadmium, and lead in sediments from Lake Roosevelt, Columbia River in Washington. They characterized chronic sediment toxicity, metal bioaccumulation, and metal concentrations in sediment and pore water from eight study sites. Their results indicate that metals in sediments from both riverine and reservoir habitats of Lake Roosevelt are available to benthic invertebrates. Vicente-Martorell (2009) measured concentrations of heavy metals (Cu, Zn, Cd, Pb and As) in sediment from the estuary of Tinto and Odei Rivers in Huelva (Spain), one of the most metallic polluted estuaries in Europe. High pollution of Zn, Pb, As and Cu were found in sediments. Availability of metals was established as following the ranking: Cd>Zn>Cu>Pb in sediment. Lin *et al*. (2008a) studied the geochemical behavior of major trace elements (As, Cd, Co, Cr, Cu, Hg, Zn, Ni, Pb, Sb, Sc, V, Mn, Ti, Al, Fe, Mg, Ca, Na and K) in 39 bottom sediment samples collected from Songhua River. Results indicated that the concentrations of As, Cd, Co, Cr, Cu, Hg, Zn, Ni, Pb, and V in the sediments, were 2.7-11.5, 0.05-1.38, 4.8-14.7, 15.9-78.9, 2.4-75.4, 0.01-1.27, 21.8-403.1, 6.2-35.8, 12.6 - 24.4, and 22.1-108.0 mg/kg, respectively. Due to the input of anthropogenic sources, temporal and spatial variations of Cd, Cu, Hg, Zn, and Pb contents in the sediment were higher than that of major elements. They discovered that generally, sediment contamination of the Songhua River by trace metals was less than that of the Zhujiang river and the Changjiang River, and similar to that of the Huabghe River. Lin *et al*. (2008 a,b) investigated trace metal contamination in the sediment of the second Songhua River in China after being subjected to large amounts of raw effluent from chemical industries in Jilin City in 1960s to 1970s, which resulted in serious mercury pollution. Total concentrations of Al, Fe, Mg, Ca, K, Na, Ti, Mn, V, Sc, Co, Cu, Cr, Ni, Pb and Zn in the sediment samples were measured by ICP-MS, following digestion with various acids. Results showed that concentrations of Co, Cr, and Ni in sediment were generally only slightly higher than or equal to their background values, while concentrations of Co, Pb, and Zn in some sediment samples were significantly higher than their background values. The sediment at Jilin City was moderately contaminated with Cu, and the sediment of second Songhua River was moderately contaminated with Pb and Zn. This buried contamination of trace metals poses a potential risk to water column under disturbance of sediment. Liu *et al*. (2012) evaluated the anthropogenic proportion and potential sources of trace metals in surface sediments of Chaohu Lake, China based on the executive geochemical data. Their analysis showed that concentrations of major and trace metals displayed significant spatial diversity and almost all elements were over the pre-industrial background value, which should be related to the variations of sediment composition partially. They highlighted the contribution of anthropogenic contamination to the elevated potential biological effects of trace metals. Though there had been no obvious human contamination of Cr and Ni in Chaohu Lake, concentrations were all over the threshold effect concentrations, which may be due to higher background levels in the parent materials of soils and bedrocks in Chaohu Lake catchment. Babale *et al*. (2011) conducted a field study to determine the level of Cd and Cr bioavailability of the sediment of Challawa River in Kano, Nigeria. The study revealed that pH and organic matter favours bioavailability of Cd and Cr. The potential risk to river water contamination was highest downstream for Cd based on the calculated contamination factor. Cd posed the highest risk to Challawa river water contamination.

Eggleton and Thomas (2004) reviewed that sediment disturbance can lead to changes in the chemical properties of sediment that stimulate the mobilization of contaminants. Research shows that changes in both redox potential and pH can accelerate desorption, partitioning, bacteria degradation and the oxidation of organic contaminants. However, these processes are both sediment and compound-specific. By affecting the affinity of contaminants to sediments, disturbance events in turn can have a significant effect on their bioavailability. The following factors were considered when assessing the release of contaminants from sediments: the fate of contaminants in undisturbed sediments and those that are not subjected to major disturbances, the kinetic processes that regulate metal release during changes in redox potential, the release of organometallic compounds from sediments re-suspension, the bioavailability of organic and organometallic compounds and the process affecting contaminant release.

2.7.2.3 Speciation of heavy metals in bottom sediments

Speciation studies of heavy metals in bottom sediments of surface water reservoirs are usually conducted in areas subjected to enhanced anthropogenic factors since an increased level of heavy metal presence is a consequence of man's activity. Metals enter the aquatic environment from a variety of sources, including those naturally occurring through biogeochemical cycles and those through anthropogenic sources. The migration behavior and bioavailability of metals is controlled by the way in which metal ions are distributed between the aqueous and particulate phases. As a result, sediments act not only as transport media of contaminants, but also as potential secondary sources of contamination of an aquatic system (Salomons and Forstner, 1984). The advantage of sequential chemical metal speciation over total metal extraction includes:

(1) Assessment of the source of a particular metal (i.e. natural or anthropogenic).
(2) Determination of the relative toxicities to aquatic biota, and
(3) A better understanding of metal-sediment interactions.

On the other hand, since the mobility of a metal and its bioavailability also depend on its speciation, considerable attention has been paid to this aspect in lacustrine systems. For example, Fityanos *et al*. (2004) employed a five-step sequential metal extraction procedure to evaluate pollution by six metals (Cd, Cr, Pb, Mn, Zn, and Cu) of two lakes of northern Greece, Volvi and Koronia. Their findings demonstrated that Cd, Cr, Pb and Cu were bound to oxidizable and residual fractions, and to a lesser extent, to carbonate fractions thus posing a low pollution risk to the lakes. In contrast, Dollar *et al*. (2001) employed the sequential extraction scheme of Tessier *et al*. (1979) to separate the portion of a metal bound to different geochemical groups at Indiana Dunes National Lakeshore. Their results showed a potential risk of pollution by release of Cd, Pb, and Cr present in the exchangeable and carbonate fractions (attributed to anthropogenic sources). In the case of the Mexican Lerma-Chapala Watershed, previous studies using total metal concentrations demonstrated that suspended sediments acted as transport vectors of six metals (Cd, Cr, Ni, Cu, Pb, and Zn) along the Lerma River, with Lake Chapala as the final destination of these pollutants (Juan *et al*., 2010).

Babale *et al*. (2011) assessed the sediment quality of River Challawa in Kano, Nigeria. Their study revealed the distribution of Cr in different fractions in the order; residual > carbonate bound > Fe-Mn oxide bound > organic bound > exchangeable in the study and in the control areas. Chromium was associated mainly (65-93.3%) with the residual fraction in all the samples and relatively small amount of chromium occur in the non-residual fractions. The Cd association with different sediment fraction followed the order: residual bound > exchangeable > carbonate bound > Fe-Mn oxide bound > organic bound. Despite the high levels of Cr, the very low percentage of the metal in the non-residual fraction indicates their limited environmental mobility. Cd is associated more with exchangeable and carbonate fractions, an indication of potential bioavailability of the metals.

2.7.2.4 Remediation of contaminated sediment

Contaminated sediment has been identified as a source of ecological impacts in marine and freshwater systems throughout the world, and the importance of the contaminated sediment management issue continues to increase in all industrialized countries. In many areas, dredging or removal of sediments contaminated with nutrients, metals, oxygen-demanding substances, and persistent toxic organic chemicals has been employed as a form of environmental remediation. In most situations, however, the documentation of the sediment problem has not been quantitatively coupled to ecological impairments. In addition, the lack of long-term, post activity research and monitoring for most projects has impeded a better understanding of the ecological significance of sediment contamination. The lack of information coupling contaminated sediment to specific ecological impairment has, in many instances, precluded a clear estimate of how much sediment requires action to be taken, why, and what improvements can be expected to existing impairments over time. A clear understanding of ecological links not only provides adequate justification for cleanup program but also represents a principal consideration in the adoption of nonintervention, alternative strategies.

Timely and effective remediation of contaminated sediments is essential for protecting human health and the environment and restoring beneficial uses to water ways. A number of site operational conditions influence the effect of environmental dredging of contaminated sediment on aquatic systems. Site experience shows that re-suspension of contaminated sediment and release of contaminants occurs during dredging and contaminated residuals remains after operations. It is understood that these processes affect the magnitude, distribution, and bioavailability of contaminants, and hence the exposure and risk to receptors of concern (Bridges *et al*., 2010). For example, Wang and Feng (2007) conducted a 5-year field monitoring study to assess the effectiveness of the environmental dredging in South Lake, China. They determined the concentrations of total nitrogen, total phosphorus, and heavy metals (Zn, Pb, Cd, Cu, Cr, Ni, Hg, and As), before and after dredging in sediment and compared the results. Multiple ecological risk indices were employed to assess the contamination of heavy metals before and after dredging. Their results showed that the total phosphorus level reduced 42% after dredging. Similar changes for Hg, Zn, As, Pb, Cd, Cu, Cr, and Ni were observed, with reduction percentages of 97.0, 93.1, 826, 63.9, 52.7, 50.1, 32.0, and 23.6, respectively, and the quality of sediment improved based on the criterion of Sediment Quality Guidelines by USEPA. Contamination degree values decreased significantly. Unexpectedly, the total nitrogen increased by 49% after dredging, compared to before dredging. Their finding was that environmental dredging was an effective mechanism for removal of total phosphorus and heavy metals from South Lake. But, the dredging was ineffective in removing nitrogen from sediment. The increase in total nitrogen level was likely due to ammonia release from the sediment, impairing the effectiveness of the dredging. Disposal of polluted dredged sediments on land may lead to certain risks. Currently, contaminated dredged sediments are often not vaporizable due to their high contents of contaminants and their consequent hazardous properties. It is generally admitted that treatment and re-use of heavily contaminated dredged sediments is not a cost-effective alternative to confined disposal.

Reports on plants growing in polluted stands without being seriously harmed indicate that it should be possible to detoxify contaminants using agricultural and biotechnological approaches. Several types of phytoremediation can be defined according to Switzguebel (2000) as:

- **Phytoextraction:** The use of pollutant-accumulating plants to remove pollutants like metals or organics from soil by concentrating them in harvestable plants parts.
- **Phytotransformation:** The degradation of complex organic molecules **o**r the incorporation of these molecules into plant tissues.
- **Phytostimulation:** Plant-assisted bioremediation, the stimulation of microbial and fungal degradation by release of exudates/enzymes into the root zone (rhizosphore).
- **Phytovolatilization:** The use of plants to volatilize pollutants or metabolites.
- **Rhizofiltration:** The use of plant roots to absorb or adsorb pollutants, mainly metals, but also organic pollutants, from water and aqueous waste streams.
- **Pump and tress (Dendroremediation):** The use of trees to evaporate water and thus to extract pollutants from the soil.
- **Phytostabilsation:** The use of plants to reduce the mobility and bioavailability of pollutants in the environment, thus preventing their migration to groundwater or their entry into the food chain.
- **Hydraulic control:** the control of the water table and the soil field capacity by plant canopies.

Phytoremediation is given as a management option for semi-terrestrial and terrestrial ecosystems affected by polluted sediments, and the process affecting pollutant bioavailablity in the sediments. The status of sediments, i.e reduced or oxidized, highly influences contaminant mobility, its (eco) toxicity and success of phytoremediation. Bert *et al*. (2009) reviewed that a large variety of plants and trees are able to colonize or develop on contaminated dredged sediments in particular conditions or events (e.g. high level of organic matter, clay and moisture content, flooding, seasonal hydrological variations). Trees, high-biomass crop species and graminaceous species could be used to dredge organic pollutants, to extract to stabillise inorganic pollutants. Choice of plants is particularly crucial for phytoremediation success on contaminated sediments. Research reports on phytoremediation of contaminated sediments in literature abound (Vervaeke *et al*., 2003; Erakhrumen, 2007; Ndimele and Jimoh, 2011; Veronica *et al*., 2011).

2.8 HEAVY METALS ABSORPTION IN VEGETATION

2.8.1 Accumulation and Toxicity of Heavy Metals in Vegetation

Water pollution of most rivers is due to millions of litre of sewage, domestic waste, industrial and agricultural effluents containing substances such as heavy metals such as lead, cadmium; mercury e.t.c. Heavy metals in the environment is increasing following their ever increasing utilization in modern technology. Substantial efforts have been made in identifying plant species and their mechanisms of hyperaccumulation of heavy metals. Variations exist for hyperaccumulation of different metals among various plant species and within populations (Pollard *et al*., 2002). Plants absorb a number of elements from soil, some of which have known biological functions and some are known to be toxic at low concentrations. Their availability in a soil-plant system depends on a number of factors which include pH of soil, soil organic matter content, cationic exchange capacity as well as plant species, stage of development, and others (Farago, 1994). It is known that the availability of some heavy metals decreases with rising pH of the soil, organic matter and clay content. Our environment has always been under natural stresses but its degradation was not as severe as it is today. The effect of environmental pollution on vegetation is astounding. Plants can face a number of foreign (xenobiotics) compounds during their life. These xenobiotics include ions of heavy metals such as lead, cadmium or copper. Study of plant response to chemical pollution is important for the management of healthy ecosystems.

Many studies have indicated that the accumulation of heavy metals in sediment has had an adverse effect on the growth and development of a wide variety of plants species. Although, low concentrations of some heavy metals, such as copper and zinc, are necessary for the proper functioning of most plant systems. Higher concentrations of copper and zinc have been found to be responsible for metabolic disturbances and growth inhibition of some plants (Fernandes and Henriques, 1991). Other studies have demonstrated that the uptake of such metals as lead, nickel, and cadmium can damage the integrity of cell membranes in certain plants. For example, excess concentration of lead, cadmium, copper and zinc significantly affected the plant water status of sunflowers, causing water deficit and subsequent changes in the plant (Kastori *et al.*, 1992). Although the uptake of heavy metals is antagonistic to a myriad number of plant systems, other studies have shown that some plants are able to absorb heavy metals, adapt to them, and thrive. Currently, those sites that contain the highest concentrations of heavy metals are situated near industrial sources such as smelters and steel refineries. Even in locations such as these, certain plant species have been able to adapt to heavy metal ions. Both the mechanisms that the plants use for adaptation and the specific effects of the metals on plant's bio-systems, however, remain unclear (Ernst *et al.*, 1992).

High level of metals in sediment does not necessarily reflect elevated doses in plants. The ability of some plants to absorb and accumulate xenobiotics makes them useful as indicators of environmental pollution. Plants absorb a number of elements from soil, some of which have no known biological function and some are known to be toxic at low concentrations. It is known that the availability of some metals decrease with rising pH of the soil, organic matter and clay content. The source of heavy metals in plant is the environment in which they grow and their growth medium (soil) from which heavy metals are taken up by roots or foliage of plants. Plants growing in polluted environment can accumulate heavy metals at high concentration causing risk to human health when consumed as food or for medicinal usage.

The study of excessive concentrations of pollutants in biological matrices has been reported in numerous publications. Muhammed (2007) evaluated the levels of arsenic and heavy metals and their genetic effects on *C. latifolia* growing in the Mamut River (Sabah, East Malaysia) riparian zone. His study revealed significantly higher levels of As (45±20µg/kg), Cd (22±2µg/kg), Cu (3678±160 µg/kg) and Zn (3773±1710µg/kg) compared to the same plant specimens from control site at Kipungit with As (16.3±11µg/kg), Cd (22±2µg/kg), Cu (450±200µg/kg) and Zn (1770±640µg/kg) at $p< 0.05$. Ozdilek *et al*. (2007) evaluated the potential impacts that metals may have on vegetation and plant tissues in the vicinity of the Blackstone River, USA. The river had been subjected to metals load that included contributions from urban runoff, waste water discharges, contaminated sediments, and also re-suspension of contaminated sediments in the river-bed. All these effects lead to the elevated concentrations of metals such as lead, copper, zinc, chromium, cadmium and arsenic. Their results showed that the metals concentrations in vegetation were generally inversely related to the distance between the vegetation and the riverbank.

Heavy metals enter the biological cycle through the roots and leaves of plants and are enriched in various plant organs. They can directly affect plant growth. The chemical composition of plants reflects the elemental composition of the sediment and the contamination of the plant surface indicates the presence of noxious environmental contaminants. Metal content will vary depending on which part of the plant is sampled. The extent of accumulation in different plant parts will vary with species and the nature of the element. Chemical composition varies not only with the age of the plant itself but with the age of the leaf/needle. For example, Thomas *et al*. (1991) studied the levels of Fe, Mn, Ni, Zn, Cr and Cu in roots, stems and leaves of aquatic plants collected at river Pimos in Central Greece in order to obtain information about the heavy metal contamination of the river. The selected species proved to be good indicators for the monitoring of heavy metals. Ahmet *et al*. (2005) investigated the heavy metal status of plants in Sultan Marsh, Turkey. Tissues of *Phragmites australis* accumulated heavy metals more than those of *Ranunculus sphaerosphermus*. They reported that heavy metal accumulation in different parts of plants followed the sequence: roots> stem > leaf. Both plants were found to be useful as biological indicators while determining environmental pressures; however, *Phragmites australis* proved more appropriate for such studies. For example, Agneta *et al.* (2002) discovered high level of Pb, Cd and Hg in spinach which served as recipients for domestic and other types of wastewater in Thailand. Reports on high accumulation of heavy metals in plants in literature abounds (Sawidis, 1995; Mustafa, 2003; Syed *et al.*, 2008). Jordao *et al.* (1997) evaluated the chromium contaminations from tannery discharges into rivers in the states of Minas Gerails, Brazil using samples of vegetation. Chromium concentration in analysed samples was higher than those normally found.

Steit and Strumm (1993) classified the exchange of chemicals between soil and plants. They divided the most common methods of assessing metal toxicity to plants from soil into three categories in a conditions closed system:

1. Monitoring of the presence or absence of specific plant ecotypes and/or plant species (indicator plant).
2. Measurements of metal concentration in tissues of selected species (accumulative bioindicators).
3. Recording of physiological and biochemical responses (biomarkers) in sensitive bioindicators.

Content of essential elements in plants is conditional, the content being affected by geological characteristics of a soil, and by the ability of plants to selectively accumulate some of these elements. Bioavailability of the elements depends on the form of their bond with the constituents of a soil. Plants readily assimilate through the roots such compounds which dissolve in waters and occur in ionic forms. Additional sources of these elements for plants are rainfall; atmospheric dusts; plant protection agents; and fertilizers, which could be absorbed through the leaf blades (Lozak *et al.*, 2001).

The advantages of using plants, as indicators are summarized below:

1. Vegetation samples are more practicable to collect than sediment because they weigh less.
2. In thick (dense) vegetation, plant sampling is quicker.

3. Large plants exploit the equivalent of many kilograms of sediment and hence can be more representative.
4. Deep-rooted plants can reveal mineralized areas not accessible by surface sampling of sediment.
5. Chemical analysis of plant tissues is less complicated and quicker than sediment analysis.
6. Where the plant accumulates an element, this can produce a more sensitive method of detection than sediment sampling.

The use of plants had been quite extensive and they are generally accepted as good and effective indicators of heavy metal pollution.

CHAPTER THREE

3.0 METHODOLOGY

3.1 DESIGN OF THE STUDY

In meeting the objectives, the following studies were carried out:

(a) Study of quality characteristics of the surface waters:

- *Total study period*: Surface water was studied for a period of twenty-four months from July, 2006 to May, 2008.
- *Frequency*: Surface water samples were collected bimonthly for twenty-four months.
- *Total number of sampling points*: Samples were collected from all the tributaries with a total of 1,080 sampling points.

Surface water was studied for the following parameters:

(i) General physicochemical parameters (pH, electrical conductivity, total solid, total dissolved solid, total suspended solid, turbidity, alkalinity, hardness, calcium and magnesium).

(ii) Trace metals (Pb, Cu, Co, Cr, Cd, Ni and Zn).

(iii) Gross organics (dissolved oxygen, biochemical oxygen demand, and chemical oxygen demand).

(iv) Anions (phosphate, sulphate, nitrate, chloride, ammonia).

(b) Study of the quality characteristics of the sediment

- *Total study period*: River sediment was also studied for the same period as the surface water.
- *Frequency*: Sediments were also collected bimonthly as for surface water.
- *Total number of sampling points*: River sediments were collected at selected locations of surface water with a total of 756 sampling points.

Sediments were studied for the following parameters:

(i) Total organic carbon.

(ii) Sediment mechanical properties (% sand, % clay and % silt).

(iii) Cation exchange capacity.

(iv) Trace metals (Pb, Cu, Cd, Co, Cr, Ni and Zn).

(c) Study of the quality characteristics of plants along river banks

- *Total study period*: plant samples were collected along the river banks.
- *Frequency:* samples were collected bimonthly for the period of study.
- *Total number of sampling points:* samples were collected at the same locations where sediments were sampled with a total of 756 sampling points.

(d) Modeling of the quality characteristics of surface water and sediment

(i) Pratti Scale Quality Classification: data obtained from all the ninety locations were fitted into Pratti scale for surface water classification (Class I - V).

(ii) Data obtained for surface water and sediment were fitted into Time Series Modelling for trend analysis and seasonality prediction of some selected tributaries for future concentration of parameters.

3.2 DESCRIPTION OF STUDY AREA/SAMPLING POINTS

Section 1.6 describes the activities along the river channel. Figure 1 describes the types of industries located along the river banks. The wastes generated from these various activities impair the water quality of the study area.

3.2.1 Map of River Osun showing sampling locations

The sampling points used for the study were selected based on the activities occurring along the river channel as shown in Figure 1. The sampling points are as shown in Figure 3.1. Thirty-one tributaries of river Osun were used. The length of Osun River is 267 km.

3.2.2 Description of Features of Sampling Points

The special features observed at the locations are as described in Table 3.1. Pictures of selected tributaries are as shown in appendices 50 to 53. The table illustrates some of the activities seen at each location. Some of these can increase the concentrations of these pollutants in the river.

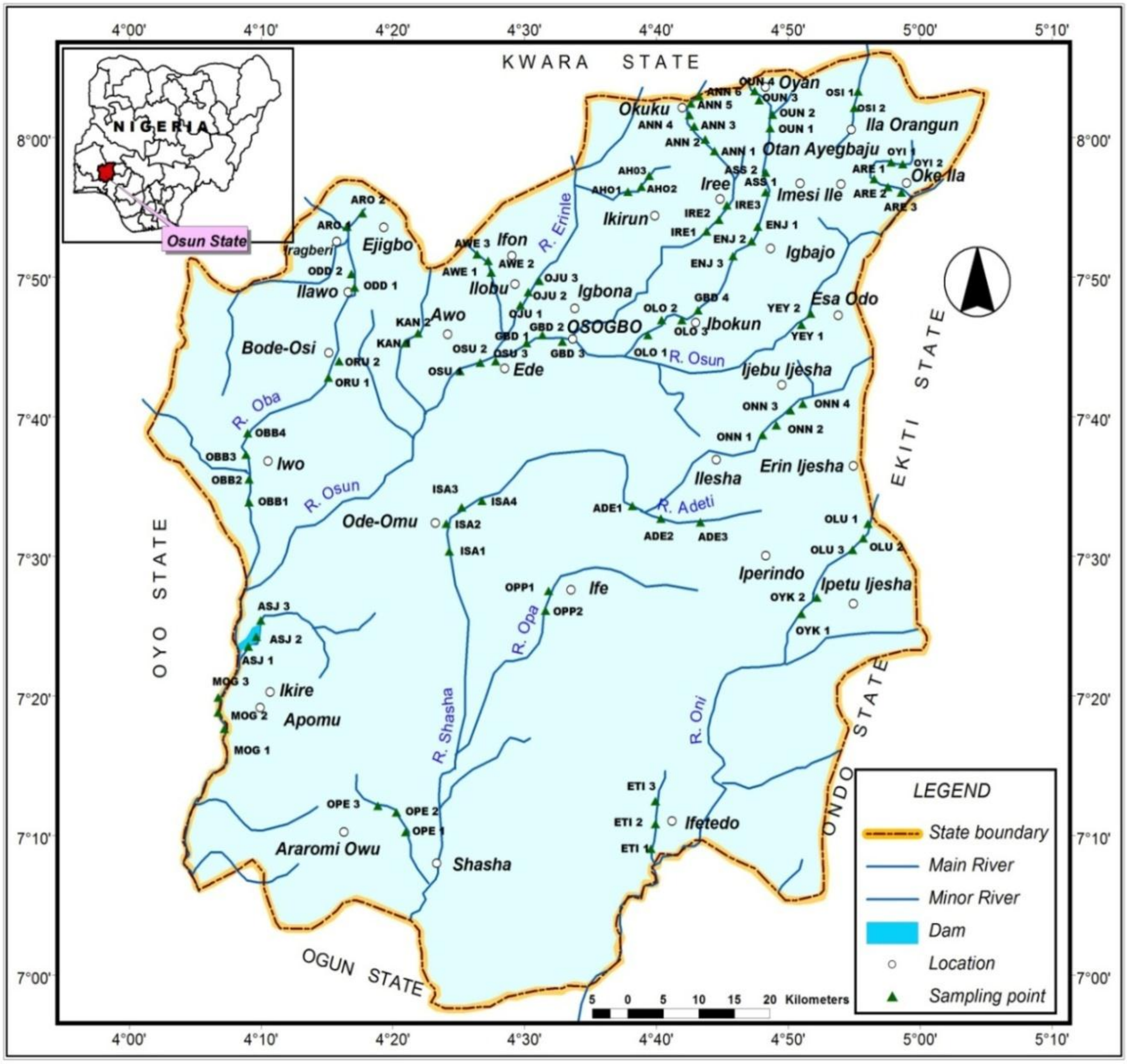

Figure 3.1: Location of sampling points on Osun River and tributaries

Table 3.1: Features of the sampled rivers

Code	Local Name	Near-by Settlement	Features
ADE 1	Adeti	Ilesha	Dirty surroundings, near foam and brewing industry
ADE 2	Adeti	Ilesha	Near slaughter house
ADE 3	Adeti	Ilesha	Dirty surroundings
AHO 1	Ahoyaya	Ikirun	Turbulent flow; bathing; near palm oil mill
AHO 2	Ahoyaya	Ikirun	Turbulent flow; bathing
AHO 3	Ahoyaya	Ikirun	Shaded with trees
ANN 1	Anne	Okuku	High flow rate; boating; suspended particles
ANN 2	Anne	Okuku	Boating
ANN 3	Anne	Okuku	Farming
ANN 4	Anne	Okuku	High flow rate
ANN 5	Anne	Okuku	Boating
ANN 6	Anne	Okuku	Boating
ARE 1	Arenounyun	Otan Ayegbaju	Farming along river bank
ARE 2	Arenounyun	Otan Ayegbaju	Near palm oil mill
ARE 3	Arenounyun	Otan Ayegbaju	Washing of clothes and materials used for palm oil production
ARO 1	Aro	Iragberi	Farming; washing of clothes; cassava processing
ARO 2	Aro	Iragberi	Cassava processing; near poultry farm

Table 3.1 contd.

Code	Local Name	Near-by Settlement	Features
ASJ 1	Asejire	Ikire	Fishing; beverage industry; near dam; boating
ASJ 2	Asejire	Ikire	Washing of clothes; under a bridge
ASJ 3	Asejire	Ikire	Boating
ASS 1	Ashahsha	Imesile	Fast flow rate; shaded with tress
ASS 2	Ashahsha	Imesile	Near palm oil mill
AWE 1	Awesin	Ifon	Washing of clothes and vehicles; near palm oil mill
AWE 2	Awesin	Ifon	Washing of motorcycles
AWE 3	Awesin	Ifon	Beside a bridge
EGU 1	Egun	Iperindo	Fast flowing; Trees along river bank
EGU 2	Egun	Iperindo	Fetching of water for drinking
EJI 1	Aro	Ejigbo	Washing of motorcycles; near soap industry
EJI 2	Aro	Ejigbo	Near soap industry
ENJ 1	Enja	Igbajo	Near palm oil mill; Farming
ENJ 2	Enja	Igbajo	Deposit of palm oil waste
ENJ 3	Enja	Igbajo	Washing of materials used for extracting palm oil
ETI 1	Etioni	Ifetedo	Turbulent flow; bathing
ETI 2	Etioni	Ifetedo	Turbulent flow; washing of clothes

Table 3.1 contd.

Code	Local Name	Near-by Settlement	Features
ETI 3	Etioni	Ifetedo	Turbulent flow; under a bridge
GBD 1	Gbodofon	Osogbo	Turbulent flow; steel rolling mill; boating
GBD 2	Gbodofon	Osogbo	Near a waste dumpsite
GBD 3	Gbodofon	Osogbo	Under a bridge; boating
GBD 4	Gbodofon	Osogbo	Turbulent flow
IRE 1	Isin	Iree	Fast flowing; near palm oil mill, washing of vehicles
IRE 2	Isin	Iree	Washing of vehicles
IRE 3	Isin	Iree	Shaded with trees
ISA 1	Ishasha	Odeomu	Fast flow rate; shaded with trees
ISA 2	Ishasha	Odeomu	Fast flow rate;
ISA 3	Ishasha	Odeomu	Near a bridge
ISA 4	Ishasha	Odeomu	boating; turbulent flow
KAN 1	Kankere	Awo	Farming; washing of clothes
KAN 2	Kankere	Awo	Near poultry
MOG 1	Moginmogin	Apomu	Dirty with bad odour; near soap industry
MOG 2	Moginmogin	Apomu	Near a market
MOG 3	Moginmogin	Apomu	Bathing

Table 3.1 contd.

Code	Local Name	Near-by Settlement	Features
OBB 1	Oba	Iwo	Fast flow rate; textile industry,
OBB 2	Oba	Iwo	Dirty environment
OBB 3	Oba	Iwo	Under a bridge; flow rate low here atimes
OBB 4	Oba	Iwo	Fast flow rate; shaded with trees
ODD 1	Odoiya	Bode Osi	Slow flow rate; washing of clothes;
ODD 2	Odoiya	Bode Osi	Washing of clothes
OJU 1	Ojutu	Ilobu	Fast flow rate; washing of clothes
OJU 2	Ojutu	Ilobu	Fast flow rate; washing of clothes and vehicles
OJU 3	Ojutu	Ilobu	Washing of various materials by spritualists
OLO 1	Oloyo	Ibokun	Near palm oil mill
OLO 2	Oloyo	Ibokun	Near a small bridge
OLO 3	Oloyo	Ibokun	Washing of motorcycles
OLU 1	Olumirin	Erin Ijesha	Tourist centre; Turbulent flow; Water coming out from the rock
OLU 2	Olumirin	Erin Ijesha	Location of fast food joint around here for tourists
OLU 3	Olumirin	Erin Ijesha	Near car pack for visitors; various anthropogenic activities
ONN 1	Oni	Ijebu Ijesha	Washing of motorcycles and clothes; bathing
ONN 2	Oni	Ijebu Ijesha	Beside a bridge

Table 3.1 contd.

Code	Local Name	Near-by Settlement	Features
ONN 3	Oni	Ijebu Ijesha	Washing of vehicles
ONN 4	Oni	Ijebu Ijesha	Washing of clothes
OPE 1	Ope	Araromi Owu	Foamy water, cassava processing
OPE 2	Ope	Araromi Owu	Under the bridge; cassava processing
OPE 3	Ope	Araromi Owu	Washing of motorcycles
OPP 1	Opa	Ile-Ife	Fast flow rate; farming
OPP 2	Opa	Ile-Ife	Shaded with trees; near soap industry
ORU 1	Orufu	Ilawo	Washing of motor vehicles; soap industry
ORU 2	Orufu	Ilawo	Slow flow rate; near palm oil mill; secretion of white liquid substance
OSI 1	Osin	Ila Orangun	Farming; near palm oil mill
OSI 2	Osin	Ila Orangun	Beside a bridge
OSU 1	Osun	Ede	Turbulent flow; boating
OSU 2	Osun	Ede	Automobile workshop
OSU 3	Osun	Ede	Washing of clothes; vehicles and motorcycles
OUN 1	Ounseku	Oyan	Foam seen in some part of the river
OUN 2	Ounseku	Oyan	Slow flow rate
OUN 3	Ounseku	Oyan	Soap industry

Table 3.1 contd.

Code	Local Name	Near-by Settlement	Features
OUN 4	Ounseku	Oyan	Bathing; Washing of Motorcycles
OYI 1	Oyi	Okeila	High flow rate; trees along river bank
OYI 2	Oyi	Okeila	Shaded with trees; log of wood inside river
OYK 1	Oyika	Ipetu Ijesha	Washing of beans and motorcycles; bathing
OYK 2	Oyika	Ipetu Ijesha	Beside a bridge; shaded with trees
YEY 1	Yeyekare	Esa Odo	Turbulent flow; boating; washing of clothes
YEY 2	Yeyekare	Esa Odo	Boating; bathing

3.3 SAMPLING

3.3.1 Sampling of Surface Water

(a) Sampling for physicochemical parameters

Methodology: Each sample was obtained as a composite. Subsamples at a given sampling location were obtained with the aid of a plastic cup at the middle and the bank of the stream/river. These were placed in a plastic bucket and mixed as the composite. Pre-cleaned plastic bottles were used to store the samples. However, preservation was by cooling in an ice chest. Samples were collected bimonthly, for twenty-four months.

(b) Sampling for trace metals (Pb, Cu, Co, Cr, Cd, Ni and Zn) analysis.

Methodology: Samples were also obtained as composites, and stored in plastic containers. However, preservation was carried out by acidifying each sample with 50% HNO_3 (3.5 ml to 1L of surface water sample). Samples were also collected bimonthly, for twenty-four months.

(c) Sampling for the determination of gross organics (DO, BOD, COD)

Methodology: Samples were collected by gently dipping the bottle into the river without allowing air bubbles, and covering the bottle immediately after collection. White BOD glass bottles were used for sample collection, and samples were preserved by cooling to 4^oC. Samples were collected bimonthly, for twenty-four months.

(d) Sampling for labile parameters

Some parameters require in-situ analysis. These are pH, electrical conductivity, temperature, total dissolved solids and dissolved oxygen. Collection and sample analysis for these are described separately under the respective sections on parameter determination.

3.3.2 Sampling of River Sediment

Methodology: Each river sediment sample was collected at several points around each sampling location, and then mixed together to form a composite sample. They were collected with a plastic hand trowel to avoid contamination, and then stored in polythene bags. Samples were preserved by storing in ice chest on the field. Air-dried, ground, sieved and then stored in the laboratory. Samples were collected bimonthly for twenty-four months.

3.3.3 Sampling of Plants

Methodology: At each location, samples of leaves and stems of particular plants found along the river bank were collected and mixed together to form composite sample and then stored in polythene bags. They were preserved by placing the polythene bags in an ice chest on the field and then air-dried, ground, sieved and stored in the laboratory for further analysis. Samples were collected bimonthly for twenty-four months. The various types of plants species used for the study are as shown in Table 3.2.

3.3.4 Summary of Sample Distribution by Location

The numbers of sampling points used for the study were chosen based on the length of each tributary as measured on the map (Fig. 3.1) and the accessibility of the river during sampling. Sediment and vegetation samples were not collected in areas where rocks were found during sampling. Table 3.3 summarizes the sampling distribution by location.

3.4 ANALYSIS OF SURFACE WATERS

Physicochemical parameters in surface water samples were determined using standard methods (USEPA, 1979; APHA-AWWA-WPCF, 1998; Department of the Environment, 1972). Other methods used are as indicated under appropriate parameters.

3.4.1 Determination of pH

pH was determined by directly dipping the battery operated pH meter (HANNAH HI96107) in a plastic container containing the surface water sample. Calibration was carried out using buffer solutions of pH 4.0 and pH 7.0.

3.4.2 Determination of Electrical Conductivity

Electrical conductivity was determined by dipping the portable EC meter (COM-100 model) into plastic container containing 200ml of the surface water. Calibration was carried out using 0.001M KCl.

Table 3.2: List of plants sampled for heavy metals along the banks of River Osun

S/N	Species*	Family	Locations
1	*Paspalum auriculatum presl*	*Cuperaceae*	Asejire
2	*Syndrella nodiflora*	*Asteraceae*	Osun
3	*Cyprus iria Linn*	*Cyperaceae*	Gbodofon
4	*Pilea ceratomera*	*Urticaceae*	Ahoyaya
5	*Brachiara lata*	*Poaceae*	Isin, Oni
6	*Rhaphio stylis beninensis*	*Icacinaceae*	Oyi
7	*Aystacia gigantic*	*Acantheceae*	Osin, Arenounyun, Esaodo, Moginmogin, Adeti
8	*Culasia sexatillis*	*Araceae*	Oloyo
9	*Chromolena odorata*	*Asteraceae*	Enja, Kankere, Aro, Adeti
10	*Bambusa vulgaris*	*Poaceae*	Ashasha
11	*Calapogonium mucuniodis*	*Papilonaceae*	Ounseku
12	*Nelsonia canescens*	*Acantheceae*	Aro
13	*Cylcasia saxatilis*	*Araceae*	Oba
14	*Brachiaria villosa (lam)*	*Poaceae*	Ope
15	*Urena lobata*	*Malvaceae*	Awesin
16	*Axonopus compressus*	*Poaceae*	Ojutu
17	*Nymphaea lotus*	*Nymphaeaceae*	Anne
18	*Furirena umbrella potts*	*Cyperaceae*	Odoiya
19	*Commelina zambesia*	*Commelinaceae*	Ishasha
20	*Commelina nigritana*	*Commelinaceae*	Etioni, Opa
21	*Centhotheca cappace deso*	*Poaceae*	Olumirin

* All identifications were made by Forestry Research Institute of Nigeria, Ibadan

Table 3.3: Summary of sample distribution by location

Code	River	No of Sub-location	Total no. of Surface water	Total no. of sediment	Total no. of of vegetation	Length of tributary (km)
ADE	Adeti	3	36	24	24	11
AHO	Ahoyaya	3	36	24	24	11
ANN	Anne	6	72	36	36	18
ARE	Arenounyun	3	36	24	24	13
ARO	Aro	2	24	24	24	5
ASJ	Asejire	3	36	24	24	25
ASS	Ashasha	2	24	24	24	8
AWE	Awesin	3	36	24	24	10
EJI	Aro	2	24	24	24	6
ENJ	Enja	3	36	24	24	10
ETI	Etioni	3	36	24	24	15
GBD	Gbodofon	4	48	24	24	12
IRE	Isin	3	36	24	24	11
ISA	Ishasha	4	48	24	24	30
KAN	Kankere	2	24	24	24	12
MOG	Moginmogin	3	36	24	24	12
OBB	Oba	4	48	24	24	16
ODD	Odoiya	2	24	24	24	5
OJU	Ojutu	3	36	24	24	18
OLO	Oloyo	3	36	24	24	11
OLU	Olumirin	3	36	24	24	12
ONN	Oni	4	48	24	24	11
OPE	Ope	3	36	24	24	22
OPP	Opa	2	24	24	24	20
ORU	Orufu	2	24	24	24	5
OSI	Osin	2	24	24	24	11
OSU	Osun	3	36	24	24	18
OUN	Ounseku	4	48	24	24	11
OYI	Oyi	2	24	24	24	13
OYK	Oyika	2	24	24	24	10
YEY	Yeyekare	2	24	24	24	15
Total		90	1080	756	756	

3.4.3 Determination of Temperature

The temperature meter (COM-100 model) was dipped directly into the river and temperature was measured and recorded immediately. The meter was calibrated according to manufacturer's instruction.

3.4.4 Determination of Total Solids

Water samples were analysed gravimetrically. A labeled evaporating dish was ignited, cooled, placed in a desiccator to cool, and weighed to constant weight. 100mL of the water sample was measured into the dish. It was evaporated to dryness on a steam bath, and dried at 105°C to constant weight.

Calculation:

$$Total\ Solids\ (mg/L) = \frac{(X2 - X1)}{Y} 1000$$

Where, $X1$ = weight (g) of empty dish
$X2$ = weight (g) of dish + sample
Y = volume (mL) of sample taken.

3.4.5 Determination of Total Dissolved Solids

A portable TDS meter was dipped into a plastic container containing the river water, and the TDS value read immediately. Replicate determinations were made to estimate precision. The TDS meter (COM-100 model) was calibrated with 0.02M KCl and 0.20M KCl.

3.4.6 Determination of Total Suspended Solids

Total suspended solids (TSS) was calculated as the difference between total solids and total dissolved solids.

Total Suspended Solids $(mg/L) = (Total\ Solids - Total\ Dissolved\ Solids)$.

3.4.7 Determination of Turbidity

Turbidity determination was carried out by visible molecular absorption spectrophotometry.

Preparation of Stock Turbidity Suspension: 10.000g of hexamethylene tetraamine $(CH_2)_6N_4$ was dissolved with distilled water in a 100mL volumetric flask, and diluted to mark. This was labelled as Solution 1. Hydrazine sulphate, $(N_2H_2)\ H_2SO_4$ (1.00g) was dissolved in distilled water and diluted to the mark in 100mL volumetric flask. It was labelled as Solution 2. 5.0mL of Solution 1 and 5.0mL of Solution 2 were added into a 100mL volumetric flask and mixed. The mixture was allowed to stand for 24 hours at 25±3℃, and then diluted to the mark with distilled water and mixed. The turbidity of this prepared solution was 400 FTU.

Procedure: Water sample for analysis was allowed to cool to room temperature. The turbidity of the water sample was measured immediately after vigorous shaking. The blank solution was also prepared without the addition of the sample.

Calibration and sample reading: Working standard (0, 2, 10, 40, 80, 100 and 150 FTU respectively) solutions were prepared from 400 FTU stock solutions. These were used to prepare calibration graph for turbidity (R^2 = 0.953) and treated as for sample. The absorbance of the water sample and blank were measured at 580nm with a visible double beam spectrophotometer (Lambda 3B). The turbidity reading of the blank was subtracted from sample reading and result read from graph and recorded in FTU.

3.4.8 Determination of Alkalinity

50 mL of water sample was pipetted and two drops of methyl orange indicator was added. This was then titrated with 0.1M HCl to an orange end point.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

$$Alkalinity\ (mg/L) = \frac{(Volume\ of\ acid\ used\ [mL]\ x\ Molarity\ of\ acid)}{Volume\ of\ sample\ (mL)}\ x\ 50{,}000$$

3.4.9 Determination of Total Hardness

50mL of water sample was measured into a conical flask and placed on a tile. Water sample containing suspended materials was filtered before measuring. 1mL of buffer solution (ethanolamine) was then added. 1mL of 0.05% sodium sulphide was added as a masking agent. Two drops of 0.005% eriochrome black T was added as indicator. The colour of the resulting solution turned wine-red showing the presence of Ca and Mg ions. This was immediately titrated with standard 0.01M EDTA solution with continuous stirring to a light blue colour at the end point.

$$\text{Total Hardness (mg/L):} \quad \frac{\text{Volume 0.01M EDTA (mL)}}{\text{Volume of sample (mL)}} \quad \text{x 1000}$$

3.4. 10 Determination of Calcium

50mL of water sample was placed in a conical flask. 2.0mL of 0.05M HCl was added to the water sample, and it was then boiled for three minutes. This was cooled to room temperature. 1mL sodium sulphide inhibitor was then added for masking. 2.0mL 0.05M NaOH was added to this and mixed. The solution was placed on a white tile and 3.5mL of glyoxalbix-2-hydroxoanil indicator was added, stirred for one minute, and titrated with 0.01M EDTA until the colour of the solution changed from orange-red to lemon-yellow.

$$\text{Concentration of Ca (mg/L):} \quad \frac{\text{Volume 0.01M EDTA (mL)}}{\text{Volume of sample (mL)}} \quad \text{x 1000}$$

3.4.11 Determination of Magnesium

The magnesium titre of the water sample was determined by subtracting titre value obtained for calcium determination from the titre value for hardness determination.

$$\text{Conc. of Mg (mg/L):} \quad \frac{[\text{Titre for hardness (mL)} - \text{Titre for Ca (mL)}]}{\text{Volume of sample (mL)}} \quad \text{x 1000}$$

3.4.12 Determination of Nitrate

Nitrate content of water sample was determined using phenoldisulfonic acid method (Gary, 1994).

Preparation of reagents:

Phenoldisulfonic Acid: 25g phenol was dissolved in 150mL concentrated H_2SO_4. 75mL of fuming H_2SO_4 was added to this solution and stirred. The resulting solution was heated for 2 hours on a hot water bath. The solution was allowed to cool before use.

Silver Sulphate Solution: 4.4g $AgSO_4$ was dissolved in 1L distilled water

Stock Nitrate Solution: 100mg/L of nitrogen was prepared by dissolving 0.722g anhydrous KNO_3 in 1L distilled water.

***Procedure*:** 100mL sample was treated with 100mL Ag_2SO_4 solution in order to remove interference by chloride. This sample was neutralized to pH 7 with dilute NaOH and filtered. The water sample was transferred to a beaker and evaporated to dryness. The residue was mixed with 2.0mL phenoldisulfonic acid reagent using a glass rod to help dissolve the solids. The resulting mixture was diluted with 20mL distilled water and 6mL concentrated ammonia of Analar grade was added until maximum colour of deep yellow was developed. The clear solution was transferred into a 50mL volumetric flask and diluted to volume with distilled water. Blank was prepared by measuring 100mL of distilled and carrying out all the procedures for sample analyses.

Calibration and Sample Reading: Working standard (0, 0.05, 1, 2, 4, 6, 10 mg/L NO_3^-) solutions were prepared by dilution of the stock and treated with appropriate reagents as for sample and used to prepare calibration graph for nitrate ($R^2 = 0.987$). Sample solution prepared above was measured at 410 nm wavelength and blank was read at the same wavelength with a double beam visible spectrophotometer (Lambda 3B). Blank reading was subtracted from sample reading and result read from the graph. NO_3^- in the sample was recorded as mg/L.

3.4.13 Determination of Chloride

Chloride in water sample was determined by mercurimetric titration.

Preparation of reagents:

0.02M Mercuric Nitrate Solution: 5.04g of mercuric nitrate, Hg $(NO_3).H_2O$ was dissolved in 50 mL distilled water containing 0.5mL nitric acid. It was diluted to 1L and filtered. This solution was standardized against standard sodium chloride.

0.02M Standard Solution of Sodium Chloride: 1.648g dried sodium chloride was dissolved in distilled water and diluted to 1L.

Indicator: 0.5g of 5-diphenylcarbazone and 0.05g bromophenol blue was dissolved in 100mL alcohol.

0.05M HNO_3: 3.2mL nitric acid was diluted to 1 L.

Procedure: 50mL of water sample was measured into a 250mL conical flask and 5 drops of mixture of 5-diphenylcarbazone and bromophenol blue was added as indicator. This changed the colour of the solution to purple. 1mL 0.05M HNO_3 was added drop wise until the colour changed to yellow. The solution was then titrated with 0.02M standard mercuric nitrate solution. The blank correction was determined by titrating 50mL distilled water by the same procedure.

$$\text{Conc. Chloride (mg/L):} \quad \frac{(A - B) \times M}{\text{Volume of sample (mL)}} \quad \times 35450$$

A = volume of mercuric nitrate used by sample (mL).
B = volume of mercuric nitrate used by blank (mL).
M = molarity of standardized mercuric nitrate (mL).

3.4.14 Determination of ammonia

Ammonia in water sample was determined by direct nesslerization colorimetrically.

Preparation of reagents:

Nessler Reagent: 35g of potassium iodide and 12.5g mercuric chloride were dissolved in 700mL distilled water. A saturated solution of mercuric chloride was added and stirred to obtain a permanent red precipitate. This was then mixed with a solution of 120g sodium hydroxide in 150mL water. After cooling, it was transferred to a 1L volumetric flask and another 1 mL saturated mercuric chloride solution was added with shaking. The reagent was allowed to settle and the supernatant was stored in a bottle in the dark. A portion of the clear supernatant was transferred periodically into a small bottle when required.

0.5% EDTA Reagent: 50g disodium tetraacetate dehydrate was dissolved in 60mL water containing 10g NaOH.

1000ppm Ammonium Chloride Stock Solution: 3.819g pure ammonium chloride, dried at 105°C, was dissolved in ammonia free water and made up to 1L with ammonia free water.

Procedure: 50.0mL of water sample was measured into 100mL volumetric flask. One drop of 0.5% EDTA solution was added to inhibit precipitation of residual calcium and magnesium ions. 2.0mL Nessler reagent was added and the reaction was left to proceed for 10 minutes for colour to develop. The blank solution was also prepared without the addition of the sample.

Calibration and Sample Reading: Working standard (0.5, 2.0, 5.0, 10, 20, 40 and 60 mg/L) solutions prepared from the stock solution were treated with appropriate reagents as for sample and absorbance read. Readings were used to prepare the calibration graph for ammonia ($R^2 = 0.988$). The absorbance of the sample solution and blank was read at 410nm with a double beam visible spectrophotometer (Lambda 3B). Blank reading was subtracted from sample reading and result read from graph. Ammonia concentration in the sample was recorded as mg/L.

3.4.15 Determination of Sulphate

Sulphate in water sample was determined turbidimetrically by absorption spectrophotometry.

Preparation of reagents:

Conditioning Reagent: 75g NaCl was dissolved in 300mL distilled water. 30 mL hydrochloric acid, 100mL 95% isopropyl alcohol and 50 mL glycerol were all added to this and mixed properly.

Sulphate Standard Solutions: 1.486g anhydrous sodium sulphate was dissolved and diluted to 1L to give 1000ppm sulphate standard solution.

***Procedure*:** 50mL of water sample was measured into 250mL conical flask. 5.0mL of conditioning reagent was added and mixed with magnetic stirrer for one minute at a constant speed. The absorbance was measured after one minute. The blank solution was also prepared without the addition of the sample.

Calibration and Sample Reading: Working standard (0, 5, 10, 30, 50, 100 and 250 mg/L) solutions were prepared from the sulphate stock solution and treated with appropriate reagents as for sample and absorbance read. These were used to prepare calibration graph ($R^2 = 0.991$). The sample and blank solutions were measured at 420nm with a double beam visible spectrophotometer (Lambda 3B). Blank reading was subtracted from sample and the result was read from the calibration graph recorded as mg/L SO_4^{2-}.

3.4.16 Determination of Phosphate

Phosphate in water sample was determined by the ammonium molybdate spectrophotometric method.

Preparation of reagents:

Reducing Agent for Phosphate: 250mL 10M sulphuric acid and 75mL ammonium molybdate solutions were added to 150mL ascorbic acid solution prepared by adding 2.6g ascorbic acid in 150mL distilled water, and mixed. 25mL potassium antimonyl tartrate solution was added and the contents mixed again.

1000 ppm Phosphate Stock Solution and Working standards: 4.3937g potassium dihydrogen phosphate, KH_2PO_4 was dissolved in 1L of distilled water. One drop of toluene was added as preservative.

50 ppm Phosphate Solution: 5 mL of 1000ppm stock solution was added to 100ml flask to give a concentration of 50 ppm.

Procedure: 20mL of the water sample was measured into a 50mL volumetric flask and diluted to 40mL mark with distilled water. 40mL of distilled water was placed in another flask as blank. To both flasks, 8mL of mixed reducing agent was added and diluted to 50mL with distilled water, and mixed. This was allowed to stand for 10 minutes. The absorbance of the sample and blank were measured at a wavelength of 880nm.

Calibration and Sample Reading: Working standard (0, 0.05, 0.1, 0.5, 1.0 and 2.0 mg/L) solutions prepared from stock solution was treated with appropriate reagents as for sample and absorbance was read. This was used to prepare calibration graph ($R^2 = 0.984$). The amount of orthophosphate in the water sample and the blank were read at 880nm with a double beam visible spectrophotometer (Lambda 3B). Blank reading was subtracted from sample reading and result read from the calibration graph. Sample was recorded as mg/L PO_4^{3-}.

3.4.17 Determination of Dissolved Oxygen

***Procedure*:** Dissolved oxygen (DO) was determined in-situ, using a battery operated HANNA H19142 dissolved oxygen meter. The probe of the meter was dipped directly and gently into the water body without disturbing the water body, and the dissolved oxygen content (mg/L) was read and recorded immediately on the field.

Calibration of Dissolved Oxygen Meter:

Zero calibration: A zero calibration was performed for maintenance purpose by dipping the probe in a HI 7040 zero oxygen solution prepared from sodium metabisulphite. The meter was adjusted to reduce to 0%.

Air calibration: This was done by dipping the probe above in 100mL beaker containing distilled water and adjusting to 100%. The meter was always re-calibrated before use.

3.4.18 Determination of Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) was determined by measuring the dissolved oxygen content of the sample on a given day, then incubating the sample, and repeating the DO determination after incubation for five days. The difference is a measure of the BOD.

Preparation of reagent:

Ferric chloride: 0.125g of ferric chloride, $FeCl_3.6H_2O$ was dissolved in 1L water.

Calcium chloride solution: 27.5g of calcium chloride, $CaCl_2$, was dissolved in 1L distilled water.

Magnesium sulphate solution: 25g magnesium sulphate, $MgSO_4.7H_2O$ was dissolved in 1L distilled water.

Phosphate Buffer Stock Solution: 42.5g potassium dihydrogen phosphate, KH_2PO_4, was dissolved in 700mL distilled water and 8.8g NaOH was added to this and mixed. This gave a pH of 7.2. Then, 2.0g ammonium sulphate was added and diluted to 1L.

Preparation of Dilution Water: 1mL of each reagent stock solution was added to 1000mL of freshly distilled water. The water was brought to incubation temperature at 20±1℃. Aerated dilution water was then prepared by saturating this with oxygen, by bubbling air through it using a vacuum pump.

Procedure: 200mL of saturated dilution water was added to 300mL BOD bottle. A measured volume of water sample was then added to this, and mixed with it. Initial dissolved oxygen content (DO_1) was then measured, using a dissolved oxygen meter as described in section 3.4.17. The sample in the BOD bottle was then incubated for 5 days at a temperature of 20℃ and in the dark. After five days of incubation, the dissolved oxygen content (DO_5) was again determined.

$$BOD_5\ (mg/L) = (DO_1 - DO_5) \times DF$$

$$\text{Dilution factor (DF)}: \frac{\text{Volume of BOD bottle (mL)}}{\text{Initial volume of sample (mL)}}$$

3.4.19 Determination of Chemical Oxygen Demand

The chemically oxidisable organic matter content of a given sample is oxidized with known excess amount of acidified potassium dichromate. Unreacted dichromate is then determined by redox titration with ferrous sulphate.

Preparation of reagents:

Potassium dichromate, 0.0625M: 6.129g potassium dichromate was dissolved in 1L distilled water.

Ferrous sulphate, 0.0625M: 34.75g ferrous sulphate, $FeSO_4.7H_2O$ was dissolved in 100mL sulphuric acid, 25% by volume, and diluted to 1L.

Indicator: Commercial ferrous phenanthroline complex was used as indicator.

Procedure: 0.2g of mercuric sulphate was added to 5mL of sample in a round-bottom flask which was then shaken thoroughly. The flask was immersed in cold running water. 5mL of 0.0625M potassium dichromate solution, 10mL concentrated sulphuric acid and 1ml saturated silver sulphate solution was added, and the mixture mixed thoroughly and cooled in a container of cold water. The flask was fitted to a condenser, and few anti-bumping granules were added. One drop of ferrous 1:10 phenanthroline indicator was added and the residual dichromate was titrated with 0.0625M ferrous sulphate. Blank determination was also carried out, following procedure used for the sample. The concentration of COD in the water sample was calculated as follows.

$$\text{COD (mg/L)} = \frac{(A - B) \times M \times 8000}{\text{Volume of sample (mL)}}$$

Where,

A = volume (mL) of standard ferrous sulphate used for blank

B = volume (mL) of standard sulphate used for sample

M = molarity of standardized ferrous sulphate

3.4.20 Determination of Heavy Metals

Heavy metals in water samples were determined by digesting the samples with nitric acid. The digests were then analysed by flame atomic absorption spectrophotometry.

Procedure

Digestion/Concentration process: 5mL of concentrated nitric acid was added to 250mL water sample in a beaker, and stirred. This was heated on a hot plate till the volume was reduced to about 20mL. This was then diluted to 50mL with distilled-deionised water and transferred to a labeled sample bottle.

Preparation of 1000 ppm Stock Solution of Metals: Stock solutions were prepared by dissolving specific amount of salts of Pb, Cu, Cr, Co, Cd, Ni and Zn in 1L flask and made up to 1000mL.

Instrumental analysis:

Calibration and Sample Reading: Working standards (0, 2, 4, 6, 8 and 10 ppm) solutions were prepared from the stock solution and treated appropriately as for sample and absorbance read. The readings were used to prepare calibration graph. The sample and blank solutions were measured at wavelength for specific metal using atomic absorption spectrophotometer (AAS) (Buck Scientific, 200A). The absorbance of blank was subtracted from absorbance of sample. The result was read from the graph and concentration of heavy metal was reported in mg/L. Heavy metals were determined at the Federal University of Technology, Akure. Table 3.4 shows the instrumental characteristics of the element determined.

3.5 Analysis of Sediment for Quality Parameters

3.5.1 Determination of Effective Cation Exchange Capacity (CECe)

Cation exchange capacity of sediment was determined by equilibrating air dried sediment sample with 1M ammonium chloride solution. The upper layer was decanted and extract used for direct measurement of CECe which involved measurement of Ca, Mg, and K by atomic absorption spectrophotometer (British Columbia, 2005).

Table 3.4: Operating conditions for the atomic absorption spectrophotometer

Metal	Wavelength (nm)	Slit width (nm)
Pb	283.3	7
Cu	217.9	7
Co	240.7	2
Cd	228.8	2
Cr	357.9	7
Ni	232	7
Zn	213.9	7

Soure: Price (1983).

Preparation of 1M NH_4Cl: 53.6g of NH_4Cl was dissolved in 1 L distilled water and made up to 1 L mark.

Procedure: 2.00g of air-dried sieved sediment sample was transferred into a 30 mL centrifuge tube. 20mL of 1M NH_4Cl was added, and the tube was then covered. This was centrifuged at 10,000 rpm and then left to settle. The upper layer was decanted carefully and the extract was used for direct analysis for CEC_e for Ca, Mg and K determination, using an atomic absorption spectrophotometer (Buck Scientific, 200 A). The concentration of Ca, Mg and K were determined from the calibration graph.

$$\text{CECe} \ (\text{meq}/100\text{g}) = (\text{Ca}/20 + \text{Mg}/12 + \text{K}/19).$$

3.5.2 Determination of Heavy Metals in Sediment

Procedure

Digestion of Samples: 5.0 g of air-dried sediment sample was extracted with 50mL 2M HNO_3 on a boiling water bath for two hours, shaking at intervals of 15 mins. The resulting extract was filtered and kept for analysis. Blanks were also prepared for every twenty samples determined (Anderson, 1976).

Instrumental analysis: Calibrations on the AAS, and readings of samples and blanks were made as previously described (see section 3.4.20). Concentrations of the metals (3.4.20) in the sample extracts were then obtained by extrapolation.

$$\text{Conc. of Heavy Metals } (\mu\text{g/g}) = \frac{\text{Conc. of metal in extract } (\mu\text{g/mL}) \text{ x Vol. of extract (mL)}}{\text{Sample weight (g)}}$$

3.5.3 Determination of Total Organic Carbon

Total organic carbon in sediments was determined by the redox titrimetric method involving oxidation of sample with an excess of acidified potassium dichromate, and back-titration of unreacted oxidant (IITA, 1979; A.O.A.C., 2000).

Preparation of reagents:

Chromic acid, 0.2M solution: 58.8g oven dried potassium dichromate $K_2Cr_2O_7$ was dissolved in 1L of 1:1 mixture of 96% H_2SO_4 and 85% phosphoric acid, H_3PO_4 and was placed in a water bath at 95-100^oC for 2 hours with occasional stirring.

Ferrous ammonium sulphate, 0.1M: 39.2g of $Fe(NH_4SO_4)_2.6H_2O$ was dissolved in 500mL distilled water containing 5mL 96% H_2SO_4. This was diluted to 1 L and stored in a stoppered bottle, away from light.

Diphenylamine Indicator: 0.20g diphenylamine was dissolved in 100mL 96% H_2SO_4. This solution was stored in an amber-glass dropping bottle.

Procedure: 0.3g of sieved sediment sample was weighed and transferred to a dry 25 x 200mm Pyrex test tube. 10mL of 0.2M Chromic acid was added to each test tube from the burette. It was heated for 3 minutes to 175°C in an electric oven. After cooling, the content of the tube was rinsed into 250mL conical flasks with enough distilled water to make 100mL. 5 drops of diphenylamine was added to the flask and it was then titrated with 0.1M ferrous ammonium sulfate solution to sharp green end point.

$$\%\ \text{Organic Carbon} = \left(\frac{[(B - U) \times D \times M \times A]}{B \times W}\right) \times 1.2 \times 100$$

Where,

B = volume (mL) of ferrous ammonium sulphate solution required for blank.
U = volume (mL) of ferrous ammonium sulphate required for sample.
D = volume (mL) of potassium dichromate used.
M = Molarity of chromic acid.
A = milliequivalent weight of C (0.003g).
W = weight of sample used.

3.5.4 Sediment Mechanical Properties

The percentages of sand, clay and silt in the sediments were determined by the hydrometer method (British Columbia, 2005).

Preparation of Reagent:

Calgon solution 5% w/v: 50g of sodium hexametaphosphate was dissolved in 1L distilled water.

Procedure: 100g of air-dried sediment, which had been passed through a 2mm sieve, was weighed and transferred into a mill shake cup. 50mL of 50% sodium hexametaphosphate and 100mL of distilled water was added. It was mixed with a stirring rod and left to set for 30 minutes. The sediment suspension was stirred for 15 minutes. The suspension was later transferred to a glass cylinder. The top of the cylinder was covered with hand and inverted several times until sediment sample was in suspension. The cylinder was placed on a flat surface and the time was noted. The soil hydrometer was then placed into the suspension until floating. The first reading on the hydrometer was taken at 40seconds as $H_{1,}$ after the cylinder was set down. The hydrometer was removed and temperature of the suspension was recorded as T_1 with a thermometer. After the first hydrometer reading, the suspension was allowed to stand for 3 hours and the second reading was taken as H_2, and temperature was also taken as T_2.

The percentage of sand, clay and silt in the sediment was calculated as follows:

% sand = $100-[H_1 + 0.2\,(T_1 - 68) - 2.0]2$

% clay = $[H_2 + 0.2\,(T_2 - 68) - 2.0]2$

% silt = 100-(% sand + % clay)

Where,

H_1 = Hydrometer reading at 40 seconds

T_1 = Temperature (^oC) at 40 seconds

H_2 = Hydrometer reading at 3 hours

T_2 = Temperature (^oC) reading at 3 hours

0.2(T-68) = Temperature correction to be added to hydrometer reading.

-2.0 = Salt correction to be added to hydrometer reading.

3.6 ANALYSIS OF PLANT SAMPLES FOR HEAVY METALS

The metals were determined by AAS.

Procedure

Solubilisation of sample by dry ashing: 5.0g of dried ground plant sample was placed in a porcelain crucible and ashed in a furnace at 500°C. 2.0g of ashed sample was completely dissolved by treatment with 50mL of 2M concentrated nitric acid, and this was evaporated to near dryness on a hot plate. Distilled water was added, and the solution was filtered into a labeled sample bottle. A blank determination was made for every twenty samples analysed.

Instrumental analysis: Calibrations on the AAS, and readings of samples and blanks were made as previously described (see section 3.4.20). Concentrations of the metals (3.4.20) in the sample extracts were then obtained by extrapolation.

$$\text{Conc. of Heavy Metals } (\mu g/g) = \frac{\text{Conc. of metal in extract } (\mu g/mL) \times \text{Vol. of extract } (mL)}{\text{Sample weight } (g)}$$

3.7 QUALITY ASSURANCE OF THE ANALYTICAL SYSTEM

The quality assurance carried out for the study involved:

- Recovery study of the analytical process for some parameters
- Analysis of standard reference material (sediment)
- Validation of results for BOD determination
- General quality control

3.7.1 Recovery Study of the Analytical Process for Metal Analysis of Sediment and Plant Samples

Sample preparation steps, particularly with the involvement of heating, often lead to some kind of losses of the analyte. It may be due to volatilization, absorption, precipitation, etc. It is imperative to estimate the effectiveness of the digestion process so as to correctly determine the average accuracy of the final results after the instrumental analysis. Recovery is done to determine if there are any losses of analyte during analysis.

This was done for the metals: lead, copper, chromium and nickel in five sediment and plant samples. The concentrations of the metals were first determined using atomic absorption spectrophotometer. 1000ppm of each metal was prepared and working standards for each metal were prepared depending on the initial concentration of the metal in each sediment and plant samples. 1.00g of selected sediment and plant samples already dried were spiked with 1.00cm^3 of 50µg/mL of heavy metals, and were taken through the process described for sediment and plant analysis using AAS. The percentage recovery was calculated as follows:

$$\% \text{ Recovery} = \frac{(\text{Concentration of metal by reanalyses} - \text{Original concentration of metal})}{\text{Level of increase in concentration, achieved by spiking}}$$

The results are as given in Tables 3.5 - 3.6. The calculated average recoveries in sediment samples were: Pb 96.0±4.6%, Cu 91.8±3.3%, Cr 93.8±7.2% and Ni 97.3±4.3% and for plant samples: Pb 98.3±2.9%, Cu 94.9±5.3%, Cr 94.9.8±9.0% and Ni 91.7±11.1. These results represent very good recovery values, and indicate that the sample analysis results are reliable.

3.7.2 Analysis of standard reference material

The quality of the interpretation of results is no better than the quality of the chemical analysis. For this reason, it is imperative to have good set of sediment standard reference materials (SRM) for use in the laboratory quality assurance program. The reference material used for this purpose was the CANMET-SO2 (soil reference of the Canada Centre for Mineral and Energy Technology). The reference sample was dried in an oven at 105^{o}C for 16 hours. 1.0g of the standard reference material was digested with 25mL aqua-regia and heated until the volume was reduced to less than 25mL. Digest was quantitatively transferred (with filtration) into a standard flask, and made up to 25mL mark and then determined by atomic absorption spectrophotometry (as in section 3.4.20). The results are given in Table 3.7.

Statistical analysis t-test shows that there is no significant difference between the values obtained and the standard reference values. This implies that the results obtained are accurate.

Table 3.5: Recovery (%) of Pb in sediment

Sample No.	Original Sample Conc. (µg/g)	Mass of Sample Spiked (g)	Concentration of Standard Spiked (µg/ml)	Volume of Standard Spiked (ml)	Increased Concentration Achieved (µg/g)	Concentration Expected by Re-analysis (µg/g)	Result of Re-analysis (µg/g)	Percentage Recoveries (%)
1	12.1	1.0	50.0	1.0	24.8	36.9	33.9	88.0
2	0.41	1.0	50.0	1.0	0.90	1.30	1.28	97.9
3	0.10	1.0	50.0	1.0	0.20	0.31	0.31	100.0
4	0.19	1.0	50.0	1.0	0.40	0.58	0.57	96.8
5	0.19	1.0	50.0	1.0	0.38	0.58	0.57	97.4
Average								96.0±4.6

Table 3.6: Average recoveries of heavy metals in sediment and plants

Heavy Metals	Recoveries (%)
Pb (in sediment)	96.0±4.6
Cu (in sediment)	91.8±3.3
Cr (in sediment)	93.8±7.2
Ni (in sediment)	97.3±4.3
Pb (in plant)	98.3±2.9
Cu (in plant)	94.9±5.3
Cr (in plant)	94.9±9.0
Ni (in plant)	91.7±11.1

Table 3.7: Results of analysis of standard reference material

Element	Reference Values (µg/g)	Results Obtained (µg/g)
Pb	21	24
Cu	7	13
Co	9	11
Cr	16	21
Ni	8	11
Zn	124	112

3.7.3 Quality assurance for BOD determination

The purpose of carrying out BOD_5 check is to determine if the results obtained in the study are accurate. This was achieved by carrying out BOD determination on a standard solution of known BOD value. A standard solution of 1:1 glucose-glutamic acid (2%) is known to have a BOD value of 198mg/L. Glucose-glutamic acid solution was prepared by drying reagent grade glutamic acid at 103^{o}C for one hour. 150mg of glucose and 150mg glutamic acid were weighed and dissolved in 400ml distilled water in a beaker and diluted to mark in a 1 L flask. BOD_5 of the prepared glucose-glutamic acid solution was determined as described in section 3.4.18. The determination was carried out five times and is as shown in Table 3.8. Statistical analysis t-test shows that there is no significant difference between the BOD values obtained and the reference values. This implies that the results obtained are accurate.

3.7.4 General quality control

Quality of reagent: All reagents used for the analysis were of high purity. Reagents blanks were also prepared and utilized, where appropriate.

Cleaning of apparatus: Sampling containers and general glassware were cleaned using appropriate methods. The plastic containers used for sampling metals and other parameters were cleaned by washing in non-ionic detergent, rinsed with tap water and pre-soaked in dilute HNO_3 for 72 hours, and finally rinsed with distilled water. Sampling bottles for phosphate determination were washed with non-phosphate soaps. They were air-dried in a dust free environment, covered up and packed in cartons until time for sample collection. The container was then labeled on the field prior to sampling. A cleaned plastic bottle with a long rope tied to it was used for collecting water from the rivers. During sampling, sample bottles were rinsed with the water sample several times, before being filled.

3.8 STATISTICAL ANALYSIS OF DATA

Statistical analysis of the data involved:

- T-test was used to test for the difference between the means of parameters obtained during the wet and dry seasons. STATISTICA Release 7 software was used for this purpose.

Table 3.8: Results of BOD check study

S/No.	BOD_5 of Reference (mg/L)	BOD_5 Value Obtained (mg/L)
1	200	205
2	200	212
3	200	189
4	200	207
5	200	186
Mean±SD		200±12

- One-Way analysis of variance was used to test for the differences between means of parameters obtained in all the tributaries. STATISTICAL Release 7 software was used for this purpose.
- Multivariate analysis involving Pearson correlation and Principal Component Analysis (PCA). STATISTICA 7 software was used for this purpose.
- Time series analysis was used to study trend and seasonality, using Number Cruncher Statistical System (NCSS 18335841) package. The method of expo-smoothing was used for trend and forecasting.

3.9 APPLICATION OF MODELING TO STUDY OF SURFACE WATER AND SEDIMENTS QUALITY

The data obtained for surface water and sediment were subjected to time series analysis and forecasting (seasonality) using the Number Cruncher Statistical System package (Lynwood *et al.*, 1990). This was used to determine the pattern of distribution of specific parameters and to project the concentrations up to year 2018.

Time series used involved trend and seasonality analysis, with the use of exponential smoothing to observe the trend and seasonality. Smoothing in time series involves some form of local averaging of data such that the nonsystematic components of individual observations cancel each other out. This method filters out the noise and converts the data into a smooth curve that is relatively unbiased by outliers.

Trend analysis

Method used here was linear trend where least squares trend computes a straight-line trend equation through the data using standard least squares techniques in which the dependent variable is time series and the independent variable is the row (sequence number).

The forecasting equation is $F(t) = a + bt$

This method is useful for those series that show a stable, long term trend. It places the largest weights in estimation on the two ends of the series, while the rows near the middle have an insignificant impact on the estimates.

Seasonality

Forecast method used was Winters with multiplicative seasonal adjustment. The season factor explains the month that the highest concentration of the parameter will be observed in that year. There are six season factors that explain the predicted values, each season correspond to months as follows: Season 1 (January and February), Season 2 (March and April), Season 3 (May and June), Season 4 (July and August), Season 5 (September and October) and Season 6 (November and December).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 AVERAGE CHARACTERISTICS (OVERALL) OF SURFACE WATER

The physicochemical parameters determined included electrical conductivity, pH, total solids, total dissolved solids, total suspended solids, turbidity, alkalinity, hardness, temperature, nitrate, sulphate, phosphate, chloride, ammonia, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand and heavy metals (Pb, Cu, Cd, Co, Cr, Ni, Zn, Ca and Mg). The overall average results obtained are as shown in Table 4.1.

Average electrical conductivity was 216±380 µS/cm. The electrical conductivity was higher compared to the amount obtained at the control site as illustrated in Table 4.1. EC in the water body was most likely derived from limestone due to dissolution of carbonate minerals (Michaud, 1991). Also, build up of salts from domestic wastes can interfere with water re-use by municipalities, industries manufacturing food product, paper and agriculture for irrigation (Hammer, 1975). Waste water effluents often contain high amounts of dissolved salts from domestic sewage. Other sources of salts include windblown sea salt, municipal storm water drainage and industrial effluent discharges. Salts such as sodium chloride, and potassium sulphate pass through conventional water and wastewater-treatment plants unaffected. Urbanization, industrialization and agricultural activities along the river channel resulted in the electrical conductivity value of the river (Fried, 1991). However, it was found to be within the SON (2007) limit for drinking water quality guidelines (1000 µS/cm) and guides for evaluating the quality of water for aquatic life (3000 µS/cm).

The overall pH obtained for the study is illustrated in Table 4.1. pH of the study area was 7.6±0.5. The pH was found to be comparable to what was obtained at the control site. pH is a general measure of the acidity or alkalinity of a water sample. This suggests that the overall pH of waters of Osun River tend to be alkaline and will be suitable for some species of fish and other aquatic organisms. High pH could alter the toxicity of other pollutants it can also alter recreational uses of water. In a river, the water's pH is affected by its age and the chemicals discharged by communities and industries. It was found to be within the range for all the drinking water quality.

Table 4.1: Average concentrations of water quality characteristics of Osun River

Parameter	Concentration	Control Area	AF*
Electrical Conductivity (µS/cm)	216±380	101±45	-
pH	7.6±0.5	7.6±0.2	-
Temperature (^{o}C)	25.3±2.6	27.5±2.0	-
TS (mg/L)	546±570	235±75	2.32
TDS (mg/L)	111±200	62±24	1.79
TSS (mg/L)	435±500	187±69	2.33
Turbidity (FTU)	34±43	1.3±3.4	-
Alkalinity (mg/L)	93±13	66±25	-
Hardness (mg/L)	116±120	61±36	-
Nitrate (mg/L)	1.80±1.50	0.70±0.30	2.57
Sulphate (mg/L)	39±30	35±82	1.11
Phosphate (mg/L)	0.20±0.20	0.05±0.03	4.00
Chloride (mg/L)	55±110	33±8	1.67
Ammonia (mg/L)	4.20±6.60	1.50±0.50	2.80
Dissolved Oxygen (mg/L)	7.90±3.00	7.00±1.00	-
Biochemical Oxygen Demand (mg/L)	6.90±7.50	4.00±2.00	-
Chemical Oxygen Demand (mg/L)	135±120	101±32	-
Ca (mg/L)	68±72	34±25	2.00
Mg (mg/L)	14±34	6.40±4.10	2.19
Pb (mg/L)	0.003±0.004	0.002±0.003	1.50
Cu (mg/L)	0.003±0.004	0.003±0.003	1.00
Cd (mg/L)	0.002±0.003	0.002±0.003	1.00
Co (mg/L)	0.004±0.004	0.004±0.004	1.00
Cr (mg/L)	0.01±0.01	0.003±0.004	3.33
Ni (mg/L)	0.004±0.010	0.004±0.010	1.00
Zn (mg/L)	0.10±0.10	0.10±0.10	1.00

* Accumulation Factor

Table 4.1 illustrates the temperature obtained (25.3±2.6 ^{o}C). Temperature in the control site was found to be higher compared to what was obtained for the study. Temperature depends on the weather, sunlight and depth, and does not undergo changes during the year in the fluvaitile environment (Egborge, 1970; Gupta, 2006; Akinyemi and Nwankwo, 2006) as compared to lacustrine environment. Generally, most of the locations in the study area were shaded with trees. Temperature was found to comply with all the guidelines for all the industries and guides for evaluating the quality of water for aquatic life and recreational water quality.

Total solids (TS) was 546±570 mg/L as shown in Table 4.1. Total solid was found to be higher in the study area compared to the control site. Osun River was found to be impaired with solids from various sources and it is as shown from the factor of accumulation obtained (2.32). TS was derived from the introduction of waste into Osun River. Dumping of solid wastes of various kinds along the river channel also leads to increased total solids content of the river. It was found to be within the limit of most of the industries but exceeds the threshold for light brewing industry (500 mg/L), pulp and paper industries (ground wood, 500mg/L) and tanning industries (100mg/L).

Table 4.1 shows the amount of total dissolved solids obtained for the study (111±200 mg/L). The total dissolved solid (TDS) measures the amount of particles that are dissolved in the river water. It was found to be higher compared to the level derived from control site with an accumulation factor of 1.79. The value indicates that the quality of the river water was impaired as a result of dissolved particles in the river. This will hamper the usage of the water for some specific purpose. It was however noticed to be within the limits for all drinking water quality guidelines and within limits for some categories of industries except power generating industry for boiler feedwater (<0.5mg/L) and food and bevearage industry (Confectionary, 50 – 100mg/L).

The total suspended solid for the study was 435±500 mg/L (Table 4.1). This signifies that the river contained some suspended particles in the river that cannot dissolve and thus impair the quality of the river and sometimes its aesthetic properties. Suspended solids are not desirable in water used for drinking and bathing. Solids are an important parameter to monitor in the control of biological and physical treatment processes and for assessing compliance with regulatory limitations. The value of total suspended solids obtained in this study has also been reported by a survey conducted by Ogunfowokan *et al*. (2005) where a high level of total suspended solids values (200.00±3.11 - 500.00±7.10 mg L^{-1}) were reported for a University sewage treatment oxidation pond at Ile-Ife. This was as a result of wastewater water which entered the river which contains human excreta, urine and other semi solid wastes. High levels obtained can affect the health of the aquatic ecosystem and can also have a deleterious effect on the health of rural dwellers that use the water for domestic purposes without treatment.

The overall turbidity for Osun River was 34±43 FTU. The flow rate of a water body is a primary factor influencing turbidity. Fast running water can carry more particles and larger-sized sediment. The turbidity of Osun River was found to be higher than what was obtained at the control site as shown in Table 4.1, signifying contamination of the river. Decaying plants and animals, bottom feeding fish, algae blooms, flooding and soil erosion can all contribute to turbidity. Slower moving streams usually contain finer particles. Turbidity is clearly related to total suspended solids. High TSS does not mean high turbidity and versa (Matthew and Michael, 2001). This anomaly may be explained by the fact that particles are effective at dispersing light and causing high turbidity readings, while not resulting in high TSS. On the other hand, large organic or inorganic particles can be less effective at dispersing light, yet their greater mass results in high TSS level. However, some authors such as Jason *et al*. (1997) reported high turbidity consistent with high levels of suspended solids. Turbidity of Osun River was found to be outside the range for most drinking water quality guidelines and some industries except for water quality tolerance for pulp and paper industry (Ground wood, 50 FTU and Kraft, <100 FTU).

Alkalinity recorded in the river was 93±13 mg/L. This level is high compared to what was obtained at the control site as shown in Table 4.1. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution. It refers to the ability of water to resist changes in pH. These buffering materials are primarily bicarbonate (HCO_3) and carbonate (CO_3), and occasionally hydroxide (OH^-), borates, silicates, phosphates, ammonium, sulfides, and organic ligands. Waters with low alkalinity are very susceptible to changes in pH. Waters with high alkalinity are able to resist major shifts in pH. Onianwa *et al*. (2001) reported that alkalinity in the waters of urban rivers and streams in Ibadan were derived primarily from bicarbonates as indicated by the pH values obtained. Alkalinity ranged from 59.0mg/L to 688 mg/L. If the alkalinity of water is too high, the water can be cloudy, which inhibits the growth of underwater plants. Too high alkalinity raises the pH level, which in turn harms or kills fish and other river organisms. A number of industries neutralize aqueous wastes to a pH of 7.0. These wastes are usually used by another industry or allowed to empty into streams, rivers and other waterways depending on the level of other pollutants. It was however noticed that alkalinity in Osun River does not exceed the range for certain industrial applications, but was found to be outside the range for power generation (boiler feedwater < 1.00mg/L).

Hardness value was 116±120 mg/L. This value was higher compared to what was obtained at the control site. Hard waters usually have concentrations greater than 200mg/L while soft water are usually less than 75mg/L (Hunter, 1997). Thus, according to Hunter (1997), the water quality of river Osun was hard due to an abundance of minerals such as calcium, magnesium, carbonate and other ions. Hard water streams usually have a large amount of plant growth and life due to the amounts of nutrients that can be used for nourishment and growth. Soft water streams have very low mineral contents. Comparison with drinking water guidelines indicated that it falls within the limit except for the EEC guideline. It was found to exceed the limit for certain industrial applications such as textiles, general dyeing and boiler feed, pulp and paper, iron and steel, power generating stations (boiler feed water, <0.07mg/L), food and beverage industry (brewing, < 70 mg/L) and sugar manufacturing.

Nitrate level was 1.8±1.5 mg/L. This concentration was higher compared to the level at the control site, with an accumulation factor of 2.57. This signifies some level of contamination of the Osun River. Nitrate is a major ingredient of farm fertilizer and is necessary for crop production. When it rains, nitrate may be washed from farmland into nearby waterways. Nitrates stimulate the growth of plankton and water weeds that provide food for fish and increase fish population. However, if algae grow too widely, oxygen levels will be reduced and fish will die. High nitrate levels in waste effluents could also contribute to eutrophication effects, particularly in freshwater (OECD, 1982; Fried, 1991; Morrison *et al.*, 2001). The level of nitrate obtained compares well with low concentration reported by Kolo (1996) (0.12 – 2.24mg/L in Oguta Lake, and 0.06-14.8mg/L in Shiroro Lake). However, low nitrate level was attributed to sedimentation, which was responsible for the reduction of nitrate to nitrite. Nitrate in Osun River network was found to comply with all the drinking water guidelines and all the guidelines for different categories of industries.

Sulphate level was 39±30 mg/L. This value was higher compared to what was obtained for the control site with an accumulation factor of 1.11. This result suggests that the water quality of Osun river system is affected and impaired by the discharge of domestic, agricultural and industrial wastes and other sulphur containing substances. The level however complied with all the guidelines on drinking water quality standards, all guidelines for various industries except sugar manufacturing where the value exceeds the recommended limit of <20 mg/L.

The overall concentration of phosphate was 0.20±0.20 mg/L. This level was about four fold of the level obtained in control sample. The accumulation factor (4.00) suggests contamination of Osun River compared to the control site. The level of phosphate in the study area was derived from anthropogenic activities. Izonfuo and Bariweni (2001) also recorded low phosphate concentrations (0.19±0.07 mg/L – 0.33±0.17 mg/L) in Epie Creek in Niger Delta, which were lower than the limit for drinking water. These were higher than the range of 0.01 – 0.03mg/L for phosphorus normally found in uncontaminated streams (USDASCS, 1975). Olele and Ekelemu (2007) recorded a low concentration of phosphorous in Tigo Lake (0.03mg/L) and Victoria Lake (0.14mg/L). The low concentration of phosphorus was supported by the assertion that over 90% of the element was obtained in bottom sediment (Ovie *et al.*, 2000). The level thus complies with the drinking water guidelines.

The concentration of chloride was 55±110 mg/L. This level was higher compared to the level at the control site, with accumulation factor of 1.67. Chloride is formed naturally when hydrochloric acid reacts with any metal in water. The presence of chloride where it does not occur naturally indicates possible water pollution. The rock salt (NaCl) applied to roads, parking lots and sidewalks to lower ice melting point, often ends up in rivers and streams. Chloride in water might be derived from anthropogenic activities. Chloride was found to comply with all the drinking water guidelines but outside the range for diary and sugar manufacturing industries.

The level of ammonia in river Osun was 4.20±6.60 mg/L. In nature, ammonia is formed by the action of bacteria on proteins and urea at high pH values (pH >8.5) and is extremely toxic to fish and other aquatic life at high concentrations (>2.0mg/L N). Realization of this undesirable consequence has led many local and national authorities to set up stringent guidelines for control of ammonia in surface water. The level of ammonia in this study was higher than the value obtained at the control site, with an accumulation factor of 2.80. This factor suggests a contamination of the surface water quality. High ammonia concentration have been reported in various studies; 249.1, 173.5 and 107.7mg/L for high, medium and low density areas of an open drain area in Ibadan (Sridhar *et al*., 1981); 8.2mg/L in Estuarino, Medras, India (Sridhar, 1982); 6.3mg/L in a Ogunpa Lake, Ibadan (Sridhar and Bammeke, 1985). The level was higher than level stipulated by S. O. N. (2007) for drinking water, and outside the range for power generating stations (boiler feedwater) and guides for evaluating the quality of water for aquatic life.

The dissolved oxygen level of river Osun was 7.9±3.0 mg/L. Dissolved oxygen level was higher than what was obtained at the control site. Which suggests that the study area was not deprived of oxygen and could be attributed to low organic enrichment. Sources of dissolved oxygen in the aquatic environment include the atmosphere and photosynthesis, and depend on its solubility while losses of oxygen include respiration, decay by aerobic bacteria and decomposition of dead decaying sediments (Gupta and Gupta, 2006). The value of DO in this study is in accordance with some findings in the literature; Oke (1998) reported that Owena reservoir had a dissolved oxygen concentration that varied from 0 to 5mg/L. Ikenweiwe and Otubusin (2005) recorded a mean value of 6.40±0.3mg/L in Oyan Lake, Abeokuta. Idowu and Ugwumba (2005) recorded dissolved oxygen concentrations ranging from 6.3-8.3mg/L in Eleiyele reservoir, Ibadan. Dissolved oxygen complied with limits set for quality for aquatic life but outside the range for power generating stations.

The biochemical oxygen demand (BOD) for river Osun was 6.9±7.5 mg/L. This was higher compared to BOD at the control site. This suggests contamination of the Osun

River because of the presence of organic material and many bacteria. Bacteria and other microorganisms decompose this organic material. In a healthy body of water, this process has only a slight impact on dissolved oxygen levels. It serves to release vital nutrients, such as nitrates and phosphates, which stimulate algae and aquatic plant growth. If the amount of decomposing organic material is too high, dissolved oxygen levels can be severely reduced. When aquatic plants die, they are fed upon by aerobic bacteria. The input of nutrients into river Osun, such as nitrates and phosphates, stimulates plant growth. Ogunfowokan *et al*. (2005) in their studies reported a BOD of range 98.85 – 31.64mg/L for University oxidation pond at Ile-Ife, the result indicates some purification and effectiveness of the oxidation pond in the removal of biochemical oxygen demanding substance from the effluent before they enter the stream. Generally, the BOD levels recorded in their study were higher than the EU guidelines of 3.0 – 6.0 mg/L for the protection of fisheries and aquatic life (Chapman, 1996). Average BOD values have been reported from various studies 3.5mg/L (Onianwa *et al.*, 2001), 2.25 – 4.28 (Izonfuo and Bariweni, 2001). BOD is not one of the parameter in some of the guidelines for some industries. Chemical oxygen demand (COD) for Osun River was 135±120 mg/L. This was higher compared to the COD at control site. The factor explains contamination of the river water as a result of discharge of organic matter from various sources. The development of unplanned houses to accommodate the rapidly growing population leads to the proliferation of refuse (waste) dumps, which invariably pose disposal problems. This is usually a common problem with many rapidly developing towns. The high population growth, poor development plan, chronic unhygienic habits and lack of enforcement of regulation have served collectively as recipe for environmental pollution. Cases where COD of river were due to industrial discharge of effluent into river have been reported. Bich and Anyata (1999) reported 5987mg/L of COD in a Kano river. Although these rivers are being used extensively for water supply, irrigation and fishing, the quality of the water was found to be unsuitable for these purposes. Morrison *et al.* (2001) reported a COD value of 32 – 63 mg/L in river Kieskamma in Eastern Cape of South Africa due to the point–source discharge. They suggested an urgent monitoring and attention by the water authorities of the area. COD in Osun River was found to be outside the range stipulated by guidelines for power generating stations.

Low levels of heavy metals were found in surface water especially for Pb (0.003±0.004 mg/L), Cu (0.003±0.004 mg/L), Cd (0.002±0.003 mg/L), Co (0.004±0.004 mg/L), Cr (0.01±0.01 mg/L), and Ni (0.004±0.010 mg/L) except for Zn (0.10±0.10 mg/L). Levels of calcium (68±72mg/L) and magnesium (14±34 mg/L) were significant in the study compared to other metals. These are as shown in Table 4.1. The levels of these heavy metals were found to be higher in the study site than control site especially for Pb and Cr with accumulation factors of 1.50 and 3.33 respectively. The levels were however found to be within the guidelines for drinking water and all the industries.

Paired t-test was used to check if there were significant differences between the means obtained for the study area and control area. The result revealed that the means were found not to be statistically significant except for pH, turbidity, hardness, temperature, nitrate and ammonia.

4.2 AVERAGE CHARACTERISTICS OF SURFACE WATER OF THE VARIOUS TRIBUTARIES

The average characteristics of surface water for the thirty-one tributaries of Osun River studied are as shown in Table 4.2. The levels of each parameter were compared with the guidelines set by various categories of water usage as shown in Tables 2.2 to 2.13.

Electrical conductivity at Adeti was found to be higher than EC stipulated by S. O. N. (2007) for drinking water guidelines. This was due to the various discharges of all forms of waste into river Adeti. The physical appearance of the river looks so dirty. pH of all the tributaries was found to be higher than the level stipulated for certain industrial applications for light brewing and laundering, steel manufacturing in iron and steel industry. The pH of these tributaries was alkaline.

All tributaries had total solids higher than the limit stipulated for certain industrial applications for tanning. Thirteen of the tributaries had values higher than limits for certain industrial applications for light brewing and pulp and paper industry (ground wood). Adeti had values higher than what was stipulated for brewing but was found to be within the limit for general dyeing boiler feed. Seven of the tributaries had total dissolved solids higher than the level stipulated for confectionary for food and beverage industry. Only two tributaries had values higher than the limit set for pulp

Table 4.2: Average characteristics of the tributaries of Osun River

Parameter	Oyi (OYI)	Osin (OSI)	Ounseku (OUN)	Arenounyun (ARE)	Ashasha (ASS)	Isin (IRE)	Anne (ANN)	Ahoyaya (AHO)	Enja (ENJ)
EC	71±32	179±84	99±46	229±150	242±160	136±120	128±49	320±390	91±51
pH	7.4±0.6	7.2±0.5	7.2±0.5	7.7±0.5	7.7±0.3	7.4±0.4	7.5±0.6	7.5±0.3	7.1±0.5
Temperature	23±2	24.6±2.3	22.9±2.1	26.0±2.1	25±2	26.5±1.7	26.0±2.2	26.7±2.7	24.3±2.0
TS	342±210	507±280	457±370	511±350	453±190	520±380	485±330	685±690	352±270
TDS	37±19	92±44	31±25	123±89	118±90	71±62	66±29	169±200	47±30
TSS	305±210	415±290	405±370	388±340	335±180	448±360	419±330	516±650	305±280
Turbidity	27±27	38±53	53±41	37±39	31±41	36±36	15±15	57±66	72±79
Alkalinity	41±9	80±24	58±23	89±17	85±34	68±63	64±15	109±98	49±20
Hardness	95±95	135±130	101±99	133±140	139±140	110±120	123±110	139±160	87±100
Nitrate	1.0±1.0	1.8±1.2	2.2±1.7	2.0±1.2	3.0±3.6	1.6±1.0	1.9±1.7	2.2±1.2	2.5±2.2
Sulphate	30±22	31±25	50±23	36±22	34±28	38±23	22±19	42±32	64±46
Phosphate	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.20±0.20	0.10±0.10	0.10±0.10	0.30±0.40	0.10±0.10
Chloride	17.7±9.7	32±13	17±12	45±23	41±28	28±21	23±17	501±39	25±15
Ammonia	3.2±2.6	2.9±1.4	4.5±3.3	3.9±3.0	3.2±2.7	4.4±4.2	3.6±2.9	5.3±4.4	4.6±2.6
DO	8.5±1.9	6.6±3.1	6.6±3.3	7.4±2.8	9.3±1.9	7.2±3.5	6.4±2.6	7.7±3.2	7.5±1.9
BOD	6.1±3.6	5.1±3.6	5.0±3.6	5.7±3.6	6.1±4.1	6.3±3.8	6.4±3.7	5.70±3.3	5.3±3.2
COD	177±150	143±130	183±170	131±120	163±120	128±140	173±160	141±110	177±190
Ca	48±42	73±80	51±42	74±71	81±71	68±76	66±58	64±69	45±41
Mg	7.10±8.30	12±13	8.40±9.90	7.40±7.50	7.90±8.80	4.80±5.10	9±11	15±17	5.70±6.50
Pb	0.003±0.100	0.003±0.004	0.003±0.003	0.003±0.003	0.002±0.003	0.002±0.003	0.003±0.004	0.003±30.004	0.003±0.003
Cu	0.003±0.003	0.003±0.003	0.003±0.003	0.004±0.009	0.004±0.003	0.002±0.003	0.003±0.003	0.003±0.003	0.003±0.003
Cd	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003
Co	0.004±0.004	0.004±0.004	0.004±0.004	0.004±0.004	0.004±0.004	0.003±0.003	0.004±0.004	0.004±0.004	0.004±0.004
Cr	0.010±0.010	0.003±0.004	0.004±0.004	0.003±0.003	0.004±0.006	0.003±0.004	0.004±0.01	0.003±0.004	0.004±0.004
Ni	0.003±0.010	0.003±0.007	0.003±0.010	0.01±0.01	0.004±0.100	0.004±0.010	0.0040.010	0.003±0.010	0.01±0.02
Zn	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.01±0.10	0.10±0.10	0.10±0.20

* units in mg/L, except EC- µS/cm, turbidity – FTU, temperature – ^{o}C and pH (no units).

Table 4.2 (contd.)

Parameter	Oloyo (OLO)	Gbodofon (GBD)	Awesin (AWE)	Ojutu (OJU)	Osun (OSU)	Yeyekare (YEY)	Oni (ONN)	Olumirin (OLU)	Orufu (ORU)
EC	80±53	173±100	243±170	113±45	139±81	139±77	113±69	39±39	55±11
pH	7.5±0.6	7.6±0.4	7.7±0.4	7.6±0.4	7.8±0.5	7.4±0.6	7.7±0.6	7.5±0.6	7.9±0.5
Temperature	23±2	26.2±2.1	26.7±1.5	26.9±1.8	25.1±1.9	24.0±1.7	23.0±1.9	23.4±2.0	26±1.4
TS	459±380	659±410	700±500	491±40	559±460	310±230	397±270	311±280	284±290
TDS	40±26	89±54	128±94	58±27	70±41	69±39	57±35	19±15	27.2±5.90
TSS	419±370	570±400	570±480	432±400	489±460	241±240	339±270	292±280	257±290
Turbidity	30±23	43±51	74±92	28±40	25±29	19±20	35±42	16±14	72±69
Alkalinity	52±24	70±26	101±138	58±15	65±29	71±20	59±19	28±11	53±27
Hardness	86±110	112±100	119±120	96±79	86±53	90±53	82±47	59±38	37±23
Nitrate	1.3±0.8	1.7±1.6	2.8±2.6	2.4±1.3	1.3±0.7	1.4±0.8	1.5±0.7	1.6±0.6	1.3±0.9
Sulphate	39±29	43±29	53±49	25±11	33±18	35±20	31±16	26±12	59±52
Phosphate	0.10±0.10	0.20±0.10	0.30±0.30	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10
Chloride	27±14	38±24	53±28	25±11	31±14	27±12	30±15	26±12	18.0±9.5
Ammonia	3.4±2.0	3.1±1.8	4.8±4.8	2.4±1.3	2.9±2.5	2.7±1.2	2.8±1.5	2.6±0.8	5.5±3.3
DO	8.2±3.6	8.3±2.4	7.5±2.6	8.0±2.3	8.5±2.2	7.4±2.8	9.9±2.8	10.6±2.2	10.4±3.8
BOD	8.0±9.8	7.0±5.0	5.5±3.9	6.5±4.1	7.8±4.7	7.3±8.2	7.2±9.4	10±13	6.6±3.4
COD	120±82	147±140	151±110	153±110	135±110	162±130	192±180	153±140	88±52
Ca	48±46	64±56	58±47	63±52	59±45	82±100	58±38	40±36	23±19
Mg	25±69	24±60	8.40±9.40	5.90±6.10	13±24	15±32	14±28	10±20	3.30±0.10
Pb	0.002±0.003	0.004±0.010	0.002±0.003	0.003±0.004	0.003±0.004	0.003±0.010	0.003±0.003	0.003±0.003	0.003±0.003
Cu	0.003±0.003	0.003±0.003	0.004±0.010	0.003±0.004	0.003±0.003	0.004±0.004	0.004±0.010	0.004±0.004	0.003±0.003
Cd	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.002	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.003±0.004
Co	0.004±0.003	0.003±0.003	0.004±0.004	0.004±0.004	0.004±0.004	0.004±0.003	0.004±0.003	0.004±0.004	0.010±0.004
Cr	0.01±0.01	0.01±0.01	0.01±0.01	0.003±0.004	0.003±0.004	0.004±0.004	0.004±0.004	0.004±0.004	0.01±0.02
Ni	0.003±0.003	0.004±0.010	0.01±0.01	0.004±0.010	0.01±0.02	0.003±0.010	0.003±0.010	0.004±0.010	0.004±0.004
Zn	0.10±0.20	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10

* units in mg/L, except EC- µS/cm, turbidity – FTU, temperature – ^{o}C and pH (no units).

Table 4.2 (contd.)

Parameter	Kankere (KAN)	Adeti (ADE)	Aro (EJI)	Aro (ARO)	Odoiya (ODD)	Oba (OBB)	Oyika (OYK)	Etioni (ETI)	Ishasha (ISA)
EC	198±82	1760±1200	143±88	147±89	83±31	192±140	53±24	98±54	212±130
pH	7.4±0.5	7.8±0.4	7.6±0.4	7.6±0.5	7.5±0.6	7.7±0.5	7.4±0.5	7.5±0.4	7.8±0.5
Temperature	25.1±1.3	24.7±2.2	24.4±2.4	24.3±2.3	26.1±1.4	26.4±1.9	24.9±1.9	26.3±1.9	25.5±1.7
TS	538±320	2000±1800	412±300	385±330	443±360	493±370	285±190	409±280	612±440
TDS	102±45	893±610	71±45	73±45	41±16	95±71	26±13	49±27	107±69
TSS	436±330	1110±1800	341±290	312±330	401±360	398±340	258±190	360±280	506±480
Turbidity	27±22	37±37	15±13	35±53	32±23	34±30	19±21	22±17	28±22
Alkalinity	72±26	657±280	72±18	102±63	53±27	82±40	36.1±2.3	54±19	98±41
Hardness	107±61	401±210	94±75	96±110	37±23	106±89	61±42	70±40	129±120
Nitrate	1.5±0.8	2.8±2.7	1.3±0.8	1.5±1.0	1.3±0.90	1.90±1.80	1.40±0.80	1.80±1.70	1.40±0.80
Sulphate	46±21	91±50	33±25	41±22	59±52	37±24	24±13	31±26	38±21
Phosphate	0.30±0.30	0.80±0.60	0.01±0.01	0.20±0.20	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10
Chloride	54±19	603±220	26±15	43±23	17±15	48±31	23±12	43±92	46±25
Ammonia	2.9±1.5	27±25	3.1±2.6	3.6±2.1	2.8±1.5	3.2±1.4	2.6±0.8	2.8±1.0	3.5±2.8
DO	5.4±3.4	5.3±3.2	8.1±2.8	7.1±4.1	7.7±2.5	7.2±3.2	8.5±2.8	9.4±2.4	9.1±2.9
BOD	7.1±4.4	13±25	6.3±4.2	6.4±4.9	6.1±4.3	6.8±4.3	6.8±8.1	7.4±8.9	8.3±8.7
COD	121±120	183±94	133±100	99±61	139±120	147±110	159±110	127±120	177±120
Ca	60±57	262±150	61±56	60±66	44±31	67±53	4.30±8.60	51±33	75±66
Mg	26±57	14±17	14±27	9±13	15±28	19±46	10±18	12±29	31±100
Pb	0.004±0.010	0.01±0.01	0.002±0.003	0.004±0.004	0.003±0.003	0.003±0.003	0.003±0.004	0.003±0.003	0.010±0.004
Cu	0.003±0.003	0.004±0.004	0.004±0.004	0.004±0.004	0.003±0.003	0.003±0.003	0.003±0.003	0.003±0.003	0.003±0.003
Cd	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003
Co	0.004±0.003	0.010±0.004	0.004±0.003	0.010±0.004	0.003±0.003	0.004±0.004	0.004±0.004	0.004±0.004	0.010±0.004
Cr	0.003±0.003	0.01±0.01	0.004±0.004	0.003±0.004	0.01±0.01	0.01±0.01	0.004±0.004	0.004±0.010	0.01±0.01
Ni	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.003±0.010	0.004±0.010	0.01±0.01	0.004±0.010	0.004±0.004
Zn	0.10±0.10	0.10±0.10	0.10±0.10	0.04±0.10	0.10±0.10	0.01±0.10	0.10±0.10	0.10±0.10	0.10±0.10

* units in mg/L, except EC- µS/cm, turbidity – FTU, temperature – ^{o}C and pH (no units).

Table 4.2 (contd.):

Parameter	Opa (OPP)	Ope (OPE)	Moginmogin (MOG)	Asejire (ASJ)
EC	176±97	287±200	604±400	167±85
pH	7.6±0.5	7.6±0.5	7.7±0.4	7.7±0.4
Temperature	25.6±1.7	26.4±2.1	28.6±2.7	28.8±3.2
TS	460±350	722±570	760±590	560±580
TDS	87±49	154±120	330±270	70±41
TSS	373±360	571±500	435±430	489±460
Turbidity	35±38	42±69	26±26	25±29
Alkalinity	88±29	139±100	195±92	64±18
Hardness	99±50	170±190	222±190	89±58
Nitrate	1.6±0.9	1.7±1.0	2.7±1.6	1.5±0.6
Sulphate	39±27	42±24	43±20	47±44
Phosphate	0.10±0.10	0.30±0.50	0.30±0.20	0.10±0.10
Chloride	32±14	50±39	144±80	34±20
Ammonia	2.8±1.7	4.4±4.4	4.1±3.1	2.7±1.1
DO	8±12	7.5±3.0	7.3±2.5	8.8±2.5
BOD	7.4±8.0	6.7±4.6	6.6±4.2	7.4±5.1
COD	135±130	123±130	127±66	118±120
Ca	63±36	74±64	122±78	54±37
Mg	6.9±5.5	14±14	4±43	21±45
Pb	0.003±0.003	0.004±0.003	0.01±0.01	0.003±0.003
Cu	0.003±0.003	0.005±0.004	0.004±0.003	0.01±0.01
Cd	0.002±0.003	0.002±0.003	0.002±0.003	0.002±0.003
Co	0.004±0.003	0.004±0.004	0.010±0.004	0.004±0.003
Cr	0.010±0.004	0.010±0.004	0.01±0.01	0.003±0.003
Ni	0.01±0.01	0.01±0.01	0.01±0.01	0.004±0.010
Zn	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10

* units in mg/L, except EC- µS/cm, turbidity – FTU, temperature – ^{o}C and pH (no units).

and paper industry (for bleached paper). Only one of the tributaries had TDS that exceeds the limit for drinking water quality guidelines and for use in the paper and pulp industry (Unbleached). Table 4.2 shows that all the tributaries had TSS greater than the limit set for the production of confectioneries in the food and beverage industries. Six out of the tributaries had their TSS values greater than the value recommended for diary production. All the thirty-one tributaries exceeded the limit stipulated for boating/aesthetic for recreational water quality. All the tribuatries had total suspended solids higher than value prescribed for food canning, freezing, dried, frozen fruits and vegetables.

All the tributaries had turbidity values greater than the drinking water quality guidelines, signifying that they need pretreatment before they can be used for drinking. All had their turbidity greater than what is stipulated for the food and beverage industries. Twenty-four out of the thirty-one tributaries had turbidity greater than the limit set for noticeable threshold of water contact for recreational water quality.

All the tributaries in Table 4.2 showed alkalinity greater than the limit set for the iron and steel industry. Only one of the tributaries had alkalinity exceeding the limit set for usage of water at the power generating stations. Four tributaries had alkalinity greater than what was prescribed for the pulp and paper industry (fine paper). Three tributaries were observed to exceed the limit stipulated for the power generating stations.

Hardness for all tributaries studied is as shown in Table 4.2. Twenty-nine tributaries had their water hardness above the guideline stipulated by EEC, two tributaries were above the limit set by S.O.N. and one tributary exceeded the Japan water quality guidelines. One of the tributaries had its hardness greater than the limit set for the petroleum industries. Five of the tributaries had hardness above the limit set for the tanning industry; all the tributaries had hardness above what was stipulated for the textiles and general dyeing industries. Twenty tributaries had hardness that exceeded the guideline set for brewing industry; fifteen tributaries had hardness above the limit set for sugar manufacturing industries; and two exceeded limit for the diary industry. This implies a level of contamination in these tributaries and will require treatment before usage.

None of the tributaries had nitrate concentration above the limit stipulated by the guidelines for various categories of water usage. All complied for the limit set for drinking water quality by all the guidelines for sulphate. All the tributaries showed higher sulphate concentration above the limit set for sugar manufacturing as shown in Table 4.2. Only one tributary had its sulphate concentration above the standard set for diary industry. The phosphate level of the thirty-one tributaries is illustrated in Table 4.2. All were within the limit set for drinking water quality guidelines.

Two out of the tributaries had chloride levels above the limit set for drinking water quality by all the guidelines. Two of them were found to have chloride level above limits stipulated for beverage and brewing industries, iron and steel industry and petroleum industry. Three tributaries were outside the limit set for brewing, textiles and pulp and paper industries. One tributary was above the guideline set for power generating stations. Twenty of the tributaries did not comply with the threshold limit for diary industry and twenty-seven had chloride values above the limit set for the usage of water by the sugar manufacturing industry.

All the tributaries had ammonia values higher than the level set by all the guidelines for various categories of water usage as shown in Table 4.2. Ammonia is formed only at high pH values (pH >8.5) and is extremely toxic to fish and other aquatic life at high concentrations (>2.0mg/L N). Ecological integrity of aquatic ecosystems is threatened when significant organic pollution exists that exceed self-purification capacity of the water bodies. Any surface water to sustain aquatic life there should be a balanced physicochemical and biological interaction. Abnormally too high or too low of each factor may lead to a deleterious ecosystem disturbance.

The dissolved oxygen (DO) for all the tributaries indicated higher concentrations above the limit set for certain industrial applications, power generating stations and guide for evaluating the quality for aquatic life. Lewis (2000) opined that oxygen conservation is an important management principle for tropical lakes and was also supported by Adeniyi *et al*. (1997). Asa Lake (3.4 –7.3mg/L), Kainji Lake (3.0 –17.8mg/L) and Onah Lake (2.00 – 11.34mg/L) in Nigeria reported by Olele and Ekelemu (2007). However, low primary productivity caused by low transparency and low nutrient load was implicated for low oxygen content of some of the tributaries (Kankere and Adeti) in river Osun. Chemical oxygen demand in Table 4.2 for all the tributaries was higher than what was stipulated by the power generating station and can not be useful except if treated. One-way analysis of variance (ANOVA) shows that the means were statistically significant at $p = 0.05$.

All the heavy metals showed compliance with all the guidelines. Which implies that the tributaries of Osun River were not contaminated with heavy metals. Four of the tributaries showed levels to be higher than the limit set for the petroleum industry and two tirbutaries with magnesium level higher than stipulated for petroleum industry. Two tributaries showed calcium level to exceed limit set for usage of water for food and beverage industry and one tributary had magnesium level greater than the limt prescribed for food and beverage industry.

4.2.1 Pratti Scale Classification of the River Waters

The water samples collected for each of the 90 locations for the thirty-one tributaries in the study were used for this classification. The classification was based on the average values of the concentrations of the parameters according to Pratti *et al*. (1971). The interpretation of these various classes are:

Class 1 – excellent
Class 2 – acceptable
Class 3 – slightly polluted
Class 4 – polluted
Class 5 – heavily polluted

Based on Table 2.14, the locations used were classified. Table 4.3 shows the quality classes that each of the locations belongs to. The study reveals that four of the locations showed excellent surface water quality and these accounts for 5%. Fifty-three of the locations showed acceptable surface water quality and accounts for 59%. Thirty-one of the locations were slightly polluted, accounting for 34%; while two of them were polluted and accounted for 2%. Ishasha (ISA-1), Isin (IRE-2, IRE-3) and OYI-1 had excellent surface water quality. This suggests why some residents along these tributaries fetch and drink water from these sources. Fifty-three locations have acceptable surface water qualities, included those on the tributaries Osun, Gbodofon,

Table 4.3: Pratti scale classification for each location of surface water samples

Tributary	Location	Pratti Scale Classification	Interpretation
Asejire	ASJ 1	3	slightly polluted
	ASJ 2	4	polluted
	ASJ 3	3	slightly polluted
Osun	OSU 1	2	acceptable
	OSU 2	2	acceptable
	OSU 3	2	acceptable
Gbodofon	GBD 1	2	acceptable
	GBD 2	2	acceptable
	GBD 3	2	acceptable
	GBD 4	2	acceptable
Ahoyaya	AHO 1	2	acceptable
	AHO 2	2	acceptable
	AHO 3	2	acceptable
Isin	IRE 1	2	acceptable
	IRE 2	1	excellent
	IRE 3	1	excellent
Oyi	OYI 1	2	acceptable
	OYI 2	1	excellent
Osin	OSI 1	2	acceptable
	OSI 2	3	slightly polluted
Oloyo	OLO 1	2	acceptable
	OLO 2	2	acceptatble
	OLO 3	3	slightly polluted
Enja	ENJ 1	2	acceptable
	ENJ 2	2	acceptable
	ENJ 3	2	acceptable
Ashasha	ASH 1	2	acceptable

Table 4.3(contd.):

Tributary	Location	Pratti Scale Classification	Interpretation
	ASH 2	2	acceptable
Ounseku	OUN 1	2	acceptable
	OUN 2	2	acceptable
	OUN 3	3	slightly polluted
	OUN 4	2	acceptable
Kankere	KAN 1	3	slightly polluted
	KAN 2	3	slightly polluted
Aro	ARO 1	2	acceptable
	ARO 2	2	acceptable
Arenounyun	ARE 1	2	acceptable
	ARE 2	3	slightly polluted
	ARE 3	3	slightly polluted
Oba	OBB 1	2	acceptable
	OBB 2	2	acceptable
	OBB 3	2	acceptable
	OBB 4	3	acceptable
Moginmogin	MOG 1	3	slightly polluted
	MOG 2	4	polluted
	MOG 3	2	acceptable
Ope	OPE 1	2	acceptable
	OPE 2	2	acceptable
	OPE 3	3	slightly polluted
Awesin	AWE 1	3	slightly polluted
	AWE 2	3	slightly polluted
	AWE 3	2	acceptable
Ojutu	OJU 1	3	slightly polluted
	OJU 2	2	acceptable

Table 4.3 (contd.):

Tributary	Location	Pratti Scale Classification	Interpretation
	OJU 3	3	slightly polluted
Anne	ANN 1	2	acceptable
	ANN 2	3	slightly polluted
	ANN 3	2	acceptable
	ANN 4	2	acceptable
	ANN 5	3	slightly polluted
	ANN 6	3	slightly polluted
Aro	EJI 1	2	acceptable
	EJI 2	2	acceptable
Orufu	ORU 1	2	acceptable
	ORU 2	3	slightly polluted
Odoiya	ODD 1	2	acceptable
	ODD 2	2	acceptable
Ishasha	ISA 1	1	excellent
	ISA 2	2	acceptable
Ishasha	ISA 3	2	acceptable
	ISA 4	2	acceptable
Adeti	ADE 1	3	slightly polluted
	ADE 2	3	slightly polluted
	ADE 3	3	slightly polluted
Oni	ONN 1	3	slightly polluted
Oni	ONN 1	3	slightly polluted
	ONN2	2	acceptable
	ONN 3	2	acceptable
	ONN 4	3	slightly polluted
Etioni	ETI 1	2	acceptable
	ETI 2	2	acceptable

Table 4.3 (contd.):

Tributary	Location	Pratti Scale Classification	Interpretation
	ETI 3	2	acceptable
Oyika	OYK 1	3	slightly polluted
	OYK 2	2	acceptable
Olumirin	OLU 1	2	acceptable
	OLU 2	2	acceptable
	OLU 3	3	slightly polluted
Yeyekare	YEY 1	3	slightly polluted
	YEY 2	3	slightly polluted
Opa	OPP 1	3	slightly polluted
	OPP 2	3	slightly polluted

Ahoyaya, Isin, Osin, Oloyo, Enja, Ashasha, Ounseku, Odoiya, part of Ishasha, Oni, Etioni, Olumirin, Aro, Oba, Ope, Anne and Aro. Olumirin is a tourist centre and pollution activities around this vicinity are minimal. But the downstream point however was exposed to visitors and anthropogenic activities accounted for the slightly polluted nature of this water body downstream. Thirty-one locations had slightly polluted surface water quality as a result of industrial, agricultural and municipal activities. These included those on Asejire, Osin, Oloyo, Ounseku, Kankere, Arenounyun, Oba, Moginmogin, Awesin, Ojutu, Anne, Orufu, Adeti, Oyika, Yeyekare and Opa. Two percent of these locations account for the polluted nature of surface water of Osun River and are located on Moginmogin (MOG-2) and Asejire (ASJ-2) as a result of the activities along this water course.

4.3 SPATIAL VARIATIONS OF PHYSICOCHEMICAL CHARACTERISTICS AND HEAVY METALS IN SURFACE WATER OF OSUN RIVER

Figures 4.1 - 4.26 illustrate the spatial variations of each physicochemical characteristic observed for all the tributaries used in this study. It can be noticed that for each of the parameters for all the tributaries, the concentration of the parameters varies depending on the tributary. This is as result of different environmental factors of industrial, urbanization and agricultural activities. The figures depict a transition from more upstream portions (such as OYI, OSI, OUN, ARE, ASS, IRE, ANN, AHO, and ENJ) to down stream portions (such as ASJ, MOG, OPE, OPP and ISA).

Figure 4.1 explains the spatial variation of electrical conductivity in surface water for all the tributaries. Changes in the electrical conductivity are not significant as the water flows from upstream to downstream except at ADE and MOG. This implies that these two tributaries contain more dissolved ions or salts among the tribuatries studied. Anthropogenic activities occurring along the river banks can increase the total dissolved ions in rivers. Some unusual spikes where noticed at some of the tributaries were as a result of random input from various sources. Spatial variation of other parameters in Figures 4.2 to 4.26 follow general pattern as for electrical conductivity.

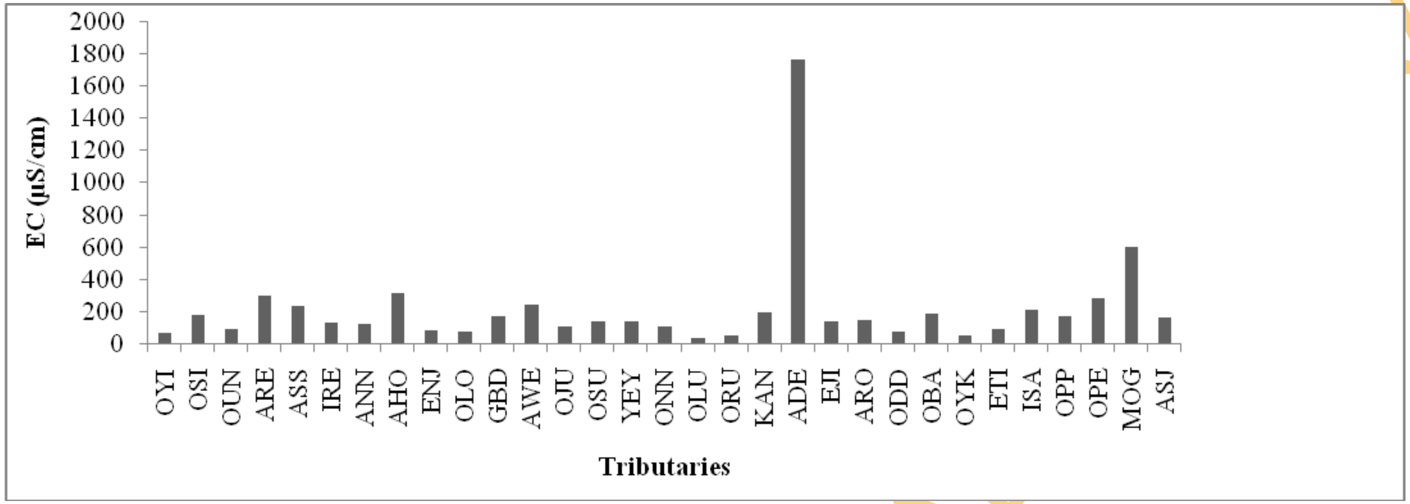

Figure 4.1:   Spatial variation of electrical conductivity in surface water

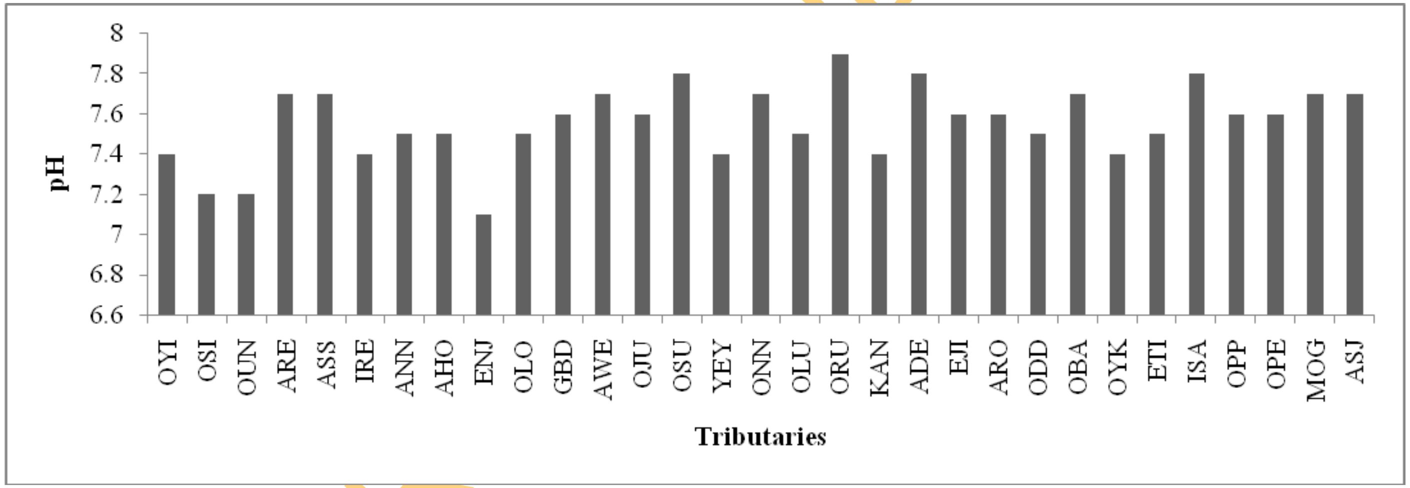

Figure 4.2: Spatial variation of pH in surface water

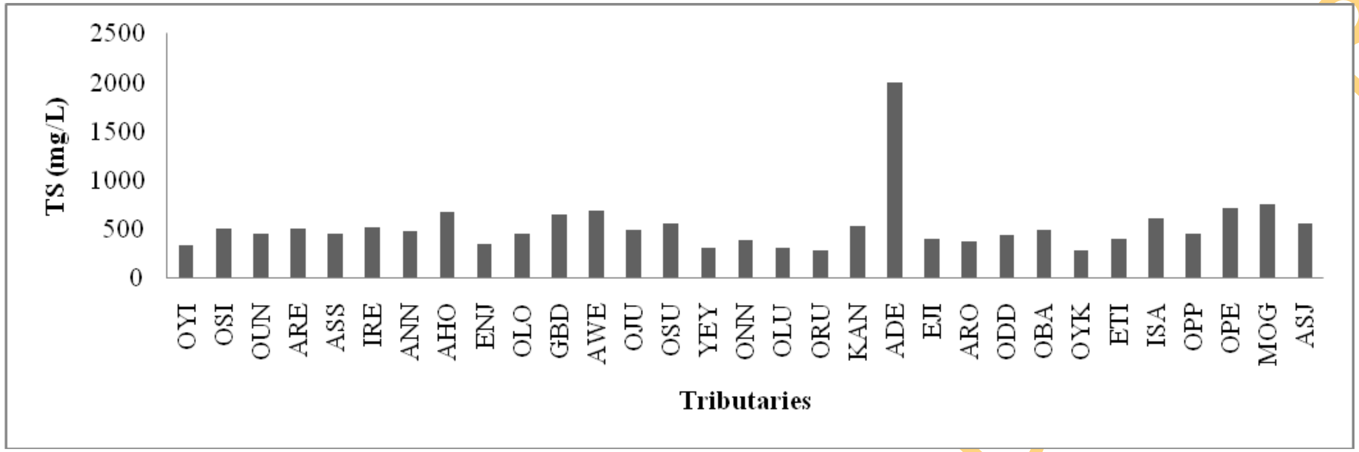

Figure 4.3: Spatial variation of total solids (TS) in surface water

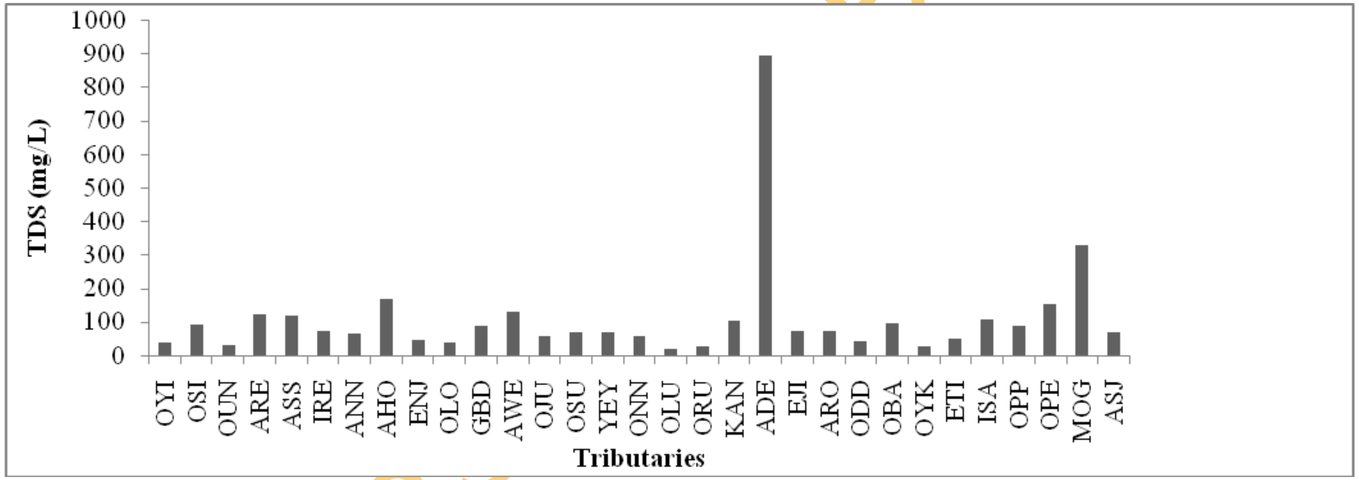

Figure 4.4: Spatial variation of total dissolved solids (TDS) in surface

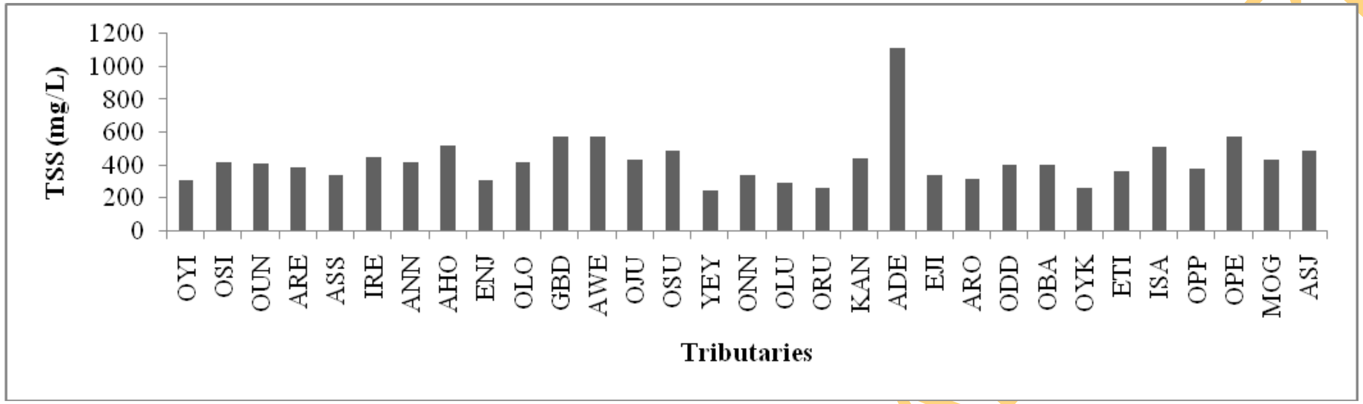

Figure 4.5: Spatial Variation of total suspended solids (TSS) in surface water

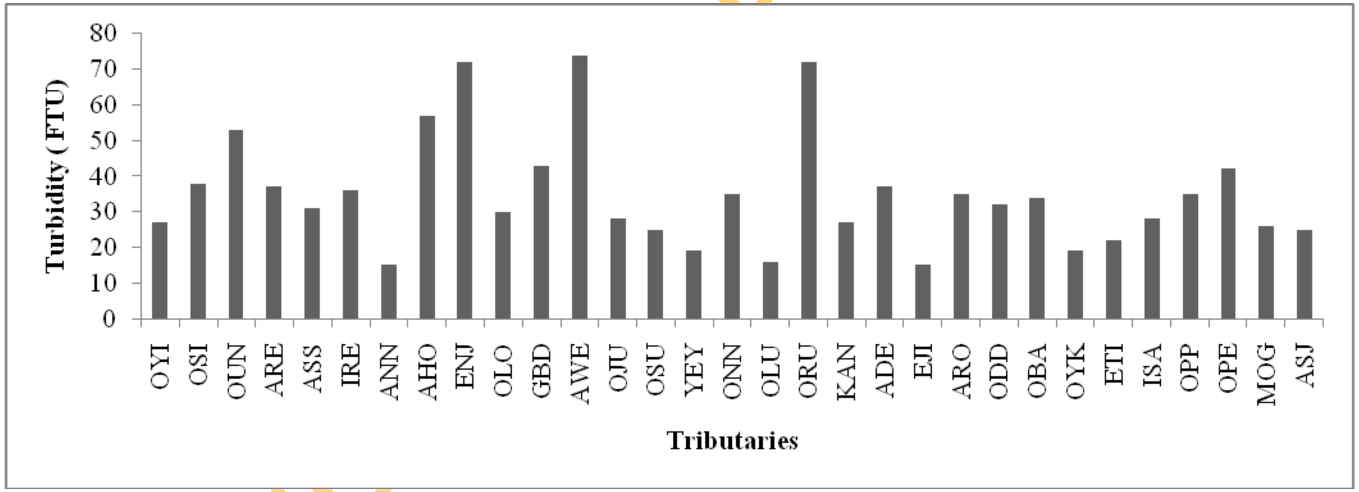

Figure 4.6: Spatial variations of turbidity in surface water

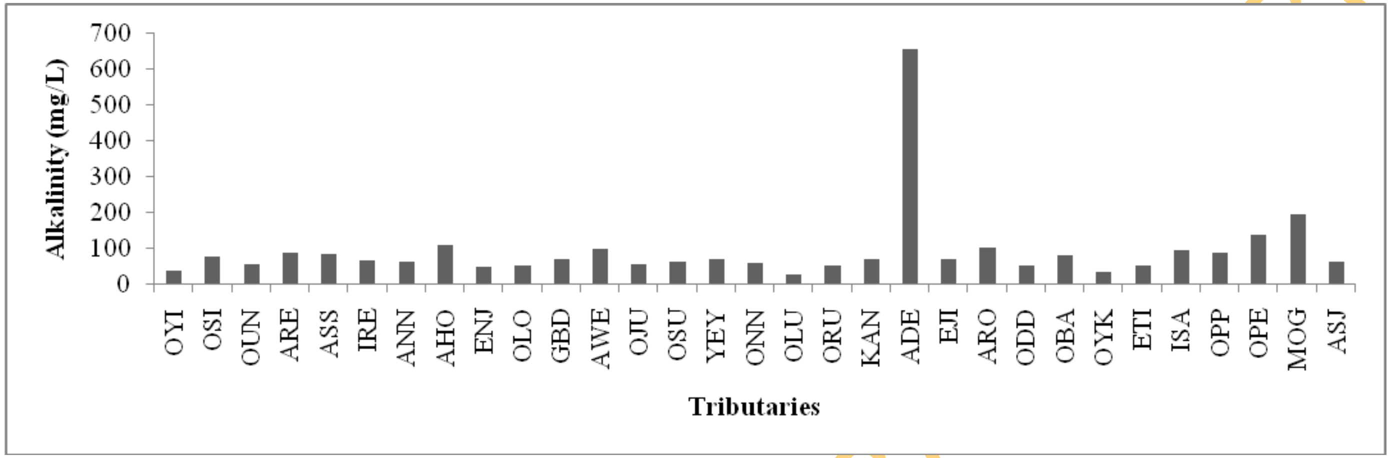

Figure 4.7: Spatial variation of alkalinity in surface water

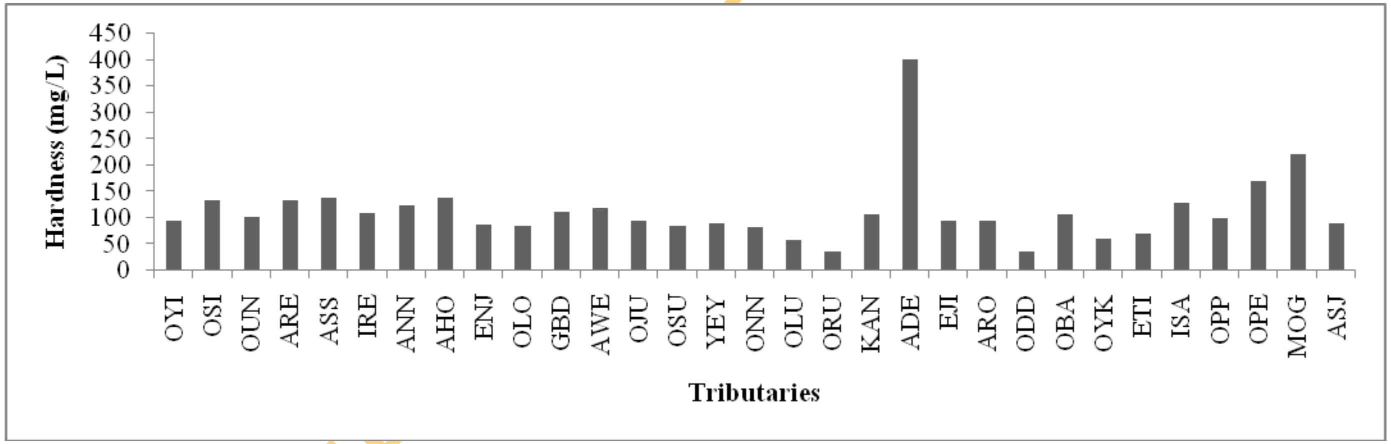

Figure 4.8: Spatial variation of hardness in surface water

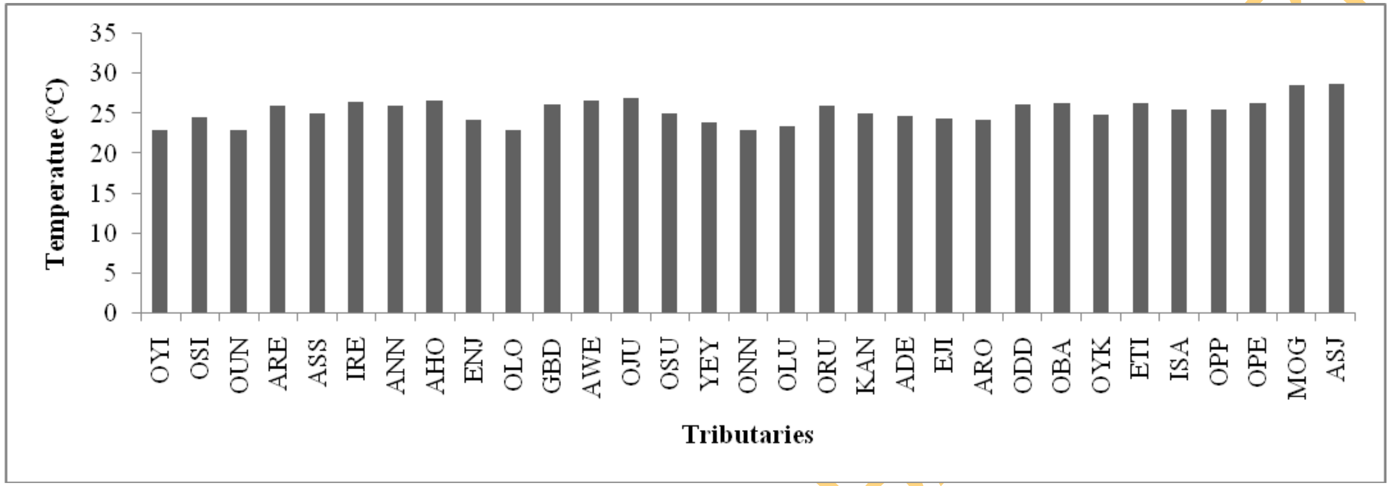

Figure 4.9: Spatial variation of temperature of surface water

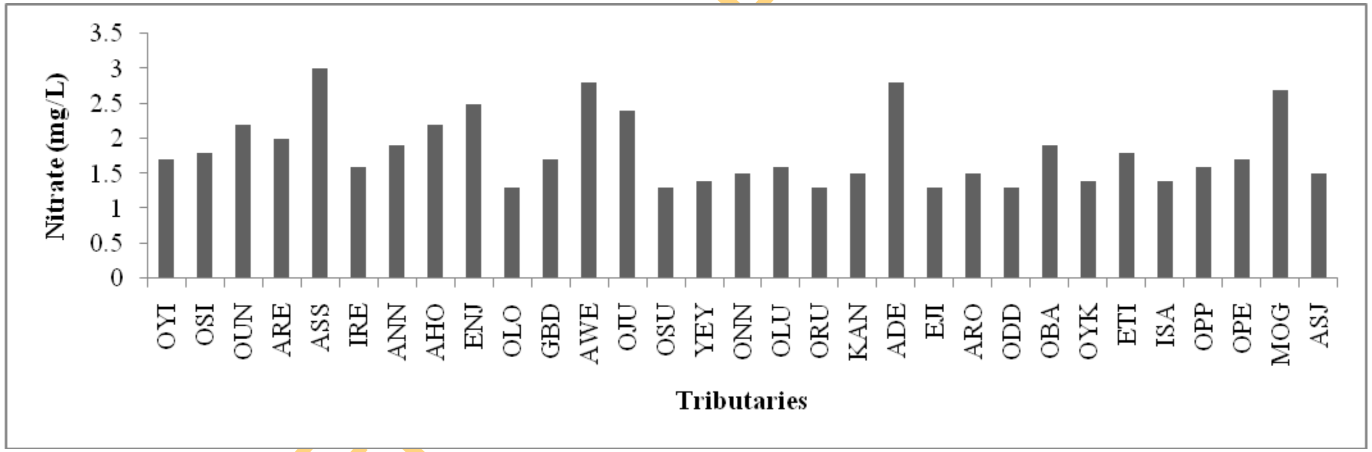

Figure 4.10: Spatial variation of nitrate in surface water

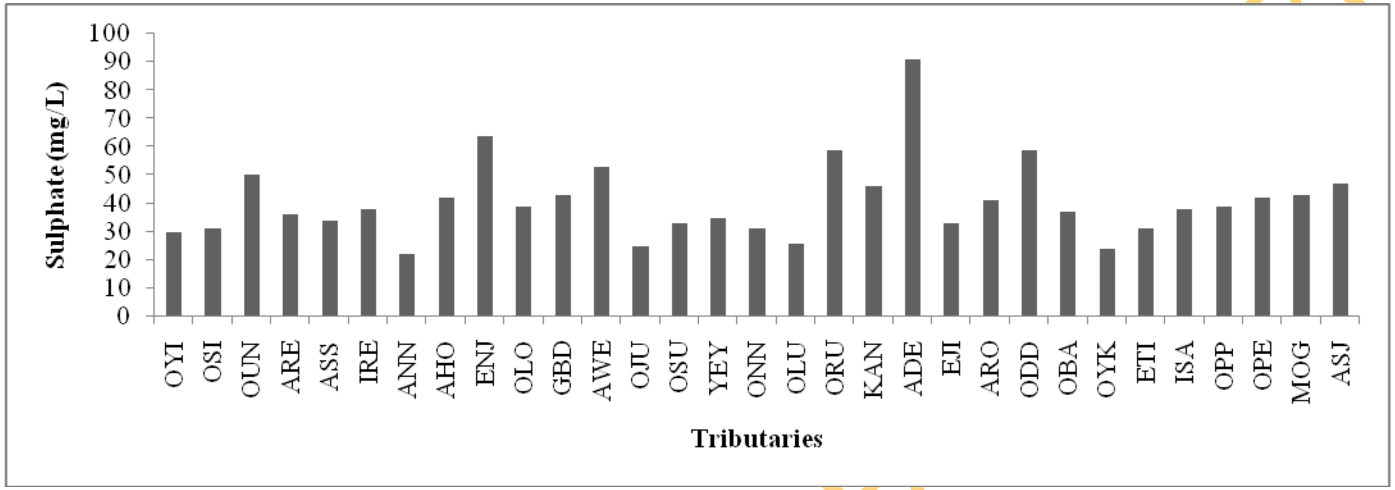

Figure 4.11: Spatial variation of sulphate in surface water

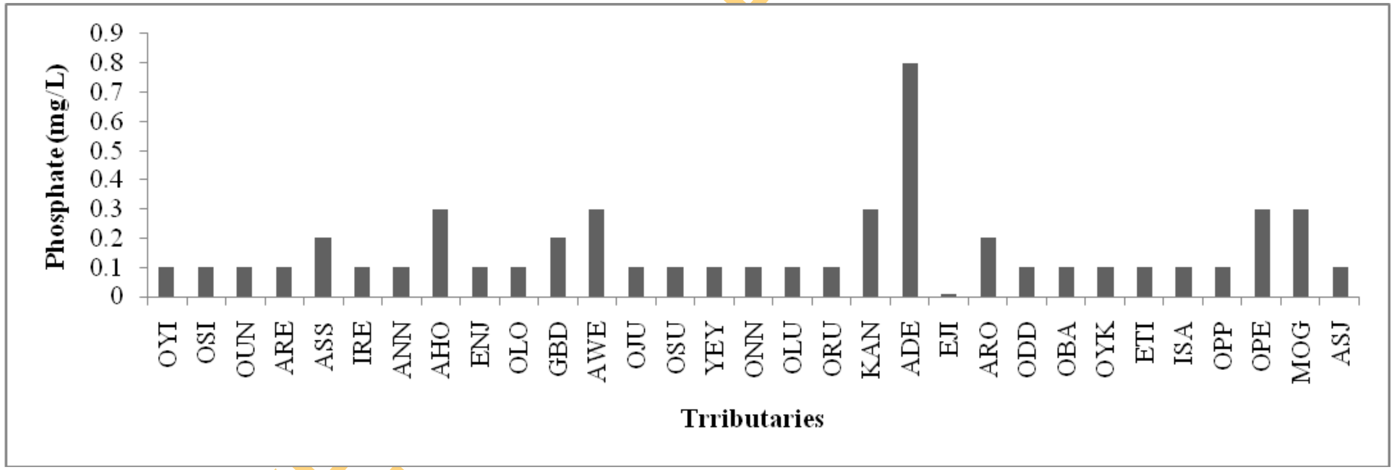

Figure 4.12: Spatial variation of phosphate in sulphate water

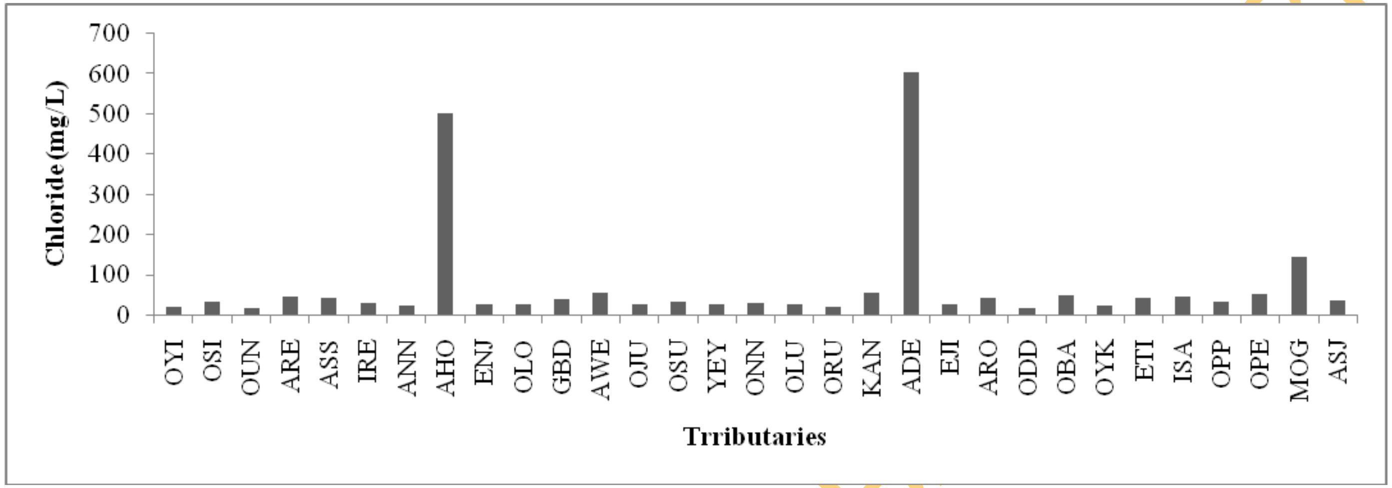

Figure 4.13: Spatial variation of chloride in surface water

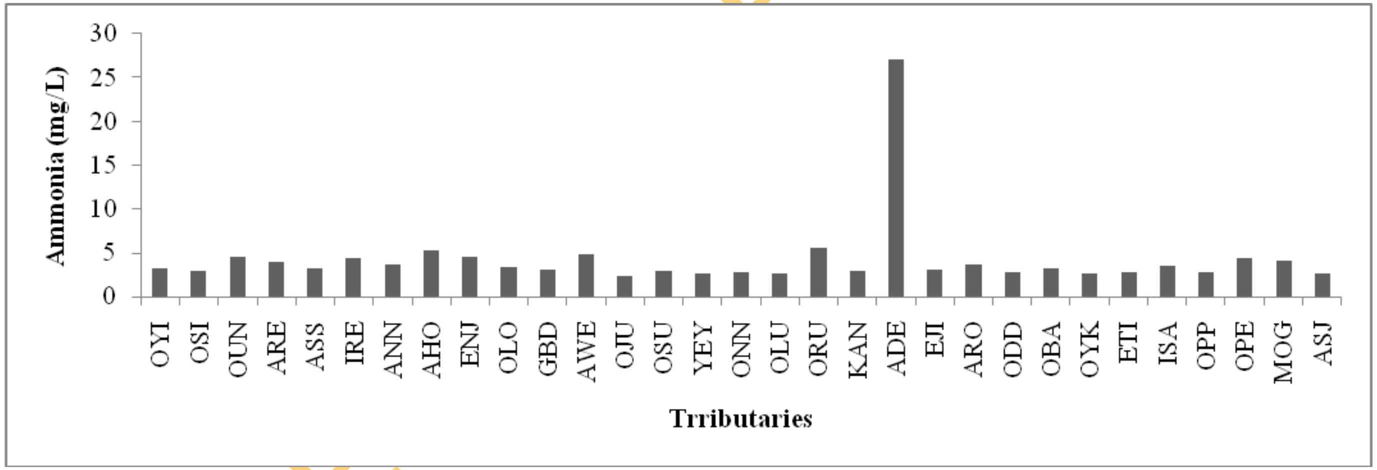

Figure 4.14: Spatial variation of ammonia in surface water

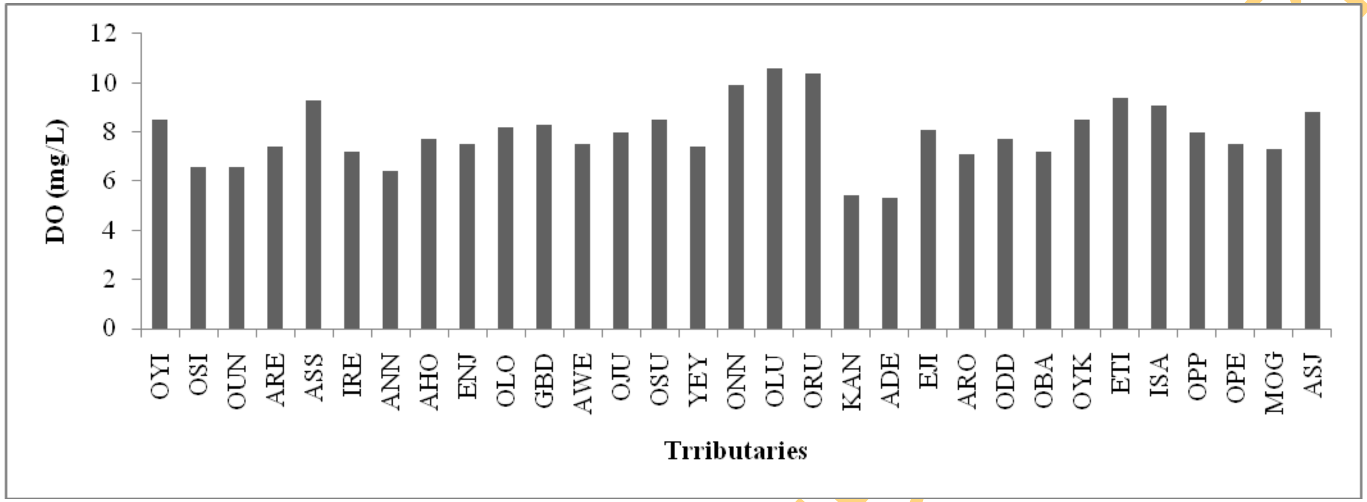

Figure 4.15: Spatial variation of dissolved oxygen of surface water

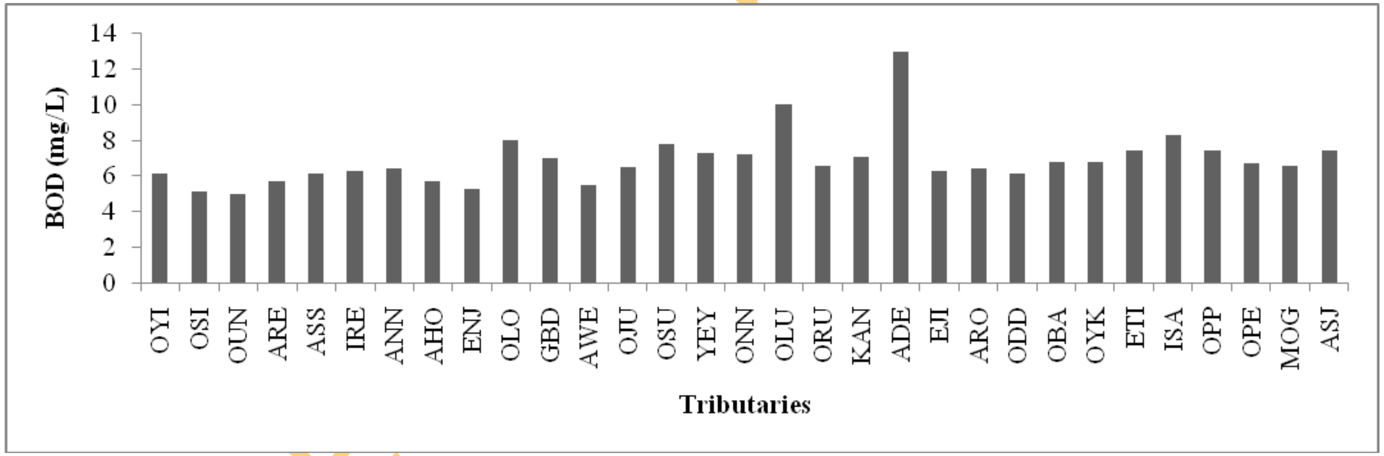

Figure 4.16: Spatial variation of biochemical oxygen demand in surface water

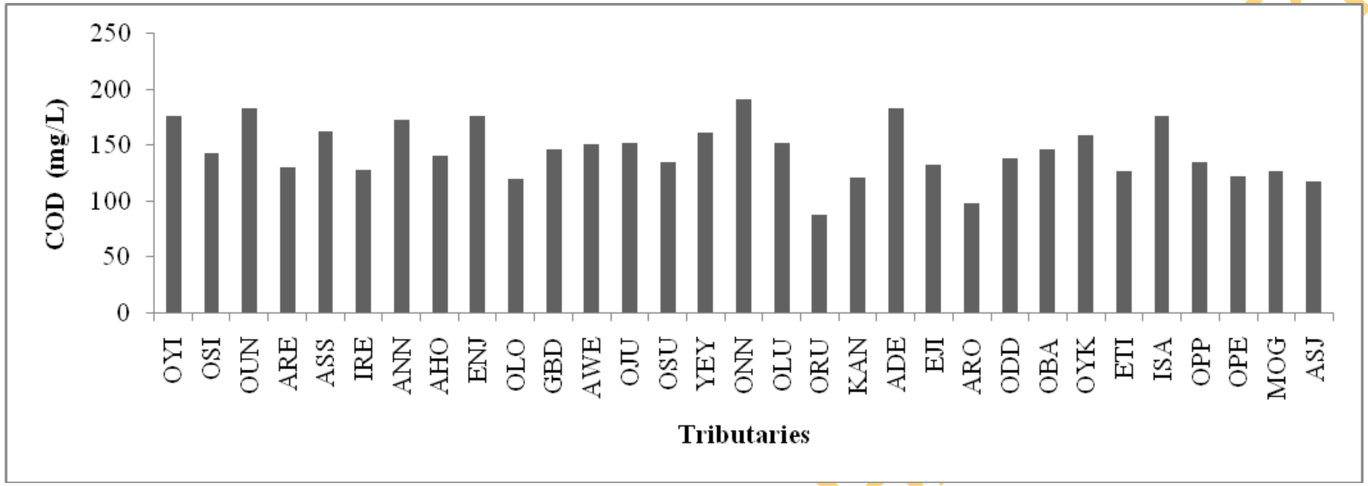

Figure 4.17: Spatial variation of chemical oxygen demand in surface water

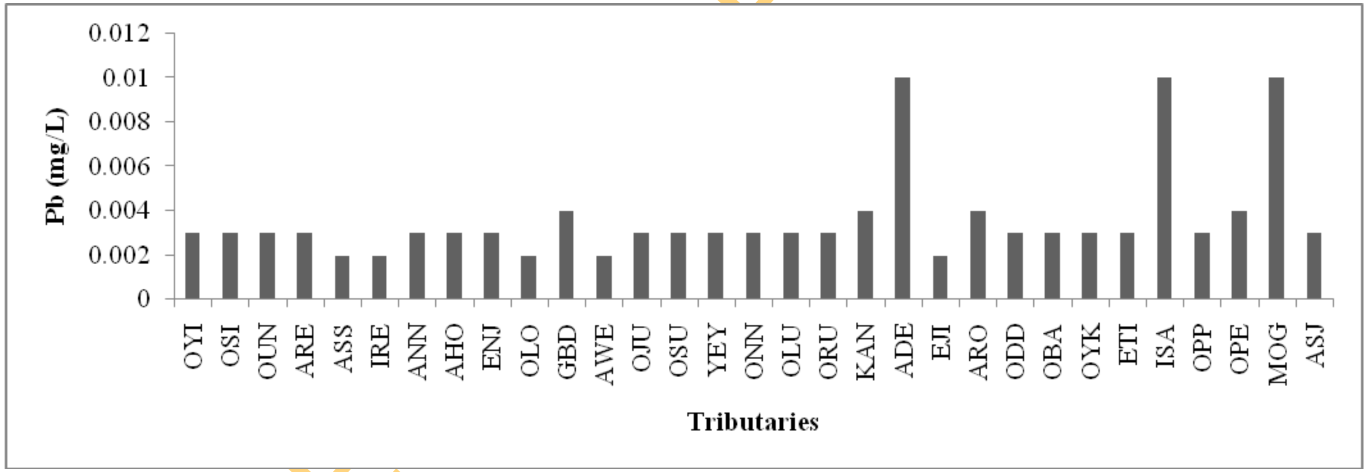

Figure 4.18: Spatial variation of lead in surface water

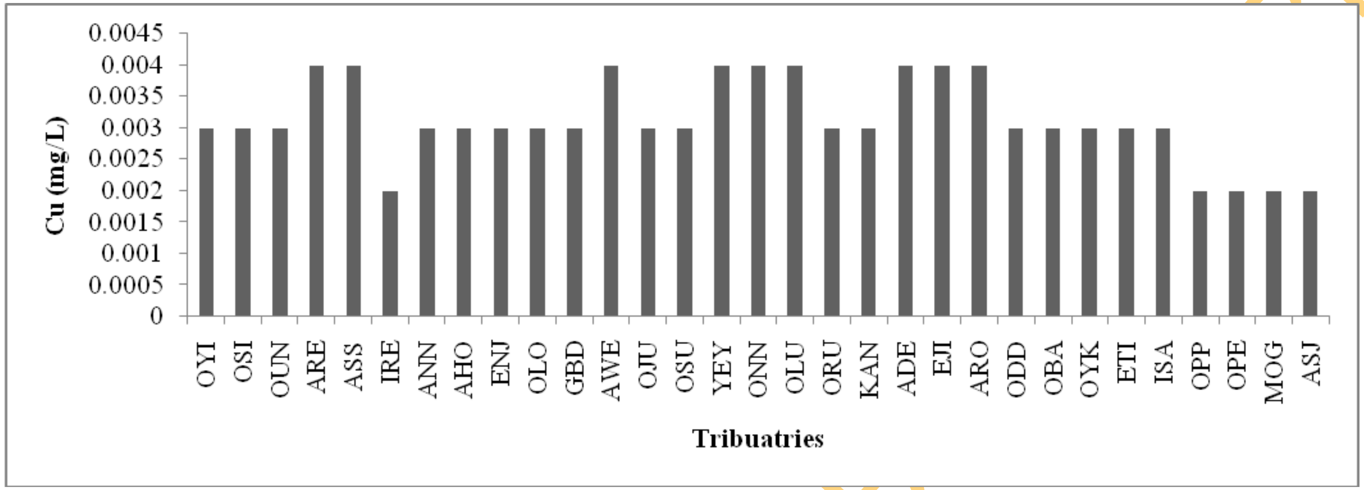

Figure 4.19: Spatial variation of copper in surface water

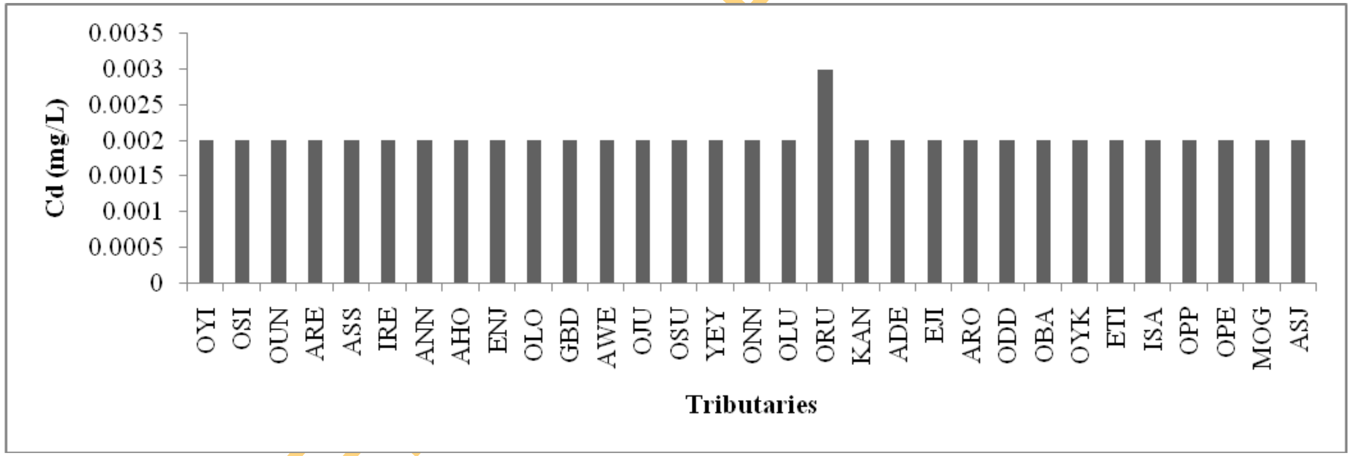

Figure 4.20: Spatial variation of cadmium in surface water

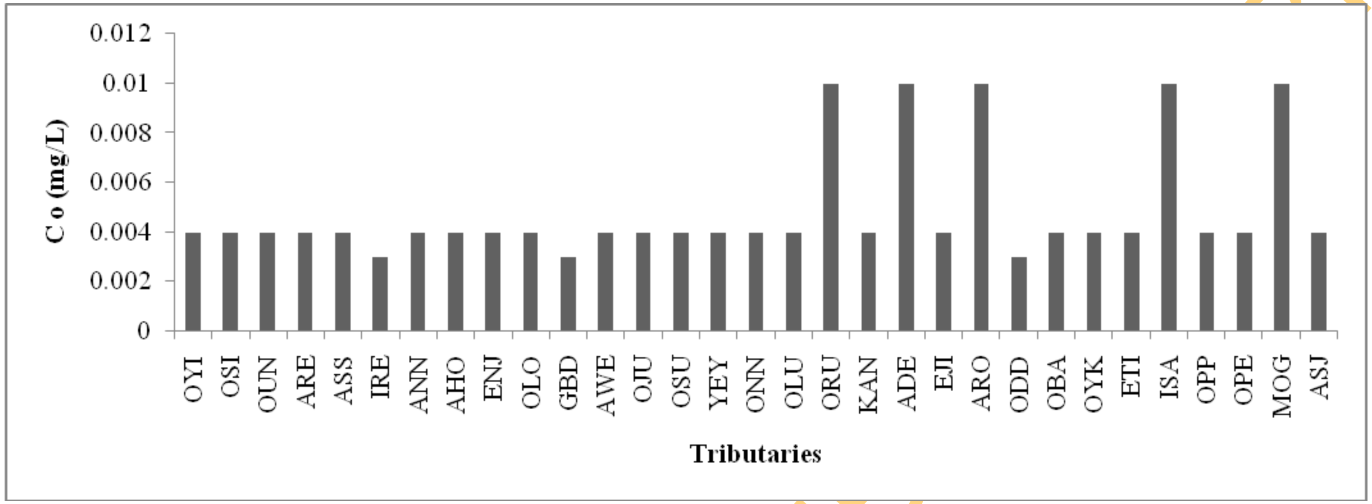

Figure 4.21: Spatial variation of cobalt in surface water

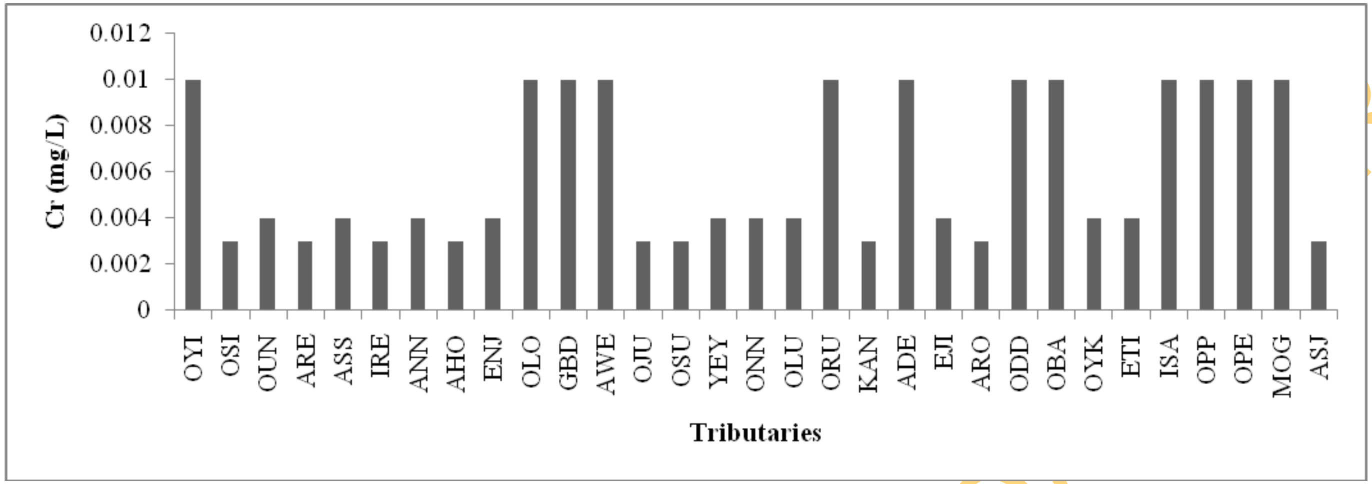

Figure 4.22: Spatial variation of chromium in surface water

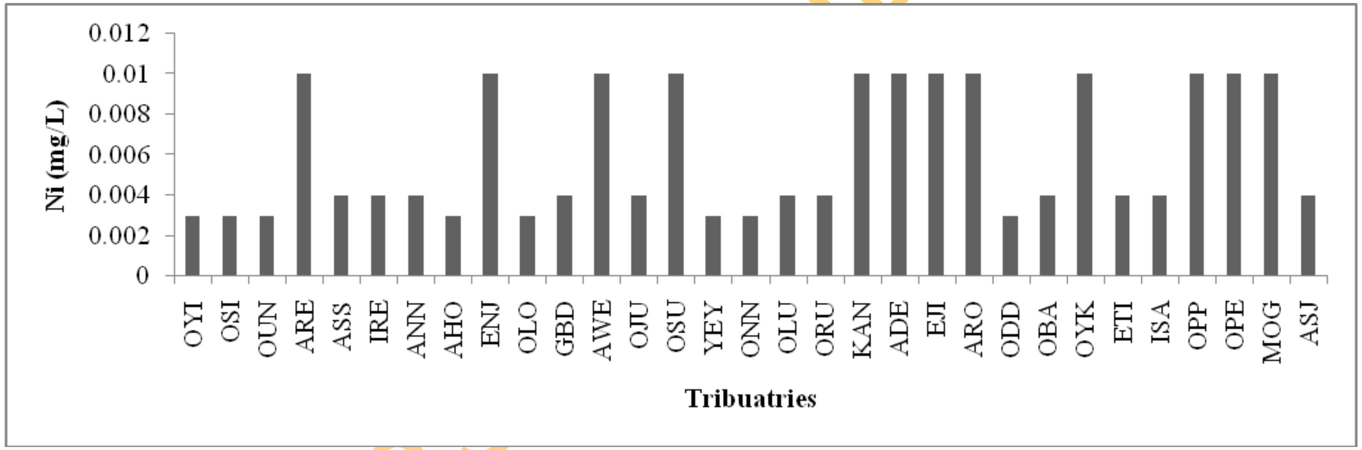

Figure 4.23: Spatial variation of nickel in surface water

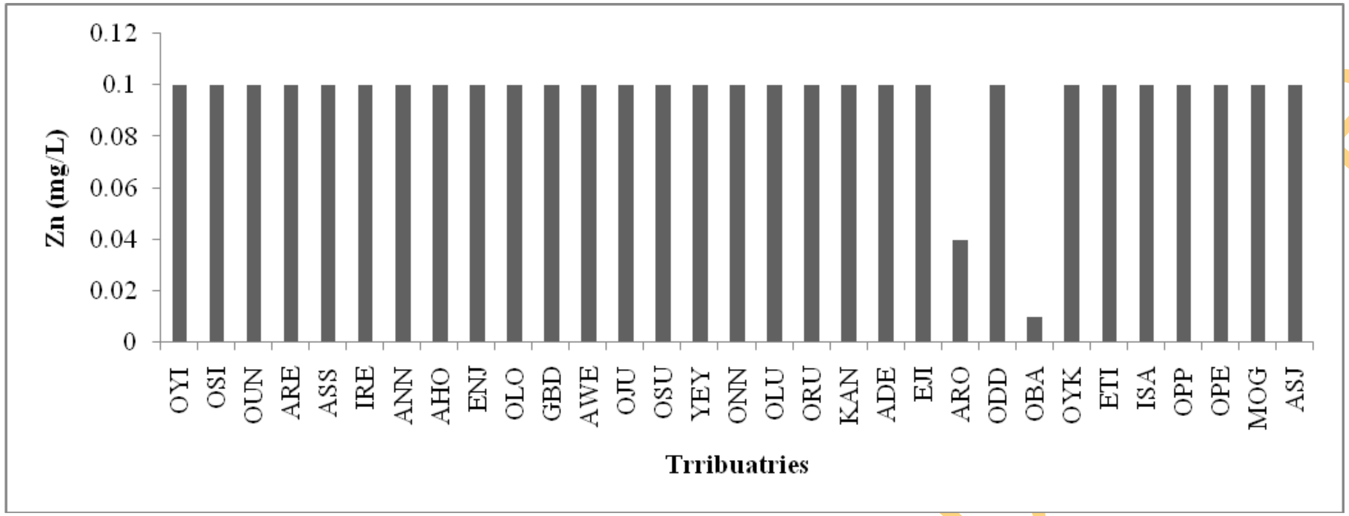

Figure 4.24: Spatial variation of zinc in surface water

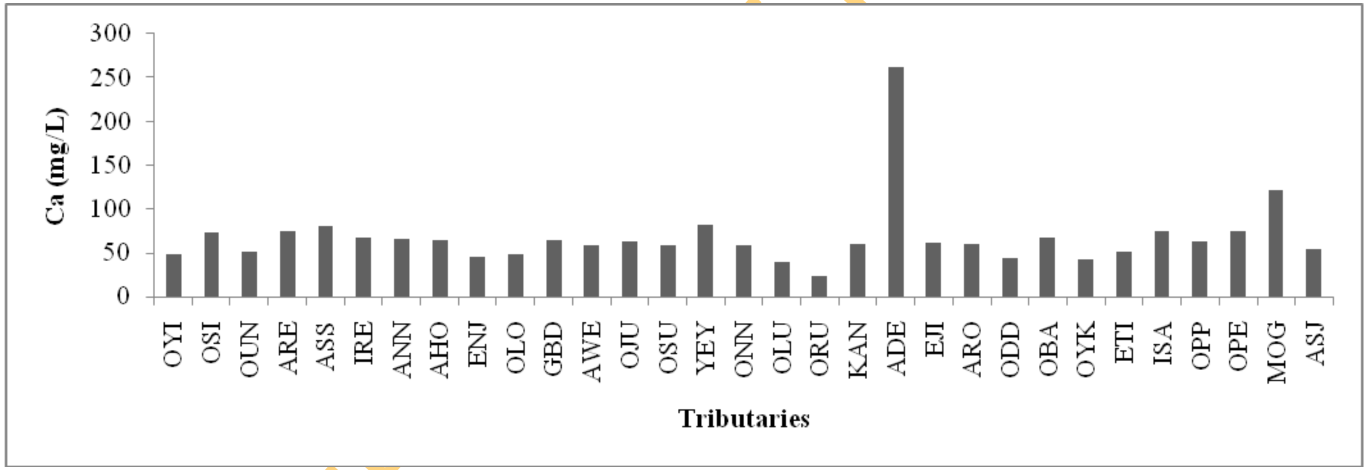

Figure 4.25: Spatial variation of calcium in surface water

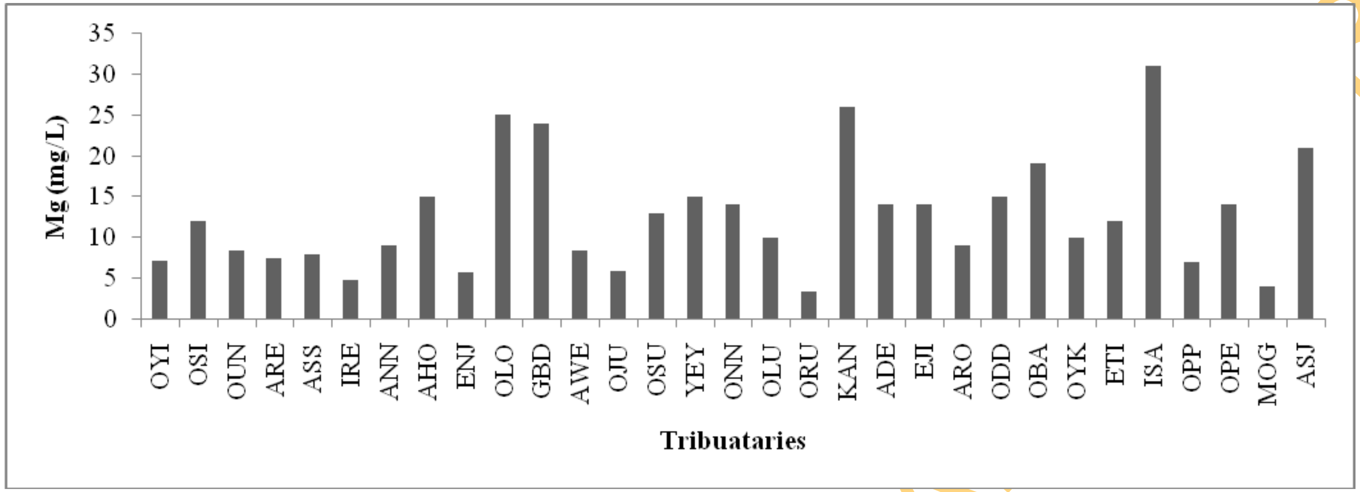

Figure 4.26: Spatial variation of magnesium in surface water

4.4 SEASONAL VARIATIONS OF THE PHYSICOCHEMICAL CHARACTERISTICS AND HEAVY METALS IN SURFACE WATER.

The seasonal variations in the physicochemical and heavy metals characteristics between wet and dry seasons are as shown in Table 4.4. This shows the variations in the physicochemical properties of Osun River in the wet and dry season.

Parameters that showed no difference between dry and wet seasons

No significant seasonal variation was recorded for temperature as shown in Table 4.4. Temperature depends on the climate, sunlight and depth and does not undergo changes during the year in the fluvaitile environment (Egborge, 1970; Akinyemi and Nwankwo 2006; Gupta, 2006) as compared to lacustrine environment. Generally, some tributaries used for the study were shaded with trees which explained why the average temperature in the wet seasons almost equal that in the dry seasons.

Parameters that were higher during dry seasons

Table 4.4 illustrates those parameters that were higher during dry seasons. These parameters included electrical conductivity, total solids, total dissolved solids, total suspended solids, alkalinity, hardness, phosphate, chloride, ammonia, nitrate, biochemical oxygen demand, chemical oxygen demand, zinc, lead, copper, cadmium, cobalt, chromium, calcium and magnesium. These parameters showed significant difference in their wet and dry season values. This was so because the volume of water in Osun River reduces in dry season because of low flow of water. In most rivers, the normal or dry weather flow is made up to exhibit their most favourable chemical water characteristics (Chov, 1964). During dry seasons much sediment at the bottom of most of these rivers are remobilized and become particulates in the river and then contributes to the pollution of the river. Chov (1964), suggests that although the river may contain extremely large amounts of suspended matter, the concentration of dissolved substances are usually low, often only a fraction of that present during dry weather. However, there are some instances where high runoff may cause deterioration in water quality. Ogunfowokan *et al*. (2005), also reported a high total solids (900±8 - 500±9 mg/L) and high suspended solids values of (500±7 - 200±3mg/L) in their study

Table 4.4: Average dry and wet season characteristics of the Osun River Water

Parameter	Dry Season	Wet Season
EC (µS/cm)	238±444	195±316
pH	7.5±0.5	7.7±0.5
Temperature	25.2±3.3	25.5±1.8
TS	591±471	504±650
TDS	126±238	97.5±160
TSS	466±397	408±55
Turbidity	24±28	43±45
Alkalinity	98±126	88±123
Hardness	132±146	102±94.9
Nitrate	1.84±1.51	1.80±1.56
Sulphate	32.1±28.7	45.9±30.1
Phosphate	0.16±0.26	0.15±0.20
Chloride	56.3±127	53.4±97.7
Ammonia	4.32±8.55	4.11±4.05
DO	7.46±3.07	8.26±2.92
BOD	7.04±7.05	6.81±7.98
COD	167±150	106±82.1
Calcium	76.0±80.4	60.1±57.7
Magnesium	17.4±46.5	9.89±14.2
Lead	0.004±0.004	0.003±0.004
Copper	0.004±0.004	0.003±0.004
Cadmium	0.003±0.004	0.001±0.001
Cobalt	0.010±0.004	0.003±0.003
Chromium	0.010±0.004	0.003±0.003
Nickel	0.003±0.004	0.01±0.01
Zinc	0.08±0.12	0.05±0.07

* units in mg/L, except EC- µS/cm, turbidity – FTU, temperature – ^{o}C and pH (no units).

and this was as a result of waste water which entered the river which contains human excreta, urine and other semi solid wastes.

Strahler and Strahler (1973) stated that all rainfall wherever it occurs carries with it a variety of ions, some introduced into the atmosphere from the sea surface, some from land surfaces undisturbed by man and some from man-made sources. The ions and other substances carried into the streams or rivers via rainfall may result into pollution. These ions during dry season now get concentrated because there is no rain to wash them away. Also many activities were carried out in most of these tributaries in the dry seasons like washing of clothes, cars and motor bicycle using different types of detergents and through this, contaminants are introduced as pollutants which impair the quality of the water body. The increase in nitrate and phosphate level in the dry seasons could lead to eutrophication in the nearest future if not controlled.

The inability of river to flow normally in dry seasons makes aerobic bacteria to consume the available dissolved oxygen in the river. This invariably means the depletion of available oxygen meant for organisms in the river. This will increase the nutrient present in the water and can result in high biochemical oxygen demand.

Parameters that were higher during wet seasons

Those parameters that showed higher concentrations during wet seasons include pH, turbidity, sulphate, dissolved oxygen and nickel. These parameters were derived mainly from anthropogenic sources. Urbanization, industrial and agricultural activities along the river channel contaminate the river. When it rains these contaminants are washed into the river and can undergo different chemical reactions which can have impact on the quality of the river water.

In the wet seasons, there is a high leaching of surrounding bodies of water. This causes the carrying of large quantities of particles and pollutants into the tributaries of Osun River characterizing the contribution of diffuse sources. Fast running water can carry more particles and larger sized sediment. Decaying plants and animals, bottom feeding fish, algae blooms, flooding and soil erosion can all contribute to disturbance of the quality of rivers. Slower moving streams usually contain finer particles, but does not mean it does not contain some amount of pollutants.

During wet seasons, there is always a rapid mixing of river water thereby increasingthe oxygen content and invariably increasing the dissolved oxygen of the river. An increase in DO during wet seasons was attributed to low organic enrichment. At alkaline pH values, photosynthetic activities result in high oxygen content.

Significant differences that existed between wet and dry seasons at most of the tributaries include: a significant difference observed for total dissolved solids at Gbodofon, Isin and Osun. Turbidity was significant at Osun, Oyi, Oloyo, Enja, Ashasha, Ounseku, Aro, Arenounyun, Oba, Moginmogin, Awesin, Ojutu, Aro (Ejigbo), Odoiya, Oni and Etioni. Alkalinity was significant at Gbodofon, Oyi, Kankere, Aro, Oba, Moginmogin, Awesin, Ojutu, Anne, Orufu and Odoiya. Differences in hardness were only observed to be significant at four tributaries (Isin, Moginmogin, Anne and Odoiya). Differences in nitrate levels were significant at Isin and Adeti. Sulphate level differences were however found to be significant at many of the tributaries (Osun, Oyi, Osin, Oloyo, Enja, Oba, Moginmogin, Ope, Awesin, Ojutu, Orufu, Odoiya, Oni, Etioni, Olumirin, Yeyekare and Opa). Differences in phosphate level were significant at Awesin, Ojutu and Adeti and could be as a result of anthropogenic activities. The differences in chloride were significant at Isin, Osin, Kankere, Arenounyun, Awesin, Ojutu and Orufu. The differences in dissolved oxygen between the two seasons were found to be significant at Gbodofon, Isin, Oloyo, Oba, Ope, Awesin, Aro (Ejigbo) and Odoiya. BOD also shows significant differences between the wet and dry seasons at Oloyo, Odoiya and Oni, while COD showed significant difference at Isin, Osin, Ashasha, Ounseku, Arenounyun, Moginmogin, Ojutu and Odoiya. Turbidity, sulphate and alkalinity showed high significant differences among the parameters studied.

Paired sample t-tests was used to see if there were any differences between the means obtained for wet and dry seasons. The results showed that there was no significant difference in some of the means obtained except turbidity, sulphate, dissolved oxygen and heavy metals that were statistically significant.

4.5 APPLICATION OF MODEL TO PREDICTION OF FUTURE WATER QUALITIES

The time series analysis for selected parameters and selected tributaries are presented in Table 4.5. The model equations and the predicted concentrations up to year 2018 are also indicated. The coefficient of determination (R^2) gives an indication about the suitability of the model. In Asejire, the model explains effectively 56% variation of EC (with predicted value of 799 µS/cm for September 2018) and 59% variation of zinc (with predicted value of 0.25 mg/L for January 2018) in surface water. For other parameters in Asejire the model could not explain significant variations. For surface water in Osun, the model explains 69% variation of nitrate with concentration of 14.1 mg/L in September, 2018. The model could not explain significant variations for other parameters. In Gbodofon, the model obtained explains 31% variation of EC with predicted concentration of 1324 µS/cm for 2018, and 34% variations of TDS (with predicted concentration of 840 mg/L for March 2018). In Oloyo, the model used could not explain significant variations of parameters in surface water. In Oyi surface water, the model explained 70% variation EC with a forecast of 549 µS/cm for July 2018, 67% variation of total dissolved solids with a concentration of 173 mg/L for July 2018. Models obtained for Olumirin surface water explained 71% variation of nitrate with a forecast of 11.1mg/L for July 2018, 59% variation of ammonia with a forecast of 3.26mg/L for September 2018. Models obtained for surface water for some parameters in the selected tributaries, the models could not explain significant variations. This is possibly due to some reactions occurring in surface water and sediment. The predictions of the parameters using the obtained models are in good agreement with observed values.

Some of the predicted values for 2018 where found to be above the limit stipulated for drinking water quality guidelines. These include Osun, Gbodofon, Olumirin and Ishasha, and strict monitoring of the water quality of the river is advisable. However, some were still within the standard stipulated for drinking water guidelines such as Oyi.

4.5.1 Time Series Analysis of Parameters of Osun River Surface Water

Table 4.6 illustrates the overall time series analysis obtained for surface water in Osun River. This explained 79% variation of nitrate with predicted concentration of 19.0

Table 4.5: Time-Series analysis results of selected parameters at selected tributaries

Tributary	Parameter	R^2	Model equation	Forecast for 2018
Asejire	EC	0.56	63.3 +18.3b	799µS/cm, September.
	Zn	0.59	42.3-4.53b	0.25mg/L, January.
Etioni	TDS	0.39	18.1 + 4.74b	684 mg/L, March.
Gbodofon	EC	0.31	68.6 + 16.1b	1324 µS/cm, March.
	TDS	0.34	31.0 + 8.97b	840 mg/L, March.
Ishasha	Nitrate	0.60	0.28 + 0.18b	5.79 mg/L,November
Moginmogin	BOD	0.35	10.4 - 0.63b	3.13 mg/L, Novenber.
Oba	pH	0.49	8.27-9.20x10^{-2}b	4.9, November.
Ojutu	EC	0.61	50.7 + 9.80b	2923 µS/cm, July.
	TDS	0.49	23.7 + 5.32b	1620 mg/L, January.
	Cu	0.44	6.89 - 1.39b	-
Oloyo	Nitrate	0.23	0.49 + 0.11b	19.9 mg/L, March.
	COD	0.27	156-9b	1300mg/L,September.
Olumirin	Nitrate	0.71	0.67 + 0.14b	11.1 mg/L, July.
	NH_3	0.59	3.24 - 0.10b	3.26mg/L, September.
	Cu	0.38	5.21x10^{-4}b- 4.70	-
Osun	Nitrate	0.69	0.39 +0.15b	14.1mg/L, September.
Oyi	EC	0.70	26.1 + 7.63b	549 µS/cm, July.
	TDS	0.67	11.2 + 4.27b	173 mg/L, July.

Table 4.6: Time series analysis of overall concentrations of surface water Parameters in Osun River

Parameter	R^2	Forecast for 2018
EC	0.27	2367µS/cm, January.
TDS	0.33	1404 mg/L, January.
Turbidity	0.06	46.9 FTU, September.
Alkalinity	0.03	129 mg/L, March.
Hardness	0.08	163 mg/L, March.
Nitrate	0.79	19mg/L, July.
Sulphate	0.03	54.7 mg/L, July.
Phosphate	0.84	18.1 mg/L, March.
BOD	0.71	21.9 mg/L, March.

mg/L for March, 2018; 84% variations of phosphate with a predicted concentration of 18.1 mg/L for March 2018, and 71% variation of BOD with predicted concentration of 21.9 mg/L in March 2018. Parameters such as EC, pH, TDS, turbidity, alkalinity, hardness and sulphate, do not show significant variations.

Nitrate, phosphate and BOD where predicted to be prevalent by March 2018. The predicted concentration of nitrate exceeded the limit stipulated by drinking water quality guidelines for SON and others except WHO guidelines and will impair the water quality of Osun River. It will not make the river water to be useful for the food and beverage industry.

4.6 PRINCIPAL COMPONENT ANALYSIS OF HEAVY METALS IN SURFACE WATER

Figure 4.27 illustrates the principal component analysis for heavy metals in water. Noticeable amount of clustering was observed among the parameters studied here. Parameters placed close to each other influence the principal component model in similar ways, which indicates they are correlated. Pb, Cu, Co, Cr, Cd, Ni and Zn are clustered together as shown in the graph; this is even supported by the Pearson correlation obtained in Table 4.7. Ca and Mg are not correlated with the other metals. The further away a parameter is from the origin, the more influential the parameter is in determining the principal component analysis model. The first principal eigenvalues captures 77.8% of the total variance which was due to the clustered heavy metals (Pb, Cu, Cd, Co, Cr, Ni and Zn). They contributed significantly to water quality variations of Osun River through anthropogenic activities such as industrial waste discharge, agricultural and domestic waste discharge. The second principal component eigenvalues accounts for 14.6% of the total variance which was due to Calcium. This probably originated from natural source. The third accounts for 7.60% of the total variance was due to presence of magnesium in the water body. The existence of magnesium ions and its compounds led to high loading of the variable.

4.7 PEARSON CORRELATION MATRIX FOR PARAMETERS IN SURFACE WATER

Table 4.7 shows the correlation matrix obtained for the physicochemical characteristics and heavy metals in surface water. Strong and positive correlations were obtained for

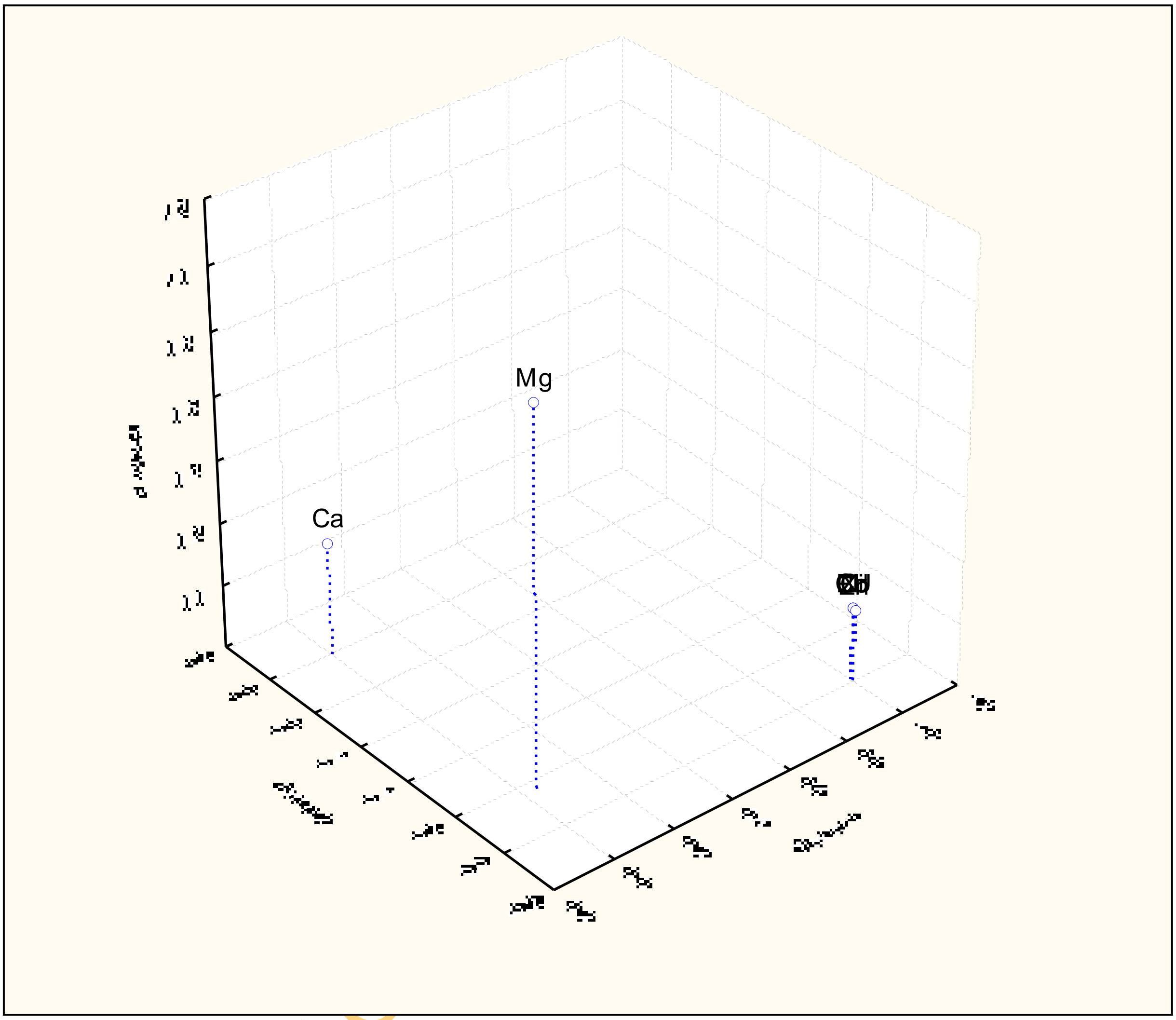

Figure 4.27: Principal component analysis of heavy metals in surface water

Table 4.7: Pearson correlation matrix for the physicochemical characteristics of surface water

Parameters	EC	TS	TDS	TSS	Turbidity	Alkalinity	Hardness	Temp.	NO_3^-	SO_4^{2-}	PO_4^{3-}	Cl^-	NH_3	DO	BOD	COD	Pb	Cu	Cd	Co	Cr	Ni	Zn	Ca	Mg
EC	1.000																								
TS	0.497	1.000																							
TDS	0.996	0.493	1.000																						
TSS	0.165	0.937	0.160	1.000																					
Turbidity	0.048	0.062	0.039	0.055	1.000																				
Alkalinity	0.860	0.488	0.843	0.217	0.055	1.000																			
Hardness	0.524	0.447	0.496	0.309	0.130	0.550	1.000																		
Temp.	0.140	0.085	0.133	0.043	-0.008	0.081	0.155	1.000																	
NO_3^-	0.142	-0.007	0.145	0.066	0.179	0.089	0.016	0.031	1.000																
SO_4^{2-}	0.219	0.199	0.205	0.144	0.551	0.245	0.238	-0.017	0.138	1.000															
PO_4^{3-}	0.540	0.345	0.526	0.181	0.379	0.543	0.449	0.081	0.220	0.394	1.000														
Cl^-	0.868	0.476	0.852	0.199	0.036	0.899	0.496	0.022	0.141	0.301	0.564	1.000													
NH_3	0.531	0.294	0.516	0.127	0.212	0.555	0.459	0.075	0.118	0.343	0.597	0.658	1.000												
DO	0.176	0.196	0.171	-0.154	0.041	0.259	-0.292	-0.044	0.090	-0.045	0.082	0.178	0.169	1.000											
BOD	0.050	0.111	0.042	0.109	0.104	0.103	0.275	0.124	0.060	0.201	0.195	0.132	0.276	-0.034	1.000										
COD	0.120	0.070	0.112	0.035	0.134	0.090	0.203	0.069	0.053	0.016	0.090	0.046	0.063	0.024	0.034	1.000									
Pb	0.036	-0.016	0.036	-0.024	-0.006	0.108	0.142	0.000	0.171	0.117	0.119	0.046	0.038	0.078	0.087	-0.002	1.000								
Cu	-0.048	0.074	-0.048	-0.070	0.040	0.027	-0.170	0.047	0.077	-0.046	0.134	-0.029	-0.016	0.022	0.100	0.100	0.417	1.000							
Cd	-0.005	-0.016	-0.005	-0.016	0.039	0.108	0.170	0.028	-0.189	0.141	0.146	0.003	-0.032	-0.052	-0.063	0.023	0.564	0.578	1.000						
Co	-0.049	-0.009	-0.048	-0.001	-0.088	0.037	-0.172	-0.012	0.141	0.161	-0.161	-0.057	-0.048	0.117	-0.056	-0.031	0.387	0.372	0.589	1.000					
Cr	-0.035	-0.022	-0.034	-0.017	-0.012	0.010	-0.228	0.046	0.104	0.075	-0.140	-0.047	-0.042	0.088	0.132	-0.014	0.438	0.273	0.313	0.413	1.000				
Ni	-0.005	-0.082	-0.005	0.087	-0.045	0.025	0.192	0.004	0.110	0.086	-0.169	0.012	-0.018	0.122	0.149	-0.023	0.368	0.397	0.201	0.112	0.285	1.000			
Zn	0.075	-0.102	-0.074	- 0.095	0.003	-0.051	0.239	0.108	-0.070	-0.052	0.086	-0.062	-0.050	0.055	-0.086	0.076	0.275	0.311	0.518	0.241	0.103	0.005	1.000		
Ca	-0.025	0.054	-0.027	0.063	-0.032	-0.054	0.169	0.124	0.078	-0.024	0.028	-0.041	0.012	0.004	0.079	0.113	-0.061	0.188	-0.181	-0.014	-0.064	-0.193	-0.266	1.000	
Mg	-0.045	0.052	0.045	0.048	-0.031	0.032	0.192	-0.036	0.034	0.009	0.000	0.059	0.032	-0.010	0.030	0.062	0.109	0.107	0.089	0.172	-0.119	-0.100	-0.149	0.337	1.000

the following pairs at p= 0.01: EC and TDS (r = 0.966), EC and alkalinity (r = 0.860), EC and chloride (r = 0.868), TS and TSS (r = 0.937), TDS and alkalinity (r = 0.843), TDS and chloride (r = 0.852), alkalinity and chloride (r = 0.899), chloride and ammonia (r = 0.658), meaning that there was a strong association between these pairs, and common sources for the pairs of polluting substances. Positive correlations were also observed for the following pairs of metals Pb and Cd (r = 0.564), Pb and Cr (r = 0.438), Cu and Cd (r = 0.578), Cd and Co (r = 0.589), Co and Cr(r = 0.413) at p< 0.01. This suggests that the metals might have originated from the same anthropogenic sources. The relationship here is not as strong as for other physicochemical properties. The probable sources of the pollutants varied widely and may include leachates from wastes waters generated municipally, domestically and industrially, and wastes from intensive agricultural practices.

4.8 COMPARISON OF THE OVERALL CHARACTERISTICS OF THE OSUN RIVER SURFACE WATER WITH DRINKING WATER QUALITY GUIDELINES.

Water is an absolute necessity for the survival of life on earth and on it depends much on man's food. The various facets of the hydrological cycle serve beneficial uses to mankind. For example, surface water sources serve multipurpose functions for drinking, cooking, bathing, laundry, irrigation, farming, livestock watering and transportation. Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered many surface water unwholesome and hazardous to man and other living resources.

People living close to river Osun use the water for variety of purposes. Water quality data are one of the important tools in environmental management. It is therefore necessary to compare the overall results obtained for the physicochemical parameters and heavy metals in these rivers with the international drinking water guidelines. Table 2.2 illustrates some international drinking water guidelines. Comparison of pH in this study (7.6±0.5) with the USEPA, Canada, EEC, WHO, Japan and SON guidelines indicates that the pH of River Osun for the study is within the acceptable level of all the guidelines at that time of sampling, indicating that river Osun was not acidic and will be useful for some purposes that do not require acidic water for the production of its products. The total solid measured in this study was 111±200 mg/L. If compared to the values in Table 2.2, with USEPA (500 mg/L), Canada (500 mg/L), WHO (1000 mg/L) and Japan (500 mg/L), it would be noticed that the TDS in the study was within the acceptable limit of most of the guidelines, meaning that the TDS in River Osun is still within the normal range and cannot be said to be polluted. Turbidity obtained was 34±43 FTU and was far above all the guidelines stipulated in Table 2.2. This means that the river water exceeded the international drinking water guidelines, because normal drinkable water should not be turbid. The reason for the high turbidity was due to disturbance of the water body and presence of particles that disperse light effectively during wet season. Sulphate and chloride were all within the acceptable limit of all the guidelines in Table 2.2. In the present study, hardness (116±120 mg/L) was above the EEC guideline (50.0 mg/L) but within that of Japan, (300 mg/L) and Nigeria (150 mg/L). Heavy metal levels were generally within stipulated limits.

4.9 COMPARISON OF SURFACE WATER CHARACTERISTICS OF THE TRIBUTARIES WITH WATER QUALITY GUIDELINES FOR VARIOUS CATEGORIES OF WATER USAGE.

Table 4.8 describes the comparison of surface water characteristics of the tributaries with water quality guidelines for some industries to determine if the water would be suitable for the classes of industries discussed in Tables 2.3 – 2.13.

Table 4.8 explains the tributaries whose water could be used for specific industry. All the tributaries were found to contain more than 10mg/L suspended solids and made them not to comply for usage in pulp and paper, and petroleum industries. The alkalinity of the waters of these tributaries was above 0.5mg/L and could not be used in the iron and steel industry. The turbidity of most of the tirbutaries was found to be greater than 10 FTU and could not be utilized in the food and beverage industries. The ammonia content of these tributaries were above 0.5mg/L and thus rendered it unuseful in power generating stations and for aquatic life support. Five of the tributaries were found to comply with regualations for boating and aesthetic activities and about thirteen for water contact alone. All the tributaries complied with the stipulated limit for livestock rearing.

The waters of these tributaries could become useful if given adequate treatment. The

Table 4.8: Tributaries with water quality meeting specific industrial and other requirements*

Industry Type	Tributaries
Pulp and Paper	None, suspended solids> 10 mg/L
Iron and Steel	None, alkalinity > 0.5 mg/L
Petroleum Industry	None, suspended solids > 10 mg/L
Power Generating Stations	None, ammonia > 0.07 mg/L
Food and Brewing	None, turbidity > 10 mg/L
Diary Production	None, turbidity > 10 mg/L
Irrigation	All tributaries
Aquatic Life Support	None, ammonia > 0.5 mg/L
Recreation	Anne, Aro, Oyika, Olumirin, Yeyekare boating and aesthetic activities
Livestock Rearing	All tributaries

***** Requirements as in Table 2.4 – 2.13

activities around them could be monitored so that level of treatment could be reduced.

4.10 COMPARISON OF THE PHYSICOCHEMICAL CHARACTERISTICS OF SURFACE WATER IN THIS STUDY WITH STUDIES ELSEWHERE.

The physicochemical characteristics of surface water in this study were compared with those obtained from rivers elsewhere. Table 4.9 reveals the comparison of the physicochemical properties in surface water with studies elsewhere. The temperature obtained in the study area (25.3±2.6 ^{o}C) was somehow comparable with what was obtained in Nigeria (26-32 ^{o}C, and 27.6±1.6 ^{o}C) by Onianwa *et al.* (2001) in Ogunpa Lake and Courant *et al*. (2007) in Benin River, Nigeria respectively. It was below the amount obtained in rivers in Lagos, Nigeria (30-40 ^{o}C) by Sangodyin (1995) but well above the temperature obtained in Boye pond, Ethiopia (21.5-21.8 ^{o}C) by Teferi *et al.* (2005). The pH of the study area (7.6±0.5) compares well with what was reported in the following rivers; Ogun River, Nigeria (7.6±0.2) by Udousoro and Osibanjo (1997), Kieskamma River, South Africa (7.3±0.1) by Morrison *et al.* (2001), in Ogunpa River, Nigeria (6.9-7.6) by Ajayi and Adelaye (1977); Epie Lake, Nigeria (6.5-7.8) by Izonfuo and Bariweni (2001); in Alaro River, Nigeria (7.7) by Fakayode (2005). Other countries however showed an acidic pH level of the surface water than that of the study area such as in Tinto River, Spain (2.6±0.2) by Elba-Poulichet *et al.* (1999) and in Nigeria (4.5±9.5 and 5.9±1.1) by Courant *et al.* (1987) in Benin River and Sangodoyin (1995) in rivers in Lagos respectively.

The total solids (546±570 mg/L) obtained for the study area falls between the values reported in Nigeria (329-1380 mg/L and 160-1480 mg/L) by Onianwa *et al.* (2001) in Ogunpa River and Fakayode (2005) in Alaro River respectively. The total suspended solids (434±500 mg/L) obtained in this studies was noticed to be higher than all the values obtained from other places according to Table 4.9. The total dissolved solids (111±200 mg/L) shows higher level than other places except in Nigeria (414 mg/L and 3300±7700 mg/L) by Ajayi and Adelaye (1977) in Ogunpa River and Courant *et al.* (1987) in Benin River.

Dissolved oxygen in this study (7.9±3.0 mg/L) falls within the range obtained in

Table 4.9: Comparison of the physicochemical parameters in surface water in this study with studies elsewhere

Country	River	Major activities in the area	Temp.	pH	TS	TSS	TDS	DO	BOD	COD	Cl$^-$	Alkalinity	References
Nigeria	Osun		25.3±2.6	7.6±0.5	546±570	434±500	111±200	7.9±3.0	6.9±7.5	136±120	55±110	93±120	This study
South Africa	Kieskamma	Industrial area	-	7.3±0.1	-	-	-	-	-	47.6±15.5	-	-	Morrison *et al.* (2001)
Nigeria	Epie	Urban Area	27.3-30.5	6.9-7.6	-	-	33.0-62.0	1.38-9.06	0.31-6.77	-	1.65-4.62	15.3-37.3	Izonfuo and Bariweni (2001)
Nigeria	Alaro	Industrial area	-	6.5-7.8	329-1380	-	-	0.63-7.0	-	-	475-1130	405-744	Fakayode (2005)
Ethiopia	Boye	Urban area	21.5-21.8	6.5-6.7	-	-	-	2.10-5.73	-	6.00-98.2	-	-	Teferi *et al.* (2005)
Nigeria	Lagos	Industrial area	30.0-40.0	4.5-9.5	-	-	-	-	-	44.0-6000	-	-	Sangodoyin (1995)
South Asia	Yamuna, Bagmati	Urban area	-	-	-	-	-	-	20.0-30.0	-	-	-	Sunil and Hideki (2001)
Nigeria	Ogunpa	Urban area	-	6.9-7.0	-	-	-	3.5-5.7		4.2-13.2	26.0-44.0	-	Sridhar and Bammeke (1985)
South Africa	Tyume	Rural community	-	-	-	-	-	4.15-11.2	-	7.5-249	-	-	Igbinosa and Okoh (2009)
Nigeria	Ogunpa	Urban area	26-32	6.6-8.1	160-1480	10-270	0.1-5.9	0.2-8.3	13-560	11.9-224	70.5-688	1.76-28.0	Onianwa *et al.* (2001)
Nigeria	Ogunpa	Urban area	-	7.7	-	-	414	2.5	16.4	-	508	25.6	Ajayi and Adelaye (1977)
U.S.A	Crooked creek	Mining, milling and smelting	-	6.7±0.7	-	7.1±7.7	200±200	-	-	10±16	-	2±11	Janneth and Foil (1979)
Spain	Tinto	Industrial area	-	2.6±0.2	-	-	-	-	-	-	11200	-	Elba-Poulichet *et al.* (1999)
Nigeria	Benin	Pet. Prospecting	27.6±1.6	5.9±1.1	-	80.4±130	3300±7700	4.7±1.0	-	-	1730±400	-	Courant *et al.* (1987) Asonye *et al.* (2007)
Nigeria	Ogun	Farming, urban and industrial area	-	7.6±0.2	-	-	-	6.6±1.5	1.9±1.2	44±80	165±654	48.4±7.70	Udousoro and Osibanjo (1997)

* all units in mg/L except temperature (°C)

Table 4.9 (contd.)

Country	River	Major activities in the area	Pb	Cu	Cd	Co	Cr	Ni	Zn	References
Nigeria	Osun		0.003±0.004	0.003±0.004	0.002±0.003	0.004±0.004	0.01±0.01	0.004±0.010	0.07±0.10	This study
Nigeria	New Calabar	Pet. Prospecting	850	2080	560	-	50	-	65.9	Wegwu and Akininwor (2006)
Nigeria	Oghoro, Ugheli	Oil Activities	ND	ND	-	-	100	-	700	Asonye *et al.* (2007)
Nigeria	Ogunpa	Urban area	<10.0-86.0	<1.00-39.0	<1.00-23.0	-	2.00-19.0	<1.00-27.0	<1.00-35.0	Onianwa *et al.* (2001)
U.S.A	Mississipi	Transportation	-	-	-	-	-	-	-	NRC (2003)
Nigeria	Man-Made Lake	Urban area	1.22±0.05	-	-	-	-	1.61±0.14	-	Adakole *et al.*(2008)
India	Brahmani	Industrial area	10.0 - 27.0	1.0 - 4.7	0.4 - 4.0	4.0 - 5.6	-	9.0 - 52	0.4 - 80.1	Reza and Singh (2010)
India	Damodar	Industrial area	-	3950	300	-	11550	-	-	Chatterjee *et al.* (2010)
Iran	Abbasa	Urban area	1.33	6.95	2.62	3.28	-	-	124	Sayyed *et al.* (2006)
Rwanda	Nyabugogo	Agriculture	0.113	-	-	-	0.110	-	-	Nhapi *et al.* (2011)
Harare	Marimba	Urban area	0.21 - 0.54	-	-	-	-	-	0.18 - 0.42	Mvungi *et al.* (2003)
South Africa	Thohoyan	Urban area	0.010 - 0.012	-	-	-	-	-	0.002 - 0.003	Okonkwo and Mothiba (2005)
Nigeria	Warri	Home Industries	0.001	0.041	0.007	0.008	-	0.039	0.009	Wogu and Okaka (2011)
India	Ganga	Industrial area	120	10.0	5.00	-	-	140	60.0	Aktar *et al.* (2010)
Nigeria	Ogun	Urban area	0.04	0.12	0.01	-	-	-	0.19	Jaji *et al.*(2007)
Nigeria	New Calabar	Urban area	0.14	0.07	0.05	-	-	0.01	-	Abu and Egenonu (2008)
Nigeria	Ogun	Farming, urban and industrial area	-	0.17±0.03	-	-	-	-	0.47±0.57	Udousoro and Osibanjo (1997)

ND –Not detected

Nigeria (1.38-9.06 mg/L, 0.2-8.3 mg/L) by Izonfuo and Bariweni (2001) in Epie Lake; Onianwa *et al*. (2001) in Ogunpa River respectively and in Tyume River, South Africa (4.15-11.2 mg/L) by Igbinosa and Okoh (2009). Lower dissolved oxygen content of some of the rivers than the study area were also noticed such as in Boye pond, Ethiopia (2.10±5.73 mg/L) by Teferi et al. (2005) and in Nigeria (3.5 ±5.7 mg/L, 2.5 mg/L, 4.7±1.0 mg/L) by Ajayi and Adelaye (1977) in Ogunpa River, in Ogun River, Nigeria (6.6±1.5 mg/L) by Udousoro and Osibanjo (1997), Courant *et al*. (1987) in Benin River and in Boye pond, Ethiopia by Teferi *et al*. (2005). The biochemical oxygen demand (6.9±7.5 mg/L) obtained for the study was well above the BOD obtained in Epie Lake, Nigeria (0.31±6.77 mg/L) by Izonfuo and Bariweni (2001) and Ogun River, Nigeria (1.9±1.2 mg/L) by Udousoro and Osibanjo (1997) but lower to values obtained in other places such as in river Yamuna, South Asia (20.0-30.0 mg/L) by Sunil and Hideki (2001) and in Ogunpa River, Nigeria (13-560 mg/L and 16.4 mg/L) by Ajayi and Adelaye (1977) and Onianwa *et al*. (2001) respectively. The COD for the study area was (136±120 mg/L) and falls within the range obtained in Nigeria (44.0-6000 mg/L, 7.5-249 mg/L, 11.9-224 mg/L) as reported by Sangodoyin (1995) in Lagos River, Onianwa *et al*. (2001) in Ogunpa Lake and Igbinosa and Okoh, (2009) Tyume River, South Africa respectively. Lower value for COD were however reported in Kieskamma River by Morrison *et al*. 2001 (47.6±15.5 mg/L) in South Africa, Ogun River, Nigeria (44±80 mg/L) by Udousoro and Osibanjo (1997) and in Crooked Creek, U.S.A. (10±16 mg/L) by Jenneth and Foil (1979) in U.S.A.

The chloride level obtained for the study area (55±110 mg/L) revealed a lower concentration when compared to what was obtained in Nigeria (475-1130 mg/L, 70.5-688 mg/L, 508 mg/L, 1730±400 mg/L, 165±654 mg/L and 11200±6300 mg/L) by Ajayi and Adelaye (1977) in Ogunpa Lake; Onianwa *et al*. (2001); Fakayode, (2005) in Alaro River; Courant *et al*. (1987) in Benin River; Udousoro and Osibanjo (1997) and Elba-Poulichet *et al*. (1999) in Tinto River, Rea of Hueva, Southwest Spain respectively. The reason might be due to the discharge of untreated waste from some of these industries into the water bodies without considering the assimilative capacity of the river.

However, a lower chloride value than in the study area was reported in Ogunpa Lake, Nigeria (1.65-4.62 mg/L; 26.0-44.0 mg/L) by Sridhar and Bammeke (1985); Izonfuo and Bariweni (2001) in Epie Lake. The level of alkalinity in the study area was 93±120 mg/L and lower to what was obtained in other countries except in Alaro River, Nigeria (405-744 mg/L) by Fakayode (2005). Sulphate (39±30 mg/L) level was lower compared to other countries whose values were used for comparison except what was reported by Sridhar and Bammeke (1985) in Ogunpa River (92.0-116 mg/L).

Table 4.9 shows comparison of heavy metals in surface water with other studies. The concentration of lead (0.003±0.004 mg/L) was found to be lower compared to values reported in in Calabar River, Nigeria (850 mg/L, <10.0-86.0 mg/L) by Wegwu and Akininwor (2006) and in Ogunpa Lake, Nigeria by Oniawa *et al*. (2001) respectively. The reason for the high lead concentration in Calabar River was as a result of the nature of petroleum activities occurring in that area. However, lead was not detected in Benin River, Nigeria by Asonye *et al*. (2007) in another oil activity region. The level of copper obtained for the study was 0.003±0.004 mg/L and low to what was obtained in Calabar River, Nigeria (2080 mg/L) by Wegwu and Akininwor (2006) and also as reported in Ogunpa Lake, Nigeria by Onianwa *et al*. (2001) (<1.00-39.0 mg/L). Copper was not detected at all in Benin River, Nigeria by Asonye *et al*. (2007) and by the report submitted in Mississipi River, U.S.A. by NRC (2003). The cadmium content of River Osun was 0.002±0.003 mg/L and was low compared to the values obtained in Ogunpa Lake, Nigeria (560 mg/L and <1.00-23.0 mg/L) as reported by Oniawa *et al*. (2001); Wegwu and Akininwor (2006) in Calabar River, Nigeria. The concentration of cobalt obtained in River Osun was 0.004±0.004 mg/L and was not reported by any of the authors used in this study. Chromium (0.01±0.01 mg/L), Nickel (0.004±0.010 mg/L) and Zinc (0.07±0.10 mg/L) had low values compared to all other values obtained in other studies used in this work. The level of lead and zinc in Osun River was higher than what was obtained in Warri River, Nigeria (0.001mg/L and 0.009 mg/L respectively) by Wogu and Okaka (2011).

The levels of heavy metals in Osun River was low compared to what were obtained in some rivers: in a man-made Lake, Nigeria by Adakole *et al.* (2010); in Marimba River, Harare by Mvubgi *et al.* (2008); in Ogun River, Nigeria by Jaji *et al.* (2007); and in New Calabar River, Nigeria by Abu and Egenonu (2008). These areas are urban settlement where most wastes from homes are discharged into the rivers without being treated. The concentration of heavy metals in industrial areas in other studies reveals a higher concentration because of industrial activities and the fact that most of the industries do not treat their wastes before discharging into rivers as reported in Brahmani River, India by Reza and Singh (2010); in Damoda River, India by Chartterjee *et al*. (2010); in Ganga River, India by Aktar *et al*. (2010). High level of lead (0.113 mg/L) and chromium (0.110 mg/L) were found in Nyabugogo River, Rwanda by Nhapi *et al*. (2011) compared to what was obtained in Rriver Osun in this study.

4. 11 AVERAGE PHYSICOCHEMICAL CHARACTERISTICS (OVERALL) OF THE SEDIMENT

The physicochemical parameters determined for sediment quality included organic carbon, sediment mechanical properties (sand, clay and silt), cation exchange capacity (CEC) and the heavy metals (Pb, Cu, Cd, Co, Cr, Ni and Zn). The overall average results obtained are as shown in Table 4.10.

The organic carbon content of Osun river sediment had an average value of 2.5%. This value was higher than the value obtained at the control site. It indicates that the study area was contaminated. Organic carbon gives an estimate of the amount of organic matter in sediment; and its concentration is largely determined by the addition of surface litter (fallen leaves, manure and dead organisms) and root material and the rate at which microbes break down organic compounds. Organic matter is a key component in assessing soil fertility, stability, and catchment health and sediment condition. The sediment contained 72.5±3.1% sand, 25.6±3.2% clay and 2.0±2.2% silt. The levels of these sediment particles at the control site were lower to the results obtained in Osun River. The results indicate that the river sediment was sandy in nature, signifying that the water holding capacity of the river sediment will be greatly influenced by draining more readily and will not hold ions for a long time. The clay content of the sediment was low compared to the sand and this can have effect on the absorbed cations and will reduce the upward movement of these cations. The silt content was not all that significant.

Table 4.10 Average physicochemical characteristics of sediment

Parameters (Unit)	Present Study	Control Site	Accumulation Factor
Organic Carbon (%)	2.5±7.3	0.7±0.4	3.57
Sand (%)	72.53.1	71.7±2.4	-
Clay (%)	25.6±3.2	25.5±2.7	-
Silt (%)	2.0±2.2	2.6±2.6	-
CEC (meq/100g)	48±16	48±11	1.00
Pb (µg/g)	0.70±5.80	0.10±0.20	7.00
Cu (µg/g)	0.40±1.90	0.10±0.10	4.00
Cd (µg/g)	0.03±0.10	0.01±0.01	3.00
Co (µg/g)	0.10±0.30	0.10±0.10	1.00
Cr (µg/g)	0.10±0.20	0.10±0.10	1.00
Ni (µg/g)	0.10±0.40	0.20±0.30	0.50
Zn (µg/g)	12±31	8.6±9.6	1.40

The sediment textures of many rivers have been reported. (Young, 1980; Zobeck and Fryrear, 1986; Davies and Abowie 2009). Davies and Abowei (2009) reported sediment consisting 57.86±2.65% sand, 17.4±1.68% silt and 24.67±1.33% clay and with significant spatial variation at $p<0.005$. Young (1980) described particle detachment and transport on particle size distribution, density and degree of the matrix sediment. Clay and silt aggregates in the 20 to 200 micrometers range are more erodible than larger or smaller particles. Very sandy sediments, not well aggregated erode as primary particles. Carolyn *et al*. (2004) obtained sediment composition of a wetland of Kerny Marsh to be 70-94% sand while the smaller particles of silt and clay ranged from 4% to 31%. The sediments at the bottom of waters play a role in the study of pollution in the rivers and can be used to ascertain the quality of the surface water (Oyeyiola *et al.*, 2006).

Walling and Moorehead (1989) reported that for rivers with relatively low solute concentrations, an order of magnitude difference exist between the medium particle size associated with the ultimate and effective grain size distributions. Carolyn *et al.* (2004) reported that Kearny Marsh grain size was dominated by sand typically at levels greater than 80%. Those sand levels were similar to those found in Massachusetts salts marshes, which averaged 80% (Hansen *et al.*, 1996). The cation exchange capacity of the river sediment obtained was 48±16 meq/100g as shown Table 4.10. The cation exchange capacity (CEC) of sediment is simply a measure of the quantity of sites on sediment surfaces that can retain positively charged ions (cations) by electrostatic forces. Thus, CEC is important for maintaining adequate quantities of plant available calcium, magnesium, and potassium in sediments. It is a good indicator of sediment quality and productivity. Cation exchange sites are found primarily on clay and organic matter surfaces. Cation exchange capacity is based on the surface area of sediment grain particles available for binding cations such as hydrogen (H^+) and free metal ions (e.g. Mn^{2+}). Sediments with a high percentage of small grains, such as silt and clay, have high surface-to-volume ratios and can absorb more heavy metals than sediments composed of large grains, such as sand (Liber *et al.*, 1996). Ali (1978) reported in his study that the level of exchangeable Ca, Mg and K as well as extractable Cu, Zn and Mn are highly influenced by the amount of organic matter present. Organic matter is largely confined to the surface horizons which invariably contain higher amounts of the nutrients than the one below. Ronald and Kennedy (1970) reported the average

CEC of clay, silt, sand and gravel fractions of steam sediment from the Mattole River of Northern California as 37.6, 11.0, 9.7 and 7.2 meq/100g respectively. Organic matter contributed about 15 percent of the total CEC of the sediment. However the CEC of the sand and gravel fractions exclusive organic matter were 5.5 to 8.0 meq/100g.

The results obtained for heavy metals in Osun River sediments as shown in Table 4.10 are 0.7±5.8 µg/g (Pb), 0.4±1.9 µg/g (Cu), 0.03±0.10 µg/g (Cd), 0.1±0.3 µg/g (Co), 0.1±0.2 µg/g (Cr), 0.1±0.4 µg/g (Ni) and 12±31 µg/g (Zn). These levels were found to be higher than what was obtained in the control site except for nickel. Lead was the most accumulated of the heavy metals in sediment with a factor of 7.00, and then copper, with factor of 4.00. The levels of heavy metals in this sediment were due to the effect of industrial, urbanization and agricultural activities along the Osun River channel. Data on levels of heavy metals in sediment of rivers abound in literature: Bonnevie *et al*. (1994) reported high metal concentrations in the sediment found in Hackensack River and Newark Bay, New Jersey to contain Cd (10±6mg/kg), Hg (2.1±2.6mg/kg), Ni (39± 49mg/kg) and Pb (421±403mg/kg). The levels of heavy metals in Shasha River sediment in Lagos Lagoon was reported by Oyeyiola *et al*. (2006) to contain 20.5 µg/g Pb, 25.3 µg/g Zn, 7.9 µg/g Cu, 30.8 µg/g Cr and 1.5 µg/g Cd. Akpan *et al*. (2002) reported concentrations in Calabar River to be below levels that are known to be harmful to aquatic biota: Pb (0.6-3.0ppm), Ni (1.2-22.5ppm), Cr (0.6-3.3ppm), Cu (0.3-48ppm), Zn (0.8-27ppm), Fe (0.2-2,880ppm) and V (0ppm).

4.12 AVERAGE PHYSICOCHEMICAL CHARACTERISTICS OF SEDIMENTS OF OSUN RIVER AND ITS TRIBUTARIES

The overall average organic carbon obtained was 2.5±7.3 %. Table 4.11 shows that all the tributaries had higher percentage organic carbon than what was obtained in the control area. This implies that the sediment of Osun River is contaminated with different types of organic material ranging from fallen leaves, decay carcasses of some animals found along the river bank and faeces seen in some of the tributaries. All these can contribute to the organic matter in sediment. Twenty-five of the tributaries had sand as the most predominant particle in its sediment texture but higher compared with the control site. All the tributaries were found to contain more clay in its texture compared to the control site except in Anne. Six out of the tributaries contained silt

Table 4.11: Average characteristics of sediments of Osun River (for all tributaries)

Parameter	Oyi (OYI)	Osin (OSI)	Ounseku (OUN)	Arenounyun (ARE)	Ashasha (ASH)	Isin (IRE)	Anne (ANN)	Ahoyaya (AHO)
Organic Carbon (%)	1.5±1.3	4.3±9.2	2.7±5.9	1.9±2.6	3.2±6.1	1.9±1.8	4.9±6.5	3.7±3.6
Sand (%)	72.7±3.5	73.8±3.5	73.6±3.6	73.1±3.2	72.3±3.7	72.2±3.5	74.6±4.0	72.5±2.2
Clay (%)	25.5±3.6	24.6±3.8	24.6±3.5	25.4±2.8	25.6±3.3	26.1±3.5	23.9±4.1	25.3±2.5
Silt (%)	1.9±1.4	1.6±1.1	1.8±1.6	1.5±1.1	2.2±1.3	1.7±1.3	1.5±1.2	2.3±1.4
CEC (meq/100g)	46±16	56±15	47±16	43±14	53±19	45.4±8.7	54±16	52±14
Pb (µg/g)	0.10±0.10	0.20±0.20	0.10±0.10	0.10±0.20	0.20±0.20	0.10±0.10	0.10±0.20	0.10±0.200
Cu (µg/g)	0.10±0.10	0.20±0.70	0.30±0.60	0.10±0.10	0.20±0.30	0.10±0.10	0.20±0.20	0.20±0.30
Cd (µg/g)	0.03±0.10	0.03±0.10	0.01±0.01	0.01	0.01±0.10	0.01	0.03±0.10	0.02±0.03
Co (µg/g)	0.10±0.20	0.10±0.40	0.20±0.40	0.10±0.10	0.11±0.10	0.10±0.20	0.10±0.20	0.10±0.10
Cr (µg/g)	0.03±0.03	0.10±0.10	0.12±0.20	0.10±0.10	0.10±0.20	0.10±0.10	0.10±0.10	0.10±0.10
Ni (µg/g)	0.10±0.10	0.10±0.20	0.10±0.20	0.10±0.20	0.10±0.10	0.10±0.20	0.10±0.20	0.20±0.60
Zn (µg/g)	7±10	15±19	5.30±5.20	13±21	17±25	10±14	14±20	22±33

Table 4.11 (contd.):

Parameter	Enja (ENJ)	Oloyo (OLO)	Gbodofon (GBD)	Awesin (AWE)	Ojutu (OJU)	Osun (OSU)	Yeyekare (YEY)	Oni (ONN)
Organic Carbon (%)	1.8±2.8	2.1±2.6	1.5±1.4	1.5±1.9	2.5±8.6	1.3±1.2	1.3±1.7	3.0±3.4
Sand (%)	73.9±2.7	72.8±2.5	73.7±3.3	72.8±2.1	72.6±3.2	71.4±1.8	72.0±2.5	71.6±3.6
Clay (%)	25.3±2.1	25.3±2.1	24.9±3.8	26±3	25.9±3.7	26.5±3.0	25.9±2.5	26.1±2.0
Silt (%)	1.5±1.2	1.8±1.1	1.4±1.4	1.3±1.1	1.5±1.2	2.2±2.9	2.1±2.4	2.2±3.8
CEC (meq/100g)	45±12	47±13	54±16	48±14	54±16	48±16	45±14	44±18
Pb (µg/g)	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.20	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10
Cu (µg/g)	0.10±0.10	0.20±0.50	0.50±0.90	0.10±0.30	0.10±0.10	0.10±0.20	0.23±0.40	0.20±0.40
Cd (µg/g)	0.04±0.10	0.03±0.10	0.10±0.20	0.02±0.10	0.03±0.10	0.03±0.10	0.02±0.04	0.03±0.10
Co (µg/g)	0.04±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.03±0.04	0.03±0.04	0.10±0.20
Cr (µg/g)	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.60
Ni (µg/g)	0.10±0.10	0.10±0.10	0.20±0.60	0.10±0.20	0.10±0.20	0.10±0.10	0.10±0.10	0.10±0.20
Zn (µg/g)	6±11	12±19	21±25	13±19	14±20	13±15	7.7±10.0	11±16

Table 4.11(contd.):

Parameter	Olumirin (OLU)	Orufu (ORU)	Kankere (KAN)	Adeti (ADE)	Aro (EJI)	Aro (ARO)	Odoiya (ODD)	Oba (OBB)
Organic Carbon (%)	2.7±7.0	1.8±3.4	2.6±4.8	2.5±3.2	1.3±1.3	1.4±2.1	1.8±1.3	1.0±1.4
Sand (%)	72.1±2.1	71.2±5.4	72.4±2.5	71.5±3.4	72.4±1.9	71.9±2.1	72.5±2.6	72.2±2.8
Clay (%)	26.0±2.4	26.0±4.4	25.4±4.6	26.5±3.3	25.7±3.0	26.1±2.9	25.6±2.4	26.3±2.7
Silt (%)	1.9±1.8	2.8±4.4	2.3±4.3	2.0±2.4	1.9±1.6	1.9±2.0	1.9±1.5	1.5±1.1
CEC (meq/100g)	43±11	45±15	46±11	49±12	48±17	40±16	44±12	43±14
Pb (µg/g)	0.10±0.10	0.10±0.10	0.03±0.10	18±28	0.10±0.30	0.10±0.10	0.10±0.10	0.10±0.10
Cu (µg/g)	0.10±0.20	0.10±0.20	0.20±0.30	6.1±8.9	0.10±0.10	0.20±0.30	0.10±0.10	0.10±0.10
Cd (µg/g)	0.03±0.10	0.01	0.03±0.20	0.10±0.20	0.01	0.01±0.01	0.01	0.02±0.03
Co (µg/g)	0.10±0.10	0.04±0.10	0.10±0.10	0.40±1.10	0.10±0.10	0.20±0.50	0.10±0.10	0.20±0.30
Cr (µg/g)	0.10±0.10	0.04±0.03	0.20±0.50	0.10±0.10	0.10±0.10	0.10±0.10	0.10±0.04	0.10±0.30
Ni (µg/g)	0.10±0.10	0.10±0.20	0.10±0.20	0.20±0.30	0.10±0.10	0.10±0.20	0.10±0.10	0.10±0.20
Zn (µg/g)	5.00±6.20	6.80±9.50	12±19	60±140	5.6±11.0	7.6±11.0	9.4±19.0	9.3±17.0

Table 4.11(contd.):

Parameter	Oyika (OYK)	Etioni (ETI)	Ishasha (ISA)	Opa (OPP)	Ope (OPE)	Moginmogin (MOG)	Asejire (ASJ)
Organic Carbon (%)	2.0±1.8	2.4±3.6	2.5±3.2	2.5±2.7	2.9±3.0	1.7±1.7	1.6±2.3
Sand (%)	72.4±3.7	72.5±2.3	71.5±3.4	74.2±2.8	71.2±2.8	73.2±3.2	71.5±1.8
Clay (%)	25.1±3.6	25.8±2.3	26.5±2.4	24.5±2.8	26.4±3.0	25.2±3.1	25.9±2.8
Silt (%)	2.4±3.6	2.2±3.8	2.0±2.4	1.2±0.9	2.5±3.1	1.6±0.9	2.7±2.8
CEC (meq/100g)	42±20	44±18	49±12	62±14	51±18	52±17	44.1±9.2
Pb (µg/g)	0.10±0.20	0.10±0.10	0.10±0.20	0.10±0.20	0.20±0.30	0.10±0.10	0.10±0.10
Cu (µg/g)	0.20±0.80	0.10±0.10	0.20±0.50	0.30±0.50	0.80±1.60	0.30±0.70	0.10±0.30
Cd (µg/g)	0.02±0.70	0.01	0.02±0.10	0.01	0.10±0.10	0.03±0.10	0.10±0.10
Co (µg/g)	0.04±0.10	0.10±0.10	0.10±0.30	0.30±0.70	0.10±0.20	0.10±0.10	0.10±0.10
Cr (µg/g)	0.10±0.10	0.10±0.10	0.20±0.20	0.10±0.10	0.10±0.20	0.10±0.10	0.10±0.10
Ni (µg/g)	0.10±0.20	0.40±1.50	0.10±0.20	0.10±0.20	0.20±0.30	0.10±0.20	0.10±0.20
Zn (µg/g)	8±14	5.40±7.60	8.30±9.20	16±31	12±20	25±34	12±18

particle higher than the control site at Egun. Cation exchange capacity was found to be very high in nine of the tributaries compared to the control site, suggesting that these tributaries will have more surfaces for exchange of cations.

The levels of heavy metals in sediment of all the tributaries in Table 4.11 were found to be below the guidelines stipulated by the Canadian and Ontario sediment quality guidelines, the consensus based sediment quality guidelines of the Wisconsin and sediment quality guideline values of ERL and ERM. Three of the tributaries had their lead level higher than what was obtained at the control site; two had an accumulation factor of 2 (Osin and Ope) and one had a factor of 180 (Adeti). These tributaries accumulated high level of lead and might be due to anthropogenic activities around the bank of the river. Eight of the tributaries had more level chromium than level obtained in the control site. The tributaries and their accumulation factor are: Osin, Ashasha, Anne, Ahoyaya, Kankere and Aro with accumulation factor of 2. Adeti had the highest accumulation factor of 61 for copper, and it's the second most accumulated of the heavy metals. These could be due to various activities by man along the river bank and dumping of electronic wastes in the river. This metal can be leached from river into sediment. None of the tributaries had its level of cadmium greater than what was obtained in the control site. Table 4.11 shows that all of the tributaries had higher cobalt level greater than the amount in control site.Those with very high accumulation factors were Ounseku (20), Ashasha (11), Adeti (40), Aro (20), Oba (20) and Opa (30). Cobalt was found to be the third most accumulated of the heavy metals in the sediment and was found in Adeti sediment. Three out of the thrity-one tributaries had higher concentration than in control site with factors of accumulation to be 1.2 (Ounseku) and 0.2 (Kankere and Ishasha). None of the tributaries had its nickel value greater than that of the control sample, sediment at Etioni with a factor of 2. Nineteen of the the tributaries had higher zinc content compared with the control sediment. Those with high factor of accumulation are Gbodofon (2.44), Ahoyaya (2.55), Moginmogin (2.91) and Adeti (6.98). Zinc was the fourth most accumulated metal in the sediment.

Contaminated sediments may be derived from inputs of suspended solids to which toxic substances are adsorbed, such as soil particles in surface water run-off from fields treated with chemicals. Alternatively, the natural suspended material in a watercourse as well as the river bed surface can adsorb chemicals from the water. When the material settles out, the toxic material forms a sink or reservoir. A one-way analysis of variance (ANOVA) revealed statistical significant differences in means of parameters in these tributaries.

4.13 SPATIAL VARIATION OF THE PHYSICOCHEMICAL CHARACTERISTICS OF SEDIMENT

The spatial variation of the physicochemical characteristics and heavy metals in sediment for all tributaries are as shown in Figures 4.28 - 4.39. From Figure 4.28, one would notice variation of some physicochemical parameters from upstream to downstream point of the river network. The organic carbon of the tributaries reduced as the river flows downstream. The figures depict a transition from more upstream portions (such as OYI, OSI, OUN, ARE, ASS, IRE, ANN, AHO, and ENJ) to down stream portions (such as ASJ, MOG, OPE, OPP and ISA). Changes were observed not to be significant except at some tributaries such as ADE, MOG, OPE, GBD, ETI and ISA where there are some unusual increase due to random input from diffuse sources. Spatial variation of other parameters in Figures 4.29 to 4.39 follow general pattern as for organic carbon.

4.14 SEASONAL VARIATION OF THE PHYSICOCHEMICAL CHARACTERISTICS AND HEAVY METALS IN SEDIMENT

The mean seasonal variations of the physicochemical characteristics and heavy metals in sediment are as shown in Table 4.12. The Physicochemical characteristic include organic carbon, sand, clay, silt, CEC, Pb, Cu, Cd, Co, Cr, Ni and Zn.

Parameters that were higher in wet seasons

The following parameters were observed to be higher in the wet seasons: Organic carbon, clay and copper. This was as a result of the high flow rate of water in the wet seasons. People dump all sorts of wastes into streams during wet seasons. These wastes contain a lot of contaminant that impair river sediment. These contaminants get absorbed by sediment and undergo various kinds of reactions. These absorption and accumulation may cause secondary pollution problem. These newly received deposits are carried into the river by storm water runoff from surrounding complex watershed which sometimes comprises of towns, villages, major roads and industries through

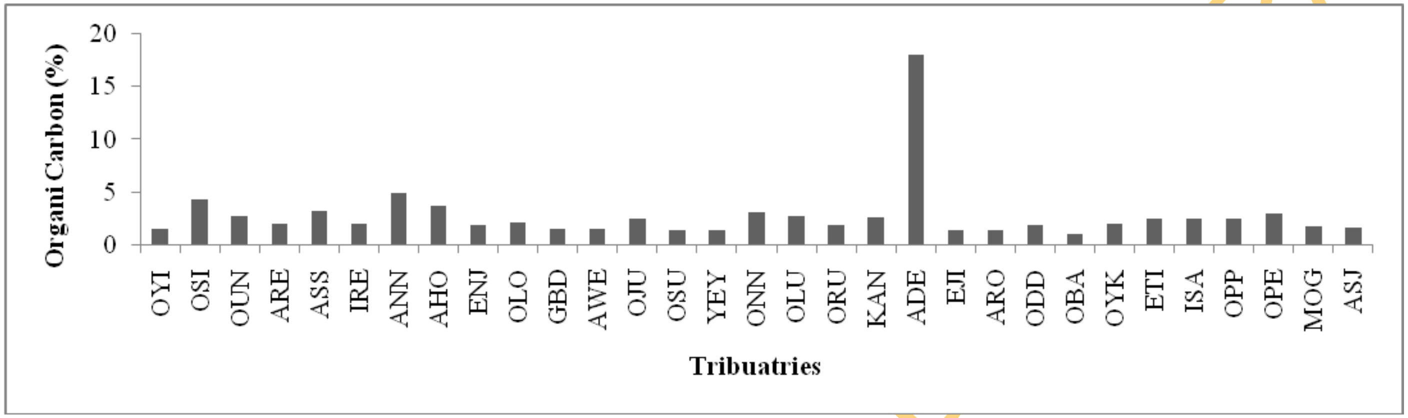

Figure 4.28: **Spatial variation of organic carbon in sediment**

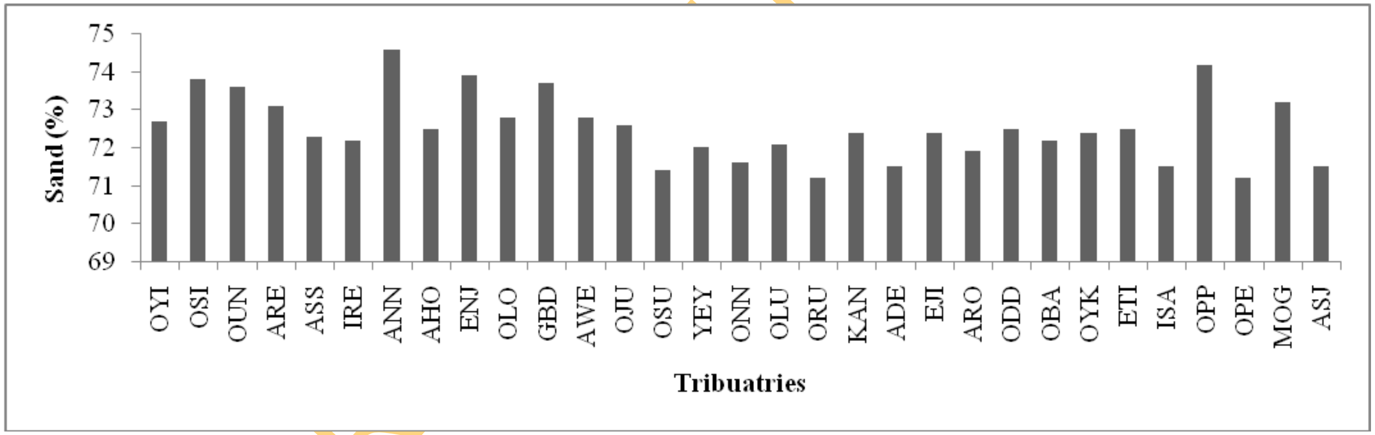

Figure 4.29: **Spatial variation of sand in sediment**

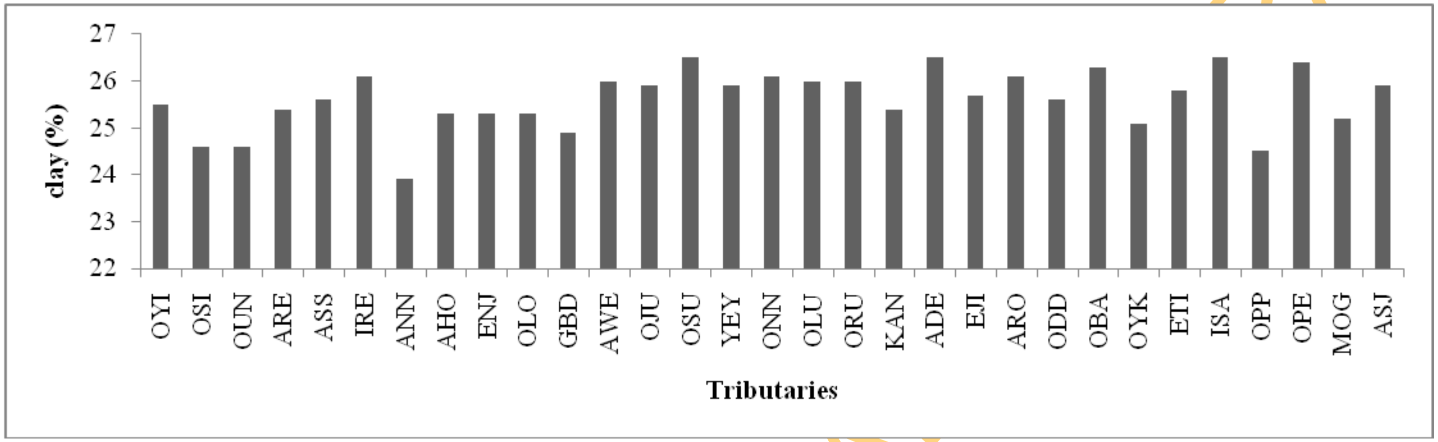

Figure 4.30: Spatial variation of clay in sediment

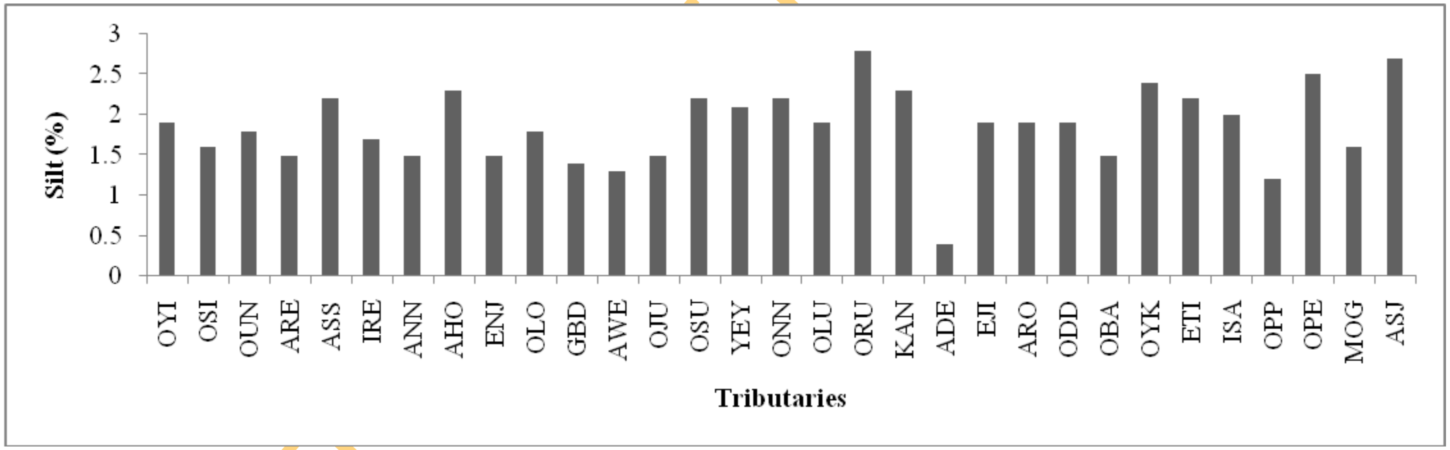

Figure 4.31: Spatial variation of silt in sediment

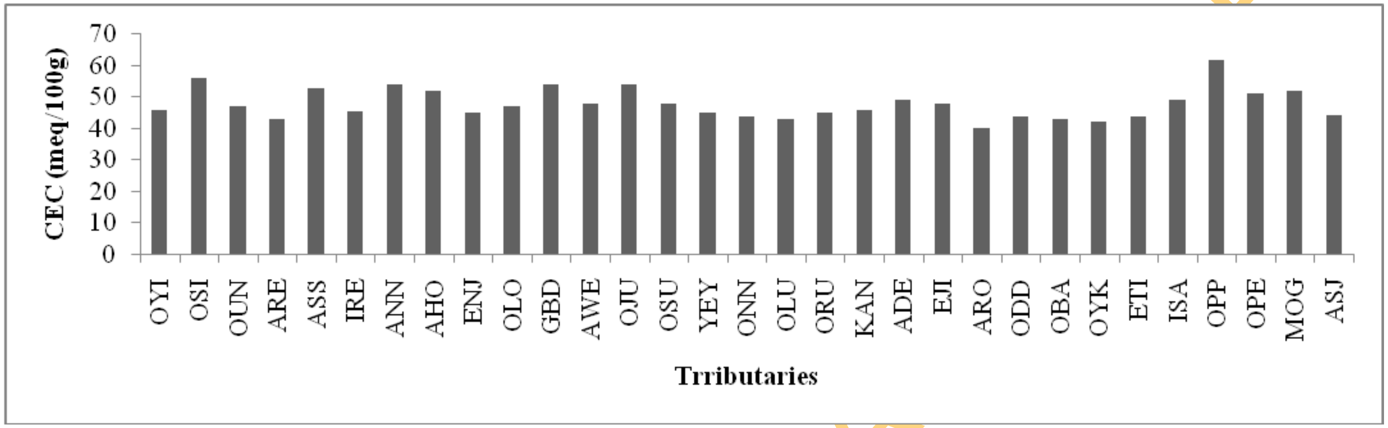

Figure 4.32: Spatial variation of cation exchange capacity in sediment

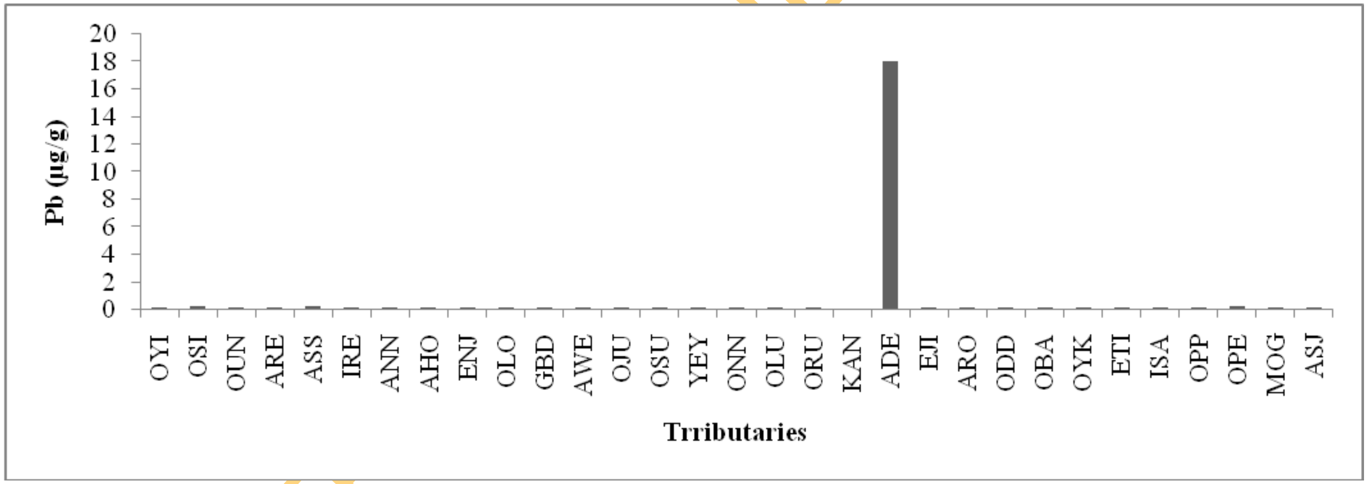

Figure 4.33: Spatial variation of Pb in sediment

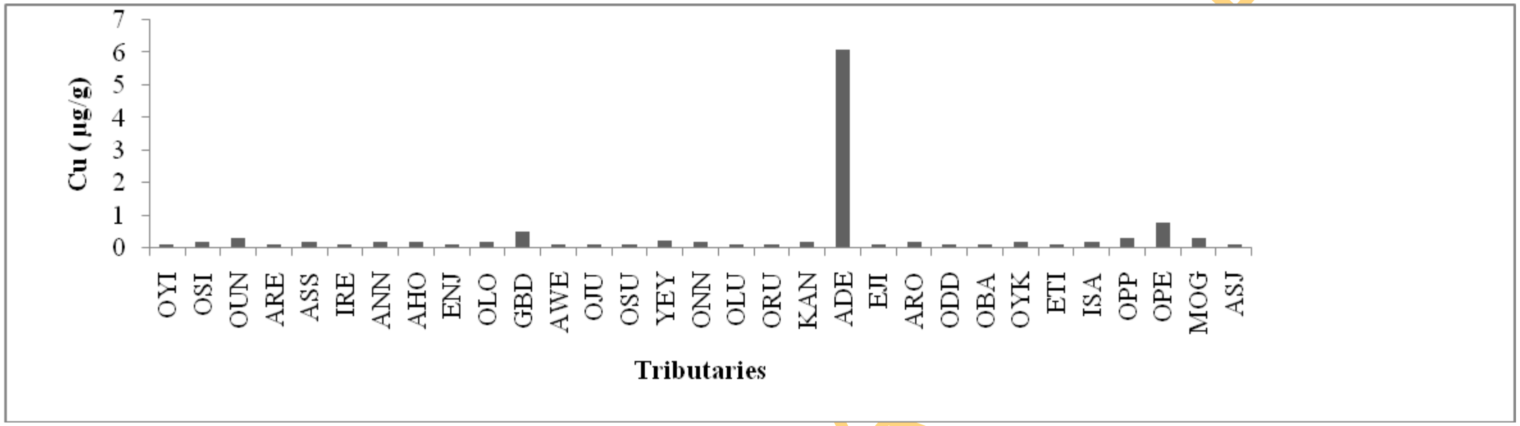

Figure 4.34: Spatial variation of Cu in sediment

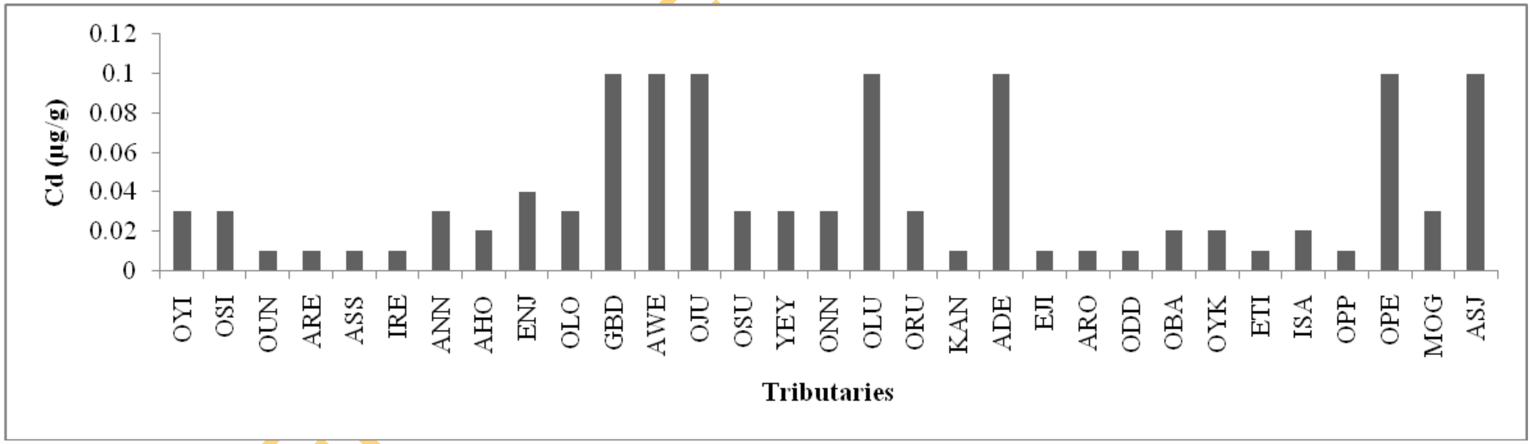

Figure 4.35: Spatial variation of Cd in sediment

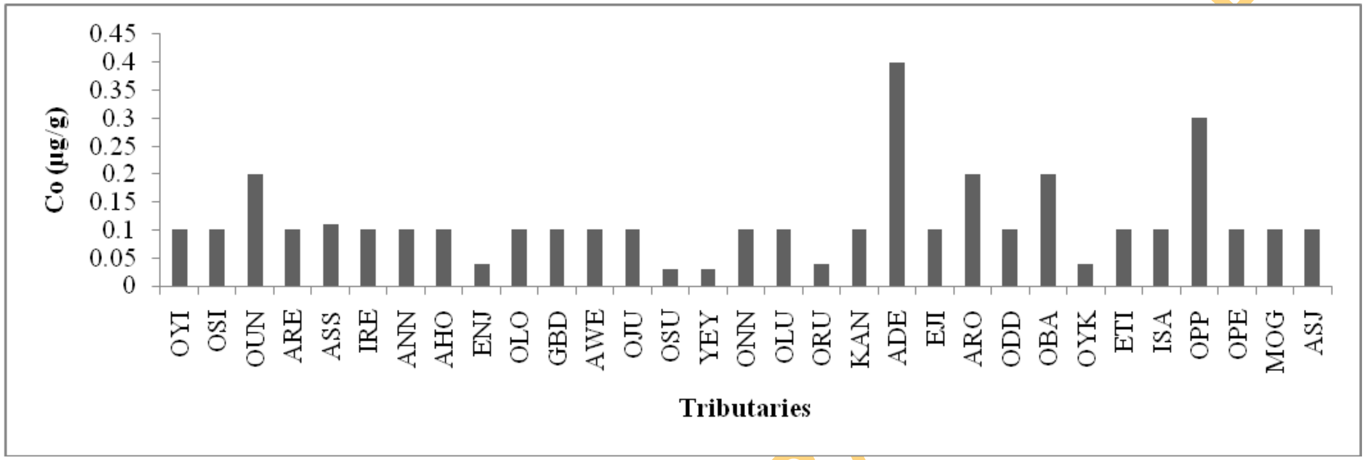

Figure 4.36: **Spatial variation of Co in sediment**

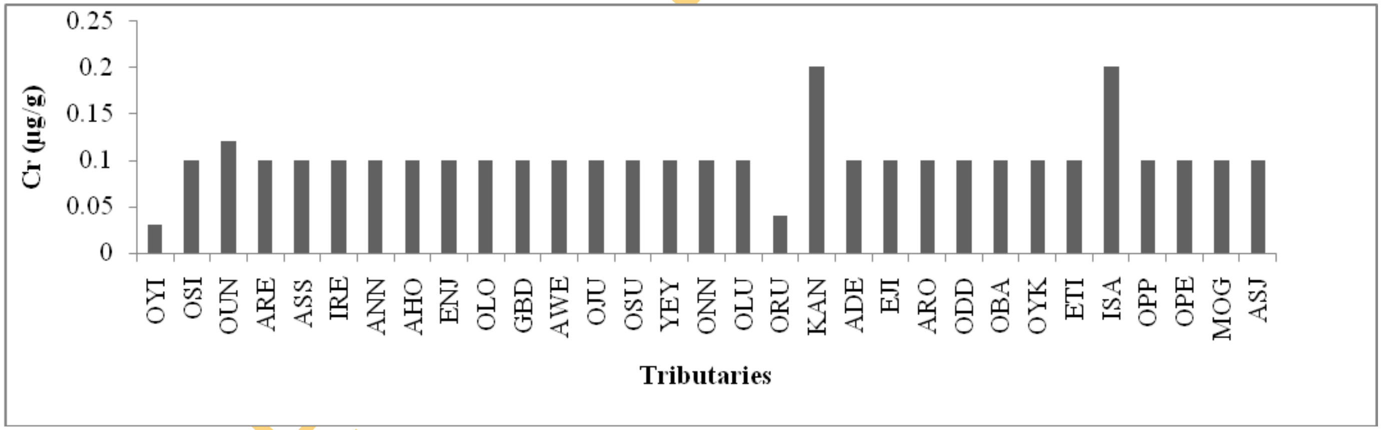

Figure 4.37: **Spatial variation of Cr in sediment**

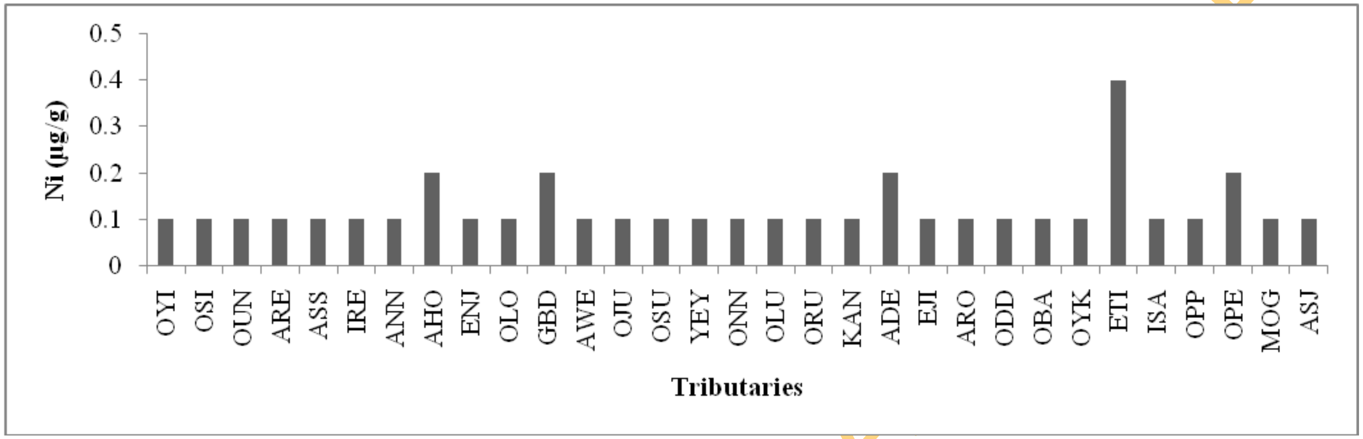

Figure 4.38: Spatial variation of Ni in sediment

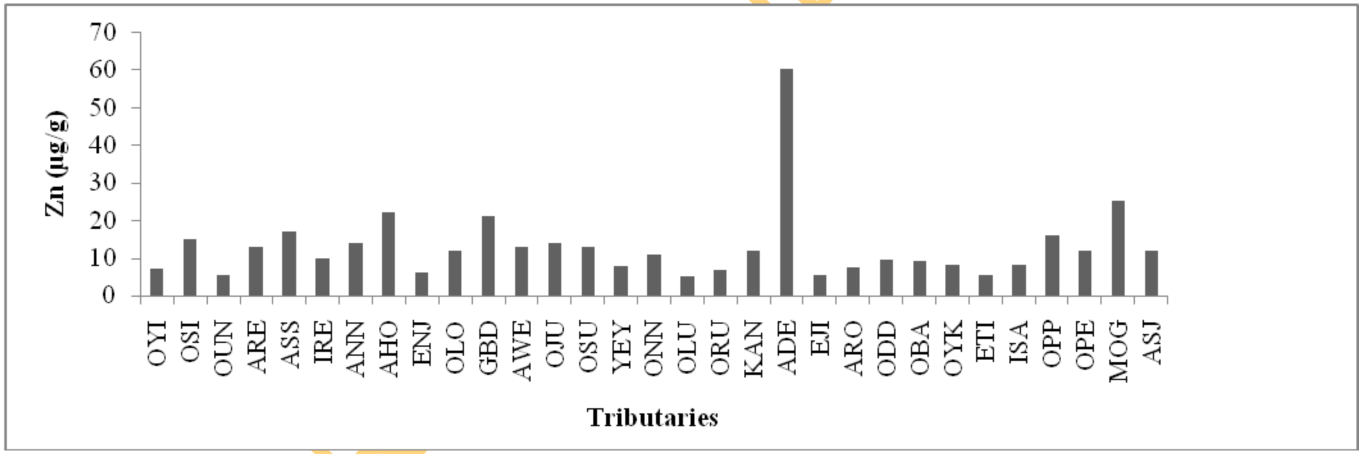

Figure 4.39: Spatial variation of Zn in sediment

Table 4.12: Seasonal variation of the physicochemical characteristics and heavy metals in sediment

Parameters	Dry Season	Wet Season
Organic Carbon (%)	1.69± 8.17	3.39±6.41
Sand (%)	73.0±3.86	71.9±2.00
Clay (%)	24.7±3.80	26.5±1.96
Silt (%)	2.30±2.81	1.61±1.28
CEC (meq/100g)	49.7±17.2	47.0±13.8
Pb (µg/g)	0.93±7.51	0.42±3.41
Cu (µg/g)	0.30±2.17	0.46±1.65
Cd (µg/g)	0.03±0.08	0.02±0.08
Co (µg/g)	0.13±0.41	0.07±0.11
Cr (µg/g)	0.10±0.19	0.07±0.11
Ni (µg/g)	0.12±0.10	0.10±0.17
Zn (µg/g)	14.4±4.10	11.1±16.1

which the river flows. Contaminants are generated in these environments. The values were high because of early flush pheneomenon. As the wet seasons progresses towards the dry seasons some of the deposits are carried further along the course of the river thus reducing the level of sediment.

Parameters that were higher during dry seasons

Sand, silt, CEC, lead, cadmium, cobalt, chromium, nickel and zinc were higher in the dry seasons. In the dry seasons, the flow rate and volume of Osun River was low and the contaminants increase in concentration, since there is no water to wash them away and dilute the river. During dry seasons all wastes from urbanization, industrial and agricultural activities settle in sediment and increase the contaminant bioavailablity. The presence of suspended matter such as leaves, sticks, carcasses of different fauna and other floating substances that can not sink are seen in these river sediments. Since the flow rate is low, deposited contaminants can not be washed away and so there is bioconcentration.

Paired t-tests performed revealed that there were no statistical significant differences at $p< 0.05$ except for organic carbon, Pb, Cu, Co and Cr that were statistically significant.

4.15 APPLICATION OF MODELS TO PREDICTION OF FUTURE SEDIMENT QUALITIES

The data obtained for sediment were subjected to modeling to determine the trend and seasonality up to year 2018. The results are as shown in Table 4.13. The model equations and the predicted concentrations up to year 2018 are also indicated. The coefficient of determination (R^2) gives an indication about the suitability of the model.

In Asejire, the model explains effectively 60% variation of Zn (with predicted concentration of 324µg/g for September, 2018). For other parameters, the model could not explain significant variations. Comparison of the predicted Zn concentration in Adeti with guidelines showed a high Zn content greater than the limit stipulated by sediment quality guidelines for ERL (150 µg/g Zn) and ERM (410 µg/g Zn), Canadian and Ontario sediment quality guidelines (123µg/g and 120 µg/g respectively) and the consensus based

Table 4.13: Time-series analysis results of selected parameters of sediment from selected tributaries

Tributary	Parameter	R^2	Model equation	Forecast for 2018
Adeti	Zn	0.46	19.5 – 20.8b	1243µg/g, November.
Asejire	Zn	0.60	42.3-4.54b	324 µg/g, September.
Etioni	Zn	0.42	15.1 -1.38b	273 µg/g, January.
Gbodofon	Co	0.53	$0.19-1.95 \times 10^{-2}b$	-
	Zn	0.69	57.0 – 5.59b	3202 µg/g, January.
Ishasha	Zn	0.45	21.3 – 1.82b	675 µg/g, January.
Isin	Zn	0.47	28.3 -2.62b	304 µg/g, November.
Moginmogin	Zn	0.68	72.3 -7.48b	1.32 µg/g, January.
Oba	Co	0.52	0.51 -5.03b	-
Ojutu	Ni	0.47	19.5-1.68b	-
Oloyo	Zn	0.43	36.9 – 3.46b	1853µg/g, November.
Osun	Zn	0.59	35.9-3.67b	3899µg/g, September.
Oyi	Ni	0.41	$0.21- 2.23 \times 10^{-2} b$	-
	Zn	0.42	31.0 – 3.13b	-

sediment quality guidelines of Wisconsin (120 µg/g Zn). This indicates that the river sediment here was contaminated with this metal.

The level of Zn in Etioni was predicted to be 273 µg/g with 42% variation and Ishasha 675 µg/g with 45% variation. The Zn level of this two tributaries were found to exceed the limit stipulated by all the guidelines except in Ishasha where Zn was lower compared with the sediment quality guidelines of the ERM which is 410 µg/g.This means the quality of the sediment will not be impaired except at Ishasha.

The predicted level of Zn at Adeti (1243 µg/g), Oloyo (1853 µg/g), Gbodofon (3202 µg/g) and Osun (3899 µg/g) were found to be higher than the level stipulated by all the sediment quality guidelines. This implies that the sediment will be grossly polluted in 2018. The sediment will therefore need to be remediated by any appropriate remediation methods. This contaminated sediment will release this toxic metal into waterbody and will also contaminate the available water meant for living organisms in the water and the usage of water for all purposes. This is so because Zn will dissolve in water and its bioavailability will increase.

Moginmogin showed predicted level of Zn (1.32 µg/g), with 68.0% variation. This level was found to be very low compared to the level of Zn in all the sediment quality guidelines. This shows that the level will not give a significant contamination but might still need to be monitored.

4.16 PRINCIPAL COMPONENT ANALYSIS OF HEAVY METALS IN SEDIMENT

The principal component analysis of metals in sediment is as shown Fig. 4.40. It reveals clustering property for the heavy metals in sediment. Cd, Co, Cr and Ni were observed to cluster together indicating correlation between these metals and were also supported from the Pearson correlation moment obtained in Table 4.14. Zn, Cd, Co, Cr, Cu and Ni are far from the origin and these parameters have more influence in determining the principal component analysis model unlike Pb with short distance from the origin. The first

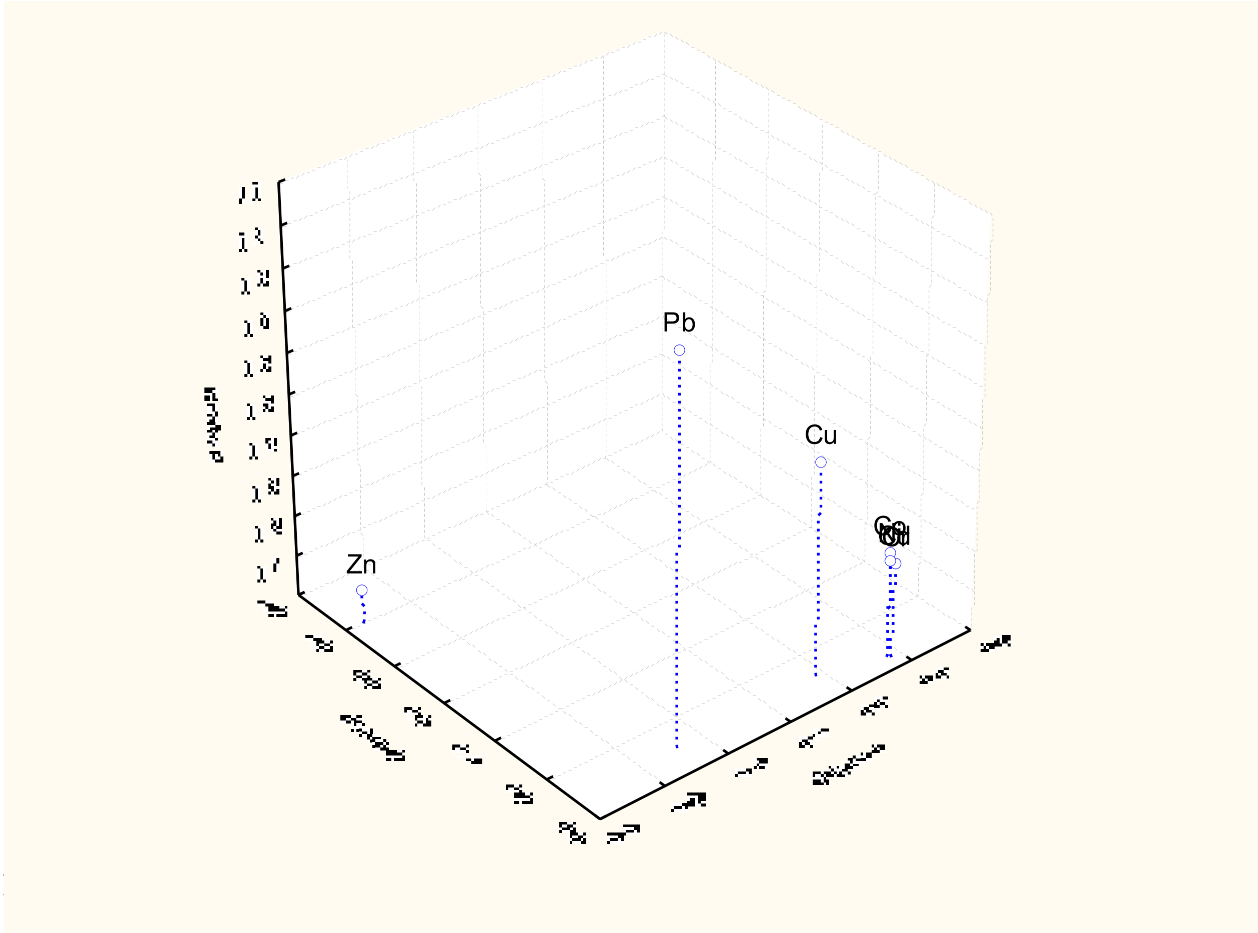

Fig. 4.40: Principal Component Analyses of Heavy Metals in Sediment

principal eigenvalues captures 74.9% of the total variance which was due to the clustered heavy metals (Cu, Cr, Cr, Cd and Ni). These metals contributed to the contamination of the Osun River sediment and were due to both industrial and domestic waste discharges. The second factor explains 14.5% of the total variance for Zn. Zn might have originated from antropogenic activities of man such as leaching of zinc material that contaminate water body and get absorbed by river sediment. The third factor explains 9.28% of the total variance for lead. Pb originated from anthropogeneic activities due to land erosion, because car exhausts which get deposited on land can be washed through erosion into river Osun and get settled at the bottom. The Figure suggests different sources of Zn, Pb and other metals.

4.17 CORRELATION OF METALS CONCENTRATIONS BETWEEN WATER AND SEDIMENT

Table 4.14 shows the correlation between metals in water and metals in sediment. It reveals a high correlation for lead (0.99), cobalt (0.99) and cadmium (0.99), signifying that the source of these metals in the two media are the same. Lower but also strong correlation was observed for copper with coefficient of correlation of 0.75.

4.18 ACCUMULATION FACTORS BETWEEN METALS IN SEDIMENT AND WATER FOR THE STUDY

Table 4.15 reveals the accumulation factors between sediment and water to be highest for lead (233) followed by zinc (171). Copper (133) also had high accumulation factor compared to the other remaining metals. A very high accumulation factor for lead indicates that lead is the most prominent of heavy metals pollutants discharged into the water course. This was probably due to instream hygrological modifications, instream sludges accumulation and air pollution fallout. The accumulation of these metals in sediment can be traced to terrestrial

4.19 PEARSON MATRIX FOR HEAVY METALS IN SEDIMENT

Table 4.16 reveals the correlation matrix obtained for heavy metals in sediment. High positive correlations were obtained for the following pairs in sediment sample analysed:

Table 4.14: Sediment-Water correlations of metal concentrations

Metal	Pb	Cu	Cd	Co	Cr	Ni	Zn
Correlation coefficient	0.99	0.78	0.99	0.99	0.92	0.89	0.97

Table 4.15: Sediment/water factors of accumulation of metal concentrations for Osun River

Metal	Accumulation Factor
Lead	233
Copper	133
Cadmium	15
Cobalt	25
Chromium	10
Nickel	25
Zinc	171

Table 4.16: Correlation matrix for heavy metals in sediment

	Pb	Cu	Cd	Co	Cr	Ni	Zn
Pb	1.000						
Cu	0.723**	1.000					
Cd	0.253**	0.398**	1.000				
Co	0.379**	0.531**	0.128**	1.000			
Cr	0.020	0.031	0.096**	0.103**	1.000		
Ni	0.155**	0.118**	0.065	0.107**	0.112**	1.000	
Zn	0.159**	0.206**	0.378**	0.234**	0.212**	0.226**	1.000

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

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

Cu/Pb (r = 0.723), Co/Cu (r = 0.532). Medium positive correlations was also observed for Cd/Cu (r = 0.378) and Zn /Cd (r = 0.378) at p= 0.01. This suggests a common source for the polluting substances such as industrialization, urbanization and agricultural activites.

4.20 CALCULATION OF ENRICHMENT FACTOR AND INDEX OF GEO-ACCUMULATION

A common approach to estimating how much sediment is impacted (naturally and anthropogenically) with heavy metals is to calculate using enrichment factor (EF) (Huu *et al*., 2010). The evaluation of the degree of metal contamination or pollution in terrestrial, aquatic and marine environment was also calculated using the index of geo-accumulation (Mediolla *et al*., 2008; Asaah and Abimbola, 2005). Table 4.17 illustrates the enrichment factor and index of geo-accumulation obtained for the sediment.

$$\text{Enrichment Factor (EF)} = \frac{(\text{C metal }/\text{C normalizer}) \text{ sediment}}{(\text{C metal }/\text{C normalizer}) \text{ control}}$$

Where C $_{\text{metal}}$ and C$_{\text{normalizer}}$ $=$ concentrations of heavy metals and normalizer in sediment and control sample.

$$\text{Index of Geo} - \text{accumulation (Igeo)} = \frac{\text{Log}_2 \;\; \text{C metal}}{1.5 \text{ C metal (control)}}$$

Enrichment factors were calculated from the mean concentrations of the heavy metals in the sampling points used for this study. The control sampling point was considered to be the unpolluted or background point. The normalizing element used was zinc according to Mendiola *et al*. (2008). Enrichment (EF) of the heavy metals in sediment showed that Zn (1), Cd (1.74), Co (0.97), Cr (0.83), and Ni (0.42) had no enrichment: Pb (3.81) had strong enrichment and Cu (2.12). Therefore, contamination of Osun River sediment by lead and copper originated from anthropogenic activities such as agriculture, urbanization, and industrialization.

Table 4.17: Overall Enrichment Factor and Indices of Geo-accumulation in sediments

	Zn	Pb	Cu	Cd	Co	Cr	Ni
C_{metal}	12.8	0.67	0.38	0.03	0.10	0.09	0.11
$C_{normalisation}$	12.8	12.8	12.8	12.8	12.8	12.8	12.8
$C_{metal/control}$	8.55	0.12	0.12	0.01	0.07	0.07	0.19
$C_{normalisation}$	8.56	8.56	8.56	8.56	8.56	8.56	8.56
EF	1.00	3.81	2.16	1.74	0.97	0.83	0.42
I_{geo}	0.08	-3.25	-7.68	-351	-31.5	-35.0	-11.1

EF< 2 is deficiency to mininmal enrichment

EF< 2-5 is moderate encrichment

EF< 5-20 is significant enrichment

EF > 20-40 very high enrichment

EF > 40 extremely high enrichment

I_{geo} <0 = unpolluted

0< = I_{geo} < 1 unpolluted to moderately polluted

1< = I_{geo} < 2 moderately polluted

2< = I_{geo} < 3 moderately to strongly polluted

3< =I_{geo} < 4 strongly polluted

The results of the calculation of geo-accumulation index (I_{geo}) in the sediment are as shown in Table 4.17. The negative values of Pb (-3.22), Cu (-7.68), Cd (-352), Co (-31.5), Cr (-35.0) and Ni (-11.1) according to Huu *et al*. (2010) showed that sediment was moderately polluted by Pb and Cu. The I_{geo} suggests pollution of the sediment mostly with lead and copper.

4.21: COMPARISON OF SEDIMENT METAL CONCENTRATIONS WITH SEDIMENT QUALITY GUIDELINES

Table 4.18 shows the number of tributaries with heavy metal values greater than what was stipulated by the sediment quality guidelines. The upper range of some of these tributaries had high heavy metal levels than some of the guidelines. Adeti had as its highest range for lead to be -70 mg/kg; copper - 24 mg/kg; cadmium - 0.5 mg/kg; cobalt - 3.0 mg/kg; and zinc - 397 mg/kg. The value for lead was greater than the limit set by the Canadian and Ontario sediment quality guidelines (35.0 mg/kg and 31.0 mg/kg Pb respectively), sediment quality guideline of ERL (46.7 mg/kg Pb) and the consensus based sediment quality guidelines of Wisconsin (36.0 mg/kg Pb). The level of copper in Adeti was found to be above the Ontario sediment quality guideline (16.0 mg/kg Cu). The level of cadmium was not as high as the limit set for the Canadian and Ontario sediment quality guidelines. The level of zinc in Adeti was higher compared to all the guidelines except for the sediment quality guidelines of ERM. Sediment is the ultimate depository of many chemical compounds including heavy metals from natural and anthropogenic sources. The reason for this accumulation of heavy metals in Adeti sediment must be as a result of discharge of waste from brewery industry located around this environment and runoff from diffuse pollution sources. Enja and Etioni had chromium and nickel concentration to be lower to other guidelines.

4.22 COMPARISON OF HEAVY METALS IN SEDIMENT IN THIS STUDY WITH STUDIES ELSEWHERE

Table 4.19 reveals the comparison of heavy metal concentration in this study with studies elsewhere. The level of lead was observed to fall below the value obtained in selected Rivers in Polland (10-126 µg/g) by Solecki and Chiboeski (1999), Ikpoba River, Nigeria

Table 4.18: Comparison of metal levels in sediment with various guideline limit

Guide/Criteria	Pb	Cd	Cr	Cu	Ni	Zn
Canadian	35.0	0.60	37.3	35.7	-	123
Ontario	31.9	0.60	26.0	16.0	16.0	120
ERM	218	70	9.6	270	51.6	410
ERL	46.7	1.2	81	34	20.9	150
CBSQG	36.0	0.99	43.0	32.0	23.0	120
No. of locations not exceeding the guidelines	30	31	30	30	31	30
No. of locations exceeding the guidelines	1	-	1	1	-	1

Ref: Wisconsin Department of Natural Resources (2003), Canadian Council of Ministers of the Environment (1999), Ontario Ministry of Environment and Energy (1993)

Table 4.19: Comparison of heavy metals in sediment in this studies with studies elsewhere (µg/g)

Country	River	Major activities in the area	Pb	Cu	Cd	Co	Cr	Ni	Zn	References
Nigeria	Osun		0.7±5.8	0.4±1.9	0.03±0.10	0.1±0.3	0.1±0.2	0.1±0.3	12±31	This Study
Pakistan	Ravi	Industrial	-	3.38±160	0.99±3.17	2.22±18.5	4.60±57.4	-	-	Rauf *et al.* (2009)
Kosova	Prishtina	Industrial	20.3-115	6.90-81.2	0.22-4.45	-	-	-	-	Fatos *et al.* (2010)
Albania	Lana	Urban area	0.21-0.34	-	0.10-0.20	-	-	54.4-87.0	-	Alma *et al.* (2010)
Hungary	Tisza	Urban/aquatic	-	53	-	-	-	75	-	Szilard *et al.* (2008)
Nigeria	Ojora	Urban/industrial	-	-	0.47±0.36	-	-	-	-	Adekoya *et al.* (2006)
Nigeria	Ibiekuma	Urban area	0.11-0.92	1.05-1.97	0.01-0.36		0.08-0.40	0.02-0.35	44.9-55.9	Obasohan (2008)
Polland	Masluchowskie	Urban area	10-126		-	-	-	-	9-169	Solecki and Chibowski (1999)
Nigeria	Ikpoba	Urban area	3.3	1.9	1.5	-	1.9	3.95	4.7	Oguzie (2002)
Bangladesh	Buriganga	Industrial	-	-	-	-	-	12.3-31.5	-	Habibet *et al.* (2009)
Australia	Swan	Industrial area	184	297	0.9	-	-	-	-	Andrew *et al.* (2004)
Turkey	Nalihan	Urban area	0.49	1.12	-	-	-	0.77	-	Ayas *et al.* (2007)
Lebanon	Jordan	Urban area	8.1	-	0.63	-	-	-	20.3	Howani and Banat (2007)
Lebanon	Yarmouk	Urban area	8.4	-	0.67	-	-	-	26.4	Howani and Banat (2007)
Portugal	Lima	Urban area	-	16.0-406	-	-	24.0-84.0	3.0-27	58-398	Raquel *et al.* (2008)
Bangladesh	Buriganga	Industrial	64.7 -77.1	21.8 -32.5	2.36 -4.25	-	119 -218	147 – 258	-	Ahmad *et al.* (2010)
Bangladesh	Shitalakhya	Industrial	54.2- 65.9	56.1 - 91.5	1.71 -2.17	-	60.1 - 91.0	121- 132	-	Ahmad *et al.* (2009)
France	Lot	Industrial	523	97.7	125	-	-	-	-	Audry *et al.* (2004)
France	Lot	Urban	105	30.7	20.4	-	-	-	-	Audry *et al.* (2004)
Spain	Tinto	Industrial	870	846	6.2	-	-	-	-	Galan *et al.* (2003)
Nigeria	Ogun	Farming, urban and industrial area	-	39.5±11.7	5.76±1.22		-	136±5	96.5±44.7	Udousoro and Osibanjo (1997)

(3.3 µg/g) by Oguzie (2002) and in Iber River, Kosova (20.3-115 µg/g) by Fatos *et a.l* (2010), Swan River (184 µg/g), Australia by Andrew *et al*. (2007) and Jordan and Yarmouk Rivers, Lebanon (8.1 and 8.4 µg/g) by Howani and Banat (2007). Lead level in this study was however found to be higher than levels obtained in Ibiekuma stream, Nigeria (0.11-0.92 µg/g) by Obasohan (2008) and in Lana River, Albania (0.21-0.34 µg/g) by Alma *et al*. (2010). The level of cadmium in the present study was found to be below the levels obtained in Ogun River, Nigeria (5.76±1.22 mg/L) by Udousoro and Osibanjo (1997); Ikpoba River, Nigeria (1.50 µg/g) by Oguzie (2002), in Igbede, Ojo and Ojora Rivers, Nigeria (0.47±0.36 µg/g) by Adekoya *et al*. (2006), in river Ravi, Pakistan (0.99±3.17 µg/g) by Rauf *et al*. (2009) and in Iber River, Kosova (0.22-4.45 µg/g) by Fatos *et al*. (2010).

The study reveals lower heavy metal levels compared to most other studies, this might be as a result of the environment of the studied river. For instance, most of the rivers elsewhere where industries are cited have their sediment contaminated. These industries discharge their wastes into these rivers without being treated and impair the quality of the river sediment. Levels of heavy metals metals were reported to be generally higher than Osun River in Yarmouk River, Lebanon by Howani and Banat (2007); in Lima River, Portugal by Raquel *et al.* (2008); Buriganga River, Bangladesh by Ahmad *et al*. (2010); in Shitalakhya River, Bangladesh by Ahmad (2009); Ogun River, Nigeria by Udousoro and Osibanjo (1997) and in River Lot, France by Audry *et al.* (2004).

Cobalt was noticed to be present in river Ravi, Pakistan (2.22±18.5 µg/g) by Rauf *et al.* (2009) and higher than the level obtained in Osun River sediment and was due to industrial waste discharge into the river.

Chromium in Osun River was higher than the lowest value obtained in Ibeikuma River, Nigeria (0.08±0.40 µg/g) by Obasohan (2008). Though still within the range in this river. Nickel in Osun River sediment was found to be greater than the lower range value of sediment in Ibeikuma, Nigeria (0.02 – 0.35 µg/g) by Obasohan (2008) and lower to the value obtained in Ogun River (136±5 mg/L) by Udousoro and Osibanjo (1997). An implication that the sediment is still comparable to sediment from this river. Zinc in this study was however higher than the level reported in Ikpoba River, Nigeria (4.7 µg/g) by Oguzie (2002) and the lower range in Masluchowskie River, Polland (9 – 169 µg/g) by Solecki and Chibowski (1999) but lower compared to the value obtained in Ogun River (96.5±44.7 mg/L) by Udouosoro and Osibanjo (1997).

Some of the metals were noticed to be below the range obtained in some other countries signifying that the pollution level of River Osun sediment is still within minimal as compared to what was obtained elsewhere.

4.23 AVERAGE METAL CONCENTRATION (OVERALL) IN PLANT

The overall average characteristics of heavy metals in plant are as shown in Table 4.20. Pb was 0.9±1.1 µg/g and higher than Pb at the control site with an accumulation factor of 1.13. Cu had an average concentration of 1.4±3.3 µg/g and higher than what was obtained at the control site with an accumulation factor of 1.40. The overall average value of Co was 1.1±1.6 µg/g and was higher than the level of cobalt at the control site with a factor of 1.22. The overall average level of Cr was 0.9±1.2 µg/g and higher than the level at the control site with a factor of 1.13. Ni had an average value of 1.3±8.4 µg/g and higher the the level obtained at the control site with a factor of 1.86. The level of Zn obtained for the study was 32±63 µg/g and higher compared to what was obtained at the control site with an accumulation factor of 1.1.

The accumulation factor showed that nickel was the most accumulated heavy metal in plants along Osun River bank and then copper. The sources of these metals could be as a result of man's activities such as industrial and urban activities. Atmospheric deposition of metals is also another source by which these metals can get deposited on plants. Nickel is mainly transported in the form of a precipitated coating on particles and in association with organic matter. Nickel may also be absorbed via uptake by plants from sediments.

The results obtained in this study was not as high as the one reported by Onianwa and Fakoyode (2000) where they reported an average value of heavy metals in plant around a battery manufacturing factory: Zn (59.2 mg/kg), Cu (18.4 mg/kg), Ni (8.26 mg/kg), Cr

Table 4.20: Average (overall) concentration of metals in Plants

Metal	Concentration (μg/g)	Control Site (μg/g)	Accumulation Factor
Pb	0.9±1.1	0.8±0.5	1.13
Cu	1.4±3.3	1.0±1.2	1.40
Cd	0.5±0.5	0.5±0.6	1.00
Co	1.1±1.6	0.9±1.1	1.22
Cr	0.9±1.2	0.8±0.8	1.13
Ni	1.3±8.4	0.7±0.9	1.86
Zn	32±63	29±31	1.10

(8.74 mg/kg), Cd (1.63 mg/kg) and Pb (1350 mg/kg). This signifies that vegetations along the river banks are not as polluted as what was obtained in the control site. Bioavailability of the elements depends on the form of their bond within the constituents of a soil. The level of heavy metals in plants in this study was as a result of anthropogenic activities around the river banks. Plants readily assimilate through the roots such compounds, which dissolve in waters and occur in ionic forms. Additional sources of these elements for plants are rainfall, atmospheric dusts, plant protection agents, and fertilizers, which could be absorbed through the leaf blades. (Lozak *et al*., 2001).

4.24 AVERAGE CONCENTRATIONS OF HEAVY METALS IN PLANTS AROUND THE TRIBUTARIES

The average characteristics of plants around Osun River for thirty-one tributaries are as shown in Table 4.21. The levels of heavy metals were compared with concentration obtained at the control site.

Fourteen of the thirty-one tributaries had higher lead values in plant than the level obtained in the control site. Isin and Adeti were found to be one of those thirteen tributaries that accumulated lead the most with accumulation factor of 1.44. Fourteen tributaries were found to have higher concentration of copper compared to the control sample and the tributary that accumulated copper the most was Asejire with accumulation factor of 2.43. This might be due to the discharge of waste from near-by source such as the Nigerian bottling company and air deposition. Only one tributary was found to have higher cadmium concentration compared to the level in the control sample, and this was Osin with an accumulation factor of 2.0. Thirteen of the tributaries had higher cobalt level greater than plant at the control site. Three of these tributaries were Ounseku, Awesin and Adeti with a factor of 1.44. The sources of this metal in these tributaries are due to man's activities around the river bank and atmospheric pollution. Six out of the thirty-one tributaries had higher nickel level compared to what was obtained at the control site. Those tributaries that accumulated nickel prominently were Arenounyun and Awesin with a factor of 1.46. Tweleve tributaries were found to have higher zinc concentration greater than the control site. Adeti was found to accumulate the highest amount of zinc, with a

Table 4.21: Average concentrations (µg/g) of heavy metals in plant in all tributaries

Parameter	Oyi (OYI)	Osin (OSI)	Ounseku (OUN)	Arenounyun (ARE)	Ashasha (ASS)	Isin (IRE)	Anne (ANN)	Ahoyaya (AHO)
Pb	1.00±1.60	0.80±0.90	1.10±1.30	0.80±0.90	1.20±1.50	1.30±1.70	1.00±1.30	0.80±0.70
Cu	0.80±0.90	1.00±1.30	1.00±1.10	3.10±5.50	1.40±2.70	1.00±1.20	1.40±3.10	0.60±0.70
Cd	0.40±0.50	0.70±0.90	0.40±0.50	0.50±0.50	0.50±0.60	0.40±0.50	0.40±0.50	0.40±0.50
Co	0.80±0.60	1.60±2.80	1.30±2.10	1.20±1.60	1.30±2.30	1.00±1.30	1.00±1.00	0.60±0.70
Cr	0.90±1.30	0.90±1.40	1.30±1.80	0.60±0.70	0.50±0.40	1.00±1.40	0.90±0.80	0.60±0.70
Ni	0.70±1.50	0.80±1.50	0.90±1.50	1.60±3.40	1.90±3.4	0.40±0.80	0.90±1.50	0.40±0.50
Zn	20±28	32±45	18±23	46±100	22±44	37±69	24±33	18±44

Table 4.21 (contd.):

Parameter	Enja (ENJ)	Oloyo (OLO)	Gbodofon (GBD)	Awesin (AWE)	Ojutu (OJU)	Osun (OSU)	Yeyekare (YEY)	Oni (ONN)
Pb	1.10±1.50	0.80±0.70	0.90±0.80	0.80±0.70	0.90±0.90	1.20±1.20	1.20±1.20	0.80±0.50
Cu	1.90±3.80	0.70±1.20	2.10±7.00	1.00±0.80	0.80±0.80	0.80±0.80	3.20±7.90	0.80±1.00
Cd	0.50±0.50	0.40±0.50	0.40±0.50	0.40±0.50	0.40±0.50	0.40±0.50	0.40±0.50	0.40±0.50
Co	0.70±0.70	1.70±2.30	0.80±1.10	0.90±1.20	1.10±2.00	1.40±2.30	1.40±0.20	0.80±1.00
Cr	0.80±1.00	1.00±2.30	0.80±0.80	1.30±1.60	0.70±1.20	1.20±1.70	0.60±0.60	0.60±0.70
Ni	0.90±1.50	0.90±1.80	1.50±5.10	1.90±3.80	1.80±4.30	1.10±1.90	0.40±0.60	0.70±1.50
Zn	32±47	20±30	49±91	28±51	43±90	41±70	30±71	18±30

Table 4.21 (contd.):

Parameter	Olumirin (OLU)	Orufu (ORU)	Kankere (KAN)	Adeti (ADE)	Aro (EJI)	Aro (ARO)	Odoiya (ODD)	Oba (OBB)
Pb	1.10±0.90	1.10±1.30	1.10±1.30	1.30±1.40	0.80±0.80	0.60±0.50	1.00±1.60	0.60±0.50
Cu	1.70±3.10	0.60±0.60	0.80±0.70	3.00±5.80	1.10±2.20	0.50±0.70	0.60±0.60	0.70±0.80
Cd	0.50±0.50	0.40±0.50	0.40±0.50	0.50±0.50	0.40±0.50	0.40±0.50	0.40±0.50	0.40±0.50
Co	1.20±1.70	0.60±0.60	0.70±0.70	1.20±1.50	1.30±2.20	0.90±1.10	0.80±1.20	1.00±1.30
Cr	0.80±0.80	0.50±0.70	0.60±1.10	1.30±1.70	1.00±1.40	0.90±1.50	0.60±0.90	0.80±1.20
Ni	1.40±3.50	0.80±1.50	0.90±1.50	0.80±1.50	0.70±1.00	0.70±1.20	0.90±1.60	1.50±2.60
Zn	27±48	13±17	26±32	57±92	53±100	30±51	10±16	41±85

Table 4.21(contd.):

Parameter	Oyika (OYK)	Etioni (ETI)	Ishasha (ISA)	Opa (OPP)	Ope (OPE)	Moginmogin (MOG)	Asejire (ASJ)
Pb	0.90±0.90	0.60±0.50	1.00±0.90	1.20±0.90	0.60±0.50	0.70±0.50	0.80±0.80
Cu	2.30±4.00	1.70±3.10	0.90±1.40	3.20±7.90	1.70±3.20	1.50±2.80	3.40±6.10
Cd	0.50±0.70	0.40±0.50	0.40±0.50	0.40±0.50	0.40±0.50	0.50±0.50	0.50±0.60
Co	0.90±1.40	0.50±0.60	1.20±1.80	1.40±0.20	1.40±1.80	0.70±0.90	1.00±1.30
Cr	0.60±0.80	1.10±1.80	1.00±1.40	0.60±0.60	1.10±1.50	1.00±1.40	0.70±0.90
Ni	0.60±1.00	0.60±0.90	0.60±1.50	0.40±0.60	0.80±1.50	0.70±0.40	0.80±1.10
Zn	41±100	31±56	34±59	30±71	32±43	44±89	35±63

factor of 1.78. This is due to the way people discharge waste containing various materials into this river. Zinc in plant can be absorbed through the river sediment and through atmospheric dust fallout. One-way analysis of variance showed statistical significant differences in the means of parameters obtained between the tributaries.

4.25 SPATIAL VARIATION OF HEAVY METALS IN PLANTS

The spatial variations of heavy metals in plants for all the tributaries are as shown in Figures 4.41 to 4.47. Figure 4.41 depicts transition of lead in plants from upstream (such as OYI, OSI, OUN, ARE, ASS, IRE) to downstream point (such as OYK, ETI, ISA, OPP, OPE, MOG and ASJ). The level of lead in plant decreases from upstream to the dowmstream of the river network. The changes in lead concentration are not significant except at some tributaries where there is an unusual increase in the level of lead due to input from diffuse point source. The spatial distribution of other heavy metals in plants follow general pattern as for lead and this is as illustrated in Figures 4.42 to 4.47.

4.26 SEASONAL VARIATION OF HEAVY METALS LEVELS IN PLANTS

The seasonal variations of heavy metals in plants are as shown in Table 4.22. The metals are discussed on the basis of the period when they are significant.

Heavy metals that are higher during dry season

Table 4.22 shows that copper, cadmium, nickel and zinc were higher in dry seasons. This can be attributed to aerial deposition of metals on leaves through chimney of some industries. The metals are absorbed and get concentrated because there is no rain to wash them away. Wind can also be a major factor in aerial deposition of heavy metals on plants. Plant can also accumulate metals from sediment. The chemical composition of plants reflects the elemental composition of the sediment and the contamination of the plant surface indicates the presence of noxious environmental contaminants. This suggests that plant uptake these metals in sediment through the waste discharged into the river by some anthropogenic activites such as industrialization, erosion and domestic activites.

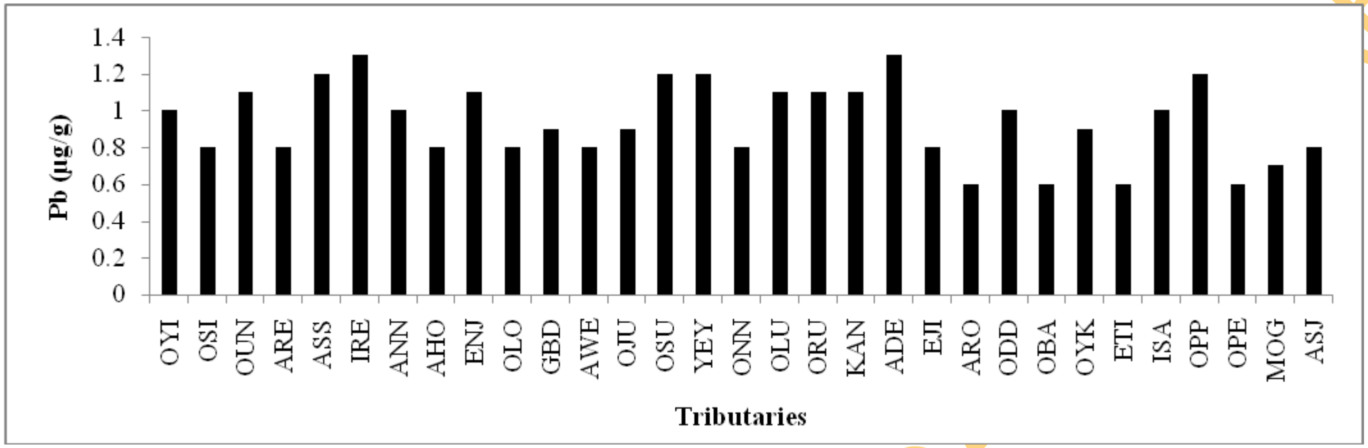

Figure 4.41: Spatial variation of Pb in plant

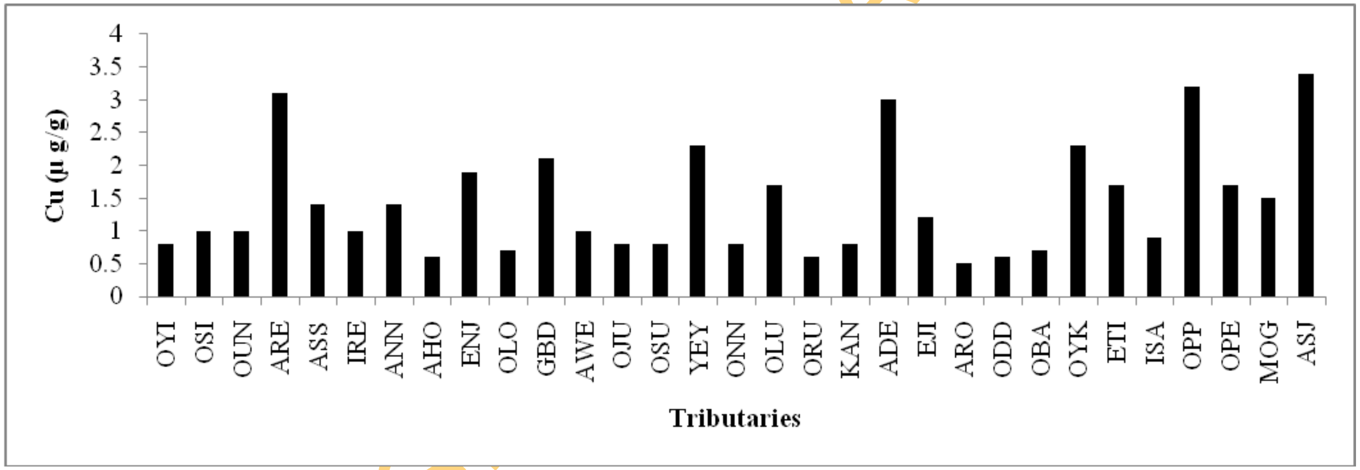

Figure 4.42: Spatial variation of Cu in plant

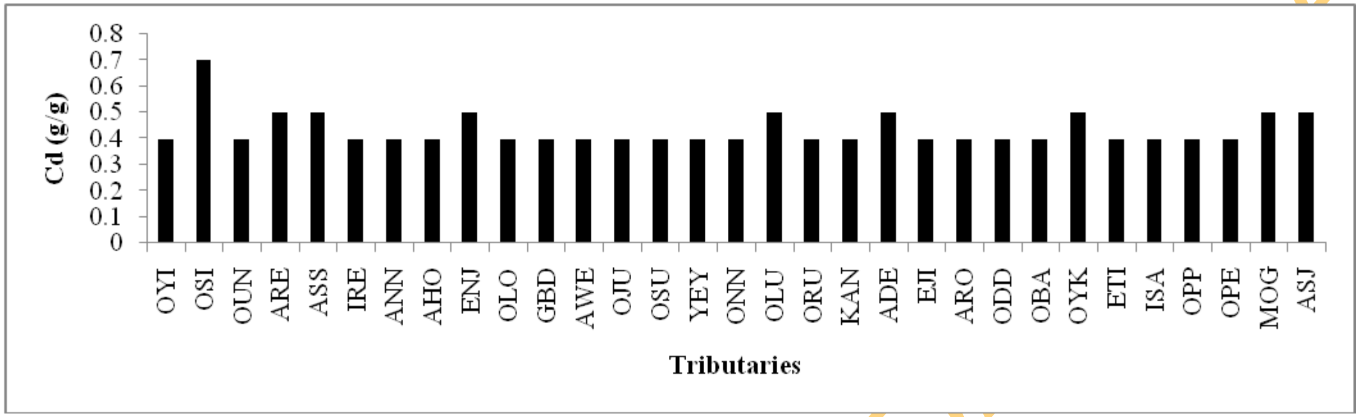

Figure 4.43: Spatial variation of Cd in plant

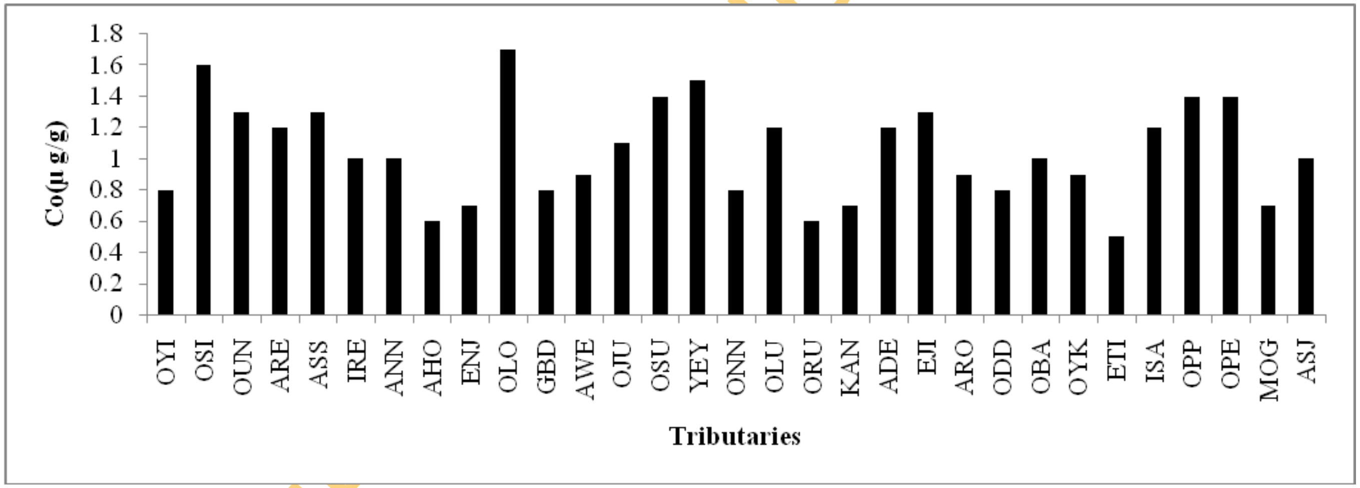

Figure 4.44: Spatial variation of Co in plant

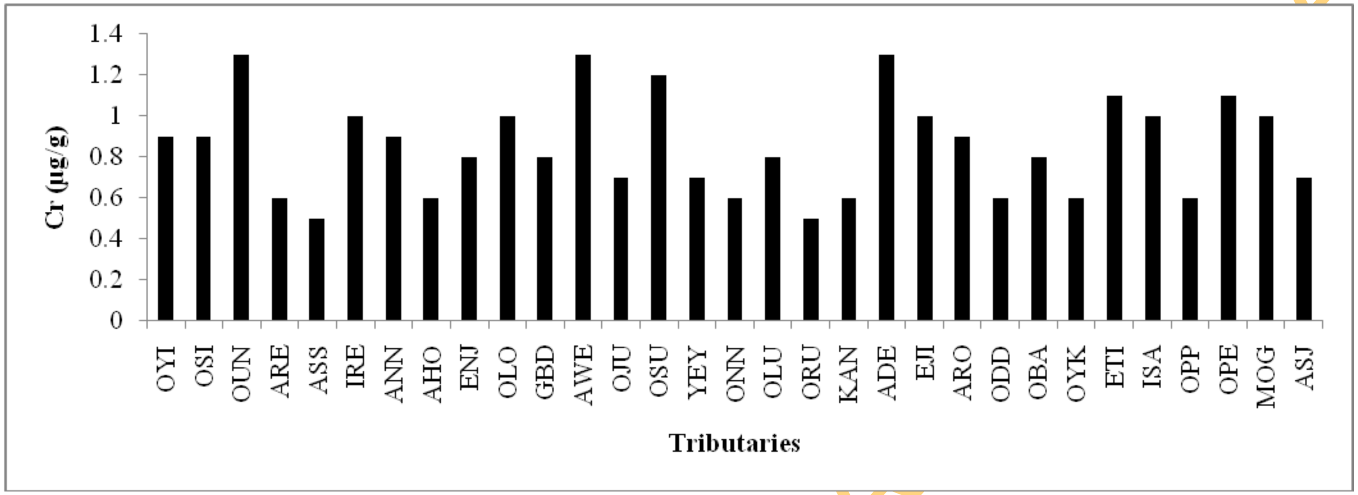

Figure 4.45: Spatial variation of Cr in plant

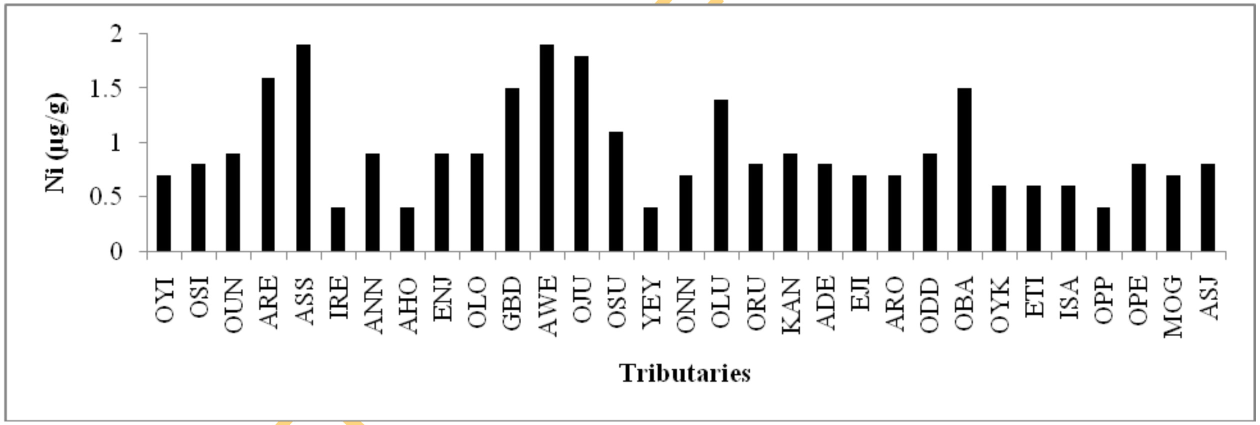

Figure 4.46: Spatial variation of Ni in plant

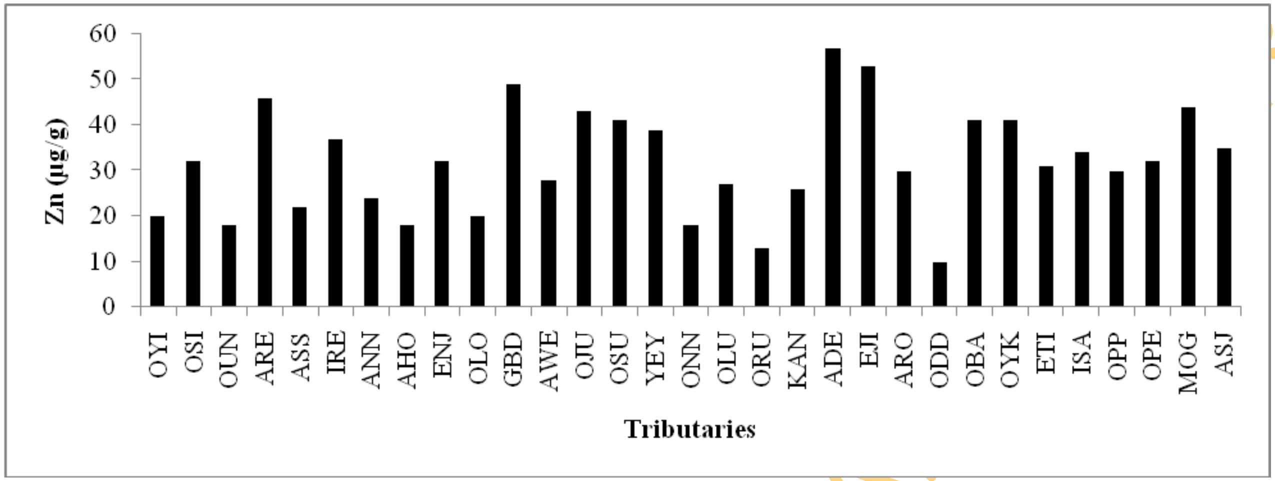

Figure 4.47: Spatial variation of Zn in plant

Table 4.22: Seasonal variation of heavy metals level in plants (µg/g)

Parameters	Dry Season	Wet Season
Pb	0.77±0.73	1.12±1.30
Cu	1.69±4.21	1.16±2.03
Cd	0.53±0.63	0.38±0.52
Co	0.57±0.63	1.56±2.07
Cr	0.66±0.94	1.07±1.40
Ni	1.70±11.8	0.82±1.54
Zn	55.9±81.4	7.82±10.1

Heavy metals that are higher during wet seasons

Lead, cobalt and chromium were observed to be higher in the wet seasons. When it rains, contaminants are carried into rivers and get absorbed by sediment. The concentrations of these metals absorbed by plant in the wet seasons implies that runoff water from industries and agricultural fields contained these metals which get into the river sediment and it was absorbed by plants. Rain water can react with fumes containing these metals from industries and get deposited on leaves of plants.

Paired t-test shows statistical significant differences between dry and wet seasons means values of all the metals. This signifies that the metals probably originated from diffuse point sources such as rainfall and anthropogenic activities such as agriculture, industrialization and municipal wastewater discharge.

4.27 CORRELATION OF HEAVY METAL LEVELS IN PLANTS

Table 4.23 illustrates Pearson correlation matrix obtained for heavy metals in plant. A medium positive correlation was obtained for the following pairs of heavy metals: Zn/Cu ($r = 0.518$), Cd/Pb ($r = 0.375$), Cr/Co ($r = 0.339$), Co/Cd (0.264), Cu/Cd ($r = 0.244$) and Zn/Cd ($r = 0.206$). All these positive correlations signify that the association among these pairs is linear but very weak. Negative correlations were however obtained between Zn/Co ($r = - 0.074$), Zn/Cr ($r = - 0.128$) and Ni/Cr ($r = - 0.009$).

4.28 PRINCIPAL COMPONENT ANALYSIS OF HEAVY METALS IN PLANTS

Figure 4.48 shows the principal component analysis model of heavy metals in plants. The first principal eigenvalues captures 75.6% of the total variance which was due to the metals Cd, Co, Cr, Pb and Cu revealing a kind of correlation between each other and from the same source. The second principal eigenvalues captures 15.2% of the total variance for Ni and the third principal eigenvalues captures 9.21% of the total variance for Zn. However, Cu, Zn and Ni did not show any clustering meaning that the source of these metals as pollutant might be from diffuse sources.

Table 4.23: Pearson correlation of heavy metals in plant

Parameter	Lead	Copper	Cadmium	Cobalt	Chromium	Nickel	Zinc
Lead	1.000						
Copper	0.159**	1.000					
Cadmium	0.375**	0.244**	1.000				
Cobalt	0.343**	0.128**	0.264**	1.000			
Chromium	0.156**	0.046	0.090*	0.339**	1.000		
Nickel	0.045	0.072*	0.102**	0.037	-0.009	1.000	
Zinc	0.034	0.518**	0.206**	-0.074*	- 0.128**	0.083*	1.000

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

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

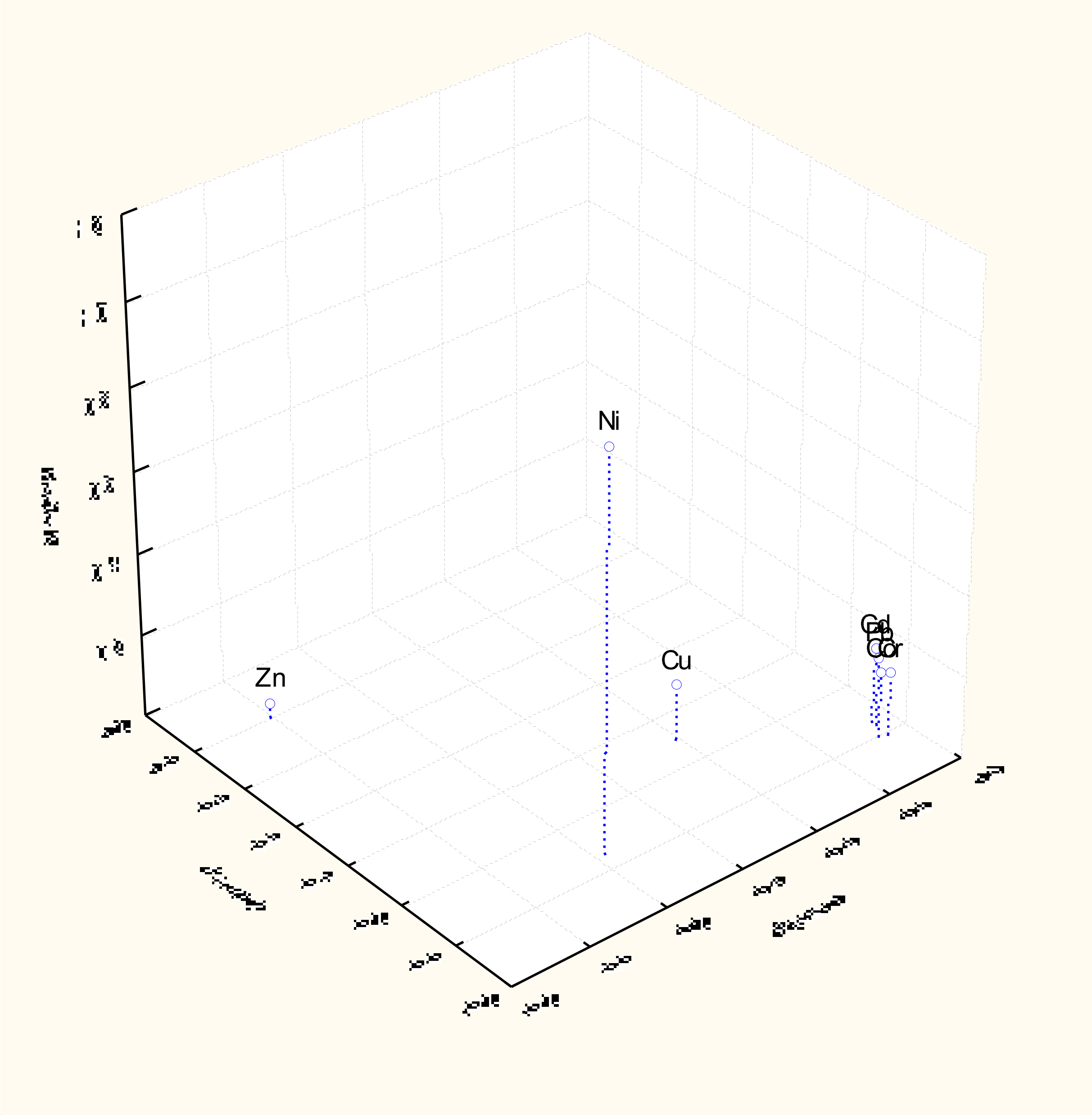

Figure 4.48: Principal Component Analyses of Heavy Metals in Plants

4.29 COMPARISON OF THE HEAVY METALS IN THIS STUDY WITH STUDIES ELSEWHERE

The comparison of heavy metals in plants in this study with levels in other places is as shown in Table 4.24. The level of lead in this study was found to be greater than levels reported in Lana River, Albani (0.01 – 0.26 µg/g) by Alma *et al.* (2010) an urban area; Msimbazi River, Tanzania (0.19 – 0.66 µg/g) by Bahamuka and Mubofu (1999); Calabar River, Nigeria (0.13 µg/g) by Edem *et al*. (2008) and in Karachi River, Pakistan (0.020±0.001 µg/g) by Syed and Muhammad (2008). The level of lead was however reported in some rivers to be greater than what obtained in this study. These include River Khetri, India (4.0 – 6.6 µg/g) by Maharia *et al.* (2010), a copper mine and in Gujarat River, India (1.9±0.4 µg/g) by Nirmal *et al*. (2009) an agricultural field.

The copper content of plants in study area was higher than levels reported in Calabar River, Nigeria (0.88µg/g) by Edem *et al.* (2009); in Khetri River, Pakistan (0.040±0.004 µg/g) by Syed and Mohammad (2008) an industrial area; in Sabah River, Malasia (1.2±1.6 µg/g) by Yap *et al.* (2009). The level of copper in plants were found to be higher than levels in this study in Tisza River, Hungary (64.0 µg/g) by Szilard *et al.* (2008) and Khetri, India (32 -77 µg/g) by Maharia *et al.* (2010).

The levels of cadmium in Khetri River, India (1.5 – 3.0 µg/g) by Maharia *et al.* (2010), Gujarat River, India (2.8±0.3 µg/g) by Nirmal *et al.* (2009) and Buriganga River, Bangladesh (0.56 – 1.40 µg/g) by Habibat *et al.* (2009) were reported to be higher than cadmium in plants of the study. All other studies showed lower cadmium levels compared to the study area.

Cobalt in plants in this study was higher than the level reported in Gujarat River, India (0.2 - 0.3 µg/g) by Nirmal *et al.* (2009) an agricultural field but lower to cobalt level in Tisza River, Hungary reported by Szilard *et al*. (2008).

Chromium in plants in this study was higher than the level reported by Edem *et al.* (2009) in Calabar River, Nigeria (0.08 µg/g) but lower compared to levels in Karachi River,

Table 4.24: Comparison of heavy metals in vegetation in this study with studies elsewhere (μg/g)

Country	River	Major activities in the area	Pb	Cu	Cd	Co	Cr	Ni	Zn	References
Nigeria	Osun		0.9±1.1	1.4±3.3	0.5±0.5	1.1±1.6	0.9±1.2	1.3±8.4	32±63	This study
Albani	Lana	Urban area	0.01-0.26	-	0.02-0.05	-	-	18.6-250	-	Alma *et al.* (2010)
Hungary	Tisza	Urban area	-	64.0		15.0	-	2.20	16.8	Szilard *et al.* (2008)
Nigeria	Lagos	Urban area	6.35-20.9	-	-	-	-	-	-	Adekunle *et al.* (2009)
Tanzania	Msimbazi	Urban area	0.19-0.66	0.25-1.60	0.01-0.06	-	-	-	1.48-4.93	Bahemuka and Mubofu (1999)
Bangladesh	Buriganga	Industrial area	-	-	0.56-1.40	-	-	1.27-5.37	-	Habib *et al.* (2009)
Nigeria	Calabar River	Urban area	0.13	0.88	-	-	0.08	-	0.03	Edem *et al.* (2009)
Pakistan	Karachi	Industrial Areas	0.020±0.001	0.040±0.004	-	-	1.11±0.90	-	0.02±0.02	Syed and Muhammad (2008)
India	Khetri	Copper mines	4.0 -6.6	32 - 77	1.5-3.0	-	2.6-5.9	3.1-9.0	24-50	Maharia *et al.* (2010)
Malasia	Sabah	Rice Field	ND	1.2±1.6	0.20±0.02	-	1.0±0.1	-	1.2±0.6	Yap *et al.* (2009)
India	Gujarat	Agricultural Field	1.9±0.4	1±55	2.8±0.3	0.2±0.3	-	0.4±0.2	3.1±0.8	Nirmal *et al.* (2009)

ND- not detected

Pakistan by Syed and Muhammad (2008); in Khetri River, India by Maharia *et al.* (2010) a copper mine; and Sabah River, Malasia as reported by Yap *et al.* (2009).

The level of nickel as reported in Lana River, Albani by Alma *et al.* (2010); Tisza River, Hungary by Szilard *et al.* (2008), an urban area and in Khetri River, India by Maharia *et al.* (2010) were higher than level of heavy metals in plant in the study. Other studies showed lower nickel level in plants.

Zinc in the study was higher than the levels reported in Tisza River, Hungary (16.8 µg/g) by Szilard *et al.* (2008); Msimbazi River, Tanzania (1.48 – 4.93 µg/g) by Bahamuka and Mubofu (1999); in Calabar River, Nigeria (0.03 µg/g) by Edem *et al.* (2009); Karachi River, Pakistan (0.02±0.02 µg/g) reported by Syed and Muhammad (2008); in Sabah River, Malasia (1.2±0.6 µg/g) by Yap *et al.* (2009) and Gujarat River, India (3.1±0.8 µg/g) by Nirmal *et al.* (2009).

The levels of these metals in plants varied as a result of environmental and the activities carried out along the bank of each river.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 SUMMARY AND CONCLUSION

As the world is ushered into the modern era of civilization, water and its management will continue to be a major issue, which will definitely have profound impact on our lives and that of our planet Earth than ever before. Indeed water is life. Everyday water systems all over the world receive polluting runoffs of industrial processes, fertilizers, pesticides, sewage, and mining drainage. River Osun flows through Osun State along with several tributaries and some man-made canals. Along this channel, rapid industrialization is taking place day by day and so this most peaceful area is changing in industries and urbanization. Most drains of these industries carry effluents from factories and also from adjacent residential colonies with their sewage which is finally discharged into River Osun and its tributaries. The study was carried out to evaluate the impact of industrial, agricultural and urbanisational activities on River Osun by studying the physicochemical properties of surface water, sediments and vegetations for twenty four months. Water quality characteristics, which include physicochemical parameters and seven heavy metals were analysed in the thirty one tributaries and control area. Sediment were analysed for organic carbon, sediment mechanical properties, cation exchange capacities and seven heavy metals in the thirty one tributaries and control area. Seven heavy metals were analysed in 26 species of plants in thirty one tributaries of Osun River so as to capture the main point of river and its tributaries of the study area and in the control area. The investigations carried out have yielded the following conclusions:

The overall mean concentrations obtained for surface water parameters indicate levels that were within the water quality guidelines with the exception of turbidity. However, some of the tributaries showed concentrations higher than the water quality guidelines. This was due to discharge of waste entering the river and its tributaries from homes and industries. The result revealed that this discharge could pose significant health and environmental risk to those who rely on River Osun as their source of domestic water without treatment. The tributaries most grossly affected include Adeti, Moginmogin, Kankere, Ope, and Awesin. Those pollutants most prominent include turbidity, nitrate, phosphate, chloride, total suspended solids and ammonia. A look at these rivers physically shows that the rivers are not healthy.

Some locations were found to contain higher sediment heavy metal levels in comparison with sediment quality guidelines. Tributaries such as Adeti, Etioni, Ahoyaya, Asejire, Moginmogin and Ope, and Enja were mostly affected.

Seasonally, River Osun shows more significant pollution during the dry seasons for most of the parameters studied, due to low flow rates and volumes of most of the rivers which helps to increase the concentration of contaminants.

Modelling of the data obtained for surface water and sediment predicted higher levels of some parameters by 2018. These include parameters such as electrical conductivity, chloride, nitrate, phosphate and biochemical oxygen demand in surface water and zinc in sediment.

5.2 RECOMMENDATION

- Regular monitoring of the water and sediment qualities of the Osun River should be carried out.
- Appropriate regulatory and enforcement agencies should ensure that effluents are properly treated before discharge into the Osun River.
- Government should inform the populace around the Osun River channel of the non-potability of the raw water.

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Appendix 1: Concentrations of Electrical conductivity (µS/cm) in surface water for all locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	58.5	47.0	47.2	45.5	44.0	72.0	60.0	53.0	58.5	110	136	126
OSI	173	124	120	136	198	129	139	130	97.5	212	331	366
OUN	99.8	43.3	58.7	68.8	153	90.0	87.0	58.0	55.8	121	178	176
ARE	158	91.0	146	250	229	231	112	94.7	100.0	490	546	302
ASS	159	78.0	111	168	302	174	287	141	90.0	347	465	589
IRE	43.0	40.7	67.6	159	273	118	37.7	31.3	43.7	239	395	186
ANN	108	98.2	101	103	107	108	100	91.0	83.0	200	215	217
AHO	109	73.0	96.0	320	*	345	62.7	75.7	72.0	515	1410	442
ENJ	75.0	48.0	52.6	63.3	*	89.0	72.0	49.0	54.0	163	202	134
OLO	61.0	43.3	43.4	53.7	219	112	67.7	63.0	42.0	52.0	*	126
GBD	108	100	94.3	90.0	339	163	99.8	89.8	91.0	254	344	299
AWE	205	100	107	163	*	214	267	174	118	441	*	636
OJU	97.3	79.7	72.4	77.3	85.3	84.5	149	91.3	70.3	176	176	194
OSU	104	95.0	94.6	92.0	115	150	113	98.7	96.0	115	377	221
YEY	96.0	97.0	96.0	108	136	144	98.0	87.0	97.0	112	338	260
ONN	102	73.8	52.1	78.0	105	113	101	51.3	71.0	92.0	269	249
OLU	33.0	26.0	23.8	37.0	29.7	31.7	28.0	19.7	21.0	24.7	126	66.1
ORU	44.0	66.0	61.1	*	*	*	36.0	62.0	60.0	*	*	*
KAN	154	154	143	165	215	159	153	149	162	185	400	342
ADE	1400	1360	1200	1590	*	1430	1030	484	1240	1680	4740	3160
EJI	90.5	91.5	83.6	103	149	136	130	73.0	87.5	122	348	310
ARO	98.0	98.0	88.0	164	*	371	139	81.5	98.5	*	*	*
ODD	77.5	72.0	58.0	61.0	78.0	68.5	74.0	82.5	64.5	59.5	156	141
OBB	88.3	77.8	87.8	172	228	250	88.8	74.5	105	185	546	400
OYK	46.0	47.5	36.0	39.5	47.5	47.0	45.0	41.0	37.5	34.5	110.0	99.1
ETI	74.7	72.7	60.2	78.7	99.3	81.0	70.0	71.0	69.3	76.7	236	188
ISA	147	122	120	163	357	213	11.0	124	124	163	556	347
OPP	171	12.0	113	144	*	129	114	116	125	145	396	348
OPE	182	153	160	619	*	301	133	118	166	599	*	443
MOG	421	261	366	249	*	86.9	620	304	365	1440	*	1150
ASJ	134	138	97.8	117	133	137	121	91	113	275	295	348

* = No water found

Appendix 2: pH in surface water for all locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	8.3	7.9	6.5	7.5	7.5	7.1	7.7	7.9	7.2	7.7	7.5	6.4
OSI	8.0	7.7	7.0	7.2	7.4	7.1	7.4	7.9	6.5	7.0	7.1	6.5
OUN	7.9	8.0	7.7	6.8	7.1	7.0	6.9	7.8	6.4	6.7	7.2	7.0
ARE	8.1	7.5	7.3	7.2	7.3	7.2	7.0	7.8	7.4	9.3	8.9	6.9
ASS	8.0	7.7	7.3	7.8	7.8	7.2	7.9	8.1	7.4	8	8	7.7
IRE	8.0	7.4	6.8	7.2	7.6	7.1	7.0	8.0	7.5	7.4	7.5	7.2
ANN	8.0	8.3	6.8	7.1	7.2	7.3	7.9	7.9	6.4	7.1	7.5	7.5
AHO	8.0	7.4	7.5	7.7	*	7.1	6.9	7.9	7.5	7.7	7.4	7.2
ENJ	7.9	7.7	0.9	6.6	*	7.1	6.9	7.9	7.1	7.0	6.8	6.6
OLO	8.0	8.2	7.5	7.2	7.0	6.9	7.2	7.1	8.6	7.7	*	6.8
GBD	8.0	7.5	6.9	7.8	7.6	7.4	7.9	7.8	8.1	7.9	7.1	7.5
AWE	8.2	7.5	7.7	7.5	*	7.2	7.9	7.8	7.5	8.4	*	7.1
OJU	8.4	7.5	7.5	7.7	7.2	7.2	7.9	7.9	7.6	8.0	7.3	7.4
OSU	8.3	8.1	8.4	7.1	7.2	7.2	7.6	7.6	8.4	7.6	8.0	7.7
YEY	8.1	8.3	7.7	7.0	7.0	7.0	7.4	7.1	7.8	8.1	7.4	6.3
ONN	8.2	8.4	7.5	7.3	7.6	7.4	8.5	6.7	7.6	8.1	7.6	7.1
OLU	8.3	7.9	7.8	7.7	7.0	7.2	7.4	7.5	7.5	8.0	7.6	6.2
ORU	8.1	8.0	8.6	*	*	*	7.6	7.9	7.3	*	*	*
KAN	8.1	8.1	8.6	7.0	7.1	7.0	7.3	7.7	7.1	7.0	7.1	7.3
ADE	8.2	8.4	7.7	7.6	*	7.9	7.9	7.6	7.4	8.3	7.4	7.6
EJI	8.2	8.2	8.4	7.1	7.4	7.1	7.2	7.9	7.5	7.4	7.7	7.5
ARO	8.3	8.0	8.6	7.5	*	7.2	7.3	7.8	7.3	*	*	*
ODD	8.2	8.1	8.7	7.2	7.1	6.9	7.4	7.8	7.0	7.4	6.6	7.7
OBB	8.3	8.1	8.7	7.4	7.6	7.1	7.7	7.7	7.6	7.4	7.2	7.3
OYK	8.1	8.2	7.7	7.6	7.0	7.2	7.4	7.3	7.5	7.5	7.4	6.1
ETI	8.2	8.1	7.9	7.5	7.1	7.4	7.2	7.6	7.3	7.9	7.4	6.8
ISA	8.1	7.6	8.0	7.8	7.8	7.8	8.0	7.8	7.6	8.5	7.9	6.7
OPP	8.0	8.1	7.8	7.5	*	7.4	8.2	7.3	7.7	8.2	7.5	6.6
OPE	8.3	7.7	6.9	7.8	*	7.2	7.1	7.9	7.3	8.1	*	7.5
MOG	8.4	8.0	7.0	7.7	*	7.3	8.1	7.9	7.3	7.3	*	7.9
ASJ	8.3	8.0	6.8	7.8	7.4	7.2	7.4	7.9	7.5	7.9	7.8	7.8

* = No water found

Appendix 3: Concentrations of TS (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	260	169	620	460	511	237	404	97.0	235	261	412	441
OSI	370	195	165	650	799	503	955	410	710	810	283	231
OUN	205	225	441	931	718	824	202	456	260	430	360	428
ARE	307	692	168	739	1640	349	404	323	405	727	601	381
ASS	320	302	695	361	596	375	363	410	370	550	420	670
IRE	647	589	139	659	1270	476	337	240	320	534	513	521
ANN	323	462	326	664	883	808	335	263	420	497	410	428
AHO	287	359	213	127	*	1550	517	239	239	919	880	1070
ENJ	333	638	72.0	973	*	258	270	300	207	263	248	313
OLO	80	458	367	840	1330	415	269	113	299	401	*	473
GBD	225	333	788	880	1400	756	553	585	601	531	530	730
AWE	273	598	1140	867	*	673	603	507	270	1010	*	1030
OJU	60.0	200	773	1200	411	943	404	273	413	466	440	303
OSU	207	700	568	847	635	1350	471	171	216	433	579	531
YEY	143	515	88.0	229	747	505	303	130	388	180	244	250
ONN	170	608	197	656	715	554	253	271	233	364	331	410
OLU	86.0	156	134	541	461	723	335	101	306	263	206	419
ORU	108	640	531	*	*	*	202	84.0	140	*	*	*
KAN	410	643	500	712	470	909	202	295	990	128	502	691
ADE	1200	1610	1000	1520	*	2340	6450	480	873	1180	3040	2340
EJI	105	236	561	517	390	707	405	102	305	349	315	950
ARO	330	920	220	530	*	505	304	182	350	*	*	*
ODD	91.0	651	631	256	1370	303	303	139	280	395	590	311
OBB	190	326	521	1020	623	657	253	200	390	394	592	755
OYK	99.0	130	291	380	630	318	303	129	250	395	181	310
ETI	163	240	579	367	720	538	202	187	353	560	413	581
ISA	208	969	421	980	946	845	253	541	392	566	739	491
OPP	360	364	372	1310	*	606	606	406	234	171	330	300
OPE	427	453	741	1750	*	943	405	161	323	893	*	1130
MOG	353	233	437	937	*	1040	606	161	323	1830	*	1170
ASJ	207	1380	507	899	473	648	302	353	393	421	646	500

* = No water found

Appendix 4: Concentrations of TDS (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	29.0	23.0	23.5	22.0	21.5	355	30.5	26.5	29.0	71.2	68.9	63.5
OSI	86.0	61.5	59.0	67.5	98.5	64.5	68.5	63.0	47.0	138	166	182
OUN	49.3	21.0	28.9	34.5	76.5	44.8	43.3	28.8	27.8	78.1	95.0	87.0
ARE	81.0	45.3	72.7	126	131	115	55.7	46.7	50.0	329	276	150
ASS	80.0	39.5	53.5	9.65	151	84.5	143	69.5	25.3	227	238	292
IRE	21.3	20.0	33.7	780	136	59.0	18.7	16.0	21.7	153	202	92.6
ANN	54.2	48.8	50.5	51.0	53.3	53.8	50.0	45.0	41.3	130	109	107
AHO	54.3	34.7	48.0	160	*	172	30.7	38.3	35.7	347	718	220
ENJ	37.3	23.3	26.3	31.0	*	37.0	34.3	24.3	26.3	106	102	67.0
OLO	30.3	21.7	21.3	27.0	109	55.7	33.3	31.3	21.0	25.7	*	63.3
GBD	54.0	49.8	13.2	44.8	169	81.0	50.0	45.0	47.3	165	171	148
AWE	103	48.7	53.0	82.0	*	107	133	86.0	58.3	295	*	318
OJU	48.3	39.9	36.0	38.3	42.3	42.7	74.3	46.3	35.0	115	85.1	96.7
OSU	51.7	47.0	47.0	46.0	57.0	74.7	56.3	49.0	49.0	57.3	190	111
YEY	47.0	48.0	47.5	53.5	68.0	71.5	49.0	43.0	47.5	56.0	170	131
ONN	51.0	35.3	26.0	39.0	52.3	56.3	50.3	25	35.3	45.8	136	126
OLU	16.0	73.0	11.3	18.7	14.3	15.7	13.7	9.67	11.0	12.3	64.6	32.7
ORU	21.5	33.0	30.5	*	*	*	17.5	30.5	30.0	*	*	*
KAN	77.0	76.0	70.5	81.0	147	79.5	76.0	74.0	81.0	92.5	199	172
ADE	700	679	595	793	*	715	512	242	618	839	2500	1630
EJI	45.0	45.5	41.5	51.0	74.0	61.0	64.5	36.5	44.0	61.0	174	156
ARO	48.5	49.0	44.0	79.0	*	186	70.0	40.0	49.0	*	*	*
ODD	38.5	36.0	29.0	30.5	38.5	34	36.5	41.0	32.5	29.5	79.4	71.3
OBB	44.0	39.0	43.8	87.3	113	125	44.0	36.8	52.0	92.0	273	195
OYK	23.0	24.0	17.5	19.0	23.5	23	22.5	20.0	19.0	17.0	56.4	50.4
ETI	37.0	36.3	30.0	39.0	49.3	40.3	34.7	35.0	34.4	38.3	116	96.3
ISA	72.8	60.5	60.0	81.0	178	107	55.5	61.3	61.8	80.8	285	17.7
OPP	85.5	63.5	57.0	71.5	*	63.5	55	57.5	62.0	71.5	200	175
OPE	90.7	76.0	79.7	306	*	150	65.7	59.0	83.0	407	*	219
MOG	210	130	180	124	*	434	310	59.0	83.0	1000	*	575
ASJ	67.0	68.3	49.0	58.0	66.3	68.0	60.7	45.3	56.3	186	142	176

* = No water found

Appendix 5: Concentrations of TSS (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	231	146	599	438	490	202	374	71.0	206	110	344	378
OSI	284	134	106	583	701	439	887	347	663	673	117	49.0
OUN	156	204	412	897	641	779	159	427	232	352	265	341
ARE	226	648	613	95.0	910	233	348	277	356	398	325	230
ASS	240	263	642	352	446	291	220	341	345	324	183	379
IRE	626	551	106	580	1130	417	318	224	298	381	311	428
ANN	269	414	275	613	832	754	285	218	379	367	301	321
AHO	232	325	165	1110	*	1380	486	201	203	573	162	847
ENJ	296	614	45.0	943	*	221	236	276	181	157	146	246
OLO	50.0	436	346	812	1223	359	236	81.0	278	375	*	410
GBD	171	288	740	836	1230	675	504	539	554	366	359	581
AWE	171	549	1090	785	*	567	470	421	212	719	*	716
OJU	11.7	160	736	1160	369	900	330	227	378	351	355	207
OSU	155	652	520	800	578	1270	415	122	167	375	359	421
YEY	96.0	467	40.0	176	678	434	254	87.0	341	124	74.0	119
ONN	106	573	171	617	663	497	202	246	197	319	195	284
OLU	70.0	143	123	522	449	707	321	92.0	295	251	141	387
ORU	86.0	609	501	*	*	*	185	53.0	110	*	*	*
KAN	333	567	430	631	323	830	126	221	909	35.5	303	520
ADE	500	929	405	728	*	1630	5940	238	255	342	531	717
EJI	60.0	191	520	466	316	647	341	66.0	261	288	141	795
ARO	282	871	176	451	*	320	234	142	301	*	*	*
ODD	53.0	615	602	226	1325	269	266	98.0	248	366	511	240
OBB	146	287	477	932	510	532	208	163	338	302	319	560
OYK	76.0	106	274	361	607	295	281	109	231	378	125	260
ETI	126	202	549	328	670	498	167	152	319	522	297	485
ISA	133	909	361	900	767	739	197	479	330	486	454	316
OPP	275	301	315	1240	*	543	551	349	172	99	131	125
OPE	356	377	661	1440	*	793	339	102	240	488	*	907
MOG	188	103	258	814	*	608	296	102	240	823	*	592
ASJ	140	1300	458	841	406	580	241	308	337	235	502	324

* = No water found

Appendix 6: Turbidity (FTU) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	31.0	36.0	13.3	9.40	12.3	30.0	38.0	100	25.3	0.70	19.0	12.4
OSI	28.3	12.4	8.80	18.00	21.0	44.0	193	25.0	11.8	3.70	42.0	43.0
OUN	51.1	23.0	14.9	32.00	79.0	57.0	72.0	50.0	23.5	3.90	92.0	140
ARE	16.8	37.3	12.9	21.4	27.0	10.8	108	13.0	107	3.82	8.23	81.0
ASS	3.80	30.6	12.7	16.0	10.6	15.0	145	18.3	20.6	0.40	20.0	76.0
IRE	110	15.0	14.5	89.0	109	31.0	38.0	22.5	13.7	2.30	28.0	45.0
ANN	9.60	21.0	14.8	12.5	14.2	17.2	21.0	20.0	13.5	1.30	29.0	8.50
AHO	41.0	20.8	8.63	50.6	*	53.0	114	26.9	27.1	1.60	45.0	236
ENJ	43.0	29.4	13.1	76.0	*	82.0	157	45.9	24.7	5.40	259	59.2
OLO	14.9	50.0	16.1	11.0	40.0	53.0	53.0	41.0	24.1	2.40	*	26.7
GBD	19.0	47.0	13.2	149	27.0	24.0	88.0	76.0	14.4	1.80	20.0	34.1
AWE	38.0	25.0	20.0	65.0	*	262	191	98.0	14.0	9.90	*	20.8
OJU	11.8	46.0	15.1	19.0	16.1	7.60	122	52.0	16.3	1.50	11.8	11.6
OSU	14.5	65.0	19.0	20.2	8.60	17.0	63.0	42.3	18.0	0.80	6.50	24.5
YEY	4.40	24.0	15.6	5.00	15.3	15.6	40.0	59.0	18.0	1.60	17.7	11.2
ONN	14.7	128	17.0	8.8	35.0	36.0	38.0	76.0	37.1	0.90	11.0	21.0
OLU	6.30	13.5	9.00	17.0	9.60	17.0	43.0	33.7	19.2	0.80	17.5	10.0
ORU	22.0	156	11.8	*	*	*	149	65.9	26.8	*	*	*
KAN	17.4	24.0	10.0	35.0	70.0	21.5	56.5	18.0	20.6	5.60	17.4	24.0
ADE	29.0	28.0	47.0	44.0	*	18.4	50.0	39.0	11.2	5.00	124	9.62
EJI	25.0	18.0	13.0	11.5	19.0	9.70	34.0	31.5	4.40	0.71	8.80	10.0
ARO	22.4	36.0	10.9	130	*	57.7	10.9	31.0	13.8	*	*	*
ODD	19.4	66.0	13.3	21	45.0	9.70	38.0	50.0	25.0	1.50	48.0	45.0
OBB	46.0	64.0	21.5	12.5	21.0	25.0	75.0	53.0	48.0	0.80	13.4	22.5
OYK	5.60	14.0	17.0	7.40	11.8	12.7	47.0	56.0	19.1	1.40	17.4	22.0
ETI	17.1	20.2	11.0	12.00	20.0	34.9	56.0	33.9	21.4	1.90	12.2	20.4
ISA	14.6	54.0	18.1	7.70	23.0	17.4	51.0	63.0	50.6	1.00	16.0	17.7
OPP	12.6	32.0	20.0	8.50	*	36.8	132	49.0	63.0	5.10	12.0	16.5
OPE	6.70	93.0	12.0	138	*	26.1	63.5	57.0	10.8	2.40	*	6.70
MOG	67.0	56.0	14.3	10.0	*	12.3	25.0	57.0	10.8	1.60	*	5.90
ASJ	20.2	62.0	14.0	24.0	17.8	14.5	92.0	37.0	13.9	0.40	3.50	9.80

* = No water found

Appendix 7: Alkalinity (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	55.3	39.8	42.0	39.9	42.4	44.9	44.9	36.0	22.8	35.0	43.0	47.0
OSI	120	73.0	81.8	79.8	112	62.0	83.3	49.0	54.0	77.8	67.0	106
OUN	74.0	46.4	45.3	42.0	80.5	91.0	50.2	38.0	36.2	51.0	64.0	80.0
ARE	104	54.6	78.1	150	109	106	52.7	44.0	59.0	120	114	81.0
ASS	104	48.7	61.9	84.6	121	62.0	109	49.0	45.6	107	98.0	133
IRE	66.3	38.0	22.1	185	147	55.6	25.6	21.0	32.0	77.0	93.0	56.3
ANN	87.0	72.2	66.3	59.0	72.3	68.7	60.5	51.0	43.0	61.0	58.0	63.9
AHO	84.0	44.2	48.6	143	*	145	35.6	33.0	52.0	121	372	120
ENJ	66.3	38.3	39.8	39.6	*	54.8	34.2	25.6	38.4	65.0	77.8	54.0
OLO	30.0	59.0	32.4	38.3	114	62.0	47.0	47.0	46.5	45.6	*	43.8
GBD	53.6	66.3	63.0	62.6	132	69.5	52.0	30.0	58.0	76.5	105	68.4
AWE	140	71.0	63.4	77.2	*	101	122	76.0	58.0	131	*	16.0
OJU	96.0	59.0	50.1	48.0	56.5	54.1	64.1	44.9	43.8	62.6	53.6	63.0
OSU	51.6	53.0	59.0	60.0	59.3	65.5	44.0	37.0	69.7	123	92.0	61.7
YEY	71.0	115	67.4	67.1	70.0	46.0	58.0	49.2	86.0	71.1	67.0	80.5
ONN	58.0	97.3	36.5	49.6	55.0	56.1	62.0	34.7	49.0	57.0	79.0	77.1
OLU	27.3	24.0	18.0	20.7	32.5	16.0	35.6	17.1	50.0	30.4	25.0	35.8
ORU	36.5	68.6	50.9	*	*	*	32.1	28.0	102	*	*	*
KAN	56.4	55.3	68.5	55.0	113	68.4	44.9	49.2	72.0	123	99.0	63.1
ADE	621	1220	483	650	*	585	423	165	569	780	1060	668
EJI	57.5	66.4	59.7	65.2	84.8	89.8	76.9	34.0	77.0	92.5	72.0	92.6
ARO	53.1	142	61.9	102	*	231	109	47.0	45.6	*	*	*
ODD	55.3	53.1	50.9	50.6	70.0	59.9	56.0	49.2	70.0	61.7	52.0	60.0
OBB	49.2	39.0	51.0	104	126	114	58.0	41.7	75.0	102	152	71.8
OYK	39.8	50.9	31.0	23.3	38.1	26.7	41.0	17.1	42.9	26.9	43.0	52.3
ETI	44.2	79.6	56.0	45.0	54.0	31.3	48.0	38.5	73.0	65.0	51.0	59.9
ISA	71.9	75.2	80.2	95.3	194	87.6	63.0	56.1	89.0	103	169	91.2
OPP	97.3	138	69.6	83.3	*	59.0	73.0	36.0	86.0	99.3	116	106
OPE	96.1	78.1	97.0	392	*	171	66.9	57.0	136	176	*	117
MOG	178	103	159	93.0	*	366	269	57.0	136	294	*	230
ASJ	68.5	72.0	61.9	54.1	53.7	78.3	83.0	26.0	71.5	44.0	81.4	73.3

* = No water found

Appendix 8: Hardness (mg/L) of surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	21.2	22.7	23.6	326	210	122	75.6	27.9	23.3	22.3	117	150
OSI	47.8	45.3	40.6	448	291	169	99.0	58.1	51.1	25.8	170	176
OUN	32.8	22.7	17.0	361	186	136	87.2	32.0	68.0	21.0	120	131
ARE	46.0	33.1	42.2	497	287	174	59.0	44.2	45.0	34.4	156	149
ASS	37.6	33.4	36.0	442	361	145	163	51.1	40.7	29.3	153	176
IRE	13.0	17.9	17.6	396	302	151	73.6	26.3	24.4	21.5	156	125
ANN	33.5	41.4	38.0	398	229	166	116	44.2	57.0	26.6	145	184
AHO	32.2	23.3	25.2	462	*	209	105	34.1	28.6	28.9	391	192
ENJ	31.0	14.1	23.0	365	*	108	89.0	36.0	24.0	21.1	129	119
OLO	20.1	16.9	21.4	85.0	358	147	97.0	40.0	26.0	26.5	*	105
GBD	30.6	39.3	32.0	295	235	186	105	43.0	47.5	27.5	179	122
AWE	54.4	38.1	26.0	407	*	175	128	72.9	53.0	32.0	*	207
OJU	32.8	32.8	29.0	279	147	143	108	43.0	35.0	21.9	129	145
OSU	25.6	41.4	38.4	101	104	167	124	44.5	58.0	29.7	176	121
YEY	29.2	36.3	47.2	114	170	157	117	46.5	37.0	57.5	153	111
ONN	42.4	32.6	22.2	92.0	115	162	62.0	34.7	49.0	57.0	79.0	77.1
OLU	22.0	30.0	27.7	88.0	76.0	95.0	85.0	20.9	19.4	23.4	113	105
ORU	14.1	31.7	26.4	*	*	*	81.0	30.2	38.1	*	*	*
KAN	37.2	47.7	46.3	149	214	174	117	62.2	92.0	37.5	173	129
ADE	305	317	285	860	*	535	364	155	471	106	516	492
EJI	16.1	31.2	35.9	102	230	169	134	36.6	45.1	24.6	179	129
ARO	28.0	38.1	40.6	119	*	378	128	39.0	55.1	*	*	*
ODD	21.3	23.7	25.5	74.5	95.0	169	93.0	23.7	31.1	24.6	153	97
OBB	25.8	25.8	32.6	137	280	195	96.0	36.0	67.0	32.9	214	133
OYK	21.6	20.0	24.0	62.9	79.2	11.0	87.2	29.7	314	21.1	117	132
ETI	22.0	24.9	30.8	112	98.0	114	109	37.2	32.5	43.3	113	107
ISA	43.2	47.6	47.0	141	482	181	102	47.0	59	70.0	200	131
OPP	58.1	47.3	42.5	154	*	163	117	54.6	58.1	85.6	153	152
OPE	54.8	57.8	52.0	660	*	266	147	60.4	209	41.4	*	155
MOG	120	79.4	103	166	*	457	329	60.4	204	61.0	*	501
ASJ	36.0	47.0	30.0	79.0	151	178	120	40.3	57.8	28.1	168	133

* = No water found

Appendix 9: Temperature (^{o}C) of surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	24.3	23.3	22.0	20.3	22.9	24.5	22.7	23.6	24.7	16.5	26.3	24.4
OSI	26.8	24.6	22.0	22.5	24.2	25.4	23.4	24.9	25.5	18.4	27.3	24.0
OUN	24.3	23.6	21.1	20.4	23.8	24.8	23.4	23	24.6	17.8	24.9	24.0
ARE	25.9	25.3	23.4	26.6	24.8	28.3	24.1	25.5	26.7	26.2	31.1	23.9
ASS	26.3	25.5	22.1	24.1	23.8	27.2	23.4	24.6	25.3	21.2	27.1	23.9
IRE	26.0	24.6	24.7	26.0	28.6	27.8	25	25.4	28.1	25.3	29.6	26.9
ANN	26.3	26.3	23.8	24.3	26.9	28.3	26.2	26.8	27.5	20.3	27.4	28.2
AHO	25.9	25.6	24.0	29.6	*	30.8	24.3	25.1	26.8	23.7	31.5	26.7
ENJ	24.7	24.7	19.6	23.4	*	27	23.3	25.1	25.3	22.6	27.3	24.0
OLO	24.2	23.5	24.3	18.1	24.0	22.9	23.9	23.5	24.1	18.3	*	24.6
GBD	24.2	25.4	25.3	22.9	29.0	26.8	25.2	24.2	26.2	26.9	28.9	29.2
AWE	26.8	25.3	25.3	28.4	*	29.2	24.4	26.3	27.0	27.2	*	27.5
OJU	26.8	25.4	25.8	25.5	26.9	28.7	25.2	26.9	26.9	25.0	30.7	28.6
OSU	25.0	24.1	27.1	20.3	25.8	26.0	23.4	24.2	25.8	23.4	26.4	27.4
YEY	24.8	23.9	25.3	20.1	24.4	24.1	25.7	24.1	24.7	21.2	23.8	26.3
ONN	24.4	23.1	24.9	19.1	22.9	22.3	24.8	23.3	24.1	19.7	22.9	24.9
OLU	24.0	23.1	25.2	20.0	22.9	22.7	23.3	23.1	24.2	19.7	26.4	25.9
ORU	25.0	24.4	27.9	*	*	*	25.7	24.3	27.1	*	*	*
KAN	25.1	25.0	27.8	23.3	24.7	25.8	25.3	24.8	26.2	22.6	26.2	24.7
ADE	24.1	23.4	26.8	19.7	*	24.9	25.5	24.1	25.8	22.3	26.1	27.4
EJI	24.9	24.7	27.9	18.7	23.8	23.5	25.6	24.8	26.7	22.1	26.5	24.3
ARO	24.7	24.7	27.9	20.0	*	23.9	24.9	24.9	26.2	*	*	*
ODD	24.5	23.8	27.2	19.2	23.8	24.7	24.5	23.7	26.6	22.9	27.0	24.4
OBB	24.9	24.6	29.0	22.7	27.0	28.4	26.1	25.2	27.3	25.7	29.0	27.0
OYK	24.0	24.1	26.7	21.4	24.5	24.7	24.6	25.5	25.8	21.5	26.5	27.8
ETI	25.9	25.2	27.1	23.3	27.7	27.5	26.3	24.9	26.2	24.9	30.0	28.1
ISA	24.5	25.1	26.5	23.4	26.4	25.0	25.2	24.4	25.6	23.1	28.1	28.5
OPP	26.3	25.2	26.7	24.4	*	25.3	24.7	25.2	25.4	23.0	28.3	27.9
OPE	24.7	24.2	26.5	24.9	*	30.7	25.5	25	27.2	27.9	*	27.4
MOG	26.0	26.7	32.4	28.2	*	32.7	27.1	25.5	27.2	26.0	*	29.6
ASJ	26.6	28.6	32.0	25.3	29.2	32.7	27.2	26.2	32.7	23.9	32.8	27.9

* = No water found

Appendix 10: Concentrations of nitrate (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	3.70	0.03	2.10	0.60	0.80	1.20	1.60	2.40	2.10	1.80	1.80	1.70
OSI	4.00	0.10	0.90	0.80	1.20	0.80	2.20	2.20	1.90	2.00	2.70	2.60
OUN	3.90	0.40	3.30	0.70	2.10	1.00	4.40	2.30	2.00	1.70	2.40	2.20
ARE	3.80	0.80	2.60	0.90	0.70	0.70	3.00	2.10	2.50	2.20	2.40	2.40
ASS	3.60	0.70	1.60	0.80	6.40	0.40	9.90	2.30	2.20	2.70	2.30	3.50
IRE	3.90	0.20	0.60	0.70	1.50	0.70	1.60	1.80	1.70	2.00	1.80	2.10
ANN	2.90	0.30	1.50	2.20	1.10	0.90	3.70	2.20	1.90	2.20	2.00	2.10
AHO	3.20	1.00	3.00	0.70	*	1.10	1.40	2.20	2.60	2.10	2.80	3.20
ENJ	2.00	1.80	0.67	6.20	*	1.30	3.80	2.10	2.20	2.00	3.10	2.40
OLO	0.80	0.20	0.70	0.70	1.10	0.60	2.00	2.40	1.80	1.80	*	2.00
GBD	1.00	0.60	0.60	3.50	1.00	0.70	1.90	3.50	1.80	1.90	1.90	2.10
AWE	3.60	0.80	2.40	1.20	*	1.40	7.50	3.80	2.40	2.40	*	2.50
OJU	3.00	0.30	1.10	3.60	1.30	0.80	2.30	2.60	1.90	1.90	1.80	1.90
OSU	0.80	0.60	0.70	0.60	1.10	1.00	1.80	2.30	1.80	1.80	1.60	2.10
YEY	0.60	0.34	0.70	0.90	1.40	1.00	1.90	2.50	2.30	1.80	1.57	2.20
ONN	0.70	0.60	1.00	1.60	1.20	0.80	1.60	2.80	2.00	2.10	1.90	1.90
OLU	0.70	0.50	1.10	1.80	1.20	1.20	2.10	2.10	2.00	2.00	2.00	2.00
ORU	0.50	0.14	0.70	*	*	*	2.00	2.20	2.20	*	*	*
KAN	0.50	0.80	0.70	0.80	1.58	0.80	1.60	2.40	2.30	2.60	2.00	2.10
ADE	0.40	0.40	10.0	1.40	*	0.42	1.80	3.80	2.60	4.20	2.70	3.20
EJI	0.40	0.24	0.60	0.60	1.10	0.50	2.20	2.20	2.00	1.80	1.80	1.90
ARO	0.50	0.20	0.80	1.60	*	0.69	2.70	2.26	2.08	*	*	*
ODD	0.40	0.40	0.90	0.43	1.20	0.77	2.50	2.50	2.10	1.90	1.94	1.80
OBB	0.60	0.40	4.10	1.30	0.90	1.20	2.10	2.60	2.70	2.10	2.00	2.70
OYK	0.60	0.40	0.60	0.70	0.80	1.01	2.10	2.50	2.21	2.00	1.40	2.00
ETI	0.90	0.40	0.90	3.00	0.80	0.80	4.10	2.70	2.10	1.94	2.00	2.00
ISA	0.60	0.40	0.70	1.00	0.70	0.70	2.40	2.50	2.40	2.00	1.60	2.20
OPP	1.00	0.36	0.80	1.40	*	0.70	2.20	3.10	1.80	2.60	2.00	2.10
OPE	0.50	0.60	0.70	1.90	*	1.10	2.20	2.60	2.30	2.10	*	2.60
MOG	1.20	2.40	2.60	2.00	*	0.90	2.30	2.60	2.30	4.30	*	3.50
ASJ	0.90	1.60	1.30	0.80	1.40	0.70	1.70	2.20	1.80	1.60	1.80	2.20

* = No water found

Appendix 11: Concentrations of sulphate (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	24.6	23.4	29.0	17.5	25.0	52.7	78.9	60.9	18.2	11.9	9.80	10.1
OSI	20.5	25.4	23.7	29.1	33.6	55.9	100	14.8	2.30	24.1	17.8	26.6
OUN	38.0	43.0	31.2	37.7	84.0	64.0	63.6	48.5	26.3	24.3	53.0	91.0
ARE	19.4	35.0	28.4	45.0	40.7	44.4	78.0	14.0	21.1	35.6	6.10	68.5
ASS	16.6	27.4	29.6	27.9	37.5	50.0	107	14.8	17.5	15.5	10.7	56.0
IRE	16.0	26.9	57.9	44.0	69.0	62.0	56.0	15.2	9.80	43.0	41.0	14.9
ANN	12.6	20.0	25.6	19.8	22.6	29.7	68.0	14.0	10.3	12.5	25.0	6.20
AHO	19.5	25.1	37.4	36.5	*	42.3	104	20.3	21.0	2.60	33.0	101
ENJ	30.2	28.7	32.8	58.3	*	94.2	112	37.1	54.0	41.7	166	43.8
OLO	53.7	22.4	30.7	32.0	30.5	62.0	105	29.8	24.4	19.9	*	13.0
GBD	25.5	36.5	25.4	90.0	76.6	46.9	77.0	52.0	19.6	19.4	14.5	37.2
AWE	19.1	32.6	32.6	38.0	*	142	142	42.0	12.7	45.0	*	19.1
OJU	14.6	34.3	35.4	22.5	28.9	27.4	70.0	26.5	20.2	16.7	14.6	9.30
OSU	55.5	24.7	30.5	22.0	27.5	43.1	77.0	33.2	17.2	21.0	13.8	31.8
YEY	48.8	25.5	32.3	20.5	43.3	77.4	49.4	53.0	20.9	15.6	26.0	11.1
ONN	50.0	24.5	28.8	25.7	24.9	41.8	46.0	58.0	29.7	12.7	10.1	17.2
OLU	49.9	27.8	26.2	20.2	28.7	37.5	39.4	23.3	13.8	13.0	21.3	12.0
ORU	41.0	35.9	26.0	*	*	*	166	61.8	26.4	*	*	*
KAN	51.0	43.7	40.8	92.9	58.0	54.4	64.2	22.7	30.4	32.8	18.5	39.0
ADE	66.0	41.5	115	*	104	130	110	50.1	83.3	114	45.8	136
EJI	63.0	24.9	23.6	33.8	20.1	43.0	84.0	33.1	12.2	13.0	34.9	8.81
ARO	55.1	32.8	24.0	70.0	*	41.0	58.0	41.9	10.7	*	*	*
ODD	32.1	40.0	70.6	20.6	30.9	30.9	68.5	34.8	16.9	11.8	24.0	18.4
OBB	61.0	32.8	32.8	34.0	21.4	51.0	85.0	56.5	33.0	12.1	8.50	36.2
OYK	35.0	21.1	33.1	17.7	28.7	39.4	40.0	23.4	12.4	13.4	11.1	11.8
ETI	29.4	25.9	32.0	16.0	25.5	47.0	101	30.0	19.2	11.5	16.2	21.2
ISA	34.7	36.0	34.0	47.0	30.5	54.2	78.8	46.9	38.7	12.3	10.5	31.0
OPP	44.0	29.3	30.5	29.9	*	56.0	96.0	68.0	34.0	20.0	11.1	11.3
OPE	47.0	48.8	30.2	52.0	*	43.8	89.4	40.7	16.7	22.9	*	33.3
MOG	71.0	39.0	40.0	65.6	*	44.2	49.0	40.7	16.7	20.5	*	45.0
ASJ	26.3	34.9	33.9	53.7	51.0	32.1	70.0	41.0	13.8	129	32.0	42.0

* = No water found

Appendix 12: Concentrations of phosphate (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.01	0.01	0.03	0.02	0.02	0.09	0.14	0.15	0.20	0.03	0.03	0.10
OSI	0.02	0.01	0.03	0.10	0.14	0.20	0.32	0.12	0.20	0.10	0.04	0.20
OUN	0.04	0.01	0.1	0.10	0.20	0.20	0.20	0.20	0.10	0.09	0.08	0.27
ARE	0.02	0.01	0.04	0.20	0.20	0.13	0.10	0.10	0.40	0.10	0.04	0.30
ASS	0.02	0.02	0.10	0.11	0.22	0.11	0.60	0.11	0.22	0.06	0.06	0.52
IRE	0.02	0.01	0.04	0.30	0.40	0.11	0.10	0.15	0.10	0.05	0.10	0.14
ANN	0.01	0.02	0.04	0.10	0.04	0.10	0.10	0.09	0.10	0.10	0.07	0.10
AHO	0.05	0.01	0.10	0.30	*	0.90	0.20	0.13	0.10	0.06	1.03	0.80
ENJ	0.01	0.02	0.10	0.16	*	0.16	0.20	0.15	0.30	0.08	0.30	0.19
OLO	0.02	0.01	0.10	0.10	0.13	0.20	0.02	0.20	0.10	0.10	*	0.12
GBD	0.04	0.02	0.10	0.30	0.40	0.20	0.20	0.20	0.20	0.10	0.10	0.20
AWE	0.02	0.02	0.10	0.20	*	0.70	0.80	0.40	0.20	0.20	*	0.10
OJU	0.01	0.10	0.10	0.04	0.10	0.10	0.20	0.20	0.20	0.05	0.03	0.07
OSU	0.01	0.01	0.07	0.10	0.10	0.20	0.03	0.20	0.20	0.07	0.04	0.15
YEY	0.01	0.01	0.10	0.02	0.04	0.10	0.10	0.21	0.20	0.10	0.10	0.11
ONN	0.03	0.04	0.10	0.04	0.10	0.10	0.10	0.30	0.21	0.03	0.02	0.14
OLU	0.02	0.004	0.02	0.10	0.10	0.10	0.10	0.22	0.10	0.04	0.04	0.20
ORU	0.01	0.10	0.04	*	*	*	0.21	0.22	0.12	*	*	*
KAN	0.02	0.50	0.13	0.20	0.90	0.54	0.02	0.21	0.50	0.62	0.20	0.38
ADE	0.40	0.13	0.20	1.50	*	0.60	0.50	0.80	0.60	1.60	1.30	0.55
EJI	0.03	0.01	0.04	0.10	0.03	0.10	0.11	0.12	0.10	0.02	0.03	0.06
ARO	0.02	0.01	0.04	0.40	*	0.30	0.10	0.11	0.20	*	*	*
ODD	0.02	0.02	0.08	0.01	0.20	0.12	0.10	0.30	0.29	0.08	0.06	0.18
OBB	0.04	0.03	0.10	0.10	0.04	0.10	0.10	0.20	0.20	0.10	0.03	0.10
OYK	0.01	0.01	0.10	0.10	0.10	0.10	0.10	0.20	0.08	0.05	0.10	0.10
ETI	0.01	0.01	0.10	0.03	0.10	0.11	0.10	0.16	0.10	0.06	0.03	0.14
ISA	0.03	0.02	0.11	0.10	0.10	0.20	0.17	0.30	0.30	0.05	0.04	0.20
OPP	0.02	0.01	0.09	0.04	*	0.10	0.09	0.20	0.26	0.04	0.03	0.12
OPE	0.02	0.04	0.10	1.00	*	1.00	0.10	0.17	0.11	0.30	*	0.16
MOG	0.03	0.10	0.23	0.40	*	0.40	0.20	0.17	0.11	0.30	*	0.29
ASJ	0.01	0.04	0.04	0.10	0.10	0.10	0.10	0.51	0.18	0.04	0.02	0.10

* = No water found

Appendix 13: Concentrations of chloride (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	33.0	12.2	10.1	18.3	20.3	18.0	14.4	23.4	14.4	27.0	14.4	7.20
OSI	53.0	20.3	16.0	28.5	32.5	39.6	47.0	32.4	25.2	28.8	25.0	34.2
OUN	37.0	9.13	11.2	21.3	24.0	18.0	14.0	13.5	7.20	20.0	8.10	14.4
ARE	49.0	24.2	19.0	19.0	79.9	70.0	50.4	34.0	28.0	24.0	62.4	58.8
ASS	38.6	12.2	16.0	33.0	102	32.4	29.0	28.8	18.0	47.0	54.0	79.0
IRE	33.0	10.8	6.77	79.8	46.0	24.0	9.60	12.0	18.0	32.4	33.6	27.6
ANN	43.0	12.2	11.5	29.8	27.1	19.2	10.8	35.0	21.0	35.0	18	16.8
AHO	45.6	12.2	14.9	7.00	*	79.0	16.8	24.0	15.6	107	116	54.0
ENJ	60.0	10.8	13.5	28.0	*	22.0	24.0	34.0	14.4	25.0	25.2	20.4
OLO	35.2	10.8	10.8	21.6	38.0	34.8	34.0	19.0	20.4	40.8	*	29.0
GBD	28.5	20.3	11.2	32.0	82.0	47.0	43.2	36.0	3.00	29.7	27.0	66.0
AWE	92.0	27.1	13.6	65.0	*	67.0	60.0	49.2	29.0	46.8	*	82.3
OJU	46.0	21.6	13.5	20.3	27.1	12.0	36.0	28.8	22.0	28.0	18.0	23.0
OSU	16.2	17.6	13.5	22.0	25.7	43.2	43.2	38.4	26.0	48.0	46.0	33.6
YEY	20.3	20.3	10.1	28.0	20.3	36.0	32.4	29.0	29.0	48.6	8.50	32.0
ONN	28.0	22.4	12.2	18.3	20.0	40.5	38.0	31.0	32.0	80.0	25.2	40.0
OLU	31.1	16.2	8.00	21.7	18.9	30.0	28.8	14.4	19.2	49.2	43.2	33.6
ORU	16.2	8.12	8.12	*	*	*	32.4	25.2	18.0	*	*	*
KAN	44.7	52.8	20.3	44.7	56.8	65.0	68.0	36.0	43.0	84.6	50.4	78.5
ADE	633	598	474	736	*	594	408	162	546	812	985	682
EJI	16.2	12.2	10.2	10.2	32.5	28.8	43.2	32.4	21.6	59.0	18.0	25.0
ARO	20.3	16.2	8.12	31.0	*	39.6	50.0	29.0	29.0	*	*	*
ODD	8.12	12.2	6.10	6.10	33.0	18.0	18.0	40.0	14.4	31.0	5.40	14.4
OBB	19.3	26.0	10.1	42.0	51.0	70.0	59.0	23.4	34.2	70.0	70.0	106
OYK	12.2	16.2	8.00	16.2	18.3	18.0	36.0	41.0	21.6	31.0	25.0	32.0
ETI	17.6	21.7	9.50	13.5	28.0	54.0	28.8	24.0	216	29.0	34.8	40.8
ISA	22.0	20.3	11.2	23.4	77.0	79.0	52.2	47.0	67.0	54.0	36.0	65.0
OPP	24.0	16.2	12.2	20.3	*	43.2	50.4	36.0	40.0	38.0	32.0	41.4
OPE	32.5	42.0	25.7	95.0	*	41.0	43.0	38.0	28.8	95.0	*	84.0
MOG	137	57.0	91.0	71.7	*	149	223	38.0	28.8	260	*	204
ASJ	27.1	27.0	14.9	30.0	16.2	38.4	36.0	33.6	52.8	52.0	22.8	61.0

* = No water found

Appendix 14: Concentrations of ammonia (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	3.60	2.90	1.90	2.30	3.10	2.20	6.10	8.50	2.80	1.20	1.60	2.10
OSI	2.50	3.20	2.30	3.70	3.80	2.90	5.60	2.20	1.70	6.20	2.20	2.70
OUN	6.50	3.00	1.80	21.0	6.20	2.80	11.1	5.30	2.80	2.30	3.30	6.00
ARE	2.20	2.60	1.80	10.4	5.40	1.50	4.20	6.90	2.90	1.90	1.60	5.20
ASS	2.00	3.10	2.20	4.20	3.00	1.90	10.7	1.70	2.00	1.55	1.59	3.90
IRE	2.30	2.40	1.90	10.3	14.1	1.50	2.30	2.20	2.00	7.70	4.10	27.6
ANN	2.10	3.90	2.50	3.90	5.80	3.80	6.90	1.70	3.70	2.40	5.10	1.70
AHO	3.20	2.60	2.30	9.30	*	2.60	4.30	4.80	2.60	1.60	13.4	11.0
ENJ	4.10	3.44	1.70	3.70	*	6.30	8.90	5.30	2.80	3.10	7.80	3.80
OLO	2.30	3.40	2.70	2.80	4.40	5.00	4.70	4.60	2.70	1.58	*	2.60
GBD	2.80	3.70	2.70	4.10	3.00	1.70	4.50	5.70	2.70	2.00	1.60	2.90
AWE	2.90	3.20	2.10	8.40	*	4.00	15.3	2.70	2.90	2.90	*	3.60
OJU	2.20	3.00	1.90	2.60	2.90	1.80	4.90	2.20	2.90	1.20	1.70	1.70
OSU	2.70	3.60	2.80	2.80	2.30	1.70	7.40	3.40	2.60	1.50	2.00	2.10
YEY	2.83	2.60	2.90	3.70	2.22	2.20	5.20	3.30	2.50	1.10	1.90	2.30
ONN	2.50	5.30	2.70	2.40	2.70	1.90	4.40	4.30	3.30	0.90	1.50	2.00
OLU	3.10	3.20	3.00	2.80	3.00	2.30	1.90	3.30	2.30	2.20	2.40	1.90
ORU	3.50	7.10	2.20	*	*	*	11.0	5.80	3.40	*	*	*
KAN	2.60	3.00	2.60	5.80	4.50	1.90	4.20	1.70	2.50	2.00	1.90	1.90
ADE	29.4	4.60	7.40	95.6	*	1.40	21.0	16.9	28.4	34.8	31.0	24.0
EJI	4.70	2.70	2.50	1.30	2.60	2.90	9.30	2.90	2.40	1.60	1.70	2.80
ARO	4.40	3.00	2.60	4.00	*	1.90	5.30	6.80	3.00	*	*	*
ODD	3.40	4.70	2.00	0.80	2.60	1.80	5.90	3.60	2.50	1.30	2.31	2.60
OBB	4.50	4.50	2.70	5.40	2.80	2.20	3.60	4.00	3.40	1.40	1.50	2.20
OYK	3.70	3.30	2.90	2.11	3.10	2.00	2.80	2.30	2.50	1.40	2.50	2.90
ETI	3.60	3.60	2.90	1.80	2.30	2.20	4.30	2.60	2.70	1.10	2.80	3.20
ISA	2.80	3.20	3.00	3.00	3.40	7.30	5.80	3.50	3.10	1.60	2.70	2.60
OPP	2.20	2.50	2.60	2.60	*	2.00	6.10	5.20	2.80	1.60	2.00	1.80
OPE	2.70	5.10	2.60	12.0	*	2.80	6.10	2.90	2.60	4.80	*	2.40
MOG	3.00	3.00	3.30	9.30	*	1.70	2.90	3.00	2.60	10.6	*	20.4
ASJ	2.80	4.00	2.80	3.90	2.20	1.70	4.40	3.20	2.30	1.70	2.30	1.50

* = No water found

Appendix 15: Concentrations of dissolved oxygen (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	7.40	8.70	6.40	7.90	5.80	9.80	10.3	11.5	10.0	8.00	8.70	7.90
OSI	1.40	2.70	4.40	6.00	4.90	11.0	6.60	12.1	8.80	7.90	6.20	7.50
OUN	1.00	6.00	2.70	3.70	3.30	8.20	10.00	9.70	10.0	8.20	9.40	6.80
ARE	5.90	6.70	6.40	5.00	0.80	8.00	10.6	10.3	11.3	8.30	7.90	7.60
ASS	7.10	9.70	7.30	9.70	7.60	8.10	9.60	11.5	11.3	9.60	12.3	7.50
IRE	7.20	8.20	5.50	1.90	1.20	7.40	9.70	12.6	11.8	8.10	4.60	7.90
ANN	4.00	4.20	5.10	2.50	4.80	7.60	7.90	8.60	8.30	8.60	7.90	7.50
AHO	3.10	6.70	6.90	4.30	*	5.10	11.8	12.7	10.4	8.70	7.10	8.00
ENJ	3.60	7.00	5.60	6.70	*	8.50	7.60	10.2	9.40	8.50	7.20	8.00
OLO	6.10	8.70	6.30	14.0	2.70	4.10	9.00	14.1	9.40	9.50	*	6.80
GBD	7.80	7.80	6.80	8.90	5.20	12.0	12.4	10.9	7.50	6.30	5.90	8.00
AWE	3.90	6.30	4.50	6.50	*	11.1	7.60	7.80	10.3	8.90	*	8.30
OJU	6.00	4.70	6.00	9.90	6.70	10.8	7.30	11.7	10.8	8.00	7.80	6.60
OSU	8.70	8.40	7.30	6.80	6.20	7.30	11.5	12.8	9.20	7.10	8.60	7.80
YEY	6.10	7.70	7.30	11.7	2.90	2.20	7.40	8.60	7.90	10.2	8.50	8.80
ONN	7.70	9.90	9.30	13.5	6.80	35.5	11.6	10.0	10.3	10.9	12.4	7.50
OLU	8.90	7.90	11.8	13.5	7.70	13.4	10.0	12.0	9.70	11.0	12.6	8.50
ORU	7.60	8.80	7.70	*	*	*	12.1	16.7	9.90	*	*	*
KAN	0.30	5.48	2.30	1.00	0.80	6.90	9.90	7.80	7.70	5.60	8.60	8.70
ADE	-0.20	2.10	6.10	1.30	*	5.50	5.30	10.6	6.50	6.80	6.60	7.50
EJI	8.40	7.00	7.70	4.70	2.30	9.40	12.2	11.1	10.4	7.30	8.40	8.50
ARO	5.20	8.20	8.40	-2.10	*	7.00	8.50	10.0	12.7	*	*	*
ODD	6.30	7.60	6.50	4.00	3.20	11.2	9.80	9.10	10.3	7.20	9.10	7.90
OBB	6.50	7.40	7.60	1.80	0.90	7.60	11.5	10.1	10.7	7.50	6.60	7.90
OYK	6.10	5.10	9.80	11.0	4.17	6.80	10.1	11.2	9.1	9.30	11.7	7.54
ETI	8.10	9.10	10.2	10.4	6.10	8.70	10.3	14.0	10.3	10.4	7.80	7.20
ISA	8.60	9.20	11.3	10.7	2.50	9.50	11.2	13.4	9.10	10.3	5.80	8.30
OPP	3.20	9.25	10.0	10.2	*	8.50	9.30	6.10	10.00	9.60	5.70	7.60
OPE	6.00	7.20	7.30	4.00	*	6.00	10.9	12.5	8.20	6.10	*	6.50
MOG	5.20	4.70	6.10	4.60	*	8.70	9.50	12.5	8.20	6.40	*	7.10
ASJ	6.90	9.00	10.7	9.70	6.50	9.50	12.7	11.1	9.20	6.30	6.70	7.50

* = No water found

Appendix 16: Biochemical oxygen demand (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	3.10	6.20	1.50	7.70	12.2	4.40	12.2	6.30	6.50	7.90	2.50	2.70
OSI	1.00	5.30	5.50	12.3	3.5	3.00	9.30	1.10	3.80	7.90	4.50	3.70
OUN	0.90	4.80	1.60	6.40	9.8	5.00	10.4	4.90	5.60	7.10	2.00	2.00
ARE	0.43	4.10	4.60	9.60	8	6.40	11.9	2.60	6.70	7.00	3.70	3.40
ASS	1.10	4.10	8.30	10.7	3.6	3.90	14.4	8.00	5.90	7.00	4.30	2.30
IRE	1.90	5.00	1.60	6.70	11.5	5.70	9.10	6.20	5.80	11.2	7.30	4.00
ANN	2.40	7.70	1.60	9.70	11.4	6.30	9.10	5.50	7.40	7.30	5.00	2.90
AHO	1.50	3.30	1.50	6.50	*	4.50	10.4	7.40	4.70	7.90	8.40	6.60
ENJ	2.00	4.90	2.10	9.50	*	5.00	10.5	4.90	4.80	6.70	5.10	3.00
OLO	2.70	2.40	2.10	6.50	7.80	35.7	10.3	13.3	3.50	2.30	*	1.10
GBD	7.30	3.10	10.0	17.1	11.5	6.40	4.90	9.90	3.90	2.70	4.20	3.40
AWE	1.70	3.40	2.80	10.9	*	1.20	7.10	7.60	7.30	6.50	*	6.80
OJU	1.10	4.60	2.40	12.7	9.60	6.00	10.8	9.40	6.90	7.60	3.60	3.60
OSU	3.33	11.7	9.80	14.0	14.3	7.70	8.10	9.60	4.40	3.10	3.30	4.00
YEY	1.00	1.70	2.20	5.70	13.1	28.0	6.90	12.5	4.20	1.70	6.50	3.50
ONN	1.50	1.70	1.50	7.40	35.5	7.40	7.40	91.0	6.50	12.1	3.80	2.20
OLU	6.10	2.50	0.90	27.0	14.7	30.6	11.6	12.7	2.80	2.70	5.50	1.70
ORU	3.90	5.00	11.2	*	*	*	6.00	9.00	4.50	*	*	*
KAN	5.40	13.5	9.40	15.8	8.60	5.60	5.30	7.10	3.80	3.00	4.00	3.60
ADE	4.40	12.7	1.70	51.0	*	29.3	8.20	14.2	5.40	7.40	6.10	1.90
EJI	7.50	6.80	7.40	15.8	0.50	7.70	6.00	7.10	5.40	5.10	2.80	3.40
ARO	1.20	4.10	10.3	16.8	*	7.20	3.30	7.80	3.90	*	*	*
ODD	4.60	6.30	9.40	15.3	5.40	5.60	3.30	9.00	4.70	2.50	5.00	1.77
OBB	6.30	10.9	10.1	14.3	6.80	4.80	7.70	7.40	4.40	2.30	5.60	0.60
OYK	1.80	3.00	2.40	6.30	11.0	29.7	201	13.2	4.10	1.10	4.20	1.00
ETI	4.10	1.80	2.90	5.90	11.9	33.4	5.20	12.3	3.20	1.80	4.90	1.20
ISA	4.10	4.80	2.30	5.90	10.7	32.5	14.7	13.1	4.10	1.90	4.60	0.70
OPP	1.00	3.30	2.40	8.30	*	26.0	11.4	15.8	3.50	2.10	5.50	1.80
OPE	2.00	7.90	9.90	11.7	*	9.90	6.30	8.70	4.10	1.30	*	4.80
MOG	2.40	9.90	9.90	12.5	*	6.20	6.50	8.70	4.10	2.90	*	1.70
ASJ	1.40	5.70	11.3	16.2	12.6	11.5	6.20	9.70	4.00	2.80	5.40	2.30

* = No water found

Appendix 17: Chemical oxygen demand (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	40.0	181	721	171	101	70.0	392	158	363	75.0	256	192
OSI	60.0	101	101	186	61.0	50.0	202	18.9	192	75.0	480	192
OUN	40.0	91.0	96.0	214	136	126	106	103	374	91.0	523	294
ARE	47.0	127	57.0	151	168	60.0	134	63.0	327	57.0	306	78.0
ASS	91.0	20.1	121	251	201	61.0	261	69.0	182	214	363	128
IRE	30.0	101	67.0	164	148	47.0	87.0	29.0	313	28.0	448	78.0
ANN	125	205	147	199	94.0	131	134	78.0	168	110	491	194
AHO	101	134	43.6	201	*	54.0	114	23.0	228	124	334	199
ENJ	91.0	154	30.0	154	*	27.0	141	34.0	327	71.0	640	277
OLO	94.0	201	40.0	134	148	154	121	84.0	71.0	84.0	*	185
GBD	956	176	111	254	96.0	50.0	126	41.0	75.0	203	347	197
AWE	60.4	141	47.0	214	*	101	315	59.0	214	121	*	242
OJU	67.0	104	74.0	201	107	188	740	63.0	213	149	391	199
OSU	167	161	107	245	104	121	121	25.0	157	50.0	192	171
YEY	170	101	20.1	241	171	91.0	222	208	107	32.0	448	139
ONN	310	206	40.0	191	185	91.0	221	63.0	96.0	229	453	222
OLU	30.0	41.0	87.1	238	31.0	208	114	97.0	114	18.0	434	142
ORU	70.0	101	30.0	*	*	*	121	101	107	*	*	*
KAN	55.0	61.0	91.0	131	55.3	30.0	231	69.0	150	64.0	256	256
ADE	127	248	121	208	*	228	249	130	128	135	223	217
EJI	40.0	161	81.0	171	81.0	61.0	141	114	171	32.0	331	213
ARO	81.0	40.0	91.0	141	*	151	171	25.0	121	*	*	*
ODD	121	50.0	161	101	61.0	60.0	121	76.0	150	102	459	203
OBB	105	126	116	221	101	106	131	56.8	117	96	389	203
OYK	40.0	202	101	221	176	65.0	201	214	85.0	150	38.0	64.0
ETI	80.0	34.0	167	168	61.0	208	94.0	126	142	57.0	266	124
ISA	53.0	91.0	106	196	116	216	156	123	277	235	456	96.0
OPP	100	40.0	20.1	171	*	181	201	101	128	107	406	32.0
OPE	37.0	125	114	411	*	167	107	59.0	85.3	33.0	*	85.0
MOG	180	144	114	154	*	74.0	101	59.0	85.3	57.0	*	213
ASJ	60.3	178	74.0	204	47.0	101	174	21.0	57.0	57.0	277	164

* = No water found

Appendix 18: Concentrations of lead (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.001	0.001	0.01	0.001	0.004	0.004	0.001	0.001	0.001	0.001	0.001	0.002
OSI	0.01	0.003	0.01	0.004	0.001	0.004	0.001	0.001	0.002	0.002	0.001	0.001
OUN	0.004	0.001	0.01	0.003	0.001	0.003	0.001	0.002	0.002	0.002	0.003	0.001
ARE	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.002
ASS	0.004	0.001	0.01	0.003	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.002
IRE	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ANN	0.004	0.01	0.01	0.01	0.001	0.002	0.001	0.001	0.002	0.001	0.001	0.002
AHO	0.01	0.001	0.01	0.004	*	0.001	0.001	0.001	0.001	0.001	0.004	0.001
ENJ	0.004	0.001	0.01	0.003	0.001	0.001	0.001	0.001	0.004	0.002	0.002	0.003
OLO	0.004	0.001	0.01	0.001	*	0.001	0.001	0.001	0.002	0.003	*	0.002
GBD	0.02	0.002	0.01	0.003	0.001	0.003	0.001	0.001	0.003	0.001	0.003	0.001
AWE	0.004	0.002	0.01	0.001	0.001	0.001	0.001	0.001	0.002	0.002	*	0.002
OJU	0.01	0.001	0.01	0.003	0.001	0.001	0.001	0.002	0.002	0.001	0.003	0.003
OSU	0.01	0.002	0.01	0.003	0.001	0.002	0.001	0.001	0.002	0.002	0.001	0.002
YEY	0.01	0.001	0.01	0.001	0.001	0.003	0.001	0.001	0.003	0.001	0.002	0.001
ONN	0.01	0.001	0.01	0.003	0.001	0.004	0.001	0.004	0.004	0.002	0.002	0.003
OLU	0.01	0.001	0.01	0.003	0.001	0.001	0.001	0.004	0.002	0.001	0.001	0.003
ORU	0.001	0.001	0.01	*	0.001	*	0.001	0.003	0.002	*	*	*
KAN	0.001	0.02	0.01	0.003	*	0.01	0.001	0.001	0.002	0.001	0.002	0.001
ADE	0.02	0.001	0.01	0.01	0.001	0.01	0.001	0.01	0.01	0.002	0.002	0.001
EJI	0.004	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	0.001	0.002
ARO	0.004	0.01	0.01	0.001	0.004	0.004	0.001	0.001	0.001	*	*	*
ODD	0.004	0.001	0.01	0.003	0.004	0.004	0.001	0.001	0.002	0.001	0.001	0.002
OBB	0.01	0.001	0.01	0.001	0.001	0.01	0.001	0.002	0.003	0.002	0.001	0.003
OYK	0.01	0.001	0.01	0.001	0.001	0.001	0.001	0.003	0.002	0.003	0.001	0.001
ETI	0.01	0.002	0.01	0.003	0.001	0.001	0.001	0.001	0.003	0.003	0.001	0.002
ISA	0.01	0.01	0.01	0.003	*	0.004	0.001	0.002	0.01	0.001	0.003	0.002
OPP	0.01	0.001	0.01	0.001	*	0.003	0.001	0.002	0.001	0.003	0.002	0.001
OPE	0.01	0.01	0.01	0.003	0.001	0.004	0.001	0.001	0.002	0.002	*	0.002
MOG	0.02	0.001	0.01	0.01	0.001	0.004	0.001	0.002	0.002	0.002	*	0.004
ASJ	0.001	0.003	0.01	0.01	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.001

* = No water found

Appendix 19: Concentrations of copper (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.002	0.001	0.01	0.001	0.001	0.001	0.001	0.002	0.01	0.002	0.001	0.003
OSI	0.004	0.003	0.01	0.001	0.002	0.001	0.002	0.003	0.01	0.001	0.002	0.002
OUN	0.004	0.001	0.01	0.001	0.001	0.002	0.002	0.001	0.01	0.001	0.002	0.003
ARE	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.002	0.002	0.01	0.001	0.002
ASS	0.002	0.003	0.01	0.001	0.002	0.002	0.01	0.004	0.01	0.01	0.002	0.01
IRE	0.01	0.001	0.01	0.001	0.002	0.001	0.002	0.002	0.003	0.001	0.001	0.002
ANN	0.002	0.002	0.01	0.001	0.001	0.001	0.001	0.001	0.004	0.002	0.004	0.004
AHO	0.002	0.001	0.01	0.001	*	0.004	0.003	0.002	0.002	0.002	0.002	0.002
ENJ	0.002	0.003	0.01	0.002	*	0.003	0.002	0.004	0.002	0.001	0.002	0.002
OLO	0.001	0.001	0.01	0.001	0.002	0.001	0.003	0.002	0.002	0.01	*	0.002
GBD	0.002	0.001	0.01	0.002	0.002	0.003	0.004	0.002	0.01	0.002	0.003	0.002
AWE	0.01	0.002	0.01	0.001	*	0.002	0.003	0.001	0.01	0.01	*	0.002
OJU	0.002	0.002	0.01	0.001	0.001	0.002	0.001	0.002	0.01	0.01	0.002	0.01
OSU	0.01	0.002	0.01	0.001	0.001	0.002	0.002	0.004	0.003	0.001	0.003	0.002
YEY	0.01	0.001	0.01	0.001	0.002	0.01	0.002	0.002	0.002	0.01	0.001	0.002
ONN	0.002	0.001	0.01	0.002	0.002	0.002	0.003	0.002	0.002	0.01	0.002	0.002
OLU	0.002	0.002	0.01	0.001	0.001	0.002	0.002	0.003	0.01	0.001	0.01	0.01
ORU	0.002	0.001	0.01	*	*	0.003	0.001	0.001	0.002	*	*	*
KAN	0.002	0.001	0.01	0.001	0.002	0.001	0.003	0.003	0.004	0.01	0.002	0.002
ADE	0.01	0.002	0.01	0.003	*	0.01	0.002	0.003	0.01	0.002	0.002	0.002
EJI	0.01	0.002	0.01	0.001	0.002	0.002	0.001	0.002	0.01	0.002	0.002	0.01
ARO	0.002	0.003	0.01	0.001	*	0.01	0.001	0.003	0.01	*	*	*
ODD	0.002	0.002	0.01	0.001	0.001	0.002	0.001	0.002	0.002	0.001	0.002	0.01
OBB	0.002	0.001	0.01	0.001	0.001	0.002	0.002	0.003	0.01	0.002	0.003	0.002
OYK	0.01	0.001	0.01	0.001	0.002	0.001	0.001	0.002	0.01	0.002	0.001	0.002
ETI	0.001	0.002	0.01	0.001	0.001	0.001	0.001	0.003	0.01	0.001	0.001	0.002
ISA	0.004	0.003	0.01	0.001	0.001	0.002	0.002	0.002	0.003	0.002	0.001	0.001
OPP	0.001	0.001	0.01	0.001	*	0.001	0.002	0.002	0.01	0.001	0.001	0.001
OPE	0.004	0.002	0.01	0.002	*	0.004	0.001	0.01	0.01		*	0.01
MOG	0.002	0.01	0.01	0.001	*	0.003	0.003	0.004	0.002	0.01	*	0.002
ASJ	0.034	0.001	0.01	0.001	0.002	0.002	0.001	0.004	0.01	0.001	0.003	0.002

*** = No water found**

Appendix 20: Concentrations of cadmium (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OSI	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OUN	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ARE	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ASS	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
IRE	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ANN	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
AHO	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ENJ	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OLO	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	*	0.001
GBD	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
AWE	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001		0.001
OJU	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OSU	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
YEY	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ONN	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OLU	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ORU	0.001	0.001	0.01	*	*	*	0.001	0.001	0.001	*	*	*
KAN	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ADE	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	0.001	0.001
EJI	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ARO	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	*	*	*
ODD	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OBB	0.002	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OYK	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ETI	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ISA	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OPP	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OPE	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	*	0.001
MOG	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	*	0.001
ASJ	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001

* = No water found

Appendix 21: Concentrations of cobalt (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.002	0.001	0.01	0.01	0.001	0.001	0.003	0.001	0.01	0.003	0.002	0.003
OSI	0.002	0.001	0.01	0.01	0.004	0.01	0.001	0.001	0.001	0.003	0.001	0.003
OUN	0.002	0.001	0.01	0.01	0.001	0.01	0.002	0.004	0.001	0.003	0.002	0.01
ARE	0.002	0.001	0.01	0.01	0.001	0.01	0.01	0.001	0.001	0.003	0.001	0.003
ASS	0.002	0.001	0.01	0.01	0.001	0.001	0.01	0.001	0.001	0.003	0.001	0.01
IRE	0.002	0.001	0.01	0.01	0.001	0.001	0.01	0.004	0.001	0.003	0.001	0.002
ANN	0.002	0.002	0.01	0.01	0.001	0.001	0.002	0.01	0.004	0.01	0.01	0.003
AHO	0.004	0.001	0.01	0.01	*	0.001	0.01	0.001	0.001	0.003	0.002	0.003
ENJ	0.002	0.001	0.01	0.01	*	0.001	0.001	0.001	0.001	0.003	0.002	0.003
OLO	0.002	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.01	0.003	*	0.003
GBD	0.02	0.001	0.01	0.01	0.001	0.001	0.001	0.002	0.003	0.003	0.001	0.003
AWE	0.002	0.002	0.01	0.01	*	0.003	0.003	0.001	0.001	0.003	0.003	0.003
OJU	0.002	0.002	0.01	0.01	0.001	0.001	0.01	0.003	0.003	0.003	0.002	0.01
OSU	0.002	0.003	0.01	0.01	0.001	0.003	0.01	0.001	0.003	0.003	0.001	0.003
YEY	0.01	0.001	0.01	0.01	0.001	0.003	0.003	0.004	0.003	0.003	0.001	0.003
ONN	0.002	0.002	0.01	0.01	0.001	0.003	0.001	0.002	0.01	0.003	0.002	0.003
OLU	0.002	0.01	0.01	0.01	0.001	0.003	0.001	0.002	0.01	0.003	0.002	0.003
ORU	0.002	0.001	0.01	*	*	*	0.01	0.001	0.003	*	*	*
KAN	0.002	0.001	0.01	0.01	0.001	0.01	0.001	0.004	0.001	0.003	0.002	0.003
ADE	0.004	0.001	0.01	0.01	*	0.01	0.002	0.002	0.01	0.003	0.001	0.003
EJI	0.004	0.001	0.01	0.01	0.002	0.01	0.01	0.001	0.003	0.003	0.002	0.003
ARO	0.002	0.002	0.01	0.01	*	0.01	0.01	0.004	0.003	*	*	*
ODD	0.002	0.001	0.01	0.01	0.001	0.001	0.003	0.001	0.001	0.003	0.001	0.003
OBB	0.002	0.001	0.01	0.01	0.001	0.001	0.003	0.001	0.01	0.003	0.002	0.003
OYK	0.004	0.002	0.01	0.01	0.001	0.001	0.001	0.001	0.01	0.003	0.001	0.003
ETI	0.014	0.002	0.01	0.01	0.001	0.001	0.003	0.001	0.001	0.003	0.002	0.003
ISA	0.004	0.001	0.01	0.01	0.001	0.01	0.01	0.002	0.003	0.003	0.001	0.01
OPP	0.002	0.001	0.01	0.01	*	0.001	0.003	0.001	0.003	0.003	0.001	0.003
OPE	0.002	0.002	0.01	0.01	*	0.01	0.01	0.002	0.001	0.003	*	0.003
MOG	0.002	0.002	0.01	0.01	*	0.01	0.01	0.002	0.001	0.003	*	0.003
ASJ	0.01	0.001	0.01	0.01	0.002	0.01	0.003	0.001	0.003	0.003	0.02	0.003

* = No water found

Appendix 22: Concentrations of chromium (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.01	0.001	0.01	0.01	0.001	0.001	0.001	0.003	0.02	0.002	0.003	0.004
OSI	0.01	0.001	0.01	0.01	0.001	0.001	0.001	0.003	0.003	0.002	0.003	0.003
OUN	0.01	0.001	0.01	0.01	0.001	0.001	0.01	0.003	0.01	0.003	0.004	0.001
ARE	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.004	0.003	0.001	0.002	0.001
ASS	0.01	0.001	0.01	0.01	0.001	0.003	0.003	0.003	0.003	0.002	0.002	0.001
IRE	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.003	0.01	0.001	0.002
ANN	0.01	0.001	0.01	0.01	0.001	0.001	0.002	0.002	0.01	0.001	0.002	0.004
AHO	0.001	0.001	0.01	0.01	*	0.001	0.001	0.003	0.003	0.001	0.001	0.003
ENJ	0.01	0.001	0.01	0.01	*	0.001	0.001	0.001	0.01	0.01	0.001	0.001
OLO	0.03	0.001	0.01	0.01	0.001	0.001	0.003	0.001	0.002	0.002	*	0.001
GBD	0.02	0.001	0.01	0.02	0.001	0.001	0.003	0.002	0.003	0.01	0.001	0.003
AWE	0.01	0.01	0.01	0.01	*	0.001	0.001	0.01	0.004	0.002	*	0.01
OJU	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.003	0.004	0.001	0.01	0.001
OSU	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.002	0.001	0.003	0.01	0.001
YEY	0.01	0.001	0.01	0.01	0.001	0.001	0.001	0.003	0.003	0.001	0.01	0.003
ONN	0.001	0.01	0.01	0.01	0.01	0.001	0.002	0.004	0.01	0.002	0.01	0.002
OLU	0.01	0.001	0.01	0.01	0.002	0.001	0.001	0.002	0.01	0.002	0.002	0.004
ORU	0.04	0.001	0.01	*	*	*	0.001	0.001	0.01	*	*	*
KAN	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.002	0.003	0.001	0.001	0.002
ADE	0.1	0.01	0.01	0.01	*	0.002	0.002	0.002	0.01	0.001	0.01	0.004
EJI	0.001	0.001	0.01	0.01	0.002	0.001	0.002	0.004	0.01	0.001	0.01	0.002
ARO	0.001	0.001	0.01	0.001	*	0.001	0.001	0.001	0.003	*	*	*
ODD	0.03	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.004	0.001	0.02	0.001
OBB	0.02	0.001	0.01	0.01	0.001	0.001	0.001	0.004	0.01	0.003	0.002	0.01
OYK	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.001	0.002	0.01	0.003
ETI	0.01	0.01	0.01	0.01	0.001	0.001	0.001	0.001	0.001	0.003	0.01	0.003
ISA	0.03	0.001	0.01	0.01	0.002	0.001	0.002	0.003	0.003	0.001	0.01	0.002
OPP	0.01	0.001	0.01	0.01	*	0.003	0.01	0.001	0.01	0.002	0.001	0.001
OPE	0.001	0.001	0.01	0.01	*	0.002	0.01	0.004	0.01	0.002	*	0.002
MOG	0.03	0.001	0.01	0.01	*	0.001	0.01	0.003	0.001	0.003	*	0.01
ASJ	0.001	0.001	0.01	0.01	0.001	0.001	0.001	0.004	0.004	0.001	0.003	0.001

* = No water found

Appendix 23: Concentrations of nickel (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.001	0.001
OSI	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001
OUN	0.02	0.001	0.01	0.003	0.001	0.001	0.003	0.001	0.001	0.001	0.002	0.001
ARE	0.03	0.001	0.01	0.001	0.001	0.003	0.001	0.001	0.001	0.003	0.001	0.001
ASS	0.02	0.001	0.001	0.001	0.001	0.001	0.004	0.001	0.01	0.001	0.001	0.001
IRE	0.03	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ANN	0.03	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.004	0.001	0.001	0.001
AHO	0.02	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.001	0.001	0.001
ENJ	0.06	0.001	0.01	0.001	*	0.001	0.001	0.001	0.003	0.01	0.001	0.001
OLO	0.01	0.001	0.01	0.001	0.002	0.001	0.001	0.001	0.001	0.001	*	0.001
GBD	0.02	0.001	0.01	0.004	0.001	0.002	0.003	0.001	0.001	0.001	0.001	0.001
AWE	0.02	0.001	0.01	0.003	*	0.001	0.001	0.003	0.01	0.001	*	0.001
OJU	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.002	0.001	0.003	0.001	0.001
OSU	0.04	0.001	0.01	0.003	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001
YEY	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.001
ONN	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OLU	0.03	0.01	0.01	0.001	0.001	0.001	0.002	0.002	0.003	0.001	0.001	0.001
ORU	0.01	0.001	0.01	*	*	*	0.002	0.001	0.003	*	*	*
KAN	0.05	0.001	0.01	0.003	0.001	0.001	0.001	0.001	0.003	0.002	0.001	0.001
ADE	0.03	0.001	0.01	0.01	*	0.01	0.001	0.003	0.001	0.001	0.001	0.001
EJI	0.03	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.001	0.001
ARO	0.04	0.001	0.01	0.001	*	0.001	0.001	0.004	0.001	*	*	*
ODD	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
OBB	0.03	0.001	0.01	0.01	0.001	0.001	0.001	0.004	0.001	0.001	0.001	0.001
OYK	0.03	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.01	0.002	0.002	0.001
ETI	0.02	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.003	0.01	0.001	0.001
ISA	0.03	0.001	0.01	0.001	0.001	0.002	0.001	0.003	0.001	0.001	0.001	0.001
OPP	0.04	0.001	0.01	0.001	*	0.003	0.002	0.001	0.001	0.001	0.001	0.001
OPE	0.03	0.001	0.01	0.001	*	0.001	0.002	0.001	0.004	0.001	*	0.001
MOG	0.03	0.001	0.01	0.001	*	0.001	0.001	0.001	0.001	0.002	*	0.001
ASJ	0.032	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001

* = No water found

Appendix 24: Concentrations of zinc (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.01	0.15	0.01	0.001	0.001	0.01	0.003	0.04	0.08	0.09	0.02	0.05
OSI	0.02	0.18	0.02	0.01	0.01	0.01	0.01	0.07	0.14	0.12	0.01	0.06
OUN	0.05	0.18	0.01	0.01	0.01	0.004	0.003	0.03	0.09	0.14	0.02	0.07
ARE	0.01	0.14	0.04	0.24	0.01	0.01	0.001	0.05	0.001	0.06	0.01	0.06
ASS	0.003	0.10	0.27	0.01	0.004	0.01	0.02	0.12	0.01	0.21	0.02	0.03
IRE	0.01	0.14	0.1	0.01	0.01	0.002	0.01	0.07	0.16	0.10	0.03	0.04
ANN	0.02	0.06	0.01	0.01	0.01	0.01	0.001	0.08	0.14	0.15	0.03	0.04
AHO	0.01	0.17	0.12	0.03	*	0.002	0.001	0.03	0.02	0.10	0.04	0.05
ENJ	0.01	0.24	0.53	0.01	*	0.01	0.01	0.09	0.06	0.20	0.02	0.01
OLO	0.02	0.06	0.52	0.01	0.01	0.01	0.01	0.08	0.06	0.16	*	0.05
GBD	0.02	0.22	0.44	0.06	0.01	0.04	0.04	0.15	0.02	0.09	0.04	0.03
AWE	0.03	0.21	0.12	0.03	*	0.01	0.01	0.10	0.08	0.15	*	0.03
OJU	0.02	0.22	0.08	0.01	0.01	0.003	0.01	0.06	0.08	0.07	0.03	0.04
OSU	0.01	0.29	0.20	0.01	0.004	0.001	0.02	0.04	0.06	0.17	0.02	0
YEY	0.02	0.02	0.49	0.03	0.01	0.01	0.01	0.04	0.12	0.09	0.01	0.04
ONN	0.01	0.01	0.25	0.01	0.01	0.01	0.01	0.05	0.10	0.15	0.11	0.03
OLU	0.02	0.01	0.31	0.01	0.001	0.01	0.01	0.06	0.14	0.11	0.01	0.07
ORU	0.01	0.28	0.02	*	*	*	0.01	0.05	0.05	*	*	*
KAN	0.01	0.001	0.40	0.01	0.004	0.01	0.01	0.09	0.12	0.12	0.02	0.03
ADE	0.02	0.10	0.25	0.05	*	0.02	0.01	0.08	0.10	0.15	0.04	0.03
EJI	0.003	0.09	0.03	0.01	0.001	0.004	0.02	0.14	0.12	0.13	0.06	0.08
ARO	0.01	0.16	0.03	0.02	*	0.01	0.01	0.06	0.05	*	*	*
ODD	0.01	0.09	0.34	0.01	0.01	0.002	0.01	0.02	0.06	0.04	0.02	0.01
OBB	0.02	0.20	0.47	0.01	0.01	0.003	0.001	0.09	0.16	0.11	0.01	0.09
OYK	0.01	0.02	0.43	0.01	0.01	0.01	0.003	0.03	0.03	0.13	0.01	0.02
ETI	0.02	0.01	0.37	0.01	0.01	0.01	0.003	0.06	0.05	0.05	0.01	0.05
ISA	0.02	0.12	0.22	0.01	0.01	0.01	0.02	0.05	0.11	0.07	0.03	0.02
OPP	0.02	0.06	0.49	0.01	*	0.002	0.04	0.07	0.15	0.14	0.03	0.01
OPE	0.01	0.13	0.32	0.02	*	0.01	0.04	0.19	0.05	0.12	*	0.03
MOG	0.03	0.28	0.28	0.02	*	0.01	0.02	0.07	0.02	0.16	*	0.03
ASJ	0.01	0.39	0.01	0.01	0.01	0.004	0.01	0.13	0.13	0.13	0.06	0.001

* = No water found

Appendix 25: Concentrations of calcium (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	16.0	13.2	11.3	96.0	146	75.6	58.0	22.1	17.0	12.0	64.5	41.1
OSI	33.0	26.2	21.7	152	295	17.4	81.0	33.7	45.0	6.40	100	64.5
OUN	29.0	16.2	5.90	111	105	108	52.0	18.2	43.0	10.0	53.0	58.6
ARE	31.0	24.2	30.2	163	256	75.6	52.0	32.5	22.1	22.3	107	70.0
ASS	39.0	27.2	20.8	175	256	93.0	99.0	36.0	34.9	22.3	99.0	70.0
IRE	14.0	12.3	15.1	111	268	128	40.7	10.5	24.4	15.3	111	64.5
ANN	28.7	27.0	17.0	159	201	89.0	66.0	33.7	39.0	16.8	62.5	50.8
AHO	26.0	21.9	15.1	215	*	105	23.0	22.2	20.9	18.8	170	59.0
ENJ	23.5	7.90	15.0	138	*	81.0	58.0	17.4	15.1	11.7	50.0	82.0
OLO	13.0	10.2	14.2	26.0	146	105	81.0	19.8	17.5	16.5	*	79.1
GBD	25.0	24.2	18.0	65.0	204	111	64.0	30.2	28.1	15.3	105	73.0
AWE	38.0	24.6	10.4	152	*	76.0	55.0	41.8	33.7	20.6	*	123
OJU	28.8	21.3	10.4	152	144	128	64.0	29.1	19.8	12.9	88.0	52.8
OSU	21.0	16.4	19.9	58.2	123	139	64.0	24.4	28.2	20.0	117	76.0
YEY	24.5	27.2	33.1	75.7	396	117	58.0	30.2	23.3	29.3	94.0	82.0
ONN	33.0	23.3	11.3	64.0	111	105	70.0	19.0	27.9	34.0	111	82.0
OLU	9.00	12.0	8.97	28.0	92.9	87.0	52.0	10.5	12.8	12.9	76.0	82.0
ORU	10.0	13.5	19.9	*	*	*	64.0	16.3	18.7	*	*	*
KAN	19.0	19.0	23.6	111	210	99.0	64.0	33.7	12.8	14.1	88.0	73.0
ADE	49.1	221	201	476	*	396	180	115	326	75.0	451	393
EJI	16.0	16.0	20.8	75.0	198	111	81.0	32.5	7.00	17.6	88.0	72.7
ARO	13.0	18.5	20.8	82.0	*	209	87.0	19.8	30.3	*	*	*
ODD	14.0	15.6	15.1	40.0	82.0	93.0	58.0	12.8	17.6	15.3	65.0	67.0
OBB	18.0	17.0	22.7	98.0	163	145	52.0	23.2	29.3	29.3	21.1	88.0
OYK	16.0	10.1	16.1	30.3	128	99.0	64.0	20.9	16.3	14.7	76.0	41.1
ETI	11.0	22.3	24.6	43.1	99.1	99.0	70.0	19.0	31.4	26.4	76.0	84.0
ISA	30.0	27.3	20.8	76.8	251	122	76.0	23.2	30.2	34.0	123	82.0
OPP	35.0	25.6	31.2	86.1	*	134	87.2	34.9	40.7	44.6	88.0	88.0
OPE	31.0	27.4	32.1	210	*	169	76.0	37.0	64.5	21.1	*	76.2
MOG	90.1	58.1	79.3	127	*	296	151	87.0	117	41.0	*	173
ASJ	15.0	27.2	14.2	60.6	105	116	76.0	26.0	35.0	17.6	100	52.8

*No water found

Appendix 26: Concentrations of magnesium (mg/L) in surface water for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.60	2.30	3.00	1.20	16.0	11.3	7.10	1.40	1.40	1.60	12.8	26.4
OSI	1.40	5.10	4.60	1.60	7.60	36.7	4.30	5.90	26.00	4.70	17.0	27.1
OUN	1.20	1.70	1.30	1.15	28.0	10.6	8.50	1.80	8.00	1.99	18.5	17.8
ARE	1.60	1.20	2.30	1.60	11.3	24.0	9.90	2.82	5.40	2.90	8.30	17.8
ASS	0.60	1.20	3.67	1.40	14.0	12.7	15.5	3.70	1.40	1.71	13.0	25.6
IRE	1.20	0.90	0.90	1.40	14.0	3.10	7.10	3.70	0.60	1.30	11.0	11.4
ANN	1.00	3.60	2.90	1.50	5.66	19.0	7.50	3.10	7.90	2.40	20.0	35.0
AHO	1.50	0.25	2.30	1.46	*	25.4	15.6	2.50	2.30	2.28	48.0	34.2
ENJ	1.00	0.97	2.80	0.99	*	7.10	11.3	5.10	1.10	2.00	20.7	9.30
OLO	2.20	1.70	2.30	0.32	237	12.7	4.20	3.39	2.10	2.28	*	6.40
GBD	2.20	24.0	1.60	1.60	19.0	17.0	13.0	4.52	5.90	3.10	17.1	11.4
AWE	4.50	3.20	2.30	1.70	*	21.0	16.0	7.60	5.10	2.70	*	20.0
OJU	0.40	3.40	5.10	0.90	4.50	4.60	7.10	1.13	3.70	2.30	10.0	22.8
OSU	2.00	6.10	4.60	0.30	86.0	7.10	13.0	4.90	8.10	4.60	12.8	10.0
YEY	2.80	1.70	3.40	0.20	111	9.90	14.1	4.00	3.40	6.80	14.2	7.10
ONN	2.40	2.20	1.80	0.10	100	12.7	14.1	8.00	3.10	5.70	3.00	11.4
OLU	3.40	1.50	4.50	0.40	71.0	4.80	5.65	2.00	2.30	2.30	10.0	7.10
ORU	0.49	5.60	1.60	*	*	*	4.20	3.40	4.60	*	*	*
KAN	3.20	6.00	5.50	1.15	211	18.4	13.0	6.90	7.80	5.70	20.7	13.7
ADE	38.0	24.1	23.7	1.60	*	35.0	42.0	10.7	33.0	7.40	26.0	22.8
EJI	1.70	4.10	3.70	0.15	84.0	14.0	13.0	1.00	9.20	1.70	22.1	13.7
ARO	1.70	3.00	4.80	0.20	*	41.0	10.0	4.70	5.90	*	*	*
ODD	14.0	1.46	2.50	0.18	96.0	18.0	8.47	4.50	3.20	2.30	21.4	7.10
OBB	1.90	17.0	1.80	0.30	145	14.1	11.3	2.30	8.80	3.40	18.5	12.8
OYK	2.20	1.90	1.80	0.20	65.1	3.30	5.70	2.10	3.70	1.60	10.0	23.5
ETI	1.00	0.49	1.60	0.40	103	2.82	9.90	4.50	0.90	4.00	7.10	5.90
ISA	3.41	4.20	7.80	0.40	290	1.00	5.65	4.20	6.40	6.60	20.0	10.7
OPP	3.70	5.10	2.75	0.40	*	7.10	7.10	4.80	4.20	10.0	15.7	15.7
OPE	5.84	8.40	3.70	2.40	*	25.4	19.8	5.10	44.0	5.13	*	20.0
MOG	6.60	5.10	6.90	0.30	*	41.0	42.0	4.50	25.2	3.70	*	109
ASJ	1.50	2.90	1.20	1.20	16.4	19.8	12.9	2.59	4.80	17.6	12.8	18.5

* = No water found

Appendix 27: Concentrations of organic carbon (%) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.50	1.30	2.50	1.00	1.70	1.40	1.00	1.10	1.20	5.30	0.70	0.60
OSI	1.60	1.10	0.40	0.38	2.00	1.40	3.10	2.40	0.80	33.9	1.90	1.40
OUN	0.30	0.70	0.40	0.24	2.00	0.70	0.70	1.20	1.20	21.6	1.03	1.09
ARE	0.20	1.30	0.50	1.10	2.10	0.50	2.20	1.70	1.20	9.00	0.70	1.30
ASS	0.30	2.80	0.60	1.50	1.00	1.50	2.80	2.50	1.40	23.0	0.50	0.70
IRE	0.36	0.37	1.20	0.50	2.53	0.50	2.80	1.60	1.00	6.10	1.20	2.70
ANN	1.00	3.00	1.30	2.50	5.60	0.60	2.10	3.70	4.20	24.1	3.80	4.30
AHO	1.49	1.57	1.00	2.60	3.10	8.40	2.54	2.80	2.10	12.5	3.00	1.70
ENJ	0.30	1.00	0.90	0.90	1.40	0.30	0.80	1.50	1.20	10.5	1.40	1.20
OLO	0.80	1.70	0.20	1.30	1.70	0.70	1.40	1.80	0.60	9.90	2.20	1.50
GBD	0.80	0.80	0.50	1.10	1.60	1.40	1.40	0.80	0.60	4.90	2.60	0.60
AWE	0.20	0.50	1.90	1.40	1.90	0.30	0.70	1.10	1.10	7.10	1.30	0.70
OJU	0.30	0.60	0.50	0.30	0.70	0.30	0.50	0.50	0.60	24.0	1.60	0.60
OSU	0.31	0.50	0.28	0.70	2.10	0.30	0.50	1.40	0.90	4.43	2.00	0.70
YEY	0.30	0.60	0.60	0.10	1.40	0.10	0.83	1.20	1.20	6.10	1.00	1.20
ONN	0.70	1.60	1.60	0.90	4.30	1.10	1.40	4.70	1.80	11.7	2.30	0.60
OLU	0.80	0.49	0.80	2.90	1.40	0.40	1.60	1.80	1.20	18.0	2.00	0.90
ORU	0.20	1.30	2.40	0.40	1.00	0.50	0.90	1.20	1.10	12.1	1.30	0.50
KAN	0.30	0.24	0.20	0.24	2.50	1.10	0.60	1.10	1.10	17.8	1.00	0.88
ADE	0.39	0.20	0.30	0.30	7.60	0.50	0.80	2.00	6.00	46.0	5.70	0.80
EJI	0.21	1.70	0.50	0.60	1.10	0.42	0.20	1.20	0.80	4.80	2.30	1.30
ARO	0.80	0.50	0.60	0.20	1.20	0.70	2.20	1.60	0.90	5.70	1.10	0.90
ODD	0.73	0.40	0.80	0.30	3.50	0.80	1.40	3.60	1.60	2.10	2.60	0.80
OBB	0.50	0.30	0.20	0.16	0.50	0.40	0.80	1.80	1.00	5.30	0.71	0.50
OYK	0.20	4.00	1.10	0.50	1.50	0.70	1.60	3.80	1.00	5.30	2.60	1.20
ETI	0.21	0.30	0.50	0.30	1.00	0.50	1.20	3.10	6.60	11.0	2.40	0.70
ISA	0.80	0.40	1.00	0.40	1.10	0.84	4.90	3.00	3.00	9.60	2.40	2.20
OPP	3.00	0.50	1.70	2.90	1.80	1.30	2.06	2.00	1.00	10.7	2.40	1.00
OPE	2.90	1.90	7.30	0.60	3.20	1.60	1.60	4.10	0.78	11.9	1.60	1.70
MOG	0.60	1.60	0.20	1.20	1.00	0.20	0.40	4.00	2.50	6.06	1.20	0.60
ASJ	0.40	0.59	0.39	0.40	1.00	0.10	0.60	6.40	0.30	4.70	2.60	0.60

Appendix 28: % sand in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	78.9	78.1	71.9	75.1	71.6	71.5	70.2	70.7	71.3	72.1	71.9	69.1
OSI	78.4	81.3	71.7	75.1	72.0	74.2	73.2	75.1	69.2	72.6	72.6	70.3
OUN	80.2	79.1	71.7	71.4	71.6	71.1	74.2	75.3	71.0	73.4	72.4	71.8
ARE	79.1	78.8	68.8	74.3	70.8	71.9	73.2	70.3	70.3	71.9	74.5	72.1
ASS	78.7	80.0	73.1	72.2	71.2	70.2	70.9	68.2	69.9	72.5	73.3	69.5
IRE	79.8	77.0	71.9	74.3	73.2	71.2	68.9	69.2	69.3	71.6	69.6	69.5
ANN	78.8	79.7	72.2	78.4	72.7	75.7	73.9	69.5	70.6	74.3	70.6	77.7
AHO	77.0	72.7	72.4	72.6	72.9	73.5	71.9	70.4	70.2	74.9	71.1	69.9
ENJ	75.1	80.6	80.5	74.2	73.5	73.4	73.2	70.1	73.5	76.2	72.2	71.5
OLO	78.3	76.3	72.4	72.9	71.5	72.8	72.5	70.1	70.9	74.3	72.3	70.8
GBD	77.3	79.0	72.0	74.4	72.3	72.5	72.1	72.1	74.1	75.5	71.8	71.0
AWE	75.1	76.9	69.9	72.6	73.0	71.8	70.9	71.2	72.0	73.0	71.9	72.5
OJU	75.6	79.4	69.4	72.7	71.5	73.5	70.0	72.3	69.6	71.5	71.8	71.6
OSU	70.1	77.4	69.0	71.4	72.6	70.5	70.9	69.1	69.8	71.1	70.2	71.1
YEY	68.6	77.3	73.9	71.2	74.1	73.4	71.2	70.2	70.5	70.7	71.9	71.2
ONN	66.6	75.8	69.6	72.7	72.9	72.2	71.2	71.0	70.0	73.2	71.2	70.4
OLU	73.6	74.7	72.3	71.3	73.0	73.9	70.2	70.7	73.9	69.4	70.8	71.3
ORU	61.0	84.8	72.6	72.4	71.2	72.3	68.8	70.9	69.2	69.8	70.2	72.9
KAN	76.7	76.6	72.1	71.4	71.8	72.0	71.9	72.1	68.8	72.9	71.8	70.5
ADE	70.2	72.7	72.5	73.7	72.3	73.2	70.5	71.3	70.7	70.7	70.2	71.5
EJI	74.1	76.1	71.7	73.9	71.9	72.9	71.5	71.7	71.7	72.5	70.5	70.9
ARO	72.0	75.3	71.9	73.4	72.5	71.6	73.5	70.9	70.1	69.2	70.0	71.6
ODD	79.6	73.6	70.1	73.3	71.3	71.2	73.2	71.2	73.2	71.9	70.9	70.0
OBB	78.2	74.7	71.7	72.8	73.2	70.5	73.8	69.8	69.6	71.6	68.4	71.0
OYK	66.9	80.0	70.9	72.6	74.8	71.5	68.8	71.9	71.9	69.6	76.2	70.9
ETI	77.0	76.4	72.4	73.8	72.6	71.9	71.2	72.0	70.6	71.6	70.8	69.3
ISA	70.8	80.0	72.0	71.8	70.8	71.8	68.2	70.5	71.0	70.5	71.3	70.6
OPP	79.1	76.7	72.1	74.6	76.1	76.2	72.2	72.1	70.0	72.9	74.1	71.2
OPE	67.5	76.4	70.2	74.0	70.8	69.8	68.8	69.9	70.3	73.3	71.2	71.3
MOG	77.8	78.9	68.6	72.1	73.0	72.3	72.2	74.6	70.2	73.8	69.1	71.8
ASJ	70.5	74.7	72.0	72.3	72.3	69.2	70.9	70.2	71.9	72.7	69.2	71.9

Appendix 29: % clay in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	17.5	19.5	27.2	24.5	26.9	27.2	26.8	27.6	27.9	26.6	27.1	27.6
OSI	20.7	23.0	26.1	24.2	25.4	25.8	25.1	29.2	27.8	23.3	26.7	27.6
OUN	18.5	18.3	26.5	27.9	24.7	26.8	24.8	22.8	28.4	25.6	27.0	26.1
ARE	20.1	20.8	25.9	23.0	26.7	27.5	26.0	27.8	28.2	26.4	25.9	26.2
ASS	20.3	18.1	25.1	24.3	27.4	29.2	25.5	28.3	27.1	26.1	25.8	27.4
IRE	18.6	20.5	25.2	25.0	25.7	27.4	28.2	30.1	29.5	26.4	28.3	28.2
ANN	18.7	18.9	25.0	20.8	26.4	22.4	24.6	28.7	27.8	23.9	26.5	23.8
AHO	21.3	21.9	25.8	25.7	24.8	24.5	26.9	26.9	28.5	22.4	27.2	27.5
ENJ	20.0	18.2	25.4	24.7	25.3	25.5	25.2	29.2	26.2	22.1	26.0	27.3
OLO	20.7	23.0	26.1	24.2	25.4	25.8	25.1	29.2	27.8	23.3	26.7	27.6
GBD	19.2	18.3	26.7	24.4	26.1	26.7	26.5	26.8	24.8	24.0	27.7	28.3
AWE	22.5	20.6	28.2	26.1	25.7	27.7	27.2	28.7	26.8	26.3	27.2	26.4
OJU	22.3	17.3	27.3	24.9	27.0	25.0	28.4	27.1	29.5	27.4	27.3	28.2
OSU	20.2	21.1	27.1	26.4	26.2	28.2	28.0	28.4	29.2	27.4	29.7	26.7
YEY	23.8	20.4	24.6	24.6	25.3	25.8	27.5	29.4	27.7	27.7	26.2	27.7
ONN	22.9	23.0	27.6	26.0	26.7	26.0	26.7	27.1	27.1	25.6	27.3	27.6
OLU	21.4	22.3	26.4	27.8	26.0	25.5	26.7	27.3	25.1	27.8	28.1	27.9
ORU	22.2	13.6	26.2	26.1	27.8	26.7	28.5	27.8	29.4	28.4	27.8	26.7
KAN	20.4	22.7	24.7	27.9	26.2	17.0	27.2	27.2	30.4	26.1	27.8	26.9
ADE	21.9	24.4	26.6	24.9	25.7	25.4	27.4	27.0	29.1	26.8	29.2	27.0
EJI	21.4	19.3	24.9	25.5	26.5	26.5	26.5	27.3	27.8	24.8	29.1	28.1
ARO	22.3	20.0	24.4	26.1	26.4	26.2	24.8	27.9	29.0	28.5	28.5	27.8
ODD	19.9	23.6	28.5	26.0	25.6	26.6	25.1	28.1	26.3	26.7	27.7	26.5
OBB	20.1	24.1	25.0	25.1	25.9	28.5	24.8	27.8	29.5	27.3	29.7	27.3
OYK	19.5	18.2	24.6	27.3	24.5	26.7	28.2	26.8	26.8	28.8	22.2	28.2
ETI	21.9	21.3	27.4	25.0	26.7	24.7	28.2	27.7	26.9	26.5	25.8	28.2
ISA	21.8	19.3	27.0	25.9	27.4	26.4	28.5	28.5	28.3	28.0	28.1	29
OPP	20.2	20.2	25.4	24.7	23.3	22.5	26.5	27.5	28.0	25.4	25.4	27.6
OPE	21.5	20.7	26.0	25.8	27.0	26.7	29.7	27.2	29.3	26.3	27.7	27.8
MOG	21.2	19.7	28.2	25.8	25.3	26.4	27.1	24.2	28.2	24.2	29.6	25.5
ASJ	18.5	22.5	26.8	26.8	25.8	27.5	27.2	28.1	27.2	26.3	27.4	27.6

Appendix 30: % silt in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	3.60	2.50	1.00	0.50	1.60	1.30	3.10	1.70	0.90	1.40	1.00	3.30
OSI	1.00	4.00	1.40	1.50	2.10	1.44	1.40	0.90	1.10	1.00	0.80	2.30
OUN	1.30	2.70	1.90	0.80	3.70	2.20	1.10	1.90	0.70	1.10	0.60	2.20
ARE	0.90	0.50	5.30	2.80	2.60	0.70	0.80	1.90	1.60	0.70	0.70	1.70
ASS	1.10	2.00	1.90	3.60	1.50	0.72	3.70	3.50	3.10	1.50	1.00	3.10
IRE	1.70	2.60	3.00	0.80	1.20	1.40	3.00	0.72	1.30	2.10	2.20	2.40
ANN	2.40	1.30	2.80	0.80	0.90	1.90	1.50	1.80	1.60	1.90	1.00	0.50
AHO	1.70	5.50	1.80	1.70	2.40	1.10	1.30	2.70	1.40	2.80	1.70	2.70
ENJ	4.00	1.30	1.70	1.20	1.20	1.10	1.70	0.70	26.0	1.80	1.90	1.30
OLO	1.10	0.80	1.60	3.00	3.10	1.44	2.40	0.70	1.30	2.50	1.10	1.60
GBD	3.50	2.50	1.40	1.30	1.70	0.80	1.40	1.10	1.20	0.60	0.50	0.80
AWE	2.50	2.50	2.00	1.40	1.40	0.50	2.00	0.10	1.30	0.80	1.00	1.10
OJU	2.10	3.40	3.30	2.50	1.50	1.44	1.60	0.60	1.00	1.20	1.00	0.20
OSU	9.80	1.50	3.90	2.30	1.30	1.40	1.10	2.50	1.10	1.60	0.20	2.30
YEY	7.70	2.40	1.60	4.30	0.70	0.90	1.40	0.50	1.90	1.70	2.00	1.20
ONN	11.0	1.30	2.90	1.40	0.50	1.90	2.16	0.80	3.00	1.30	1.60	2.10
OLU	5.20	3.10	1.30	1.20	1.00	0.70	3.10	1.10	1.10	2.80	1.20	0.90
ORU	16.9	1.70	1.30	1.50	1.10	1.10	2.70	1.30	1.50	1.80	2.10	0.50
KAN	2.90	0.70	3.30	0.80	2.10	11.0	0.90	0.72	0.80	1.10	0.40	2.60
ADE	8.00	3.00	1.00	1.40	1.40	2.10	2.10	2.30	0.20	2.50	0.70	1.60
EJI	4.50	4.60	3.50	0.70	1.70	0.80	2.10	2.20	0.50	2.80	0.50	1.10
ARO	4.80	4.80	3.70	0.60	1.20	2.30	1.70	1.30	1.00	2.40	1.00	0.60
ODD	0.60	2.90	1.50	0.70	3.20	2.30	1.80	0.70	0.50	1.50	1.50	3.60
OBB	2.10	1.30	3.40	2.20	1.00	1.10	1.40	2.40	1.00	1.20	1.90	1.80
OYK	13.6	1.9	4.50	0.20	0.80	1.80	3.00	1.60	1.40	1.70	1.70	1.00
ETI	1.10	2.40	0.30	1.30	0.80	3.44	0.70	0.30	2.60	2.00	3.50	2.60
ISA	7.50	0.70	1.10	2.30	1.90	1.80	3.40	1.10	0.80	1.60	0.60	0.50
OPP	0.80	3.20	2.50	0.80	0.70	1.30	1.40	0.40	2.10	1.70	0.60	1.30
OPE	11.10	3.00	3.90	0.20	2.20	3.40	1.60	2.90	0.50	0.50	1.20	0.90
MOG	1.10	1.60	3.30	2.20	1.80	1.40	0.80	1.30	1.60	2.10	1.30	2.70
ASJ	11.1	2.90	1.30	1.00	2.00	3.20	1.90	1.70	1.00	1.10	3.50	0.60

Appendix 31: Cation exchange capacity (meq/100g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	16.9	80.8	44.2	47.1	39.5	51.5	50.3	44.9	63	53.4	33.8	37.0
OSI	19.0	65.9	65.7	58.8	64.0	62.6	69.7	43.2	65.6	50.4	61.5	47.4
OUN	14.2	57.0	35.0	44.0	45.0	55.1	55.4	51.0	66.0	38.9	46.1	43.1
ARE	23.8	76.0	46.8	47.6	57.5	60.8	67.7	57.0	51.3	42.5	44.9	48.4
ASS	21.9	88.6	40.9	39.4	48.5	80.0	71.0	51.6	48.1	35.1	54.2	52.6
IRE	24.3	49.3	35.0	42.3	39.5	47.1	52.4	55.4	51.7	48.5	47.8	47.2
ANN	28.2	52.0	54.9	58.0	58.0	58.6	57.5	49.0	65.7	45.7	53.0	51.0
AHO	31.3	71.8	61.7	47.7	58.5	77.9	48.9	38.3	47.9	40.3	46.7	56.4
ENJ	18.0	55.3	31.3	46.5	39.5	58.5	56.2	53.4	50.8	36.8	50.0	39.5
OLO	20.7	58.1	34.4	35.0	33.0	60.9	56.1	54.9	57.4	42.0	51.5	55.8
GBD	28.4	82.0	48.3	40.4	62.5	67.3	62.0	47.4	57.7	49.0	39.0	51.0
AWE	24.5	44.2	67.0	53.0	48.5	0.30	51.7	48.0	57.1	52.7	37.9	56.0
OJU	18.5	77.0	18.6	54.4	34.0	60.6	51.4	50.0	51.6	51.8	41.0	50.2
OSU	18.9	60.0	32.7	33.0	42.5	56.5	50.0	58.4	75.1	36.0	52.0	57.0
YEY	19.1	52.0	37.3	56.0	37.0	48.4	51.6	45.5	73.1	41.8	37.9	40.0
ONN	16.0	81.0	54.8	43.0	49.0	63.0	49.4	56.5	68.0	49.7	36.3	52.7
OLU	23.0	49.0	23.5	40.0	42.0	55.0	53.9	31.1	54.9	41.3	44.3	44.8
ORU	13.4	59.8	34.2	43.7	38.0	65.8	45.9	29.5	55.4	45.6	59.9	45.7
KAN	17.5	50.9	26.2	44.0	50.0	57.3	49.8	50.2	40.2	41.9	41.3	44.1
ADE	38.0	43.0	44.0	61.0	70.0	63.3	58.6	54.0	62.2	47.4	60.4	41.0
EJI	17.2	77.5	35.8	47.0	37.0	54.3	52.5	44.5	51.1	51.2	64.8	51.8
ARO	26.9	53.3	49.4	18.8	30.5	52.8	54.1	60.5	69.0	37.5	32.9	23.7
ODD	19.5	31.7	16.1	35.1	55.0	54.6	48.4	28.6	53.0	48.6	40.2	52.5
OBB	14.9	54.0	30.2	37.0	37.0	57.8	58.0	43.0	46.9	37.0	46.5	44.7
OYK	15.7	89.0	50.0	17.3	28.0	47.8	57.8	38.9	36.3	51.3	42.3	57.8
ETI	12.9	70.0	21.5	30.7	22.0	55.2	42.6	52.2	57.5	57.2	47.6	58.4
ISA	26.5	56.7	50.7	35.0	47.5	60.6	63.0	56.2	52.5	44.4	43.0	52.4
OPP	30.0	52.3	65.7	77.9	66.0	73.0	75.6	58.8	77.5	53.5	63.8	53.2
OPE	47.9	96.4	76.3	22.1	43.0	61.5	55.6	49.9	49.3	47.0	42.0	50.0
MOG	32.0	76.6	38.0	61.0	31.5	61.0	49.2	58.9	67.0	45.4	51.1	61.0
ASJ	36.8	47.4	50.6	30.4	36.5	47.2	66.4	41.1	50.5	48.2	44.3	44.2

Appendix 32: Concentrations of lead (μg/g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.10	0.01	0.20	0.10	0.01	0.01	0.01	0.01	0.10	0.10	0.01	0.01
OSI	0.60	0.01	0.20	0.10	0.32	0.23	0.01	0.10	0.10	0.10	0.10	0.01
OUN	0.20	0.10	0.21	0.30	0.20	0.01	0.20	0.01	0.10	0.09	0.10	0.01
ARE	0.01	0.01	0.30	0.20	0.32	0.30	0.01	0.01	0.10	0.01	0.10	0.01
ASS	0.10	0.18	0.21	0.01	0.01	0.80	0.01	0.10	0.10	0.10	0.10	0.01
IRE	0.30	0.01	0.20	0.01	0.32	0.01	0.21	0.08	0.10	0.01	0.01	0.01
ANN	0.20	0.01	0.40	0.10	0.10	0.20	0.01	0.10	0.10	0.10	0.10	0.01
AHO	0.80	0.10	0.30	0.10	0.01	0.20	0.01	0.11	0.10	0.01	0.01	0.01
ENJ	0.10	0.01	0.40	0.01	0.01	0.01	0.01	0.01	0.20	0.10	0.01	0.01
OLO	0.10	0.01	0.30	0.20	0.01	0.23	0.30	0.11	0.10	0.01	0.10	0.01
GBD	0.10	0.01	0.30	0.01	0.20	0.01	0.21	0.01	0.10	0.01	0.10	0.01
AWE	0.40	0.01	0.50	0.01	0.01	0.10	0.01	0.10	0.10	0.01	0.01	0.01
OJU	0.10	0.01	0.20	0.01	0.20	0.01	0.01	0.10	0.10	0.01	0.01	0.01
OSU	0.10	0.01	0.20	0.10	0.20	0.01	0.01	0.10	0.20	0.01	0.20	0.01
YEY	0.04	0.01	0.30	0.01	0.01	0.10	0.01	0.30	0.20	0.01	0.20	0.10
ONN	0.10	0.01	0.42	0.10	0.01	0.01	0.01	0.24	0.20	0.10	0.10	0.01
OLU	0.04	0.10	0.21	0.20	0.20	0.23	0.01	0.30	0.30	0.10	0.01	0.01
ORU	0.01	0.01	0.10	0.10	0.01	0.10	0.01	0.01	0.20	0.01	0.10	0.01
KAN	0.10	0.01	0.10	0.30	0.01	0.01	0.01	0.01	0.10	0.01	0.01	0.01
ADE	8.60	21.0	39.0	10.0	4.40	70.0	63.0	0.34	0.41	0.20	0.01	0.01
EJI	0.04	0.01	0.90	0.01	0.20	0.01	0.01	0.20	0.10	0.10	0.01	0.01
ARO	0.01	0.01	0.10	0.10	0.01	0.10	0.01	0.01	0.10	0.10	0.01	0.01
ODD	0.10	0.01	0.42	0.01	0.32	0.01	0.01	0.01	0.11	0.01	0.01	0.01
OBB	0.04	0.18	0.21	0.19	0.20	0.01	0.10	0.10	0.10	0.10	0.20	0.01
OYK	0.04	0.20	0.60	0.01	0.20	0.01	0.01	0.30	0.10	0.01	0.01	0.01
ETI	0.01	0.18	0.30	0.01	0.32	0.01	0.01	0.10	0.30	0.01	0.01	0.01
ISA	0.30	0.18	0.40	0.10	0.01	0.1	0.01	0.23	0.20	0.01	0.10	0.01
OPP	0.21	0.20	0.70	0.10	0.32	0.01	0.01	0.10	0.20	0.10	0.10	0.01
OPE	0.20	0.39	0.90	0.10	0.01	0.23	0.01	0.10	0.20	0.09	0.10	0.01
MOG	0.20	0.10	0.10	0.10	0.20	0.01	0.01	0.11	0.10	0.1	0.01	0.01
ASJ	0.40	0.10	0.20	0.01	0.32	0.01	0.01	0.11	0.10	0.01	0.01	0.01

Appendix 33: Concentrations of copper (μg/g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.01	0.10	0.10	0.10	0.08	0.01	0.01	0.10	0.08	0.10	0.03	0.03
OSI	0.03	0.10	0.10	0.10	0.10	0.10	0.17	0.10	0.08	0.40	0.03	0.03
OUN	0.01	0.06	0.10	2.20	0.08	0.01	0.10	0.10	0.20	0.26	0.20	0.06
ARE	0.01	0.10	0.10	0.10	0.08	0.01	0.17	0.10	0.08	0.06	0.03	0.03
ASS	0.01	0.30	0.17	0.70	0.08	0.05	0.20	0.10	0.10	0.30	0.30	0.05
IRE	0.01	0.03	0.10	0.30	0.10	0.07	0.01	0.08	0.10	0.20	0.20	0.03
ANN	0.30	0.03	0.40	0.50	0.08	0.04	0.04	0.10	0.30	0.20	0.10	0.06
AHO	1.20	0.17	0.30	0.10	0.10	0.05	0.01	0.23	0.10	0.20	0.10	0.10
ENJ	0.02	0.03	0.10	0.03	0.08	0.10	0.09	0.08	0.20	0.20	0.10	0.03
OLO	0.02	0.10	1.80	0.40	0.01	0.05	0.01	0.10	0.03	0.03	0.10	0.03
GBD	0.01	0.40	1.00	1.90	1.60	0.03	0.10	0.20	0.20	0.09	0.20	0.01
AWE	0.01	0.08	0.25	0.70	0.01	0.01	0.01	0.25	0.17	0.10	0.03	0.06
OJU	0.01	0.08	0.08	0.20	0.01	0.01	0.01	0.01	0.08	0.20	0.10	0.06
OSU	0.01	0.03	0.13	0.40	0.01	0.03	0.01	0.01	0.25	0.06	0.40	0.03
YEY	0.01	0.08	1.30	0.40	0.01	0.01	0.01	0.50	0.25	0.10	0.10	0.03
ONN	0.10	0.08	1.20	0.10	0.01	0.05	0.01	0.20	0.30	0.20	0.40	0.20
OLU	0.01	0.03	0.10	0.60	0.10	0.05	0.10	0.10	0.30	0.10	0.30	0.03
ORU	0.01	0.03	0.20	0.50	0.01	0.03	0.01	0.08	0.30	0.10	0.20	0.03
KAN	0.01	0.30	0.30	2.20	0.01	0.05	0.01	0.01	0.10	0.10	0.03	0.10
ADE	3.80	5.00	11.6	12.0	8.60	6.40	24.0	0.10	0.10	0.80	0.10	0.10
EJI	0.01	0.03	0.30	0.03	0.10	0.10	0.01	0.08	0.25	0.20	0.12	0.03
ARO	0.01	0.10	0.90	0.20	0.10	0.01	0.09	0.08	0.30	0.20	0.03	0.03
ODD	0.01	0.03	0.20	0.03	0.10	0.05	0.01	0.01	0.20	0.10	0.03	0.10
OBB	0.01	0.10	0.20	0.03	0.10	0.01	0.10	0.20	0.10	0.06	0.12	0.10
OYK	0.01	0.08	0.10	1.90	0.01	0.01	0.01	0.01	0.30	0.10	0.10	0.03
ETI	0.01	0.03	0.10	0.10	0.01	0.01	0.10	0.01	0.50	0.10	0.10	0.03
ISA	0.02	0.10	1.30	0.50	0.01	0.03	0.10	0.40	0.20	0.10	0.12	0.04
OPP	0.70	0.60	1.60	0.20	0.08	0.05	0.01	0.01	0.17	0.30	0.10	0.03
OPE	0.10	2.70	5.40	0.50	0.01	0.05	0.10	0.20	0.30	0.18	0.03	0.10
MOG	0.10	1.60	0.30	1.20	0.01	0.10	0.01	0.10	0.10	0.10	0.10	0.10
ASJ	0.07	0.03	0.38	0.70	0.08	0.01	0.01	0.01	0.06	0.06	0.03	0.03

Appendix 34: Concentrations of cadmium (µg/g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.20	0.01	0.1	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OSI	0.30	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OUN	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ARE	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ASS	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
IRE	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ANN	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
AHO	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ENJ	0.40	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OLO	0.20	0.01	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
GBD	0.29	0.01	0.01	0.30	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
AWE	0.01	0.01	0.01	0.20	0.01	0.01	0.01	0.25	0.01	0.01	0.01	0.01
OJU	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OSU	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
YEY	0.01	0.01	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ONN	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OLU	0.10	0.01	0.01	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ORU	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
KAN	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ADE	0.30	0.14	0.20	0.50	0.10	0.10	0.17	0.01	0.01	0.01	0.01	0.01
EJI	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ARO	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ODD	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OBB	0.04	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OYK	0.01	0.01	0.01	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ETI	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ISA	0.01	0.10	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OPP	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
OPE	0.03	0.01	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MOG	0.20	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ASJ	0.01	0.01	0.01	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Appendix 35: Concentrations of cobalt (µg/g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.40	0.02	0.20	0.02	0.14	0.24	0.01	0.02	0.02	0.02	0.02	0.02
OSI	0.90	0.20	0.16	0.40	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.02
OUN	1.10	0.10	0.01	0.02	0.10	0.30	0.30	0.02	0.02	0.02	0.02	0.02
ARE	0.10	0.02	0.40	0.10	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
ASS	0.10	0.02	0.30	0.20	0.01	0.50	0.01	0.02	0.02	0.10	0.10	0.02
IRE	0.75	0.10	0.30	0.02	0.02	0.22	0.01	0.02	0.02	0.02	0.02	0.02
ANN	0.30	0.02	0.16	0.02	0.01	0.60	0.01	0.10	0.02	0.02	0.02	0.02
AHO	0.12	0.02	0.30	0.02	0.02	0.20	0.01	0.02	0.02	0.02	0.02	0.02
ENJ	0.10	0.02	0.10	0.02	0.20	0.01	0.01	0.02	0.02	0.02	0.02	0.02
OLO	0.02	0.02	0.30	0.02	0.02	0.22	0.01	0.02	0.02	0.02	0.02	0.02
GBD	0.29	0.01	0.01	0.30	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
AWE	0.10	0.02	0.30	0.02	0.01	0.10	0.01	0.10	0.02	0.02	0.02	0.02
OJU	0.10	0.10	0.20	0.02	0.10	0.01	0.01	0.10	0.02	0.02	0.02	0.02
OSU	0.02	0.02	0.10	0.02	0.02	0.01	0.01	0.10	0.02	0.02	0.02	0.02
YEY	0.02	0.01	0.02	0.10	0.02	0.01	0.01	0.02	0.10	0.02	0.02	0.02
ONN	0.10	0.02	0.30	0.10	0.01	0.40	0.01	0.02	0.02	0.02	0.02	0.02
OLU	0.10	0.10	0.30	0.02	0.10	0.22	0.01	0.10	0.02	0.02	0.20	0.02
ORU	0.02	0.02	0.10	0.02	0.01	0.10	0.01	0.02	0.10	0.02	0.02	0.02
KAN	0.19	0.02	0.30	0.02	0.01	0.22	0.01	0.02	0.02	0.02	0.02	0.02
ADE	0.50	0.50	0.16	0.10	0.50	0.30	3.00	0.02	0.02	0.10	0.14	0.02
EJI	0.30	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.20	0.02
ARO	0.20	0.20	0.30	0.02	0.14	1.80	0.01	0.02	0.02	0.02	0.02	0.02
ODD	0.10	0.02	0.40	0.02	0.14	0.20	0.01	0.02	0.02	0.02	0.02	0.02
OBB	0.90	0.20	0.10	0.10	0.01	0.22	0.10	0.02	0.02	0.10	0.02	0.02
OYK	0.10	0.02	0.30	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
ETI	0.02	0.02	0.16	0.02	0.01	0.22	0.01	0.02	0.11	0.02	0.20	0.02
ISA	0.60	0.02	0.30	0.20	0.01	0.01	0.01	0.02	0.10	0.02	0.02	0.02
OPP	2.50	0.30	0.01	0.02	0.01	0.01	0.01	0.02	0.10	0.10	0.10	0.02
OPE	0.02	0.02	0.10	0.02	0.01	0.4	0.10	0.10	0.02	0.02	0.02	0.02
MOG	0.20	0.20	0.30	0.02	0.01	0.10	0.01	0.02	0.02	0.10	0.02	0.02
ASJ	0.20	0.02	0.10	0.02	0.14	0.30	0.01	0.02	0.02	0.02	0.02	0.02

Appendix 36: Concentrations of chromium (μg/g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.03	0.10	0.01	0.10	0.01	0.01	0.01	0.03	0.03	0.03	0.03	0.03
OSI	0.50	0.03	0.01	0.03	0.01	0.01	0.01	0.11	0.06	0.10	0.03	0.03
OUN	0.50	0.10	0.01	0.10	0.13	0.01	0.10	0.11	0.10	0.11	0.10	0.03
ARE	0.03	0.30	0.10	0.03	0.01	0.01	0.01	0.22	0.03	0.11	0.19	0.03
ASS	0.35	0.02	0.30	0.20	0.01	0.50	0.01	0.02	0.02	0.10	0.10	0.02
IRE	0.18	0.10	0.01	0.02	0.01	0.01	0.20	0.03	0.03	0.22	0.10	0.03
ANN	0.20	0.10	0.04	0.10	0.13	0.01	0.01	0.10	0.10	0.2	0.03	0.10
AHO	0.13	0.03	0.01	0.10	0.01	0.01	0.01	0.10	0.03	0.10	0.03	0.03
ENJ	0.34	0.03	0.01	0.03	0.20	0.01	0.01	0.20	0.10	0.10	0.03	0.03
OLO	0.20	0.03	0.01	0.10	0.10	0.01	0.01	0.03	0.08	0.11	0.03	0.03
GBD	0.03	0.10	0.10	0.10	0.20	0.01	0.01	0.22	0.10	0.03	0.10	0.03
AWE	0.32	0.10	0.01	0.10	0.01	0.01	0.01	0.03	0.08	0.10	0.10	0.03
OJU	0.03	0.03	0.01	0.03	0.10	0.01	0.01	0.10	0.10	0.10	0.10	0.30
OSU	0.32	0.03	0.01	0.03	0.01	0.01	0.01	0.11	0.03	0.30	0.27	0.03
YEY	0.32	0.20	0.10	0.03	0.01	0.01	0.01	0.20	0.08	0.20	0.10	0.30
ONN	0.03	0.10	0.10	0.03	0.01	0.01	0.01	0.03	0.08	0.22	0.10	0.03
OLU	0.32	0.03	0.01	0.10	0.01	0.01	0.01	0.10	0.10	0.11	0.10	0.20
ORU	0.03	0.03	0.01	0.03	0.01	0.01	0.01	0.10	0.08	0.10	0.10	0.03
KAN	1.80	0.03	0.01	0.10	0.01	0.15	0.01	0.21	0.03	0.10	0.10	0.03
ADE	0.40	0.20	0.10	0.03	0.01	0.01	0.10	0.20	0.10	0.20	0.10	0.03
EJI	0.03	0.03	0.01	0.03	0.10	0.01	0.01	0.30	0.10	0.10	0.03	0.03
ARO	0.20	0.40	0.01	0.03	0.01	0.01	0.01	0.03	0.08	0.10	0.03	0.03
ODD	0.03	0.03	0.01	0.03	0.13	0.01	0.01	0.11	0.10	0.03	0.03	0.03
OBB	0.70	0.30	0.01	0.10	0.01	0.01	0.01	0.10	0.20	0.10	0.03	0.15
OYK	0.03	0.10	0.01	0.04	0.01	0.01	0.01	0.03	0.10	0.22	0.03	0.10
ETI	0.19	0.03	0.01	0.03	0.01	0.01	0.01	0.20	0.10	0.10	0.03	0.03
ISA	0.60	0.10	0.01	0.03	0.01	0.01	0.01	0.20	0.10	0.30	0.30	0.20
OPP	0.20	0.30	0.01	0.03	0.13	0.01	0.01	0.20	0.10	0.13	0.03	0.03
OPE	0.03	0.50	0.01	0.10	0.01	0.10	0.10	0.03	0.08	0.20	0.20	0.10
MOG	0.03	0.10	0.10	0.03	0.01	0.01	0.01	0.11	0.10	0.11	0.10	0.03
ASJ	0.03	0.10	0.01	0.03	0.01	0.01	0.19	0.03	0.20	0.10	0.10	0.03

Appendix 37: Concentrations of nickel in (μg/g) sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	0.11	0.27	0.40	0.40	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
OSI	0.10	0.70	0.40	0.20	0.01	0.15	0.01	0.02	0.02	0.10	0.02	0.02
OUN	0.04	0.50	0.10	0.10	0.20	0.01	0.20	0.02	0.02	0.10	0.02	0.02
ARE	0.07	0.60	0.40	0.02	0.01	0.15	0.01	0.02	0.02	0.02	0.02	0.02
ASS	0.20	0.27	0.24	0.10	0.01	0.20	0.01	0.02	0.02	0.20	0.02	0.02
IRE	0.39	0.01	0.02	0.01	0.02	0.01	0.22	0.03	0.02	0.02	0.02	0.02
ANN	0.30	0.50	0.30	0.20	0.10	0.10	0.01	0.02	0.02	0.10	0.02	0.02
AHO	0.11	0.20	0.40	0.02	0.01	0.01	0.01	0.02	0.14	0.02	0.02	0.02
ENJ	0.10	0.48	0.10	0.02	0.01	0.01	0.15	0.02	0.02	0.02	0.02	0.02
OLO	0.09	0.10	0.20	0.02	0.01	0.15	0.01	0.02	0.02	0.10	0.02	0.02
GBD	0.20	1.60	0.40	0.10	0.10	0.15	0.01	0.02	0.20	0.02	0.02	0.02
AWE	0.01	0.10	0.48	0.20	0.01	0.10	0.01	0.02	0.10	0.02	0.02	0.02
OJU	0.01	0.01	0.40	0.02	0.01	0.20	0.01	0.02	0.02	0.02	0.02	0.02
OSU	0.02	0.30	0.24	0.02	0.01	0.01	0.01	0.02	0.02	0.20	0.02	0.02
YEY	0.49	0.10	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
ONN	0.04	0.10	0.60	0.10	0.01	0.10	0.01	0.02	0.10	0.10	0.02	0.02
OLU	0.10	0.02	0.02	0.40	0.01	0.01	0.01	0.02	0.02	0.14	0.02	0.02
ORU	0.01	0.20	0.50	0.10	0.01	0.01	0.01	0.02	0.02	0.10	0.02	0.02
KAN	0.40	0.20	0.60	0.10	0.01	0.15	0.01	0.02	0.02	0.10	0.02	0.02
ADE	0.50	0.20	0.60	0.02	0.20	0.40	0.50	0.02	0.10	0.02	0.02	0.02
EJI	0.07	0.40	0.24	0.02	0.10	0.01	0.01	0.02	0.10	0.02	0.02	0.02
ARO	0.25	0.02	0.80	0.10	0.01	0.01	0.01	0.01	0.10	0.10	0.02	0.02
ODD	0.07	0.10	0.24	0.02	0.01	0.01	0.01	0.10	0.02	0.02	0.02	0.02
OBB	0.20	0.30	0.50	0.02	0.01	0.01	0.01	0.02	0.10	0.02	0.10	0.02
OYK	0.10	0.15	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
ETI	3.70	0.02	0.20	0.02	0.01	0.01	0.01	0.02	0.10	0.02	0.10	0.02
ISA	0.50	0.10	0.10	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.10	0.02
OPP	0.18	0.02	0.80	0.10	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
OPE	0.20	0.80	0.60	0.10	0.01	0.20	0.01	0.02	0.10	0.10	0.02	0.02
MOG	0.01	0.50	0.40	0.10	0.01	0.01	0.01	0.02	0.02	0.20	0.02	0.02
ASJ	0.11	0.50	0.40	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02

Appendix 38: Concentrations of zinc (μg/g) in sediment for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	28.9	7.10	25.7	5.60	0.80	0.70	0.20	1.20	1.10	7.50	0.70	5.60
OSI	60.0	17.0	43.0	10.0	0.50	20.10	0.70	7.20	5.50	12.8	2.80	5.00
OUN	8.10	4.60	11.4	9.60	2.10	0.14	0.60	3.50	2.40	16.0	0.99	4.70
ARE	58.0	0.30	50.1	23.0	0.50	3.50	0.22	2.00	2.10	6.40	0.90	7.30
ASS	75.6	39.0	22.0	27.0	0.40	15.30	0.60	1.20	3.90	11.5	1.50	4.30
IRE	46.6	7.00	27.9	9.00	0.50	4.80	0.54	4.70	2.20	10.7	2.80	4.40
ANN	64.9	29.0	32.9	11.7	0.70	1.50	0.30	2.70	4.40	10.4	2.90	3.30
AHO	109	3.70	54.0	22.0	0.80	9.79	0.20	1.60	0.14	16.3	2.80	4.90
ENJ	41.5	5.80	5.30	0.30	0.60	0.80	1.20	0.70	2.10	9.24	3.80	2.90
OLO	32.0	178	62.0	8.00	2.50	0.50	0.11	0.90	4.20	13.7	2.10	5.05
GBD	66.0	40.0	54.0	49.0	7.10	8.90	0.55	2.00	6.10	7.70	4.00	1.80
AWE	17.0	19.3	62.0	26.0	0.40	0.40	0.11	3.00	5.00	8.70	2.00	8.90
OJU	15.2	24.0	26.3	9.90	1.40	6.00	0.30	1.70	4.60	9.50	1.20	3.30
OSU	39.0	26.9	36.0	30.0	0.20	0.10	0.20	2.20	7.70	9.20	0.80	6.10
YEY	35.8	10.0	13.4	5.30	0.43	0.20	0.11	5.70	6.60	9.60	1.20	3.90
ONN	31.0	10.0	48.0	17.0	0.20	5.50	0.22	3.10	2.90	13.3	0.55	1.30
OLU	14.9	1.20	13.4	13.0	0.40	0.80	0.40	0.50	3.90	9.60	0.80	1.20
ORU	19.1	10.0	29.6	4.60	0.20	0.14	0.11	1.10	3.40	9.20	0.90	3.30
KAN	64.5	8.00	28.9	9.60	0.20	11.8	0.20	0.70	1.60	15.6	0.70	3.40
ADE	397	90.0	91.0	62.0	10.0	28.0	8.30	3.00	16.3	16.3	1.30	3.40
EJI	28.0	8.00	7.30	4.30	0.29	0.60	0.40	2.30	2.60	6.60	0.90	6.10
ARO	14.0	11.0	33.7	12.0	0.20	0.40	0.40	2.50	2.60	11.0	1.20	1.90
ODD	66.2	2.10	26.0	0.80	0.80	0.01	0.34	0.30	1.90	9.40	1.30	3.30
OBB	61.0	11.5	14.0	7.40	0.40	0.40	0.50	4.70	4.70	3.00	4.80	3.55
OYK	14.1	28.8	32.6	8.00	0.40	0.40	0.10	0.65	1.70	5.50	1.20	2.80
ETI	26.6	6.20	11.1	3.40	0.20	0.40	0.36	1.60	3.40	8.20	0.50	3.10
ISA	17.0	15.4	23.1	15.0	0.40	1.40	0.30	3.50	5.60	12.4	2.20	3.80
OPP	114	13.0	32.3	9.00	1.00	1.50	0.30	0.70	6.70	8.70	2.60	3.30
OPE	33.0	29.0	50.6	4.70	0.50	5.10	0.70	3.20	5.30	8.80	0.70	6.90
MOG	79.0	88.0	56.4	56.0	0.60	0.10	0.11	3.30	3.90	11.8	1.90	1.50
ASJ	60.1	19.0	25.0	11.0	0.50	0.14	0.60	0.70	8.50	9.60	1.10	0.02

Appendix 39: Concentrations of lead (μg/g) in plant for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	6.00	0.01	0.20	1.00	1.00	1.00	1.00	0.01	0.40	0.40	0.01	0.10
OSI	2.80	0.01	0.80	1.00	1.00	1.45	1.00	0.01	0.70	0.30	0.30	0.10
OUN	3.50	3.0	1.16	1.00	1.00	1.20	1.00	0.01	0.70	0.30	0.01	0.10
ARE	1.90	0.01	2.00	1.70	1.50	1.10	1.00	0.01	0.40	0.10	0.01	0.30
ASS	2.80	4.50	2.12	1.00	1.00	2.70	1.00	0.01	0.01	0.30	0.10	0.30
IRE	5.00	4.50	1.00	1.00	1.00	1.20	1.00	0.70	0.10	0.10	0.01	0.30
ANN	3.30	2.00	1.60	1.00	1.00	1.30	1.00	0.20	0.50	0.10	0.01	0.40
AHO	1.00	1.50	1.32	1.00	1.00	1.20	1.00	0.01	0.70	0.10	0.01	0.10
ENJ	2.70	0.01	1.00	1.00	1.00	4.10	1.00	0.70	1.60	0.10	0.30	0.10
OLO	2.09	0.01	1.00	1.10	1.50	1.20	1.00	0.70	0.10	0.32	0.86	0.10
GBD	1.29	1.50	2.00	1.18	1.00	1.20	1.00	0.01	0.70	0.10	0.01	0.34
AWE	1.20	0.01	1.00	1.00	1.50	2.00	1.00	0.40	0.10	0.10	0.30	0.57
OJU	2.10	3.00	0.80	1.00	1.00	1.20	1.00	0.40	0.40	0.10	0.01	0.30
OSU	2.88	1.50	1.20	1.10	1.00	1.45	1.20	0.01	0.10	0.40	2.70	0.30
YEY	2.10	0.01	3.30	1.00	1.00	3.3	1.00	1.10	0.65	0.60	0.90	0.10
ONN	1.29	0.01	1.00	1.18	1.00	1.20	1.00	1.41	0.40	0.10	0.30	0.30
OLU	1.80	1.50	1.20	1.00	1.00	2.91	1.00	0.40	1.00	0.80	0.01	0.10
ORU	1.20	4.50	2.00	1.00	1.00	1.20	1.00	0.01	0.10	0.10	0.60	0.90
KAN	1.00	4.50	1.00	1.00	1.00	2.60	1.00	0.01	0.10	0.30	0.30	0.10
ADE	3.10	3.00	2.00	1.70	1.00	2.20	1.00	0.70	0.70	0.30	0.01	0.10
EJI	2.30	0.01	1.00	1.10	1.00	1.20	1.00	0.40	0.10	0.10	0.80	0.10
ARO	1.20	0.01	1.00	1.00	1.00	1.00	1.00	0.01	0.01	0.60	0.01	0.30
ODD	1.20	1.50	1.32	1.00	4.50	0.90	1.00	0.01	0.40	0.10	0.01	0.10
OBB	1.20	0.01	1.00	1.00	1.00	1.00	1.00	0.40	0.65	0.30	0.01	0.10
OYK	1.90	0.01	2.00	1.00	1.00	2.00	1.00	1.10	0.10	0.10	0.30	0.10
ETI	1.00	0.01	1.00	1.10	1.00	1.00	1.00	0.01	0.40	0.10	0.01	0.30
ISA	1.90	1.50	1.32	1.10	1.00	2.00	1.00	1.10	1.00	0.10	0.30	0.10
OPP	1.20	3.00	1.32	1.00	1.00	2.60	1.00	0.01	0.65	0.30	2.27	0.30
OPE	1.20	0.01	1.32	1.00	1.00	1.00	1.00	0.01	0.40	0.10	0.01	0.57
MOG	1.29	0.01	1.20	1.10	1.00	1.00	1.00	0.70	0.70	0.30	0.30	0.10
ASJ	1.29	1.50	1.00	1.00	1.50	1.45	1.00	0.40	0.10	0.01	0.01	0.30

Appendix 40: Concentrations of copper (µg/g) in for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	2.08	2.60	0.30	0.01	0.01	0.76	0.80	0.80	1.10	0.40	0.30	0.10
OSI	3.10	0.01	0.30	0.20	0.30	0.01	0.80	0.01	2.90	0.30	0.01	0.10
OUN	1.50	2.60	0.30	0.20	0.01	0.40	0.50	0.01	2.60	0.90	2.18	0.30
ARE	1.00	0.90	17.6	0.50	6.00	7.90	0.80	0.01	0.30	0.80	0.01	1.40
ASS	1.00	3.50	2.60	6.10	0.01	0.01	0.80	0.53	0.52	0.80	0.10	0.80
IRE	2.08	0.01	0.10	0.20	0.01	1.00	0.80	0.80	2.40	2.50	1.10	0.10
ANN	1.40	0.60	5.60	0.30	0.01	0.01	0.50	1.10	1.90	0.10	0.90	4.60
AHO	2.60	2.60	0.01	0.01	0.01	0.01	0.10	0.53	0.80	0.30	1.10	0.60
ENJ	3.15	0.01	13.4	0.01	0.01	0.01	2.80	0.30	2.10	0.30	0.30	0.80
OLO	2.08	1.10	2.60	0.20	0.01	0.80	0.01	0.01	1.30	0.10	0.01	0.30
GBD	2.08	0.01	18.0	0.50	0.50	0.40	0.80	0.50	1.10	0.10	1.60	0.30
AWE	2.08	1.80	0.01	1.20	0.30	1.10	0.51	1.05	0.52	0.30	1.40	1.40
OJU	1.50	2.60	0.80	0.20	0.01	0.40	0.80	0.53	1.30	0.30	0.80	0.55
OSU	1.50	0.90	0.50	0.01	0.30	0.80	1.50	0.53	1.80	0.10	1.10	0.80
YEY	2.08	1.20	20.8	0.20	0.01	0.01	0.51	1.30	0.80	0.50	0.30	0.10
ONN	1.00	0.90	0.30	0.20	0.30	0.01	0.51	1.80	1.30	2.30	0.30	0.55
OLU	1.70	0.30	8.00	0.20	0.01	0.76	2.10	1.10	4.20	0.73	0.80	0.60
ORU	1.00	0.01	1.30	0.01	0.40	0.40	1.03	0.01	1.80	0.80	0.01	0.30
KAN	1.00	0.01	0.80	0.20	0.30	0.76	1.03	0.53	1.60	1.40	1.60	0.30
ADE	13.0	6.80	1.10	0.20	0.50	9.00	0.50	0.50	2.40	0.50	0.01	0.60
EJI	1.50	1.75	7.90	0.20	0.01	0.40	0.30	0.80	0.30	0.60	0.70	0.10
ARO	2.08	0.01	0.30	0.01	0.01	0.01	0.01	0.30	1.80	0.40	0.01	0.80
ODD	1.50	0.01	0.80	0.20	0.01	0.40	0.60	0.53	1.10	0.10	0.30	0.30
OBB	2.08	0.90	0.80	0.01	0.01	0.01	0.01	0.53	1.80	0.10	1.40	0.30
OYK	7.08	2.60	12.9	0.50	0.30	0.40	0.90	0.53	1.10	0.60	0.40	0.30
ETI	1.00	2.60	10.5	0.20	0.30	0.40	0.01	0.01	1.60	2.50	0.50	0.60
ISA	2.60	0.90	0.80	0.20	0.01	0.01	0.30	1.10	3.70	0.30	0.80	0.30
OPP	1.50	3.50	25.0	0.20	0.30	1.40	1.30	1.80	1.30	0.30	0.80	0.10
OPE	1.50	4.00	11.3	0.01	0.30	0.01	1.00	0.30	1.30	0.30	0.30	0.30
MOG	5.10	0.90	6.00	1.20	0.01	0.01	0.30	0.50	2.40	0.90	0.01	0.30
ASJ	4.12	0.01	15.3	17.4	0.20	0.01	0.51	0.53	2.10	0.10	0.01	0.30

Appendix 41: Concentrations of cadmium (µg/g) in plant for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 200	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OSI	1.00	3.10	1.10	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OUN	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ARE	1.00	0.01	1.00	1.00	1.30	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ASS	1.00	0.01	1.00	1.50	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
IRE	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ANN	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
AHO	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.10	0.01	0.10
ENJ	1.00	0.01	1.10	1.00	1.00	1.10	0.01	0.01	0.10	0.01	0.01	0.10
OLO	1.00	0.01	1.00	1.00	0.01	1.10	0.01	0.01	0.10	0.01	0.01	0.10
GBD	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
AWE	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OJU	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OSU	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
YEY	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ONN	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OLU	1.20	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ORU	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
KAN	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ADE	1.20	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
EJI	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ARO	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ODD	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.50	0.01	0.10
OBB	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OYK	2.00	0.01	1.10	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ETI	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ISA	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OPP	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
OPE	1.00	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
MOG	1.20	0.01	1.00	1.00	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10
ASJ	1.00	0.01	1.00	1.50	1.00	1.00	0.01	0.01	0.10	0.01	0.01	0.10

Appendix 42: Concentrations of cobalt (μg/g) in plant for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	1.00	0.01	1.00	1.00	1.00	1.35	1.54	1.30	0.69	0.10	0.01	0.10
OSI	3.10	9.92	0.01	1.00	1.02	2.20	1.54	0.01	0.10	0.10	0.01	0.10
OUN	1.50	7.40	1.02	1.00	1.50	1.00	1.00	0.50	0.10	0.10	0.01	0.10
ARE	5.20	0.01	2.60	1.00	2.10	2.00	1.00	0.01	0.10	0.40	0.01	0.10
ASS	1.00	7.40	0.01	1.20	1.00	2.50	2.30	0.01	0.10	0.10	0.01	0.10
IRE	4.20	0.01	0.50	1.00	1.00	1.86	2.30	0.01	0.40	0.10	0.01	0.10
ANN	1.70	1.70	1.70	1.00	1.00	1.20	1.70	0.30	0.30	0.10	0.01	0.60
AHO	2.08	7.40	0.01	1.00	1.00	1.20	1.00	0.01	0.10	0.10	0.01	0.10
ENJ	1.50	0.01	0.01	1.00	1.00	1.00	1.00	1.77	0.10	0.10	0.01	0.50
OLO	4.20	7.40	1.02	1.00	1.00	1.20	2.70	1.30	0.40	0.10	0.01	0.10
GBD	3.10	0.01	0.50	1.20	2.10	1.00	1.54	0.01	0.40	0.10	0.01	0.10
AWE	2.60	3.20	0.01	1.00	1.02	1.00	1.30	0.50	0.10	0.10	0.40	0.10
OJU	2.08	5.70	0.01	1.00	1.00	1.20	1.30	0.01	0.10	0.70	0.01	0.10
OSU	2.60	7.40	0.01	1.20	1.02	1.20	2.10	0.01	0.10	0.10	0.01	0.50
YEY	1.50	7.40	1.50	2.60	1.02	2.00	1.00	0.01	0.40	0.10	0.01	0.10
ONN	1.00	2.50	0.01	1.00	1.00	1.00	1.00	0.89	0.10	0.10	0.01	0.50
OLU	4.20	2.50	0.01	1.00	1.00	3.40	1.30	0.90	0.40	0.10	0.01	0.10
ORU	1.00	0.01	1.50	1.00	1.00	1.20	1.00	0.01	0.10	0.10	0.01	0.10
KAN	1.50	0.01	1.30	1.00	1.00	1.20	1.80	0.01	0.10	0.10	0.01	0.10
ADE	3.10	4.96	1.50	1.00	1.02	1.35	1.30	0.01	0.10	0.20	0.01	0.10
EJI	2.60	7.40	0.01	1.00	1.50	1.20	1.00	0.50	0.10	0.10	0.60	0.10
ARO	3.70	0.01	1.50	1.00	1.54	1.00	1.00	0.01	0.69	0.10	0.01	0.10
ODD	4.20	0.01	0.50	1.20	1.00	1.00	1.00	0.01	0.10	0.10	0.40	0.10
OBB	1.50	4.96	0.50	1.00	1.00	1.35	1.00	0.50	0.10	0.10	0.01	0.50
OYK	3.60	0.01	1.50	1.00	1.00	1.90	1.54	0.01	0.10	0.10	0.01	0.10
ETI	1.50	0.01	0.50	1.00	1.00	1.00	1.00	0.01	0.10	0.10	0.01	0.10
ISA	3.60	4.96	0.01	1.90	1.00	1.35	1.00	0.01	0.40	0.10	0.01	0.10
OPP	1.00	7.40	1.50	1.00	1.00	2.00	1.54	0.89	0.10	0.10	0.01	0.10
OPE	5.20	4.96	1.02	1.00	1.00	1.20	1.54	0.01	0.10	0.10	0.01	0.10
MOG	2.60	0.01	0.50	1.39	1.00	1.00	1.00	0.50	0.40	0.10	0.01	0.10
ASJ	4.20	0.01	1.02	1.00	1.00	1.10	2.90	0.01	0.10	0.10	0.01	0.01

Appendix 43: Concentrations of chromium (μg/g) in plant for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	3.60	0.01	0.01	0.01	1.00	1.20	1.80	1.00	1.66	0.10	0.40	0.10
OSI	1.00	4.70	1.00	0.01	1.90	0.01	1.00	0.01	0.10	1.40	0.03	0.10
OUN	3.60	3.79	0.30	0.01	1.00	1.00	1.00	0.70	1.30	0.70	2.80	0.10
ARE	1.00	0.01	0.80	0.01	1.00	2.40	1.00	0.01	0.10	0.10	0.40	0.10
ASS	1.00	0.01	0.01	0.01	1.00	0.50	1.00	0.69	0.83	0.40	0.10	0.10
IRE	1.00	4.70	0.01	0.01	1.00	0.50	1.00	0.01	1.30	0.40	0.02	0.10
ANN	1.00	1.90	0.70	0.01	1.60	0.60	1.00	0.70	1.10	0.30	0.30	1.40
AHO	1.00	4.70	0.80	0.01	1.90	0.50	1.00	0.01	0.10	0.10	0.03	0.40
ENJ	1.00	2.80	0.01	0.40	1.00	0.01	2.10	0.01	1.77	1.40	0.40	0.40
OLO	1.00	4.70	0.53	0.01	1.00	0.01	1.00	1.39	0.83	0.40	1.40	0.10
GBD	1.00	1.89	0.01	1.10	1.90	0.50	1.20	0.40	0.50	1.10	0.03	0.40
AWE	5.20	1.00	0.01	0.80	2.72	0.50	1.00	0.01	0.50	0.70	1.40	1.40
OJU	3.60	0.01	0.01	0.01	1.00	0.50	1.00	0.01	0.83	0.10	0.01	1.10
OSU	3.60	1.90	0.80	0.01	3.20	0.50	1.00	0.01	0.83	0.10	1.90	1.10
YEY	1.00	1.89	0.80	0.01	0.01	1.00	1.00	0.01	1.25	0.30	0.03	0.10
ONN	6.25	1.89	0.01	0.01	1.90	0.01	1.00	0.69	1.30	0.10	0.10	0.10
OLU	1.10	1.89	0.30	0.01	1.90	1.40	1.42	0.40	0.83	0.10	0.03	0.10
ORU	1.00	0.01	1.30	0.01	1.00	1.50	1.00	0.01	0.10	0.10	0.03	0.40
KAN	1.00	0.01	0.01	0.01	3.20	0.01	1.00	0.40	1.30	0.40	0.03	0.10
ADE	3.60	1.00	0.01	0.01	1.90	0.50	1.20	0.01	0.40	0.50	0.40	0.10
EJI	3.60	0.01	0.30	0.01	1.90	0.96	1.00	0.40	2.10	1.40	0.50	0.40
ARO	3.60	0.01	0.01	0.01	1.00	0.01	1.00	1.39	1.30	0.30	2.10	0.40
ODD	1.00	2.80	0.01	0.40	1.00	0.50	1.00	0.01	0.10	0.10	0.03	0.40
OBB	1.00	1.00	0.53	0.01	1.00	0.01	1.00	0.40	0.50	0.40	2.80	1.05
OYK	1.00	0.01	0.80	0.01	1.90	0.50	2.10	0.40	0.50	0.10	0.20	0.10
ETI	6.25	1.89	0.01	0.01	1.90	0.01	1.00	1.30	1.30	0.10	0.10	0.10
ISA	3.60	2.80	0.01	0.40	1.00	0.50	1.00	0.70	0.50	0.40	0.70	0.40
OPP	1.00	1.89	0.01	0.01	1.00	0.96	1.00	0.01	0.10	0.10	1.10	0.10
OPE	3.60	2.80	0.30	0.01	1.00	0.01	1.00	0.40	0.83	0.10	2.40	0.80
MOG	3.60	2.80	0.30	0.40	1.00	0.01	1.00	0.40	0.90	0.40	0.70	0.10
ASJ	1.00	2.80	0.40	0.01	1.00	0.50	1.00	0.01	1.30	0.10	0.03	0.10

Appendix 44: Concentrations of nickel (μg/g) in plant for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	1.46	0.01	5.20	1.00	0.01	0.01	0.01	0.01	0.10	0.10	0.40	0.10
OSI	1.20	5.00	1.20	1.00	0.01	0.01	0.01	0.01	0.10	0.10	0.70	0.10
OUN	1.20	5.00	1.20	1.00	0.50	0.01	0.01	0.40	0.50	0.50	0.02	0.10
ARE	1.00	3.40	3.70	9.00	0.01	0.95	1.40	0.01	0.50	0.10	0.02	0.10
ASS	3.00	5.00	7.40	6.50	0.01	0.50	0.01	0.01	0.10	0.10	0.02	0.10
IRE	2.00	0.01	1.00	1.70	0.01	0.01	0.01	0.01	0.10	0.10	0.01	0.10
ANN	1.80	3.36	3.10	1.00	0.3	0.01	0.60	0.01	0.10	0.10	0.02	0.30
AHO	1.00	5.00	0.50	1.00	0.01	0.01	0.01	0.87	0.50	0.10	0.02	0.10
ENJ	1.46	5.00	1.20	1.10	0.01	0.50	0.95	0.01	0.10	0.10	0.02	0.10
OLO	1.00	5.04	3.50	1.10	0.01	0.01	0.01	0.01	0.10	0.10	0.40	0.10
GBD	1.00	0.01	14.0	1.83	0.50	0.01	0.01	0.01	0.10	0.10	0.02	0.10
AWE	2.00	5.00	1.00	10.0	1.30	0.50	1.00	0.01	0.90	0.90	0.40	0.10
OJU	1.20	1.20	15.6	1.80	0.50	0.01	0.50	0.01	0.10	0.50	0.02	0.10
OSU	1.00	6.72	1.00	1.10	0.90	0.01	1.40	0.40	0.10	0.10	0.02	0.10
YEY	1.20	2.20	1.20	7.80	0.01	0.01	0.01	0.01	0.10	0.10	0.02	0.10
ONN	1.00	0.01	4.20	1.00	0.01	0.01	0.01	0.01	0.10	1.00	0.10	0.10
OLU	2.00	2.20	1.20	9.00	0.01	0.50	1.00	0.01	0.10	0.10	0.02	0.10
ORU	1.44	5.00	1.20	1.00	0.50	0.01	0.01	0.01	0.10	0.10	0.02	0.10
KAN	1.00	5.00	1.20	1.00	1.30	0.01	0.01	0.01	0.10	0.50	0.02	0.10
ADE	1.20	3.40	2.20	1.22	0.50	0.50	0.01	0.01	0.10	0.10	0.02	0.40
EJI	2.00	1.90	1.00	1.00	0.50	0.01	0.01	0.01	0.10	1.90	0.02	0.40
ARO	1.40	2.50	1.20	2.90	0.01	0.01	0.01	0.01	0.50	0.10	0.02	0.10
ODD	1.00	2.80	2.20	1.70	0.01	0.01	0.01	0.01	0.50	0.50	0.02	0.10
OBB	4.20	5.00	1.20	5.40	0.50	0.01	0.01	0.90	0.10	0.10	0.02	0.10
OYK	1.46	1.20	3.00	1.00	0.01	0.50	0.01	0.01	0.10	0.10	0.10	0.10
ETI	3.00	0.01	1.10	1.00	0.50	0.01	0.01	0.01	0.10	0.50	0.02	0.40
ISA	1.00	0.50	4.50	1.10	0.01	0.01	0.01	0.01	0.10	0.10	0.02	0.10
OPP	1.00	0.01	1.00	1.70	0.01	0.01	0.01	0.01	0.10	0.10	0.40	0.10
OPE	1.00	0.01	2.70	3.60	0.01	0.01	0.50	0.01	0.10	0.50	0.70	0.10
MOG	2.20	0.01	1.13	3.70	0.01	0.01	0.01	0.01	0.10	0.90	0.02	0.10
ASJ	1.20	0.01	2.20	3.40	0.90	0.01	0.95	0.10	0.10	0.02	0.02	0.10

Appendix 45: Concentrations of zinc (μg/g) in plant for all the locations

Sample Code	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
OYI	10.4	2.25	70.0	1.00	0.30	1.77	1.00	8.90	79.0	20.0	23.7	8.00
OSI	15.3	7.30	159	39.0	1.90	4.00	3.10	13.4	33.6	60.9	14.9	25.4
OUN	1.04	1.80	36.0	18.0	2.80	1.30	1.40	19.1	60.0	24.0	41.1	8.90
ARE	1.00	4.90	357	88.0	12.0	12.0	1.99	3.25	27.5	24.7	8.30	9.10
ASS	1.60	3.50	52.0	104	1.50	4.00	3.20	9.40	24.6	55.0	3.40	5.40
IRE	5.40	5.30	30.0	30.0	1.20	2.20	1.70	15.4	34.1	185	10.9	0.10
ANN	1.80	3.00	86.2	34.0	4.10	1.80	2.30	21.0	50.0	29.0	12.0	42.0
AHO	8.30	4.90	1.00	109	0.60	2.70	0.10	6.10	27.0	47.0	5.40	4.70
ENJ	32.7	2.30	140	59.0	0.30	0.89	4.60	11.8	66.0	59.6	3.40	6.00
OLO	15.6	4.90	2.70	64.0	0.90	0.89	4.50	30.9	56.0	49.3	4.30	5.70
GBD	11.0	2.30	240	162	3.07	0.89	1.70	18.3	47.0	34.0	48.0	15.0
AWE	11.7	5.08	14.3	165	3.70	1.80	3.10	8.10	43.0	36.0	10.3	32.8
OJU	1.90	5.10	322	87.0	2.20	1.30	3.10	9.40	53.0	17.0	6.00	8.00
OSU	9.30	6.30	163	151	3.70	1.80	5.80	26.0	66.0	48.0	6.50	7.70
YEY	8.20	2.82	211	81.0	0.60	2.20	1.70	15.0	103	31.0	11.7	6.00
ONN	2.50	4.60	3.60	56.0	2.80	1.80	1.70	3.30	33.0	79.0	17.0	5.10
OLU	2.90	2.80	103	46.0	1.50	3.10	6.60	14.0	81.0	21.0	30.0	15.0
ORU	1.05	4.00	5.40	6.40	0.90	1.30	0.01	28.4	36.0	18.0	8.80	47.0
KAN	1.60	5.30	65.2	18.0	4.60	2.20	4.46	8.10	62.4	77.0	2.60	23.4
ADE	64.0	7.80	277	207	8.90	24.0	7.54	13.8	26.0	15.7	12.0	14.8
EJI	1.20	0.90	353	83.0	1.90	0.89	3.10	20.0	73.0	88.0	1.70	15.0
ARO	1.04	4.90	170	58.0	0.90	0.89	1.37	7.70	4.00	49.8	11.7	4.00
ODD	5.40	1.10	4.50	35.0	0.01	0.89	3.10	3.30	33.0	51.0	4.00	12.0
OBB	11.1	2.10	209	137	19.0	0.89	0.69	15.0	69.0	25.3	19.0	13.1
OYK	4.90	2.90	365	19.0	3.40	1.30	0.40	3.70	21.0	46.2	2.00	19.7
ETI	2.00	3.50	146	26.0	3.40	0.89	0.40	15.0	31.0	134	2.20	6.90
ISA	3.10	2.90	35	200	1.84	1.77	2.10	19.0	77.0	40.0	2.00	17.1
OPP	4.50	2.33	258	1.20	0.60	5.80	10.0	6.10	13.0	22.8	15.4	0.60
OPE	31.9	3.90	140	16.0	2.80	1.80	2.06	13.4	67.0	81.0	12.0	14.9
MOG	22.0	3.00	184	197	0.90	1.80	2.40	16.0	54.0	31.0	5.10	10.9
ASJ	3.70	5.30	201	89.0	1.20	1.30	3.40	6.10	53.5	17.9	33.0	5.10

Appendix 46: Physicochemical properties of surface water obtained from control sites (Egun)

Parameter	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
EC (µS/cm)	67.8	87.5	139	181	177	10.6	69.1	48.2	92.1	131	143	62.2
pH	8.1	7.9	7.9	7.6	7.5	7.8	7.7	7.5	7.5	7.6	7.6	7.3
TS (mg/L)	150	196	230	233	246	291	280	133	334	252	178	299
TDS (mg/L)	33.5	73.5	91.0	99.5	56.0	82.5	63.2	51.5	61.5	37.7	61.6	28.2
TSS (mg/L)	117	122	139	133	190	209	217	81.0	274	214	280	271
Turbidity (FTU)	13.6	10.4	14.7	12.1	8.25	14.3	14.9	9.85	6.85	7.25	9.35	13.8
Alkalinity (mg/L)	55.3	85.4	91.7	94.5	91.7	57.1	56.2	27.4	50.9	99.6	53.8	31.5
Hardness (mg/L)	28.0	32.5	32.7	74.5	133	39.2	58.1	53.1	47.6	60.7	129	43.0
Temperature (°C)	25.9	27.6	29.8	30.0	29.5	27.4	28.1	24.0	27.2	28.0	27.7	24.7
Nitrate (mg/L)	0.53	0.66	1.03	1.11	0.81	0.40	0.98	0.60	0.54	0.60	0.20	0.39
Sulphate (mg/L)	30.2	36.7	35.7	53.7	39.1	27.9	28.7	43.5	34.4	31.0	30.8	33.8
Phosphate (mg/L)	0.02	0.03	0.04	0.04	0.05	0.04	0.06	0.11	0.04	0.09	0.06	0.04
Chloride (mg/L)	32.4	30.4	37.8	38.2	32.7	42.0	41.7	30.2	28.5	36.1	29.7	18.2
Ammonia (mg/L)	1.12	1.12	1.62	1.21	2.23	1.41	2.17	1.94	1.29	0.96	1.77	1.25
DO (mg/L)	6.55	6.90	6.55	6.45	5.67	8.25	7.91	8.83	6.56	5.50	5.91	7.72
BOD (mg/L)	0.60	1.55	3.15	4.00	7.72	4.97	3.67	4.75	4.77	6.17	3.27	3.85
COD (mg/L)	94.6	111	106	122	86.2	70.4	65.0	155	127	138	69.8	66.6

Appendix 47: Concentration of heavy metals (mg/L) in surface water of control sites

Parameter	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
Pb	0.001	0.002	0.001	0.003	0.001	0.03	0.001	0.001	0.001	0.001	0.002	0.001
Cu	0.01	0.001	0.01	0.001	0.002	0.003	0.002	0.01	0.002	0.001	0.002	0.001
Cd	0.001	0.001	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Co	0.002	0.001	0.01	0.01	0.001	0.01	0.001	0.001	0.01	0.003	0.001	0.003
Cr	0.01	0.001	0.01	0.01	0.001	0.001	0.002	0.003	0.003	0.002	0.001	0.001
Ni	0.03	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Zn	0.02	0.21	0.09	0.02	0.02	0.003	0.01	0.11	0.14	0.18	0.07	0.07
Ca	19.0	16.8	12.3	36.3	97.1	26.6	44.0	23.3	23.4	16.6	70.3	27.8
Mg	2.23	2.83	4.96	9.29	8.76	3.06	3.43	7.23	5.88	10.7	14.3	3.71

Appendix 48: Physicochemical characteristics and heavy metals in sediments of control sites

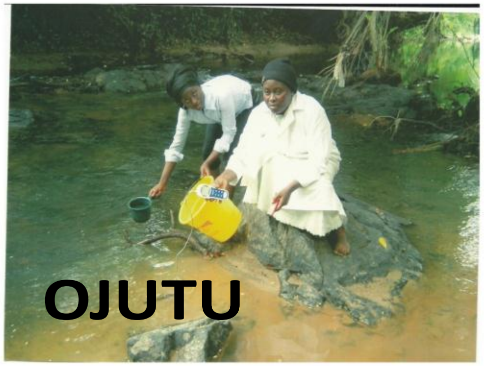
Parameter	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
Org. Carbon %	0.21	0.21	0.40	0.46	0.46	0.30	1.19	1.15	0.96	0.96	0.96	1.00
Sand (%)	71.7	72.6	69.0	73.1	70.5	70.2	70.9	69.1	73.0	76.1	74.3	70.6
Clay (%)	22.2	21.0	26.2	25.4	25.6	27.7	27.3	30.3	24.4	23.3	25.0	27.8
Silt (%)	3.73	6.50	4.85	1.60	4.00	2.15	1.82	0.65	2.70	0.70	0.75	1.60
CEC (meq/100g)	44.1	37.3	34.4	44.2	40.9	38.1	60.5	50.9	63.9	44.1	65.6	50.4
Pb (µg/g)	0.16	0.10	0.16	0.17	0.32	0.07	0.11	0.11	0.17	0.05	0.01	0.01
Cu (µg/g)	0.21	0.10	0.21	0.12	0.08	0.03	0.09	0.13	0.17	0.18	0.13	0.01
Cd (µg/g)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Co (µg/g)	0.25	0.08	0.09	0.08	0.08	0.12	0.01	0.08	0.02	0.02	0.02	0.02
Cr (µg/g)	0.03	0.07	0.01	0.01	0.13	0.01	0.10	0.07	0.12	0.17	0.08	0.03
Ni (µg/g)	0.48	0.35	0.36	0.01	0.01	0.08	0.76	0.02	0.02	0.16	0.02	0.02
Zn (µg/g)	19.7	21.9	27.9	0.57	0.95	3.3	0.87	3.45	6.67	9.50	1.77	6.22

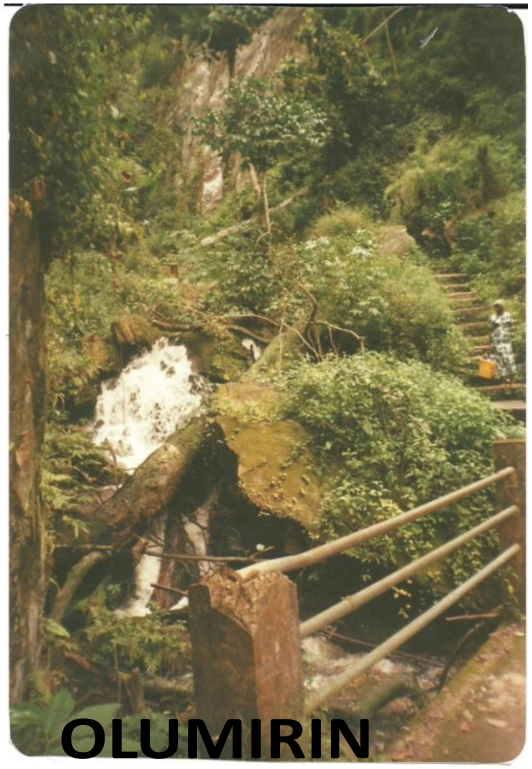
Appendix 49: Concentrations of heavy metals (µg/g) in plants of control sites

Parameter	July 2006	September 2006	November 2006	January 2007	March 2007	May 2007	July 2007	September 2007	November 2007	January 2008	March 2008	May 2008
Pb	1.15	0.01	1.16	1.00	1.00	1.23	1.00	1.00	1.00	0.77	0.29	0.01
Cu	2.60	2.63	0.53	0.48	0.01	0.39	0.77	0.79	2.62	0.33	0.87	0.33
Cd	1.54	0.01	1.00	1.00	1.00	1.38	0.01	0.01	0.01	0.01	0.01	0.10
Co	1.00	2.49	0.52	1.20	1.02	1.18	1.89	0.45	0.35	0.10	0.01	0.10
Cr	1.00	1.89	0.14	1.14	1.86	0.49	0.98	0.35	0.87	0.28	0.48	0.40
Ni	1.23	1.69	1.24	1.72	0.45	0.01	0.48	0.44	0.10	0.10	0.35	0.10
Zn	8.30	6.54	54.5	106	6.14	2.66	7.21	11.8	51.1	52.5	42.8	6.60

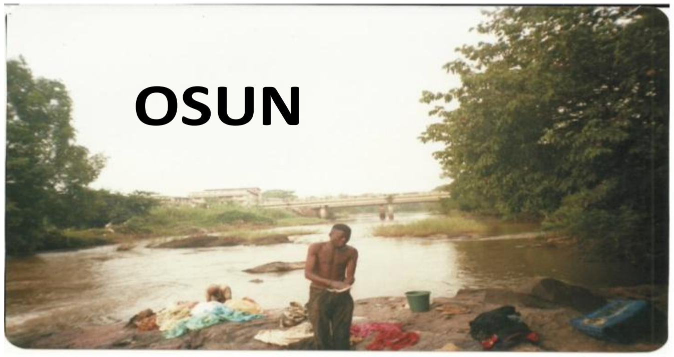
Appendix 50: Description of sampling locations at Adeti, Oyika and Anne

Appendix 51: Description of sampling locations at Ojutu, Gbodofon and Olumirin

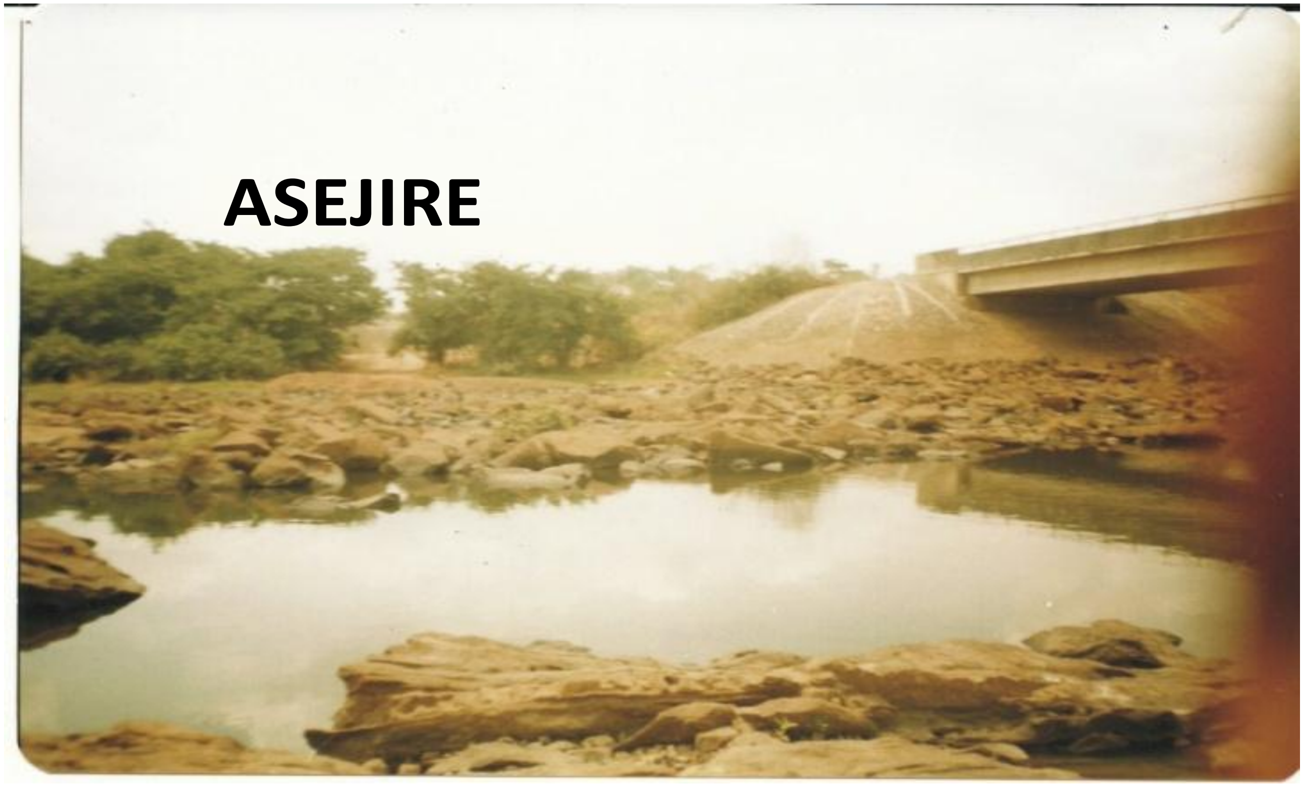




Appendix 52: Description of sampling locations at Osun, Yeyekare and Olumirin



Appendix 53: Description of sampling location at Asejire



LIST OF ACRONYMS/ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
APHA	American Public Health Association
AWWA	American Water Works Association
BOD	Biochemical Oxygen Demand
CBSQG	Concensus Based Sediment Quality Guidelines of Wisconsin
CECe	Effective Cation Exchange Capacity
COD	Chemical Oxygen Demand
Conc.	Concentration
DO	Dissolved Oxygen
EEC	European Economic Community
ERL	Effect Range Low
ERM	Effect Range Medium
FMHE	Federal Ministry of Health and Environment
FTU	Formazin Turbidity Unit
NCSS	Number Cruncher Statistical System
PCA	Principal Component Analysis
SON	Standard Organization of Nigeria
SPSS	Statistical Package for Social Sciences
TDS	Total Dissolved Solids
TS	Total Solid
TSS	Total Suspended Solid
USEPA	United State Environmental Protection Agency
UV/Visible	Ultraviolet/Visible
WHO	World Health Organization
WPCF	Water Pollution Control Federation