KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

KUMASI

COLLEGE OF SCIENCE

IMPACT OF OIL REFINERY EFFLUENT ON THE WATER QUALITY:

CASE STUDY OF EKERIKANA CREEK IN NIGERIA

A Thesis Submitted to the Department of Environmental Science, of the Kwame Nkrumah University of Science and Technology in Partial Fulfilment of the Requirements for the Degree of Master of Science (Environmental Science)

By

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DECLARATION

I, Anaero-Nweke George N. hereby declare that this submission is my own work towards the MSc Environmental Science and that, to the best of my knowledge it contains no material previously published by another nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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ABSTRACT

Over the years Ekerikana creek in Okrika Local Government Area of Nigeria has served as the recipient water body where refinery effluents are discharged. The level of chemical contaminant in the treatment refinery waste water has always been a controversy. In the same way the level of impact of these discharges on the adjoining river has been a cause of worry to the community. A study was conducted on Ekerikana creek and its adjourning river to determine the impact of refinery effluent on the water quality. Standard methods were used to determine the physicochemical parameters of Refinery effluent and the effluent receiving river water bodies at four selected sites; Refinery effluent (S1), Point of Discharge (S2), Upstream river water (S3), and Downstream river (S4). The results obtained indicated that the physicochemical parameters of refinery effluent and river water bodies varied significantly ($P<0.05$). Parameters such as turbidity, Biochemical Oxygen Demand, Chemical Oxygen Demand, phosphate, ammonia, phenol, lead, cyanide, nickel and total coliform were all above maximum permissible limit as specified by Environmental Standards and Guidance for the Petroleum Industries in Nigeria (EGASPIN) in all stations while Parameters such as pH, temperature, sulphide, cyanide, vanadium, copper and zinc were all below permissible limit in all stations. Other parameters such as total suspended solids, total dissolved solids, and total chromium were above permissible limit in the river water than in the refinery effluent. However the concentration of heavy metals analysed on sediment samples in the river water were higher than the river water sample while other parameters were below permissible limit. Phytoplankton distribution and abundance among the sampling stations were very poor. A total of 40 taxas were recorded with 3 families namely; Bacillariophceae, Cyanobacteria and Chlorophyceae with Bacilliarophyceae dominating the entire phytoplankton distribution. Benthic organism distribution and abundance amongst the sampling stations were also very poor, a total of six species from the family Nereidae were recorded namely; *Leonates decipiens*, *Dendronereis arborifera*, *Lopdorhynchus ucinatus*, polycheate larvae, *Capitella capitata* and *Arenicola spp*. It was established from the results of this study that the refinery discharges had negative impact on the creek and adjoining river water qualities. Hence, extraction of water from these rivers for domestic and agricultural purposes requires some forms of physical and chemical treatment.

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LIST OF ABBREVIATIONSAND ACRONYMS

API: American Petroleum Institute

ARM: Artificial Refinery Mixture

APHA: American Public Health Association

$AgNO_3$: Silver nitrate

AAS: Atomic Absorption Spectrophotometer

Al^{3+}: Aluminium ion

BOD: Biological Oxygen Demand

COD: Chemical Oxygen Demand

CO_2: Carbon dioxide

Cr: Chromium

DO: Dissolved Oxygen

EROD:Ethoxyresorufin-O-deethylase

E_1: Untreated effluent

E_2: Treated effluent

EGASPIN: Environmental Guardians and Standard for Petroleum Industries in Nigeria

FAO: Food and Agriculture Organisation

$Fe(NH_4)_2\ SO_4$: Ferrous Ammonium Sulphate

$Fe(CN)_6$: Ferri cyanide

HF: Hydrogen Flouride

HCO^-_3 : Bicarbonate

H^+: Hydrogen

H_2SO_4: Sulphuric Acid

HNO_3: Nitric Acid

$KBr0_3$: Potassium Bromate

K_2HPO_4: Dipotassium Phosphate

K_2CrO_4: Potassium Chromate

$K_2Cr_2O_7$: Potassium dichromate

LC50: Median Lethal Concentration

LDH: Lactate Dehydrogenase

Mg^{2+}: Magnesium ion

NNPC: Nigerian National Petroleum Company

Na^+: Sodium ion

Ni: Nickel

NaOH: Sodium Hydroxide

$(NH_4)_2OH$: Ammonium hydroxide

O_2: Oxygen

OP: Observation Pond

PPM: Parts Per Million

PPB: Parts Per Billion

pH: Potential Hydrogen

Pb: Lead

PAHs: Polycyclic Aromatic Hydrocarbons

PSI: Pounds per Square Inch

SO_4^{2+}: Sulphate ion

S1: Refinery Station (site 1)

S2: Ekerikana Creek (site 2)

S3: Upstream river (site 3)

S4: Downstream river (site 4)

THC: Total Hydrocarbon Concentration

TDS: Total Dissolved Solids

TSS: Total Suspended Solids

TOC: Total Organic Carbon

CHAPTER ONE

1.0 INTRODUCTION

1.1Background to the Study

In the past, human and other animals enjoyed clean water and air, but industrial revolution in the 19th century and its perfection in 20th century, gradually caused air, water and soil to become polluted by the activities of man (Sadatipour *et al.*, 2004).

The high rise in production of industrial goods and services, coupled with the diverse sophistication in technology have led to tremendous increase in waste and other by-products. The interaction and impact of such waste with the immediate environment (ecosystem) creates pollution problems (Kanu and Achi, 2011).

In a more strict sense the indiscriminate discharge of untreated industrial and domestic wastes into the water-ways, spewing of thousands of tons of particulates and airborne gases into the atmosphere, the throw-away attitude toward solid wastes, and the use of newly developed chemicals without considering potential consequences have resulted in major environmental disasters. For instance the formation of smog in the Los Angeles area since the late 1940s and the pollution of large areas of the Mediterranean Sea have stood out as specific references (Kanu and Achi, 2011).

Nowadays, the level of environmental pollution has already risen to a critical scale that threatens and endangers the health and survival of humans and other living things. This situation has lead to loss of biodiversity of assorted species. The awareness on this has made some highly industrialized countries to device and adopt certain fundamental measures for the prevention of environmental pollution (Osibanjo *et al.*, 2011).

Pollution of the aquatic environment stem from different industrial sources / activities. The major activities in this regards includes but not limited to Oil and Gas resources development, siting manufacturing industries / factories along the coast of running waters, movements of vessels and other marine activities (Sangodoyi, 1991).The present situation and the worsen environmental status is worrisome. This calls for serious caution while tackling our social needs on earth.

Therefore, the environment resources around us should be exploited in such a reasonable way to provide our daily needs and at the same time not to be exposed to damage, loss of esthetics. By such a cautious approach, our future may be guaranteed (Kanu and Achi, 2011).

1.2 Problem statement

Refining of crude oil into petroleum products for energy is essential to human development. The industrial setting requires large volumes of process water which in the process need to be recycled to meet up the demand. Unavoidably large scale contamination by process chemicals / biological additives do occur. The contaminants constitute pollution if discharged into the immediate environment without treatment (Basheer *et al.*, 2011).

It is evident that both the waste water and process water are treated in a water treatment plant, but the level of treatment can only be ascertained through the analysis of the discharged effluent at different points of their exit into the adjoining environment (Osibanjo *et al.*, 2011).

Similarly, no matter how little the contaminants may be in the discharged waste water, the interactions of such residual chemical / biological contaminants with the existing physical environment at risk may subject the environmental composition therein to partial or outright pollution / loss of environmental esthetics (ie pollution) (Kanu and Achi, 2011).

Over the years Ekerikana creek in Okrika Local Government Nigeria has served as the recipient water body (environment) where the refinery effluents / run off are discharged.

The level of chemical contaminant in the treatment refinery waste water has always been a controversy. In the same way the level of impact of these discharges on the adjoining creek have always been a cause of worry to the community. It is therefore the main objective of this research to provide some valuable information on the status of the treated waste water and also the level of impact on the creek.

1.3 Objectives

The main objective of this study was to determine the impact of oil refinery effluent on the water quality of the Ekerikana river in Nigeria.

1.4 Specific objectives

The specific objectives of this project include to:

- Determine the composition of the effluent from the Port-Harcourt refinery.
- Analyse the physico-chemical parameters on the treated effluent from waste water treatment plant, untreated effluent from oily pond and observation pond (outlet effluent).
- Analyse the effluent at the Point of Discharge into the creek.
- Analyse river water from Upstream / Downstream from the discharge point of the refinery effluent.
- Analyse some physico-chemical parameters on sediments in each site.

- Determine the existence of flora and fauna in the rivers and discuss the overall impact of the observed results on the recipient ecosystem.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Water as resource for life on earth, has several unique properties that makes it an essential to support life. The water environment exists in form of running streams, marine and estuary, lakes/seasonal water bodies. These form natural habitat for a great diversities of fish species, worms (annelids), plants of all sizes and species, different classes and species of micro-organism. These species (flora and fauna) interact with one another and also with their immediate environment (water and mudflat/sediment) as well as the atmosphere for a balanced energy transfer / exchange (Nweke, 2002). These interactions are perfect when the environment is natural (ie without pollution).

It is good to also recall that estuaries and their interconnecting creeks are known to constitute great economic value to the immediate population. They serve as major source of dietary protein to man by way of supporting artesian fishery activities of local fishermen (Nweke, 2002). This occupational support, stem from the fact that such an ecosystem serves as major habitats for several fresh water and marine species.

Estuarine and coastal waters offer important services to human development (Nweke, 2002). One of such is the site for industrial operations which frequently require large volume of water. The water environment therefore serves as a receiver where large volumes of effluent waste waters are discharged.

The discharges of waste water go on in an unrestricted manner in some coastal environment without regards to their impact on the aquatic ecology. This is done with the view that water has the capacity of transferring substances from one point to another and allows interactions

to occur between solutes without the water been seriously affected (Nweke, 2002). This notion maybe misleading especially if we accept the fact that pollution is a gradual process. Therefore, allowing the toxicants to accumulate overtime may impose serious stress on the environment thereby causing harm or gradual elimination of some important sensitive flora and fauna (Nweke, 2002).

2.2 Petroleum-Hydrocarbon Pollution

The presence of petroleum hydrocarbon in water and sediments has been a major source of concern, especially as it affects the colonies of macro-invertebrate (Fish etc). There are informations in literature on the ambient levels of hydrocarbons in the surface benthic sediments of marine and aquatic environments subjected to various degrees of pollution (Emoyan *et al.*, 2008).

These studies used a synoptic approach to get the hydrocarbon distribution, which were achieved in each case by collection of samples in a given geographical area over a stated period. Ekweozor *et al.* (1989) reported the effect of hydrocarbon pollution on the distribution of mullet species along Elechi creek in Port-Harcourt, which showed that the total hydrocarbon concentration (THC) in water and sediment around the industrial jetty was significantly ($P<0.05$) higher than the other sites in Okrika, Rivers State of Nigeria throughout the sampling period. Benthic and Non-benthic organisms were affected physiologically as well as their attitudes such as their feeding habits and reproductive system (Nwabueze and Agbogidi, 2010).

Snowden and Ekweozor (1990), also reported that at spill-sites, there was a near total elimination of littoral in fauna and a highly significant oyster mortality, plus 30% oiling of mangrove prop roots and 32% oiling of seedling which resulted in partial defoliation and death of seedling with $500m^2$ area.

Heavy metals, phenolic substances and polycyclic aromatic hydrocarbons are considered to be the most toxic and carcinogenic component of crude oil and its related compound; however some microbes are resistant to such prevailing condition (Nwabueze and Agbogidi, 2010).

In the same vein, as cited in Port Maritime Protection (2013), it was found that many protozoan survived in an oil-polluted river but noted that the more sensitive species had been eliminated. Chindah (1998) concluded that the pollution of the upper new Calabar River had impacted on periphytonic photosynthesis in the oil-polluted water. In addition, photosynthetic activities of algae are known to be obstructed due to the exclusion of light by black oil colour (Port Maritime Protection, 2013). Port Maritime Protection (2013), also observed declining rates in phytoplantonic photosynthesis in oil-polluted water. Oxygen is also reported excluded from organisms following oil pollution (Port Maritime Protection, 2013). Obstruction of photosynthetic activities due to refined petroleum products was imminent in sensitive algae species such as diatoms, but not in less sensitive euglenoid. Camphuysen (1989) had also observed the toxic effects of oil on zooplanktons. Other marine organisms and the sediment environment are however not left out of the effects of pollution. It is relatively easy to monitor the effects of oil in water for instance, the number of oiled seabirds and mortality of littoral invertebrates. The effects become less easy to distinguish if components of oil passing through the water column become trapped in the sediment (Camphuysen, 1989).

Some water soluble fractions, particularly aromatic compounds are toxic to aquatic animals and plants. They are acutely lethal in concentrations of a few parts per million (ppm) and chronically lethal in sub-lethal concentrations in parts per billion (ppb), although plants and animals vary widely in their sensitivity (Piere, 1980). The water-soluble fractions depress phytoplankton photosynthesis, respiration and growth, kill and cause developmental

abnormalities in zooplankton and the young stages of many aquatic organisms. Eggs and young ones are more sensitive than adults, and crustaceans are more sensitive than most other groups (Nwabueze and Agbogidi, 2010).

Oil spills in water kill shellfish and finfish by its smothering actions. Ingested oil may interfere with fish nutrition. In shallow inshore sites contamination may persist for years (Chima, 2013). Oil on the surface of water may limit gaseous exchange, entangle and kill surface organisms and coat the gills of fishes. Birds at risk of oil pollution are those, which spend most of their time sitting on the surface of the water and gregarious water birds, which dive rather than fly up when disturbed (Chima, 2013).

When marine, shore and fresh water birds become very heavily oiled, the feathers lose their insulation against temperature losses or cannot act as water-proof covering or be used for flight and hence the birds drown and are washed ashore. When oiled birds preen their plumages they ingest some crude oil which was reported to affect absorption, cause haemolysis and disrupt osmotic regulation (Camphuysen, 1989). Oiling maybe teratogenic to birds (Camphuysen, 1989). When oil comes ashore it kills shore animals by smothering them, or if sufficiently fresh, it kills them because of its toxic constituents (Camphuysen, 1989)..

In the Funiwa-5 oil well blow out, Emoyan *et al.* (2008) observed total decimation of shell fish, polychaete worms and crustaceans in the mangrove area. Defoliation and death of Rhizophora racemosa occurred 2-3months after the spill in mangrove swamp (Orji *et al.*, 2012). The damage was due to smothering of the pneumatophores of mangroves, prop roots and attached fauna were killed (Orji *et al.*, 2012).

Akani *et al.* (2008) observed that when oil spillage occurs on land, such as the ejamah-ebubu oil spill incident near Eleme, Rivers state in 1970 which was not clean, farmlands and swamps were heavily impacted, the soils were no longer fit for farming and streams were no

longer being used for fishing. He also observed that the lighter and low molecular weight hydrocarbons had evaporated and inter-mediate heavier fractions had permeated into the soil. Orji *et al.* (2012) observed at oil spillage sites the soil farmlands in the immediate vicinity were completely oil-logged and all economic crops such as seedlings of yam and cassava were scorched to death and the farmlands remained barren ten months after the spill incident (Akani *et al.,* 2008).

Oil degrading bacteria in oiled soil became more abundant while nitrifying bacteria became reduced in number (Amadi and Braide, 2003). Groundwater may be contaminated by spilled crude oil. After 18months of the Funiwa-5 oil well blow-out, Emoyan *et al.* (2008) observed ground water contamination in coastal villages in Bayelsa State.

The inhabitants of the riverine area where petroleum exploration and exploitation were carried out are the most obvious victims of the environmental and socio-economic hardships that are associated with oil exploration and oil spillages.

2.3 Oil Refinery Pollution

Pollution of the aquatic environment occurs from many different sources including from oil refineries. Oil refinery effluents contain many different chemicals at different concentrations. The exact composition cannot however be generalised as it depends on the refinery and which units are in operation at any specific time. It is therefore difficult to predict what effects the effluent may have on the environment. In a typical crude oil (petroleum) refining system, waste water are commonly generated from the following:

- Production process
- Oily sewer water pond
- Ballast water release
- Sanitary waste water

- Chemical waste water
- Cooling towers
- Dimersol effluent from specially designed plant.

Each of these sections are essential in the refinery process. All the water generated are channelled into the waste water treatment chamber and thereafter into the observation pond before being discharged.

The operations of each of the above sections are summarized below:

2.3.1 Production Process

Petroleum refining process plants are grouped into 3-5 sections depending on the capacity and a waste water treatment plant is essential for the proper management of effluent.

The three vital components include:

- Crude distillation unit and or vacuum distillation unit
- Chemical / catalytic cracking treatment section which handles cracking
- Fractionization chamber where different forms of petroleum gases are produced. Though other units do exist but their relevance is outside the scope of this research.

All the generated petroleum products above are subjected to primary treatment inside the plant.

2.3.2 Oily Sewer Water

The oily sewer water (containment pond) consists of rain water, run off from oil contaminated paved areas, drain water from vessels, pumps and tanks. These are channelled down to oily pond where separation is done by an American Petroleum Institute (API) separator that separates oil from water.

In this process, oil is sent to ballast tank which is finally sent to waste water treatment plant for treatment and water is sent down to observation pond for discharge together with treated effluent.

2.3.3 Ballast Water

Ballast water tank contains oil from oily sewer pond and ballast water from jetty. These are channelled to waste water treatment unit for treatment before discharge into the environment.

2.3.4 Sanitary Water

The sanitary waste water consists of toilet effluents, kitchen effluent produced in the refinery which is also sent to waste water treatment unit.

2.3.5 Chemical Waste Water

The chemical waste water consists of laboratory waste water, spent chemicals and detergents from sour water, caustic treatment unit and dimineralized effluent.

The effluent produced from this section contains neutralized spent detergent (caustic) which in turn contains some phenol and monoethanolamine solution.

The contaminated process waste water from this section is sent to waste water treatment unit while the demineralised effluent is neutralized and sent to observation pond directly.

2.3.6 Water from Cooling Towers (clean water system)

Water from cooling towers are considered clean (ie free from chemical / biological contamination). They do not require further treatment in the water treatment plant according to some existing company policy and therefore were discharged directly into the observation pond.

This water comes directly from:

- Boiler Blow down and condensate
- Cooling Tower blow down
- Cooling Tower for HF-Alkylation blow down
- Raw water treater blow down and
- Clean water from process units.

The overall treated waste water from the water treatment plant and the volume coming from the untreated oily sewer pond are discharged into adjoining creek.

The total quantity of aqueous effluent that is being discharged by oil refineries has decreased over the years, for example European refineries discharged 3119×10^{6} t year $^{-1}$ from 80 refineries in 1969 reducing to 2543×10^{6} t year $^{-1}$ from 84 refineries in 2000. The decrease between 1974 and 1978 is thought to be due to more refineries using air cooling and recirculating cooling water systems (Concawe, 2004).

Over the years the complexity of refineries has increased and since 1969 there has been the introduction of more effective treatment systems. The three main treatment processes for effluent before its discharge are gravity separation (API separators, tank separation), advanced treatment (flocculation, sedimentation, filtration) and biological treatment (biofilters, activated sludge, aerated ponds) (Concawe, 2004). The percentage of refineries that have all three treatment processes has increased over the years from only 23%(of 82 refineries) in 1969 to 91% (of 84 refineries) in the year 2000 as not all refineries have the same processes, but the effluents that are produced will have different chemical compositions depending on the type of treatment they receive (Wake, 2005). Petroleum refinery waste water are made up of many different chemicals which include oil and greases, phenols

(creosols and xylenols), sulphides, ammonia, suspended solids, cyanides, nitrogen compounds and heavy metals like chromium, iron, nickel, copper, molybdenum, selenium, vanadium and zinc (Wake, 2005). Oil consists of five types of components, saturated non-cyclic hydrocarbons (paraffins), cyclic hydrocarbons (cycloalkanes), olefinic hydrocarbons (alkenes), aromatics and non-hydrocarbons (sulphur compounds, nitrogen-oxygen compounds and heavy metals) (Wake, 2005). Refinery effluents tend to have fewer of the lighter hydrocarbons than crude oil but more polycyclic aromatics which tend to be more toxic and more persistent in the environment (Wake, 2005).Since 1969, the amount of oil that is discharged in the refinery effluents of Europe has decreased from 44,000 t year $^{-1}$ from 73 refineries to 747 t year $^{-1}$ from 84 refineries in 2000. The discharge levels of ammonia and phenols have also reduced by 45% and 60%, respectively from 1993 to 2000.

Wake (2005) noted that the number of components in the original crude oil stock, plus the resultants from the fractionation process, plus any addition of chemical additives during the refinery operations determine the number of components in a wastewater. This means that each effluent is generally unique and can vary on a daily basis depending on which units within the refinery are in operation.

2.4 Fate of oil Refinery Effluent

The fate of oil refinery effluent once it is discharged into the environment depends on the conditions and hydrodynamics of the receiving water. The effluent is inevitably diluted within the receiving water but to what extent depends on the size of the recipient and where the outfall is located, whether it is intertidal or subtidal. Wake (2005) dyed the discharge water from an offshore operation and found that the discharge was unevenly distributed in the recipient waters.

Most studies on the fate of refinery wastes just consider the hydrocarbons within the effluent. The volatile compounds are lost from the water column through weathering (Wake, 2005).

The remaining compounds undergo sedimentation and biodegradation. The most important removal mechanism was sedimentation. In Southampton Water, 70% of the hydrocarbons were found in the sediments. Compounds with high water solubility such as aromatics were absorbed slower than non-polar aliphatic compounds. In Southampton water biodegradation occurred rapidly, hydrocarbon concentrations were reduced by 70% after 40 days, much faster than in other areas (Wake, 2005). The increased speed of biodegradation was attributed to the substantial population of oil degraders in the area that had accumulated over the 50 years of sustained discharge. Most of the hydrocarbons that are degraded are lower molecular weight aliphatic fractions. This means that over time hydrocarbon concentrations do decrease but due to the constant effluent discharge they are always being replenished. Therefore if the discharges were to cease or the hydrocarbon concentration within effluents were to be reduced then there is the potential for the hydrocarbon concentrations to decrease to lower levels within the sediment.

Around a petroleum refinery in the Gulf of Fos (South France) there were three zones of contamination of the sediment. Firstly a highly contaminated zone near the refinery (50 g kg^{-1} sediment dry weight), followed by a less contaminated zone in the deep creek (3g kg^{-1} sediment dry weight), with a final slightly contaminated zone in the open sea (0.1g kg^{-1} sediment dry weight). Other studies have also shown that the area of high contamination is often localised to the vicinity of the outfall and decreases with distance. The hydrocarbons seem to sediment out near to the discharge point (Wake, 2005).

There also seems to be a pattern of hydrocarbon distribution with depth but this varies depending on the history of the discharge and sedimentation rates of the area concerned. Wake (2005) observed that around the NesteOy's oil refinery in Finland the maximum concentration of oil was at 4–14 cm and that there seemed to be no further degradation at this depth. In Narragansett Bay it was discovered that the hydrocarbon concentration decreased

with depth and that with increasing depth a greater percentage of the oil was of biogenic origin (Wake, 2005). This would suggest that in this area degradation of the light fractions was occurring within the sediment leaving the heavier biogenic hydrocarbons, which could be due to a slow sedimentation rate. The pattern of the concentration of contaminants with depth of the sediment can also be linked to the history of the inputs to the area.

Cranthorne *et al.* (1989) found that at Kinneil in the Forth Estuary the aliphatic concentration increased with depth, which could be a reflection of the reduced hydrocarbon content of the effluent over the years. Wake, (2005) observed that in Southampton Water there was a distinct oil horizon within a core at 90–100 cm depth, which they attributed to the expansion of the oil refinery in this area in around 1950 and a subsequent reduction in discharges. This again shows that no generalisations can be made between different areas as to the fate of the components in the effluent.

2.5 Effects of oil Refinery Effluent

There are many different ways of testing the toxicity of different compounds but there are two main types of tests. Firstly, the acute lethal test which usually lasts 96 hours. The aim of this type of test is to find out the lethal concentration of a substance. Secondly, there are sub-lethal tests. These can take many forms but basically test for any sub-lethal reactions that a substance may cause a problem for the individual and / or the population over a long period of exposure (Wake, 2005).

Measurements of sub-lethal effects that are often used are respiration rate, growth rate, reproductive success and behavioural changes. Acute tests are the most common but sub-lethal tests are also important especially when looking at the impact of a chronic problem like refinery effluents. Many different species have been used to test for the toxicity of oil refinery effluents including species of fish, crustaceans, and algae.

The toxicity of oil refinery effluent is dependent on a number of factors. The volume, quality, salinity and variability of the discharge, the siting of the outfall, the physical and chemical conditions of the discharge area, the proximity of other effluents and pollutants, and the biological condition of the discharge area (Wake, 2005). Some of the different components of the refinery effluent such as pH, temperature, total dissolved solid, total suspended solids, turbidity, biological oxygen demand, phenol, ammonia, sulphides, nitrates and phosphate, phenol, total hydrocarbon concentration, heavy metals and faecal coliform can have varying effects and toxicities (Wake, 2005).

2.5.1 Effects of some physico-chemical parameters on water quality:

2.5.1.0 pH

Most freshwater lakes, streams, and ponds have a normal pH in the range of 6 to 8. Acid deposition has many harmful ecological effects when the pH of most aquatic systems falls below 6 and especially below 5 (Lenntech, 2013). Some effects of increased acidity on aquatic system are:

a) As the pH approaches 5, non-desirable species of plankton and mosses may begin to invade, and populations of fish such as smallmouth bass disappear.

b) Below a pH of 5, fish populations begin to disappear, the bottom is covered with undecayed material, and mosses may dominate near shore areas.

c) Below a pH of 4.5, the water is essentially devoid of fish.

d) Aluminium ions (Al^{3+}) attached to minerals in nearby soil can be released into lakes, where they can kill many kinds of fish by stimulating excessive mucus formation. This suffocates the fish by clogging their gills. It can also cause chronic stress that may not kill individual fish, but leads to lower body weight and smaller and makes fish less able to compete for food and habitat (Lenntech, 2013).

e) The most serious chronic effect of increased acidity in surface waters appears to be interference with the fish' reproductive cycle. Calcium levels in the female fish may be lowered to the point where she cannot produce eggs or the eggs fail to pass from the ovaries or if fertilized, the eggs and/or larvae develop abnormally (Lenntech, 2013).

Extreme pH can kill adult fish and invertebrate life directly and can also damage developing juvenile fish. Water pH level may cause the stripping of a fish of its slime coat and high pH level 'chaps' the skin of fish because of its alkalinity. When the pH of freshwater becomes highly alkaline (e.g. pH 9.6), the effects on fish may include: death, damage to outer surfaces like gills, eyes, and skin and an inability to dispose of metabolic wastes. High pH may also increase the toxicity of other substances. For example, the toxicity of ammonia is ten times more at a pH of 8 than it is at pH 7. It is directly toxic to aquatic life when it appears in alkaline conditions. Low concentration of ammonia is generally permitted for discharge (Lenntech, 2013).

2.5.1.1 Temperature

Changes in temperature affect aquatic life. Temperature determines which organisms will thrive and which will diminish in numbers and size. For each organism there is a thermal death point. Also, there is a range of temperature which produces optimal abundance. The effects of temperature upon life of a cold blooded or poikilotherm are profound. Poikilothermic animals, such as fish, are those whose body temperatures follow closely the temperature of their medium (Science Fair Water, 2013).These animals have coped with temperature problems in different ways. Not only the organism survival, but growth and reproduction of each organism have critical temperature preference ranges. Each organism must be favored by the proper temperature if the individual or its population is going to survive. For instance, temperature influences enzymatic reactions through hormonal and

nervous control to digestion, from respiration and osmo-regulation to all aspects of an organism's performance and behavior (Science Fair Water, 2013).

High and low temperatures that are lethal to individual organism of a species determines the distribution and abundance of its population. However, more often the distribution and abundance of populations is determined by less than lethal temperatures interacting with other environmental factors that either tend to favor or not to favor reproduction and growth.

Increased water temperature is an important consideration when toxic substances are present in water. Many substances (i.e. cyanides, phenol, xylene, zinc) exhibit increased toxicity at elevated temperatures. These toxicities and other physiological interactions are also influenced by temperature acclimation or history of the species. High temperature of receiving water has the following effects:

-Higher temperature diminishes the solubility of dissolved oxygen and thus decreases the availability of this essential gas

- Elevated temperatures increase the metabolism, respiration and oxygen demand of fish and other aquatic life, approximately doubling the respiration for each 10° C. rise in temperature. Hence the demand for oxygen is increased under conditions where oxygen supply is lowered.
-The solubility of many toxic substances is increased as well as intensified as the temperature rises

-Higher temperatures militate against desirable fish life by favoring the growth of sewage fungus and the purification of sludge deposits, and finally,

-Even with adequate dissolved oxygen, there is a maximum temperature that each species of fish or other organism can tolerate. Higher temperatures results in death of organisms. The

maximum temperatures that adult fish can tolerate vary with the species of fish, prior acclimatization, oxygen availability and the synergistic effects of other pollutants (Science Fair Water, 2013).

2.5.1.2 Total dissolved solids

Total Dissolved Solid (TDS) is a measurement of inorganic salts, organic matter and other dissolved materials in water. Water with total dissolved solids concentrations greater than 1000 mg/l is considered to be "brackish". Total dissolved solids cause toxicity through increases in salinity, changes in the ionic composition of the water and toxicity of individual ions. Increases in salinity have been shown to cause shifts in biotic communities, limit biodiversity, exclude less-tolerant species and cause acute or chronic effects at specific life stages (Phylis *et al.,* 2007). Phylis *et al.* (2007) found a significant and negative correlation between concentrations of chlorophyll-a (an estimate of primary production) and concentrations of Na^{+}, Mg^{2+}, SO_4^{2+}, HCO_3^{-} and CO_3^{2-} and also reported substantial changes in marsh communities. When TDS increased from 270 to 1170 mg/l, both coontail (*Ceratophyllum demersum*) and cattails (*Typha spp*.) were nearly eliminated. Salinity and aquatic biodiversity are inversely related in lake water (Phylis *et al.,* 2007). Changes in the ionic composition of water can exclude some species while promoting population growth of others (Phylis *et al.,* 2007).

2.5.1.3 Total Suspended solids

The term suspended solids refers to the mass (mg) or concentration (mg) of inorganic and organic matter, which is held in the water column of a stream, river, lake or reservoir by turbulence. Total suspended solids are typically comprised of fine particulate matter with a diameter of less than 62 mm (Bilotta and Brazier, 2008), though for the majority of cohesive solids, research has demonstrated that transport frequently occurs in the form of larger

aggregated flocs (Bilotta and Brazier, 2008). All streams carry some suspended solids under natural conditions. However, if concentrations are enhanced through, for example, anthropogenic perturbations, this can lead to alterations to the physical, chemical and biological properties of the water body. Physical alterations caused by Suspended Solids, SS. include reduced penetration of light, temperature changes, and infilling of channels and reservoirs when solids are deposited. These physical alterations are associated with undesirable aesthetic effects such as; higher costs of water treatment, reduced navigability of channels and decreased longevity of dams and reservoirs (Bilotta and Brazier, 2008). Chemical alterations caused by SS include the release of contaminants, such as heavy metals and pesticides, and nutrients such as phosphorus, into the water body from adsorption sites on the sediment. Furthermore, where the suspended solids have a high organic content; their in-situ decomposition can deplete levels of dissolved oxygen in the water, producing a critical oxygen shortage which can lead to fish kills during low-flow conditions (Bilotta and Brazier, 2008).

2.5.1.4 Turbidity

Turbidity is a measurement of how cloudy water appears. Technically, it is a measure of how much light passes through water, and it is caused by suspended solid particles that scatter light. These particles may be microscopic plankton, stirred up sediment or organic materials, eroded soil, clay, silt, sand, industrial waste, or sewage. Bottom sediment may be stirred up by such actions as waves or currents, bottom-feeding fish, people swimming, or wading, or storm runoff (Science Fair Water, 2013).

Clear water may appear cleaner than turbid water, but it is not necessarily healthier. Water may be clear because it has too little dissolved oxygen, too much acidity or too many contaminants to support aquatic life. Water that is turbid from plankton has both the food and

oxygen to support fish and plant life. However, high turbidity may be a symptom of other water quality problems. Turbidity however has the following effects on water bodies:

• Turbidity diffuses sunlight and slows photosynthesis. Plants begin to die, reducing the amount of dissolved oxygen and increasing the acidity (decaying organic material produces carbonic acid, which lowers the pH level). Both of these effects harm aquatic animals (Science Fair Water, 2013).

• Turbidity raises water temperature because the suspended particles absorb the sun's heat. Warmer water holds less oxygen, thus increasing, the effects of reduced photosynthesis. In addition, some aquatic animals may not adjust well to the warmer water, particularly during the egg and larval stages.

• Highly turbid water can clog the gills of fish, stunt their growth, and decrease their resistance to diseases (Science Fair Water, 2013).

• The organic materials that may cause turbidity can also serve as breeding grounds for pathogenic bacteria (Science Fair Water, 2013). When drinking water reservoirs are turbid, the water treatment plant usually filters the water before disinfecting it. Industrial processes and food processing, require clear water (Science Fair water, 2013).

2.5.1.5 Conductivity

Conductivity is a measure of the capability of a solution such as water in a stream to pass an electric current. This is an indicator of the concentration of dissolved electrolyte ions in the water. It doesn't identify the specific ions in the water. However significant increases in conductivity may be an indication that pollution discharges have entered the water. Every creek will have a baseline conductivity depending on the local geology and soils. Higher conductivity will result from the presence of various ions including nitrate, phosphate and sodium (Sharon, 1997).

2.5.1.6 Biological Oxygen Demand

"The amount of oxygen that would be consumed if all the organic materials in 1L of water were oxidized by bacteria and protozoa"(Food Science and Technology, 2012).

Micro-organisms such as bacteria/ protozoa are responsible for decomposing organic matters (Food Science and Technology, 2012). When organic matter such as plant material (leaves, dried grass) sewage, or even food waste is present in a water supply, the bacteria starts to break down this waste. In this process much of the available dissolved oxygen is consumed by aerobic bacteria, reducing the requisite amount of oxygen for the other aquatic organisms to live (Food Science and Technology, 2012).

It is the most commonly used parameter for determining the oxygen demand on the receiving water of a municipal or industrial discharge. BOD can also be used to evaluate the efficiency of treatment processes, and is an indirect measure of biodegradable organic compounds in water. If there is a large quantity of organic waste in the water supply, there will also be a lot of bacteria present working to decompose this waste through oxidation. In this case, the demand for oxygen will be high to fulfil the demand for oxidation process and aquatic organisms, so the BOD level will be high. As the waste is dispersed through the water, BOD levels will begin to decline. Phosphates and nitrates are plant nutrients and can help the plant life and algae to grow quickly. Phosphates and nitrates in a body of water can contribute to high BOD levels. Because, when plants grow quickly, they also die quickly. This contributes to the organic waste in the water, which is then decomposed by bacteria. This results in a high BOD level. When BOD levels are high, dissolved oxygen (DO) levels decrease because the demand for oxygen by the bacteria is high as dissolved oxygen in the water. If there is no organic waste present in the water, there would not be as many bacteria present to decompose it and thus the BOD will tend to be lower and the DO level will tend to be higher. At high BOD levels, organisms such as macro invertebrates that are more tolerant of lower dissolved

oxygen (i.e. leeches and sludge worms) may appear and become numerous. Organisms that need higher oxygen levels (i.e. caddis fly larvae and mayfly nymphs) may not survive. If increased levels of BOD lower the concentration of DO in a water body, there is a potential for effects on the water body itself, and the aquatic life. When the dissolved oxygen concentration falls below 5 mg/L, species intolerant of low oxygen levels become stressed. Eventually, species sensitive to low dissolved oxygen levels are replaced by species that are more tolerant of adverse conditions, significantly reducing the diversity of aquatic life in a given body of water. If dissolved oxygen levels fall below 2 mg/L for more than even a few hours, fish kills can result. At levels below 1 mg/L, anaerobic bacteria replace the aerobic bacteria. As the anaerobic bacteria break down organic matter, foul smelling hydrogen sulfide can be produced (Food Science and Technology, 2012).

2.5.1.7 Chemical Oxygen Demand

High COD levels decrease the amount of dissolved oxygen available for aquatic organisms. Low (generally under 3mg/l) dissolved oxygen or hypoxia causes reduced cell functioning, disrupts circulatory fluid balance in aquatic species and can result in death or individual organisms. Hypoxic water can also release pollutant stored in sediment (Kanu and Achi, 2011).

2.5.1.8 Oil and grease

The oil in the refinery effluent can affect marine organisms in a number of different ways. Animals coated by even small amounts of oil may be unable to swim or fly properly, maintain their body temperature, feed or even reproduce. Oil can also cover beaches and other vital habitats, making it difficult for animals to find uncontaminated food, nesting and resting places (Etkin, 1997).

Some animals are more vulnerable to oil than others. For example, young may be less able to deal with either coatings or exposure to toxic substances than adults due to their size,

underdeveloped immune systems and behaviour's. Marine mammals, seabirds (especially penguins) and sea turtles are all particularly vulnerable to oil on surface waters as they spend considerable amounts of time on the surface feeding, breathing and resting (Etkin, 1997).

Turtles and marine mammals are vulnerable to floating oil at all life stages as they do not appear to avoid oil slicks and they must inhale large amounts of air prior to diving. Turtles also feed in convergence zones, areas where air flows and currents meet, which tend to collect floating oil. It can kill them directly through coating and asphyxiation, contact poisoning, or through exposure to water-soluble components. It can also cause the destruction of more sensitive juveniles or of the food organisms therefore wiping out a population. Lastly oil is capable of causing sub-lethal and stress effects, carcinogenic and mutagenic effects and can affect the behaviour of individuals (Etkin, 1997).

2.5.1.9 Ammonia

The toxicity of ammonia is dependent on pH, oxygen concentration and temperature (Wake, 2005). With increasing pH (Wake, 2005) and decreasing O_2 (Wake, 2005) ammonia becomes more toxic. Ammonia is removed by bacteria in well-oxygenated areas and is therefore not likely to be accumulated by marine organisms (Wake, 2005).

2.5.1.10 Nitrates and Phosphates

Nitrates and phosphates in water bodies may have considerable effect on the water quality. Nitrogen in its various forms is considered to be the limiting nutrient in marine water. Therefore an increase in nitrogen compound should lead to phytoplankton blooms and when blooms occur, water conditions (such as reduced water clarity and dissolved oxygen) may become unfavourable for aquatic organisms. Inorganic phosphates are also rapidly taken up by algae and other aquatic plants although phosphates are usually not the limiting nutrient in

marine waters. Ecological alterations result from biotic response to nutrient inputs, most noticeable are the massive algal blooms (Dang *et al.,* 1997), that at times the algae are known to cover heavily 50% of the pelagic surface Dang *et al.* (1997).

An international environmental research center (Royal Swedish Academy of Sciences) through satellite remote-sensing technology has detected an important source of nutrient that is killing lake Victoria, the world's largest fresh water lake. They reported that these nutrients are feeding a carpet of water hyacinth that is rapidly choking the life out of the lake. Also a Kenyan-based international center for research in Agro-forestry discovered that the satellite imagery had discovered a plume of colouring water. The plume was showing a flow of sediment causing eutrophication (the process by which a body of water become enriched in dissolved nutrients that stimulate the growth of aquatic plants), the satellite imagery also showed that the nutrients were not coming solely from agricultural runoff as previously suspected, but also largely from low-lying deforestation riparian zones and other areas surrounding the lake that are not in private hands. The discovery further stated that the over supplies of nutrients and untreated sewage may have led to massive fish die-off, toxic algae blooms and the rampant spread of the aggressive flotation of weed water hyacinth. The hyacinth starves fish and plantation of oxygen and sunlight and also reduces the diversities of important aquatic plants. The hyacinth is also blocking water-ways traffic, it also causes water to stagnate, making the chocked shoreline a breeding ground for mosquitoes Dang *et al.* (1997).

2.5.1.11 Sulphides

Sulphides on the other hand are also removed by bacteria (Wake, 2005) but have the opposite relationship with pH. The toxicity of sulphides increases with decreasing pH (Wake, 2005).

2.5.1.12 Cyanide

Cyanides are also very toxic to marine organisms and the toxicity is affected by synergism with other compounds like ammonia and zinc. Cyanide affects the transport of oxygen from the blood to the tissues (Palmes, 1991). Aquatic lives are killed by cyanide concentrations in the microgram per liter (parts per billion) range as where birds and mammals deaths result from cyanide concentration in the milligram per liter (part per million). Concentration of free cyanide in the aquatic environment ranging from 5.0 to 7.2 micrograms per liter, blocks the absorption of oxygen by cells and causes aquatic species to suffocate, reduces swimming performance, inhibits reproduction, and alters growth (Palmes, 1991).

2.5.1.13 Phenols

Phenol has been observed to be very toxic to humans and other aquatic organism and has nearly unique properties of tainting the taste of fish if present in marine environment in concentration ranging from 0.1 to 1.0 mg/l, depending on the chemical nature of the phenol, fish species and the developmental stage, with embryo-larvae stages being many times more susceptible than adults. On the other hand are readily biodegraded by bacteria within 200 minutes given the right conditions (Otokunefor and Obiukwu, 2005). The exact effects of refinery effluent and its constituents thus can and do vary between species and from one location to another (Otokunefor and Obiukwu, 2005).

2.5.1.14 Total Hydrocarbon Concentration

Petroleum hydrocarbons have been observed to be toxic to aquatic life. It has been observed that river water that accommodated a fraction of crude oil or dispersed crude oil increased the activity of gill citrate synthase, Lactate Dehydrogenase LDH, and hepatic ethoxyresorufin-0-deethylase (EROD) at a concentration of 14.5mg/l. Lipophilic hydrocarbons have been

observed to accumulate in the membrane lipid bilayers of microorganisms and interfered with their structural and functional properties. Otokunefor and Obiukwu (2005) concluded that hydrocarbons are the most significant cause of toxicity in sediment sample obtained from around The North Sea oil platform contaminated by large piles of oil-based drill cuttings and polar organic compounds.

2.5.1.15 Fecal coliform

Fecal coliform bacteria are naturally occurring organisms that can be found in the feaces of humans and other animals, and their presence is used as an indicator of biological contamination of water sources. The bacterium has a number of impacts on both the environment and public health, and is consequently monitored closely by municipal water districts, governmental and environmental agencies. A high level of fecal coliform bacteria usually indicates large amounts of untreated feaces or other organic material in water, which has a number of environmental impacts. The organic matter that plays host to the bacteria decays aerobically, which can severely diminish oxygen levels and kills fish and other oxygen-dependant wildlife. The presence of feacal pollutants in water also contributes to the growth of algae and weeds, which can lower oxygen levels and block water flow. Feacal coliform bacteria can also have severe impacts of public health. Bodies of water with high levels of this bacterium can contain a wide range of disease-causing parasites, bacteria, and viruses. Illnesses contracted by people exposed to such water can range from mild conditions like ear infections to life-threatening conditions like typhoid fever or hepatitis. Parasitic worms and bacterial pathogens like *Salmonella* are also commonly found in water that tests positive for high levels of feacal coliform bacteria (Emily *et al.*, 2013).

2.5.1.16 Heavy and trace metals

Heavy metals can have toxic effects. The occurrence of trace elements in excess of natural loads in most part of the Niger Delta area of Nigeria from exploration and exploitation of mineral resources have become a problem of increasing concern (Kakulu and Osibanjo, 1998). Beyond the tolerance limits, there have been implications in some metabolic malfunctions in humans as they can be taken up directly in drinking water or indirectly by consumption of contaminated aquatic fauna and flora. Agbozu and Ekweozor (2001) therefore concluded that analysis of fish has been a valuable source of information in the evaluation of the concentration and effects of trace elements in the environment. Wegwu *et al.* (2000), had reported in their study of trace elements in aquatic fauna, that the high levels of metals recorded could be attributed to the greater industrial activities and constant discharge of effluent into Bonny River in Rivers state of Nigeria.

The concentration of metals dissolved in water may give a highly misleading picture of the degree of metal pollution and in some cases may significantly underestimate the total metal concentration in water. Mercury concentration measured by Wakawa *et al.* (2008) in the Mississippi indicated that 60% of the mercury in the water was associated with suspended sediment.

pH value also affects the concentrations of metals in the environment. Wakawa *et al.* (2008) in their study of fish in lakes with different pH values, reported deviated metal concentration in water of low pH, attributing it to the absorption of CO_2 and minerals from soils by H^+ ions with resultant increase in a direct bearing on the elevated heavy metal concentration (Wakawa *et al.*, 2008).

Evidence from studies on heavy metal pollution in aquatic environment reveals that heavy metals are partitioned among the three major compartments of such ecosystem, the water,

biota and sediments (Wakawa *et al.,* 2008). The amount and form of these metals in the aquatic system depends primarily on the number of physico-chemical factors of the compartment itself. Heavy metals are known to have been introduced through the food chain to higher trophic levels through accumulation by primary producers (algae).

Heavy metals and other crude components, other than settling down on the sediment environment, have been found to accumulate on different body tissues of marine organisms. This however has been observed to affect some of these organisms (benthic and non-benthic) physiologically as well as change their nutritional attitudes and reproduction (Fakayode and Onianwa, 2002).

In addition, the toxic effects of these marine organism has been shown to be due to their various abundance (productivity and diversity) and changes in species composition in such environment. The structure and productivity of aquatic ecosystems are affected by the concentrations and chemical forms of various metals (Fakayode and Onianwa, 2002). Obasohan and Oransay, (2000) who studied the heavy metals in water, sediment and some important commercial fish species from Ikpobu River found that all fish noticeably accumulated heavy metals. The value varied amongst the different heavy metals and fish species. Some non-essential metals such as: Ni, Cr and Pb exceeded the FAO acceptable limits in food fish. Dambo and Ekweozor (2000) found a correlation between concentrations of lead in oyster shells and those in sediment and concluded that Lead (Pb) had a preferential accumulation in oyster shells than in the tissues of the oysters. Therefore, different metals have varying effects that with temperature, salinity, pH and valence can act synergistically with one another (Abowei, 2010).The exact effects of refinery effluent and its constituents thus can vary between species and from location to location.

2.5.2 Effects of refinery effluent on Phytoplankton

There are very few studies that looked at the effects of refinery effluent or its components on algae. Phytoplankton abundance is influenced by water temperature, velocity of current, availability of nutrient and light penetration into the water. Ogamba (2004) reported that pollution affects the distribution, standing crop and chlorophyII concentration of phytoplanktons. Wake (2005) used 90-day toxicity tests on phytoplankton; he found that at the highest concentration tested (5.84% refinery effluent) the phytoplankton numbers decreased. Abowei (2010) concluded that, the algal flora of refinery effluent polluted river was found to be sparce. The species diversity of the phytoplankton was low, and that was why the primary production and productivity were equally low. Phytoplankton density was higher at the unaffected area of tidal movement even though the species diversity was relatively low. The spatial variation was no doubt related to both geographical influences and the influx of the pipeline discharge. Abowei (2010) studied the effect of refinery effluent on phytoplanktons and recorded that *Bacillariophyceae* were the most dominant species followed by *Cyanophyta* and *Pyrophyta*. The low phytoplankton density and diversity recorded have also been confirmed by earlier investigation (Ogamba, 2004), attributing it to oil pollution. Nevertheless, the general reduction in species diversity must be seen as evidence of the polluting effects of the oil industry in the phytoplankton. Reduced productivity of phytoplankton and/or algae will have a reduction effect to the other organisms in the environment, such as crustaceans and fish because they serve as food to them and other zooplanktons (Joseph and Joseph, 2002).

2.5.3 Effect of refinery effluent on Invertebrates

Many studies have used freshwater and marine invertebrates as test organisms to observe the effects of refinery effluent and its individual components. Crustaceans seem to be more sensitive than other aquatic organisms. Tests of the toxicity of refinery effluent from BP

Grangemouth on four species of marine invertebrate found that the most sensitive to the effluent was *Praunus flexuosus>Corophium volutator>Macoma balthica>Hydrobia ulvae*. Other studies have found marine/estuarine species to be more sensitive than fresh water species (Bleckmann *et al.*, 1995).

The conditions of the toxicity tests are also very important. Using sediment within a toxicity experiment has varied effects. Wake (2005) found that during acute toxicity tests the presence of a substrate caused enhanced survival for all four species (*Praunus flexuosus, Corophium volutator, Macoma balthica, and Hydrobia ulvae*). Contrary to these Wake (2005) found that the addition of sediment actually increased the toxicity of the refinery effluent to the tadpole snail and grass shrimp. The toxicity of the effluent was also found to change with storage. There was a significant loss in toxicity when the effluent was stored for 24 h before use in an experiment (Bleckmann *et al.*, 1995).

Sublethal toxicity tests on invertebrates have concentrated on the changes in reproductive success. Norbert- King and Mount (1986) observed that *Ceriodaphnia* resident in diluted refinery wastewater produced fewer young per female than the controls. Bleckmann *et al.* (1995) also found that an artificial refinery mixture (ARM) decreased the egg production and the number of broods in the estuarine crustacean *Mysidopsis bahia*. The effects of the two effluents that were discharged from BP Grangemouth on four marine invertebrates have been compared. It was found that the petrochemical effluent was more toxic than the oil refinery effluent (Wake, 2005). This suggests that it is not necessarily the oil, per se, but may be some of the other chemicals in the petrochemical waste that have the greatest toxic effects.

Some studies have tried to identify the relative toxicity of individual components so that the chemical or group of chemicals that cause the toxic effects can be determined. Wake (2008) investigated the toxicity of six components of refinery effluents on the Grass shrimp P*alaemonetes pugio* using 96 h tests. The order of toxicity was determined starting with the

most toxic. Fuel oil>sulphide>ammonia>phenol>chromium>kalinite. Fuel oil was also found to be the most toxic component of an artificial refinery mixture ARM (Wake, 2005), and ammonia was more toxic than phenol to C*orophium volutator*, as where oil was found to have no acute toxic effect. Wake (2005), tried to isolate the fractions of refinery wastewaters that were lethal to D*aphnia magna* using stepwise treatments and toxicity tests. The components that were found to be most toxic were the steam volatile, base neutral, and aromatic compounds. Eleven polycyclic aromatic hydrocarbons (PAHs) were identified but it was noted that although all these compounds were toxic they must be working in an additive or synergistic manner to produce the toxic effects shown in the experiments. The test conditions also affected the toxicity of the individual components. Low salinity was found to enhance the toxicity of ammonia for *Corophium volutator*. (Wake, 2005) discovered that temperature was the most important environmental variable for *Palaemonetes pugio* whereas light intensity, photoperiod and salinity had no effect. Animals from different locations and different genera showed the same effects, but larvae were more sensitive than adults (Wake, 2005). Sublethal effects of effluent components to changes in reproductive success have also been considered. Wake (2005) looked at the effects of ammonia, phenol, chromate and fuel oil on the reproduction and growth of M*ysidopsis bahia*. No animals that were exposed to ammonia survived to reproductive maturity. Those animals exposed to phenol, chromate and fuel oil experienced reproductive impairment. Phenol also caused growth inhibition whereas chromate caused the animals to swim in spirals. Changes in behaviour have also been noticed in other studies. During 96 h tests zooplankton (D*aphnia magna*) became erratic and uncoordinated in the water column when exposed to n-heptane, cyclohexane, benzene, diesel oil, mobile oil and oil refinery effluent (Wake, 2005).

Genotoxic effects have been evaluated in the cells of bivalve and gastropod molluscs inhabiting different sites of Klaipeda port area in Lithuania (Barsiene, 2002), with the highest

genotoxicity levels being found in the zone of sewage effluents from Palanga town and effluents from the Mazeikai oil refinery.

2.5.4 Effect of refinery effluent on Fishes

Fish have been used for the toxicity testing of oil refinery effluent in many different studies, most of which have looked at sublethal effects. Many different species of fish have been tested over the years. Wake (2005) used acute toxicity tests to determine the sensitivity of 57 species of fish to refinery wastewater. It was discovered that there was a variation both within and between species. The guppy (*Libestes reticulatus*) was the most resistant of the 57 species that were tested. Wake (2005) observed the effects of refinery effluent on five species of fish and found that the goldfish (33.1%) was the most resistant followed by the green sunfish (23.3%), red shiners (18.8%), golden shiners (18.7%) and lastly fathead minnows (17.0%). Two experiments have looked at the effects of Haldia refinery effluent on *Tilapia mosambica* using 96 h toxicity tests. The LC_{50} (median lethal concentration) value of refinery effluent was 54%. At 80–100% refinery effluent, the fish usually died within 24 hours showing signs of respiratory distress, surfacing and secretion of mucus (Wake, 2005). Wake (2005) observed the respiratory and feeding rates of *T. mosambica* exposed to different concentrations of effluent. At 2.10% and 5.84% of refinery effluent there was an increase in respiratory rate but no effect on feeding rate (Wake, 2005)

Wake (2005) used longer 90-day toxicity tests to look at several sub-lethal effects on *Tilapia mosambica*. None of the fish died over the 90-day experiments. At 2.10% refinery effluent, the fish yield was significantly reduced, the fish showed signs of respiratory distress and hampered growth. At 0.58% and 5.84% refinery effluent, the maturity index for females varied significantly from the controls. Fecundity of the fish in contact to refinery effluent was discovered to decrease but not significantly. Rowe et al. (1983a) also found that fecundity was affected by refinery wastewater. In 28% effluent concentration the fish produced fewer

eggs per spawn, spawned less frequently and had delayed spawning. They also showed that the 1st generations were smaller and that spinal curvature was present in the 2nd generation and all fish showed haemorrhaging of the fins. Rainbow trout have been observed to have erosion of the caudal fins when in contact with 31% refinery effluent (Rowe et al., 1983b). The growth of rainbow trout in 30% refinery effluent was severely reduced and was still reduced at 10% concentration of refinery effluent. Wake (2005) looked at the effects of pre-exposure to refinery effluent on rainbow trout. There was no increase in tolerance; in-fact pre-exposure caused the fish to become more sensitive to the effluent at lethal concentrations. Wake (2005) also observed the behavioural effects of refinery effluent on fathead minnows. When in contact with the effluent the fish showed signs of distress, had a sluggish or no response to disturbance. Erratic swimming, darkening of the integument, paralytic spasms and periods of immobility indicated severe stress, after which death usually followed within a few hours.

Wake (2005), recorded the acute toxicity of several petrochemical compounds to four species of fish; bluegills were the most sensitive followed by fathead minnows, goldfish and guppies. Of the compounds that were tested *O*-chlorophenol and *O*-cresol were the most toxic and methyl methacrylate and isoprene were the least toxic. Three of the petrochemical toxicities were affected by water quality. Soft water increased the toxicity of methyl methacrylate, styrene and vinyl acetate. Tests using fathead minnow fry and adults showed that the fry were more tolerant to methyl acethacrylate and less tolerant to vinyl acetate than the adults. Wake (2005) used rainbow trout to determine the effects of acclimation on the toxicity of zinc, cadmium, ammonia, phenol. With both heavy metals, an increase in tolerance and resistance after pre-exposure was seen in both adult and juveniles. The adults were more sensitive to the toxic effects of the heavy metals than the juveniles. Concentration of ammonia as low as 0.08mg/l with increase in temperature was observed to reduce the swimming performance of

coho salmon, an effect attributed to metabolic changes as well as depolarization of white muscle.There was however no change in the tolerance of the fish to phenol with pre-exposure (Wake, 2005).

2.6 Field Surveys

Many ecological monitoring programmes have been undertaken in areas near to oil refineries to assess the impact they have on the environment. The majority of the surveys have looked at the impact on the estuarine or marine environment especially refineries that discharge into intertidal areas. Most of these intertidal areas are mudflats or soft bottomed sandy areas although rocky shores and salt marshes are also found. The main community that was studied in these surveys was that of the macro benthos, as they were relatively easy to sample (Wake, 2005)

2.6.1 Effect of refinery effluent on benthic organisms

The areas around oil refinery outfalls all show a similar response to the refinery effluent, whether it is a rocky shore, soft sediment or the water column. The area around the discharge is often found to have a low diversity and abundance of fauna due to the inability of many species to survive in such close proximity to the effluent (Wake, 2005)). In some cases the area adjacent to the outfall can be completely devoid of any fauna, such as in the Hooghly Estuary, India, where no bottom fauna was found around the refinery outfall (Wake, 2005). There were a few cases where no effect was detected in an area close to an effluent discharge (Dean, 2008).

Often the impacted area is limited to a specific distance from the discharge point. This distance varies depending on the site and the effluent. In Milford Haven the impacted area was limited to 200 m from the outfall (Dean, 2008), whereas in the Hoogly Estuary it extended to 700 m (Wake, 2005) who noted that the impacted area in the Medway Estuary was limited to an area of 1.5 km around the outfall.

In Southampton Water two distinct groups could be defined based on the level of impact. Group 1, the area of gross pollution, included the stations around the discharge that had elevated hydrocarbon and trace metals. This group was dominated by the polychaetes *Hediste diversicolor*, *Capitella capitata*, *Polydora spp*. Group 2 which was situated above and below the affected zone had more diverse fauna. The larvae of the species that were found only in Group 2 were not able to survive settlement at Group 1 sites, possibly due to a toxicity effect of the sediment in that area (Dean, 2008).Wake (2005) investigated the spatial distribution of the benthic community of the Kinneil mudflat in the Forth Estuary, Scotland. The two effluent outfalls at Kinneil also produced a similar pattern, and four zones of pollution were observed. Gross pollution occurred within 250 m of the outfall, where there was no fauna found. Between 250 and 500 m from the outfall (severe pollution) the community was characterised as having a low abundance, species diversity and biomass. Between 0.5 and 1.5 km (pollution) the fauna had a high abundance and biomass but still a relatively low diversity. Lastly, the zone furthest away from the effluent (1.5–2.25 km) was described as moderate pollution and recovery. This zone had a higher diversity and a lower abundance than the previous zone. Dean (2008) also considered the changes in the species within these areas. In the area of severe pollution only the two opportunistic species (*Manayunkia aestuarina* and *Oligochaetes*) were abundant and *Hydrobia ulvae*, *Macoma balthica* and *Nereis diversicolor* were present in low numbers. The Spionids were found in the 0.5–1.5 km zone and *Corophium volutator* and *Cerastoderma edule* were only found after 1.5 km from the discharge. The species that were found close to the refinery outfalls were mainly opportunistic species (Dean, 2008); typical species found in organically enriched areas. Often the abundance/biomass distribution reflects the typical species abundance biomass (SAB) relationship (Wake, 2005). Wake (2005) observed the Kinneil mudflat on the Forth estuary had a higher biomass of *Oligochaetes* and *Nereis diversicolor* than other similar mudflats in

the estuary. There was also some evidence to suggest that refinery effluent may reduce the growth of some species. Dean (2008) found that close to the refinery effluent discharge *Macoma balthica* and *Hydrobia ulvae* were smaller than those recorded from further away.

Effects on the flora have also been seen. In both the Medway Estuary and Milford Haven, algal growth has been seen to increase near the effluent; algae are notably abundant around the outfalls in these areas (Dean, 2008). Often oil is thought to be the main component of the effluent to cause the adverse effects as it is thought to be toxic. Wake (2005) suggested that the reason for the death of *Spartina* and the appearance of bare patches of mud was repeated light oiling of the *Spartina* shoots. The oil content of the soil, the pH of the water and soil, the sulphide concentration and temperature of the effluent did not seem to have an effect and *Spartina* was found to grow in jars of outfall water and pots of soil from the denuded area. Studies of the macrophytes in experimental wetlands have shown that petrochemical effluent was not the limiting factor for the growth of three species (*Scirpus californicus*, *Typhasubulata* and *Zizaniopsis bonariensis*) and that water and/or nutrients had a greater effect (Dean, 2008).

Some field studies however suggested that it may be other components within the effluent that could be causing the effects. Wake (2005) found that the species numbers negatively correlated with the oil concentration of the sediment but *Nereis diversicolor* was present in areas contaminated with oil. Therefore, it was concluded that oil alone could not be responsible for the effects seen in the area around BP Colemouth Creek. The oil content of the refinery effluent at Milford Haven was reduced but no reduction in the area of impact was seen. It was considered that the low salinity of the effluent might be an important factor for causing the impact to this area rather than the oil (Wake, 2005).

2.7 Recovery

It can be seen that if the toxicity of the effluent is reduced or the effluent is stopped completely, the area of impact is able to recover. The time taken for the area to recover varies and depends on the area and the type of organisms involved. In Porvoo, Finland, the subtidal area was monitored to observe the effects of the addition of a new treatment plant to the oil refinery there in 1973 (Wake, 2005). An improvement in the macro-fauna was seen with an increase in the number of species and diversity. The species that were found to re-colonise most successfully included the amphipods *Pontoporeia affinis* and *Corophium volutator*, the Oligochaete *Tubifexco status*, the polychaetes *Polydoraredeki* and the bivalve *Cerastoderma edule* (Dean, 2008).

The addition of a biological treatment system to oil refineries in both the Forth estuary, Scotland and the Peace river, Canada caused a decrease in the opportunistic species and again allowed the less tolerant species to recolonise (Wake, 2005). The size of the area of enrichment gradually decreased over time (Wake, 2005) and recent unpublished studies of the area have shown that the area affected by the petrochemical discharges has now disappeared completely. The improvement in the quality of the effluent at an oil refinery in Southampton water in 1971 produced a dramatic improvement in the condition of the nearby salt marsh (Wake, 2005).

The oil refinery at Milford Haven closed in March 1983 and monitoring of the rocky shore area was carried out to see if there was any change (Wake, 2005). The year 1984 saw increased recruitment of juvenile limpets all along the shore but especially near the outfall. During the following years further recruitment was noted, the average limpet became smaller but where found at increased densities. The barnacle population showed a different pattern. In 1984 there was an increase in the numbers of juvenile and adult barnacles but not near the outfall where there were fewer still. In 1985 a distinct gradient of density could be seen with

increased densities going away from the outfall, however in 1986 this gradient was less pronounced and only one station near to the old outfall had reduced numbers of barnacles. Therefore it was concluded that the effluent had been the main factor causing the exclusion of limpets and barnacles from the area around the outfall (Wake, 2005).

2.8 Pollution from other sources

As industrial activities continued to increase in Nigeria expecially as it relates to agricultural and urban development, large scale of waste water was constantly discharged into the aquatic environment. Unnatural inputs of silt, nutrients and other contaminations have hastened the eutrophication process in many water bodies. Eutrophication of large tropical and sub-tropical water bodies have been studied less in comparison, although it has been recognized as an important environmental issue (Dang *et al.*, 1997). Imbalance of biogeochemical cycle was minor, relative to bacteria fixation cycles, which have become a central environmental problem; while in nitrogen fixation, there has been dramatic changes due to combustion and run-off from agricultural processes (Dang *et al*., 1997).

Sources of marine pollution can be classified in two main classes: point sources and non-point or diffuse sources. At the point sources, waste water is flowing into the marine environment through a definite point. Control of wastes generated from a point source is relatively simple because their collection is easy. Non-point sources are more troublesome. As these sources are diffused, it is very difficult to dispose of or treat them. They flow freely as surface or underground runoff to the marine environment (Dang *et al.*, 1997).

2.8.1 Point Sources

There are many different point sources of marine pollution. Among them the ones discussed briefly below can be considered as the major examples

- **Domestic areas:** mainly in developing and less developed parts of the world many cities discharge the waste which are generated from residential areas directly into the sea. The modern tendency to consider septic tanks as out of date and primitive has resulted in a considerable increase in the amount of domestic waste water discharged in to the marine environment. These wastes are mainly rich in organic materials and have unpleasant effects on the receiving body such as microbial pollution. Increase in the concentration of nitrogen, phosphorus and sometimes solid materials, heavy metals and toxic elements and depletion of oxygen levels. Rapid increase in population and growth of urban areas have also contributed to the increase in population growth of urban of urban areas have also contributed to the increase of the amount of domestic waste water generated (Dang *et al.*, 1997).
- **Storm water:** Rain water collected by sewer and carried into the marine environment constitutes a point source. These waters are significantly sources of pollution because they carry almost all kinds of impurities which can be found on the surface of the earth, such as solid wastes, leaves, soil and even sometimes lead generated from the exhaust gases of vehicle (Dang *et al.*, 1997).

2.8.2 Non-point sources

The main sources of these kind of wastes are as follows:

- **Urban areas**: Pollutant generated from urban areas may occur in liquid or solid form. Rain water not collected by sewers, leachate generated by open dump or landfills, the content of septic tanks which overflow accidentally and oils are examples of the liquid waste. On the other hand, particulate matter such as dust generated by air pollution and precipitating on the marine environment, constitutes an example of solid pollutants which may be discharged into the marine environment. The wastes

generated from the sources mentioned above contains all kinds of pollutants such as toxic materials, heavy metals, bacterial and nutrient (Dang *et al.,* 1997).

- **Agricultural areas:** waste water originating from agricultural areas may contain excess amount of nutrients such as nitrogen and phosphorus generated from natural and synthetic fertilizers. The concentration of bacteria, suspended solids and pesticides in the marine environment is also increased by discharge of the waste water. Also runoff from the area contaminated by livestock and poultry wastes, particularly from the feedlots, may contribute to marine pollution (Dang *et al.*, 1997).
- **Mines:** waste water generated from minning activities can be rich in toxic metals, such as mercury and cadmium, which may be harmful to aquatic life (Dang *et al.,* 1997).
- **Forest:** mainly solid materials, such as leaves carried to the marine environment by storms, cause an increase in the concentration of solid materials of the marine water (Dang *et al.,* 1997).
- **Ships and other vehicles:** commercial passenger and transport ships, private boats and yatch many times discharge their wastes (sewage, bilge water, solid waste, litter etc) into the marine environment, thus contributing to its pollution (Dang *et al.*, 1997).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of the study area

The four sampling stations were established along the creek of Okrika Local Government

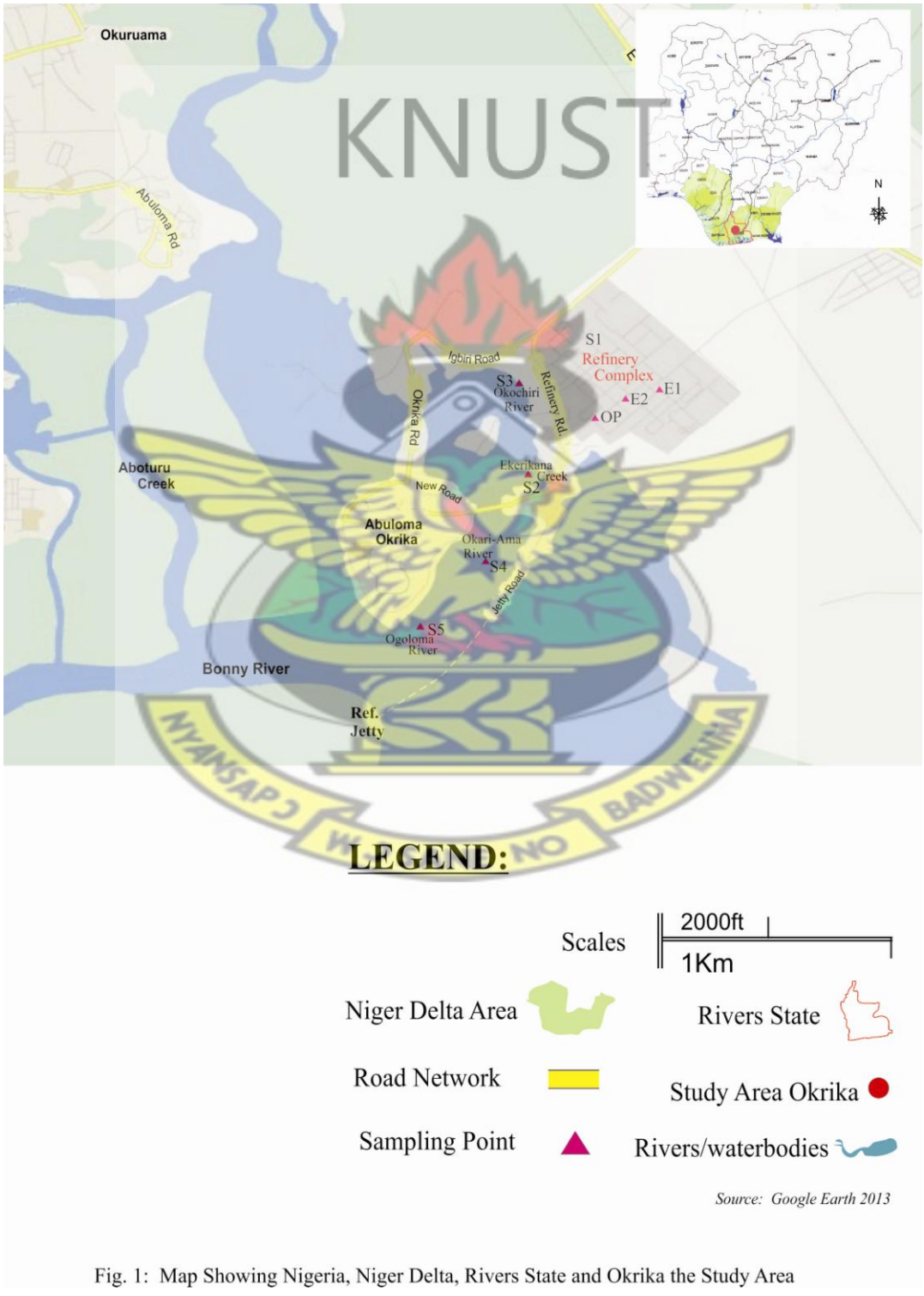


Fig. 1: Map Showing Nigeria, Niger Delta, Rivers State and Okrika the Study Area

Area in the Niger Delta of Rivers State, Nigeria. The creek were all brackish as evident in their vegetation. The Vegetations consist of Rhizophora racemosa which lined the shores of these stations. The creek is tidal in both wet and dry seasons. Anthropogenic activities along the creek include sand mining or dredging, fishing, navigation, washing, bathing and recreational activities. A major industrial outfit which is situated in station 2 (Ekerikana) is the Nigerian National Petroleum Co-operation (NNPC) refinery complex which generates several volumes of effluents that is channelled into the creek via a drainage system. These activities have undoubtedly influenced the natural balance of the aquatic ecosystem and consequently its biota, such as phytoplankton and benthos composition.

3.2 Sample points

Four (4) main sample collection sites were selected in the study area. These includes;

1. The refinery effluent: In this location 3 sampling points were taken namely;
    - Untreated effluent (E_1) (map 1)
    - Treated effluent from treatment plant (E_2) (map 1)
    - Observation Pond waste water (OP): The combination of both untreated and treated effluent (map 1)
2. Ekerekana creek which serves as the Point Of Discharge into the river (S.2) (map 1)
3. Okochiri river as site 3 (S.3): This represents the Upstream of the River (map 1)
4. Okari-ama river as site 4 (S.4): Representing the Downstream of the River (map 1)

3.3 SAMPLE COLLECTION /METHOD

Plate 1: Using earthman grab in collecting benthos sediment sample at S.4

Plate 2: Sediment collection for total hydrocarbon concentration analysis from S.5 (Ogoloma river)

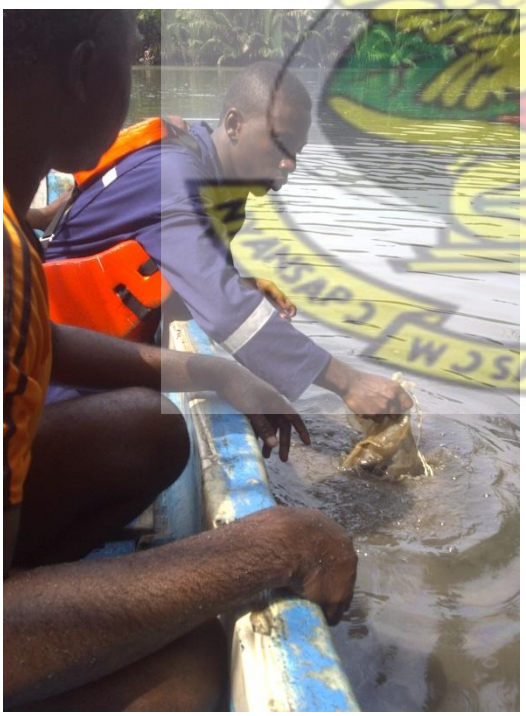


PLATE 3: Sieving of benthos sample into the brackish water at S.3

PLATE 4: Point of Discharge of refinery effluent into the creek at S.2

Samples from each of the four (4) sites were collected on a monthly basis.

The Samples were collected at low tide at about 30 cm deep with a 2 litre plastic hydrobios sampler bottle by lowering and allowing water to over flow before it was withdrawn and transferred to a clean 2 litre polyethylene container, 250 ml capacity borosilicate glass bottle (for oil and grease determination) and a 1 litre sterilized plastic polyethylene container covered with foil (for determination of total coliform) in each of the sites. The collected samples were stored in an ice box at 4^{o}C before taken to the laboratory within six (6) hours for analysis. All analysis were completed within two weeks (14 days). Plates 1-4 show the sampling methods employed for the study.

3.4 Physico-Chemical parameters and analysis

Analysis of physico-chemical parameters

3.4.1 pH

The water pH was determined in the laboratory by the use of a pH meter (APHA 4500-H^{+}B). The procedure followed the standard method for water and waste water analysis. According to this method the pH meter was calibrated using two buffer solutions at the range of pH 7.0-pH 4.0. After calibration, the electrodes were rinsed thoroughly with distilled water and blotted dry with soft tissue paper before the electrodes were inserted inside the sample and read after 120 seconds (2minutes).

3.4.2 Conductivity

The conductivity of the samples were determined in the laboratory by the use of a conductivity meter (APHA 2510B).

Calibration

Plug the conductivity and temperature probes into the unit. Calibrate the meter with standard 0.001N and 0.1N KCL solution for analysis of samples with low conductivity. Calibrate the meter with standard 0.39N KCl solution for sea water samples or samples with high conductivity.

Sample Analysis

The conductivity and temperature probes were plugged into the unit setting the display to read in ^{o}C and µS/cm or mS/cm respectively by the use of the MODE keypad before the probes were immersed in to the samples and measured. The display was read directly in ^{o}C for temperature and µS/cm or mS/cm for conductivity.

3.4.3 Temperature

The temperature of the samples were determined in the laboratory by the use of a conductivity meter (APHA 2510B). Calibrations was done same way as in conductivity.

Sample Analysis

The temperature was plugged into the unit setting the display to read in ^{o}C by the use of the MODE keypad before the probe was immersed into the samples and measured. The display was read directly in ^{o}C for temperature.

3.4.4 Total dissolved solids

The total dissolved solids of the samples were determined in the laboratory by the use of a conductivity meter (APHA 2510B). Calibration was done same was as in conductivity.

Sample Analysis

The probes were pluged into the unit setting the display to read in mg/l by the use of the MODE keypad before the probes were immersed in to the samples and measured.

3.5.5 Total suspended solid

The total suspended solids of the samples were determined following standard method for water and waste water analysis (APHA 2540D). According to this procedure, a whitman's filter paper was weighed on a weighing balance, 100ml of sample was measured and poured inside a beaker. The filter then folded to funnel before the sample was added to pass through gradually. After filteration, the filter paper was cooled and dried in an oven at a temperature of 103-105^{o}C before been weighed. Total suspended solids were calculated as:

$$\text{Total suspended solid, mg/l} = \frac{A-B \times M \times 1000}{Volume\ of\ sample, mg/l}$$

Where: A = weight of filter + residue, mg

B = weight of filter, mg

3.5 Chemical Analysis

3.5.1 Biological Oxygen Demand (BOD_5)

The five (5) days Biochemical Oxygen Demand (BOD_5) were determined following standard procedure of water and waste water by (APHA 5210B).

According to this method, samples were measured to corresponding BOD measuring ranges as shown in the Table 3.1 below:

Table 3.1 BOD sample volume and measuring range for analysis

Sample volume (ml)	Measuring range (mg/l)	Factor
432	0-40	1
365	0-80	2
250	0-200	5
164	0-400	10
97	0-800	20
43.5	0-2000	50

In this procedure 97 ml of sample was placed in the BOD bottle, a magnetic stirrer was inserted inside the bottle and a rubber quiver into the neck of the bottle before two (2) pellets of NaOH was added and incubated in an oxitop BOD incubator thermostatic box at a temperature of 20^{o}C for 5 days. BOD was calculated as:

BOD_5 mg/l = measured value (digits) × factor.

3.5.2 Chemical Oxygen Demand

The Chemical oxygen demand of the samples were determined by closed reflux, titrimetric method. The procedure followed the modification as suggested in the standard methods for chemical analysis of water and waste water (APHA 5220C). According to the procedure 2ml of sample was added in a 16 × 100mm tube, also 1ml of digestion solution and 3ml of H_2SO_4 were added

The tubes were caped tightly and agitated severally for thorough mixing before being placed in a block digester for pre-heating at a temperature of 150^{o}C for 2 hours. After heating, the samples were cooled at room temperature slowly to avoid precipitation before removing the caps. One to two drops of ferroin indicator was added and stirred up rapidly before titrating

with standard ferrous ammonium sulphate $Fe(NH_4)_2SO_4$(0.10m) to a sharp redish end point. Blank sample (distilled water) and standards was also prepared and allowed to pass through the same procedure.

Reagents

a) Standard potassium dichromate digestion solution (conc. 0.01667M): 500ml of distilled water was added to 4.903g $K_2Cr_2O_7$ that was previously dried at 150^oC for 2 hours, 167ml of concentrated H_2SO_4 and 3.3 g of $HgSO_4$ and then dissolve. Cool to room temperature and dilute to 1 litre.

b) Sulphuric Acid mixture: Ag_2SO_4 crystal was added to H_2SO_4 at the rate of 5.5 Ag_2SO_4/kg H_2SO_4 and was left to stand for 1 or 2 days to dissolve.

c) Ferroin indicator solution: 1.485g of 1,10-phenethroline monohydrate and 695 mg $FeSO_47H_2O$ was dissolved in distilled water and diluted to 100ml. 10ml of the solution was added into 50ml of volumetric flask and filled to 50ml mark with distilled water.

d) Standard Ferrous Ammonium Sulphate titrant ($Fe(NH_4)_2SO_4$) 0.10 M: 39.22g $Fe(NH_4)_2(SO_4)_2.6H_2O$ was dissolved in distilled water. 20ml of conc. H_2SO_4 was added cooled and diluted to 100ml.

COD was calculated as mg O_2/l = $\frac{A-B \times M \times 8000}{Volume\ of\ sample}$

Where: A = ml Ferrous Ammonium Sulphate used for blank

B = ml Ferrous Ammonium Sulphate used for sample

M = molarity of Ferrous Ammonium Sulphate

8000 = milliequivalent weight of oxygen × 1000ml/l

3.5.3 Phenol

Phenol in water were determined following standard chemical procedures of water and waste water (APHA 5530D) using spectrophotometer. According to the procedure, 250 ml of sample was poured inside a distillation flask and 100 ml was distilled using simple distillation unit. 100 ml of the distillate was added inside a 250ml beaker, 2.5 ml of 0.5N NH_4OH solution was added and immediately adjusted to pH of 7.9± 0.1 with phosphate buffer. 1.0 ml of 4-Aminoantipyrine solution was added and mixed well, also 1.0ml of $K_3Fe(CN)_6$ solution was added and mixed well then the solution was allowed to stand for 15minutes before the absorbance was measured at 500 nm using 10 mm cell in the Ultraviolet spectrometer.

Reagent

a) Stock solution: 100 mg phenol was dissolved in distilled water and diluted to 100 ml.
b) Intermediate phenol solution: 1.0 ml stock phenol solution was diluted in freshly boiled and cooled water to 100ml (1ml = 10.0µg phenol).
c) Bromate-bromide solution: 2.784 g of anhydrous $KBrO_3$ was dissolved in water, and 10g of KBr crystals was added, and diluted to the 1000ml mark with distilled water.
d) Ammonium hydroxide, NH_4OH,0.5N: 35ml of fresh concentrated NH_4OH was diluted to 1litre with distilled water.
e) Phosphate buffer solution: 104.5g of K_2HPO_4 and 72.3g of KH_2PO_4 was dissolved in water and diluted to 1litre ensuring that the pH is 6.8.
f) 4-Aminoantipyrine solution: 2.0g of 4-Aminoantipyrine was dissolved in distilled water and diluted to the 100ml mark.

Calibration curve preparation

0.00ml, 10.00 ml, 20.00 ml, 40.00 ml and 50.00 ml of the intermediate standard phenol solution was measured into a separate 100ml volumetric flask and diluted to the mark with distilled water, 2.5 ml of 0.5N NH_4OH solution was added and immediately adjusted to pH of 7.9± 0.1 with phosphate buffer. 1.0 ml of 4-Aminoantipyrine solution was added and mixed well, also 1.0ml of $K_3Fe(CN)_6$ solution was added and mixed well then the solution was allowed to stand for 15 minutes before the absorbance was measured at 500 nm using 10 mm cell in the Ultraviolet spectrometer. Phenol is calculated as:

mg Phenol/l = $\frac{A \times 1000}{B}$

Where: A = µg phenol in sample, from calibration curve (µg/l),

B = Volume of original sample (ml)

1000 = Conversion to mg.

3.5.4 Oil and Grease

Oil and grease in water samples was determined following standard procedures of water and waste water (ASTM D3921). According to the procedure, 500 ml of the sample was added in a calibrated glass bottle, 20ml of tetrachloroethane (solvent) was added to the sample and shaked vigorously for two minutes. The sample together with solvent was emptied into a separatory funnel. The separatory funnel was shaked vigorously and intermittently the stopper is released to reduce pressure build up. Allow the contents of the separatory funnel to settle and then the bottom layer of the sample was transferred into a clean bottle through a glass funnel in which

cotton wool and about 1.0 g of anhydrous sodium sulphate was placed at the aperture to absorb water. Then an aliquot of the extract is measured. Oil and grease is calculated as follows:

$$\text{Oil and grease concentration in mg/l} = \frac{Instrument\ reading\ \frac{mg}{l} \times volume\ of\ extract\ (ml)}{Volume\ of\ sample\ (ml)}$$

3.5.5 Phosphate

Phosphate in water was determined by automation using a multi-parameter photometer (Hanna Instrument HI 83200). According to the procedure 10ml of sample was added into the photometer cuvette to zero the instrument. After that 1(one) packet of HI 93713-O phosphate reagent was added into the cuvette, shaken gently for 2minutes using a stop watch before reinserting the cuvette into the instrument for 5minutes countdown before reading the result.

3.5.6 Sulphate (SO_4^{2-})

Sulphate in water was also determined by Automation using a multi-parameter photometer (Hanna Instrument HI 83200), According to the procedure 10ml of sample was poured into the cuvette before zeroing, 1 (one) packet of HI 93751-0 (powdered sulphate reagent) was added into the cuvette and shake gently for one minute using a stop watch before reinserting the cuvette into the instrument for five minute count down before reading the result.

3.5.7 Ammonia (NH_4^-)

Ammonia in water was also determined by automation using a multi-parameter photometer (Hanna Instrument HI 83200). According to the procedure 10ml of sample was added inside the cuvette to zero the instrument, 4 to 6 drops of Ammonia reagent (HI 93700A-0) was added into the sample and mixed. After that 4 to 10 drop of second Ammonia reagent (HI 93700B-0) was also added and mixed properly before reinserting the cuvette into the instrument for 3 minutes 30 seconds count down before reading the result.

3.5.8 Chloride / Salinity

Salinity in water samples was determined titrimetrically. According to the procedure a reddish-brown comparison solution was prepared as blank by adding 100ml distilled water inside a clean conical flask, 1ml of K_2CrO_4 (Potassium Chromate solution) was added and 0.2ml of 0.0282M of $AgNO_3$ (Silver nitrate solution) was also added and shaked gently. In analysing the sample, 100 ml of sample was added into another conical flask, 1ml of K_2CrO_4 indicator was added before titrating with constant stirring with 0.0282M $AgNO_3$ to the colour of the blank (reddish-brown). Salinity is calculated as follows:

Salinity as Cl (mg/l) = $\frac{A-B \times M \times 1000}{ml of sample}$

where A = ml of $AgNO_3$ used for titrating sample

B = 0.2ml of $AgNO_3$ used for titrating the blank

M = Molarity of $AgNO_3$

CL × 1.65 = Salinity

Note : 0.1ml of $AgNO_3$ = 2drops of $AgNO_3$

0.2ml of $AgNO_3$ = 4drops of $AgNO_3$

3.5.9 Cyanide (CN^-)

Cyanide in water samples were determined by Automation using a multi-parameter photometer (Hanna Instrument HI 83200). According to the procedure, the water temperature must not exceed 20^oC. The cuvette was filled up to 1.5cm ($^3/4$) below rim with 10ml of sample before zeroing the instrument. After zeroing, 1 level spoon of cyanide reagent (HI 93714A) was added and shaked gently for 30seconds using a stop watch, after 30 seconds 1

packet of cyanide reagent B (HI 93714B-0) was added again and shaked gently for 10 seconds, immediately 1 packet of cyanide reagent C (HI 93714C-0) was added and shaked vigorously for 20 seconds, reinserting the cuvette into the instrument for 25minutes countdown before reading the result.

3.5.10 Sulphide (SO_3^2)

Sulphide content of the water samples were determined titrimetrically by iodine method as described in standard method (APHA 1975). According to the procedure 15ml of standard iodine solution was measured into a 250ml conical flask, 5ml of distilled water was added to make the volume up to 20 ml. 2.0 ml of standard hydrochloric acid was added using a 2.0 ml pipette before 200 ml of sample was carefully measured and added into the iodine-acid water mixture, then 0.1ml of starch indicator was added, the colour changed to deep blue before the mixture was titrated with standard Sodium thiosulphate solution to a colourless end point. Sulphide was calculated as:

$$\text{Sulphide mg/s}^{-2} = \frac{A-B \times M \times 8000}{Volume of sample}$$

a = volume of iodine used

b = volume of thiosulphate ($Na_2S_2O_3$)

v = volume of sample

3.5.11 Total / Faecal coliform

Total and Faecal coliform in water samples were determined following standard procedure of water and waste water (APHA 9222B). According to the procedure, 5.2 g of Macconkey Agar powder was measured with an electronic balance into a conical flask and mixed with 100 ml of distilled water, it was stired thoroughly with a stirring rod, covered with a non- absorbent

cotton wool and aluminium foil before auto-claved at 121oc for 15 minutes. 3.6 g of powder Eosin-methylene blue Agar was added in 100ml of water and the procedure above was also repeated. After 15 minutes, the media in the autoclave was brought out, cooled in a bowl of cold water, after that it was poured into labelled Petri dishes and allowed to gel, further heat-dried in the incubator at 45^{o}C to remove moisture content. Test tubes were brought out and labelled with dilution factor 10^{-1} to 10^{-3} after that 9ml of the diluent (distilled water) was put into each of the tubes and 1ml of the water sample was then put into the 1st test tube for each set, serial dilution was carried out from tube 10^{-1} to 10^{-2} to 10^{-3} after serial dilution, 0-1ml of 10^{-3} on Petri dishes and incubated for 24 hours, after 24 hours the colony count and microscopic report was obtained.

3.6 Heavy Metals

Heavy metals in water samples were determined by Atomic Absorption Spectroscopy method (A.A.S). According to the procedure 10ml of HNO_3 (Nitric acid) was diluted with 500ml of distilled water. The Atomic Absorption spectrophotometer had already been calculated according to wavelength of different heavy metal parameter. An aliquot of the stock solution was used as blank by aspirating for 5minutes to enable flushing of burner system and to auto-zero the instrument before measurement.

3.7 Phytoplankton Analysis

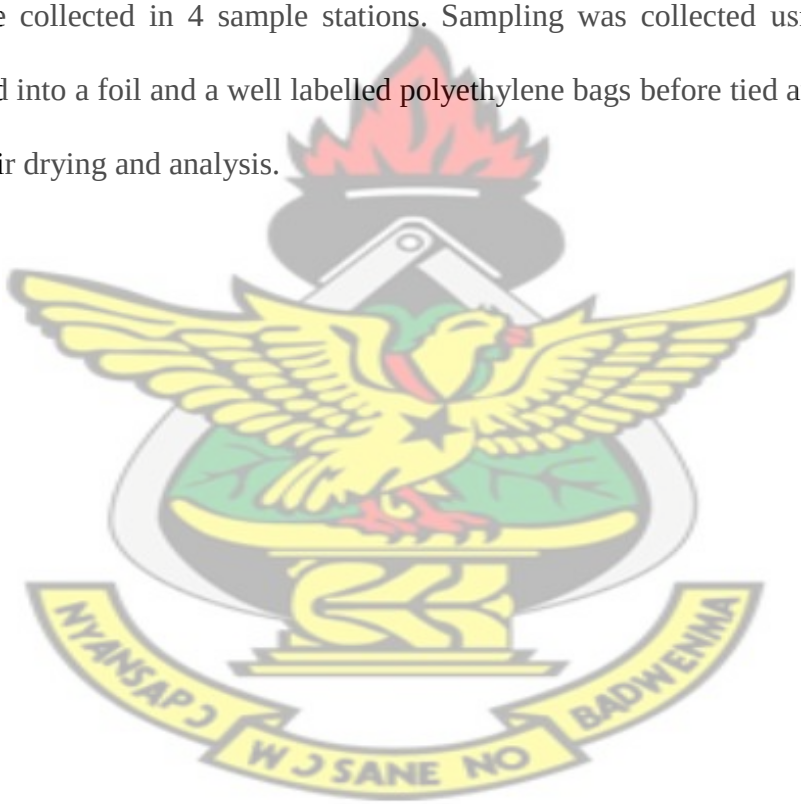
Phytoplankton samples were collected in three sample stations and one control station(S.4). Samples were collected with a vial bottle and preserved with 5% formaline and stained with Rose Bengol solution before transported to the laboratory for microscopy identification and taxonomic grouping.

3.8 Benthos analysis

Benthos samples were collected in 3 sampling stations and 1 control station (S.4). Sampling was done using Earthman's grab and a net for sieving of mudflat before samples were transfered to a well labelled plastic container fixed with 10% formalin and also stained with Rose Bengol solution before taking to the laboratory to isolate benthic organisms using a microscope, pairs of forceps and a tray.

3.9 Sediment Analysis

Sediments were collected in 4 sample stations. Sampling was collected using Earthman's grab, transferred into a foil and a well labelled polyethylene bags before tied and taking to the laboratory for air drying and analysis.



CHAPTER FOUR

4.0 RESULTS

4.1 Physical composition and concentration of refinery effluent and river water

The physical quality of the effluents generated and river water in all sampling sites was investigated by analysis and the levels of contaminants were estimated. The mean concentration of pollutants are shown in Table 4.1 below:

Table 1: Mean concentration of Physical parameters and EGASPIN compliance limit

Parameter	untreated effluent (E1)	Treated effluent (E2)	observation pond (OP)	Point of discharge (POD) station 2	Upstream river station 3	Downstream river (station 4)	EGASPIN Compliance limit
pH	7.27 ±0.15	7.13±0.11	6.24±1.31	6.91±0.18	6.83±0.32	7.143±0.25	6.5-8.5
Temp ^{o}C	25.00 ±2.04	25.36±1.87	25.43±1.66	25.66±1.56	25.26±2.01	26.70±3.20	30
Cond(µS/cm)	2403.33±366.10	341.00±21.51	986.00±204.97	1145.33±19.29	2563.00±427.07	2877.66±177.45	1400
TDS(mg/l)	760.00±60.00	181.00±51.50	338.66±29.48	250.33±87.29	2256.33±264.87	2058.00±320.95	<2000
TSS(l)	36.33±8.08	28.33±8.14	20.33±9.29	207.33±170.73	99.66±6.42	52.00±8.88	30
Turbidity (NTU)	22.89±5.29	62.50±3.96	48.26±4.10	45.14±6.85	24.85±6.19	19.83±8.46	5
Salinity(mg/l)	173.26±92.56	3.60±0.78	35.66±9.12	22.33±3.44	26.56±5.80	28.13±15.24	N/A
TOC(mg/l)	177.43±27.77	138.66±68.53	129.73±78.21	176.00±58.92	202.33±101.86	239.50±183.30	N/A

The mean concentrations and statistical analyses of the physical parameters are explained below:

4.1.1 pH

The pH value in all the sampling stations as presented in Table 1 ranged from 7.27 ±0.15 to 6.24±1.31. Untreated effluent recorded the highest pH value 7.27 ±0.15 followed by Downstream river, Treated effluent, POD, Upstream river and Observation pond effluent with mean values of 7.14±0.25, 7.13±0.11, 6.91±0.18, 6.83±0.32, and 6.24±1.31 respectively. Turkeys multiple comparison at ($P<0.05$) showed that the values were not significant. However the values were all within permissible limit as specified by EGASPIN except observation pond effluent.

4.1.2 Temperature

The temperature of the effluent and river water presented in Table 1 ranged from 26.70±3.20^{o}C to 25.00±2.04^{o}C. Downstream river recorded the highest temperature of 26.70±3.20^{o}C, followed by POD, Observation pond effluent, Treated effluent, Upstream river and Untreated effluent with mean values of 25.66±1.56^{o}C, 25.43±1.66^{o}C, 25.36±1.87^{o}C, 25.26±2.01^{o}C, and 25.00±2.04^{o}C respectively. Turkeys multiple comparison at ($P<0.05$) showed that the values were not significantly different.

However the values were all within the permissible limit as specified by EGASPIN.

4.1.3 Conductivity

The values of electrical conductivity in all the sampling stations in Table 1 ranged from 2877.66±177.4µS/cm to 341.00±21.5µS/cm. Upstream river recorded the highest electrical conductivity value 2877.66±177.45 µS/cm followed by Downstream river, Untreated effluent, POD, Observation pond effluent and Treated effluent with mean values of 2563.00±427.07µS/cm, 2403.33±366.10µS/cm, 1145.33±19.29µS/cm, 986.00±204.97µS/cm and 341.00±21.51µS/cm respectively. Turkeys multiple comparison at ($P<0.05$) showed that

the values were significantly different. However the values were all above permissible limit as specified by EGASPIN in Table 1, except outfall effluent, outlet effluent and meeting point which is below the permissible limit.

4.1.4 Total dissolved solids (TDS)

The mean values of total dissolved solids in all the sampling stations in Table 1 ranged from 2256.33±264.87mg/l to 181.33±51.50 mg/l. Upstream river recorded the highest total dissolved solids mean values 2256.33±264.87 followed by Downstream river, Untreated effluent, Observation pond effluent, POD, and Treated effluent with mean values of 2058.00±320.95mg/l, 760.00±60.00mg/l, 338.66±29.48mg/l, 250.33±87.29mg/l and 181.33±51.50mg/l respectively. Turkeys multiple comparison at ($P<0.05$) showed that the mean values were significant.

However the mean values in all stations were all below permissible limit as specified by EGASPIN except upstream and downstream of the river which were above the permissible limit.

4.1.5 Total suspended solids (TSS)

The mean values of total suspended solid in all the sampling stations in Table 1 ranged from 207.33±170.73(l) to 20.33±9.29(l). POD recorded the highest total suspended solid mean value 207.33±170.73(l), followed by Upstream river, Downstream river, Untreated effluent, Treated effluent and Observation pond effluent with mean values of 99.66±6.42(l), 52.00±8.88(l), 36.33±8.08(l), 28.33±8.14(l), and 20.33±9.29(l) respectively. Statistically using turkeys multiple comparison at ($P<0.05$) showed that the mean values were significant.

However the mean values were all above permissible limit as specified by EGASPIN except outfall effluent and outlet effluent which were below the permissible limit.

4.1.6 Turbidity

The observed turbidity in all the sampling stations in Table 1 ranged from 62.50±3.96(NTU) to 19.83±8.460(NTU). Treated effluent recorded the highest turbidity value 62.50±3.968 followed by Observation pond effluent, POD, Upstream river, Untreated effluent, and Downstream river with mean values of 48.26±4.100(NTU), 45.14±6.852(NTU), 24.85±6.195(NTU), 22.89±5.293(NTU) and 19.83±8.460(NTU) respectively. Turkeys multiple comparison at (P<0.05) showed that the values were significantly different. However the values were all above permissible limit as specified by EGASPIN.

4.1.7 Salinity

The mean values of salinity in all the sampling stations in Table 1 ranged from 173.26±92.56(mg/l) to 3.60±0.78(mg/l). Untreated effluent recorded the highest salinity mean value 173.26±92.56(mg/l) followed by Observation pond effluent, Downstream river, Upstream river, POD, and Treated effluent with mean values of 35.66±9.12(mg/l), 28.13±15.24(mg/l), 26.56±5.80(mg/l), 22.33±3.44(mg/l) and 3.60±0.78(mg/l) respectively. Turkeys multiple comparison at (P<0.05) showed that the mean values were significantly different.

4.1.8 Total organic carbon

The mean concentration of total organic carbon in all the sampling stations in Table 1 ranged from 239.50±183.30(mg/l) to 129.73±78.21(mg/l). Downstream river recorded the highest total organic carbon mean value 239.50±183.307(mg/l) followed by Upstream river, Untreated effluent, POD, Treated effluent and Observation pond effluent with mean values of 202.33±101.86(mg/l), 177.43±27.71(mg/l), 176.00±58.92(mg/l), 138.66±68.53(mg/l) and 129.73±78.21(mg/l) respectively. Turkeys multiple comparison at (P<0.05) showed that the mean values were not significantly different.

4.2 Chemical composition and concentration of the refinery effluent and river water

The chemical quality of the effluents from all the sampling sites were analysed and the levels of contaminants were estimated. The mean concentration of pollutants are shown in Table 2 below:

Table 2: Mean concentration of chemical parameters and EGASPIN compliance limit

Parameter	Untreated effluent (E1)	Treated effluent (E2)	Observation pond (OP)	Point of Discharge (POD) station 2	Upstream river station 3	Downstream river station 4	EGASPIN Compliance limit
oil & grease (mg/l)	160.14±29.81	6.81±4.09	21.5±1.36	4.41±4.15	6.39±1.45	1.66±1.15	10
BOD(mg/l)	113.00±45.57	40.00±18.02	63.00±20.66	30.66±10.06	66.00±12.16	81.33±20.13	10
COD(mg/l)	183.50±51.10	65.00±24.36	106.03±16.31	83.56±6.44	102.33±31.10	93.83±23.25	40
HCO_3^-(mg/l)	166.00±24.020	40.26±6.100	117.10±41.983	105.86±27.630	143.86±22.948	135.70±64.89	N/A
PO_4^{3-}(mg/l)	2.20±1.10	1.25±0.42	3.68±0.98	1.29±0.28	0.32±0.12	0.21±0.17	0.2
SO_4^{2-}(mg/l)	3.75±1.11	8.07±1.88	7.64±2.16	5.67±2.03	134.09±57.08	351.33±88.75	250
NH_4^+(mg/l)	1.21±0.16	0.90±0.49	0.35±0.26	0.25±0.14	2.24±0.39	0.67±0.35	0.2
T. phosphorus (mg/l)	2.94±0.59	1.74±0.58	4.16±1.43	1.68±0.56	0.38±0.07	0.39±0.07	1
Cyanide(mg/l)	0.01±0.109	0.01±0.00	0.01±0.10	0.01±0.00	0.01±0.00	0.01±0.00	0.01
SO_3^-(mg/l)	0.01±0.005	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01
Phenol(mg/l)	0.39±0.015	0.14±0.05	0.25±0.01	0.28±0.02	0.27±0.03	0.24±0.02	0.2
Pb(mg/l)	0.16±0.06	0.34±0.17	0.32±0.21	0.13±0.10	0.14±0.09	0.13±0.10	0.05
Zn(mg/l)	0.71±0.52	0.05±0.01	0.40±0.30	0.16±0.04	0.03±0.02	0.04±0.01	1.0
Cu(mg/l)	0.04±0.00	0.03±0.02	0.03±0.02	0.03±0.15	0.23±0.16	0.05±0.01	1.5
T. Chromium (mg/l)	0.07±0.04	0.09±0.01	0.07±0.04	0.08±0.02	0.09±0.03	0.13±0.05	0.3
Nickel(mg/l)	0.07±0.05	0.11±0.01	0.10±0.00	0.23±0.051	0.38±0.07	0.43±0.15	0.05
Vanadium (mg/l)	0.13±0.10	0.17±0.05	0.17±0.05	0.13±0.10	0.14±0.04	0.17±0.05	0.33

4.2.1 Oil and grease

The oil and grease concentration in all the sampling stations in Table 2 ranged from 160.14±29.81(mg/l) to 1.66±1.15(mg/l). Untreated effluent recorded the highest concentration of oil and grease with mean value 160.14±29.810(mg/l) followed by Observation pond effluent, Treated effluent, Upstream river, POD and Downstream with mean values of 21.53±1.36(mg/l), 6.81±4.099(mg/l), 6.39±1.45(mg/l), 4.41±4.15(mg/l) and 1.66±1.15(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the values were significantly different. However the values for inlet effluent and outlet effluent were above permissible limit as specified by EGASPIN.

4.2.2 Biological Oxygen Demand

The mean Biological Oxygen Demand in all the sampling stations as shown in Table 2 ranged from 113.00±45.57(mg/l) to 30.66±10.06(mg/l). Untreated effluent recorded the highest value of Biological Oxygen Demand with mean 113.00±45.57(mg/l) followed by Downstream river, Upstream river, Observation pond effluent, Treated effluent and POD with mean values of 81.33±20.13(mg/l), 66.00±12.16(mg/l), 63.00±20.66(mg/l), 40.00±18.02(mg/l) and 30.66±10.06(mg/l), respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were statistically significant. However the mean values in all stations were above permissible limit as specified by EGASPIN.

4.2.3 Chemical Oxygen Demand

The mean Chemical Oxygen Demand levels in all the sampling stations as shown in Table 2 ranged from 183.50±51.10(mg/l) to 65.00±24.36(mg/l). Untreated effluent recorded the highest level of Chemical Oxygen Demand with mean value 183.50±51.10(mg/l) followed by Observation pond effluent, Upstream river, Downstream river and POD with mean values

of 106.03±16.31(mg/l), 102.33±31.10(mg/l), 93.83±23.25(mg/l), 83.56±6.44(mg/l) and 65.00±24.36(mg/l) respectively. Turkeys multiple comparison showed that the mean values were statistically significant at P<0.05.

However the mean values were all above permissible limit as specified by EGASPIN.

4.2.4 Bicarbonate (HCO_3^-)

The levels of bicarbonate in all the sampling stations as shown in Table 2 varied from 166.00±24.02(mg/l) to 40.26±6.10(mg/l). Inlet effluent recorded the highest level of bicarbonate with mean value of 166.00±24.02(mg/l) followed by Upstream river, Downstream river, Observation effluent, POD and Treated effluent with mean values of 143.86±22.94(mg/l), 135.70±64.89(mg/l), 117.10±41.98(mg/l), 105.86±27.63(mg/l), and 40.26±6.10(mg/l) respectively. Turkey's multiple comparison showed that the mean values were statistically significant at P<0.05.

4.2.5 Phosphate

The mean levels of phosphate in all sampling stations as shown in Table 2 varied from 3.68±0.98(mg/l) to 0.21±0.17(mg/l). Observation pond effluent recorded the highest level of phosphate with mean levels of 3.68±0.98(mg/l) followed by Untreated effluent, POD, Treated effluent, Upstream river and Downstream river with mean values of 2.20±1.10(mg/l), 1.29±0.28(mg/l), 1.25±0.42(mg/l), 0.32±0.12(mg/l), 0.21±0.17(mg/l) respectively. Turkey's multiple comparison at (P<0.05) showed that the mean levels were significantly different.

However, the mean values for all stations except downstream river were all above permissible limit as specified by EGASPIN.

4.2.6 Sulphide (SO_3^{2-})

The mean sulphide levels in all the sampling stations as shown in Table 2 recorded 0.01±0.00(mg/l). Turkeys multiple comparison at ($P<0.05$) showed that the mean levels were not statistically significant. However the mean levels for all stations were within permissible limit as specified by EGASPIN.

4.2.7 Ammonia (NH_4^-)

The mean concentration of ammonia in all the sampling stations as shown in Table 2 ranged from 2.24±0.39(mg/l) to 0.25±0.14(mg/l). Upstream river effluent recorded the highest concentration of ammonia with mean values of 2.24±0.39(mg/l) followed by Untreated effluent, Treated effluent, Downstream river, POD and Observation effluent with mean values of 1.21±0.16(mg/l), 0.90±0.49(mg/l), 0.67±0.35(mg/l), 0.35±0.26(mg/l),and 0.25±0.14(mg/l) respectively. Turkeys multiple comparison at ($P<0.05$) showed that the mean values were statistically significant.

However, the mean values for all stations were all above permissible limit as specified by EGASPIN.

4.2.8 Total phosphorus

The mean levels of total phosphorus in all sampling stations as shown in Table 2 ranged from 4.16±1.43(mg/l) to 0.38±0.07(mg/l). Observation pond effluent recorded the highest mean of total phosphorus 4.16±1.43(mg/l) followed by Untreated effluent, Treated effluent, POD, Downstream of the river and Upstream of the river with mean values of 2.94±0.59(mg/l), 1.74±0.58(mg/l), 1.68±0.56(mg/l), 0.39±0.07(mg/l) and 0.38±0.07(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean levels were statistically

significant. However the mean levels for all stations except Upstream and Downstream of the river were all above permissible limit as specified by EGASPIN.

4.2.9 Phenol

The mean phenol concentration in all the sampling stations as shown in Table 2 ranged from 0.39±0.01(mg/l) to 0.14±0.05(mg/l). Untreated effluent recorded the highest concentration of phenol with mean values of 0.39±0.01(mg/l) followed by POD, Upstream river, Observation pond effluent, Downstream of the river and Treated effluent with mean values of 0.28±0.02(mg/l), 0.27±0.03(mg/l), 0.25±0.01(mg/l), 0.24±0.02(mg/l), and 0.14±0.05(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were statistically significant. However, the mean values for all stations except outfall effluent were above permissible limit as specified by EGASPIN.

4.2.10 Sulphate (SO_4^{2-})

The mean levels of sulphate in all the sampling stations as shown in Table 2 ranged from 351.33±88.75(mg/l) to 3.75±1.11(mg/l). Downstream of the river recorded the highest level of sulphate with mean 351.33±88.754(mg/l) followed by Upstream of the river, Treated effluent, Observation pond effluent, POD and Untreated effluent with means 134.09±57.08(mg/l), 8.07±1.88(mg/l), 7.64±2.16(mg/l), 5.67±2.03(mg/l), and 3.75±1.11(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the values were statistically significant.

The mean for all stations except Downstream of the river were below permissible limit as specified by EGASPIN.

4.2.11 Cyanide (CN^-)

The mean concentration of cyanide in all the sampling stations were the same that is 0.01±0.00(mg/l). Turkey's multiple comparison at ($P<0.05$) showed that the mean values were not statistically significant for each other. However, the mean values were all within permissible limit specified by EGASPIN.

4.2.12 Total coliform

The number of total coliform in all the sampling stations in Table 2 varied from 13.00±2.64(mg/l) to 3.00±1.00(mg/l). Observation pond effluent recorded the highest number of total coliform with mean number of 13.00±2.64(mg/l) followed by POD, Untreated effluent, Treated effluent, Upstream of the river and Downstream of the river with mean numbers of 11.33±2.30(mg/l), 8.33±1.52(mg/l), 6.00±3.60(mg/l), 3.00±1.00(mg/l), 0.66±0.57(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean numbers were statistically significant. However, the mean numbers for all stations were above permissible limit except downstream of the river as specified by EGASPIN.

4.2.13 Lead

The concentration lead in all the sampling stations shown in Table 2 ranged from 0.34±0.17(mg/l) to 0.13±0.10(mg/l). Treated effluent recorded the highest concentration of lead with mean values of 0.34±0.17(mg/l) followed by Observation pond effluent, Untreated effluent, Upstream of the river, POD and Downstream of the river with mean values of 0.32±0.21(mg/l), 0.16±0.06(mg/l), 0.14±0.09(mg/l), 0.13±0.10(mg/l), 0.13±0.10(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were not statistically significant. However, the mean values for all the stations were above the permissible limit as specified by EGASPIN.

4.2.14 Zinc

The concentration of zinc in all the sampling stations shown in Table 2 varied from 0.71±0.52(mg/l) to 0.03±0.02(mg/l). Untreated effluent recorded the highest concentration of zinc with mean values of 0.71±0.52(mg/l) followed by Observation pond effluent, POD, Treated effluent, Downstream of the river and Upstream of the river with mean values of 0.40±0.30(mg/l), 0.16±0.04(mg/l), 0.05±0.01(mg/l), 0.04±0.01(mg/l), and 0.03±0.02(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were not statistically significant. However, the mean values for all the stations were below permissible limit as specified by EGASPIN.

4.2.15 Copper

The concentration of copper in all the sampling stations shown in Table 2 ranged from 0.23±0.16(mg/l) to 0.03±0.15(mg/l). Upstream of the river recorded the highest concentration of copper with mean value of 0.23±0.162(mg/l) followed by Downstream of the river, Untreated effluent, POD, Observation pond effluent, and Treated effluent with mean values of 0.05±0.01(mg/l), 0.04±0.00(mg/l), 0.03±0.15(mg/l), 0.03±0.02(mg/l), 0.03±0.02(mg/l), and 0.03±0.15(mg/l), respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were not statistically significant. However, the mean values were below permissible limit as specified by EGASPIN.

4.2.16 Total chromium

The mean concentration of total chromium in all the sampling stations shown in Table 2 ranged from 0.13±0.05(mg/l) to 0.07±0.04(mg/l). Downstream of the river recorded the highest concentration of total chromium with mean values of 0.13±0.05(mg/l) followed by Treated effluent, Upstream of the river, POD, Untreated effluent, and Observation pond

effluent with mean values of 0.09±0.03(mg/l), 0.09±0.03(mg/l), 0.08±0.02(mg/l), 0.07±0.04(mg/l), and 0.07±0.04(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were not statistically significant.

The mean values for all the stations were below permissible limit except Upstream and Downstream of the river as specified by EGASPIN.

4.2.17 Nickel

The concentration of nickel in all the sampling stations shown in Table 2 ranged from 0.43±0.15(mg/l) to 0.07±0.05(mg/l). Downstream of the river recorded the highest concentration of nickel with mean values of 0.43±0.15(mg/l) followed by Upstream of the river, POD, Treated effluent, Observation pond and Untreated effluent with mean values of 0.38±0.07(mg/l), 0.23±0.051(mg/l), 0.11±0.01(mg/l), 0.10±0.00(mg/l) and 0.07±0.05(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were statistically significant. However, the mean values for all stations were above the permissible limit as specified by EGASPIN.

4.2.18 Vanadium

The concentration of vanadium in all the sampling stations shown in Table 2 ranged from 0.17±0.05(mg/l) to 0.13±0.10(mg/l). Treated effluent recorded the highest concentration of vanadium with mean value of 0.17±0.05(mg/l) followed by Observation Pond, Downstream of the river, Upstream of the river, Untreated effluent, and POD with mean values of 0.17±0.05(mg/l), 0.17±0.05(mg/l), 0.14±0.04(mg/l), 0.13±0.10(mg/l) and 0.13±0.10(mg/l) respectively. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were statistically significant. However the mean values for all stations were below the permissible limit as specified by EGASPIN.

4.3 Some physico-chemical profile of the Sediment

The levels of contaminants by some physico-chemical characteristics in sediment are shown in table 3 below:

Table 3: Physico-chemical properties of the indicated sampling points

Parameters	Point of Discharge (POD) (station 2)	Upstream (station 3)	Downstream (station 4)
pH	7.60	7.17	6.56
Temperature ^{o}C	28.9	28.3	28.6
Conductivity(µS/cm)	5140	7920	4670
Salinity (mg/l)	2.7	4.3	2.4
Sulphate(mg/l)	95.7	30.3	185.5
Phosphate(mg/l)	<0.05	<0.05	<0.05
Phenol (mg/l)	BDL	BDL	BDL
Lead (mg/l)	<0.001	8.27	3.66
Zinc (mg/l)	53.27	11.59	23.02
Copper (mg/l)	2.35	2.46	0.87
Nickel (mg/l)	6.41	0.42	4.87
Chromium (mg/l)	<0.001	<0.001	<0.001
THC(mg/l)	2328.82	126.47	964.12

The pH values in the sediment ranged from pH 7.60 to 6.56. POD, Upstream and Downstream of the with values 7.60, 7.17 and 6.56 respectively. Temperature values ranged from 28.9^{o}C to 28.3^{o}C. Point of Discharge, Downstream and Upstream of the river with values 28.9, 28.6, 28.3(mg/l) respectively. Upstream has the highest concentration of salinity 4.3(mg/l) followed by POD

2.7(mg/l), Downstream 2.4(mg/l).Upstream sediment has the highest concentration in conductivity 7920(mg/l) followed by POD 5140(mg/l), and downstream 4670(mg/l). POD sediment has the highest concentration of zinc 53.27 followed by Downstream 23.02 and Upstream 11.59. POD has the highest concentration of nickel 6.41 followed by Downstream 4.87, and Upstream 0.42. POD also has the highest concentration of total hydrocarbon content 2328.82, followed by Downstream 964.12 and Upstream 126.47. Downstream sediment has the highest concentration in sulphate 185.5 followed by POD 95.7 and Upstream 30.3.

Upstream had the highest concentration of copper 11.59(mg/l), followed by POD 2.35(mg/l) and Downstream 0.87(mg/l).Lead was not present in the Upstream of the river but was present in POD 8.27(mg/l), and downstream 3.66(mg/l). Phenol, phosphate and chromium were not detected in any of the stations in the sediment. POD has the highest concentration in THC 2328.82(mg/l), Downstream 964.12 (mg/l) and Upstream 126.47(mg/l)

4.4 Level of abundance and distributions of phytoplankton

The level of abundance and distributions of phytoplanktons are shown in Table 4 below:

Table 4: Results for phytoplankton distribution, abundance, density and richness

S/N	Family Bacillariophyceae	POD station 2	Upstream station 3	Downstream station 4	Control station 5	Total
1	*Nitzschia spp.*		1	1	3	5
2	*N. palea*		1	3		4
3	*N. sigma*		3	1	1	5

Table 4: Cont'd

4	*N. lanceolata*		1	2		3
5	*N. filiformis*		3	2	1	6
6	*N. vermicularis*				7	7
7	*N. ricta*		1		1	2
8	*N. linearis*				2	2
9	*N. denticula*				1	1
10	*N. kutzingiana*				1	1
11	*N. acicularis*				9	9
12	*N. dissipata*		1			1
13	*N. longissima*		1			1
14	*N. sigmoides*		3			3
15	*N. paleacea*		1			1
16	*Achnanthes spp.*		1	1		2
17	*A. lanceolata*		1			1
18	*Melosira italic*			31		31
19	*M. granulate*		1	4		5
20	*M. distans*			1		1
21	*Pinnularia spp.*			1		1
22	*P. viridis*		1			1
23	*Eunotia spp.*		1		1	2
24	*Stauroneis anceps*				2	2
25	*Caloneis spp.*		3		14	17

Table 4: Cont'd

26	*Diatom spp.*		1		2	3
27	*Synedra spp.*	1				1
28	*S. ulna*				2	2
29	*Cymbella spp.*				3	3
30	*C. lanceolata*				1	1
31	*C. cistula*				1	1
32	*Epithemia argus*				1	1
33	*Surirella elegans*				1	1
34	*Cyclotella comta*				1	1
35	*Cocinodiscus lacustris*				1	1
	Density (cells/L)	1	25	50	53	129
	No of Species	1	17	12	19	49
	Family Chlorophyceae					
36	*Phytoconis spp.*	45			2	47
37	*Anacystis spp.*	65		11		76
	Density (cells/L)	110	0	11	2	123
	No of Species	2	0	1	1	4
	Family Cyanobacteria					
38	*Lyngbya spp.*	3	1	1		5

Table 4: Cont'd

39	*L. limnetica*		8		13	21
40	*Oscillatoria putrida*			1		1
	Density (cells/L)	3	9	2	13	27
	No of Species	1	2	2	1	5
	Density / station	114	34	63	68	279
	Total Species	4	19	15	21	58
	Relative abundance (%)	40.9	12.2	22.6	24.4	100
	Margalef richness index	80.7	11.3	23.8	22.3	

Table 4 represents each of the major families of phytoplankton distribution and abundance during the period of study. A total of 40 species belonging to 3 families were recorded namely; Bacillariophyceae (35), Chlorophyceae (2) and Cyanobacteria (3).

The most diversed family with the highest distribution is Bacillariophyceae which was represented by 35 species and constituted 49% of total species. The dominant genus of the Bacillariophyceae were *Nitzschia* with 15 species though poorly distributed.

Highest density (cells/L) of (53) with 19 species were found in the Control station, followed by Downstream river water which recorded (50) density (cells/l) with 12 species, Upstream river recorded (25) density (cells/l) with 17 species and Only one (1) specie and density (cells/l) (*Synedra spp.*) was found in the POD (Point of Discharge) close to the refinery.

Chlorophyceae recorded 2 species with 123 total number of density (cells/l) and constituted 4% of total species. POD close to the refinery recorded 2 species (*Phytoconis spp.* and *Anacystis spp.*)with the cell counts of 45 cells/L and 65 cells/L respectively which culmulated to dencity (cells/L) of 110, Downstream river recorded 1 specie (*Anacystis spp.)* and 11 density (cells/l), Control station had 1 specie (*Phytoconis spp.*) and 2 density (cell/l) and Upstream river had no specie.

Cyanobacteria had the least number of density (cells/l) 27 and constituted 5% of total specie higher than chlorophyceae. Control station had 13 density(cells/l) with 1 specie (*L. limnetica*), Upstream river recorded 9 density (cells/l) with 2 species (*Lyngbya spp.* and *L. limnetica*) 1 and 8 respectively, POD close to the refinery recorded 3 density (cells/l) with 1 specie (*Lyngbya spp.),* while Downstream recorded 2 density (cells/l) and 2 species (*Oscillatoria putrida* and *Lyngbya spp.).*

Highest relative abundance (40.9%) was in the POD river (station 2), followed by (24.4%) in the control station, (22.6%) in the Downstream river water (station 4), and the least (12.2%) was in upstream river water (station 3), this culminated to the specie richness of 80.7, 22.3, 23.8, and 11.3 respectively.

4.5 Level of abundance and distributions of benthic organisms

The level of abundance and distributions of benthic organisms are shown in Table 5 below:

Table 5: Benthos distribution, abundance, density and richness

S/N	Nereidae	POD station 2	Upstream station 3	Downstream station 4	Control station 5	Total
1	*Lopdorhynchus ucinatus*				13	13
2	*Ceratonereis keiskama*			4	72	76
3	*Dendronereis arborifera*			2	38	40
4	*Leonates decipiens*				49	49
	Density (organisms/cm^2)	0	0	6	172	178
	No of Taxa	0	0	2	4	6
	Polycheates					
5	*Capitella capitata*	8		3	7	18
6	*Arenicola spp.*	2		9	6	17
7	Polycheates larvae				11	11
	Density (organisms/cm^2)	10	0	12	24	46

Table 5: Cont'd

	No of Taxa	2	0	2	3	7
	Density / Station	10	0	18	196	224
	Total Specie	2	0	4	7	13
	Relative Abundance (%)	4.5	0	8.0	87.3	100
	Margalefs richness index	12.8	0	12.1	102.6	

Data on benthic organism in respect to distribution and abundance among sampling stations are presented in Table 5. The Table showed very poor distribution and low abundance of benthic organism. A total of 6 species from the family Nereidae were recorded. POD (Point of Discharge) river close to the refinery discharge point had 2 species *Capitella capitata* and *Arenicola spp.* with cell counts of 8 and 2 respectively. No benthic organism was found in the Upstream river. Downstream river recorded 4 species *Arenicola spp., Ceratonereis keiskama, Capitella capitata,*and *Dendronereis arborifera* with cell counts of 9,4,3,2 respectively. All the 6 species were however found in the control station with *Ceratonereis keiskama* dominated the control with 72 individuals followed by *Leonates decipiens, Dendronereis arborifera, Lopdorhynchus ucinatus,* polycheate larvae, *Capitella capitata* and *Arenicola spp.* with cell counts of 49,38,13,11,7. The Relative abundance in the POD was 4.5% with a corresponding low richness index of 12.8, Downstream 8.0% with richness index of 12.1, and control station 87.3% with richness index of 102.6.

CHAPTER FIVE

5.0 DISCUSSION

The tidal flood nature of the creek distributes industrial pollutants back and front thereby localizing pollution within the axis. It was seen from the result statistically using turkey's multiple comparison that the discharge of untreated effluent into the observation pond was the major cause of pollution in the creek though the treatment plant was not efficient to remove pollutant to appreciable levels.

5.1 Physical Parameters

Result from this study showed that pH values at all stations were all below the permissible limit as specified by EGASPIN except Observation pond effluent which had a pH of 6.24±1.31. Turkey's multiple comparison at ($P<0.05$) showed that the mean values were not statistically significant. In effect, continuous discharge could result in acid deposition in the recipient water body.

The temperature of all the sampling stations (Table 1) was within permissible limit as specified by EGASPIN. Turkeys multiple comparison at ($P<0.05$) showed that the temperature of all sampling stations were not significant different from each other.

Total suspended solid levels (Table 1) were above the permissible limit at all stations except in the Treated effluent and Observation pond which might have been due to dilution by rain water. The higher levels recorded in the river water could have also be due to frequent discharging of effluent into the water and its accumulation therein. Turkey's multiple comparison at ($P<0.05$) revealed that mean values of refinery effluent and the river water were significantly different which could have been due to higher levels recorded in the river water. Conductivity values recorded at all sampling stations were above the permissible limit

except at the Treated effluent, Observation pond effluent and POD river water (Table 1). Statistically the mean values were significantly different from each other due to higher values recorded in the Untreated effluent, Upstream and Downstream points. The significant increases in the conductivity of water Upstream and Downstream may be an indication that pollutant might have entered the water which could adversely affect the survival of aquatic animals and increase the level of toxicity measured by other parameters.

Total Dissolve Solid levels measured inside the refinery showed that the effluent discharged out of the refinery were below permissible limits (Table 1). The river water had lower concentration at the POD point but higher concentration above permissible limit in the Upstream, and Downstream points. Turkey's comparison at ($P<0.05$) showed that the values were significant. The increase in values of total dissolved solid in the Upstream, and Downstream river may be attributed to prolonged accumulation in the river water without proper dilution.

The observed turbidity in all sampling stations were above the permissible and limits (Table 1).Turkey's multiple comparison at ($P<0.05$) revealed that there was a significant change which could be attributed to high turbidity of the refinery effluent discharged into the river water. Increase in turbidity of water can cause problems in the treatment plant and also result in the death of plants and animals present in the river.

5.2 Chemical Parameters

Generation of phenol, phosphate, and ammonia, were all above permissible limit at all station as specified by EGASPIN. Turkey's multiple comparison (at $P<0.05$) showed that the results were significant. The observed high concentration may be traced to large quantities of Untreated effluent which is channeled into the Observation pond without treatment and the slow dilution there of the river.

Natural sources of water typically contain little ammonia, usually in concentrations below 0.1mg/l, EGASPIN recommended maximum permissible limits in refinery effluents as 0.2mg/l. The concentration of ammonia in the effluent and river water were above permissible limit which was due to higher concentration from the Untreated effluent, inefficient treatment plant and bioaccumulation of the Observation pond and river water.

The concentration of phosphate was above the permissible limit at all stations, statistically the values were significant using turkeys multiple comparison at ($P<0.05$). These recorded concentrations could also be attributed to the flow of Untreated effluent and the inefficiency of treatment plant leading to slow dilution and bioaccumulation in the Observation pond and river water.

The mean levels of total phosphorus in all sampling stations in the refinery were all above permissible limit as shown in Table 2 except Upstream and Downstream of the river. Turkeys multiple comparison showed that the mean values were significant at ($P<0.05$). This showed the inefficiency of treatment plant and high concentration of Untreated effluent discharged into the Observation pond which is released to the recipient environment. Reduction below permissible limit in the Upstream and Downstream of the river could be attributed to dilution of the river water. In effects, High levels of total phosphorus and other nutrients have been reported to encourage eutrophication which could further deplete the dissolved oxygen levels of the rivers and adversely affect aquatic life's (Dang et al., 1997).

Oil and grease concentration in the Untreated effluent was responsible for the increased concentration of oil and grease in the Observation pond which was above permissible limit as as (Table 2). The effluent-receiving water body had low concentration of oil and grease which could be attributed to proper dilution of the effluent in the creek.

Total hydrocarbon content in sediment Point of Discharge, POD was 2328.82(mg/l), Upstream sediment 126.47(mg/l), Downstream sediment 964.12(mg/l). These concentrations were found to be higher than the maximum permissible limit as shown in Table 2 with the POD having the highest concentration of total hydrocarbon content. In effect, the water quality at the point of effluent discharge POD may be considered to be similar to an improperly treated effluent in need of further treatment action in order to reduce the contaminant concentration to acceptable levels. Petroleum hydrocarbons have been observed to be toxic to aquatic life. The high total hydrocarbon content in the sediment of the effluent-receiving water body in combination with other pollutant could be responsible for the depletion of fishes and other aquatic life at the Point of impact of the effluent. Evidence from local fishermen during interview suggests that the area around the point of discharge of the effluent is devoid of fishes and hence no fishing activity is carried out there anymore.

The concentrations of sulphate was above permissible limit only in Downstream side of the River as shown in Table 2. Sulphide and cyanide concentrations however were not significant and below the permissible limit at all sampling stations.

Salinity, Total organic carbon and bicarbonate concentrations were significantly different in all station but their permissible levels were not applicable in the study.

The levels of Biological Oxygen Demand were high in all stations than the permissible limit shown in Table 2; comparison of the mean values were also significant ($P<0.05$) using turkey's multiple comparison. This may be as a result of escape of organic matter from the biological treatment plant, and the Untreated effluent which flowed into the Observation pond (OP), the most important of which outside the refinery could be the faecal waste deposition by the surrounding communities.

The Chemical Oxygen Demand values recorded at all stations were all above permissible limits and standard set by EGASPIN (Table 2). Statistically the results were significant using turkey's multiple comparison at ($P<0.05$). The results indicated that the water bodies sampled had suffered deterioration and degradation due to continuous discharge of partially treated and untreated effluent into the recipient water body.

The mean numbers of total coliform was very high at all station. This is unacceptable when compared to regulatory permissible limit (EGASPIN). The result obtained for total coliform in Table 2 showed that the microbial water quality of the refinery and the river water was very poor. Total coliform pollution are wide spread and the entire course of the river as sampled was not suitable for domestic consumption without treatment. The result also reveals that the water may pose a serious health risk to man, animals and plants accentuated by the fact that the community defecate into the water in addition caused by the refinery effluent.

5.3 Heavy metal concentration

Heavy metal concentration such as zinc, copper, total chromium and vanadium in the effluent and river water were below the permissible limit as shown in Table 2. Metals such as lead and nickel recorded levels were above permissible limit of 0.05mg/l at all the stations. Higher concentration of nickel and lead in the river water could be attributed to slow dilution due to accumulation of the metals.

Sediment concentration in Table 3 showed that all the heavy metals (zinc, copper, nickel) were above permissible limit apart from total chromium which was not detected at all stations and lead which was not detected in the Upstream river sediment. It is very interesting to know that zinc and copper which was not present in the effluent and river water was present in high concentration in the sediment. This however could affect some organisms present in

the river (benthic and non-benthic) physiologically as well as change their attitude such as their nutritional attitudes and reproduction (Fakayode and Onianwa, 2002).

5.4 Phytoplankton distributions and abundance

In Table 4 phytoplankton distribution and abundance was very poor, and the algal flora of the creek / river water was found to be sparce. The species diversity of phytoplankton was low, and that was why the primary production and productivity was equally low. Phytoplankton density was higher at the unaffected areas of discharge (Downstream and control station) of the river, even though the species diversity was relatively low. The spatial variation was no doubt related to both geographical influences and influx of the discharge. Nevertheless, the general reduction in species diversity must be seen as evidence of the polluting effects of the oil industry on the phytoplankton population. Reduced productivity of phytoplankton and/or algae will have a knock on effect to the other organisms in the environment, such as crustaceans and fish because they provide nutritional base for them and other zooplanktons. (Joseph and Joseph, 2002). However, the dominance of Bacillariophyceae in this study is not an unusual occurrence. Many phytoplankton studies have reported the dominance of Bacillariophyceae in rivers and creeks of the Niger Delta in Nigeria. (Ogamba *et al*., 2004) concluded that the species with the highest self-sustaining natural mechanisms of natural increase usually become dominant. This may account with the widespread dominance of Bacillariophyceae in this study.

5.5 Benthic organism distribution and abundance

Data on benthic organisms with respect to distribution and abundance among sampling stations showed poor distribution and low abundance of benthic organisms (Table 5). The low diversity of benthic organism in this study is not unusual. The dominance of polychaetes in the Point Of Discharge (*Capitella capitata* and *Arenicola spp.)* where the refinery effluent

is emptied can be attributed to their high level of pollution- tolerance. No benthic organism was seen in the Upstream of the river. Downstream of the river had more species (Table 5) while at the control station all 6 species were present though in low abundance and distribution which could be due to low pollution as compared to other stations. The results showed strong relationship between the results of the physico-chemical of the river water quality and the distribution of organisms along the creek. This is an indication of the ability of the organisms to survive, adapt, migrate or die under favorable and unfavorable environmental conditions. Similar trends in the correlation between the physico-chemical quality and the distribution of organisms have been reported by Wake, (2005) and Dean, (2008). The weak correlation of some of the fauna such as *Lopdorhynchus ucinatus, Ceratonereis keiskama, Dendronereis arborifera and Leonates decipiens* to water quality parameters can be attributed to their physiological adaptations to the unfavorable environmental conditions. The differences in species composition and abundance may be attributed to the ecological differences of the different habitat locations and period of investigating the water quality. The diversity of benthic macro-invertebrates in the study areas were generally very low.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

- The refinery effluent was composed of some physic-chemical parameters such as; pH, temperature, conductivity, total dissolved solids, total suspended solids, turbidity, salinity, total organic carbon, oil and grease, biological oxygen demand, chemical oxygen demand, bicarbonate, phosphate, sulphate, sulphide, ammonia, total phosphorus, cyanide, phenol, Heavy metals such as; lead, zinc, copper, total chromium, nickel, vanadium and microbial contaminant such as Total coliform bacteria.
- The untreated effluent from the refinery were above the permissible limit, which was the major cause of worry and the treatment plant was not efficient enough to remove pollutants to acceptable limits which led to high concentrations in the observation pond.
- At the point of discharge into the river it was therefore realised that the concentration of some of the physico-chemical parameters such as: total suspended solids, turbidity, biological oxygen demand, chemical oxygen demand, phosphate, ammonia, total phosphorus, total coliform, phenol, lead, and nickel were above permissible limit which could be as a result of high bioaccumulation and slow dilution of the river.
- Due to the tidal movement of the river water which disperses pollutant upstream and downstream, there was no significant difference in the concentrations of the physico-chemical parameters recorded.
- The physico-chemical parameters analysed on the sediment were below permissible limit except the heavy metals which were not present in the effluent but was detected

in high concentration in the sediment which could also be as a result of bioaccumulation.

- Fauna and flora composition, abundance and distribution in the river water were very low due to the high concentration of pollutants present. However fauna and flora found at the point of discharge into the river were pollution-tolerant but further downstream it was noted that they slowly increased in their number.

It was therefore noted at the end of this study that the impact of oil refinery effluent invariably resulted in pollution of the river water bodies and hence usage of this water by surrounding communities for domestic and agricultural purposes will require some form of physico-chemical treatment.

6.2 Recommendations

- Careless disposal of untreated effluent into the observation pond without pre-treatment should be discouraged.
- The treatment plant should be efficient enough to remove pollutant to appreciable level.
- Regulating agencies should impose direct charges on industrial effluents, as well as continuous monitoring and surveillance in order to ensure the protection of water resources from further degradation.

REFERENCES

Abowei, J.F.N., (2010). Salinity, dissolved oxygen, pH, and surface water temperature conditions in Nkoro River, Niger Delta, Nigeria. *Adv.J. Food Sci. Technol.,* 2(1):16-21.

Agbozu, I.E. and Ekweozor,I.K.E. (2001). Heavy metal levels in a non-tidal freshwater swamp in the Niger Delta area of Nigeria. *Afr. J. Sci.,* 2: 175-182.

Ahn, I.Y., Kang, Y.C. and Cho, J., (1995). The influence of industrial effluents on intertidal benthic communities in Panweol, Kyeonggi Bay (Yellow Sea) on the west coast of Korea. Mar. Pollut. Bull. 30: 200-206.

Amadi, E.N., and Braide, S.A., (2003). Distribution of petroleum hydrocarbon degraders around petroleum – related facilities in a mangrove swamp of the Niger Delta. *Journal of Nigerian Environmental Society. 1(2)* 187-192.

American Public Health Association (APHA) (1998). Standard Methods for the examination of water and waste water, 20th edition. Washington DC,USA pp. 1244.

Akani, N. P., Braide, S. A., and Amadi, E. N.,(2008). Physicochemical and Microbiological Assessment of Oil-impacted Sediment in Ejama-Ebubu in Rvers State. *Nigerian Journal of Microbiology, Vol. 22(1): 1725 – 1731 2008*

Barsiene, J., (2002). Genotoxic impacts in Klaipeda Marine Port and Butinge oil terminal areas (Baltic Sea). Marine Environmental Research : 475–479.

Basheer H.D., Wan M.A, A.R. Aziz, A.B.,(2011). Treatment technologies for petroleum refinery effluents.Process Safety and Environmental Protection 89: 95–105

Belan, T.A.,(2003). Benthos abundance patterns and species composition in conditions of pollution in Amursky Bay (the Peter the Great Bay, the Sea of Japan). *Mar. Pollut. Bull.* 46: 1111-1119.

Berthet, B., C., Mouneyrac, J.C. Amiard, C., Amiard-Triquet, Y. B., (2003). Accumulation and soluble binding of cadmium, copper, and zinc in the polychaete *Hediste diversicolor* from coastal sites with different heavy metal bioavailabilities. *Arch. Environ. Con. Tox.* 45: 468-478.

Bilotta, G.A., and Brazier, R.E., (2008). Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research*. 42: 2849– 2861.

Bleckmann, C.A., Rabe, B., Edgmon, S.J., Fillingame, D., (1995). Aquatic toxicity variability for fresh- and saltwater species in refinery wastewater effluent. *Environmental Toxicology and Chemistry* 14:1219–1223.

Camphuysen, C.J.,(1989). Beached-bird Surveys in the Netherlands 1915-1988; Seabird Mortality in the southern North Sea since the early days of Oil Pollution. *Techn. Rapport* Vogelbescherming 1, WerkgroepNoordzee, Amsterdam 322 pp.

Chima, (2013). EnvironmentalConsequences of Nuisance Accessed on 4 june 2013 from http://www.martinslibrary.com/2013/01/environmental-consequences-of-nuisance.html.

Chindah, A. C., (1998). The effect of industrial activities on the periphyton communities of Upper New Calabar River, Nigeria. *Water Res*.,32 (4): 1137-1143.

Cranthorne, B., Roddie, B., Bolton, C., Jonston, D., Munro, D. (1989). Collaborative research programme: the effects of oily discharges upon the Forth estuary. Water Research Centre, Marlow, Bucks, Report no. PRS 2001-M/3, 71 pp.

Concawe, (2004). Trends in oil discharged with aqueous effluents from oil refineries in Europe: 2000 survey. Concawe (address as above) Report no. 4/04, 9 pp. (available at www.concawe.org).

Dang, O.H, Atle, H., and Gjertved H., (1997).'The significant of Nitrogen runoff for eutrophication of fresh water and Marine reciepients' *Ambio* 26 (5): 32-43.

David, A.R., Fairbridge,R.W.,(1999). Encyclopedia of Environmental Science. Pg 741.

Dambo, W.B., and Ekweozor, I.K.E., (2000). The determination of lead in mangrove oyster, *Crassostrea gasar* from the lower bonny estuary, nigeria. *J. Appl. Sci. Environ. Mgt*., 4`: 101-108

Dean, H.K. (1996). Subtidal benthic polychaetes (Annelida) of the Gulf of Nicoya, Costa Rica. Rev. Biol. Trop. 44 (suppl. 3): 69-80.

Dean, H.K. (2008). The use of polychaetes (Annelida) as indicator species of marine pollution.Rev. Biol. Trop. (*Int. J. Trop. Biol. Vol*. 56 (Suppl. 4): 11-38,

Ekweozor, I.K.E., (1989). A review of the effect of oil pollution in a West African environment. Discovery Innovation, 1: 27-37.

Ekweozor, I.K.E., Ikomah B.F., Dambo,W.B. and Daka,E.R., (2001). The effect of hydrocarbon pollution on the distribution of mullet species along Elechi Creek , Port Harcourt. *J. Appl. Sci.,* 4: 2169-2179.

Ekweozor, I.K.E., A.W. Granville, E.E., Nkanga and Ogbalu,O.K., (2002). The effects of crude oil contaminated feeds on the yield and quality of eggs of poultry birds (*Gallus domesticus*). *J. Agric. Trop. Sub.,* 103: 89-97.

Ekweozor, I., Agbozu, I.E., (2001). Surface water pollution studies of Etelebou oil field in Bayelsa State, Nigeria. *African Journal Sci*. 2:246-254.

Environmental Guidelines and Standards for the Petroleum Industries in Nigeria (EGASPIN) DPR Lagos 1991 Revised Edition 2002.

Emoyan, O.O., Akpoborie, I.A., and Akporhonor, E.E., (2008). The Oil and Gas Industry and the Niger Delta: implications for the environment. Journal *Appl. Sci. Environ. Manage. Vol*. 12 (3) 29-37.

Etkin, D.S.,(1997): The impact of oil spills on marine mammals OSIR Report 13 March 1997 Special Report.

Fakayode, S.O., (2005). Impact assessment of industrial effluent on water quality of the receiving Alaro River in Ibadan, Nigeria. *AJEAMRAGEE,* 10: 1-13.

Fakayode, S.O., and Onianwa, P.C., (2002). Heavy metals contamination of soil and bioaccumulation in Guinea grass (*Panicum maximum*) around Ikeja Industrial Estate, Lagos, Nigeria. *Environmental Geology*, 43: 145-150.

Food Science and Technology (2012). Effects of Biological Oxygen Demand on the water quality Accessed on 4 june 2013. www.fst.bod.com

Imeh, J., Okop, T.U., Sunday, C.H and Ekpo, K.D., (2012): Determination of total hydrocarbon content in soil after oil spillage. *Biol. Chem. Research Volume* 30 (1) 2013 Pages No. 1-12

Joseph, V., and Joseph, A., (2002). Ecology and seasonal variation of microalgal community in an Oil refinery effluent holding pond: monitoring and assessment. Environmental Monitoring and Assessment 80:175–185.

Kakulu, S.E.,and Osibanjo, O., (1998). Trace heavy metal pollutional status in sediments of Niger Delta area. *Nig. J. Chem. Soc*. 13: 9-11.

Kanu, I., and Achi, O.K., (2011). Industrial Effluents and Their Impact on Water Quality of Receiving Rivers in Nigeria. *Journal Appl. Technol in Env. San. vol* 1 (1): 75 – 86.

Kumar, R., (2011). Effect of dairy effluents on seed germination and early seedling growth of Pennisetumtyphoides. *International Journal of Research in Science and Technology* http://www.ijrst.com/ (IJAER). Vol. 1 issue No (V).

Nwabueze, A.A., and Agbogidi, O.A., (2010): Impact of water soluble fractions of crude oil on Growth performance of the catfish *Heterobrancuhus Bidorsalis.*Journal of Agricultural and Biological Science Nigeria.

Nweke, A. A., (2002). Impact of Organic Waste Pollution on the macrobenthos and fish fauna of Elechi creek. Ph.D. thesis, Rivers state University of Science and Technology, Port Harcourt, Nigeria, PP: 287.

Obasohan E.E., and Oronsaye, J.A.O., (2000) ' Heavy metals in water sediments and some important commercial fish species from Ikpoba Rivers, Benin city Nigeria. *J. Appl. Sc. Env. Mana.*4: 263-268.

Obire, O., and Amusan, F.O., (2003). "The Environmental Impact of Oilfield Formation Water on a Freshwater Stream in Nigeria", *Journal of Applied Sciences and Environmental Management* 7 (1) : 61-66.

Orji, F.A., Ibiene, A.A., and Ugbogu, O.C., (2012). Petroleum Hydrocarbon Pollution of mangrove swamps:The Promises of Remediation by Enhanced Natural Attenuation. *American Journal of Agricultural and Biological Sciences* 7 (2): 207-216.

Osibanjo, O., Daso, A.P. and Gbadebo .A.M.,(2011). The impact of Industries on Surface Water quality of River Ona and River Alaro in Oluyole Industrial Estate, Ibadan, Nigeria. *Afr. J. Biotechnol*. 10(4): 696-702.

Ogamba, E.N., Chindah, A.C., Ekweozor, I.K.E., and Onwuteaka, J. N., (2004). Water quality and phytoplankton in Elechi creek complex of the Niger Delta. *Journal of Nigerian Environmental Society* (JNES) 2: (2) 121-130.

Otokunefor, T.V., and Obiukwu, C., (2005). Impact of refinery effluent on the physicochemical properties of a water body in the Niger Delta. *Appl. Biol. and Environ. Research* 3 (1):61-72

Palmes, J., (1991). Cyanide: A Review of Literature on the Toxicity of Cyanide to Fish and Wildlife Related to Its Use in Mining: Alaska Dept. of Fish and Game, unpublished internal document, available at: Alaska Dept. of Fish and Game, Habitat Div., P.O. Box 25526, Juneau, AK 99802, p.47-57.

Pierre, N., (1980). The Oil Spill Age: Fate and effects of Oil in Marine Environment.

Phylis, K., and Lawrence, K.D., (2007). Effects of Total Dissolved Solids on Aquatic Organisms: A Review of Literature and Recommendation for Salmonid Species. *American Journal of Environmental Science* Volume 3, Issue 1 Pages 1-6.

Port and Maritime Protection (2013). Oil and its impact on the Environment. Accessed on 4 June 4, 2013. *www.maritime.protection.com*

Rowe, D.W., Sprague, J.B., and Heming, T.A., (1983a). Sublethal effects of treated liquid effluent from a petroleum refinery, I. Chronic toxicity to flagfish. *Aquatic Toxicology 3:149–159.*

Rowe, D.W., Sprague, J.B., Heming, T.A., and Brown, I.T., (1983b). Sublethal effects of treated liquid effluent from a petroleum refinery, II. Growth of rainbow trout. *Aquatic Toxicology* 3:161–169.

Sangodoyin, A.Y., (1991). Groundwater and Surface Water Pollution by Open Refuse Dump in Ibadan, Nigeria. *Journal of Discovery and Innovations, 3 (1): 24-31*.

Science Fair Water (2013). Water Turbidity effects on fish and Aquatic Life Accessed on 4 june 2013. *www.sciencefairwater.turbidity.com*

Science Fair Water (2013).Water Temperature effects on fish and Aquatic Life Accessed on 4 june 2013.*www.sciencefairwater.turbidity.com*

Sharon, B., (1997). Testing the Waters: Chemical and Physical Vital Signs of a River. River Watch Network. ISBN-0-782-3492-3. *http://www.fosc.org/WQData/WQParameters.htm*

Snowden, R.J. and Ekweozor, L.K.E., (1990). The Littoral Infauna of the West African Estuary: a baseline Survey for the Monitoring of Oil Pollution. *Mar. Biol*., 105(1): 51-59.

Sadatipour, L., Mirzaie, L.J andRezaei, A.A.,(2004).An investigation on Kangan gas refinery wastewater. *International Journal of Enviornmental Science and Technology, Vol. 1, No. 3, Autumn 2004, pp.205-213.*

Udotong, I.R.,(2003).Evironmental Pollution of oil spill in Bayelsa State, Nigeria. In: EN Adinna, OB Ekop, VA . *J Hum Ecol*, 33(1):41-46.

Wakawa, R. J., Uzairu, A., Kagbu, J. A., and Balarabe, M. L., (2008). Impact assessment of effluent discharge on physico-chemical parameters and some heavy metal concentrations in surface water of River Challawa Kano, Nigeria. *African Journal of Pure and Applied Chemistry Vol*. 2 (9), pp. 100-106.

Wake, H., (2005). Oil refineries: a review of their ecological impacts on the aquatic environment. *Estuar. Coast Shelf Sci.* 62, 131–140.

Welch, E.B., and Lindell, T., (1992). Ecological Effects of Wastewater: Applied Limnology and Pollution Effects. ERFN Spon. An Imprint of Chapman and Hall, New York. Pg 1-343.

Wegwu, M.O., Abbey, B.W., and Ibeh, G.O., (2000). Spectrophotometric determination of some trace elements in aquatic fauna. *J. Appl. Sci. Environ. Mgt*. 4(2), 5-8.

Wokoma-Aleleye, L.P., and Hart, S.A.,(1999). The Effect of Industrial Activities on the Primary Productivity in the lower Bonny Estuary, Rivers State, Nigeria. *J. Appl. Sc. Environ.mgt.,2:139-42.*

Yakubu, A.F., Sikoki,F.D., and Horsfall, J.R.M.,(1998). An Investigation into the Physicochemical Conditions and Planktonic Organisms of the Lower Reaches of the Nun River, Nigeria. *J. Appl.Sc. Environ. Mgt*., 1(1): 38-42.

APPENDICES

Appendix 1: Statistical analysis of physico-chemical parameters at sampling sites

Table 1: Statistical analysis of pH at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Observation pond	3	6.2433
	Upstream river water	3	6.8333
	POD	3	6.9167
	Treated effluent	3	7.1333
	Downstream river water	3	7.1433
	Untreated effluent	3	7.2700

Table 2: Statistical analysis of Temperature at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Untreated effluent	3	25.0000
	Upstream river water	3	25.2667
	Treated effluent	3	25.3667
	Observation pond	3	25.4333
	POD	3	25.5667
	Downstream river water	3	26.7000

Table 3: Statistical analysis of Conductivity at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Treated effluent	3	341.0000		
	Observation pond	3		986.0000	
	POD	3		1145.3333	
	Untreated effluent	3			2403.3333
	Upstream river water	3			2563.0000
	Downstream river water	3			2877.6667

Table 4: Statistical analysis of TDS at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Treated effluent	3	181.0000		
	POD	3	250.3333		
	Observation pond	3	338.6667		
	Untreated effluent	3		760.0000	
	Downstream river water	3			2058.0000
	Upstream river water	3			2256.3333

Table 5: Statistical analysis of TSS at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	Observation pond	3	20.3333	
	Treated effluent	3	28.3333	
	Untreated effluent	3	36.3333	
	Downstream river water	3	52.0000	
	Upstream river water	3	99.6667	
	POD	3		270.3333

Table 6: Statistical analysis of Turbidity at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Downstream river water	3	19.8333		
	Untreated effluent	3	22.8900		
	Upstream river water	3	24.8533		
	POD	3		45.1400	
	Observation pond	3		48.2667	
	Treated effluent	3			62.5000

Table 7: Statistical analysis of Salinity at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	Treated effluent	3	3.6033	
	POD	3	22.3333	
	Upstream river water	3	26.5667	
	Downstream river water	3	28.1333	
	Observation pond	3	35.6667	
	Untreated effluent	3		173.2667

Table 8: Statistical analysis of TOC at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Observation pond	3	129.7333
	Treated effluent	3	138.6667
	POD	3	176.0000
	Untreated effluent	3	177.4333
	Upstream river water	3	202.3333
	Downstream river water	3	239.5000

Table 9: Statistical analysis of Oil and grease at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	Downstream river water	3	1.6667	
	POD	3	4.4133	
	Upstream river water	3	6.3933	
	Treated effluent	3	6.8167	
	Observation pond	3	21.5333	
	Untreated effluent	3		160.1400

Table 10: Statistical analysis of BOD at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	POD	3	30.6667	
	Treated effluent	3	40.0000	
	Observation pond	3	63.0000	63.0000
	Upstream river water	3	66.0000	66.0000
	Downstream river water	3	81.3333	81.3333
	Untreated effluent	3		113.0000

Table 11: Statistical analysis of Sulphate at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Untreated effluent	3	3.7533		
	POD	3	5.6733		
	Observation pond	3	7.6433		
	Treated effluent	3	8.0733		
	Upstream river water	3		134.0900	
	Downstream river water	3			351.3333

Table 12: Statistical analysis of COD at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	Treated effluent	3	65.0000	
	POD	3	83.5667	
	Downstream river water	3	93.8333	
	Upstream river water	3	102.3333	
	Observation pond	3	106.0333	
	Untreated effluent	3		183.5000

Table 13: Statistical analysis of Bicarbonate at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	Treated effluent	3	40.2667	
	POD	3	105.8667	105.8667
	Observation pond	3	117.1000	117.1000
	Downstream river water	3		135.7000
	Upstream river water	3		143.8667
	Untreated effluent	3		166.0000

Table 14: Statistical analysis of Phosphate at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Downstream river water	3	.2133		
	Upstream river water	3	.3233		
	Treated effluent	3	1.2533	1.2533	
	POD	3	1.2967	1.2967	
	Untreated effluent	3		2.2067	
	Observation pond	3			3.6833

Table 15: Statistical analysis of Sulphide at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	untreated effluent	3	.0167
	POD	3	.0167
	Upstream river water	3	.0167
	Downstream river water	3	.0167
	Observation pond	3	.0183
	Treated effluent)	3	.0197

Table 16: Statistical analysis of Ammonia at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	POD	3	.2500		
	Observation pond	3	.3533		
	Downstream river water	3	.6733	.6733	
	Treated effluent	3	.9000	.9000	
	Untreated effluent	3		1.2133	
	Upstream river water	3			2.2467

Table 17: Statistical analysis of Total phosphorus at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Upstream river water	3	.3800		
	Downstream river water	3	.3933		
	POD	3	1.6867	1.6867	
	Treated effluent	3	1.7400	1.7400	
	Untreated effluent	3		2.9400	2.9400
	Observation pond	3			4.1600

Table 18: Statistical analysis of Total coliform at sampling sites

	Site	N	Subset for alpha = 0.05			
			1	2	3	4
Tukey Ba	Downstream river water	3	.6667			
	Upstream river water	3	3.0000	3.0000		
	Treated effluent	3	6.0000	6.0000	6.0000	
	Untreated effluent	3			8.3333	8.3333
	POD	3			11.3333	11.3333
	Observation pond	3				13.0000

Table 19: Statistical analysis of Phenol at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Treated effluent	3	.1400		
	Downstream river water	3		.2400	
	Observation pond	3		.2533	
	Upstream river water	3		.2767	
	POD	3		.2867	
	Untreated effluent	3			.3967

Table 20: Statistical analysis of Cyanide at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Treated effluent	3	.0117
	Upstream river water	3	.0117
	Untreated effluent	3	.0133
	Observation pond	3	.0133
	POD	3	.0133
	Downstream river water	3	.0133

Appendix 2: Statistical analysis of heavy metals at sampling sites

Table 1: Statistical analysis of Vanadium at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Untreated effluent	3	.1367
	POD	3	.1367
	Upstream river water	3	.1433
	Treated effluent	3	.1700
	Observation pond	3	.1700
	Downstream river water	3	.1700

Table 2: Statistical analysis of Nickel at sampling sites

	Site	N	Subset for alpha = 0.05		
			1	2	3
Tukey Ba	Untreated effluent	3	.0700		
	Treated effluent	3	.1033		
	Observation pond	3	.1100		
	POD	3	.2300	.2300	
	Upstream river water	3		.3833	.3833
	Downstream river water	3			.4367

Table 3: Statistical analysis of Total chromium at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Untreated effluent	3	.0733
	Treated effluent	3	.0733
	POD	3	.0867
	Observation pond	3	.0933
	Upstream river water	3	.0933
	Downstream river water	3	.1300

Table 4: Statistical analysis of Copper at sampling sites

	Site	N	Subset for alpha = 0.05	
			1	2
Tukey Ba	Treated effluent	3	.0367	
	Observation pond	3	.0367	
	POD	3	.0367	
	Untreated effluent	3	.0433	
	Downstream river water	3	.0567	
	Upstream river water	3		.2367

Table 5: Statistical analysis of Zinc at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	Upstream river water	3	.0367
	Downstream river water	3	.0433
	Observation pond	3	.0500
	POD	3	.1667
	Treated effluent	3	.4033
	Untreated effluent	3	.7167

Table 6: Statistical analysis of Lead at sampling sites

	Site	N	Subset for alpha = 0.05
			1
Tukey Ba	POD	3	.1367
	Downstream river water	3	.1367
	Upstream river water	3	.1467
	Untreated effluent	3	.1633
	Treated effluent	3	.3233
	Observation pond	3	.3467