KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF SCIENCE

BASELINE ENVIRONMENTAL QUALITY ASSESSMENT AT OFFSHORE CAPE THREE POINT, GHANA

BY

BERNARD KWAKU SACKITEY

FEBRUARY, 2019

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF SCIENCE

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

BASELINE ENVIRONMENTAL QUALITY ASSESSMENT AT OFFSHORE CAPE THREE POINT, GHANA

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY IN THE COLLEGE OF SCIENCE IN FULFILMENT OF THE REQUIREMENTS OF MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE

BY

BERNARD KWAKU SACKITEY

FEBRUARY, 2019

DECLARATION

It is hereby declared that this thesis is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any degree of the University, except where due acknowledgement has been made in the text.

BERNARD KWAKU SACKITEY

(STUDENT) … ……………………… …….. ……………………

Signature Date

Certified by:

Dr. Jonathan N. Hogarh

Supervisor ………………………. ……………………………

Signature Date

Certified by:

Prof. M. G. Addo

Head of Department ………………………. ……………………………

Signature Date

DEDICATION

I dedicate this work to God Almighty my creator, my strong pillar, my source of inspiration, wisdom, knowledge and understanding. He has been the source of my strength throughout this program and on His wings only have I soared. I also dedicate this work to my awesome beloved wife, Abigail Effah who has encouraged me all the way ensuring I give all it takes to finish that which I have started as well as my sweet mother Augustina Dedo Odonkor for her constant love and support. To my children, Ann Dedo Sackitey and Bernard Kwaku Sackitey Junior who have been affected in every way possible by this quest.

Thank you. My love for you all can never be quantified. God bless you.

LIST OF ABBREVIATIONS

AAS - Atomic Absorption Spectrophotometer

APHA - American Public Health Association

BOD- Biochemical Oxygen Demand

BTEX- Benzene, toluene, ethylene benzene and xylene

DO - Dissolved Oxygen

EC- European Commission

FAAS - Flame Atomic Absorption Spectrophotometer

FPSO- Floating Production Storage and Offloading

MARPOL - Marine Pollution

NE- North East

NOAA- National Oceanic and Atmospheric Administration

NPA - National Petroleum Authority

NW- North West

OCTP- Offshore Cape Three Points

PAH- Polycyclic Aromatic Hydrocarbons (PAHs).

PEL- Permissible Exposure Level

SE- South East

SOD - Sediment Oxygen Demand

SW- South West

TEL - Threshold Effect Level

TPH - Total Petroleum Hydrocarbon

UNEP- United Nations Environmental Program

USEPA - United States Environmental Protection Agency

VOC - Volatile Organic Carbon

ACKNOWLEDGEMENTS

I wish to express my sincere and profound gratitude to the Almighty God for his divine protection and guidance throughout my life and during the entire study.

My greatest appreciation also goes to my supervisor Dr. Jonathan N. Hogarh, Department of Theoretical and Applied Biology, Faculty of Biological science, College of Science for his constructive critism, guidance, corrections and significant contributions made during the entire execution of the thesis.

God bless you all

ABSTRACT

Baseline assessment and monitoring of physico-chemical water quality parameters in a marine environment are required in order to understand the pollution status for strategic mitigation measures to be put in place to address significant environmental impacts. Environmental monitoring is often required to obtain information on the actual and potential environmental impacts of an activity so that it will inform authorities to adopt better environmental regulations. Offshore environmental assessment was conducted on the quality of marine water and sediment at Cape Three Point, Ghana.

During the study, water and sediment samples were collected from near shore area, pipeline route and well/cluster area (Gye Nyame, FPSO, Sankofa NE, Sankofa SE, Sankofa NW and Sankofa SW fields). Data was taken monthly for a period of three months (March - May, 2018). The geographical locations of the study sites were determined using global positioning system (GPS). Physical and chemical parameters were determined for water and sediment samples using accepted international methods and standards for the examination of water. The results showed that total petroleum hydrocarbon (TPH) levels in the sediment were high in the well/cluster fields with mean values of 71.9 mg/kg and 1165 mg/kg for pipeline route and Sankofa NE fields, respectively. Iron, As, Ni and Cu in the sea water and sediment exceeded the NOAA threshold limits and were comparatively higher in the well/cluster area compared to the nearshore and pipeline route region. Concentrations of TOC, BTEX, SOD, BTEX, VOC, Pb, Cd, Cr and Hg in sediment was below detected limit and safe for marine ecosystem health. Phosphate and nitrates in the sea water were lower throughout the water column, increasing slightly with depth in the order; surface (<100m), middle (100-500m) and bottom (>500m).

This is an indication that adverse biological effects cannot occur in the short term but constant monitoring are needed in the well/ cluster field.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER ONE

INTRODUCTION

1.1 Background of study

An environmental survey and assessment of an area or locality is usually conducted to obtain information on its chemical and biological status before a new activity starts (Trabucco et al., 2006). The significance of offshore environmental monitoring and assessment is to provide an overview of the environmental safety/pollution and trends over a period of time in relation to offshore oil and gas activities. Baseline surveys are always required before exploration drilling in new areas begins. It is therefore very important that environmental monitoring and assessment are done taking into account the state of the marine environment as well as the discharge history over a the past period (Ray and Engelhardt, 1992). International conventions such as the convention on the pollution of the sea requires that baseline surveys should be carried out before commencing any exploration drilling in new and previously unsurveyed areas within established regions (MARPOL Convention, 1978). This depends on the distance from already surveyed areas especially where vulnerable environmental resources including species and habitats have been found to exist in order to protect the entire marine ecosystem from pollution (Erakhrumen, 2015).

Environmental monitoring activities at offshore are carried out in a way that makes it possible to verify the risk that pollutant discharges from oil and gas activities impact on the pelagic environment. The baseline information on the pristine conditions established would help to compare against exploration drilling, development and post-development impacts over a period of time (Fakhru'l-Razi et al., 2012). When baseline assessment and monitoring of quality parameters in a marine environment are conducted and pollution status are known, strategic mitigation measures can then be put in place to address significant environmental impacts in the marine ecosystem (Onojake and Abanum, 2012).

Eni Ghana exploration and production involves developing the Offshore Cape Three Points Project, consisting of the development of 19 wells, the installation of a Floating Production Storage and Offloading (FPSO) and the associated pipeline at Cape Three Point in Ghana. A baseline assessment and environmental quality monitoring are required in order to obtain information on the actual and potential environmental impacts of the marine ecosystem prior to commencement of drilling and exploration. The information obtained based on the assessment and monitoring serve as a benchmark on how the general regulatory requirements can be fulfilled (Hansen and Davies, 2012).

The monitoring and assessment of physical, chemical and vulnerable benthic habitats are intended to ascertain extent to which organisms in the sea waters are affected by pollution generated through oil and gas activities (Neff et al., 2013). This study therefore sought to conduct a baseline environmental quality at offshore Cape Three Point.

1.2 Problem statement

Offshore operating companies are required to carry out environmental assessment to obtain information on the actual existing conditions and potential environmental impacts of their activities. This gives environmental protection authorities a better basis for regulating the release of pollutants into marine ecosystem (Onojake and Abanum, 2010).

Specific requirements and regulations for environmental assessment are established relating to petroleum activities which deal with environmental surveys of the water column, and sediment analysis for physico-chemical parameters required before petroleum exploration begins (Hansen and Davies, 2012). Regulations provide information on petroleum activities at both offshore and onshore environment have been set out and include environmental reporting of water, sediment and benthos quality (Neff et al., 2013).

Locations where oil and gas explorations are sited have possibility of affecting the flora and fauna in aquatic environs. Hence, there is the need for environmental assessment to investigate the environmental conditions before these explorations to assess their impacts. This is necessary to inform possible mitigation measures to augment the effects caused by the petroleum exploration activities Offshore Cape Three Point, Ghana.

1.3 Justification

Environmental pollutants such as hydrocarbons (BTEX, PAH, TPH, and VOC), heavy metals and high levels of nutrients can significantly impact on the aquatic environment. Water column assessment and sediment analysis at offshore drilling need to be determined because discharges of pollutants in the marine environment continue to increase by oil and gas companies. The findings of this study will provide relevant information on the current environmental quality status of the offshore Cape Three Points. The findings will also be of help to relevant authorities of offshore oil and gas to continuously monitor the marine environment in accordance with the requirements of Marine Pollution (MARPOL) convention and subsequently avoid significant environmental impacts.

Furthermore, the findings of this study will serve as baseline for Eni Ghana to improve on their environmental performance by supporting a good environmental management practice at the site, assist in meeting regulatory requirements and provide relevant data about the environmental status at the operation sites.

1.4 Main objective

The overall objective was to conduct a baseline environmental quality assessment at offshore Cape Three Point.

1.4.1 Specific objectives

- To determine the levels of some physical and chemical parameters present in the sea water (pH, TDS, temperature, nitrates, phosphates, DO, TOC, BOD_5 ,Pb, Cu, Cd, Cr, Hg, As, Ni, Fe, Zn).
- To determine the levels of selected physical and chemical variables in (redox potential, BTEX, VOC, TPH, Pb, Cu, Cd, Cr, Hg, As, Ni, Fe and Cu) sea sediment.

1.4.2 Research questions

- What was the state of physical and chemical characteristics of the seawater prior to offshore oil drilling project by ENI Ghana Limited?
- What was the state of physical and chemical characteristics of sea sediment prior to the offshore oil drilling project by ENI Ghana Limited?

CHAPTER TWO

LITERATURE REVIEW

2.1 Physical and chemical characteristics of sea water quality

The determination of physico-chemical characteristics of sea water quality is of significant concern in order to effectively address future contaminants that have the potential to pollute the marine ecosystem (Cianelli et al., 2011). Some studies have been conducted to measure sea water and sediment quality parameters in both developed and developing countries since their levels beyond recommended limit have the potential to affect the marine ecosystem. This include pH, conductivity, total suspended solids, temperature, dissolved oxygen, chemical oxygen demand, total organic carbon, biological oxygen demand and heavy metals such as Pb, Cu, Zn, Cr, Ni, Co, Fe and As (Hansen and Davies, 2012; Neff et al., 2013). Other hydrocarbons such as volatile organic compounds, total organic carbon, benzene, toluene and xylene (BTEX) are also significant parameters whose present beyond recommended limit can affect the entire marine ecosystem and subsequently affect fauna and flora (Neff et al., 2013).

More so, oil rig platform can also discharges produced water which contain high levels of heavy metals, total mineral oils, phenols, aromatic and aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (Onojake and Abanum, 2012). The specific chemical composition of the produced water depends on the geological reservoir, the field operations and the exploitation level (Cianelli et al., 2011).

2.2 Sources and occurrence of oil pollution in water

Studies have identified three major sources of oil pollution in the marine ecosystem and this includes; oil spills, gas effluent and waste discharges (Neff et al., 2013; Cianelli et al., 2011). The major causes of the spill incidences include; pipelines and flow lines leakage/blowouts, blowouts from well-heads due to poor maintenance and damage and spills from flow stations (Hansen and Davies, 2012). Oil spills involve the release of dangerous hydrocarbons such as benzene and Polycyclic Aromatic Hydrocarbons (PAHs) into the soil and water sources. These spillages influence marine life and subsequently affect the entire ecosystem (Saro, 2007).

2.3 Effluent and Waste discharges into water

The discharge of effluents into sea water by the oil companies is one significant phenomenon that needs to be addressed for the protection of the sea. For instance during exploration or seismic surveys by oil companies, drill cuttings, drilling mud and fluids are used for stimulating production (Onojake and Abanum, 2012). The major constituents of drill cuttings such as baryotes and bentonitic clays when dumped on the ground prevent local plant growth until natural processes develop new topsoil. In the water, these materials are dispersed and sink and may kill benthic living plants and organisms by burying them (Armstrong et al., 2004). In addition to the pollutants introduced into the environment from exploration operations, refinery wastes also have characteristics which constitute potential water pollutants such as phosphates, nitrates and organic compounds (Saro, 2007).

The major element involved in the process of environmental impact assessment is the identification of physico-chemical parameters as it helps to quantify and evaluate the extent of pollution. Hence it is necessary to identify the critical impacts that are likely to cause significant effects on various components of the environment due to proposed exploratory drilling (Onojake and Abanum, 2012).

2.4 Chemical composition of petroleum

"Petroleum is a naturally occurring toxic, flammable liquid that consist of a complex combination of hydrocarbons of diverse molecular weight and other organic compounds" (Onojake and Abanum, 2012). Liquefied petroleum gas (LPG) such as methane, ethane, and ethane among others are part of petroleum but it is a mixture of lighter hydrocarbons (Neff et al., 2013). The other organic compounds that are part of petroleum are; carbon, nitrogen, oxygen and sulphur and most importantly compounds incuding persistent organic pollutants (POPs). "There are also other heavy metals such as iron, nickel, copper and vanadium which may pollute the immediate environment when the oil spills (Saro, 2007).

2.4.1 Persistent Organic Pollutants (POPs)

Persistent Organic Pollutants (POPs) are groups of organic compounds classified as persistent, bio-accumulating and toxic (Neff et al., 2013). These are created through anthropogenic industrial processes which have potential substantial effects on the environment and human health (Onojake and Abanum, 2012). Persistent Organic Pollutants persist in the environment because there is an extensive resistance to degradation in the environment by means of biological processes, together with photolytic and chemical processes. Persistent Organic Pollutants also have other qualities which include capability to be easily transported at long-range distances, bio-magnification in the food chain systems, and histological bioaccumulation in both animals and humans (Rittler, et al., 2007).

Initially, in 1995, only about 12 POPs were set as priority POPs and investigated by the Governing Council (GC) of the United Nations Environmental Program (UNEP). The list was later expanded with the inclusion of carcinogenic polycyclic aromatic hydrocarbons (PAHs). An international treaty was signed that regulates these pollutants and also encourages a strategic plan to reduce and possibly ban all chemicals named under the POP group by the Stockholm Convention on POPs in 2001 (Bilcke, 2002). Chronic exposures to POPs are potentially hazardous and are capable of resulting in fatalities, diseases such as cancers, illnesses and impairments of the immune systems. Accessibility to POPs exposure is possible through accidental ingestion in diets and direct exposures in the marine environment (Fakhru'l-Razi et al., 2012).

Guo et al. (2012) conducted a study and extracted PAHs in sediments from a sea sample from New Delhi, India by using the soxhlet extraction technique and separated and quantified them using a

GC-MS process. The concentrations varied between 6 and 46 μg/g dry weight. Petersen et al. (2011) also investigated the distribution of PAHs in superficial sediments of the western Mediterranean Sea using GC-MS. The PAH concentrations ranged between 1 and 20500 ng/g dry weight in the sediments.

2.5 Effects of petroleum exploration on marine ecosystem

Oil and gas exploration can significantly influence the marine ecosystem and subsequently pollute marine resources if care is not taken. For instance 40% of inhabitants species in the Niger delta in Nigeria was found to have been lost due to release of contaminants such as VOC, PAH, TPH and heavy metals such as Cu, Ni, Cr, Co and As during the oil exploration and drilling processes (Onojake and Abanum, 2012).

"The flaring of gas which is also a major component during oil and gas exploration subsequently releases gases and compounds including nitrogen dioxide, sulphur dioxide and volatile organic compounds such as benzene, toluene, and xylene"(Cambel and Tessier, 1996).

Produced water that is produced as a byproduct of oil drilling contains polycyclic aromatic hydrocarbons (PAHs) and at high levels may have the potential to cause harm to marine life usually have high levels (Cianelli et al., 2011).

2.6 Effect of oil exploration activities in marine organisms

"The drilling of oil either offshore and onshore have a significant implications and have the potential to alter the existing conditions of the environment where such activities are operated" (Fakhru'l-Razi et al., 2012). Onojake and Abanum, (2012) reported that some species of fish have been driven away both from offshore and onshore and others found to be dead due to pollution of marine resources from oil exploration

Produced water which contain soluble compounds and heavy metals such as Cu, Pb, Zn, Ni, among other toxic metals may be a significant source of marine pollution. These have the potential to destroy both fauna and flora as they can pass through the system and be discharged with the produced water into the sea which tends to have negative effect on marine organisms (Neff et al., 2013).

“According to Onojake and Abanum, (2012), offshore spills which are usually much greater in scale contaminate coastal environment and cause a decline in local fishing production” (Neff et al., 2013). Barros et al. (2001). Reported that accidental spills from tanker ship in Alaska, Galapos Island in France and many have significantly impacted on their marine ecosystem and subsequently affected benthic species leading to a decline in fish.

One of the most significant routes through which oil spills affect marine habitats is by essentially suffocating plants and animals. Marine plants could be covered in a film of oil which leads to reduction of oxygen and water exchange thereby causing the plants to die and marine life threatened to survive”(Neff et al., 2013). The inhalation and ingestion of toxic compounds as a result of oil spillage can also harm marine life, both in the long and short term. “In the long term, oil spills affect marine life by interfering with the ability to breed, reproduce, grow, or perform other vital functions” (Eastmond, 2008).

“Some of the impacts of oil exploration on the marine environment include; significant reduction of fisheries resources or damage to wild life resources including sea birds and marine mammals, decrease of aesthetic values beaches, alteration of marine ecosystems by elimination of species with an initial decrease in diversity” (Hansen and Davies, 2012).

2.7 Effects of spillage of low toxicity oil based mud in water

"Drilling activities and the maintenance of machines and equipment in oil exploration generate solid waste such as well cuttings, drilling muds and cement slurry "(Onojake and Abanum, 2012). Drill cuttings describe the rock formation being drilled that are returned to the surface with drilling fluid. "The cuttings then become a waste stream from the drilling process and are eventually dumped into the sea" (Hansen and Davies, 2012).

Studies conducted on the Jubilee Oil Fields in Ghana revealed elevated levels of lead (Pb), manganese (Mn), cadmium (Cd) and nickel (Ni) in the marine water samples around the Jubilee oil fields. The source to attribute this could be partly be attributed to the discharged of low toxicity oil based mud and other drill cuttings which contains these toxic chemicals. However, there was high concentrations of oil and grease, and organic based compounds such as TPH, VOC and PAH in sediment and water samples. "The occurrence the elevated levels of these compounds in both sea water and sediment samples is an indication of oil pollution from the operations of the Jubilee Field" (Erakhrumen, 2015).

2.8 Carcinogenic metallic elements

2.8.1 Lead (Pb)

Lead (Pb) forms from natural processes and it has been widely investigated due to its toxicological attributes and extensive distribution capabilities in the environment. Anthropogenic sources account for the majority of Pb pollution in the environment; most notable is the pollution from vehicular exhausts due to additives such as lead tetraethyl in commercially available gasoline prior to recent exclusions by the U.S. EPA (USEPA, 1999) and also by the European Union (European Directive 98/70/CE). These additives, though, banned in the United States and European Union are still been used in other countries, like Nigeria. Lead (Pb) compounds are classified as both organic and inorganic; where the inorganic Pb compounds are classified as human carcinogens (Toscano and Guilarte, 2005).

Lead (Pb) is considered a multi-effect pollutant in humans leading to a variety of undesirable health problems such as encephalopathy (Gordon et al., 2002). The kidney and hematopoietic defects, cardiovascular and gastrointestinal impediments, and immunological and nervous system breakdown are also common symptoms of lead poisoning in humans (USEPA, 1999).

2.8.2 Cadmium (Cd)

Cadmium (Cd) is a prevalent heavy metal with natural origins from the earth's crust and it is dispersed in the environment through natural processes such as forest fires, rock weathering, and volcanic eruptions (Pinot et al., 2000). Anthropogenic sources of Cd pollution are over 10 times higher than sources from natural causes (Elinder, 1992). Industrial effluent discharges from energy generation and other industrial activities largely contribute to Cd pollution (Toscano and Guilarte, 2005).

Produced water from oil exploration activities also release high levels of Cd into the environment and when ingested by fishes and eventually transfer to man through the food chain (Erakhrumen, 2015). The routes of exposure of Cd to the human body are through inhalation and ingestion (Llobet et al., 1998; Domingo, 1994). Although the primary route of Cd into the human body is through inhalation with about 50% absorbed in the lungs, it is effectively circulated in the blood and hoarded in the kidney and liver, resulting in adverse human health problems (Goyer, 1991; Hopkins et al., 1968).

2.8.3 Chromium (Cr)

Chromium (Cr) is a widespread element present in all environmental media continental dust flux has been identified as the main natural source of exposure (Shanker et al., 2005). However, increasing levels is largely attributed to human induced and mostly contribute significantly to ecosystem impacts than the natural sources. "Chromium enters the atmosphere via anthropogenic stationary and mobile point sources, including gas, oil and coal combustion and industries that manufacture metals or use metals as active ingredients in their operations" (Vincent, 2003). "Anthropogenic sources such as coal and petroleum combustions are responsible for the elevated levels of Cr in the environment" (Stoecker, 2001; Porte, et al., 2003; Katz and Salem, 1992).

2.8.4 Nickel (Ni)

Nickel (Ni) compounds are abundantly found naturally. The earth's core is composed of 10% Ni and the majority reaches the earth's surface through volcanic processes. Elements of Ni found in the environment are found as alloys of Cr, Cu, Zn and Fe. The distribution of Ni in ecological materials occurs from petroleum combustion plants and coal plants, waste discharge from ships as well as from trash incinerators and produced water (Erakhrumen, 2015; Maggi et al., 2010).

The potential human health responses to extensive exposures to Ni include damage to blood cells and to the kidney (USEPA, 1999) as well as irritation of the nasal cavities, and developmental and immune system defects (Erakhrumen, 2015). Nickel have been reported as potentially carcinogenic to humans with chronic exposures (IARC, 1999). The chronic inhalation minimal risk level for Ni has been determined as 9.0×10^{-05} mg Ni/m^3 (USEPA, 1999) and an oral reference dose (RFD) of 2.0×10^{-02} mg/ kg per day (Toscano and Guilarte, 2005).

2.9 Sedimentological analysis

Studies show that sediment analysis is a significant factor to determine the pollution of a water body (Onojake and Abanum, 2012; Erakhrumen, 2015). Grain size is the most fundamental physical property of sediment. Sediments consisting of grains of different size and mainly categorized as sand, silt or clay; they are classified according to the size and size distribution of their grains in the categories described in the Wentworth classification (Pinot et al., 2000). The information on sediment grain size allows study trends in surface processes related to the dynamic conditions of transportation and deposition. Moreover, sediments are the ultimate sink for contaminants in the marine environment (Pinot et al., 2000). The relationships between physical properties and chemical characterization of sediment are a basic point of environmental impact assessment in order to determine whether or not contamination related to offshore activities has occurred. In studies conducted to determine the environmental quality of offshore oil exploration in developing world, the parameters of interest analysed in the sediments included: Total Organic Carbon (TOC), Benzene Toluene Xylene (BTEX), Polycyclic Aromatic Hydrocarbon (PAH), Aliphatic compounds, Volatile Organic Compounds (VOCs), Total Petroleum Hydrocarbon (TPH), heavy metals (Pb, Cu, Cd, Cr, Hg, As, Ni, Al, Ba, Fe, V and Zn), temperature, conductivity, turbidity (suspended matter) and dissolved oxygen (Chloudhry, 1983).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study site

The Offshore Cape Three Points (OCTP) block is located offshore of Ahanta West District in the Western Region of Ghana. It has about 1100 meters of water depth and approximately 60 km from the coast. The OCTP block is regulated by a Petroleum Agreement signed on 15th March, 2006 between the Republic of Ghana (Minister of Energy) and the Contractor group, formed by ENI Ghana E & P Limited P.I., Vitol Upstream Ghana Limited and Ghana National Petroleum Commission. The OCTP field shall be produced from five main regions (Sankofa North East, South East, South West, North West and Gye Nyame) (NPA, 2010).

3.2 Sampling Methods

A reconnaissance survey was conducted for selection of the sampling locations. The locations were classified into three clusters based on the area of operation by ENI Ghana Exploration. Three sampling areas were demarcated from each cluster and their respective coordinates were determined using global positioning satellite (GPS) device (Model, GARMIN etrex 20). These sampling areas are; near shore area, pipeline route and well/cluster area (Gye Nyame, FPSO, Sankofa NE, Sankofa SE, Sankofa NW and Sankofa SW fields). Data was taken monthly for a period of three months (March – May, 2018). Triplicate samples were taken during the study period (Fig 3.1). In all, a total of 216 each of water and sediment samples were analyzed during the entire study period.

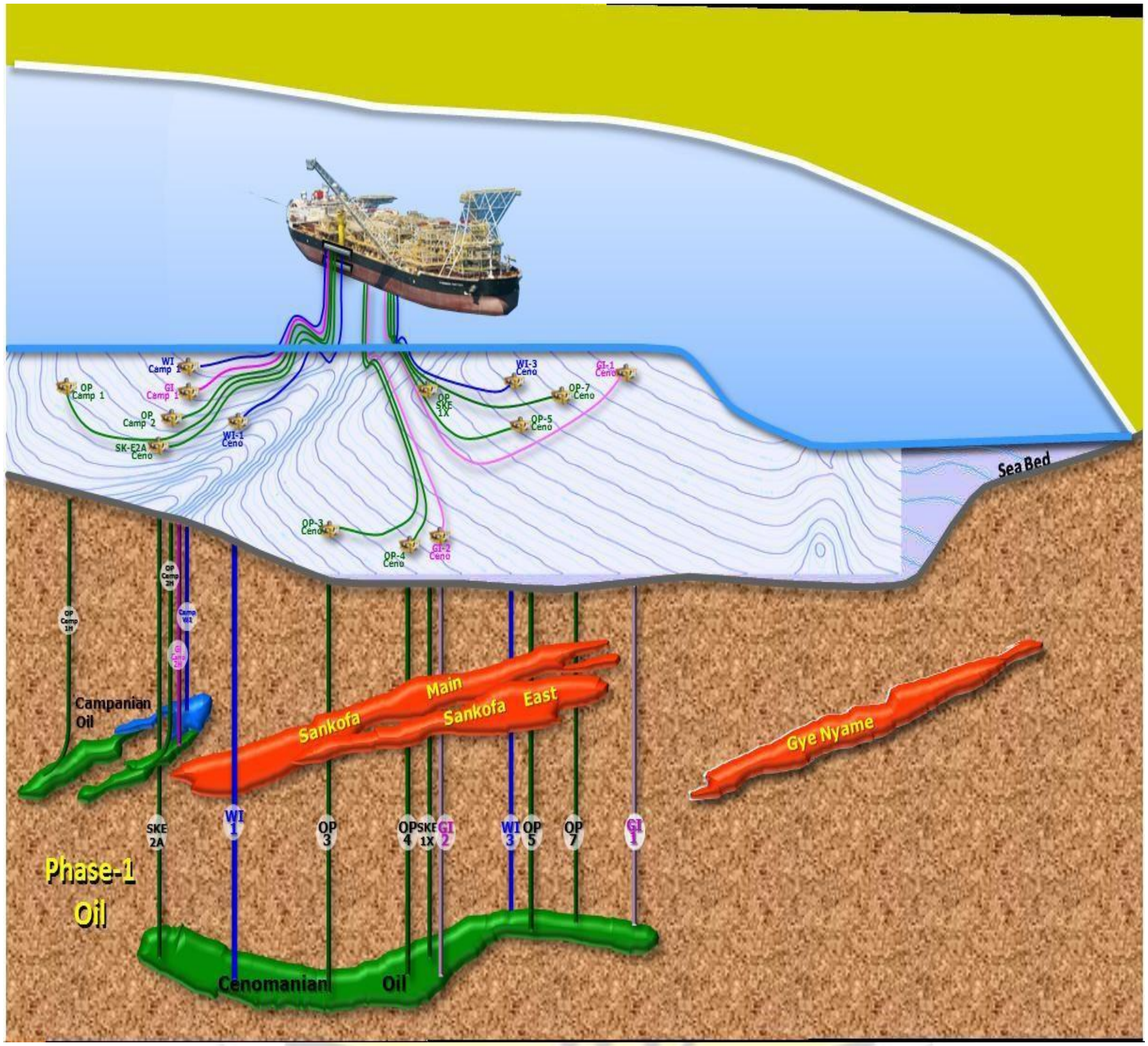

Fig 3.1 Map of the study area

3.3 Sampling procedures

3.3.1 Sea water sampling

All heavy metals were sampled with plastic containers whilst hydrocarbon samples were taken in glass bottles. Strict measures were adhered to in order to avoid any external influence that could contaminate the samples during collection, handling, transportation and preservation.

Plastic bottles of 500 ml capacity with stopper were used for collecting the water samples. The containers were pretreated by washing with acetone to get rid of organic substances such as grease and fat residues. Each bottle was washed with detergents and finally rinsed with de-ionized water. The sampling containers were then soaked in 1 M nitric acid solution for 24 hours. The containers were finally rinsed three times with distilled water before transporting them to the sampling site.

At the site, the sampling bottles were rinsed thoroughly with some of the water samples to be sampled. Water samples were taken at three depths; surface (<100 m from surface), mid-column (100-500 m), and more than 500m m from the seabed. Samples were taken with a carrousel of 12 x 5L Niskin bottles Sea Bird Electronics 32A clean grab sampler. At each of the sampling site, physical parameters were measured in-situ with the deployment of a conductivity, temperature and depth (CTD) sensor (Model: Sea Bird Electronics 32). The depth of the water was determined by means of a controlled T-count (Hy-Tec) cable meter installed on board. The water samples were then transferred into appropriate bottles. Each container was clearly marked with the name, address of the sampling station, sample description and the date of sampling. Samples that were not analyzed at the sampling location were put in an ice chest and finally transported to the laboratory and stored in a refrigerator below 4℃ (APHA, 2010).

Physico-chemical parameters measured were pH, temperature, total dissolved solids, nitrate, phosphates, biological oxygen demand (BOD), dissolved oxygen (DO) and total organic carbon (TOC). Hydrocarbons (BTEX, VOC, and TPH) as well as heavy metals (Cr, As, Pb, Cd, Hg, Ni, Fe and Zn) in the water and sediment samples were also measured.

3.3.2 Sediment sampling

Sediment samples were taken using a grab sampler (Model: Van Veen) which is capable of collecting sediment material up to about 20 cm in depth. Glass bottles were used for storage of sediment for the analysis of hydrocarbons and were kept in an ice chest. Three replicates were obtained in each sampling location. The parameters that were measured in the sea sediment were; sediment oxygen demand, benzene, toluene, ethylene benzene and xylene (BTEX), TPH (total petroleum hydrocarbons), VOC (volatile organic compounds) and heavy metals (Pb, Cu, Cd, Cr, Hg, As, Ni and Fe). Sediment oxygen demand was measured in-situ using Electrometric Laboratory respirometer (Bench Model)

3.4 Water Sample Analysis

All the water analyses were determined using appropriate certified and acceptable standard methods of water and waste water (APHA, 2010). The physical parameters including; pH, temperature and dissolved oxygen were measured in-situ using CTD Sea Bird Electronics 25 sensors. The heavy metals (Cr, As, Pb, Cd, Hg, Cu, Ni and Fe) were analyzed with Flame Atomic Absorption Spectrophotometry (FAAS) (ST-AAS-7000) and mercury was analyzed using a mercury analyzer. Nitrate and phosphates were determined using HACH direct reading spectrophotometer (APHA, 2010).

The BOD was analyzed using potassium dichromate method. Total organic carbon (TOC) was analyzed using catalytic method by oxidative combustion at high temperature. The hydrocarbons (BTEX, VOC and TPH) were analyzed using high resolution gas chromatography-mass spectrometry (HR GC-MS) (APHA, 2010).

3.4.1 Nitrate-Nitrogen- (NO_3-N) Analysis

The method used for the nitrate analysis was the cadmium reduction method. The nitrate level in each sample was measured using nitrate powdered pillows in a direct reading HACH spectrophotometer (Model DR. 2010). Ten (10) ml of the sample was measured into sample cell of the spectrophotometer. One nitraver 5 nitrate reagent powder pillows was added to the sample.

The mixture was then shaken vigorously for 1 minute. Five minutes was allowed for the solution to react. An orange colour of the mixture indicated the presence of nitrate. A blank was placed into the cell holder to calibrate it. The prepared sample was then placed into the cell holder to determine the nitrate-nitrogen concentration at 500 nm in mg/l (HACH, 1996).

3.4.2 Phosphate -Phosphorus (PO_4-P)

A 25 ml of the sample was placed in the sample cell. Phos ver 3 phosphate reagent powder pillow was added to the sample content and swirled immediately to mix. A two-minute reaction period was allowed. A blue coloration of the mixture indicates the presence of phosphate. A blank was placed into the cell holder to calibrate it. After the sample had reacted, the prepared sample was lifted and placed into the cell holder and the level of phosphate-phosphorus was determined at 890 nm" (APHA, 2010).

3.4.3 Biochemical Oxygen Demand (BOD)

The BOD test was done by filling and hermetically sealing BOD bottle with the sample of water and was put in an incubator at 20^{o}C for five days. The initial dissolved oxygen measured was taken and recorded and the value obtained after the incubating period was also recorded. "The BOD was calculated by subtracting the final value from the initial value. The samples taken from the field for the BOD analysis were diluted. The dilution was done since BOD concentration in the water samples was suspected to exceed the concentration of DO available in the water sample as initial measurements recorded was very low. Because the initial DO was determined immediately after the dilution was made, all oxygen uptake, including that occurring during the first 15 minutes was included in the BOD measurement. The dilution water was prepared by 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride and iron (III) chloride solution per litre of water" (APHA, 2010).

Mathematically the BOD was computed as below;

$$BOD_5 \text{ mg/l} = \frac{DI - D2}{P}$$

Where,

D1 = DO of diluted sample immediately after preparation, mg/l

D2 = DO of diluted sample incubated for 5 days at 20℃ mg/l

P = Decimal volumetric fraction of sample used.

3.5 Determination of Heavy Metals

3.5.1 Digestion of water samples

100 ml of the water sample was measured with a measuring cylinder and 5 ml of concentrated hydrochloric acid was added to it. The solution was then transferred into a conical flask and heated on hot plate for two hours at 105 °C to 25 ml. It was then transferred into 100ml volumetric flask and distilled water was added to fill up to the mark where it was filtered and transferred into the pre-cleaned sample bottle and subjected to atomic absorption spectrophotometer (AAS) analysis (Serfor Armah et al., 2006).

3.5.2 Digestion of sediment samples

The sediment samples were air- dried for three days. It was then ground into smaller particles, sieved and finally subjected to digestion process: Two grammes of the sediment sample was weighed and poured into a beaker, 5 ml of nitric acid (HNO_3) was added together with 2 ml of perchloric acid and 5ml of hydrogen fluoride (HF) and heated for 1 hour on a heater at 160°C. After proper digestion, the sample was allowed to cool down and then filtered. The filtrate was transferred into 100 ml volumetric flask and made up to the mark with distilled water. The prepared sample solution was transferred into the pre-cleaned labeled sample bottles in readiness for atomic adsorption spectrophotometer (AAS) analysis (Serfor Armah et al., 2006).

Instrumental Analysis of Heavy metals in water and sediment

The digestates were assayed for the presence of heavy metals (Cr, As, Pb, Cd, Hg, Ni, Fe and Zn) using Atomic Absorption Spectrometer (VARIAN AA 240FS) in an acetylene-air flame. The concentrations were then calculated based on the absorbance obtained using the Beer Lambert law. Responses of standards were used to establish accurate performance of machine and accurate concentration values of elements. The machine was calibrated after every three analyses to ensure accuracy. Light was generated from a hollow cathode lamp at wavelength characteristic to each analyte. The sample was introduced as an aerosol into the flame and the burner aligned in the optical path to allow the light beam pass through the flame where the light was absorbed. The light was then directed into a monochromator which then isolated the specific analytical wavelength of the light emitted by the hollow cathode lamp from the non-analytical. The sensitive light detector then measured the light and translated the response into the analytical measurements (Whitemore, 2001).

Calculation of concentration of heavy metals in sediment was done using the following formula;

$$Final\ conc. (mg/L\ or\ \ mg/kg) = \frac{Conc. (analytical\ measurement)\ x\ Nominal\ volume}{Sample\ weight\ (gramme)}$$

Where: Conc. (analytical measurement) = instrumental measurement

Nominal volume = final volume of digestate sample solution

Final Concentration (mg/kg) = concentration of metals in sediment.

3.5.3 Determination of Total organic carbon (TOC)

The materials including glass wares that were used in the sample processing were combusted at 400°C for at least 4 hours following standard procedures. The samples were kept frozen at -20°C until the final processing. The sediment samples were then allowed to be thaw, and was homogenized and finally dried in an oven at a temperature of 40°C. A portion of the sample was then removed, ground and homogenized to obtain a uniform mixture. An aliquot of the dried, homogenized sample was then placed in an aluminum-weighing pan and further dried at temperature of 105°C. The LECO CR-412 Carbon Analyzer was calibrated before the analysis of samples. Different quantities of high purity calcium carbonate standard (99.95% purity, carbon content of 12.0%) were used to calibrate the instrument. An empty carbon-free combustion boat was analyzed as a blank for the calibration curve. Total organic carbon was analyzed by placing approximately 0.350 g of the dried, ground and homogenized sample into a clean, carbon-free combustion boat. Each sample boat was then treated with phosphoric acid drop by drop until the sample stops “bubbling” and the sample was completely moist with acid. The sample was placed in an oven and the temperature was set at 40°C for 24 hours and then transferred to an oven set at 105°C. Once the sample was dried, the boat was placed on the auto sampler rack assembly and loaded onto the LECO carbon analyzer for the determination of Total organic carbon” (Weisman et al., 2008).

3.5.4 Determination of TPH using Gas Chromatography

The TPH of sediment sample was analyzed using the revised EPA 8015D called "NonHalogenated Organics Using GC/FID method. This method has the ability to provide some necessary information on the product type. The solid samples were extracted with soxhlet device (EPA 3540). The extracts were then subjected to alumina (EPA 3611) with which the fatty matter was removed on the basis of polarity and petroleum hydrocarbons (fractionated into aliphatic and aromatic fractions). Each fraction was then injected directly into a gas chromatograph equipped with a nonpolar capillary column for analytical determination. Identification of the analytes was done by comparing the retention time of an individual compound to that of a reference standard.

Calibration standards were used to prepare calibration curves with which the TPH were quantified (Weisman et al., 2008).

3.5.5 Determination of BTEX

One gram of sediment sample was weighted in a 10 ml standard glass vial. The sample was then heated in headspace auto sampler at 90 °C for 10 min whilst shaking. The syringe temperature was selected at 100 °C. The oven temperature program started from 40 °C and was held for 10 minutes, increased at a rate of 20 °C/min, up to 200 °C and finally held for 2 minutes. Electron impact ionization (EI) was used at 70 eV. A transfer line temperature was fixed and held at 250 °C. The detector temperature was set to 230 °C. A Hewlett Packard HP 5MS column (Palo Alto, CA, USA) (30 m × 0.32 mm i.d., 0.25 μm film thickness) was then used to obtain the reference data by chromatography. For instrumental control and intensity measurements, vendor software Xcalibur from Thermo was used (Waltham, MA, USA). Calibration data were developed with the help of Turbo Quant Analyst 6.0 software (Thermo Nicolet Corp. Madison, USA). The mass spectra were obtained at a mass-to-charge ratio (m/z) scan range from 75 to 200. The specific ions generated at m/z 77 and 78 for benzene, m/z 91 and 92 for toluene and m/z 91 and 106 for ethyl benzene and xylenes, respectively were then determined (Medunić and Šmit, 2015).

3.6 Quality control

The following quality control and quality assurance techniques were used during the analysis.

Blanks were used throughout the study to check contamination during sample preparation. Duplicates samples were analyzed to check the reproducibility of the method used and also to check the efficiency of the equipment being used. Blanks and duplicates of samples were digested under the same conditions as the samples. These served as internal controls.

3.7 Data Processing and Analysis

Data collected for all parameters were entered into Microsoft excel spreadsheet version 2010 and finally imported onto STATA software version 14 for statistical analysis. Descriptive statistics such as means, standard deviation, minimum and maximum ranges were computed. One way analysis of variance (ANOVA) was used to determine if statistical significant differences in concentrations of physical and chemical parameters exist among the sampling locations and statistical significance was accepted at $p \leq 0.05$.

CHAPTER FOUR

RESULTS

4.1 Physico-chemical parameters of sediment

4.1.1 Sediment Oxygen Demand (SOD)

Figure 4.1 illustrates the mean values of sediment oxygen demand. High mean values were recorded in the cluster/well area of the sea with the highest value of 3.5 mg/l recorded at Sankofa NE sampling station. Pipeline route station registered mean value of 0.5 mg/l whilst the near shore region recorded a value of 0.7 mg/l .The highest values were found in Sankofa NE and SE (Fig 4.1). Analysis of variance at 95% confidence level revealed statistically significant differences in SOD among the sampling sites ($p = 0.024$). Post hoc multiple comparison using Tukey's Honestly Significant Difference (HSD) revealed that there were no differences in mean SOD among Sankofa NE, Sankofa SE, Sankofa NW and Sankofa SW ($p > 0.05$). There were also no differences between the nearshore region, Pipeline region, Gye Nyame fields and FPSO fields (p > 0.05).

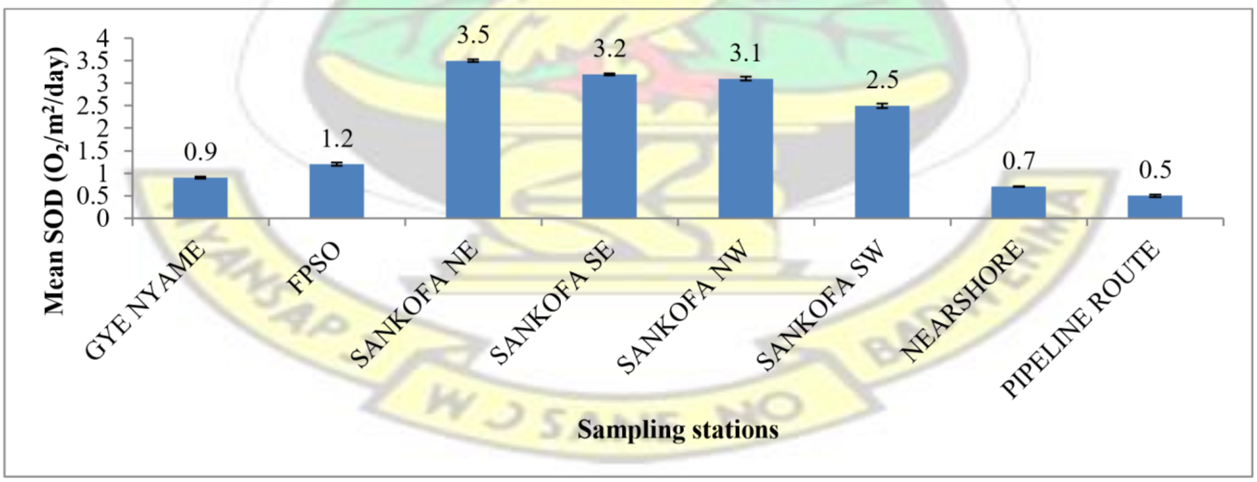

Fig 4.1: Mean SOD values of sea sediment.

4.1.2 Total Organic Carbon (TOC)

The mean total organic carbon (TOC) of the sediment samples ranged from a minimum of 2.4 mg/kg (Nearshore region) to a maximum 4.4 mg/kg (Gye Nyame sampling station) (Fig 4.2). There was a statistically significant difference in concentrations of TOC among the sampling stations (p = 0.032). Tukey's HSD revealed that there were no differences in mean TOC among Sankofa NE, Sankofa SE, Sankofa NW and Sankofa SW, FPSO and Gye Nyame fields ($p>0.05$). They were however different from Nearshore region and Pipeline route region ($p = 0.025$). Concentrations of the nearshore and pipe route region were not statistically different ($p = 0.128$). The TOC concentrations homogeneity along nearshore area and pipeline route region was generally lower compared to those at the well/cluster regions.

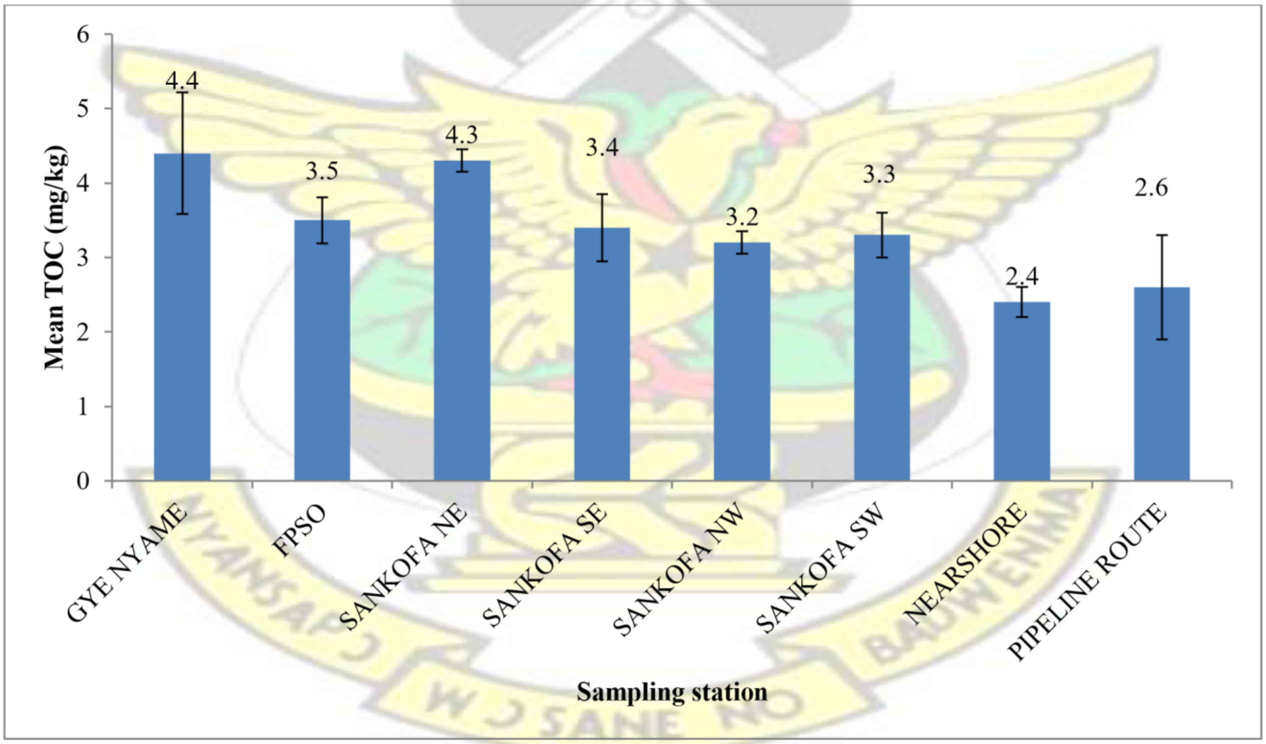

Fig 4.2: Mean TOC of sea water samples.

4.1.3 Total petroleum hydrocarbon (TPH)

The highest content of TPHs was recorded at Sankofa NE with mean value of 1165 mg/kg. The lowest mean values were recorded at Nearshore and pipeline route regions with mean values of 68.2 mg/kg and 71.9 mg/kg respectively (Fig 4.3). The TPH concentration homogeneity along nearshore area and pipeline route region were lower compared to those at the well/cluster regions and showed statistically significant differences among sampling stations (p = 0.025). Tukey's HSD multiple comparison showed that there were no differences in mean TPH among Gye Nyame fields, FPSO, Sankofa NE and Sankofa NW ($p > 0.05$). There were no differences in TPH between Sankofa SE and Sankofa SW ($p > 0.05$). There was also no significant difference between Nearshore and pipeline route sampling stations ($p = 0.432$).

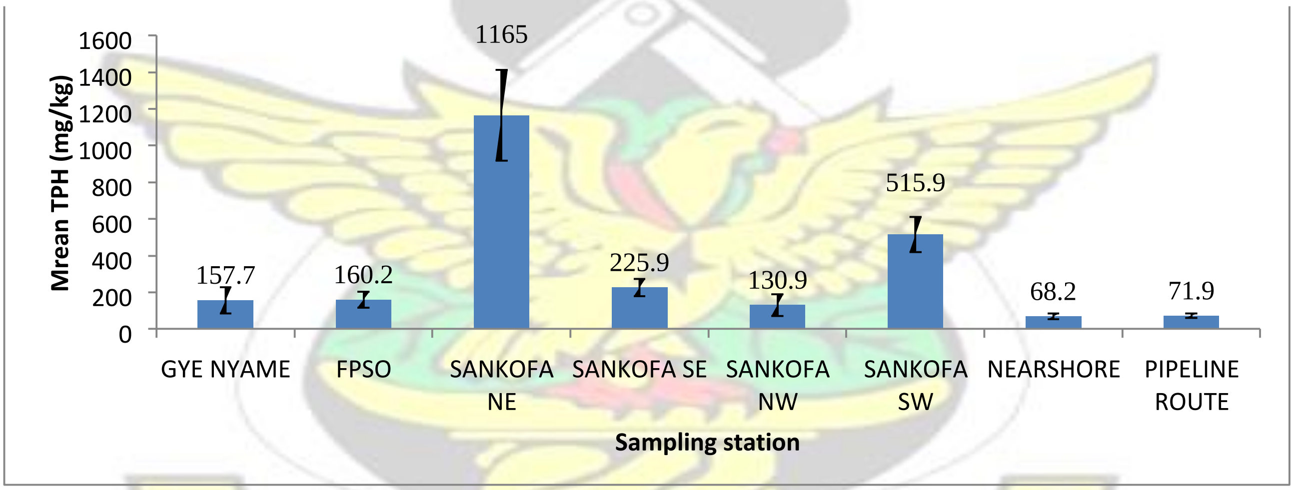

Fig 4.3: Mean TPH concentrations of sea sediment samples at sampling stations.

4.1.4 Volatile organic compounds (VOC)

Acetone and tetrachloroethane were the two volatile organic compounds that were investigated in this study. The mean acetone levels in sea water samples ranged from 0.02 mg/kg (Sankofa SE) to a maximum of 0.18 mg/kg (Sankofa SE) and 0.19mg/kg (Nearshore region). Concentrations of tetrachloroethane also ranged from a minimum of 0.02 mg/kg (pipeline route) to a maximum of 0.15 mg/kg (Gye Nyame sampling station). Mean VOC did not differ significantly among the sampling stations (p = 0.482).

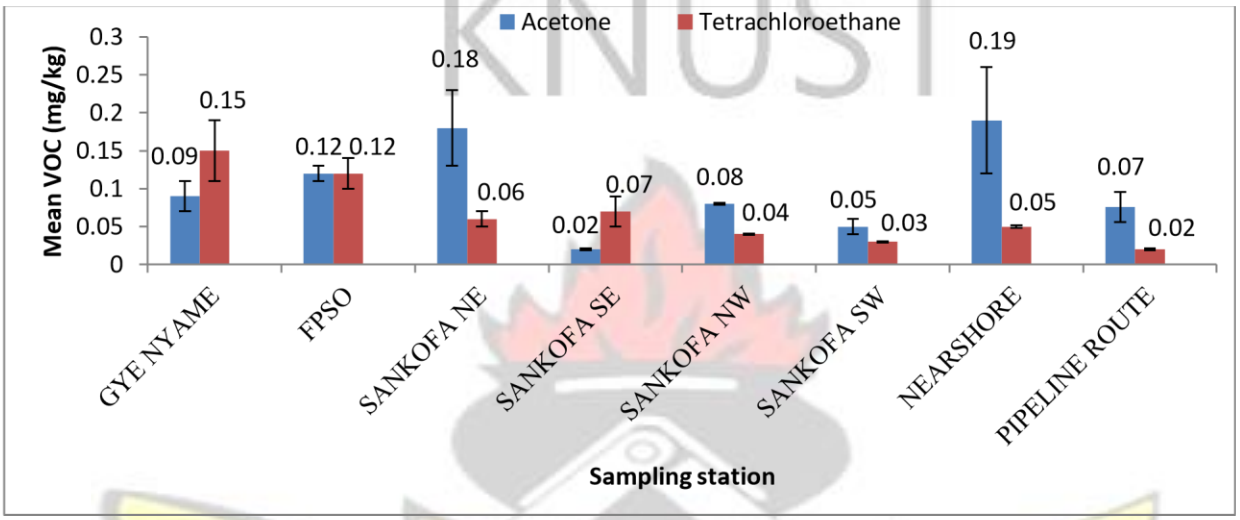

Fig 4.4: Mean VOC concentrations of sea sediment.

4.1.5 Volatile Monoaromatic hydrocarbons (BTEX).

The mean BTEX of the sediment samples at each of the sampling stations is illustrated in Fig 4.5. The highest concentration of benzene was recorded at Sankofa NW with mean value of 0.05 mg/kg. The lowest concentrations of BTEX were recorded at both FPSO sampling stations and Sankofa SW sampling station (Fig 4.5). Analysis of variance at 95% confidence level revealed that the BTEX of sediment samples did not differ significantly among sampling stations (p = 0.034).

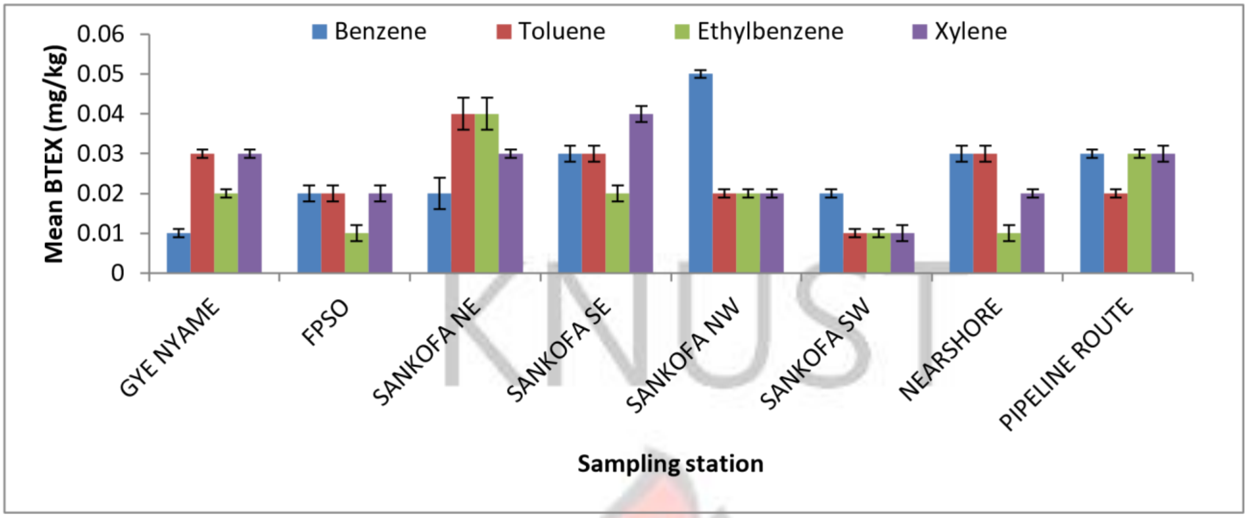

Fig 4.5: Mean BTEX concentrations of sea sediment.

4.1.6 Heavy metal levels in sea sediment

Table 4.1 shows the individual average and standard deviations of heavy metals concentrations in sea sediment samples obtained in each sampling station during the survey. In general, Nearshore stations showed lower values than Pipeline route regions and cluster/well regions. The mean iron concentrations ranged from 15.4 g/kg (Nearshore region) to a maximum of 44.1 g/kg (Pipeline region). The highest Fe value at the cluster/ well sampling station was recorded at Sankofa SE with mean value of 29.4 g/kg. There was no statistically significant difference in Fe concentrations among the sampling stations ($p = 0.184$) (Table 4.1).

Chromium concentrations ranged from 25.88 mg/kg (Nearshore region) to 78.30 mg/kg (Pipeline region). With regard to the cluster/well region, the lowest concentration was recorded at FPSO with a mean value 60.43 mg/kg whilst the highest was recorded at Sankofa SE with a mean value of 70.9 mg/kg. There was a statistically significant difference in Cr concentrations among the sampling stations ($p = 0.002$).The Tukey's HSD revealed that there were no differences in Cr levels between the Pipeline route region and the well/cluster region but were however different from the nearshore area (Table 4.3).

In the Nearshore region, Cd and Hg concentrations were below detection limit (<0.120 mg/Kg and <0.100 mg/Kg, respectively). Cadmium average concentrations in the wells/clusters region ranged from 0.13 mg/kg at FPSO to 0.33 mg/kg at Sankofa NE. Mercury average concentrations ranged from 0.11 mg/Kg at Pipeline fields to 0.53 mg/Kg at Sankofa SW region. There was a statistically significant difference in Cd concentrations among the sampling stations ($p = 0.042$) and that of Hg was also statistically significant ($p = 0.016$) (Table 4.1). The Post hoc test revealed that there were no differences in Hg levels between pipeline region, Gye Nyame and Sankofa SW ($p = 0.654$).

In the Nearshore area, a mean Pb concentration of 3.47 mg/kg was recorded. In the Pipeline region, average concentration obtained was 7.29 mg/Kg which was comparatively higher than that at the Nearshore region. In the cluster/well region the highest mean value of 262.89 mg/kg was recorded at Sankofa SW. There was a statistically significant difference in Pb concentrations among the sampling stations (p = 0.033). Tuckey's HSD post hoc comparison revealed that there were no significant differences in Pb concentrations among the following stations; Nearshore region, pipeline route region, Gye Nyame fields, Sankofa SE, Sankofa NW and FPSO fields ($p>0.05$) (Table 4.3).

Table 4.1 Heavy metals concentrations (mg/kg) in sea sediment sample

			Well/cluster Area Mean ± SD						
Var	Nearshore	Pipeline	Gye Nyame	San. NE	San. SE	San. SW	San. NW	FPSO	P-value
Fe	15441.67±3428	44183.3±15551.	2778 ± 3838	28766.7±2025	29433.3±917	29016±1820	31633.3±1234	28050 ± 2025.0	0.184
Cr	25.88± 5.65	78.30± 23.90	58.25±4.56	68.44±4.80	70.90±1.90	63.00±6.20	69.26±4.20	60.43 ± 3.56	0.002*
As	10.85± 2.10	15.60±4.90	8.7± 1.40	7.3±1.70	6.70±1.30	12.10±4.20	6.70±2.40	5.3 ± 0.50	0.172
Pb	3.47± 0.76	7.29± 1.80	10.25±1.45	35.26±15	11.90±1.10	262.89±131	10.65 ± 151	9.40 ± 0.93**a**	0.033*
Hg	ND	0.113± 0.02	0.145±0.01	0.234±0.10	0.15±0.20	0.527±0.236	0.274 ± 0.10	0.143 ± 0.01	0.016*
Ni	4.91± 1.4	24.15± 7.30	29.86±2.93	35.67±2.50	39.70± 1.60	35.03±4.30	38.00± 3.79	28.9 ± 3.03	0.116
Cu	3.45± 0.50	13.07± 4.52	15.72±1.42	20.17±1.81	21.37±0.70	37.89±18.43	19.71 ± 2.00	15.82 ± 1.58	0.001*
Cd	ND	0.181± 0.04	0.227±0.03	0.31±0.10	0.29 ± 0.10	0.14 ± 0.0-	0.31 ± 0.00	0.127 ± 0.04	0.042*

***Significant (p≤0.05)** Note: San: Sankofa, NE: North East, SE: South East, SW: South West, NW: North West; FPSO: Floating Production Storage and Offloading, ND: Not detected.

Table 4.2 Heavy metals concentrations in sea sediment (mg/kg) showing where differences in means lie.

Var	Nearshore	Pipeline	Well/cluster Area Mean ± SD						P-value
			Gye Nyame	San. NE	San. SE	San. SW	San. NW	FPSO	
Fe	15441.67±3428	44183.3±15551.	2778 ± 3838	28766.7±2025	29433.3±917	29016±1820	31633.3±1234	28050 ± 2025.0	0.184
Cr	25.88± 5.65$_{a}$	78.30± 23.90$_{b}$	58.25±4.56$_{b}$	68.44±4.80$_{b}$	70.90±1.90$_{b}$	63.00±6.20$_{b}$	69.26±4.20$_{b}$	60.43 ± 3.56$_{b}$	0.002*
As	10.85± 2.10	15.60±4.90	8.70± 1.40	7.30±1.70	6.70±1.30	12.1±4.20	6.70±2.40	5.30 ± 0.50	0.172
Pb	3.47± 0.76$_{a}$	7.29± 1.83$_{a}$	10.25±1.45$_{a}$	35.26±15$_{abc}$	11.90±1.10$_{a}$	262.89±131$_{b}$	10.65 ± 151$_{a}$	9.40 ± 0.93$_{a}$	0.033*
Hg	ND	0.113± 0.02$_{a}$	0.15±0.01$_{a}$	0.234±0.10$_{b}$	0.15±0.20$_{a}$	0.52±0.23$_{ab}$	0.274 ± 0.10$_{b}$	0.14 ± 0.01$_{a}$	0.016*
Ni	4.91± 1.40	24.15± 7.30	29.86±2.93	35.67±2.50	39.70 ± 1.60	35.03±4.30	38.0 ± 3.79	28.90 ± 3.03	0.116
Cu	3.45±0.50$_{abc}$	13.07± 4.52$_{a}$	15.72±1.42$_{a}$	20.17±1.81$_{b}$	21.37±0.70$_{b}$	37.89±18.40$_{b}$	19.71 ± 2.00$_{a}$	15.82 ± 1.58$_{a}$	0.001*
Cd	ND	0.181± 0.04$_{a}$	0.23±0.03$_{a}$	0.331±0.10$_{b}$	0.29 ± 0.10$_{a}$	0.14 ± 0.00$_{a}$	0.31 ± 0.00$_{b}$	0.13 ± 0.04$_{a}$	0.042*

Means in the same rows with different letters are significantly different

4.2 Physical Parameters of water samples

4.2.1 pH

The lowest mean pH values obtained ranged from 7.1 of depth (>500m) at Sankofa SE to a maximum of 8.6 (<100m) at Sankofa SW. The results revealed that shallow waters show higher pH values compared to middle and deep waters. In the Nearshore region, all samples (surface, medium and bottom) showed high and homogeneous values, given the low depth of all stations. The pH recorded during the sampling period did not differ significantly with depth among sampling stations (P = 0.452).

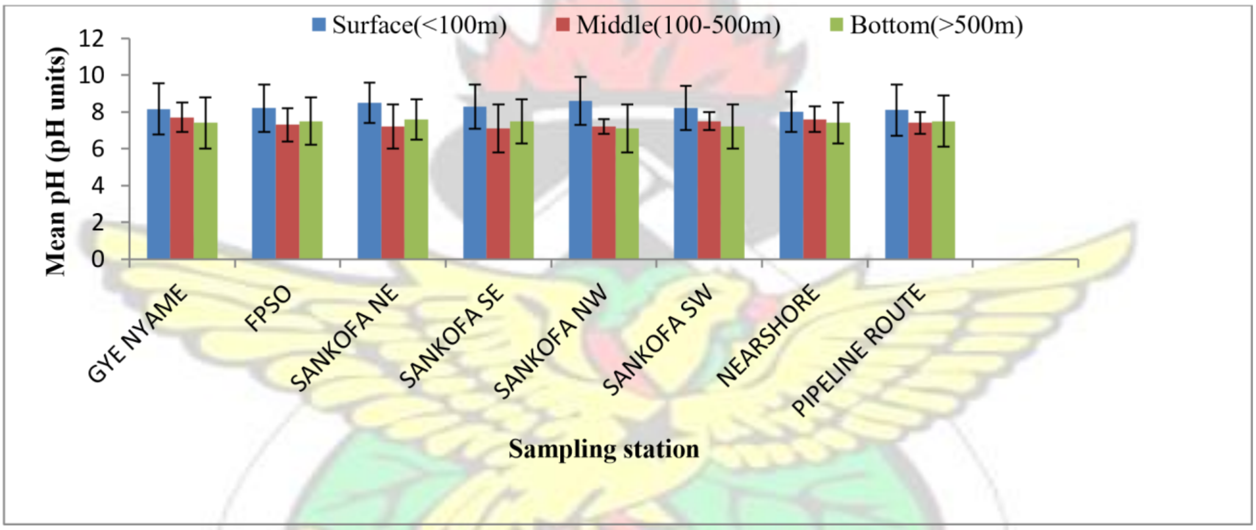

Fig 4.6: Mean pH of sea water at sampling stations

4.2.2 Dissolved Oxygen (DO)

The mean DO of the sea water samples ranged from a minimum of 4.8 mg/l at Gye Nyame sampling station at depth greater than 500m to a maximum of 15.5 mg/l at FPSO sampling station which is within the cluster/well region at depth <100m.The mean values and their depths are as illustrated in (Fig 4.7). The DO recorded during the sampling period differed significantly with depth among the sampling stations (P = 0.002). Post hoc test using the Least LSD revealed that there were no differences in dissolved oxygen in relation to depth between surface (<100m) and middle (100-500m) but were however significantly different from depth (>500m).

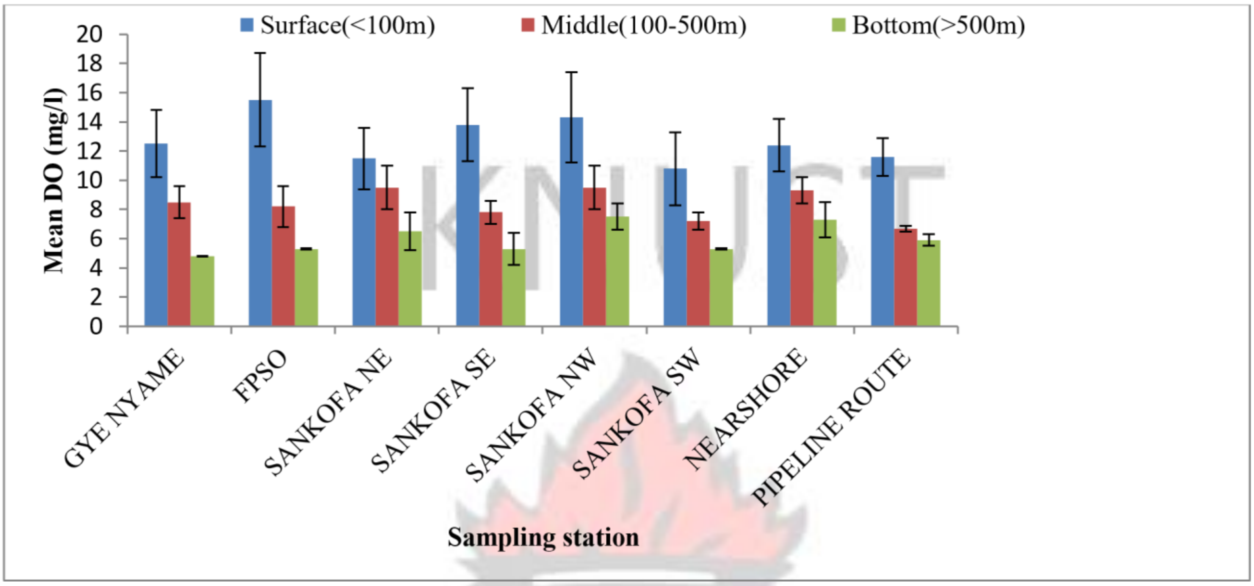

Fig 4.7 Mean dissolved oxygen concentrations of sea wáter.

4.2.3 Biological Oxygen Demand (BOD)

The mean BOD of the sea water sample ranged from a minimum of 10.8 mg/l at Gye Nyame sampling station at depth <100m to a maximum of 35.4 mg/l at Sankofa SE sampling station at depth >500mm (Fig 4.8). There was a statistically significant difference in BOD with depth among the sampling stations at 95% confidence level (P = 0.028). When the Least Significant Difference (LSD) was used to compare the means, there were no differences in BOD in relation to depth between middle portion (100-500m) and bottom (>500m) but were significantly different from the surface (<100m).

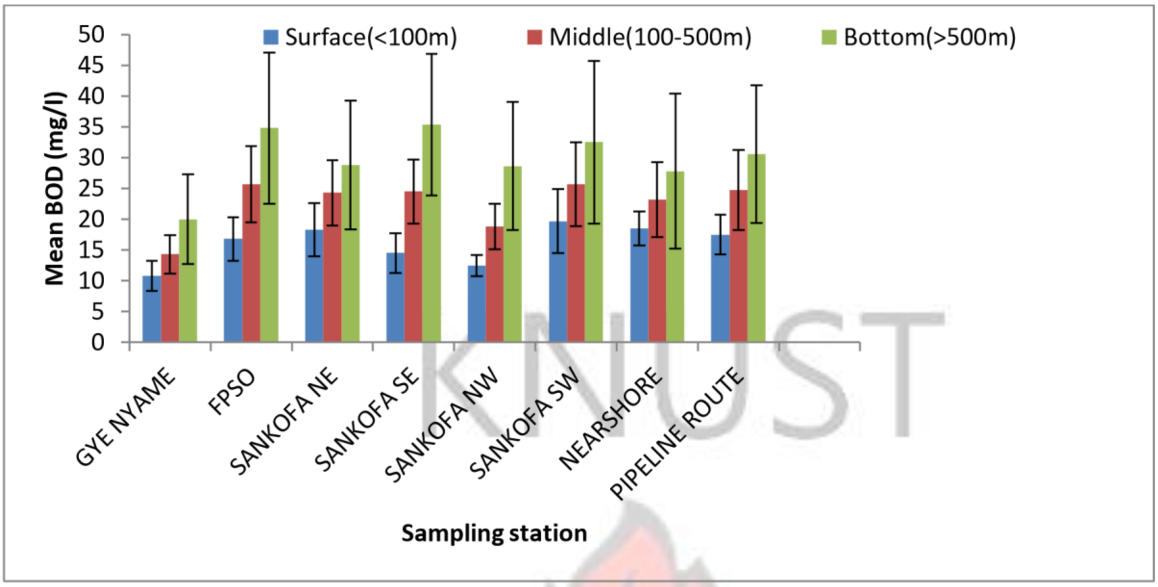

Fig 4.8 Mean BOD levels of sea wáter.

4.2.4 Temperature

The mean water temperature ranged from a minimum of 22.5°C at site Sankofa NE fields (bottom) with depth >500m to a maximum of 32.6°C at site Sankofa SW (surface) with distance greater than 100m (Fig 4.9). Analysis of variance at 95% confidence interval revealed no statistically significant differences ($P = 0.724$) in temperature in relation to depth over the study period.

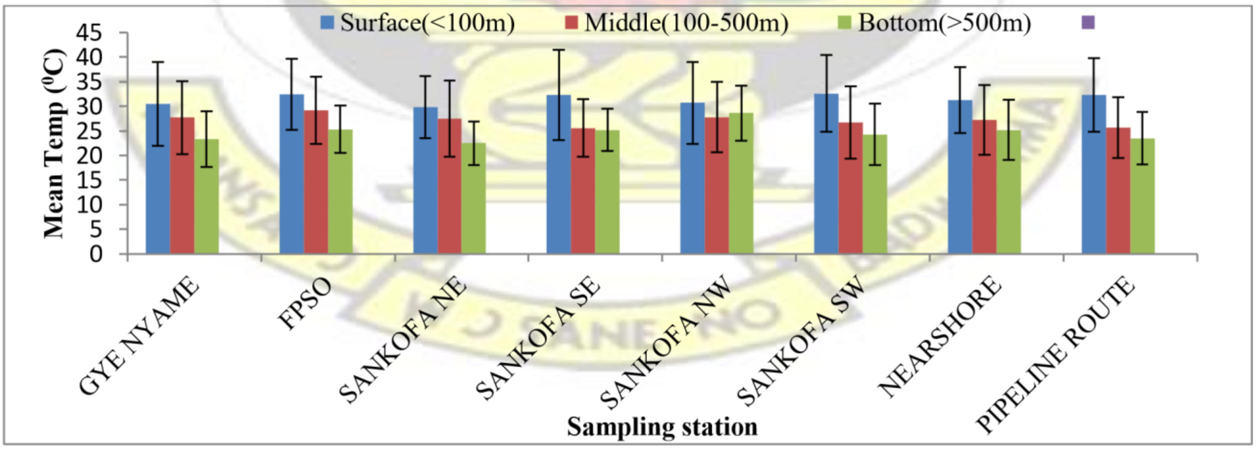

Fig 4.9: Mean temperatura reading of sea wáter.

4.2.5 Total dissolved solids

The mean TDS values obtained ranged from 29600mg/l of depth (100-500m) at Sankofa SW to a maximum of 36234mg/l (>500m) at Pipeline route. In the Nearshore region all samples (surface, medium and bottom) did not show much variation with depth. The TDS recorded during the sampling period did not differ significantly with depth among the sampling stations (*P* = 0.347).

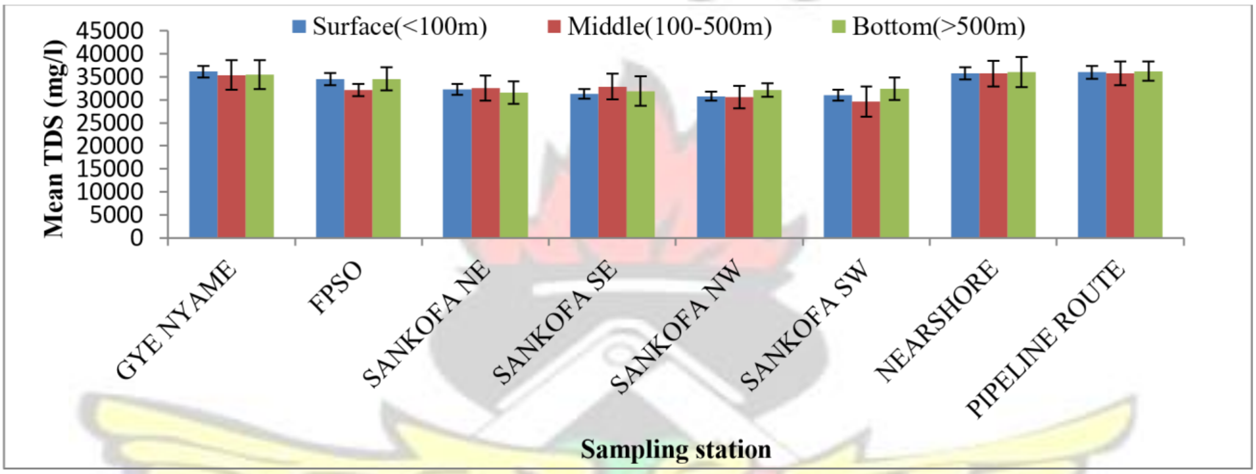

Fig 4.10: Mean TDS levels of sea wáter.

4.3 Nutrients

4.3.1 Nitrates

At the Nearshore region and Pipeline route sampling stations the highest mean nitrate concentrations recorded were 0.7 mg/l and 9.7 mg/l respectively. At the cluster/well region, the highest concentration was recorded at Sankofa NE with mean value of 38.3 mg/l and the lowest values of 0.1 mg/l each were recorded at FPSO and Sankofa NE sampling station at depth <100m (Fig 4.11). There was a statistically significant difference in nitrates with depth among the sampling stations (*P* = 0.018). When the Least Significant Difference (LSD) was used to compare the means, there were no differences in nitrates concentrations in relation to depth between middle portion (100-500m) and bottom (>500m) but were significantly different from those from the surface (<100m).

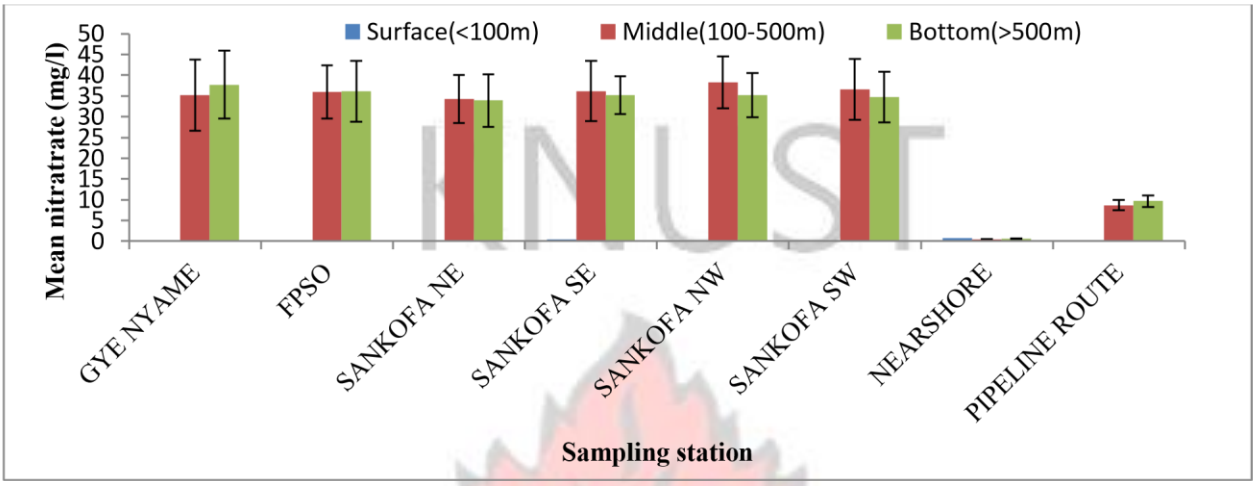

Fig 4.11 Mean nitrate concentrations in sea water

4.3.2 Phosphates

The mean phosphate of the sea water sample at pipeline route region ranged from a minimum of 0.4 mg/l (surface) to a maximum of 0.6 mg/l (middle).The Nearshore region also recorded concentrations between 0.4 mg/l and 0.6 mg/l (Fig 4.12). There was a statistically significant difference in phosphates with depth among the sampling stations at 95% confidence level (P = 0.01).The Least Significant Difference (LSD) revealed that there were no differences in phosphate concentrations in relation to depth between middle portion (100-500m) and bottom (>500m) but were significantly different from those from the surface (<100m).

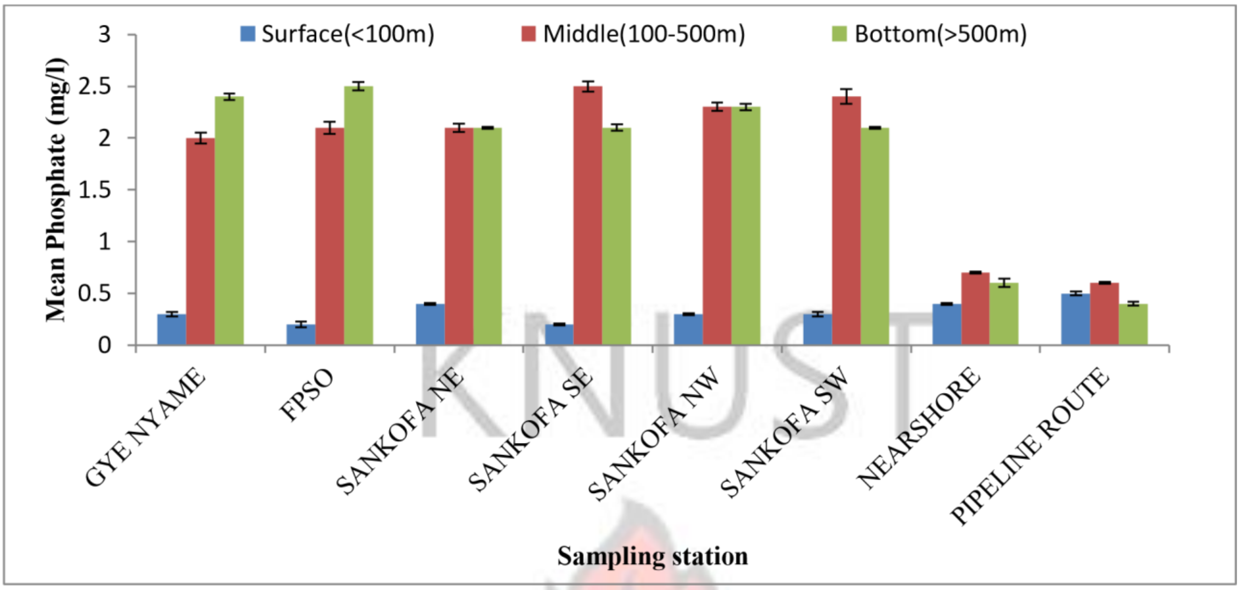

Fig 4.12: Mean phosphate concentrations in sea water.

4.4 Heavy metals in Sea water

4.4.1 Heavy metals concentrations of sea water

Table 4.4 illustrates the mean and standard deviations of heavy metals concentrations in sea water samples obtained at the surface (<100m), middle (100-500m) and bottom (>500m) from the sea bed in each sampling station. In general, Nearshore stations showed lower values than Pipeline route regions and cluster/well regions. Chromium (Cr), Pb, Hg and Cd levels in sea water were below the detectable limit of <2.0 mg/l, <1.0 mg/l, <0.01 mg/l and <0.05 mg/l respectively. The mean iron concentrations ranged from 4.1 mg/kg (Pipeline route) to a maximum of 102.7 mg/kg (Nearshore region). The Fe levels recorded at Nearshore sampling stations were higher compared to that of pipeline route and well/cluster region.

Table 4.4 Heavy metals concentrations (mg/l) in sea water

Metal/Site	**Nearshore**			**Pipeline route**			**Well/Clusters**		
	Surface	Middle	Bottom	Surface	Middle	Bottom	Surface	Middle	Bottom
Fe	52.6±10	57.9±12	102.7±22	4.4±1.2	7.6±1.5	4.10.8	4.9±1.1	4.0±0.8	5.5±0.7
Cr	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
As	2.0± 0.03	1.9±0.07	2.2±0.0	1.7±0.04	1.8±0.06	1.9±0.03	1.7±0.02	1.9±0.04	1.9±0.03
Pb	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	3.0±0.2	1.5±0.6	2.0±0.3	<1.0	<1.0	<1.0	2.1±0.3	2.3±0.5	1.7±0.4
Cu	1.5±0.4	1.4±0.3	1.8±0.2	1.1±0.2	1.5±0.5	1.2±0.1	1.2±0.3	1.0±0.2	1.1±0.1
Cd	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

CHAPTER FIVE

DISCUSSION

5.1 Sediment oxygen demand, total organic carbon, TPH, VOC, BTEX

Sediment oxygen demand is the rate at which DO is removed from the overlying water column by biochemical processes in the stream bed sediments (Hatcher, 2011). Sediment oxygen demand is a major oxygen sink and helps in respiration by aquatic plants and the oxidation of organic materials and other reduced matters in the water column (Justice et al., 1994). It is defined as the rate of oxygen consumption, biologically or chemically in sediment at the bottom of a water body (Veenstra and Nolen, 1991). The National Oceanic and Atmospheric Administration (NOAA) does not have specific values for SOD, however for marine ecosystem health; it varies between 0.11 and 0.19 g O_2/m^2 /day (Bosch et al., 2002). The SOD of all the study sites investigated in this study exceeded this guideline value with the highest values found in well/cluster region (Sankofa NE and SE). The high values obtained at the cluster region could be attributed to high levels of organic materials in bottom sediment due to intense activities in this region whose decomposition could lead to oxygen depleting effect in the bottom sediment.The high SOD recorded in this region could limit benthic respiration as it contributes significantly to oxygen depletion. In some water systems, SOD can account for more than half of the total oxygen demand and play a primary role in the water quality (Hanes and Irvine, 2016). This finding is consistent with the work of Onojake and Abanum (2012) who conducted a study at off shore oil fields in Niger delta, Nigeria and reported SOD value to be between 0.5 and 4.6 g O_2/m^2 /day. The findings however disagree with the work of Erakhrumen, 2015 who conducted a similar study in Saudi Arabia and found SOD values below 0.11 g O_2/m^2 /day.

The total organic carbon concentration along nearshore area and pipeline route region was generally lower compared to those at the well/cluster regions during the entire study period.

This may be attributed to the fact that the deep sea experience rapid inputs of organic carbon from the overlying surface waters with rapid responses by micro and macro fauna mainly from primary production from the surface waters and material originating from primary consumers such as phaecal pellets and dead bodies (Robison et al., 2005). High levels of total organic carbon in marine sediment may be attributed to the level of productivity and/or low levels of oxygen in the sediment water interface as compared to the nearshore and pipeline region which receives lower inputs of organic materials hence are more likely to have high levels of oxygen which could convert most organic carbon into carbon dioxide and water. This is due to the susceptibility of the organic matter degradation in the presence of oxygen (Gooday, 2002). The findings are consistent and agree with the work of Onojake and Abanum (2012) who reported high values of total organic carbon during an environmental Impact assessment (EIA) in some oil fields in the Niger delta, Nigeria.

The total petroleum hydrocarbons (TPH) is used to describe a large group of chemicals originally derived from crude oil. The highest concentration was obtained in the Sankofa NE in the well/ cluster sampling stations. This could partly be attributed to the fact that TPHs have the potential to enter aquatic ecosystems either as components of uncombusted petroleum and petroleum products such as crude oil, fuel, lubricating oils or as products of incomplete combustion in exhaust emissions which might have occurred during the exploration stages of the projects by Eni Ghana, the company tasked to manage the offshore Cape Three point project (Hanes and Irvine, 2016). Since petroleum is a naturally occurring organic compound that is found deep under the earth's crust, the natural geochemistry of the underlying rocks could also contribute significantly to the inputs of TPH in water ecosystem in the well cluster area as compared to the pipeline route region and the nearshore region. Other anthropogenic activities such as oil refineries, off shore oil production, transportation and tanker accidents could not also be ruled out as a potential source to contribute significantly to the TPH inputs of the marine ecosystem in this study. In general, average concentrations of TPH in the sediment were high throughout the study region, especially in the wells/clusters region. This phenomenon is not surprising since sediment often acts as sinks for TPH and its concentrations have been reported to be higher than that in water (Erakhrumen, 2015). There is no threshold effect level (TEL) or permissible exposure level (PEL) or equivalent values for TPH by WHO. However, for the purpose of ecosystem health, a maximum value of 1000 mg/l has been recommended (Metwally et al., 2010). The reference concentrations found in literature however depend on different factors including composition and nature of sediments, possible natural seeps, anthropogenic activities near studied location (Candler et al., 2000). The values obtained in the well/cluster region especially Sankofa NE is an indicator of contamination and this could be attributed to previous drilling activities in the sampling fields. During exploration or seismic surveys by oil companies, drill cuttings, drilling mud and fluids are used for stimulating production (Onojake and Abanum, 2012).

Volatile Organic Compounds (VOCs) are organic chemicals that have a high vapour pressure at ordinary temperature given its low boiling point. Some VOCs are dangerous to human health or cause harm to the environment. In the sampling stations, all values for all stations were below the detection limit (<0.5 mg/kg) set by the World Health organization (WHO, 2010) and National Oceanic and Atmospheric Administration (NOAA, 2012).

Since BTEX compounds are volatile, when discharged into the sea it is quickly lost through evaporative processes, thus the time of exposure to aquatic organisms may be short enough to avoid ecosystem effects. BTEX compounds are severely toxic to aquatic organisms if contact is maintained. All BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) concentrations measured in all samples were below detectable limit of <0.1mg/kg (WHO, 2010). The findings obtained in this study with regards to the concentrations of VOC and TPH are consistent with the findings of Fakhru'l-Razi et al. (2012) in the Niger delta, Nigeria, in which environmental survey report revealed low concentrations of VOC and TPH in the entire marine environment during oil exploration and drilling processes.

5.2 Heavy metals

The concentrations of total arsenic in uncontaminated nearshore marine and estuarine sediments usually fall in the range of 5 to 15 mg/kg dry weight. The average concentration of arsenic in deep-sea sediments is estimated to be about 40 mg/kg. According to the World Health Organization, concentrations of arsenic above 70 mg/kg are expected to be associated frequently with adverse effects in benthic organisms (WHO, 2010). The arsenic levels reported in all sampling stations at the nearshore, pipeline and cluster/well regions were below this recommended limit. This indicates that there would be no significant impact on the marine ecosystem. The values obtained in sediment samples were comparatively higher and statistically significant than that of water and their concentrations increased with an increase in depth. This is so since sediment acts as sink for heavy metals and are more likely to have higher levels compared to the water.

Mercury, cadmium, nickel and chromium and lead have no biological role in human and are considered to be toxic heavy metals (Meador et al., 1994). “They are potent toxins even at relatively low concentrations and their bioaccumulation in tissues can lead to cell death” (Swicka-Kapusta, 2003). “Cadmium and mercury have been included in the regulations of the European Union for hazardous metals” (EC, 2001). Lead, mercury and chromium were below the detection limit in sea water samples. High values of mercury were recorded in cluster/well fields which slightly exceeded the recommended limit of 0.199 mg/kg by the World Health Organization (WHO, 2014). This might have arisen due to the dumping of electronics and other mercury containing compounds by vessels that flout international conventions of the protection of the marine pollution. This finding disagrees with the work of Onojake and Abanum, (2012) who reported mercury values to be very low at Niger delta. The results obtained in this study suggest that, impacts on the due marine ecosystem due to mercury -contamination would be observed at the well/cluster region.

The highest cadmium values among the wells/clusters region were observed in Sankofa NE fields and Sankofa SW fields. Cadmium concentrations in all sediment samples were below the threshold exposure limit (TEL) of 0.680 mg/kg. It can therefore be concluded that significant impacts would be rarely observed and pose no threat to the marine ecosystem in general in the short term.

With regard to the concentration of lead, it occurs naturally from the decomposition of parent rocks and may accumulate from anthropogenic sources such as traffic exhaust, lead-zinc smelters, paints and batteries (Cameron, 1992). Lead entering aquatic systems through aerial deposition or runoff is deposited in bed sediments in association with particulate matter, such as iron and manganese oxides, or is precipitated out of solution with carbonate or sulphide (Hanes and Irvine, 2016). Sediments, therefore, act as an important route of exposure to lead (Pb) for aquatic organisms. Lead (Pb) is listed as a toxic substance of the Canadian Environmental Protection Act (CEPA, 2010). The National Oceanic and Atmospheric Administration (NOAA) and threshold exposure limit (TEL) of WHO for Pb are 46.7 and 30.24 mg/kg respectively. Lead in sediment at Nearshore and Pipeline regions were below NOAA and TEL values and therefore biological effects would be rarely observed.

Copper is an essential trace element that can be toxic to aquatic biota at elevated concentrations Fakhru'l-Razi et al. (2012). Copper is necessary for the synthesis of haemoglobin and is an essential part of several enzymes (Underwood, 2013). However, a high intake of Cu has been recognized to cause adverse health problems (Gorell et al., 1997). In the wells/clusters region, higher copper values were observed compared to the pipeline route and nearshore fields. This difference may be due to the fact that this regions had some level of exploration or seismic surveys by some oil companies, and activities such as drill cuttings, drilling mud and fluids could introduce some levels of heavy metals such as Cu into the surrounding media and this could have accounted for the high levels of Cu in this regions. Copper had also been used as principal biocide in antifouling marine paints for over 100 years. Even with the advent of TBT, copper is still used in paint alongside the TBT biocide and hence its high presence in the well/cluster region. Copper concentrations in almost all studied samples were below NOAA ERL value of 34 mg/kg and hence biological effects may not occur.

Chromium (Cr) is generally produced by industrial processes. Trivalent and hexavalent forms are used in chemical industries including chrome plating, dye and pigment manufacture, leather tanning and wood preserving (Lin et al., 2013). Chromium concentrations in sea sediment at the well/cluster fields were comparatively higher than that of the nearshore and pipeline route fields, though they were all below the recommended guidelines set by the NOAA and WHO. The reason could be attributed to the fact that the nearshore area and pipeline route had no intense activity compared to the well/cluster area where pervious drill cuttings had taken place and could have introduced some levels of Cr into the surrounding media and subsequently act as sinks in the sediment.

Nickel concentrations in all Nearshore, Pipeline and Cluster/well sediment samples fell below the NOAA and WHO limits of 20.9 mg/kg and 15.9 mg/kg respectively. This is an indication that adverse biological effects would be rarely observed. This finding is consistent with the work of Fakhru'l-Razi et al. (2012) in oil fields in Saudi Arabia who also reported nickel values below the NOAA and WHO recommended limits.

5.3 Temperature, pH, and DO

Ocean temperatures typically range from -2 to 35ºC (28.4 to 95.0 ºF). In the Nearshore region, temperatures ranged from 25.2ºC (surface column) to 31.3ºC (bottom column). The temperatures of the various sampling stations decreased with depth. This this may be attributed to the turbulence of the sea and also the presence of a thermocline also known as the thermal layer or the metalimnion in lakes which is a thin but distinct layer in a large body including the ocean where temperature changes more rapidly with depth than it does in the layers above or below. In the ocean, the thermocline divides the upper mixed layer from the calm deep water below making temperature below colder compared to the surface (Sahmoun et al., 2005). The natural background limit for NOAA and WHO for ecosystem health is between 22℃ and 27℃ (WHO, 2010). The temperatures recorded for all the sampling fields were above the natural background limit and this could partly be attributed to the absorption of sunlight during the day causing an increase in temperature since data was taken during the day. Temperature of water needs to monitored closely as it is a very critical factor of significance for aquatic ecosystem and its fluctuations can affect organism as well as the physico-chemical properties of ocean (Nkansah, 2010).

The mean pH values obtained ranged from 7.1 of depth (>500m) at Sankofa SE to a maximum of 8.6 (<100m) at Sankofa SW. The results revealed that shallow waters show higher pH values compared to middle and deep waters. The pH of sea water samples fell within the WHO range for portable water of 6.5-8.5. This indicates neutral to alkaline conditions and it is not surprising since sea water contains high levels of carbonate, bicarbonates and hydroxyl ions which have very high buffering capacity (Erakhrumen, 2015; Manoukian et al., 2010).

The dissolved oxygen concentrations of the sea water samples decreased with depth. According to WHO (2010), fishes in aquatic water body cannot survive when the DO of the water falls below 5 mg/l. The DO levels of all the samples recorded for the entire study period were within the guideline value for fishes to thrive in an aquatic body. This is an indication that ecosystem health will not be affected.

5.4 Phosphates and Nitrates

The essential nutrients for primary production in the marine environment are basically nitrogen and phosphorus (Porte et al., 2003). This is as a result of a condition called eutrophication, which is a biological effect in which there is an increase in plant nutrients such as nitrogen and phosphates (Lin et al., 2013; Olawoyin, 2012). The concentrations of these compounds are decisive for the regulation of phytoplankton populations, as the higher or lower concentrations of these nutrients are the cause of eutrophication and oligotrophication episodes, respectively. The results showed that the concentrations of phosphate and nitrates in the sea water were lower throughout the water column, increasing slightly with depth in the order (<100m), middle (100-500m) and bottom (<500m). The levels obtained might have arisen from refinery wastes since they also have characteristics which constitute potential water pollutants such as phosphates, nitrates and organic compounds (Saro, 2007; Perera et al., 2012). Values measured for nitrates and phosphates at the cluster/well region tend to be higher than that at the nearshore and pipeline route. This is not surprising since no intensive activities are realized in this region as compared to the cluster region which is the project field.

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

Baseline environmental quality assessment at offshore Cape Three Point was done to find out the physical and chemical quality of the sea water and sediment samples for protection of the marine environment. High SOD levels were recorded in the well cluster region and this could limit benthic respiration due to oxygen depletion from possible high organic loads in the marine sediment. The total organic carbon concentrations along nearshore area and pipeline route region were generally low compared to those at the well/cluster regions during the entire study period.

In general, average concentrations of TPH in the sediment were high throughout the study, especially in the wells/clusters region. Iron, As, Ni and Cu concentrations in sea water exceeded the NOAA threshold limits. They were comparatively higher in the well/cluster area than the nearshore and pipeline region. Iron (Fe) and chromium (Cr) in sediment exceeded the NOAA threshold limit. Nickel in well/cluster area exceeded the recommended limit but those at the nearshore and pipeline region fell below the limits. This is an indication that adverse biological effects could potentially be observed in the well/cluster area.

The pH of sea water samples fell within the range of 7.5-9.5. Phosphate and nitrates in the sea water were lower throughout the water column, increasing slightly with depth in the order (<100 m), middle (100-500 m) and bottom (<500 m). The study therefore concluded that majority of the parameters investigated did not cause a significant challenge to marine ecosystem health but environmental protection measures need to be put in place during offshore oil drilling phase at Cape Three Point in order to protect the marine environment.

6.2 Recommendations

- Further studies can consider heavy metal fractionation of the sea sediment to determine the actual concentrations in each fraction of the sediment.
- Further research should be conducted on the benthic species, their abundance and species richness.

LIST OF REFERENCES

Anderson, R. (1987). Chromium. In: Trace Elements in Human and Animal Nutrition, *Journal. Geophys.Res*.74:6995–7008.

APHA (2010). Standard methods for the examination of water and wastewater. USA: American Public Health Association.

Armstrong, B., Hutchinson, E., Fletcher, T. & Unwin, J. (2004). Lung cancer risk after exposure topolycyclic aromatic hydrocarbons: A review and meta-analysis. *J. Environmental Health*
p 21-34.

Barros, F., Underwood, A. J. & Lindegarth, M. (2001). The influence of rocky reefs on structure of benthic macrofauna in nearby soft-sediments. *Estuarine, Coastal and Shelf Science*, Vol. 52, pp.191-199.

Bilcke, CV. (2002). The Stockholm convention on persistent organic pollutants. Review of Clinical Pharmacology 53: 451-458.

Bosch, D. R., Lowrance, G., Vellids, J., Sheridan, T., & Williams, R. (2002). Dissolved Oxygen and Stream Flow Rates: Implications for TMDLs. In: Proceedings of the Total Maximum Daily Load (TMDL) Environmental Regulations Conference, A. Saleh (Editor). ASAE, St. Joseph, Michigan, p. 92.

Canadian Environmental Protection Agency (CEPA) (2010). "Methodology Framework for the Design of Digital Ecosystem," ISIC IEEE International Conference Systems, Man and Cybernetics, Montreal, Canada.

Candler, J.E., Hoskin, S., Churan, M., Lai, C.W., Freeman, M. (2000). Seafloor monitoring for synthetic-based mud discharged in the Western Gulf of Mexico. In: 1997 SPE/EPA Exploration and Production Environmental Conference, Houston, Texas. Society of Petroleum Engineers, Inc., Richardson, Texas.

Cameron, W. (1992). Ammoniumadsorption in superficial North Sea sediments. Cont. Shelf Res.16:1415–143.

Campbell, P.G.C. and Tessier, A. (1996). Ecotoxicology of metals in aquatic environments: Geochemical aspects. In: Ecotoxicology: A hierarchical treatment, M.C. Newman and C.H. Jagoe, eds. Lewis Publishers, Boca Raton. FL.

Choudhry, G.G., (1983). Humic substances: Sorptive interactions with environmental chemicals, *Toxicol. Envir. Chem*. 6, 127-171.

Cianelli, D., Manfra, L., Zambianchi, E., Maggi, C. & Cicero, A.M. (2011). Modelling and Observation of Produced Formation Water (PRODUCED WATER) at Sea. In: Fluid Waste Disposal, Canton, K.W. (Ed.), 113-135, Nova Science Publishers, Inc., ISBN 9781-60741-915-0, and New York.

Domingo, J. L. (1994). Metal-induced developmental toxicity in mammals: A review. *Journal of Toxicology and Environmental Health,* 42: 123-141.

Eastmond, H. (2008). Variability in particle attenuation and stimulated fluorescence in the tropical and equatorial Pa-cific: Scales, patterns and some biogeochemical implications. *J. Geophys*. Res.104:3401–3422.

EC (European Commission), (2001). The European commission Water Framework Directive (2000/60/EC).

Elinder, C.G. (1992). Cadmium as an environmental hazard. IARC scientific publications 118: *Environmental Health,* 15: 299-323.

Erakhrumen, A. A. (2015).Concentrations of heavy metals in untreated produced water from a crude oil production platform in Niger-Delta, Nigeria. *Journal of Research in Forestry, Wildlife and Environmental*, (1), 2141 -1778.

Fakhru'l-Razi, A., Pendashteh, A., Biak, D. R. A., Madaeni, S. S. & Abidin, Z. (2012). Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials,* 170, 530-55.

Gordon, J.N., Taylor A, Bennett, P.N. (2002). Lead poisoning: Case studies.*J. Geophys.Res*.74:6995–7008

Goyer, R. (1991). Toxic effects of metals. In: Amdur MO, Doull JD and C.D. K. 180, 512-539.

Gooday, A.J. (2002). Biological responses to seasonally varying fluxes of organic matter to the ocean floor: A review. *J. Oceanogr.* 58: 305-332.

HACH (1996). Standard methods for the examination of water and waste water, (20th ed.), Washington DC, USA

Hansen, B. R. & Davies, S. R. H. (2012). Review of potential technologies for the removal of dissolved components from produced water. Chemical Engineering Research & Design, 72, 176-188.

Hanes, N. and Irvine, T. (2016). Ocean deoxygenation in a warming world. Annual Review of Marine Science, 2: 199–229

Hopkins, Jr. L.L, Ransome-Kuti, O., & Majaj, A.S. (1968). Improvement of impaired carbohydrate metabolism by chromium (III) in malnourished infants. *Am J Clin Nutr*, 21:203-11.

IARC (1999). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 74,

Katz, S. A., Salem, H. (1992). "The toxicology of chromium with respect to its chemical speciation: A review". *Journal of Applied Toxicology*, 13 (3): 217-224.

Lin, Y.C., Chang-Chien, G.P., Chiang, P.C., Chen, W.H., & Lin, Y.C. (2013). Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbour in Southern Taiwan. *Mar. Pollut*. Bull. 76, 266-275

Maggi, C., L. Manfra, O. Nonnis, R. Di Mento, M. Mannozzi, C. VirnoLamberti, A. M. Cicero and Gabellini, M. (2010). Monitoring of Impacts of Offshore Platforms in the Adriatic Sea (Italy), *ISPRA Italian Institute for Environmental Protection and Research, Rome, Italy.*

Manoukian, S., Spagnolo, A., Scarcella, G., Punzo, E., Angelini, R. & Fabi, G. (2010*).* Effects of two offshore gas platforms on soft-bottom benthic communities (Northwestern Adriatic Sea, Italy), *Marine Environmental Research*.

MARPOL (1978). Prevention of vessel-source marine pollution: a note on the challenges and prospects for Chinese practice under international law. Retrieved from file:///c:/users/hp/desktop/project%20akpama/data/247594.pdf

Meador, K., E. M. Thorndike, A., and Mathieu, S. (1994). Nepheloid layers and bottom currents in the Arctic Ocean. *J. Geophys.Res*.74:6995–7008

Medunić, G. & Šmit, Z. (2015). Organic micropollutants in the Sava and Bosna river overbank and floodplain sediments during the May through June 2014 catastrophic flood. The Mining-Geology-Petroleum Engineering Bulletin http://dx.doi.org/10.17794/rgn.2016.1.4

National Petroleum Authority (NPA), (2010).Municipality information.www.npa.ghana.gov.gh. Accessed: February, 2018.

Neff, J.M., Lee, K., DeBlois, E.M. (2013). Produced Water: Overview of Composition, Fates, and Effects In: Lee, K., Neff, J. (Eds.), Produced Water, Springer New York, pp. 3-54.

Nkansah, M. A., Boadi, M. O. & Badu, M. (2010). “Assessment of the Quality of Water from Hand-Dug Wells in Ghana”, Environmental Health Insights 4, 7–12.

NOAA (2012). Protocol for determination of total suspended matter in oceans and coastal zones. JRC Technical Note I.98.182.

Olawoyin, R.O. (2012). Application of expert systems in the characterization and impact of petroleum derivatives on human health, A Dissertation in Energy and Mineral Engineering Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at The Pennsylvania State University.

Onojake, M.C. & Abanum, U.I. (2012). Evaluation and Management of Produced Water from Selected Oil Fields in Niger Delta, Nigeria. *Archives of Applied Science Research*, 4(1): 39-47.

Perera, F.P. Tang, D., Wang, S., Vishnevetsky, J. (2012). "Prenatal Polycyclic Aromatic *Perspectives*, 112: 970-978.

Petersen, M., Bleuten, W., & Jorgensen, S. (2011).Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. *Journal of Hydrology., (271)*: 213-225

Pinot, F., Kreps, SE., Bachelet, M., Hainaut P, Bakonyi M, Polla BS (2000). Cadmium in the environment : Sources, mechanisms of biotoxicity, and biomarkers. Reviews on pollutants. United Nations Environmental Programme. Retrieved on 2007-09-16.

Porte, K., E. M., Thorndike, S.A. and. Mathieu, M. (2003). Nepheloidlayers and bottom currents in the Arctic Ocean. *J. Geophys.Res*.74:6995–7008.

Ray, J.P. & Engelhardt, F.R. (1992). Produced Water - Technological/Environmental Issues And Solutions. Eds.; Plenum Press, New York & London. Rev; 49:163-239.

Rittler, D. W., P. R., Can, L., and Carder, T. (2007). Particle transport from the West African shelves of Liberia and SierraLeone to the deep sea: A chemical approach. Mar. Chem.9:283–306.

Robison, W., VanderZwaag, D. L., and Fennel, K. (2005). Recovery planning for pacific marine species at risk in the wake of climate change and ocean acidification: Canadian practice, future courses. Journal of Environmental Law and Practice, 27: 23–56

Sahmoun, A.E., Case, L.D., Jackson, S.A. & Schwartz, G.G. (2005). Cadmium and prostate cancer: A critical epidemiologic analysis. Cancer Investigation 23: 256-263.

Saro, J. (2008). Bio-physical forcing of particle production and distribution during a spring bloom in the North Atlantic. Deep-Sea Res. II42:757–775.

Sarfo-Armah, W. W. L., Dunne, J., Sarmiento, J. L., and Pauly, D. (2006). Integrating ecophysiology and plankton dynamics into projected maximum fisheries catch potential under climate change in the Northeast Atlantic. ICES Journal of Marine Science, 68: 1008–1018.

Shanker, A.K., Cervantes, C., Loza-Tavera, H., Avudainayagam, S. (2005). Chromium toxicity in plants. *Environment International*, 31: 739-753.

Stoecker, C. M., and McDonald, D. G. (2001). Global Warming: Implications for Freshwater and Marine Fish. Cambridge University Press, Cambridge, UK

Switka-Kapusta. (2003). Protocol for determination of total suspended matter in oceans and coastal zones. JRC Technical Note I.98.182.

Toscano, C. D. & Guilarte, T. R. (2005) Lead neurotoxicity: From exposure to molecular effects, Brain Research Reviews, Volume 49, Issue 3, November 2005, Pages 529-554.

Trabucco, B., Maggi, C., VirnoLamberti, C., Bacci, T., Marusso, V., Vani, D., Gabellini, M. & Cicero, A.M. (2006b). Marine benthic assemblages around a gas platform (Central Adriatic Sea). Coastal Innovations and Initiatives - Proceedings Littoral, pp.39- 46.

Veenstra, B. A., Chan, F., Nielsen, K. J., Fox, D. S., Barth, J. A., Huyer, A., Lubchenco. (1991). Upwelling-driven nearshore hypoxia signals ecosystem and oceanographic changes in the northeast Pacific. Nature, 429: 749–754.

Vincent, K. (2003). The tides of the continent of Australia. Research paper 37, Horace Lamb Centre for Oceanographic Research, Flinders University of South Australia. pp. 326

Whittemore, R.C. (2001). Recent Studies on the Comparison of in-Situ and Laboratory Sediment Oxygen Demand Techniques. Tech. Bull. No. 489. Nat. Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York.

USEPA (United States Environmental Protection Agency), (1999).National primary drinking water regulations. EPA 816-F-09-004. Washington, D.C.

Weisman, C. E., Bianucci, L., and Fennel, K. (2008). Sensitivity of northwestern North Atlantic shelf circulation to surface and boundary forcing: a regional model assessment. Atmosphere-Ocean, accepted for publication.

WHO/UNICEF (2014). Global Water Supply and Sanitation Assessment Report, World Health Organization, Geneva.

WHO (2010). Guidelines for drinking-water quality, third edition, incorporating the first and second addenda volume 1, Recommendations. WHO, Geneva.