

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

KUMASI

COLLEGE OF SCIENCE

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

**DETERMINATION OF HYDROCARBON CONTAMINATION OF
UNDERGROUND WATER AROUND FUEL FILLING STATIONS IN SELECTED
RESIDENTIAL AREAS IN THE KUMASI METROPOLIS IN THE ASHANTI
REGION OF GHANA**

By

ESTHER BADU

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**A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL AND
APPLIED BIOLOGY, KWAME NKRUMAH UNIVERSITY OF SCIENCE AND
TECHNOLOGY, KUMASI, IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF THE DEGREE OF
MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE**

BY

ESTHER BADU

OCTOBER, 2015

DECLARATION

I, Esther Badu hereby declare that this thesis, “Determination of hydrocarbon contamination of groundwater around fuel filling stations in some selected residential areas in the Kumasi Metropolis in the Ashanti Region of Ghana”, is my own work produced from research undertaken under supervision, and that no part of it has been published or presented for another degree elsewhere, except for permissible excerpts/references from other sources, which have been duly acknowledged.

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(Head of Department)	Signature	Date

DEDICATION

This work is dedicated to my dear mother, Madam Christiana Kyeiwaa and my siblings for their love, care, support and guidance throughout my entire life.

ACKNOWLEDGEMENT

This work would not have been successful without the perfect grace of the Almighty God under whose canopy I continue to seek refuge.

My heartfelt gratitude goes to the Academic Board of the Theoretical and Applied Biology Department that admitted me to pursue my graduate studies here at the Kwame Nkrumah University of Science and Technology (KNUST).

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Finally, I owe all my colleagues especially Mr. Adjei Yeboah, Mr. Ransford Boah and Mr. William Asante Nnuro an appreciation for motivating me all through this study. May God richly bless you.

ABSTRACT

Underground water is vulnerable to contamination from numerous anthropogenic activities. These human activities include improper installation of septic tanks, improper disposal of wastes, leaking underground storage tanks (LUST), and accidental spill of chemicals. Petroleum hydrocarbons are released into underground water due to leakages in fuel storage facilities from the numerous fuel filling stations. Once underground water is contaminated, it is very difficult, time consuming and expensive to clean up. In this study, the physico-chemical parameters - temperature, electrical conductivity (EC), Total Dissolved Solids (TDS), Salinity and Total Petroleum Hydrocarbon (TPH) as well as the distance from fuel storage tanks to underground water sources were measured to ascertain the level of contamination by hydrocarbons in the underground water studied. The mean temperature ranged from 28.69°C at Oforikrom to a high value of 31.87°C at Kentinkrono. The lowest pH recorded was 4.84 at Denyame and the highest of 7.03 at Ahinsan. The mean electrical conductivity results ranged from a low value of 24.5 $\mu\text{S}/\text{cm}$ at Ayeduase and a high value of 519.5 $\mu\text{S}/\text{cm}$ at Oforikrom. TDS were highest at Oforikrom (260 mg/l) and lowest at Ayeduase (10 mg/l). None of these samples recorded TDS values exceeding the permissible limit of 1000 mg/l. The highest mean salinity value recorded was 0.25 ppm at Oforikrom and the lowest of 0.01 ppm at Ayeduase. The highest mean concentration of TPH was 9.48 mg/l recorded at Oforikrom and three sampling points (Abrepo, Kentinkrono and New Suame) recorded zero (0) concentration of TPH. Three sampling points (Oforikrom, Asafo YF and Kwadaso Nsuom) recorded TPH concentrations above the permissible limit. The shortest distance between fuel storage tank and underground water source recorded was 25 m at Ahinsan and the longest distance of 535 m at Aboabo which recorded average TPH concentrations of 3.71 mg/l and 1.12 mg/l respectively. This indicates that, as the distance between the underground storage tanks (UST) and an underground water source increases, there was reduction in the TPH concentration of the water sampled. This shows that the locations of UST had an influence on the contamination of underground water close to fuel filling stations within the Kumasi metropolis in the Ashanti Region of Ghana.

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LIST OF ABBREVIATIONS AND ACRONYMS

APHA	American Public Health Association
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
BTX	Benzene, Toluene, and Xylene
EDB	Ethylene Dibromide
EPA	Environmental Protection Agency
GPRS	Growth and Poverty Reduction Strategy
GWC	Ghana Water Company
KMA	Kumasi Metropolitan Area
LNAPL	Light Non-aqueous Phase Liquids
LUFST	Leaking Underground Fuel Storage Tanks
LUST	Leaking Underground Storage Tanks
MTBE	Methyl tertiary-butyl ether
NAPL	Non-aqueous Phase Liquid
PHC	Petroleum Hydrocarbons
RIDEM	Rhode Island Department of Environmental Management
TDS	Total Dissolved Solids
TPH	Total Petroleum Hydrocarbons
USEPA	United States Environmental Protection Agency
UST	Underground Storage Tanks
VOC	Volatile Organic Compounds

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Water is essential to the existence of man and all living things and it is a cross-cutting element of the Growth and Poverty Reduction Strategy (GPRS II) of the Republic of Ghana which is linked to the Millennium Development Goals. The availability of water has always been of vital importance to life, both for animals and plants. It has always played a life sustaining role in growth and welfare of humankind. The water resources of a country constitute one of the most important economic assets.

It is a matter of great pleasure that Ghana as a nation along with the rest of the world have started highlighting life on the earth. Studies to protect life and other resources such as air, freshwater and the like have been initiated throughout the world. It is unfortunate; however, that we are leaving behind a legacy that will make the life of tomorrow more threatened than it is felt today. The anthropogenic activities have shaken the environment of this planet earth and we are facing the danger of contamination, degradation, destruction and the elimination of ecological infrastructure that is essential for us now as much as it is for the future generation. Presently, we can observe with dismay that rare species of wildlife are disappearing, the forests are at devastation, the earth is so much polluted that, it is pouring out acidic rains, and freshwater resources are severely degraded (Mohammed,1997).

Contrary to the popular impression that at least the waters from our springs and wells are pure, we are uncovering a pattern of pervasive pollution which is generally irreversible due to the fact that the rate of groundwater renewal is very slow as compared to that of surface water (USEPA, 1990).

Sources of underground water contamination are widespread and include thousands of accidental spills, landfills, surface waste ponds, underground storage tanks, pipelines, injection wells, land application of wastes and pesticides, septic tanks, radioactive waste disposal, salt water intrusion, and acid mine drainage.

The contamination of underground water could be attributed to the boom in automobile sales followed by the construction of thousands of gasoline stations across the country where bare steel tanks are installed underground to store gasoline (Marxsen, 1999). Contamination of underground water with respect to underground fuel tanks according to Marxsen, (1999) could be linked to corrosion of steel tanks, faulty installation and operation, leaking storage tanks and spills.

There have been more than 450,000 confirmed fuel leaks from underground storage tanks (UST) in the US, including 44,000 in California. Because of these, many communities need to find alternative sources of freshwater (Marxsen, 1999).

These UST hold toxic materials, such as gasoline and waste oil, which contain dangerous substances that can cause cancer and harm developing children. Chemicals in UST can quickly move through soil and pollute underground water. There is no safe level of exposure to many of these toxic substances as stipulated by Moran *et al.*, (2005). Once underground water is contaminated, it is very difficult, time consuming and expensive to clean up. The time and cost of clean-up depends on the extent of contamination even a small amount of contamination can be costly to clean up. It is best to prevent underground water contamination from occurring.

A study made by Kamrin (1992) found out that the vulnerability of underground water to existing or potential sources of contamination underscores the need for a systematic, detailed process by which these potential threats can be recorded and evaluated. This

research work would describe how tank owners can help prevent contamination by properly using and storing fuels.

1.2 Problem Statement

The sources of underground water contamination are many and varied because, in addition to natural processes, practically every type of facility or structure installed by man and each and every human physical activity may eventually cause underground water quality problems.

In recent years, numerous fuel filling stations established have increased possible leakages in underground fuel storage tanks which have had a significant adverse environmental impact on the world at large. Leaking underground storage tanks (LUST) hold gasoline, diesel fuel, waste oil and other toxic materials that contain dangerous chemicals and heavy metals that are known to cause cancer, injure developing children and harm the human reproductive and nervous systems. Smith (1986) buttressed the above when he reported that living near a leaking UST or drinking water from a well that is polluted by an UST may present a serious threat to vulnerable people, such as children.

Harris *et al.* (2008) recorded that petroleum fuels contain a number of potentially toxic compounds, including common solvents such as benzene, toluene and xylene (BTX), as well as additives such as ethylene dibromide (EDB) and organic lead compounds. EDB is a carcinogen, a cancer-causing agent, in laboratory animals, and benzene is considered a human carcinogen. Methyl tertiary-butyl ether (MTBE) is a fuel oxygenate added to gasoline to reduce air pollution and increase octane ratings. Widespread use of this chemical according to Harris *et al.* (2008) has resulted in frequent detections of MTBE in samples of shallow underground water from urban

areas throughout the United States. However, the substances in gasoline can threaten humans in another way as toxic contaminants of drinking water (Kamrin, 1992). Underground fuel tanks are a major source of underground water contamination since they have a life span of 15 to 25 years, and the probability that they will begin to leak increases with age (Marxsen, 1999).

When leaks occur, fuel seeps through the soil to the groundwater. Harris *et al.* (2008) reported that a leakage rate of just two drops per second can contaminate nearly half a billion gallons of water to the point where odor and taste make it unacceptable for drinking.

The time it takes leaking fuel to reach the underground water depends on soil composition, geological and hydrological factors and the distance between the tank and the aquifer. Once the leaking fuel reaches the underground water, fuel tends to accumulate because it cannot evaporate, as it does on the surface; it is not easily broken down by micro-organisms; and underground water moves very slowly. These factors lead to accumulation and persistence of these contaminants in the water (Kamrin, 1992).

Smith (1986) indicated that the restoration after contamination is often complex and expensive. Thus, the vulnerability of underground water to pollution coupled with our dependence on it for our drinking, agriculture and industry necessitates the creation of a strong, uniform policy to address the contamination problem.

Underground water contamination and its sources must be identified and assessed, and their impacts on underground water quality determined for comprehensive groundwater protection strategy.

1.3 Aim and Objectives of the Study

The main aim of the research was to determine hydrocarbon contamination of underground water around fuel filling stations in selected residential areas in the Kumasi Metropolis.

Specifically, the research aimed at achieving the following objectives:

- To identify fuel filling stations, their storage facilities and underground water sources close to the fuel storage facilities around fuel stations.
- To determine the distance between underground fuel storage tanks and the underground water collected, and relate it to the total petroleum hydrocarbon (TPH) levels in the underground water samples studied.
- To determine the TPH concentration levels of samples from underground water sources close to fuel storage facilities around fuel stations.
- To determine some physicochemical parameters in selected underground water samples in relation to contamination by hydrocarbons.

1.4 Scope of Study

Geographically, the study area covered the Kumasi Metropolis in the Ashanti Region of Ghana. Kumasi was chosen because it is a growing metropolis just like other Metropolitan areas such as Accra and Sunyani which are flooded with automobiles and hence several fuel filling stations which have underground storage tanks. Contextually, the study focused on contamination of underground water by leaking underground fuel storage tanks (LUST). This is because leaking fuel tanks are one of the major sources of underground water contamination but with little or no attention.

CHAPTER TWO

LITERATURE REVIEW

2.1 Underground water Contamination

Underground water contamination happens when naturally occurring or man-made substances seep into underground water (Matsumoto, 2009). This chapter addresses man-made underground water contamination, which might be as a result of accidental or deliberate releases of chemical products into the subsurface. For example, leaky underground storage tanks and pipelines have often discharged chemicals into underground water (Figure 2.1). Improper disposal at commercial (and sometimes residential) facilities has also resulted in chemicals being dumped on or into the ground. Matsumoto (2009) stated that in some cases, transportation accidents may release chemicals at ground surface and thence into the ground.

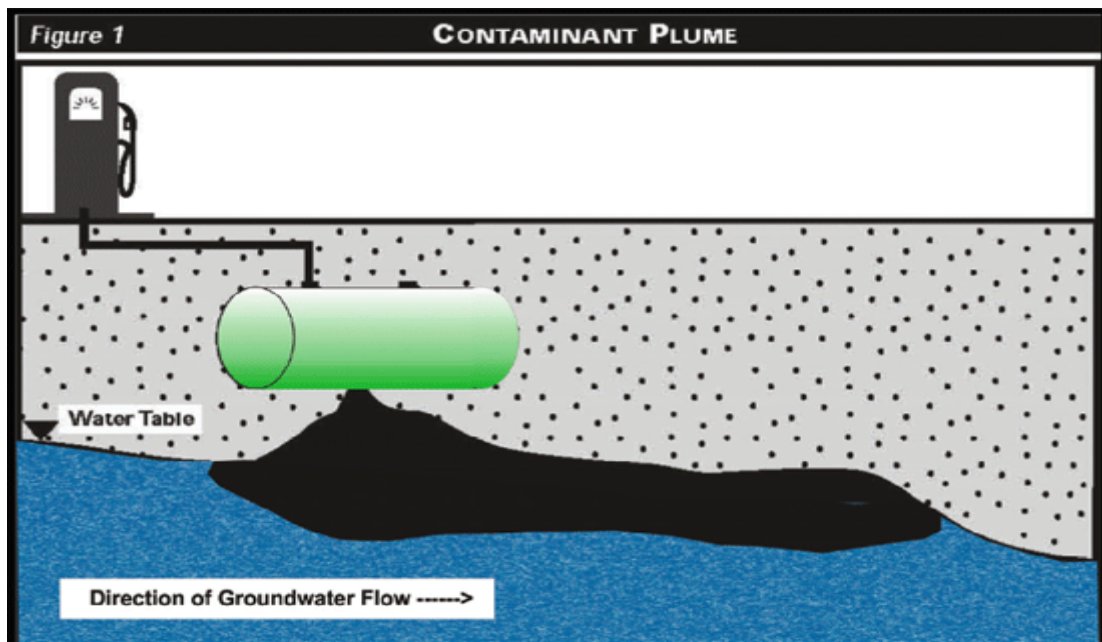


Figure 2.1: Groundwater flow and contaminant plume

Underground water Contamination is the detrimental alteration of the naturally occurring physical, thermal, chemical, or biological quality of underground water.

Underground water Contamination may be defined as the artificially induced degradation of natural underground water quality according to Todd (1980).

Any addition of undesirable substances to underground water caused by human activities is considered to be contamination. It has often been assumed that contaminants left on or under the ground will stay there.

According to Metthess *et al.* (1985), contaminated underground water may be defined as groundwater which has been effected by man to the extent that it has higher concentrations of dissolved or suspended constituents than maximum permissible concentration fixed by national or international standards for potable, industrial or agricultural purpose.

Metthess (1982) separated the natural underground water which is not influenced by man but contaminated as contamination should be defined in these cases as any increase in concentration of the respective constituent above its natural variations.

Zaporozec (1981) also proposed the term “Groundwater pollution” for any minor alteration or degradation of the natural quality of underground water, resulting from process or man’s activities.

Pollution means too much of any given contaminant such that it renders the receiving water unusable in its existing state for its desired best use (Mohammed, 1997).

Unfortunately until recently, no scientific campaign has been launched to protect underground water pollution.

2.2.1 Causes of Underground water Contamination

The type, extent and duration of anthropogenic changes of underground water are controlled by the influence of man, the geochemical, physical and biological processes

underground and hydrogeological conditions in underground water (Golwer, 1983). Underground water is vulnerable to contamination from numerous anthropogenic activities. Smutko *et al.* (1993) reported that these human activities include improper installation of septic tanks, improper disposal of wastes, leaking underground storage tanks, and accidental spills of chemicals. These are all sources of underground water contamination.

The sources of underground water pollution could be point source or non-point source. Leaking underground storage tanks (LUST), as this work seeks to determine, is an example of a point source of underground water contamination. On the other hand, a typical example of non-point source of groundwater contamination is the applications of fertilizers to agricultural fields.

The terms point and non-point do not reflect where the contamination takes place but rather refer to how the contamination is dispersed. Point sources are dispersed locally whereas non-point sources are dispersed over wide areas or regions. While the distribution of a pollutant may be classified as point or non-point, changes in underground water quality are closely related to patterns in land-use and waste disposal practices (Smutko *et al.*, 1993).

Again, according to Smutko *et al.* (1993), the sources of underground water contamination as a result of human activities could be classified into four categories as:

1) Waste disposal, 2) storage and handling, 3) agricultural, and 4) salt water intrusion. Methods of waste disposal commonly associated with underground water contamination include landfills, septic systems, surface impoundments or lagoons, injection wells, and direct land application of waste. The physical, chemical and biological states of underground water vary in accordance with the environment

through which it passes during the course of hydrological cycle and becomes a part of underground water. The USEPA (1990) has categorized the various sources of deteriorating underground water quality into three main categories. These are waste dumps, industrial effluents and leaking underground fuel storage tanks (LUFST). However, emphasis will be laid on only leaking underground storage tanks (LUST) in this study.

2.3 Fuel Storage Tanks

USEPA (1997) reported that gasoline stations, dry cleaners, and other industrial establishments store large quantities of liquids in tanks. Some are above ground, some are below ground. Underground tanks tend to cause underground water contamination because small leaks often go undetected.

The United States Environmental Protection Agency (USEPA) defines an underground storage tank (UST) as “a tank and any underground piping connected to the tank that has at least 10 percent of its combined volume underground” (United States Code of Federal Regulations (2002). UST are of particular concern because of their potential to lose tightness over time and leak their contents into the subsurface. This can result in severe contamination of soil and underground water, and in the worst cases, impairs the ability of an underground aquifer to provide drinking water for entire communities. USEPA (1997) reported that LUST is known as the highest priority threat to underground water resources in the State. When these tanks leak their contents into the subsurface, serious public health risks can result. A leak in a gasoline UST could be responsible for contaminating the wells in town with methyl tertiary-butyl ether (MTBE), which is a volatile organic compound known by the EPA to have

carcinogenic effects in laboratory animals (USEPA, 1997), and considered to be a potential human carcinogen at high doses (USEPA,1998).

According to the USEPA, (1998), if an underground petroleum tank is more than 20 years old, especially if it is not protected against corrosion, the potential for leaking increases dramatically. Newer tanks and piping can leak, too, especially if they were not installed properly. Even a small gasoline leak of one drop per second can result in the release of about 400 gallons of gasoline into the underground water in one year. Even a few quarts of gasoline in the underground water may be enough to severely pollute a drinking water. At low levels of contamination, fuel contaminants in water cannot be detected by smell or taste, yet the seemingly pure water may be contaminated to the point of affecting human health (USEPA, 1998).

2.3.1 Contamination by Leaking Underground Storage Tanks

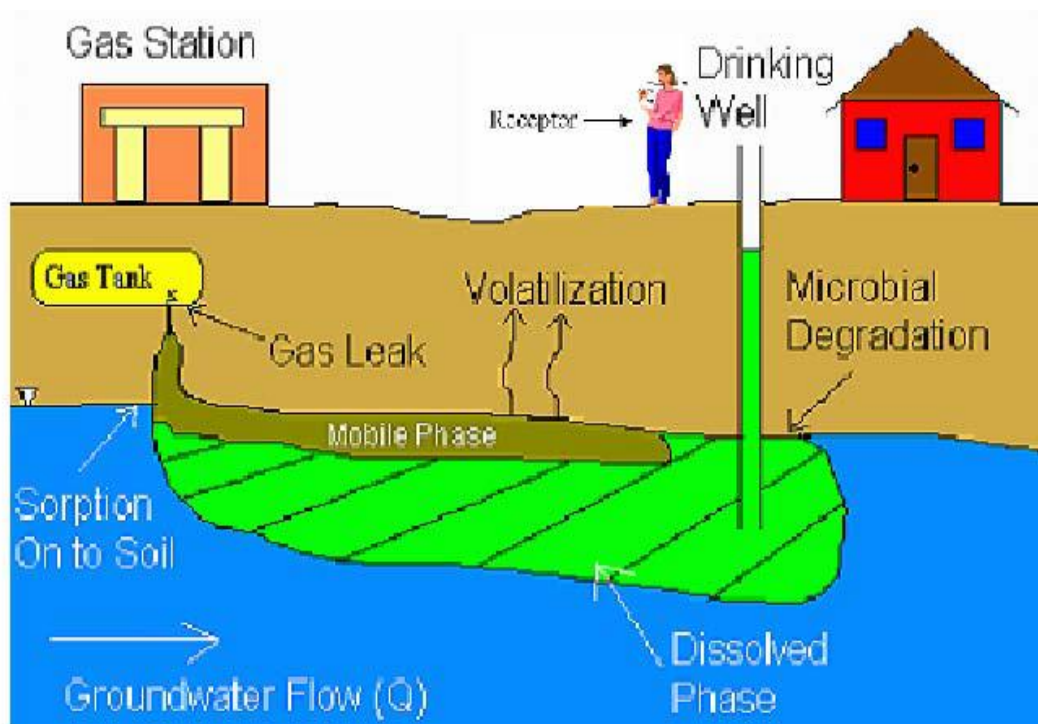


Figure 2.2 Example of Environmental Risk Assessment Scenario Caused by Leaking UST

DiGiano *et al.* (1988) reported that a fluid that is immiscible with water is termed as a non-aqueous-phase liquid (NAPL). NAPL may be either less dense (e.g. petroleum products) or more dense (e.g. chlorinated solvents) than water. A spill of a low- density NAPL released into the subsurface environment from a leaking underground storage tank will move vertically the partially-saturated zone (unsaturated zone) in response to gravity. As the NAPL moves vertically: a portion of the immiscible fluid is retained by capillary forces in the pore spaces (USEPA, 1997); soluble components of the NAPL are transferred to the pore water phase; volatile components of the NAPL are transferred to the vapor phase; and the NAPL eventually intercepts the water table and begins migration in the direction of underground water movement if a sufficient volume of NAPL is released (DiGiano *et al.*, 1988).

The above scenario according to DiGiano *et al.*, (1988) leads to the distribution of contaminants in four phases: the NAPL phase, the aqueous phase, the vapor phase, and the solid (soil, partially-saturated sands, silts, or clays, and aquifer materials) phase.

Releases of non-aqueous phase liquids (NAPL) to underground water systems are a serious and widespread problem (USEPA, 1996; USEPA, 1998). Each release has the potential to threaten human health and the environment which then contaminate soil and underground water and act as a source for dissolution of soluble hydrocarbon constituents. The contamination is further dispersed as the water soluble components flow with the underground water.

It has been recognized by USEPA (1990) that the major sources causing soil and underground water contamination are resulting from leaking underground storage tanks (LUST) which are enormously applied by commercial, industrial and residential sectors.

Of course, similar contamination can also occur during land-farming, petroleum sludge disposal, heavy oil upgrading, and other processes (DiGiano *et al.*, 1988).

United States Geological Survey (2003) reported that there is no safe level of exposure to many of these toxic substances released into the environment from LUST.

Leaking underground storage tanks can hold substances such as fuel (e.g. gasoline or diesel), used oil and other toxic substances (USEPA, 1997).

Leaks of petroleum products have been increasing because underground steel tanks installed in large numbers in about two decades ago become corroded. Most underground tanks too made of steel without adequate corrosion protection, leak by the time they are 15 years old (USEPA, 1997).

2.4 Underground water Contamination by Hydrocarbons from LUST

An underground storage tank (UST), include any underground piping connected to the tank itself, which is used to contain an accumulation of regulated substances. Several hundred thousand UST that are used for storing petroleum products are leaking (USEPA, 1997).

Mackay *et al.* (1985) added more flesh on leaking underground storage tanks when they indicated that leaking underground storage tanks are one of the most frequent causes of underground water pollution in the United States. A recent survey according to Sun (1986) estimated that most gasoline storage tanks were leaking, while many other tanks are approaching their design life.

Upon release of gasoline in the subsurface, each of the many organic components in gasoline is transported by bulk movement and inter phase transfer (i.e., to the groundwater, soil and vapor); some of these components may also be degraded or

transformed by either biotic or abiotic processes. The result is a spatial and temporal distribution of contaminants in the subsurface environment (Sun, 1986).

Petroleum hydrocarbons are classified as priority pollutants; some are at least somewhat water soluble, making them a common underground water contaminant. Petroleum hydrocarbons are known for their acute toxicity (Valentinetti, 1989); thus small concentrations can be of concern. Hydrocarbon contamination from fuel leaks and spills is one of the most common underground water pollution problems (Valentinetti, 1989).

A survey conducted by Taylor (1989) revealed that approximately 30 % of existing underground tank facilities is leaking in Chelsea. These leaks in underground storage tanks and underground fuel transfer lines are difficult to detect and locate. Taylor (1989) further reported that underground storage tanks (UST) hold toxic material, such as gasoline and waste oil, which contain dangerous substances that can cause cancer and harm developing children. Chemicals in UST can quickly move through soil and pollute underground water. The greatest harm caused by a leaking underground storage tank, which holds petroleum or petroleum by-products, is the contamination of soil and underground water (Taylor, 1989). For instance, petrochemical compounds that seep down to an underground water formation will tend to float on top of the water table due to their lighter specific gravity. Also, volatile components can exist in gaseous phase and escape as fumes or odors. Other components, such as benzene, toluene, and various xylenes (or BTX), can attach to the soil and exist in adsorbed phase.

Taylor (1989) indicated that most often the leaks are so small that inventory studies are ineffective in locating the source of the pollutant. The rate of dissipation or natural degradation of fuel contamination in soil is extremely slow in many cases and even a

small fuel leak can produce serious contamination that is extremely costly to remediate (Taylor, 1989). The next sub-section gives a brief description of petroleum hydrocarbons commonly found in underground storage tanks.

2.4.1 Petroleum Hydrocarbons

Petroleum and petroleum products are highly complex and varied mixtures. Hydrocarbons (compounds containing only carbon and hydrogen atoms) form the major components in petroleum. Crude oil can consist of thousands of individual compounds with hydrocarbons representing from 50 to 98 percent of the total weight of crude oil (Taylor, 1989). When petroleum compounds such as crude oil are released into the environment, the compounds undergo physical, chemical, and biological changes which are collectively known as 'weathering'. Taylor (1989) added that each of these processes required to enhance the degradation of various types of petroleum hydrocarbons become successful depending on the physical and chemical properties of the hydrocarbons. The next sub-section hence discusses the classification and composition of petroleum hydrocarbons.

2.5 Classification and Composition of Hydrocarbons

Petroleum hydrocarbons are mostly compounds which are made up of hydrogen and carbon atoms only. They are characterized by their chemical composition as well as their structure.

According to Parcher (1999), there are typically four major classes of Petroleum hydrocarbons. These are:

- Alkanes
- Cycloalkanes

- Alkenes
- Aromatics

The Alkanes, Cycloalkanes and Alkenes are collectively called Aliphatics. The carbon atoms in alkanes are joined by single bonds. They are commonly known as Paraffins or saturated hydrocarbons. Alkanes have a general formula of C_nH_{2n+2} . Alkanes with cyclical structure are called Cycloalkanes or Cycloparaffins. These compounds are also called Naphthenes which has a formula of C_nH_{2n} . Alkenes (also known as unsaturated hydrocarbons or Olefins) are made up of carbon-carbon double bonds. The general formula for alkenes is C_nH_{2n} .

Aromatic hydrocarbons are characterized by at least one 6-carbon benzene rings. They are unsaturated and hence; resemble benzene in chemical behavior. Monoaromatics as the name implies; are aromatics with one benzene ring as part of their structure. Polycyclic aromatic hydrocarbons (PAH) on the other hand, are aromatics with two or more fused benzene rings. Some monoaromatics like benzene, toluene, ethylbenzene and xylenes (BTEX) are the most common aromatics petroleum. Aromatic compounds are of great concern in relation to environmental pollution because they are relatively soluble in water and as such have a high mobility potential in groundwater (Parcher, 1999).

Parcher (1999) added that many aromatic compounds are carcinogenic and can pose health risks when dissolved in drinking water aquifers. Petroleum hydrocarbons are derived from crude oil, which is refined into various petroleum products by several processes. Like the parent crude oil, refined petroleum products are also mixtures of as many as several hundred compounds. The bulk products may be classified on the basis of composition and physical properties. Products typically stored in UST include the following main groups:

- Gasolines
- Middle Distillates
- Heavy Fuel Oils

2.5.1 Gasolines

There are over 70 individual hydrocarbon compounds in regular gasoline (Parcher, 1999), and they are mainly compounds of aliphatic hydrocarbons and aromatic hydrocarbons. The aromatic compounds, such as benzene and toluene, are characterized by a ring structure of carbon atoms (Parcher, 1999). Gasolines are mixtures of petroleum hydrocarbons and other non-hydrocarbon chemical additives, such as alcohols (*e.g.*, ethanol) and ethers (*e.g.*, methyl tertiary-butyl ether, or MTBE). Gasolines are more mobile than either the middle distillates or the fuel oils. The higher mobility of gasoline is primarily due to the fact that its components tend to have lower molecular weights; hydrocarbon compounds usually found in gasoline have between 4 and 10 carbon atoms per molecule. The lower molecular weight results in lower viscosity, higher volatility, and moderate water solubility. Fresh gasolines contain high percentages of aromatic hydrocarbons (*i.e.*, those with a 6-carbon benzene ring), which are among the most soluble and toxic hydrocarbon compounds. The most frequently encountered aromatic compounds are benzene, toluene, ethylbenzene, and xylene (BTEX). Because of their relatively high volatility, solubility, and biodegradability, BTEX compounds are usually among the first to be depleted from free product plumes. At sites of older gasoline releases, the free product plume may contain relatively little BTEX, being instead enriched in heavier, less soluble, and less readily biodegradable components. As a consequence, the product will be more viscous, slightly denser, less volatile, and less mobile than fresh product.

Methyl tertiary-butyl ether (MTBE) is produced in very large quantities and is almost exclusively used as a fuel additive in motor gasoline (Parcher, 1999). It is one of a group of chemicals commonly known as "oxygenates" because they raise the oxygen content of gasoline. At room temperature, MTBE is a volatile, flammable and colorless liquid that dissolves rather easily in water. MTBE has been used in gasoline at low levels to replace lead as an octane improver (helps prevent the engine from "knocking"). Oxygen helps gasoline burn more completely, reducing harmful tailpipe emissions from motor vehicles. In one respect, the oxygen dilutes or displaces gasoline components such as aromatics (e.g., benzene) and sulfur. In another, oxygen optimizes the oxidation during combustion. Most refiners have chosen to use MTBE over other oxygenates primarily for its blending characteristics and for economic reasons. USEPA (1997) reported that refiners may choose to use other oxygenates, such as ethanol (USEPA, 1997). The non-hydrocarbon additives (*e.g.*, ethanol, MTBE) are readily soluble and preferentially dissolve into groundwater, which diminishes their concentration in the free product, but results in formation of longer dissolved plumes. MTBE also moves away from the source faster than free product and because it is relatively non-degradable, it is difficult to remediate (USEPA, 1997).

2.5.2 Middle Distillates

Middle distillates (*e.g.*, diesel fuel, kerosene, jet fuel, lighter fuel oils) may contain 500 individual compounds, but these tend to be more dense, much less volatile, less water soluble, and less mobile than the compounds found in gasolines (Parcher, 1999). The major individual components included in this category of hydrocarbons according to Parcher (1999), contain between 9 and 20 carbon atoms each. Lighter aromatics, such as BTEX, are generally found only as trace impurities in middle distillates, and if

initially present, they are generally not present in plumes at older release sites, because they have biodegraded, evaporated, and dissolved into groundwater (Parcher, 1999).

2.5.3 Heavy Fuel Oils

Parcher (1999) reported that heavy fuel oils and lubricants are similar in both composition and characteristics to the middle distillates. These types of fuels are relatively viscous and insoluble in groundwater and are, therefore, fairly immobile in the subsurface. Parcher (1999) further added that most of the compounds found in heavy fuel oils have more than 14 carbon atoms; some have as many as 30. Like the older releases of middle distillates and gasolines, the lighter end components are present only in trace amounts as they are more readily biodegraded and dispersed. The next sub-section discusses how the petroleum hydrocarbons are distributed in the subsurface.

2.6 Phase Distribution of Petroleum Hydrocarbons in the Subsurface

According to Parcher (1999), when petroleum hydrocarbons have been released into the subsurface, they can partition into one or more of the following phases:

- Mobile Liquid – the mobile free product is maintained at the water table and capillary fringe or /perched above a low permeability layer in the unsaturated zone;
- Residual Liquid – the liquid hydrocarbon is trapped within the soil matrix both above and below the water table, depending on water table movement;
- Aqueous – the soluble hydrocarbon components dissolve in the groundwater and soil moisture;
- Sorbed – the soluble hydrocarbon is adsorbed to soil particles
- Vapor – the volatile hydrocarbon components enter a gaseous state, which occurs primarily in the unsaturated zone.

Generally, the presence of all the above phases results when a sufficient volume of NAPL has been released into the subsurface (USEPA, 1996). The petroleum hydrocarbon constituents that comprise free product may partition into four phases in the subsurface—**vapor** (in soil gas), **residual** (adsorbed onto soil particles including organic matter), **aqueous** (dissolved in water), and **free or separate** (liquid hydrocarbons). Figure 2.3 below illustrates the distribution of the hydrocarbon phases in the subsurface from a leaking UST.

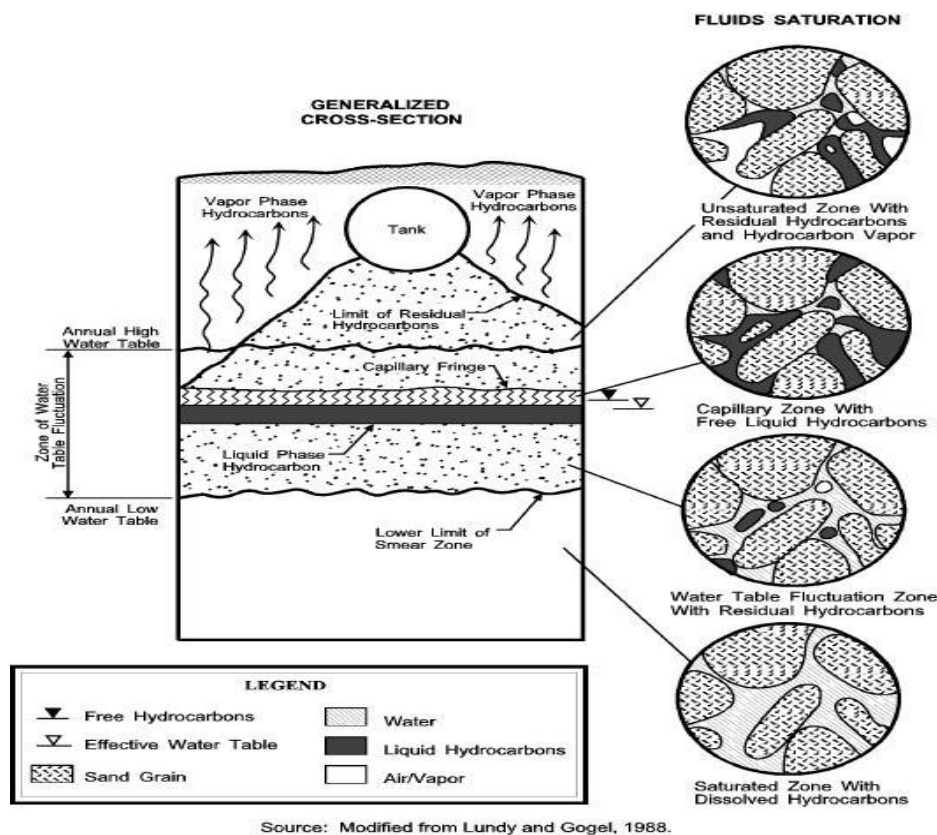


Figure 2.3 Vertical Distributions of Hydrocarbon Phases

The partitioning between these phases, according to Pacher (1999) is determined by dissolution, volatilization, and sorption. When released into the subsurface environment, liquid hydrocarbons tend to move downward under the influence of gravity and capillary forces. The effect of gravity is more pronounced on liquids with higher density. The effect of capillary forces is similar to water being drawn into a dry

sponge. As the source continues to release petroleum liquids, the underlying soil becomes more saturated and the leading edge of the liquid migrates deeper leaving a residual level of immobile hydrocarbons in the soil behind and above the advancing front. If the volume of petroleum hydrocarbons released into the subsurface is small relative to the retention capacity of the soil, then the hydrocarbons will tend to sorb onto soil particles and essentially the entire mass will be immobilized (Parcher, 1999). For petroleum hydrocarbons to accumulate as free product on the water table, the volume of the release must be sufficient to overcome the retention capacity of the soil between the point of release and the water table. Figure 2.4 below illustrates the progression of a petroleum product release from a leaking UST as illustrated by Parcher (1999).

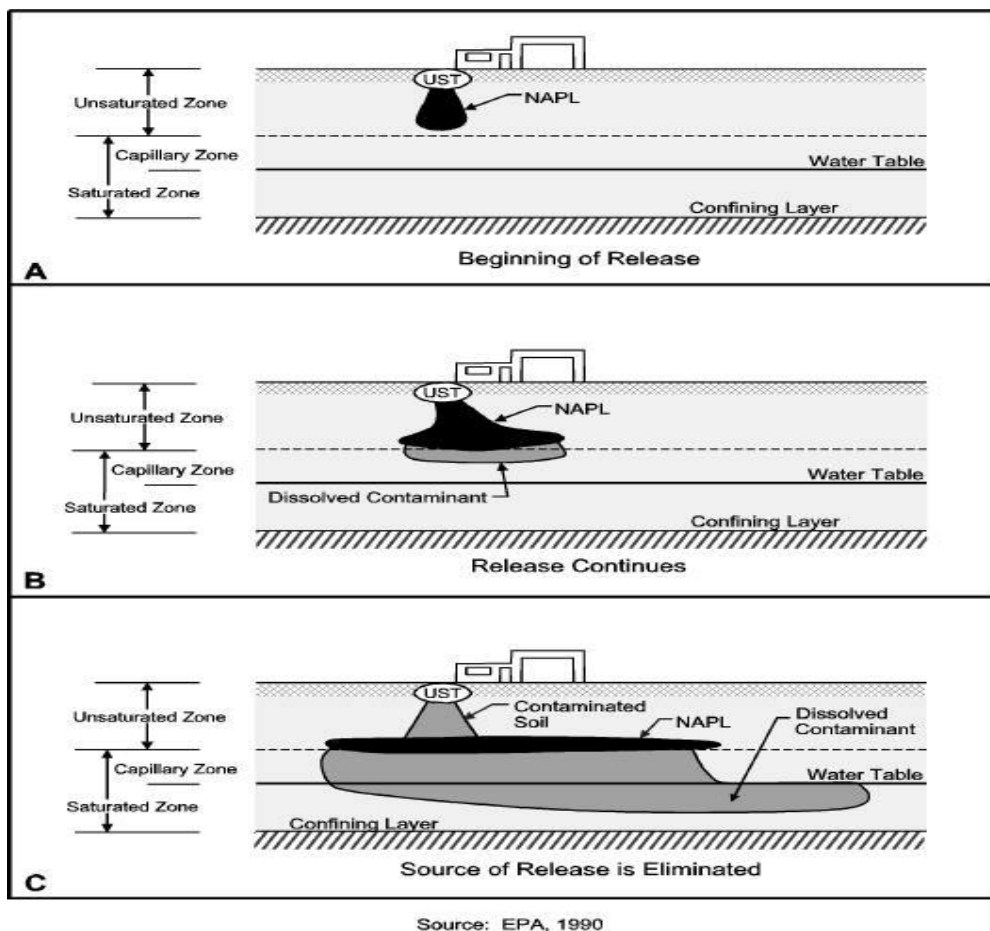


Figure 2.4 Progression of a Typical Petroleum Product Released from an Underground Storage Tank

Parcher (1999) explained that frame A shows the hydrocarbon mass before it reaches the capillary fringe. If the release were to be stopped at this point, there would probably be no accumulation of free product. In Frame B, the release has continued and the volume of the release is sufficient for free product to begin accumulating on, and displacing, the capillary fringe. The free product is beginning to displace the capillary fringe and some of the soluble constituents are dissolving into the groundwater. The source of release has been stopped in Frame C. Residual hydrocarbons remain in the soil beneath the UST. The free product plume has spread laterally, and a plume of dissolved contaminants is migrating down gradient (Parcher, 1999).

Portions of the hydrocarbon mass from both the residual and free phases according to Parcher (1999), will volatilize (evaporate) and dissolve to become components of the soil vapor and groundwater, respectively. Volatilization and solubilization (dissolution) of the lighter fractions tend to make the remaining hydrocarbon mass more dense and even less mobile. Hydrocarbons that are in the vapor phase are much more mobile and can migrate relatively great distances along preferential flow paths such as fractures, joints, sand layers, and utility line conduits (Parcher, 1999). Accumulation of vapors in enclosed structures (*e.g.*, basements, sewers) potentially can cause fires or explosions. The more soluble components of the hydrocarbon mass will dissolve into underground water, both above and below the water table. The dissolved hydrocarbons move with the flowing underground water and can contaminate drinking water supplies (Parcher, 1999).

2.6.1 Processes that affect the fate and transport of Hydrocarbons in Underground water

There are various processes such as physical, chemical and biological processes that affect the fate and transport of petroleum hydrocarbons in the subsurface (Parcher, 1999). Some of these processes are described in greater detail below.

2.6.1.1 Dissolution

Dissolution is the transfer of soluble hydrocarbon constituents from free phase or residual NAPL into the aquifer and is the primary physical property that controls the extent of a contaminant plume (Salanitro, 1993). Dissolution of soluble hydrocarbons is affected by factors like the surface area contact between NAPL and water as well as contact time. The rate of dissolution depends on the effective solubility of the hydrocarbon constituents in the aquifer and the amount and type of NAPL in the subsurface (Parcher, 1999).

2.6.1.2 Advection

Advection is the process by which solutes (dissolved hydrocarbons) are transported in flowing groundwater (Parcher, 1999). High advection can cause increased spreading and dilution of dissolved contaminants.

2.6.1.3 Hydrodynamic Dispersion

Hydrodynamic dispersion is the term applied to the combined effects of mechanical dispersion and molecular diffusion in causing a contaminant plume to spread within a underground water system (Parcher, 1999). Mechanical dispersion is the mixing of the solute with uncontaminated water, thus reducing the concentration of the contaminant. Variations in pore size, flow path, and pore friction cause dispersion. Longitudinal dispersion occurs in the direction of advective underground water flow while transverse

dispersion occurs perpendicular to underground water flow. Diffusion is the movement of dissolved molecular species in response to concentration gradients (Parcher, 1999). Molecular diffusion occurs even in the absence of underground water flow. Under normal advective flow systems, mechanical dispersion predominates (ASTM, 1998).

2.6.1.4 Adsorption

The term adsorption describes the partitioning of organic contaminants from the soluble or gaseous phase onto a solid phase, usually the soil matrix. Since most petroleum constituents are non-ionic, they adsorb more readily to organic carbon rather than mineral particles in soil (Parcher, 1999). Therefore, adsorption is a more important process in aquifers with high organic carbon content. In addition, adsorption reactions between NAPL constituents and organic particles are usually chemical in nature, and therefore, are reversible equilibrium reactions (Parcher, 1999). In general, adsorption retards the movement of contaminants in aquifers (Parcher, 1999).

2.6.1.5 Volatilization

The transfer of a chemical from the aqueous or liquid phase to the gas phase is termed volatilization (Parcher, 1999). The USEPA, (1995) reported that the rate of volatilization is controlled by molecular weight, solubility, and vapor pressure of the liquid as well as the gas-liquid interface. Volatilization can result in the mass loss of substances from the subsurface into the atmosphere. While this process accounts for mass loss, especially in shallow water table environments, this mechanism may not be significant compared to other processes and diminishes in importance over time as volatile organics are depleted from the subsurface (USEPA, 1995). McAllister and Chiang (1994) stated in their report that at a typical site, about 5 to 10 percent of benzene mass loss is due to volatilization while biodegradation accounts for the

remaining mass loss. The anticipated mass loss due to volatilization is even lower for less volatile hydrocarbon constituents.

2.6.1.6 Biodegradation

Biodegradation is a process by which hydrocarbons are consumed by micro-organisms through a series of enzyme-catalyzed oxidative-reduction reactions (Parcher, 1999). When oxygen is the electron acceptor, aerobic bacteria convert hydrocarbon contaminants to carbon dioxide and water by transferring electrons from the hydrocarbon to oxygen, thus reducing it to water. Approximately three units of oxygen are required to convert one unit of hydrocarbon to carbon dioxide and water (ASTM, 1998). Under anaerobic conditions, alternate electron acceptors are utilized by the micro-organisms. Alternate electron acceptors, in order of preference, include nitrate, manganese, ferric iron, sulfate and carbon dioxide (ASTM, 1998).

The capability of petroleum hydrocarbons to biodegrade depends on composition and chemical structure. Lighter, more soluble hydrocarbons are typically more biodegradable than heavier, less soluble hydrocarbons. Hydrocarbons with simple chemical structures are more biodegradable than complex hydrocarbons (Parcher, 1999). For example, straight-chain hydrocarbons degrade faster than branched structures and mono-aromatic compounds, such as benzene, are more easily degraded than polycyclic aromatic compounds, such as naphthalene (Chiang *et al.*, 1989).

Chiang *et al.* (1989) further reported that in the past 15 years, microbial degradation of petroleum hydrocarbons has been widely studied in the laboratory and in the field. The presence of microbial populations capable of oxidizing petroleum hydrocarbons has been demonstrated in numerous locations and for diverse hydrologic conditions. Biodegradation has been shown in numerous studies to be the primary mechanism for

attenuation of petroleum hydrocarbons in the subsurface (McAllister and Chiang, 1994).

2.6.2 Properties of Geologic Media

The extent and rate of petroleum hydrocarbon migration depends in part on the properties of the subsurface medium in which it is released (Parcher, 1999). The subsurface medium may be naturally occurring geologic materials (*e.g.*, sedimentary, metamorphic, or igneous rock or sediments) or artificial fill that has been imported to the site by human activity. Characterization of both the type and the distribution of geologic media (or fill material) are necessary to determine the likely migration routes and travel times of hydrocarbons in underground water (Parcher, 1999). In the context of fluid flow in the subsurface, geologic media can be classified on the basis of the dominant characteristics of pore space, fractures, or channels through which fluids move. In porous media, fluids move through the interconnected voids between solid grains of soil. Fractured media are those in which fluids migrate readily through fractures rather than the adjacent soil or rock matrix.

Parcher (1999) further stated that porosity and permeability are the two most important media-specific properties of a natural geologic material. Porosity characterizes the ability of media to store fluids, and permeability characterizes the ability of the media to transport fluids.

2.6.2.1 Porosity

Porosity, or more specifically effective (“drainable”) porosity as indicated by Parcher (1999), is an important factor to be considered in the evaluation of groundwater contamination by hydrocarbons. Porosity defines the storage capacity of a subsurface media. All rocks and unconsolidated media contain pore spaces. Parcher (1999)

defined porosity as the percentage of the total volume of an unconsolidated material or rock that consists of pores. Porosity according to Parcher (1999) is classified as either primary or secondary. Primary porosity is created when sediments are deposited (or crystalline rocks are formed), and it depends on the shape, sorting, and packing of grains. Primary porosity is greatest when grains are nearly equal in size (*i.e.*, are well graded or sorted) and non-spherical in shape. Unconsolidated sediments that contain a wide range of grain sizes (*i.e.*, are poorly graded or sorted) tend to have a low primary porosity because smaller grains fill the pore spaces between the larger grains (Parcher, 1999).

Secondary porosity develops after rocks have been formed or sediments deposited. Examples are joints, foliations, fractures, and solution openings. Also included in this category are animal burrows, root holes, and desiccation cracks in clay soils. While the latter examples typically facilitate free product migration only very locally, the former examples can exert a much more regional influence. Once free product enters these larger openings, it can migrate undetected over relatively great distances (miles in some cases) in a matter of weeks or months (Parcher, 1999).

Total porosity as reported by Parcher (1999) is based on the volume of all voids (primary and secondary), whether or not the pores are connected. When pores are not connected and dead-end pores exist, underground water cannot move through the rock or sediments. Effective porosity is the term that characterizes the ratio of the volume of interconnected pores to the total volume of unconsolidated materials or rock. Parcher (1999) concluded that there is no direct correlation between effective and total porosity. Effective porosity is approximated by drainable porosity and can be significantly less than total porosity. In general, the smaller the grains in the rock, the smaller the effective porosity (and the greater the retention capacity or residual saturation). For

example, clays and limestones can have an upper range of total porosity that is in excess of 55 percent, but a lower range of drainable porosity of 1 percent or less (Parcher, 1999).

2.6.2.2 Permeability

Permeability is one of the most critical properties to be considered in the contamination of underground water by hydrocarbons. Parcher (1999) stipulated that the rates of underground water flow and free product migrations are related directly to permeability. The rate of free product migration also depends on other parameters, but permeability exhibits the greatest range in values (varying over 5 or 6 orders of magnitude for common geologic media). The intrinsic permeability of the geologic media is independent of the nature of the fluid flowing through the media. Intrinsic permeability is related to hydraulic conductivity, which is a measure of the ability of the geologic medium to transmit water, but the terms are not interchangeable. Hydraulic conductivity is a function of properties of both the media and the fluid. Hydraulic conductivity is often referred to as simply “permeability” (Parcher, 1999).

Geologic media with high hydraulic conductivities according to Parcher (1999) are highly permeable and can easily transmit non-viscous fluids, especially water and many types of petroleum products. Various geologic media tend to have hydraulic conductivity values within predictable ranges.

A geologic medium is described as “isotropic” if the measured permeability is the same in all directions (Parcher, 1999). Flow through an isotropic medium is parallel to the hydraulic gradient. This condition might exist in uniform, well-graded sand. The permeability of a geologic medium is often observed to vary depending upon the direction in which it is measured (Parcher, 1999). Known as “anisotropy”, this

condition can cause the flow of underground water and free product to occur in a direction that is not necessarily the same as the principle direction of the hydraulic gradient (Parcher, 1999).

Parcher (1999) recorded that the nature of geologic processes results in the non-uniform deposition and formation of rocks and sediments. Geologic media often are characterized by the degree of uniformity in grain size and properties such as permeability. Geologic media with uniform properties over a large area are referred to as being homogeneous. By contrast, geologic media that vary in grain size from place to place are called heterogeneous (Parcher, 1999). In nature, heterogeneity according to Parcher (1999) is much more common than homogeneity. Soil properties (*e.g.*, permeability, texture, composition) can be dramatically different over short distances. These changes strongly influence the direction and rate of the flow of underground water, free product, and vapor through the subsurface (Parcher, 1999). For example, free product may migrate farther and faster than it would in homogeneous media because hydrocarbons tend to move through the most permeable pathways and bypass extremely low permeability zones. Fine-grained fractured media are heterogeneous in the extreme. Migration distances in fractured media can be large because of the very small storage capacity of the fractures (Parcher, 1999).

2.6.3 Properties of Fluids

The physical properties of fluids that are most significant to free product and migration are density and viscosity (Parcher, 1999). Density determines the tendency of free product to accumulate above the water table or to sink to the bottom of the aquifer. Common petroleum hydrocarbons tend to accumulate above the water table because of their low density. Viscosity is a factor controlling the mobility of liquid hydrocarbons. Petroleum hydrocarbons with low viscosity are more mobile than those with high

viscosity. A third fluid property is interfacial tension, which is important because it determines how easily a geologic media will be wetted with a fluid and also controls (with pore size) the height of the capillary rise in a porous media. All three properties are inversely related to temperature (Parcher, 1999).

2.6.3.1 Density

According to Parcher (1999), density, which refers to the mass per unit volume of a substance, is often presented as specific gravity (the ratio of a substance's density to that of some standard substance, usually water). The densities of petroleum hydrocarbons typically found in UST are less than 1.0 g/ml and typically range from 0.75 g/ml to as high as 0.99 g/ml (Parcher, 1999). Density varies as a function of several parameters, most notably temperature, however, in most subsurface environments the temperature (and hence the density) remains relatively constant. The density of water is about 1.0 g/ml at normal groundwater temperatures (Eastcott *et al.*, 1988). Petroleum hydrocarbons that are less dense than water will float; these are also referred to as light non-aqueous phase liquids, or LNAPL.

2.6.3.2 Viscosity

Viscosity, which describes a fluid's resistance to flow, is caused by the internal friction developed between molecules within the fluid (Parcher, 1999). For most practical applications, viscosity can be considered to be a qualitative description in that the higher a fluid's viscosity, the more resistive it is to flow. Parcher (1999) reported that fluids with a low viscosity are often referred to as "thin", while higher viscosity fluids are described as "thick". Thinner fluids move more rapidly through the subsurface than thicker fluids. This means that a thinner petroleum product (*i.e.*, gasoline) is generally more easily recovered from the subsurface and leaves a lower residual saturation than a thicker petroleum product (*e.g.*, fuel oil). Parcher (1999) reported further that viscosity

is inversely proportional to temperature: As the temperature of the fluid increases, the viscosity decreases. The viscosity of free product in the subsurface environment typically changes over time, becoming thicker as the thinner, more volatile components evaporate and dissolve from the liquid hydrocarbon mass. Parcher (1999) gave three different terms that are commonly used to describe viscosity are *absolute*, *dynamic*, and *kinematic*. Absolute and dynamic are synonymous terms and are typically reported in units of centipoise (cP). Kinematic viscosity, which is equal to dynamic (or absolute) viscosity divided by density, is typically reported in units of centistokes (cSt) (Parcher, 1999).

2.6.3.3 Interfacial Tension

Parcher (1999) stated that the characteristics of free hydrocarbon movement are largely determined by interfacial tension that exists at the interface between immiscible fluids (*e.g.*, hydrocarbon, air, and water). Interfacial tension causes a liquid to rise in a capillary tube (or porous medium) and form a meniscus. In general, higher surface tensions result in higher capillary pressure, which may produce higher residual saturation (Mercer and Cohen, 1990).

The interfacial tension between a liquid and its own vapor is called surface tension. Interfacial tension is the primary factor controlling wettability. The greater the interfacial tension, the greater the stability of the interface between the two fluids. The interfacial tension for completely miscible liquids is 0 dyne cm⁻¹. Water (at 25°C) has a surface tension of 72 dyne cm⁻¹. Values of interfacial tension for petroleum hydrocarbon water systems fall between these two extremes (Mercer and Cohen, 1990). Interfacial tension decreases with increasing temperature and may be affected by pH, surface-active agents (surfactants), and gas in solution (Parcher, 1999).

2.6.4 Properties of Fluids and Geologic Media

The movement of free product in the subsurface according to Parcher (1999) also depends upon several factors which are functions of the properties of both the fluid and the geologic media. These factors are capillary pressure, relative permeability, wettability, saturation, and residual saturation. Although all of these factors are interrelated, the most important are capillary pressure and relative permeability (Parcher, 1999).

2.6.4.1 Capillary Pressure

Parcher (1999) explained that capillary pressure is the difference in pressure observed between two phases (*e.g.*, hydrocarbon liquid and water) that occupy the same pore space. As the result of interfacial tension, the boundary between two immiscible phases is a curved surface, or interface. Capillary pressure is the change in pressure across this curved interface (Parcher, 1999). In the vadose zone capillary pressure is negative (*i.e.*, less than atmospheric) and it is referred to as suction or tension. Capillary pressures are larger in fine-grained media (*e.g.*, silt, clay) than in coarse-grained media (*e.g.*, gravel).

The distribution and accumulation of free product in the subsurface according to Schwille (1967) is influenced by capillary pressure. When the petroleum product (the non-wetting fluid) begin to displace water (the wetting fluid) it enters the largest pores. The pressure required for this to occur is referred to as the “threshold entry pressure” (Schwille, 1967). According to Schwille (1967), free product can penetrate a water-saturated porous medium when the hydrocarbon pressure head exceeds the resistance of the capillary forces in a saturated zone.

2.6.4.2 Relative Permeability

The mobility of free products of hydrocarbons in the subsurface is strongly controlled by the relative permeability of the petroleum hydrocarbons and water, which in turn is dependent upon saturation. Relative permeability is the ratio of the effective permeability of a fluid at a specified saturation to the intrinsic permeability of the medium at 100 percent saturation (Mercer and Cohen, 1990). The relative permeability of a particular geologic media that is completely saturated with a particular fluid according to Parcher (1999) is equal to the intrinsic permeability. When more than one fluid (*i.e.*, air, water, petroleum hydrocarbon) exist in a porous medium, the fluids compete for pore space thereby reducing the relative permeability of the media and the mobility of the fluid. This reduction can be quantified by multiplying the intrinsic permeability of the geologic media by the relative permeability (Parcher, 1999).

2.6.4.3 Wettability

Wettability, which depends on interfacial tension, refers to the preferential spreading of one fluid over solid surfaces in a two-fluid system (Mercer and Cohen, 1990). Because of the dependence on interfacial tension, the size of the pore spaces in a geologic medium strongly influences which fluid is the wetting fluid and which fluid is the non-wetting fluid. The dominant adhesive force as indicated by Bear (1972) between the wetting fluid and media solid surfaces causes porous media to draw in the wetting fluid (typically water) and repel the non-wetting fluid (typically hydrocarbon or air).

The factors affecting wettability relations in immiscible fluid systems include mineralogy of the geologic media, the chemistry of the underground water and the petroleum hydrocarbon, the presence of organic matter or surfactants, and the saturation history of the media. Sometimes, such factors can lead to the preferential wetting of only a portion of the total surface area; this is called fractional wettability.

With the exception of soil containing a high percentage of organic matter (*e.g.*, coal, humus, and peat), most geologic media are strongly water-wet if not contaminated by NAPL (Mercer and Cohen, 1990).

This means that free product will be less mobile and generally leave a higher residual saturation in the soil, than will water.

2.6.4.4 Saturation

The level of saturation possible in a subsurface media has several implications for evaluating the level of hydrocarbons in underground water. First, it controls the mobility of fluids; second, it defines the volumetric distribution of petroleum hydrocarbons; and third, it is a function of other properties such as capillary pressure and relative permeability as indicated by Newell *et al.* (1995). The mobility of a particular phase is reduced with decreasing saturation until flow ceases to occur. Saturation of a porous medium may be defined as the relative fraction of total pore space containing a particular fluid (Newell *et al.*, 1995).

The mobility of a liquid through a porous medium is a function of the saturation of the porous medium with respect to that liquid. In order for it to flow through a porous medium, a liquid must be continuous through the area where flow occurs (Parcher, 1999).

2.6.4.5 Residual Saturation

Residual saturation refers to the saturation level at which a continuous mass of petroleum hydrocarbons (NAPL) becomes discontinuous and immobilized by capillary forces (Newell *et al.*, 1995). Following a release of petroleum hydrocarbons into the subsurface, the hydrocarbon mass seeps downward into the unsaturated zone. If the volume of the release is enough to sufficiently saturate the soil, the leading edge of the

hydrocarbon mass continues to move deeper into the subsurface. Behind and above the leading edge, a significant portion of the hydrocarbon mass is retained in pore spaces by capillary forces.

The amount of hydrocarbon that is retained against the force of gravity is referred to as the residual saturation. The corresponding term for water is irreducible water saturation.

Generally, the finer-grained the soil, the higher the residual saturation. Fluids that are more dense for a given viscosity drain to a greater degree under the influence of gravity than do less dense fluids. Fluids that have high interfacial tension also tend to exhibit higher capillary pressure, which may result in higher residual saturation (Parcher, 1999).

Because residual hydrocarbons are both tightly bound and discontinuous in pore spaces, they are essentially immobile. However, the residual phase often represents a potential long-term source for continued underground water contamination. Although some portion of the residual mass will be slowly diminished (*i.e.*, will naturally attenuate) over time as the result of dissolution, volatilization, and biodegradation, more aggressive remedial action may be required to mitigate this source within a reasonable amount of time (Mercer and Cohen, 1990).

2.7 Monitoring Underground water Contamination by Hydrocarbons

The progress of underground water contamination can be monitored through physicochemical parameters such as pH, temperature, salinity, conductivity, total dissolved solids (TDS) and total petroleum hydrocarbons (TPH) as well as the location of fuel storage tanks to the underground water sources.

2.7.1 pH of Underground water

The standard permissible limits of pH in underground water are 6.5 – 8.5 (USEPA, 1990). pH is defined as the negative log of the hydrogen ion concentration. The concentration is normally expressed in moles per liter. The liter component is nearly always the universal solvent, water. When most hydrocarbons are added to water, they do not mix; hence they are immiscible. No hydrogen ions are formed, and the pH of the original water remains unchanged. However, some types of hydrocarbons do have a hydrogen ion component when mixed with water. Thus, the more available one or more hydrogen ions are in the hydrocarbon being considered, the lower the pH (Ayotamuno and Kogbara, 2007).

2.7.2 Total Petroleum Hydrocarbons (TPH) of Underground water

Total Petroleum Hydrocarbons (TPH) is a term used to describe a broad family of several hundred chemical compounds that originally come from crude oil. In this sense, TPH is really a mixture of chemicals which are called hydrocarbons because almost all of them are made entirely from hydrogen and carbon atoms. Hence, the cumulative concentrations of petroleum hydrocarbons are commonly referred to as total petroleum hydrocarbons (Parcher, 1999). Crude oils can vary in how much of each chemical they contain, and so can the petroleum products that are made from crude oils. Most products that contain TPH will burn. Some are clear or light-colored liquids that evaporate easily, and others are thick, dark liquids or semi-solids that do not evaporate. Many of these products have characteristic gasoline, kerosene, or oily odors. Because modern society uses so many petroleum-based products (for example, gasoline, kerosene, fuel oil, mineral oil, and asphalt), contamination of the environment by them is potentially widespread. Contamination caused by petroleum products will contain a variety of these hydrocarbons. Because there are so many, it is not usually practical to

measure each one individually. However, it is useful to measure the total amount of all hydrocarbons found together in a particular sample of soil, water, or air. The amount of TPH found in a sample is useful as a general indicator of petroleum contamination at that site (Parcher, 1999).

Many different analytical techniques including gravimetric, immunoassay, and gas chromatography (GC) have been used to measure TPH in soil and water. None of the techniques measure the entire range of petroleum hydrocarbons. The subsets of hydrocarbons detected by the techniques vary depending on the extraction and analytical methods used. Total petroleum hydrocarbons (TPH) in groundwater samples are commonly extracted and analyzed for comparison to regulatory standards and for forensic evaluation of the source of spilled petroleum (Parcher, 1999). The standard measurements of TPH in underground water do not only include dissolved petroleum hydrocarbons, but commonly also include contributions from: (1) hydrocarbons sorbed on particulate matter; (2) droplets or micellar forms of liquid hydrocarbon contamination; (3) biogenic hydrocarbons; (4) contamination by field or laboratory equipment; and (5) dissolved polar organics (non-hydrocarbons), which may be naturally occurring or derived from spilled petroleum products. These factors complicate the regulatory and forensic interpretation of standard TPH data for underground water samples (Parcher, 1999). The maximum permissible value of TPH in underground water is 5.0 mg/l (USEPA, 1990).

2.7.3 Total Dissolved Solids (TDS) of Underground water

TDS indicates the salinity behavior of underground water. TDS is the term used to describe the inorganic salts and small amount of organic matter present in solution of water. Although not a direct evidence of biodegradation, TDS is a geochemical

parameter that closely links groundwater electrical properties to hydrocarbon degradation (Parcher, 1999).

TDS of natural waters can be measured by standard gravimetric techniques or by TDS/Conductivity meters. The specific conductance (electrical conductivity normalized to 25°C) of underground water is directly related to TDS based on the assumption that the TDS in the water consists mainly of ionic constituents that conduct electricity (Hem, 1985).

In underground water contaminated with hydrocarbons, it is not clear if the TDS calculated from specific conductance measurements is entirely due to ionic species. There is always a possibility that, a groundwater contaminated by dissolved hydrocarbons, there may be a reduction of specific conductance due to higher resistivity of hydrocarbon components. Also, it is possible that there could be an enhancement of specific conductance of underwater from polar ionic compounds (e.g., organic acids and bio-surfactants) produced during degradation (Parcher, 1999).

According to Zaporozec and Miller (2002), there is no evidence of adverse health effects at TDS levels over 1,000 mg/l, although at about 1,200 mg/l taste problems are likely to arise, and at levels over 1,500 mg/l, gastrointestinal irritation may occur.

2.7.4 Electrical Conductivity and Salinity of Underground water

Solids can be found in nature in a dissolved form. Salts that dissolve in water break into positively and negatively charged ions. Conductivity is the ability of water to conduct an electrical current, and the dissolved ions are the conductors. Hence, Electrical Conductivity (EC) can be described as a measure of the ability of water to pass an electric current which is affected by the presence of inorganic dissolved solids. The

major positively charged ions are sodium, (Na^+) calcium (Ca^{2+}), potassium (K^+) and magnesium (Mg^{2+}). The major negatively charged ions are chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-). Nitrates (NO_3^{2-}) and phosphates (PO_4^{3-}) are minor contributors to conductivity, although they are very important biologically (CWT, 2004).

Organic compounds like grease, alcohol and phenol have low conductivity in water. Conductivity is affected by temperature and salinity. As the temperature of underground water increases, its conductivity increases as well.

Salinity is a measure of the amount of salts in the water. Because dissolved ions increase salinity as well as conductivity, the two measures are related. The salts in sea water are primarily sodium chloride (NaCl). However, other saline waters, owe their high salinity to a combination of dissolved ions including sodium, chloride, carbonate and sulfate (CWT, 2004).

Increasing salinity increases conductivity. Conductivity and Salinity almost go together as well as TDS. A higher TDS means that there are more cations and anions in the water. With more ions in the water, the water become saline and increases the electrical conductivity (Hayashi, 2004). The likely reason for a low salinity in a study area can be attributed to the effective recharge from both precipitation and surface /river drainages (Ayotamuno and Kogbara, 2007).

2.7.5 Temperature of Underground water

Norris and Spieker (1996) reported that the temperature of underground water is generally equal to the (ambient) mean air temperature above the land surface. It usually stays within a narrow range year-round. Groundwater temperatures in the shallow

subsurface are dominantly affected by the solar radiation (Lee *et al.*, 2000). Conductivity is affected by temperature. Electrical Conductivity (EC) is strongly dependent on temperature (Hayashi, 2004). As the temperature of underground water increases, its conductivity increases as well. Groundwater textbooks frequently cite '2% increase of EC per 1 °C increase of temperature' (Matthess, 1982; Hem, 1985).

2.7.6 Distance from Fuel Storage Tanks to Underground water Sources

Fuel storage tanks must be far enough away from underground water sources. Leaks from any size of tank can enter the underground water and contaminate existing wells (Kamrin, 1992). Leaks from aboveground storage tanks can also enter the soil and contaminate underground water. Regulations for siting aboveground storage tanks have been concerned more with preventing explosion and fires than preventing underground water pollution.

Aboveground fuel tanks should be located at least 40 feet from existing buildings. Underground storage tanks must be located downslope and more than 100 feet from underground water sources. The distance required may be more than this in some cases, depending on the type of fuel, the design and material of the tank, and the amount of fuel being stored (<http://www.ncpma.org>).

2.8. Effects of Underground water Contamination by Hydrocarbons

Access to safe water remains an urgent human need in many countries for which Ghana is no exception. Major part of the problem is underground water contamination which is becoming more alarming in recent years. Kamrin (1992) made an assertion that underground water contamination has many damaging effects as it can harm human health, reduce economic productivity, and lead to the loss of amenities.

Petroleum fuels contain a number of potentially toxic compounds, including common solvents such as benzene, toluene and xylene, and additives such as ethylene dibromide (EDB) and carbon-based lead compounds. Kamrin (1992) reported that EDB is a carcinogen (cancer-causing) in laboratory animals, and benzene is considered a human carcinogen (USEPA, 1998: (<http://extension.missouri.edu/explore/envqual/wq0654.htm>)). Petroleum hydrocarbons (PHC) are used in nearly every facet of human life. They provide energy to heat our homes and places of work, fuel our transportation systems and power manufacturing processes and tools, as well as providing a source for the numerous synthetic materials we take for granted in our lives. When they are used as intended, PHC provide great benefits to society. However, when released to the soil environment (e.g. groundwater) as raw feed stocks or refined fuels or lubricants, problems can result. These problems include fire and explosion hazard, human and environmental toxicity, movement through soil to air or water, odour and impairment of soil processes such as water retention and nutrient cycling (USEPA, 1990).

According to the USEPA (1990), the health of hundreds of millions of people is threatened by contaminated underground water. The USEPA (1990) reported on underground water contamination that emphasizes that the contamination of groundwater may lead to several inconveniences.

Tremendous human suffering is caused by diseases that are mostly conquered when there is the availability of safe water supply. The problem is compounded in some areas by growing scarcity of portable water, which makes it difficult to meet increasing demand except at escalating cost (USEPA, 1990).

The BTEX compounds (Benzene, Toluene, Ethylene and Xylenes) in petrol are recognized by The World Health Organization as being toxic and in some cases

potentially carcinogenic to humans. Benzene, a significant component of petrol, is linked to leukaemia. These compounds are also potentially carcinogenic and deadly to some animal and aquatic life (Kamrin, 1992).

Underground water contamination can be harder to contain. It can extend far beyond the source site, lying as a 'plume' of petrochemicals on top of underground water on the water table. This may be quite close to the surface, rising further in seasons of heavy rainfall. A residual contaminated plume can sit under flat land or be carried to bore water, streams, lakes and the sea, threatening human and environmental health (Kamrin, 1992).

The detection frequency of MTBE is relatively highest in monitoring wells located in urban areas and in public supply wells. The detection frequency of any gasoline hydrocarbon also is dependent on study type and generally is less than the detection frequency of MTBE. The probability of detecting MTBE in underground water is strongly associated with population density, use of MTBE in gasoline, and recharge (USEPA, 1997). Underground water in areas with high population density, in areas where MTBE is used as a gasoline oxygenates, and in areas with high recharge rates has a greater probability of MTBE occurrence. The probability of detecting MTBE in ground water is weakly associated with the density of leaking underground storage tanks, soil permeability, and aquifer consolidation, and only concentrations of MTBE $>0.5 \mu\text{g/l}$ is associated with dissolved oxygen (USEPA, 1997).

The fact that MTBE is been detected in the underground water with increasing frequency is not surprising, given its suite of chemical properties according to USEPA (1998). It is highly hydrophilic and soluble, does not readily sorb to soil particles, and migrates faster and over greater ranges than do other gasoline constituents.

Additionally, it is quite resistant to biodegradation (USEPA, 1998). Thus, a leak from a UST containing MTBE-enhanced gasoline can be potentially catastrophic to local water supplies, and can be costly and difficult to remediate. The health effects of MTBE are not well understood. When inhaled in high concentrations, it causes cancer in some research animals. There is little data on its effects when humans ingest the chemical. Benzene is classified as a human carcinogen by the International Agency for Research on Cancer and as a hazardous waste and a priority pollutant by the USEPA (1997). Many other petroleum hydrocarbons, including toluene, xylene and ethylene dichloride, are also classified as either priority pollutants or hazardous substances. In addition, some compounds can be in soluble phase contained within the underground water (USEPA, 1990). The leakage represents an increasing danger to underground water resources and public health. If the chemical concentrations are high enough, the people are susceptible to various health risks.

2.9 Safeguarding our Underground water Supply

Underground water is an essential resource that moves so slowly hence, it is so difficult and expensive to clean up a contaminated aquifer (if it can be done at all). However, many underground water aquifers are vulnerable to contamination because contaminants can move rapidly through the ground and throughout the aquifer. It is then preferable by far to prevent contamination from happening in the first place. For instance, in the petrochemical industry, leaking underground storage tanks (LUST) can be replaced by tanks that will not corrode. Monitoring wells need to be established in all fuel filling outlets to help control possible groundwater contamination. A well-managed UST program that emphasizes leak detection can reduce the overall cost of LUST damage. This is because the cost of addressing LUST may exceed its benefits. Rice *et al.* (1995) found out that LUST contamination tends to be shallow so it may not

affect deeper public drinking water wells. In addition, if the source of the leak is removed, passive bioremediation processes may naturally contain the spread of contamination.

CHAPTER THREE

METHODOLOGY

3.1 The study area

The study was conducted in the Kumasi Metropolitan Area (KMA), which is the capital town of the Ashanti Region of Ghana. Kumasi is a fast growing city in the southern part of Ghana. Like every developing city, there is high population growth rate with increasing automobile density to ensure easy movement of people. The increasing number of automobiles in the metropolis has contributed to the establishment of several fuel filling stations across the length and breadth of the city in recent years. Figure 3.1 is a map of Ghana showing the study area.

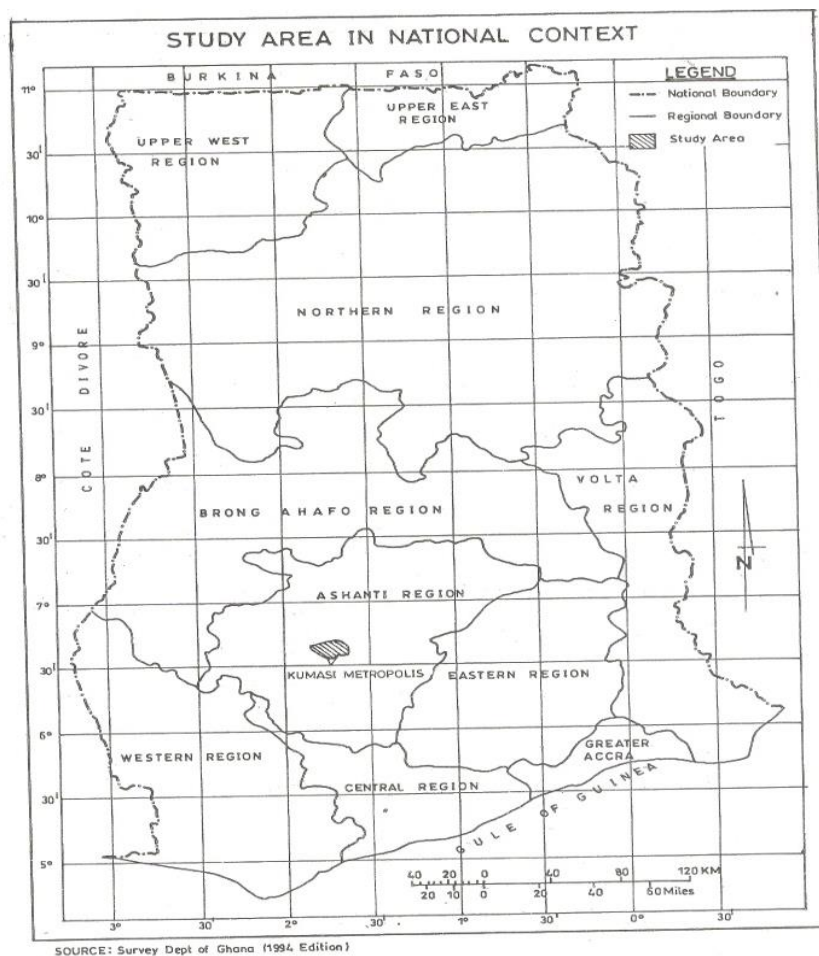


Figure 3.1: Map of Ghana Showing the Study Area (Kumasi Metropolis)

The study centered on eighteen (18) selected residential areas within the metropolis. These areas were selected based on the availability of underground water sources around fuel filling stations in the metropolis (Figure 3.2). The map indicates the locations of some of the fuel filling stations found in the metropolis. They include Shell, Total, Modex Oil, Pacific Oil, Sky Oil, Engen Oil and Unity Oil just to mention but a few that have flooded the study area.

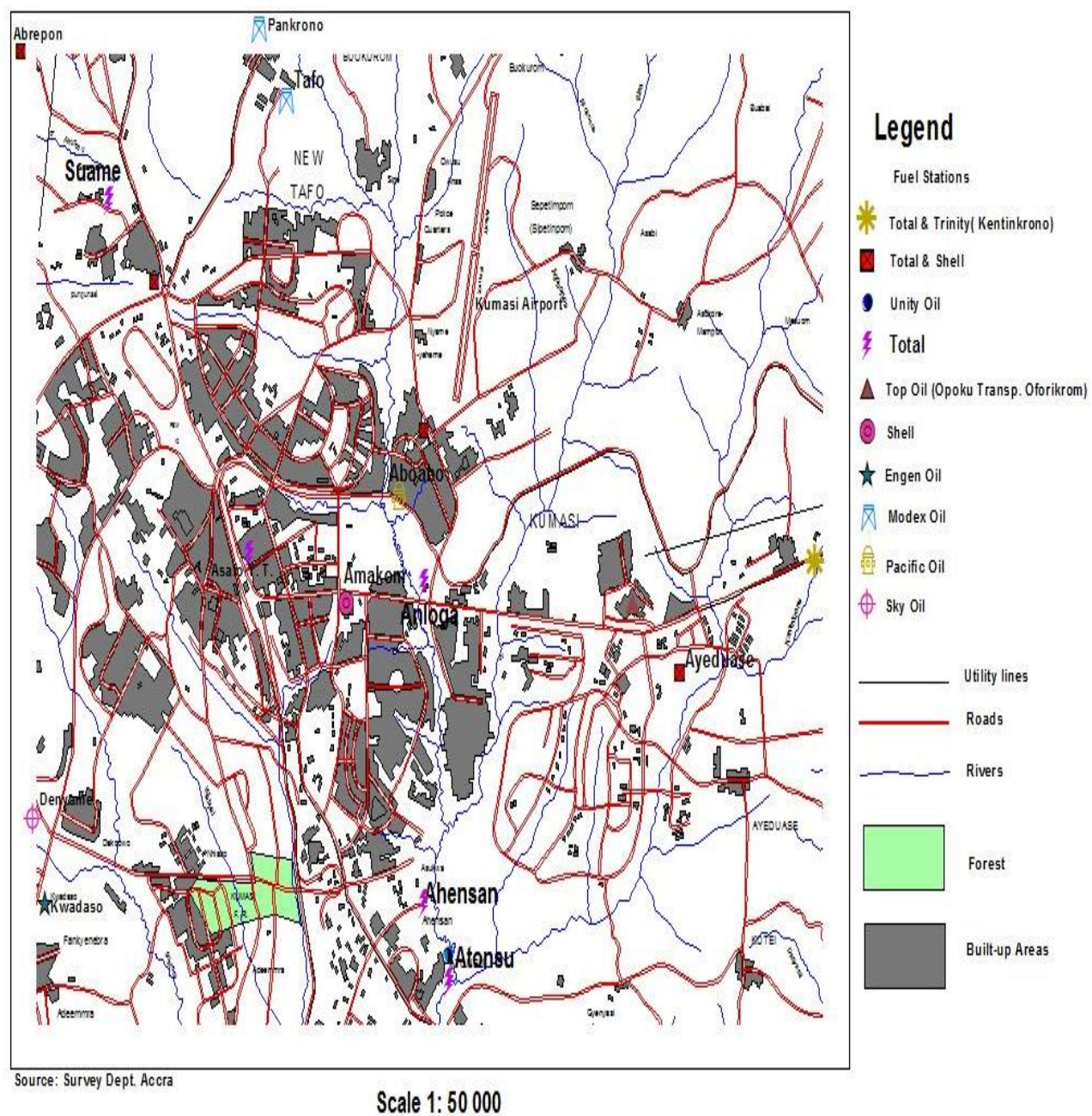


Figure 3.2: Map of Kumasi Metropolis showing locations of selected fuel stations

3.1.1 Size and location of KMA

Kumasi metropolis is relatively located at the central part of the Ashanti Region. It is located 300 kilometres northwest of Accra. According to Corubolo and Mattingly (1999), KMA is the second largest city of Ghana (Figure 3.1). Kumasi is within latitudes 6.38° and 6.45° north as well as longitudes 1.41° and 1.32° west. It lies within an elevation which ranges between 250 – 300 metres above sea level. The northern part of Kumasi shares a boundary with Kwabre District and to the southern part with the Bosomtwe-Kwanwoma district (Corubolo and Mattingly, 1999). Ejisu-Juaben and the Atwima districts are the western and eastern boundaries to Kumasi, respectively. The metropolitan area covers an area of 245 square kilometres. It also serves as a link between the northern and the southern sectors of Ghana.

3.1.2 Topography and Climate of KMA

Nsiah-Gyabaah (2000) indicated that the general topography of Kumasi metropolitan area is undulating with gentle slopes, commonly of 5° to 15° . Kumasi itself as described in the work of Nsiah-Gyabaah (2000) lies on top of a local watershed at approximately 282 m high, but altitudes in the peri-urban interface around Kumasi according to Holland *et al.* (1996) vary from 250 to 300 meters. There are relatively slightly hilly areas and few ridges in the Kumasi metropolis and the landform is an advanced dissection of a tertiary erosion surfaces (Holland *et al.*, 1996).

Kumasi lies within the moist semi-humid climatic zone of the country which has led to two rainfall seasons experienced annually with the annual mean rainfall of about 1345 mm (Holland *et al.*, 1996). The first rainy season is from mid-March to early July, and the second season begins from late August to October. The periods between November to early March are much drier throughout the year.

Holland *et al.* (1996) stipulated that the mean annual temperature is about 28°C with average monthly temperatures varying from 24°C to 33°C. The humidity in Kumasi varies from about 50 percent in the dry season to about 76 percent at the end of the main wet season. The average humidity is about 84.16 per cent at 0900 GMT and 60 per cent at 1500 GMT (Holland *et al.*, 1996). The Kumasi metropolis is affectionately called ‘the Garden City of Ghana’ due to the green forest zone. The vegetation has been characterized under the moist semi-deciduous forest zone of the country, affirming the fact that it occurs within wet semi-equatorial climatic region (Dickson and Benneh, 1988). But due to rapid increases in population and urbanization in the Kumasi metropolis, very little of the original forest remains.

3.1.3 Soil Resources in KMA

According to Holland *et al.* (1996), the soils in the Kumasi metropolis belong to the Forest Ochrosol great group, though formerly high in organic matter, intensive agriculture has led to many areas now being low in organic matter.

The soils in the Kumasi metropolis are developed on granite or phyllites. The soils on the granites are quite acidic but those on the phyllites are less acidic. The dominant textures are sandy loams with relatively high nitrogen and organic matter content. However the soils are often seriously deficient in other most important soil nutrients like potassium and magnesium due to land pollution.

3.1.4 Geohydrology and Drainage of KMA

The Kumasi Metropolis lies within the plateau of the South–West physical region which ranges from 250-300 metres above sea level, according to Dickson and Benneh, (1988). Dickson and Benneh, (1988) stated in their study that the topography of KMA is undulating. The Metropolis is located within the Pra basin. It is drained by a

relatively dense network of streams whose natural drainage runs generally from north to south, and some of which include the Daban, Subin, Aboabo, Wiwi and Santang streams, exhibiting some dendritic patterns and stemming out of the Sisa, Oda, Sokoban and the Owabi rivers, whose valleys are flat-bottomed (Dickson and Benneh, 1988). These converge into the Sisa, which flows into the Oda approximately 9 kilometers south of Kumasi.

Cornish *et al.* (1999) indicated that a small portion of the North-west to the Kumasi city, where a vehicle repair area is located, drains into the north-west catchment of the Owabi dam and thence into the Ofin River.

Kesse (1985) described the Birimian rocks in the KMA as generally strongly foliated and jointed, and where they outcrop or lie near the surface, considerable water may percolate through the joints, fractures or other partings. This implies that the granitic rocks associated with the Birimian rocks are not inherently permeable but have secondary permeability. Thus, the porosity developed as a result of joints, fractures and weathering of rocks contributed to the relatively average higher yields of underground water found in wells within the Kumasi granitic rocks (Kesse, 1985).

3.1.6 Water resources and utilization in KMA

To characterize the water resources in an area, it is necessary to define the sources of supply; the quality of water at the sources; the range of uses of the water; the types and scale of abstraction; and the contamination of the sources, sinks, and pathways. The main sources of water in the metropolis for households are piped supply from treated water sources; untreated piped water from underground water sources; shallow boreholes; wells; and ponds, springs, lakes, rivers and streams.

In Ghana, water is harnessed from rivers at dams and other structures to supply urban communities in the country. Most surface water sources have to be treated to meet health standards. Groundwater from shallow wells and boreholes is generally a good source of potable water in the Kumasi metropolis most especially in the new communities. Underground water sources such as hand-dug wells and boreholes appear to be less polluted in the KMA.

Ghana Water Company (GWC) which is under the Ministry of Works and Housing is responsible for the provision of quality water in the metropolis. GWC utilizes Owabi and the Barekese reservoirs to supply piped water to its customers in the KMA. The major water resource for this reservoir is the River Owabi which flows through Maase, Atafua and eventually into the Owabi reservoir for water supply by the GWC to Kumasi (McGregor *et al.*, 2000).

3.2 Data Collection Procedures

Secondary data were obtained from books, articles, and internet sources. Articles and journals were also obtained from the Kumasi Metropolitan Assembly. Primary data were collected through field investigation and questionnaire survey. Detailed procedures for the data collection are discussed in the sections below.

3.2.1 Preliminary Field Investigation

The field observation involved the researcher moving through the study area to assess the following:

- Fuel filling stations in the study area
- Fuel filling stations in residential areas within the study area
- Locations and types of fuel storage facilities
- Underground water sources close to fuel stations

3.2.2 Questionnaire Survey

Questionnaires (Appendix 7.1) were administered to fuel filling station managers in the study area at residential areas with underground water sources close by (Figure 3.2).

Information collected was on the following variables:

- How to establish fuel filling stations
- Fuel Storage Facilities
- Means of Monitoring Leakages of Storage Facilities
- Measures to Combat Fuel Storage Tank Leakages
- Monitoring of underground water for possible contamination
- Distance from fuel storage facility to underground water source

3.3 Sampling Techniques

The cluster and purposive sampling methods were used. Firstly, the study area was zoned into ten clusters, namely: Subin, Manhyia, Asokwa, Oforikrom, Suame, Old Tafo, Bantama, Kwadaso, Nhyiaeso and Asawase Sub-Metros. Secondly, purposive sampling was used to select eighteen (18) sampling points from the ten sub-metros for the survey (Appendix 7.2 for selected areas and their GPS coordinates).

3.4 Collection of Water Samples

Water samples were collected from underground water sources around eighteen (18) fuel stations in the study area. They were collected from already sunk private bore holes and wells. They were collected into 1500 ml plastic bottles. The collected samples were labelled at the point of collection and stored in ice chest prior to taking them to the laboratory. Duplicate samples were taken from the sampled water sources. Bottles were already rinsed with water to be sampled before sample collection. Sufficient air space was left to create space for water expansion.

3.5 Measurements of Parameters

In the course of the study physicochemical parameters were monitored, Total Petroleum Hydrocarbons (TPH) and the distance from underground water sources to fuel storage facilities were measured.

3.5.1 Measurement of Distance from Underground water Sources to Fuel Storage Tanks

The distances from fuel storage facilities to the sampled groundwater sources were obtained from fuel station managers and others were measured with the surveyor's tape during the administration of the questionnaires (Appendix 7.3 for details).

3.5.2 Measurement of Physicochemical Parameters

The pH, salinity, temperature, Total Dissolved Solids (TDS) and conductivity were determined on the spots where samples were taken with the Coleman pH meter, conductivity/TDS meter (APHA, 1985).

3.5.2 .1 Procedure for on the spot Measurement of Parameters

Distilled water was used to wash the probe and a 1000 ml measuring cylinder thoroughly. A water sample of about 500 ml was transferred into the measuring cylinder. Some amount of sampled water from each underground water source was used to rinse the probe and the measuring cylinder thoroughly each time before measuring the physicochemical parameters. The probe was then dipped into the water sample and the physicochemical parameters were measured and recorded (Appendix 7.5).

3.5.2.2 Measurement of TPH

Precise detection of hydrocarbons in water requires sophisticated laboratory analysis of water samples. The USEPA (1996) promotes two different types of analyses to measure

total petroleum hydrocarbons (TPH) in underground water samples. These are EPA method 418.1 and EPA method 8015. In EPA method 418.1, a solvent is added to water, extracting the hydrocarbons, which are then exposed to infrared light. The rate of light absorption provides a number value for the TPH found in the water sample, but does not determine the composite mixture of hydrocarbons, whereas EPA Method 8015 evaporates hydrocarbons into representative ions that can reveal varying concentrations of gasoline and diesel fuels (USEPA, 1996).

3.5.2. 3 Procedure for extraction of Organic Phase from water samples

1500 ml of sampled water was extracted three times with an organic solvent called methylene chloride using a separating funnel. An electronic shaker was employed to homogenize a mixture of 100 ml methylene chloride and the water sample which were well shaken for about 10 minutes. About 500 ml of the homogenized mixture containing methylene chloride was transferred into a 1000 ml separating funnel. The mixture in the separating funnel was again shaken for 5 minutes and it was then allowed to stand for about 10 minutes which allowed the separation of the organic phase from the aqueous phase. The organic phase (containing the hydrocarbons) was drained gently into a beaker. The extraction of the organic phase was repeated three times using the methylene chloride in each case. The organic phase (containing the hydrocarbons) obtained from the various extractions were altogether put into a beaker. The beaker containing the supposedly organic phase (containing the hydrocarbons) was then subjected to the soxhlet apparatus to get rid of traces of water. The organic extract (free from water) was transferred into a 2 ml vial carefully. In all, a total of eighteen (18) samples (including duplicates) were treated in the same manner as indicated above.

3.5.3 Measurement of Total Petroleum Hydrocarbons (TPH)

Many different analytical techniques including gravimetric, immunoassay, and gas chromatography (GC) can be used to measure TPH in soil and water. None of the techniques measure the entire range of petroleum hydrocarbons. This study however, utilized the gas chromatography (GC) in addition to Flame Ionization Detector (FID) for TPH analysis in the oil extracts. This method measured C₉ to C₃₆ range of hydrocarbons. The average response factor of alkanes was employed to convert the total peak area of a sample chromatograph into a TPH concentration. In this method, the extracted organic phase, organic compounds in chromatographic column in addition to those detected by the FID may form part of the calculated TPH. Table 3.1 indicates the conditions under which the GC analysis was done.

Table 3.1 Conditions for GC Analysis

Parameter	Condition
Initial Temperature	50°C, hold for 0.2 minutes
Final temperature	270°C, hold for 20 minutes
Injector Temperature	270°C
Detector Temperature	300 °C
Carrier gas flow rate	1.0 ml / minute
Program	50°C to 300°C at 5°C/ minute
Make-up gas	28 ml /minute

The Gas Chromatographic (GC) analysis procedure started with a solvent blank followed by calibration verification standard, method blank and finally the extracts (oil extracts) analysis. The calibration verification standard was an n-alkane mixture which contained C₉ to C₃₆ range of hydrocarbons. 500 mg/l working concentration was prepared for both the standard and oil extracts (Environmental Research Institute, 1999).

3.6 Statistical Analysis

The physicochemical parameters were statistically analyzed with anova in relation with the TPH concentrations of the underground water samples studied (Appendix 7.6). The relationship between distance of fuel storage tanks to the underground water and TPH values of the underground water was tested by conducting Spearman's correlation analysis. This type of correlation analysis was opted for because the data was not normally distributed.

CHAPTER FOUR

RESULTS

4.0 Introduction

The results obtained from the questionnaire survey, physicochemical parameters and the TPH concentrations of water samples taken from the eighteen sampling points are represented below, with their statistical analysis (Appendix 7.3 to 7.6).

4.1 Fuel Storage Facilities in Fuel Stations

The questionnaire survey revealed that 16 out of the fuel stations studied represented by 88.9% store their fuel in underground storage tanks while 2 of them represented by 11.1% use barrels as their storage facilities. With regards to the metal used to manufacture the fuel storage tanks, 14 stations represented by 77.8% used steel and 4 stations cumulatively; used iron and 11.1% of respondents use unknown metals for storage tanks. Three fuel stations (16.7%) had the age of the fuel storage tanks being exactly 5 years. Majority of the fuel stations (50%) had the exact age of their storage tanks to be 10 years. Two fuel stations (11.1%) had the age of their fuel storage tanks being more than 20 years (Appendix 7.4).

4.2 Respondents detection of leakages of fuel storage facilities

Majority of fuel stations (15) represented by 83.3% detect leakages in their fuel storage facilities. Three fuel stations do not detect leakages in their fuel storage tanks (Table 4.1).

From figure 4.1, all the 18 fuel stations (100%) detect leakages through the use of leakage monitoring device. Out of the 18 fuel stations, 16 of them (88.9%) detect

leakages with reduction in fuel quantity and 9 of them represented by 50% detect leakages through spills.

Table 4.1 Detection of leakages in storage facilities

Variable	Category	Frequency (n)	Percent (%)
Leakage detected sometimes from fuel tanks	Yes	15	83.3
	No	3	16.7

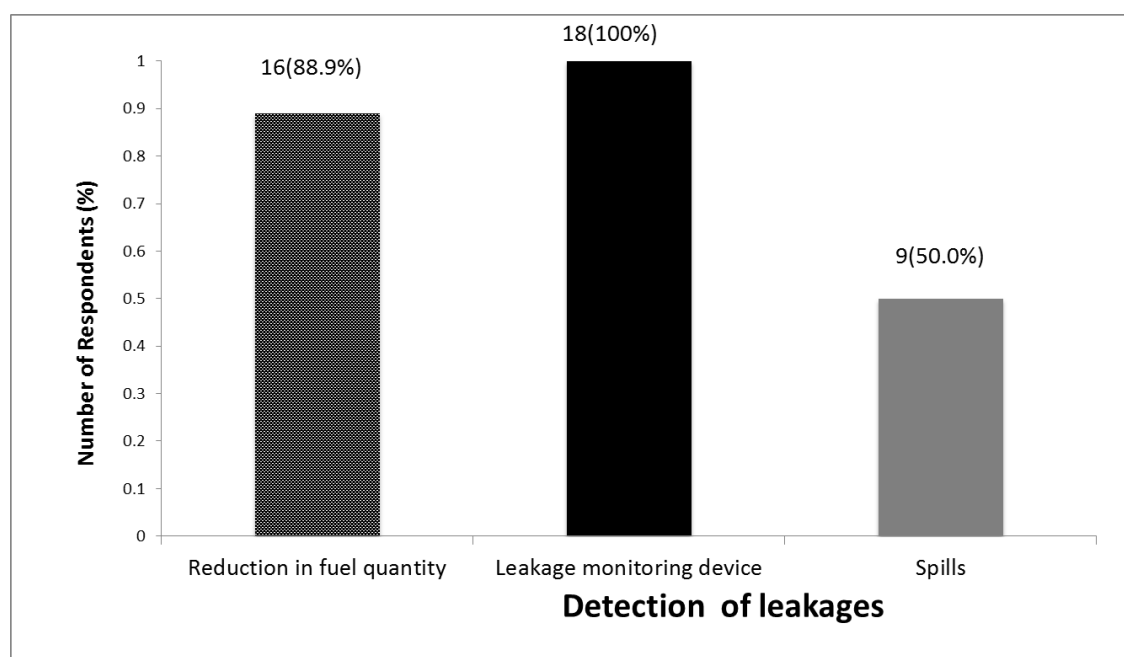


Figure 4.1: How fuel tank leakages are detected

4.3 Management of fuel storage tank leakages

All fuel stations studied (18) represented by 100% manage fuel storage tanks leakages by leak backup containment. 94.4% also ensure proper installation of fuel storage tanks to manage leakages. 38.9% use leak testing to manage fuel storage tanks leakages. 5.6% manage leaking fuel storage tanks by the removal of abandoned tanks. When leakages are detected, majority of the fuel stations (83.3%) do reinstallation of tanks to combat the leakages. 38.9% of the respondents repaint their fuel storage tanks when

they detect leakages. On the other hand, 33.3% of the respondents remove the leaking fuel storage tanks for repairs (Figure 4.2).

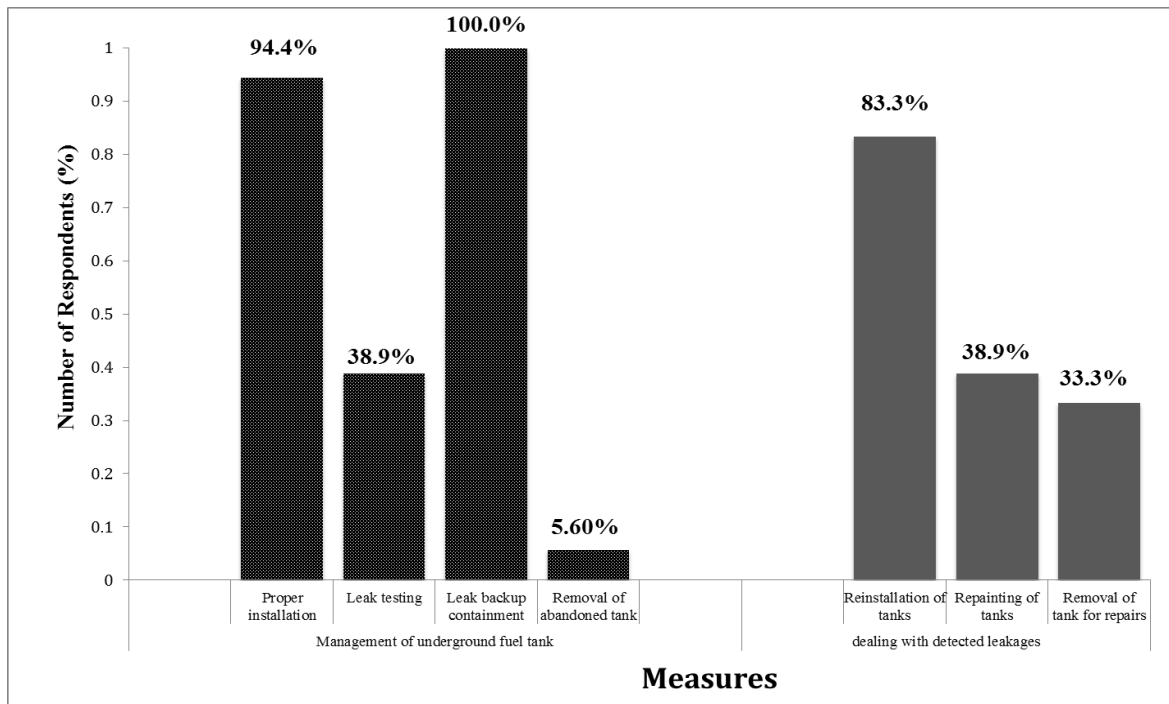


Figure 4.2 Measures to combat fuel storage tank leakages in fuel stations

Majority of the respondents (12) represented by 66.7% do not have monitoring wells/boreholes for easy detection of fuel leakages as against 33.3% (6) who had monitoring wells/boreholes (Table 4.2).

Table 4.2: Monitoring of groundwater

Variable	Category	Frequency (n)	Percentage (%)
Presence of groundwater monitoring boreholes or wells	Yes	6	33.3
	No	12	66.7

4.4 Distances of Fuel Storage Tanks to Underground water Sources

In this study, the lowest distance between fuel storage tank and underground water source recorded was 25 m at Ahinsan and the highest distance of 535 m at Aboabo.

Samples collected from these two locations recorded average TPH concentrations of 3.71 mg/l and 1.12 mg/l respectively. The location of the underground water at Ahinsan was below the permissible limit of more than 100 feet (30.48m) from underground water sources from fuel storage facilities (WHO, 2008). All the other locations (17 sample sites) were within the permissible limit of the distance between fuel storage tanks and underground water sources (Table 4.3). There was a negative correlation between the distance of the underground water sources sampled to the fuel storage tanks ($r = -0.26$).

Table 4.3: Distances of Fuel Storage Tanks to Underground water Sources in relation to TPH Concentrations

Sample	Distance from UST to underground water source	Average
Location	(m)	TPH (mg/l)
Oforikrom	185	9.48
Asafo Y.F.	205	6.16
Anloga Junction	85	3.82
Airport Roundabout	112	2.06
Suame Roundabout	100	1.41
Pankrono	235	1.61
Tafo Mile 4	358	2.43
Ahinsan	25	3.71
Atonsu	56	1.45
Abrepo	486	0.00
Denyame	403	2.15
Kentinkrono	200	0.00
New Suame	350	0.00
Maakro	105	0.35
Kotei	218	0.03
Ayeduase	45	0.86
Aboabo-Akorem	535	1.12
KwadasoNsuom	110	9.34

4.5 Mean Temperature of Water samples

Mean temperature values ranged from 28.69°C at Oforikrom to a high of 31.87°C at Kentinkrono (Appendix 7.5). With a permissible limit of 29.0°C for temperature (WHO, 2008), only samples from Oforikrom were within this limit, with the remaining seventeen (17) points exceeding (Figure 4.3).

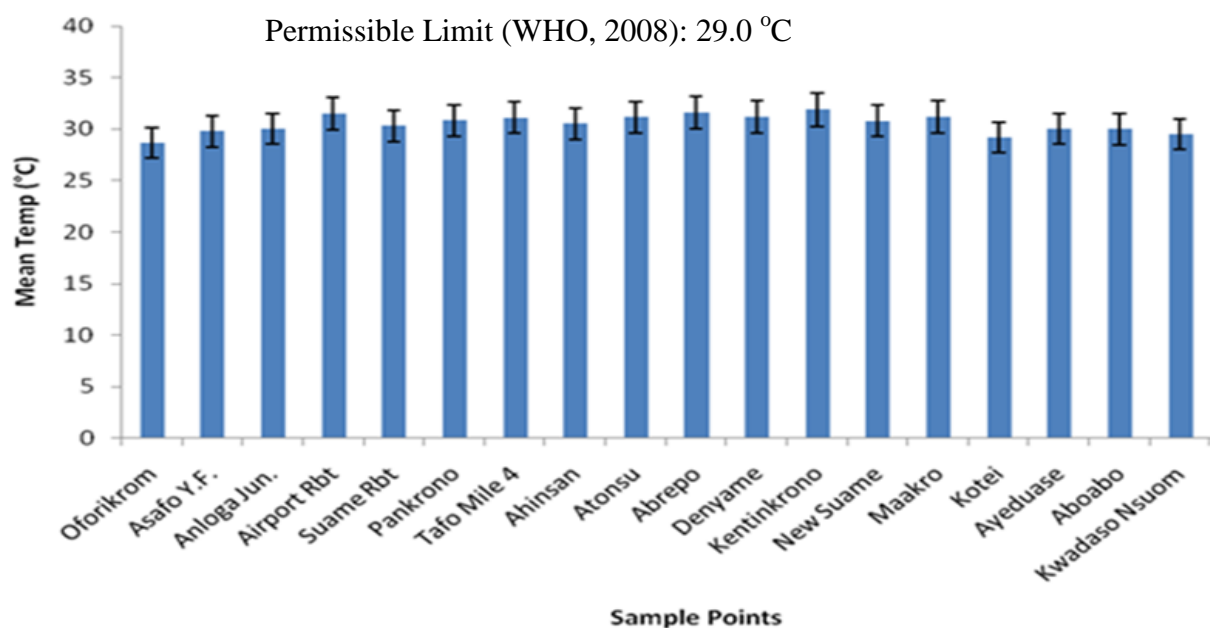


Figure 4.3: Mean Temperature values across all the sampling points

4.6 Mean pH levels in the water samples

The permissible range for pH in drinking water is 6.5-8.5 (USEPA, 1990). In this study, the lowest pH recorded was 4.84 at Denyame and the highest of 7.03 at Ahinsan (Figure 4.4). Correlation analysis of the pH values and TPH concentration showed that there was a positive relationship (r value = 0.43) between them (Appendix 7.6).

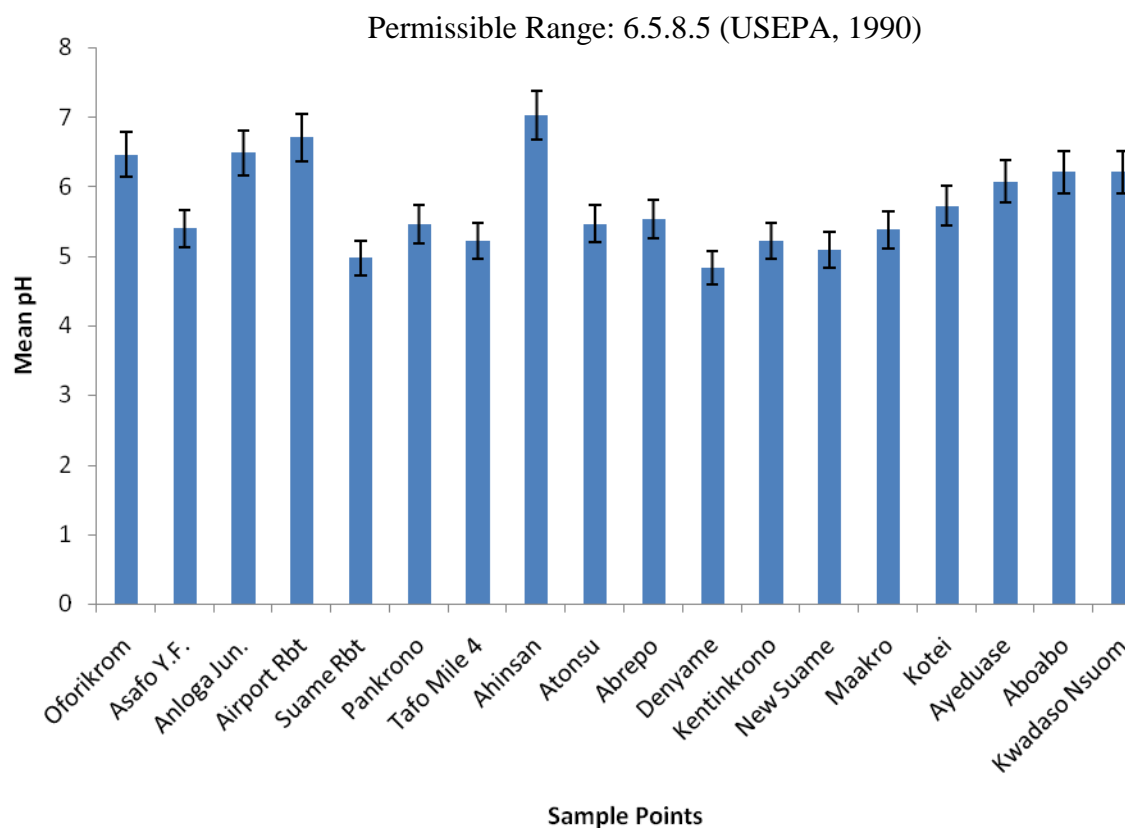


Figure 4.4: Mean pH readings of the water samples from the study area.

4.7 Mean Conductivity, Total Dissolved Solids and Salinity levels in the Water

Samples

The permissible limit of electrical conductivity according to WHO (2008) is 1000 $\mu\text{S}/\text{cm}$ for drinking water; however in this study the mean conductivity results ranged from a low of 24.5 $\mu\text{S}/\text{cm}$ at Ayeduase and a high of 519.5 $\mu\text{S}/\text{cm}$ at Oforikrom (Figure 4.5 and Appendix 7.5). Total Dissolved Solids (TDS) were again highest at Oforikrom (260 mg/l) and lowest at Ayeduase (10 mg/l). None of these samples recorded TDS values exceeding the permissible limit of 1000 mg/l (Figure 4.6). There was a positive correlation ($r\text{-value} = 0.99$) between the values of conductivity and TDS reported in this study (Appendix 7.6).

The permissible limit for Salinity in drinking water is 200 parts per million (WHO, 2008); however, in this study the highest mean value recorded was 0.25 ppm at Oforikrom and the lowest of 0.01ppm at Ayeduase (Figure 4.7 and Appendix 7.5). There was a positive correlation between the values of salinity recorded and conductivity (r-value = 0.99) as well as TDS (r-value = 0.99). These three parameters were also linked to the concentrations of the TPH in the water samples. Correlation figures (r-values) of 0.58, 0.58 and 0.59 were recorded for conductivity, TDS and salinity values against TPH concentrations respectively (Appendix 7.6).

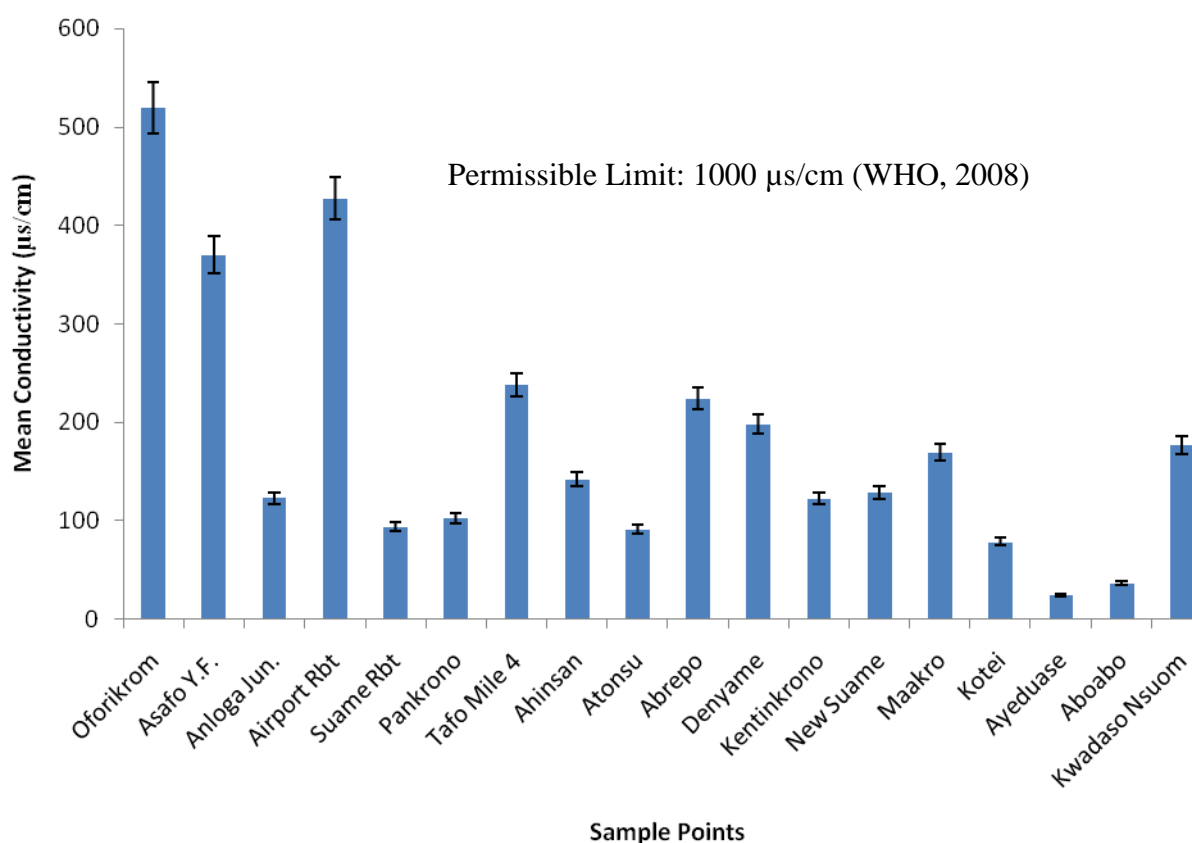


Figure 4.5: Mean Conductivity values of water from the study area

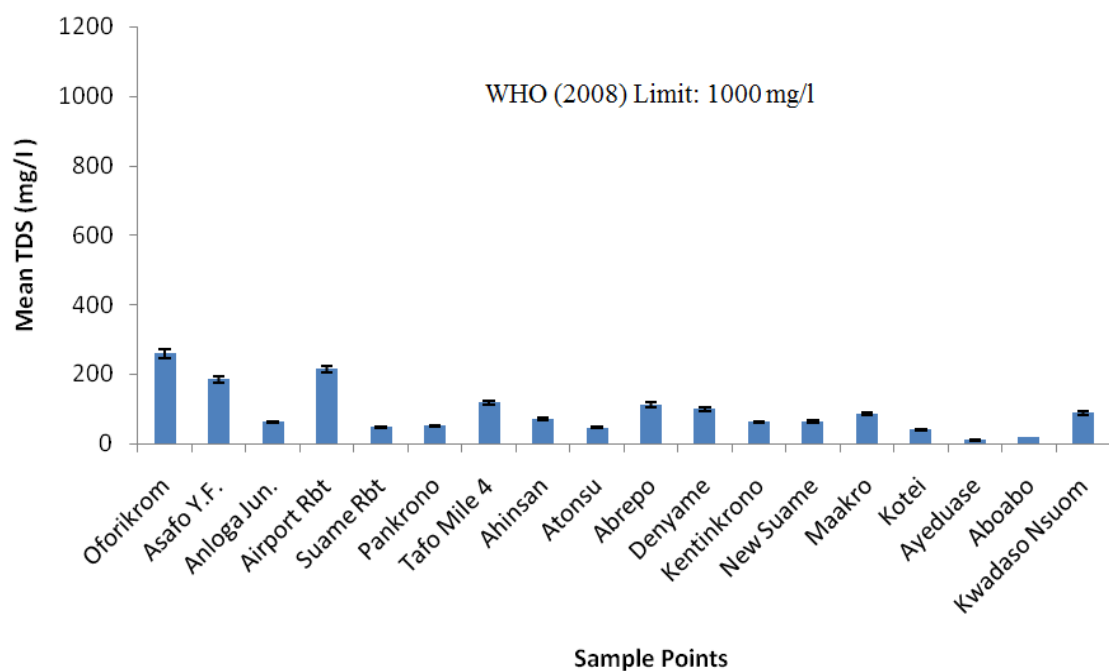


Figure 4.6: Mean Total Dissolved Solids of water for the sampling points in study area

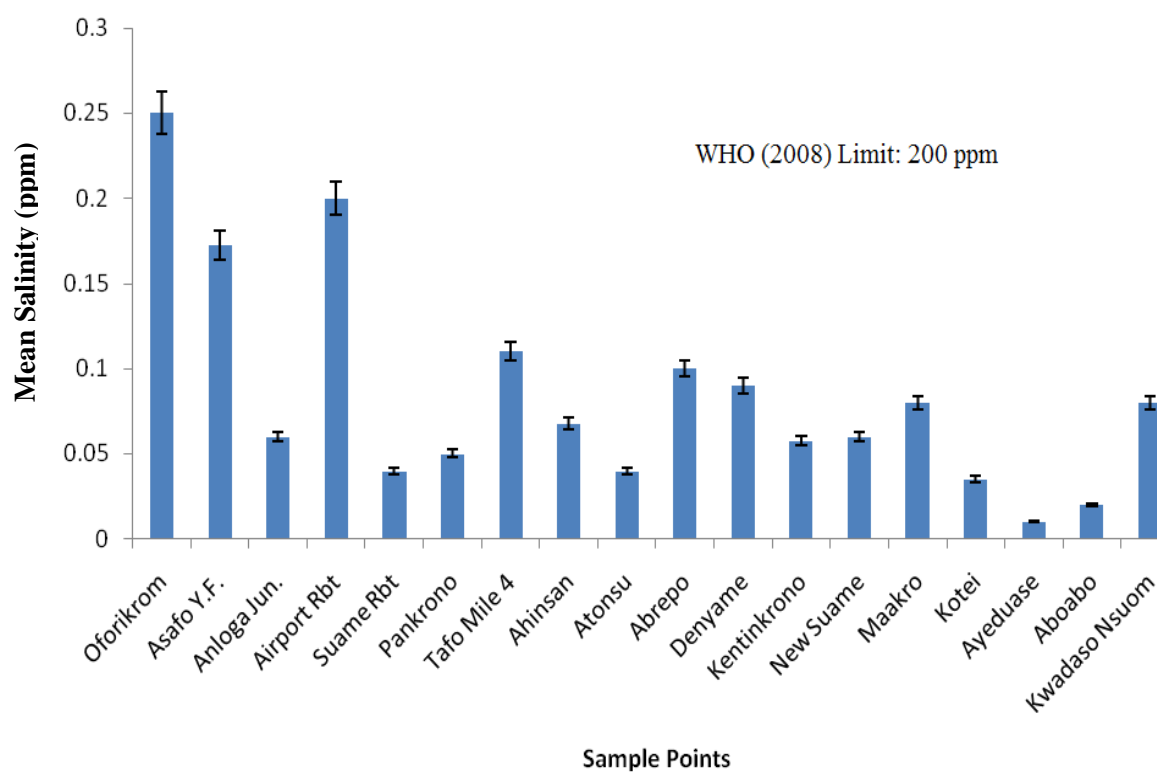


Figure 4.7: Mean Salinity values of water for the sampling points

4.8 Mean Total Petroleum Hydrocarbon concentration in the water samples

The permissible limit for Total Petroleum Hydrocarbon (TPH) concentration for drinking water is 5.0 mg/l (USEPA, 1990; WHO, 2008); however in this study, the highest mean concentration of TPH was 9.48 mg/l recorded at Oforikrom. Three sampling points (Abrepo, Kentinkrono and New Suame) recorded no contamination with TPH (Appendix 7.5). Three points (Oforikrom, Asafo YF and Kwadaso Nsuom) recorded TPH concentrations above the permissible limit (Figure 4.8 and Appendix 7.5).

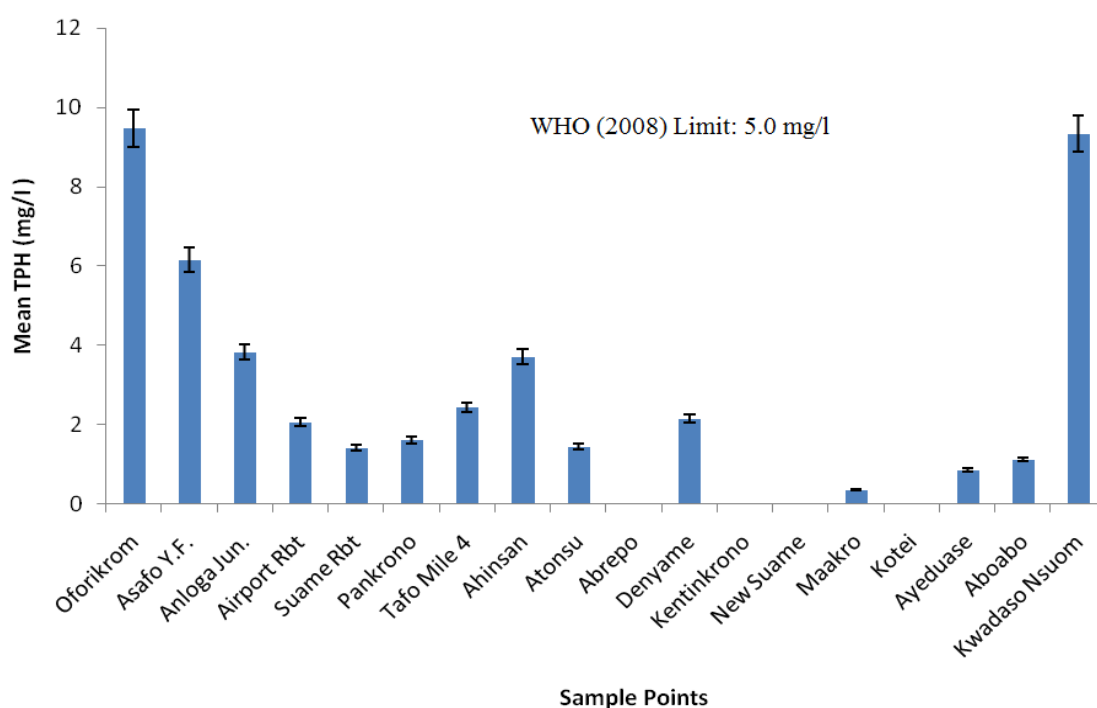


Figure 4.8: Mean TPH values of water samples for the sampling points

CHAPTER FIVE

DISCUSSION

5.1 Introduction

Underground water sources could be contaminated by hydrocarbons from leaking underground fuel storage tanks close to them. Underground water contamination can be harder to contain if it does occur. The contamination can extend far beyond the source site, lying as a ‘plume’ of petrochemicals on top of underground water on the water table. Early detection could be a plus for assessing the level of contamination of underground water sources such as boreholes or wells for effective control of the contamination. The progress of underground water contamination by hydrocarbons can be monitored through physicochemical parameters such as pH, temperature, salinity, conductivity, total dissolved solids (TDS) and total petroleum hydrocarbons (TPH) as well as the location of fuel storage tanks to underground water sources.

5.2 Management of fuel storage tank leakages by fuel filling stations in KMA

Majority of the fuel station respondents (50%) had the exact age of their storage tanks to be 10 years. Two of the fuel stations (11.1%) had the age of their fuel storage tanks being more than 20 years (Appendix 7.4). The age of fuel storage tanks can increase the rate at which leakages occur in fuel storage tanks as indicated by Sampat (2000). Sampat (2000) supported this finding by stating that underground storage tanks have a life of 15 to 25 years, and the probability that they will begin to leak increases with age. Small leaks of fuel go undetected into underground water (USEPA, 1997).

When leaks occur, fuel seeps through the soil to the underground water. The study reported that most of the fuel filling stations detected leakages in their fuel storage tanks (Table 4.1). This shows that the underground water samples studied which

recorded total petroleum hydrocarbons (TPH) could be as a result of leakages from these underground storage tanks (Table 4.3). Harris *et al.* (2008) suggested that leakage rate of just two drops per second can result in the loss of almost 500 gallons of fuel in one year and can contaminate nearly half a billion gallons of underground water to the point where it becomes unacceptable for drinking. In order to manage fuel leakages in storage tanks, fuel stations could do proper installation, leak testing, leak backup containment and removal of abandoned tank respectively to manage leakages in fuel storage tanks. Dealing with detected leakages of fuel storage tanks, reinstallation of tanks, as reported by majority of respondents (83.3%) must be the best practice to combat storage tank leakages and if possible remove the tanks for repairs as indicated by 33.3% of respondents (Figure 4.2).

5.3 Effects of Temperature and pH on Underground water Contamination by Hydrocarbons

Temperature is a factor of great importance for aquatic ecosystem, as it affects water organisms, as well as the physical and chemical characteristics of water. Temperature is one of the physical aspects of underground water quality. Water temperature plays an important role in determining the quality of life it could support. The temperature of underground water is generally equal to the mean air temperature above the land surface. This usually stays within a narrow range all year-round. A study conducted by Norris and Spieker (1996) is in support of the above assertion.

Oforikrom recorded the lowest average underground water temperature of 28.69°C and the highest temperature recorded at Kentinkrono was 31.87°C (Appendix 7.5). Underground water temperatures in the shallow subsurface are dominantly affected by the solar radiation (Lee *et al.*, 2000). Hence the results obtained in this study for mean temperature was not surprising as the results obtained (Appendix 7.5 and Figure 4.3)

were similar to the ambient temperature of the Kumasi Metropolis at the time of sampling.

The permissible limit for pH of drinking water is 6.5-8.5 (USEPA, 1990); this limit ensures that water is not too acidic or basic that can lead to adverse health effects. However, in this study, sixteen out of a total of eighteen sample sites of the Kumasi Metropolis recorded very low pH values, as low as 4.84 (Appendix 7.5 and Figure 4.4). This indicates that the majority (88.89%) of the water covered in this study were too acidic for human consumption. Most of the residents at the locations where underground water were sampled use the underground water for drinking and other domestic purposes. Low pH could result in the metallic taste frequently associated with some groundwater. High pH levels are undesirable since they may impart a bitter taste to the water. Ayotamuno and Kogbara (2007) in their study had similar assertion in relation to pH levels of groundwater and their taste during consumption.

It can be deduced that there are slight traces of dissolved acidic salts. This may be linked with the characteristics of the underground water at the sixteen sample locations (Figure 4.4) since movement of such salts from the surface of the soil to underground water might have occurred during seepage as underground water pollution can occur through seepage of pollutants and by migration of contaminants from the surface of the soil. This could be aided by the high infiltration and permeability of the soils (sandy loam soils) which implies that any contaminant on the surface has the potential to leach or move fast into the subsurface, which could lead to underground water contamination. Ayotamuno and Kogbara (2007) supported the idea that contaminants from the surface of the soil could leach into the subsurface to pollute underground water sources.

Acidic water (low pH) can leach metals from underground storage tanks, which can cause health problems. This low pH of the water as reported (Appendix 7.5) could however be attributed to the presence of TPH and other contaminants in the underground water samples.

There was a positive correlation (0.43) between the pH of the water samples and the TPH concentrations, confirming the relationship, indicating that as TPH concentrations increased in the water samples there was a correspondent increase in underground water pH (Appendix 7.5 and 7.6).

5.4 Effects of Electrical Conductivity and TDS on Underground water

Contamination by Hydrocarbons

The source of TDS in drinking water is attributed to natural sources, domestic wastewaters, municipal runoffs and industrial wastewaters. As suggested by Hem (1985), the electrical conductivity of underground water is related to the TDS of underground water. The electrical conductivity of underground water is directly related to TDS based on the assumption that the TDS in the water consists mainly of ionic constituents that conduct electricity. Although not a direct evidence of biodegradation, TDS is a geochemical parameter that closely links underground water electrical properties to hydrocarbon degradation as indicated by a study conducted by Hem (1985). However, in this study, a correlation figure of 0.58 was recorded for TDS (Appendix 7.6).

The higher readings of salinity and conductivity in this study (Appendix 7.5) could be attributed to the contamination of the water samples with hydrocarbons, which have the potential of increasing the ionic content of the groundwater. Conductivity and Salinity

almost go together as well as TDS. As indicated by Hayashi (2004), higher TDS means that there are more cations and anions in the underground water.

As evidenced in this study results (Appendix 7.5), Oforikrom recorded the highest electrical conductivity and TDS. On the other hand, Ayeduase recorded the lowest electrical conductivity and TDS. These two areas (Oforikrom and Ayeduase) at the same time recorded the highest mean salinity value of 0.25 ppm and lowest mean salinity value of 0.1 ppm respectively. Correlation analysis of the results obtained for TDS and conductivity gave a result of 0.99(Appendix 7.6) indicating a strong relationship between the two parameters. Again, salinity and conductivity gave a correlation figure of 0.99 (Appendix 7.6). This is an indication that, salinity levels in an underground water body directly influences the ability of that underground water to conduct electricity.

5.5 Effects of Total Petroleum Hydrocarbons on Underground water

Contamination

The amount of TPH according to USEPA (1998) and ASTDR (1999) found in a underground water sample is a useful indicator of petroleum contamination in that water. The permissible limit for total petroleum hydrocarbons is 5.0 mg/l (USEPA, 1990). However, in this study, only three of the underground water samples out of the eighteen areas studied had mean values exceeding this standard (Appendix 7.5). These areas were Oforikrom, Kwadaso Nsuom and Asafo YF. These areas recorded TPH concentrations of 9.48 mg/l, 9.34 mg/l and 6.16 mg/l respectively (Appendix 7.5). This could be as a result of waste dumps, spills from garages and leaking underground fuel storage tanks. Most underground storage tanks (UST) leak their contents into the environment. Giese *et al.* (1987) supported this assertion by reporting that the use of underground storage tanks (UST) to store petroleum products has been practiced for

long, with reports of leakages in these tanks. In line with this, Valentinetti (1989) also suggested that leakage from underground storage tanks (UST) is one of the major contaminants of underground water which is similar to the results of this study.

In addition, according to Valentinetti (1989), petroleum hydrocarbons enter underground water through several sources such as leakages from UST. This was evidenced in this study where most underground water sampling points had the influx of mechanic shops as well as fuel storage tanks close to them. These mechanic shops spill petroleum products onto the environment which might end up reaching the underground water to increase the TPH concentrations of the underground water as reported by Sun (1986). Similarly, the numerous fuel filling stations may have leakages in their underground storage tanks (UST). The petroleum products may leak into the environment and eventually into the underground water close by due to factors such as soil types and underground water flow. According to Sun (1986), upon the release of gasoline in the subsurface, each of the many organic components is transported by bulk movement and transfers them to the underground water, soil and vapour. Some of the components of the gasoline may also be degraded or transformed either biotically or abiotically resulting in spatial and temporal distribution of contaminants in the subsurface environment.

Also, at the time of sampling, there were several vehicle washing bays close to some of the underground water sources sampled. In the course of their activities, some amount of hydrocarbons might be released unto the environment from leaking engine tanks which might eventually find its way into the underground water source.

The TPH concentrations recorded in this study could also be attributed to the distance between the underground water sources and the fuel storage facilities in the study area.

The TPH concentration (9.34 mg/l) recorded for Kwadaso Nsuom for instance could be as a result of the location of the underground water source sampled. It was located downstream from the fuel storage tank which was installed up hill. There is therefore the possibility that the hydrocarbons from the fuel storage tank could easily leak into the underground water.

The amount of TPH found in a sample is useful as a general indicator of petroleum contamination at that site as reported by ASTDR (1999). This is because, low levels of TPH (fuel contaminants) in underground water cannot be detected by smell or taste, yet the seemingly pure water may be contaminated to the point of affecting human health as stipulated by USEPA (1998).

Although the TPH concentrations of fifteen (15) sampled underground water sources did not exceed the permissible limit of 5.0 mg/l (WHO, 2008); it is an area of concern because once hydrocarbons reach the underground water, they tend to accumulate due to the inability to evaporate, as it does on surface water. It is also not easily biodegraded by micro-organisms as it does in surface water. Moreover, underground water moves very slowly therefore leading to the accumulation and persistence of these hydrocarbon contaminants in the underground water as evidenced in a report by Kamrin (1992).

According to Sampat (2000), the hydrocarbon contamination of underground water could be attributed to the boom in automobile sales followed by the construction of thousands of gasoline stations across the country where bare steel tanks are installed underground to store gasoline. As evidenced in this study, the Kumasi metropolis is no exception as seen in the results (Appendix 7.4 and 7.5).

The contamination of underground water with respect to underground fuel tanks as indicated in this study could be linked to corrosion of steel tanks, faulty installation and operation, leaking storage tanks and spills as stated by Sampat (2000). In line with a study by Sampat (2000), the study recorded 6 fuel stations in the Kumasi Metropolis (Appendix 7.3) have their storage tanks with the age of 20 years and above. Sampat (2000) buttress his findings by stating that underground storage tanks have a life of 15 to 25 years, and the probability that they will begin to leak increases with age.

When leaks occur, fuel seeps through the soil to the underground water. Harris *et al.* (2008) suggested that leakage rate of just two drops per second can result in the loss of almost 500 gallons of fuel in one year and can contaminate nearly half a billion gallons of underground water to the point where odor and taste make it unacceptable for drinking.

5.6 Effects of Distances from Fuel Storage Tanks to Underground water Sources on Underground water Contamination

The distance between Underground Storage Tank (UST) to an underground water source plays a major role in determining the concentration levels of TPH in underground water bodies. The recommended distance between underground storage tanks (UST) to an underground water source must be at least 100 m according to Harris *et al.* (2008). The closer the UST are to the underground water sources, the higher the TPH concentration of that particular underground water (www.ces.ncsu.edu).

In this study, the lowest distance from the UST to the underground water sampling point was measured to be 25 m and the highest was 535 m at Ahinsan and Aboabo respectively (Appendix 7.3). These locations recorded TPH concentrations of 3.71 mg/l and 1.12 mg/l respectively (Appendix 7.5). These results indicate that, as the distance

between underground storage tanks (UST) to an underground water source increases, the TPH concentrations in those underground water decreases. The correlation analysis of the TPH concentrations in water samples from the underground water sources to the location of the UST gave an r-value of -0.26 (Appendix 7.6). This shows that the locations of UST had some influence on the contamination of underground water close to fuel filling stations within the Kumasi metropolis. This correlation value suggests that there are other factors that attributed to the TPH concentrations recorded in this study. This may include the soil type, rock type, and other geologic properties such as porosity and permeability of the geologic materials in those underground water sources as well as the properties of those petroleum hydrocarbons present in the underground water. This assertion is evidenced in a study conducted by Parcher (1999) where factors such as capillary pressure, wettability, saturation and viscosity of the fluid (petroleum hydrocarbon) in question as well as the geologic properties of that particular area being studied.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSION

Total petroleum hydrocarbon concentration in underground water affects different aspects of the water's quality. In this study, it can be concluded that fifteen (15) represented by 83.3% of the fuel stations sometimes detected leakages in their fuel storage tanks. Again, fifteen (15) underground water sources out of the eighteen (18) showed the presence of TPH. TPH concentrations were within the permissible limit of 5.0 mg/l (WHO, 2008) except three locations (Appendix 7.5). The underground water source that recorded the highest TPH concentration (9.48 mg/l) was at Oforikrom but the least were recorded at Kentinkrono, New Suame and Abrepo which recorded 0 mg/l each. The presence of the hydrocarbon contaminants in the groundwater affected the pH, conductivity, TDS temperature and salinity of the underground water samples analyzed. 94.4% of the fuel stations studied had their storage facilities located within the required distance. The distance between UST and underground water sources such as wells and boreholes in the Kumasi Metropolis had some effect on the quality of the water, thus the closer the UST and wells/boreholes the higher the concentration of TPH in the water.

6.2 RECOMMENDATIONS

The outcome of this study raises issues of public health and safety; therefore the following recommendations are made.

1. The distance between the wells/boreholes and the UST had an influence on the concentration of TPH, therefore it is suggested that wells should be cited far

away from UST so as to reduce the amount of TPH that may get into the underground water sources.

2. Since the age of the UST greatly influences leakages, it is suggested that a regulation that requires the replacement of older storage tanks (over ten years) is enforced.
3. During the installation of the UST, it is suggested that there is a comprehensive geological survey of the area so as to ascertain the impact of a possible leakage on underground water sources.
4. Further studies must be carried out to look at the properties of the soil in areas where boreholes/wells as well as areas where fuel storage tanks could be located.
5. The oil (hydrocarbons) properties must be looked at against the soil types since they affect the movement or leaching of hydrocarbons in the subsurface.
6. Underground water sources in the metropolis must be registered to enhance easy identification during studies of this nature in future.
7. An appropriate incentive package could be put in place for fuel filling station managers (respondents) to support studies of this nature.

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APPENDICES

APPENDIX 7.1 QUESTIONNAIRE SURVEY

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

COLLEGE OF SCIENCE

Kwame Nkrumah University of Science and Technology, Kumasi.

M.Sc. Environmental Science

QUESTIONNAIRE FOR ASSESSING UNDERGROUND WATER CONTAMINATION BY HYDROCARBONS FROM LEAKING UNDERGROUND FUEL STORAGE TANKS AT SELECTED FUEL STATIONS IN THE KUMASI METROPOLIS.

This questionnaire seeks to find out the possible contamination of groundwater by hydrocarbons due to closeness of underground water sources to fuel filling stations. Your contribution and co-operation to the success of this study would be highly appreciated. Give your responses to the questions below with all objectiveness, sincerity and honesty. Be rest assured that you and your responses shall be kept with the highest degree of confidentiality. Please, read the questions and statements carefully and respond to them accordingly. Tick in the box [☐] or write the item which best describes your responses.

General Information of Fuel Station

Name of fuel station.....

Location.....

Public [☐]

Private [☐]

Date:2012

How to establish fuel filling stations

1. Are there any laid down procedures for putting up fuel filling stations in Ghana?
 - a. Yes []
 - b. No []
2. If your answer to the above question (**Q 1**) is yes, who supervises compliance to those rules?
 - a. Metropolitan Assembly []
 - b. Environmental Protection Agency []
 - c. Energy Commission []
 - d. Others, specify.....
3. Do those authorities visit proposed site for fuel station before the establishment of proposed fuel filling stations?
 - a. Yes []
 - b. No []

Fuel Storage Facilities

4. Where do you store the fuel?
 - a. Underground tank []
 - b. Aboveground tank []
 - c. Barrels []
5. Which metal was used to manufacture your fuel storage tank?
 - a. Steel []
 - b. Iron []
 - c. Others, specify.....
6. What is the exact age of your fuel storage tank?
 - a. 5 years []

- b. 10 years []
- c. 20 years []
- d. Others, specify.....

Means of Monitoring Leakages of Storage Facilities

7. Do you sometimes detect leakages from the fuel storage tanks?

- a. Yes []
- b. No []

8. How do you detect the leakages of the fuel tanks?

- a. Reduction in fuel quantity []
- b. Leakage monitoring device []
- c. Spills []
- d. Others, specify.....

Measures to Combat Fuel Storage Tank Leakages

9. How do you manage underground fuel tanks?

- a. Proper installation []
- b. Leak testing []
- c. Leak backup containment []
- d. Removal of abandoned tank []
- e. Others, specify.....

10. If leakage is detected, what do you do?

- a. Reinstallation of tanks []
- b. Repainting of tanks []
- c. Removal of tank for repairs []
- d. Abandon tanks []
- e. Filling with inert material []

Monitoring of groundwater

11. Do you have groundwater monitoring well at your fuel station outlet?

a. Yes []

b. No []

12. How far is your storage tank from boreholes or wells?

a. 25m []

b. 45m []

c. 100m []

d. 200m []

e. Others, specify.....

APPENDIX 7.2 GPS COORDINATES OF SAMPLING POINTS

GPS COORDINATES FOR SAMPLING LOCATIONS FOR THE UNDERGROUND WATER SAMPLES

LOCATION	SERIAL NO.	NORTH COORDINATES	WEST COORDINATES
Oforikrom	1	06°41'18.5''	001°35'22.0''
	2	06°41'18.5''	001°35'22.0''
	3	06°41'18.6''	001°35'21.9''
	4	06°41'18.5''	001°35'21.9''
	5	06°41'18.5''	001°35'22.0''
Asafo Y.F.	1	06°40'59.2''	001°36'37.2''
	2	06°40'59.3''	001°36'37.2''
	3	06°40'59.2''	001°36'37.2''
	4	06°40'59.3''	001°36'37.2''
	5	06°40'59.3''	001°36'37.2''
Anloga Junction	1	06°41'21.6''	001°35'49.4''
	2	06°41'21.7''	001°35'49.3''
	3	06°41'21.8''	001°35'49.4''
	4	06°41'21.8''	001°35'49.4''
	5	06°41'21.8''	001°35'49.4''
Airport Roundabout	1	06°42'34.6''	001°35'59.2''
	2	06°42'34.6''	001°35'59.2''
	3	06°42'34.7''	001°35'59.3''
	4	06°42'34.8''	001°35'59.4''
	5	06°42'34.7''	001°35'59.4''
Suame Roundabout	1	06°42'31.9''	001°37'35.7''
	2	06°42'31.9''	001°37'35.7''
	3	06°42'31.9''	001°37'35.7''
	4	06°42'31.9''	001°37'35.7''
	5	06°42'31.9''	001°37'35.7''
Pankrono	1	06°44'39.9''	001°36'36.2''
	2	06°44'39.9''	001°36'36.3''
	3	06°44'40.1''	001°36'36.2''
	4	06°44'40.2''	001°36'36.2''
	5	06°44'40.0''	001°36'36.5''
Tafo Mile 4	1	06°44'24.7''	001°36'45.8''

	2	06°44'24.7''	001°36'45.9''
	3	06°44'24.7''	001°36'45.9''
	4	06°44'24.5''	001°36'46.0''
	5	06°44'24.6''	001°36'45.8''
Ahinsan Breweries	1	06°39'55.6''	001°36'13.4''
	2	06°39'55.5''	001°36'13.5''
	3	06°39'55.4''	001°36'13.5''
	4	06°39'55.5''	001°36'13.4''
	5	06°39'55.5''	001°36'13.4''
Atonsu	1	06°39'18.5''	001°35'24.5''
	2	06°39'18.5''	001°35'24.5''
	3	06°39'18.5''	001°35'24.5''
	4	06°39'18.6''	001°35'24.4''
	5	06°39'18.7''	001°35'24.4''
Abrepo Junction	1	06°42'37.8''	001°38'25.3''
	2	06°42'37.7''	001°38'25.3''
	3	06°42'37.7''	001°38'25.3''
	4	06°42'37.7''	001°38'25.3''
	5	06°42'37.8''	001°38'25.2''
Denyame	1	06°41'23.3''	001°38'19.7''
	2	06°41'23.4''	001°38'19.7''
	3	06°41'23.3''	001°38'19.7''
	4	06°41'23.4''	001°38'19.8''
	5	06°41'23.4''	001°38'19.7''
Kwadaso Nsuom	1	06°41'57.4''	001°39'15.1''
	2	06°41'57.5''	001°39'15.1''
	3	06°41'57.6''	001°39'15.1''
	4	06°41'57.5''	001°39'15.2''
	5	06°41'57.5''	001°39'15.2''
Kentinkrono	1	06°41'29.2''	001°33'05.2''
	2	06°41'29.2''	001°33'05.1''
	3	06°41'29.2''	001°33'05.1''
	4	06°41'29.1''	001°33'05.1''
	5	06°41'29.2''	001°33'05.1''

New Suame	1	06°42'57.6''	001°37'45.9''
	2	06°42'57.6''	001°37'46.0''
	3	06°42'57.7''	001°37'46.0''
	4	06°42'57.8''	001°37'46.0''
	5	06°42'57.8''	001°37'46.0''
Maakro	1	06°43'49.7''	001°37'57.5''
	2	06°43'49.8''	001°37'57.5''
	3	06°43'49.7''	001°37'57.6''
	4	06°43'49.7''	001°37'57.6''
	5	06°43'49.7''	001°37'57.6''
Kotei	1	06°39'49.8''	001°33'23.8''
	2	06°39'49.8''	001°33'23.7''
	3	06°39'49.9''	001°33'23.7''
	4	06°39'49.9''	001°33'23.7''
	5	06°39'49.9''	001°33'23.7''
Ayeduase	1	06°40'22.9''	001°33'31.6''
	2	06°40'23.0''	001°33'31.5''
	3	06°40'23.0''	001°33'31.5''
	4	06°40'23.1''	001°33'31.6''
	5	06°40'23.0''	001°33'31.6''
Aboabo-Akorem	1	06°42'00.8''	001°35'29.3''
	2	06°42'00.9''	001°35'29.3''
	3	06°42'00.9''	001°35'29.5''
	4	06°42'00.8''	001°35'29.4''
	5	06°42'00.9''	001°35'29.5''

**APPENDIX 7.3 DISTANCE OF FUEL STORAGE TANKS TO
UNDERGROUND WATER SOURCES**

SampleLocation	Distance from UST to Underground Water (m)
Oforikrom	185
Asafo Y.F.	205
Anloga Junction	85
Airport Roundabout	112
Suame Roundabout	100
Pankrono	235
Tafo Mile 4	358
Ahinsan	25
Atonsu	56
Abrepo	486
Denyame	403
Kentinkrono	200
New Suame	350
Maakro	105
Kotei	218
Ayeduase	45
Aboabo-Akorem	535
Kwadaso Nsuom	110

APPENDIX 7.4: QUESTIONNAIRE RESPONSES ON FUEL STORAGE FACILITIES IN FUEL STATIONS

Fuel stations	Where do you store the fuel		Metal used to manufacture fuel storage tank			Exact age of fuel storage tank			
	Underground tank	Barrels	Steel	Iron	Other unknown metal	5 years	10 years	20 years	>20 years
Ahinsan	1		1				1		
Atonsu	1		1				1		
Anloga junction	1			1					1
Suame Roundabout	1		1					1	
Maakro	1		1				1		
Kwadaso Nsuom	1		1				1		
Airport Roundabout	1		1					1	
Oforikrom	1		1				1		
Kentinkrono	1				1		1		
Asafo Y.F.	1		1						1
Pankrono	1		1				1		
New Suame	1		1				1		
Tafo Mile 4	1		1			1			
Denyame	1		1					1	
Abrepo	1		1				1		
Aboabo-Akorem	1		1					1	
Ayeduae		1			1	1			
Kotei		1		1		1			
Respondents (%)	16 (88.9%)	2 (11.1%)	14 (77.8%)	2 (11.1%)	2 (11.1%)	3 (16.7%)	9 (50.0%)	4 (22.2%)	2 (11.1%)

APPENDIX 7.5 MEAN RESULTS FOR ALL PARAMETERS

	Average	Average	Average	Average	Average	Average	
Location	Temperature (°C)	pH	Electrical Conductivity (µs/ cm)	TDS (mg/L)	Salinity (ppm)	TPH (mg/L)	Distance (m)
Oforikrom	28.69	6.46	519.50	260.00	0.25	9.48	185
Asafo Y.F.	29.77	5.40	370.25	185.00	0.17	6.12	205
Anloga Junction	30.03	6.48	123.00	61.50	0.06	3.82	85
Airport Roundabout	31.52	6.71	427.25	213.75	0.20	2.06	112
Suame Roundabout	30.31	4.97	94.25	47.50	0.04	1.41	100
Pankrono	30.84	5.46	102.50	51.50	0.05	1.61	235
Tafo Mile 4	31.13	5.22	237.75	118.75	0.11	2.43	358
Ahinsan	30.54	7.03	142.00	71.00	0.07	3.71	25
Atonsu	31.15	5.47	91.25	46.00	0.04	1.45	56
Abrepo	31.64	5.53	224.00	112.00	0.10	0.00	486
Denyame	31.16	4.84	198.25	99.25	0.09	2.15	403
Kentinkrono	31.87	5.22	122.75	61.50	0.06	0.00	200
New Suame	30.81	5.09	128.25	64.25	0.06	0.00	350
Maakro	31.21	5.38	169.75	85.00	0.08	0.35	105
Kotei	29.21	5.72	78.50	39.25	0.04	0.03	218
Ayeduase	30.03	6.07	24.50	10.00	0.01	0.86	45
Aboabo-Akorem	29.99	6.21	36.50	18.50	0.02	1.12	535
Kwadaso Nsuom	29.51	6.21	176.50	88.25	0.08	9.34	110
PERMISSIBLE LIMITS OF PARAMETERS	29.00	6.5-8.5	1000	1000	200	5.00	30.48

APPENDIX 7.6: STATISTICAL ANALYSIS OF RESULTS

ANOVA ANALYSIS OF TEMPERATURE

Table Analyzed	Temp		
One-way analysis of variance			
P value	< 0.0001		
P value summary	***		
Are means significantly different? (P < 0.05)	Yes		
Number of groups	18		
F	76.89		
R squared	0.9603		
ANOVA Table	SS	df	MS
Treatment (between columns)	59.40	17	3.494
Residual (within columns)	2.454	54	0.04544
Total	61.85	71	

ANOVA ANALYSIS OF pH

Table Analyzed	pH		
One-way analysis of variance			
P value	< 0.0001		
P value summary	***		
Are means significantly different? (P < 0.05)	Yes		
Number of groups	18		
F	1267		
R squared	0.9975		
ANOVA Table	SS	df	MS
Treatment (between columns)	28.05	17	1.650
Residual (within columns)	0.07033	54	0.001302
Total	28.12	71	

ANOVA ANALYSIS OF ELECTRICAL CONDUCTIVITY (E.C)

Table Analyzed	E.C		
One-way analysis of variance			
P value	< 0.0001		
P value summary	***		
Are means significantly different? (P < 0.05)	Yes		
Number of groups	18		
F	12110		
R squared	0.9997		
ANOVA Table	SS	df	MS
Treatment (between columns)	1227000	17	72160
Residual (within columns)	321.8	54	5.958
Total	1227000	71	

ANOVA ANALYSIS OF TOTAL DISSOLVED SOLIDS (TDS)

Table Analyzed	TDS		
One-way analysis of variance			
P value	< 0.0001		
P value summary	***		
Are means significantly different? (P < 0.05)	Yes		
Number of groups	18		
F	12240		
R squared	0.9997		
ANOVA Table	SS	df	MS
Treatment (between columns)	306500	17	18030
Residual (within columns)	79.50	54	1.472
Total	306500	71	

ANOVA ANALYSIS OF SALINITY

Table Analyzed	Salinity		
One-way analysis of variance			
P value	< 0.0001		
P value summary	***		
Are means significantly different? (P < 0.05)	Yes		
Number of groups	18		
F	2696		
R squared	0.9988		
ANOVA Table	SS	df	MS
Treatment (between columns)	0.2759	17	0.01623
Residual (within columns)	0.0003250	54	0.000006019
Total	0.2762	71	

ANOVA ANALYSIS OF TOTAL PETROLEUM HYDROCARBONS (TPH)

Table Analyzed	TPH		
One-way analysis of variance			
P value	< 0.0001		
P value summary	***		
Are means significantly different? (P < 0.05)	Yes		
Number of groups	18		
F	6.894		
R squared	0.8669		
ANOVA Table	SS	df	MS
Treatment (between columns)	298.8	17	17.57
Residual (within columns)	45.88	18	2.549
Total	344.6	35	