KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF ENVIRONMENTAL SCIENCE

PHYTOREMEDIATION OF HYDROCARBON CONTAMINATED SOIL - A CASE STUDY AT NEWMONT GHANA GOLD LIMITED – AHAFO KENYASI

BY

BONIFACE BAAH

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A Thesis Submitted to the Department of Environmental Science in partial fulfillment of the requirement for the award of the Master of Science Degree in Environmental Science

BONIFACE BAAH

DECEMBER, 2011

DECLARATION

I, **Boniface Baah**, hereby certify that this report is a true outcome of the research carried out at Newmont Ghana Gold Limited (NGGL), Ahafo Kenyasi on phytoremediation of hydrocarbon contaminated soil at the Volatilization Pad facility of the company to accelerate the breakdown of hydrocarbons. I hereby declare that, except for reference to other people's work which has been duly acknowledged, this research work consists of my own work produced from research undertaken under the supervision of Dr. Bernard Fei – Baffoe (Biological Science Department – K.N.U.S.T.) and that no part has been presented for any degree elsewhere. This report is submitted in partial fulfillment for the award of MSc. (Hons.) Environmental Science.

…… ……..

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PROJECT STUDENT

…… ……..

DR. BERNARD FEI-BAFFOE DATE

(PROJECT SUPERVISOR)

…… ……

DR. PHILIP.K. BAIDOO DATE

(HEAD OF DEPARTMENT)

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Firstly, I ascribe all thanks to God Almighty who provided the life, strength, energy, commitment and academic zeal needed to overcome the task of the project.

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Finally, I thank all men of Goodwill whose dynamic strength and passion saw the work completed. Such are men of honor.

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ACRONYMS

NGGL	Newmont Ghana Gold Limited
Vol. Pad	Volatilization Pad
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
DRO	Diesel-Range Organics
EPA	U.S. Environmental Protection Agency
GRO	Gasoline-Range Organics
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
MTBE	Methyl Tert Butyl Ether
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated biphenyl
TPH	Total Petroleum Hydrocarbons
VOC	Volatile Organic Compound
DOE	U.S. Department of Energy
AEHS	Association for Environmental Health and Science
HCS	Hydrocarbon Contaminated Soil

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ABSTRACT

Phytoremediation technology was employed to remediate hydrocarbon contaminated soil from Newmont Mining site using *Chromolaena odorata* (Siam Weed).

Physicochemical, Microbiological, Total Petroleum Hydrocarbon (TPH) and Oil and Grease were used as parameters in assessing the efficiency and optimization of the phytoremediation process of the hydrocarbon contaminated soil. Parameters such as pH, moisture content and temperature of the contaminated soil and the various media used for augmentation (Topsoil, Compost and Fertilizer) were determined using calibrated meters.

Contaminated soils were analyzed for TPH (Infra-red method) and Oil and Grease (gravimetric method). The levels of these parameters in the contaminated soil were high and had thus reduced the nutrients in the soil responsible for plant growth. Topsoil, Compost and Fertilizer were used to augment the nutrient levels in the contaminated soil. *Chromolaena odorata* was then planted in the contaminated soils. As the plants matured, Oil and Grease/TPH mean values in the soil decreased to the barest minimum in the soil. The plants were subjected to analyses for Oil and Grease and TPH. Some plants picked at random and subjected to analyses showed contaminants stored at the root, leaf and stem zones. The percentage storage at the various sites were approximately 45%, 37% and 18% for the root, leaf and stem zones respectively. About 83% - 88% of the Oil & Grease/TPH concentrations in the contaminated soil were gotten rid of in the soil within the six months period that the experiment was carried out.

Phytoremediation technology had worked for the degradation of contaminants in the soil and thus rendered the soil good for other useful purposes including agriculture and also to be kept for future reclamation activities.

CHAPTER ONE

1.0 INTRODUCTION

There are a significant number of petroleum hydrocarbon impacted sites across the world resulting from a wide range of past industrial, military, and petroleum production, and distribution practices (Total Petroleum Hydrocarbon Criteria Working Group Series, 1998). Difficulties in evaluating and remediating these sites arise from the complexity of the regulatory, scientific, and economic issues regarding impacted soil and water. Most investigations involving petroleum hydrocarbons are regulated by the states with different requirements in methodologies, action levels, and cleanup criteria. The chemical composition of petroleum products is complex and varied and changes over time and distance when released to the environment (Bellmann & Otto, 2003). These factors make it difficult to select the most appropriate analytical test methods for evaluating environmental samples and to accurately interpret and use the data.

Oil pollution in soils can cause interference with the ecosystem and causes the land no longer productive. Therefore, it needs an effective remedy which is fast, precise and does not disturb the environment. Many methods can be used for the remediation of oil pollution. Methods of oil pollution remediation in the environment can be done in three ways i.e. physical, chemical and biological (Okoh & Trejo-Hernandez, 2010).

Phytoremediation is a broad term that has been in use since 1991 to describe the use of plants to reduce the volume, mobility, or toxicity of contaminants in soil, groundwater, or other contaminated media (McCutcheon & Schnoor, 2003). Phytoremediation is an emerging technology that uses various plants to degrade, extract, contain, or immobilize contaminants from soil and water. This technology has been receiving attention lately as

an innovative, cost-effective alternative to the more established treatment methods used at hazardous waste sites (U.S. EPA, 2000). Furthermore, Phytoremediation defines a technique of reducing and cleaning pollutant concentrations in contaminated soils, water, or air with plants. This technique differs from bioremediation in that the former uses plants while the later uses biological (plant or bacterial). Such as bioremediation, phytoremediation technologies are based on two methods: ex-situ and in-situ. Ex-situ method requires removal of contaminated ground for treatment on or off site, and returning the treated ground to the resorted site (the practice at NGGL Volatilization Pad), while in-situ method defines a remediation without excavation of contaminated site. Phytoremediation has advantages and limitations. Like bioremediation, the cost of phytoremediation is lower than that of traditional remediation both in-situ and ex-situ. However, it requires a longer treatment period. It is effective if land contamination is limited to within 0.9144 meters (3 feet) of the surface, and if groundwater is within 3,048 meters (10 feet) of the surface. Sites must be low to moderate soil contamination over large areas, and to sites with large volumes of groundwater with low levels of contamination.

For at least 300 years, the ability of plants to remove contaminants from the environment has been recognized and taken advantage of in applications such as land farming of waste. Over time, this use of plants has evolved to the construction of treatment wetlands or even the planting of trees to counteract air pollution. In more recent years, as recognition grew of the damage around the world from decades of an industrial economy and extensive use of chemicals, so did interest in finding technologies that could address the residual contamination (McCutcheon & Schnoor, 2003).

Phytoremediation takes advantage of a plant's natural ability to absorb, accumulate, or metabolize contaminants from the soil or other media in which it grows. Interactions between these plants and microorganisms that live in the soil can also contribute to phytoremediation (Khyde, 2010).

Plants have been used for remediation in the past. A number of free-floating aquatic and aquatic emergent plant species and their associated microorganisms have been used for more than a decade in constructed wetlands for municipal and industrial wastewater treatment. Several fast-growing tree plantations have been established and are under active study for their potential use in wastewater cleanup in land discharge systems (Suthersan, 1999).

Controlled incineration is the most common method used to dispose plants that have absorbed large amounts of contamination. This process produces ashes, which can then be discarded at appropriate waste sites. For plants that have absorbed metals, controlled incineration produces ashes with a high metal content. Researchers are working on methods to recover the original metals from these ashes (Belz, 1997).

Phytoremediation technologies are in the early stages of development, with laboratory research and limited field trials being conducted to determine processes and refine methods. Additional research, including genetic engineering, is being conducted to improve the natural capabilities of plants to perform remediation functions and to investigate other plants with potential phytoremediation applications (Ralinda & Miller, 1996).

Although phytoremediation may not be the perfect remedial solution that some envisioned when its use at hazardous waste sites was first pioneered, its implementation continues to be appropriate or even preferable at a variety of sites. As the technology matures and its use expands beyond research laboratories and government-funded remediation, site owners and consultants will want comparative data on phytoremediation to determine its appropriateness for a particular site (Amanda, 2006).

1.1. JUSTIFICATION

Ghana over the years has experienced environmental pollution of different forms (land, water, air) and all efforts has been made by both governmental and non-governmental organizations in the drive towards finding a lasting solution to this menace. The influx of companies (locals and multinationals) engaged in all manner of activities across the length and breadth of the country impact negatively on our environment. Mining companies are no exception. Due to the use of all kinds of equipment that use fuel and other oils, there is a high tendency of spillage onto the ground and also into water bodies. Newmont Ghana Gold Limited (NGGL), as a mining company that holds the environment in high esteem, has serious concerns about the destruction of the environment through pollution.

As part of policies to reduce the negative impacts of mining activities on the environment, NGGL has put in place policies to pursue the conservation of the environment. Numerous chemicals are used on site and these chemicals mostly get to contaminate the environment if not handled properly. Hydrocarbon management is a

fundamental environmental management tool especially in mining companies that deals with large volumes of hydrocarbons and its hydrocarbon related waste.

In view of this and for best practices, Newmont Ghana Gold Limited has embarked on volatilization of hydrocarbon contaminated waste which commenced full operation in March 2009. Available data indicates that the rate of breakdown is not as fast as expected. Data on Total Petroleum Hydrocarbon (TPH) and Oil and Grease collected so far has values ranging between 45,000 ppm and 53,000 ppm respectively. These figures are far above the 5,000 ppm Australian guideline (guideline adopted by NGGL).

This research work, therefore, seeks to assess the efficiency of phytoremediation technology of the hydrocarbon contaminated soil as an alternative to the volatilization process being practiced at Newmont. The findings will be useful in the remediation of contaminated soils on Newmont site and other Oil Contamination in Ghana in the near future.

1.2. OBJECTIVES OF RESEARCH

The main objective of this project is to investigate the rate of breakdown of hydrocarbons in oil contaminated soil from Newmont's Volatilization Pad facility using phytoremediation technology with *Chromolaena odorata* (commonly known as Siam Weed).

1.2.1 Specific Objectives

- To design a phytoremediation set up of fertilizer, compost and topsoil blend.
- To determine an appropriate monitoring regime for the degradation process.
- To determine the initial levels of TPH/Oil and Grease of soil samples (contaminated and non- contaminated) and that of the 'Siam Weeds' taken from the forested areas around the Newmont site.
- To monitor the rate of reduction of TPH/Oil and Grease in soil and the accumulation of contaminants in plant with time.
- To determine pollutant concentrations in the plants and to find out the parts of the plant where these pollutants are stored (root, stem, leaf).
- To identify which media combinations is most suitable for the effective breakdown of hydrocarbons in contaminated soils.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 HYDROCARBON CONTAMINATION

Hydrocarbons in whatever form are generally the most common contaminant that requires remediation due to their widespread occurrence and the risks they pose to human health and controlled waters (Churngold, 2009).

Total Petroleum Hydrocarbons (TPH) is a term used to describe hydrocarbon compounds derived from Petroleum Sources (ATSDR, 1999). Common fuels such as Petrol, Diesel and Kerosene and Lubricating Oils/Greases all fall within the TPH banner. Due to the diversity of compounds that comprise TPH and the environmental and human health risks they pose, the remedial methods used to address them need to be considered on a site-specific basis.

Although hydrocarbons are simple organic substances (comprising only carbon and hydrogen), there are a huge number of different compounds, each exhibiting different chemical and physical properties. To rationalize the behavior of TPH once released into the environment, it is easiest to look at the structure and size of specific compounds. TPH compounds that have an aliphatic structure (i.e. straight or branched chains of carbon molecules) will behave differently to aromatic compounds (ringed chains of carbons). Similarly TPH compounds that have less carbon molecules will also act differently (Churngold, 2009).

Lighter end TPH compounds (i.e. less than 16 carbon atoms) tend to be more mobile due to greater solubility, greater volatility and lower organic partitioning coefficients. Lightweight aromatic compounds, such as benzene, are also more toxic making them of greater concern if released into the environment. Heavier TPH compounds typically have opposing properties, tending to adsorb into the organic fraction of soil. Heavier aromatic compounds, referred to as Polycyclic Aromatic Hydrocarbons (PAH), can also have higher toxicity and are typically more persistent in the environment. PAH's are commonly found in coal tar, heavy oils and creosotes.

Typically the majority of TPH mass will be partitioned within the soil phase. In certain instances TPH can also be encountered as a phase separated liquid, which due to its buoyancy, results in them floating on the surface of the water-table (ATSDR, 1999). Commonly phase separated TPH is referred to as Light Non-Aqueous Phase Liquid (LNAPL). A percentage of TPH will also be dissolved into the groundwater or trapped as a vapor within the soil 'pore-space' in the unsaturated zone. The exact split between phases is linked to the original composition of the source, geological and hydrogeological conditions and the age since the spillage occurred (Churngold, 2009).

2.2 TYPES / COMPOSITION OF HYDROCARBONS

In organic chemistry, a hydrocarbon is an organic compound consisting entirely of hydrogen and carbon. The majority of hydrocarbons found naturally occur in crude oil, where decomposed organic matter provides an abundance of carbon and hydrogen which, when bonded, can catenate (i.e. the ability of a chemical element to form a long chain-like structure via a series of covalent bonds) to form seemingly limitless chains (Clayden *et al.*, 2001).

The classifications for hydrocarbons defined by IUPAC nomenclature of organic chemistry are as follows:

1. Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon species and are composed entirely of single bonds and are saturated with hydrogen. The general formula for saturated hydrocarbons is C_nH_{2n+2} (assuming non-cyclic structures) (Silberberg, 2004). Saturated hydrocarbons are the basis of petroleum fuels and are either found as linear or branched species. Hydrocarbons with the same molecular formula but different structural formulae are called structural isomers (Silberberg, 2004).
2. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes. Those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures) (Silberberg, 2004). Those containing triple bonds are called alkynes, with general formula C_nH_{2n-2}.

3. Cycloalkanes are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is C_nH_{2n} (Silberberg, 2004).
4. Aromatic hydrocarbons, also known as arenes, are hydrocarbons that have at least one aromatic ring.

Hydrocarbons can be gases (e.g. methane and propane), liquids (e.g. hexane and benzene), waxes or low melting solids (e.g. paraffin wax and naphthalene) or polymers (e.g. polyethylene, polypropylene and polystyrene).

2.3 VARIOUS METHODS EMPLOYED IN REMEDIATING CONTAMINATED SOILS

Numerous hydrocarbon remediation technologies have been developed in recent years. However, most of these are on1y applicable to southern climates. Remediation technologies include both physical (mechanical) and biological methods (e.g. phytoremediation). Physical methods include i) soi1washing, ii) excavation and land filling, iii) incineration and thermal desorption and iv) Vacuum extraction while biological methods include i) infiltration galleries and ii) biopiles and Iandfarming. Generally, biological processes are one half to one third the cost of physical methods (Torma, 1994). Physical and biological methods are outlined with reference to their particular strengths and weaknesses.

2.3.1 Soil Washing

Soil washing involves an on-site set-up to scrub soil and remove Hydrocarbons which are then treated separately. Soil washing can be carried out with the aid of surfactants. Emulsifiers and other additives are added to increase hydrocarbon solubility (Kosaric, 1993). The major drawback with this technology is that abrasive additives can harm the natural microbial flora and damage the soil environment (Loss of minera1 cycling capacities) (Atlas and Bartha, 1993).

Additional steps to remove soi1 additives after cleanups, non-specificity of cleaning agents, high labor requirements and low treatment volumes may also serve to reduce efficiency and increase costs of soil washing.

2.3.2 Excavation and Landfilling

This option involves excavating Hydrocarbon contaminated soil with heavy equipment and placing it in a regulated landfill. When on-site landfilling is not feasible, soil must be containerized and shipped to a licensed waste manager. These factors and the need for ongoing monitoring to control fugitive leachate emissions make excavating and landfilling costly and logistically difficult to implement.

2.3.3 Incineration and Thermal Desorption

Thermal desorption and incineration use heat to volatilize and destroy Hydrocarbon contaminants. Incineration uses a closed-vessel combustion unit to completely destroy Hydrocarbon components at high temperature, whereas thermal desorption can be carried out *in* or ex-*situ* and uses lower temperature ranges to volatilize Hydrocarbon

components from the soil. Volatilized components are then captured and or treated. Influent/effluent streams for both processes face varying regulatory restrictions and monitoring requirements (Kostecki and Calabrese**,** 1990). These factors combined with low treatment volumes reduce efficiency and increase costs for large-scale treatment, making incineration and/or thermal desorption inappropriate.

2.3.4 Vacuum Extraction

In vacuum extraction, a pump draws air through wells constructed above the water table within the contaminated soil. Contaminants volatilize into the vapour phase where they are then captured, treated or exhausted. This in- situ treatment method removes the need for excavation and ex-situ remediation. It is not possible, however for treatment of soils with tight formations (clay) (Kostecki and Calabrese, 1990).

2.3.5 Biopiles and Landfarming

Biopiles are similar to landfarms in that they are both above-ground, engineered systems that use oxygen, generally from air, to stimulate the growth and reproduction of aerobic bacteria which, in turn, degrade the petroleum constituents adsorbed to soil. While landfarms are aerated by tilling or plowing, biopiles are aerated most often by forcing air to move by injection or extraction through slotted or perforated piping placed throughout the pile (U.S. EPA, 2007).

They can be coupled with biostimulation (addition of nutrients) and or bioaugmentation (inoculation with microbes). Biopiles involve placing soil in mounds or windrows to

promote higher temperatures. For landfarming, soil is excavated, spread thinly (15-30 cm) over a large area to ensure adequate aeration and periodically tilled.

The amount of equipment required depends on the degree of process control required. Regulatory guidelines for volatile organic carbon (VOC) emissions may require that Off-gases from the treatment cells be captured and treated. Biopiles and/or landfarms can be used for al1 soil types and can treat large volumes of soi1 efficiently and economically.

2.3.6 Rhizoremediation

Plant enzymes establish the degradation of pollutants during phytoremediation; whereas, during natural attenuation or bioaugmentation, the (indigenous) microbial population performs the degradation. In many of these studies, an important contribution to the degradation of pollutants is ascribed to microbes present in the rhizosphere of plants used during phytoremediation or of plants which are emerging as natural vegetation on a contaminated site. This contribution of the rhizomicrobial population is referred to as rhizoremediation (Anderson *et al.*, 1993). In some cases, rhizosphere microbes are even the main contributors to the degradation process. A plant can be considered to be a solar-driven biological pump and treatment system, attracting water with its root system, accumulating water-soluble pollutants in the rhizosphere, and concluding with the degradation or translocation of the pollutant (Erickson, 1997). Although the importance of the rhizosphere community for degradation of pollutants has been recognized, very little is known about the exact composition of the degrading population.

The first studies toward degradation of compounds in the rhizosphere mainly focused on the degradation of herbicides and pesticides (Hoagland *et al.*, 1994; Jacobsen, 1997;

Zablotowicz *et al.*, 1994). These studies suggested that plants are protected against these compounds by the degrading bacteria.

Today, many reports deal with degradation of hazardous organic compounds such as TCE, PAHs and PCBs (Walton and Anderson, 1990; Radwan *et al.*, 1995; Brazil *et al.*, 1995). In many of these reports, the composition of the microbial population has not been analyzed in detail. In addition, in many reports, no information about the survival, proliferation, and activity of these populations in the rhizosphere was provided.

2.4 PHYTOREMEDIATION OVERVIEW

Phytoremediation is defined as the use of plants to extract, sequester, or detoxify pollutants. This remediation method is environmentally friendly and visually attractive, and the structure of the soil is highly maintained (Khan *et al.*, 2000). Pollutants which can be a target for phytoremediation can be divided into two groups, the elemental pollutants and the organic pollutants (Meagher, 2000).

Phytoremediation uses plants to clean up pollutants in the environment. Plants can help clean up many kinds of pollutants including metals, pesticides, explosives, and oil. The plants also help prevent wind, rain, and groundwater from carrying pollutants away from sites to other areas.

Phytoremediation works best at sites with low to medium amounts of pollution. Plants remove harmful chemicals from the ground when their roots take in water and nutrients from polluted soil, streams, and groundwater. Plants can clean up chemicals as deep as their roots can reach. Tree roots grow deeper than smaller plants, so they are used to reach pollutants deeper in the ground.

Once inside the plant, chemicals can be:

- Stored in the roots, stems, or leaves
- Changed into less harmful chemicals within the plant
- Changed into gases that are released into the air as the plant transpires (breathes) (U.S. EPA, 2001).

Phytoremediation can occur even if the chemicals are not taken into the plant by the roots. For example, chemicals can stick or *sorb* to plant roots. Or they can be changed into less harmful chemicals by bugs or *microbes* that live near plant roots (U.S. EPA, 2001). The plants are allowed to grow and take in or sorb chemicals. Afterward, they are harvested and destroyed, or recycled if contaminants (e.g. metals) stored in the plants can be reused. Usually, trees are left to grow and are not harvested.

Plants grown for phytoremediation also can help keep harmful chemicals from moving from a polluted site to other areas. The plants limit the amount of chemicals that can be carried away by the wind or by water that soaks into the soil or flows off the site (U.S. EPA, 2001).

2.5 MECHANISMS OF PHYTOREMEDIATION

Phytoremediation utilizes physical, chemical, and biological processes to remove, degrade, transform, or stabilize contaminants within soil and groundwater.

Phytoremediation uses one basic concept: the plant takes the pollutant through the roots. The pollutant can be stored in the plant (phytoextraction), volatized by the plant (phytovolatization), metabolized by the plant (phytodegradation), or any combination of the above (Belz, 1997). Figure 1 shows the mechanisms in phytoremediation.

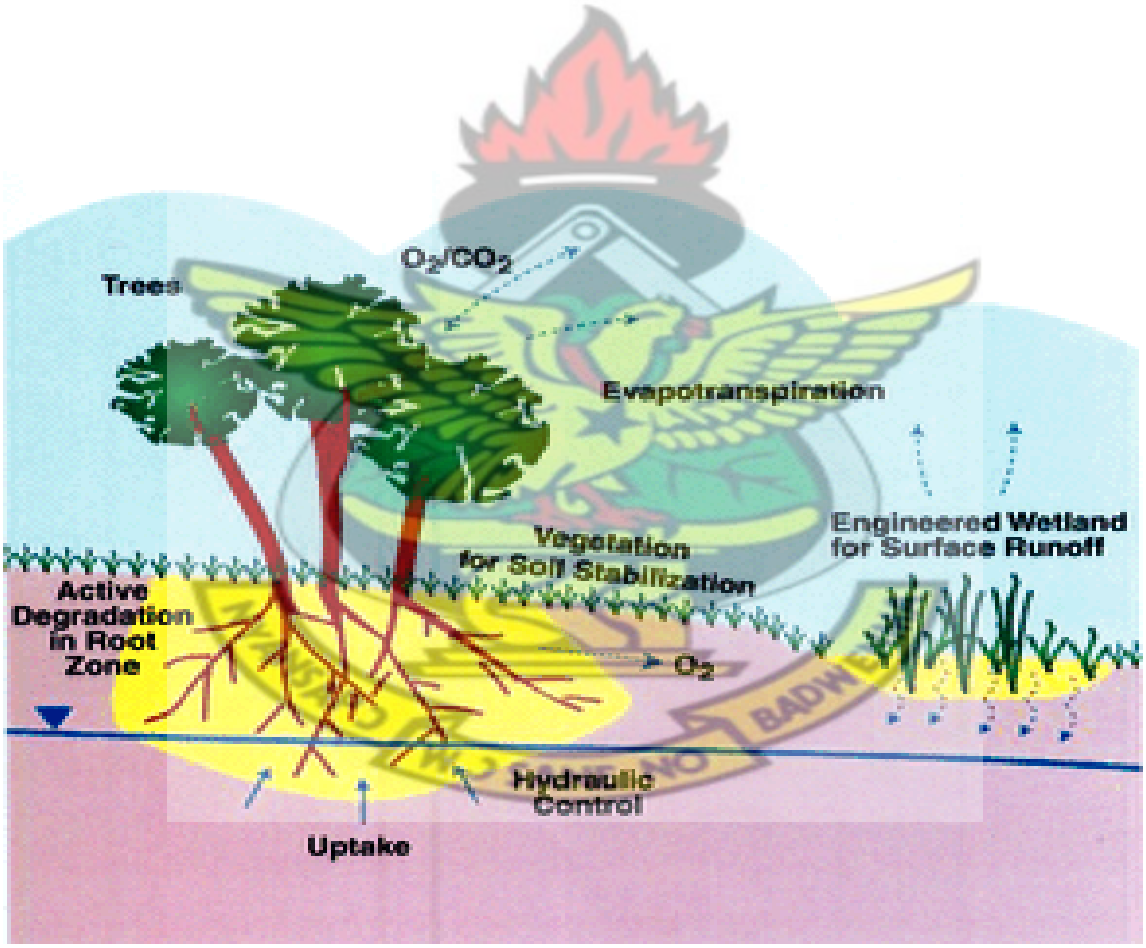

Figure 1: Mechanisms of Phytoremediation (U.S. EPA, 2000)

Researchers have identified mechanisms by which plants can affect contaminant mass in soil, sediments, and water. Although overlap or similarities can be observed between some of these mechanisms, and the nomenclature varies, reference is made to six phytoremediation mechanisms, which include: i) Phytoextraction, ii) Phytovolatilization, iii) Phytodegradation, iv) Rhizodegradation, v) Rhizofiltration, vi) Phytostabilization .

Each of the above mechanisms will have an effect on the volume, mobility, or toxicity of contaminants, as the application of phytoremediation is intended to do (U.S. EPA, 2000b).

2.5.1 Phytoextraction

The first phytoremediation patent applied for in the United States related to phytoextraction (McCutcheon and Schnoor, 2003). Phytoextraction refers to the ability of plants to remove metals and other contaminants from the subsurface and translocate them to the leaves or other plant tissues. The plants may then need to be harvested and removed from the site. Even if the harvested plants must be landfilled, the mass disposed of is much smaller than the original mass of contaminated soil. Incineration and disposal of the plants is cheaper than traditional remediation methods. As a comparison, it is estimated that a site containing 5000 tons of contaminated soil will produce only 20-30 tons of ash (Black, 1995). Use of phytoextraction is usually limited to metals and other inorganic compounds in soil or sediment. From the figure 2 below, Nickel is removed from the subsurface of a plant in A and translocated to the leaves of the same plant in B.

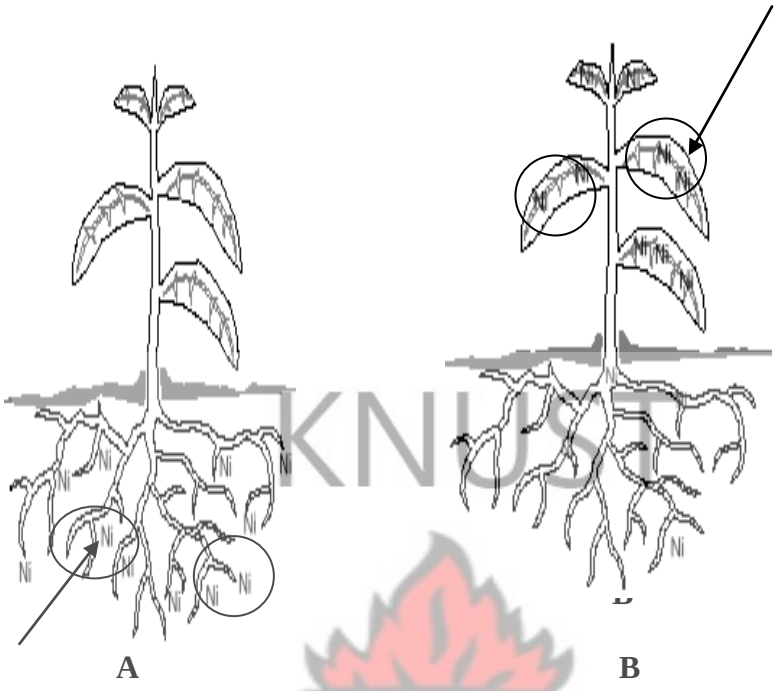

Figure 2: Phytoextraction (U.S. EPA, 2000)

2.5.2 Phytovolatilization

Phytovolatilization also involves contaminants being taken up into the body of the plant, but then the contaminant, a volatile form thereof, or a volatile degradation product is transpired with water vapor from leaves. Phytovolatilization may also entail the diffusion of contaminants from the stems or other plant parts that the contaminant travels through before reaching the leaves (McCutcheon and Schnoor, 2003). This mechanism takes a solid or liquid contaminant and transforms it to an airborne vapor. The vapor can either be the pure pollutant, or the pollutant can be metabolized by the plant before it is vaporized, as in the case of mercury, lead and selenium (Boyajian and Carriera, 1997; Black, 1995; Wantanbe, 1997). Phytovolatilization can occur with contaminants present in soil, sediments, or water and has been found to occur with volatile organic compounds, including trichloroethene, as well as inorganic chemicals that have volatile forms, such as

selenium, mercury, and arsenic (U.S. EPA, 2000b). Figure 3 shows contaminants (c) undergoing metabolism i.e. photochemical oxidation and being transformed into a volatilized contaminant (C1).

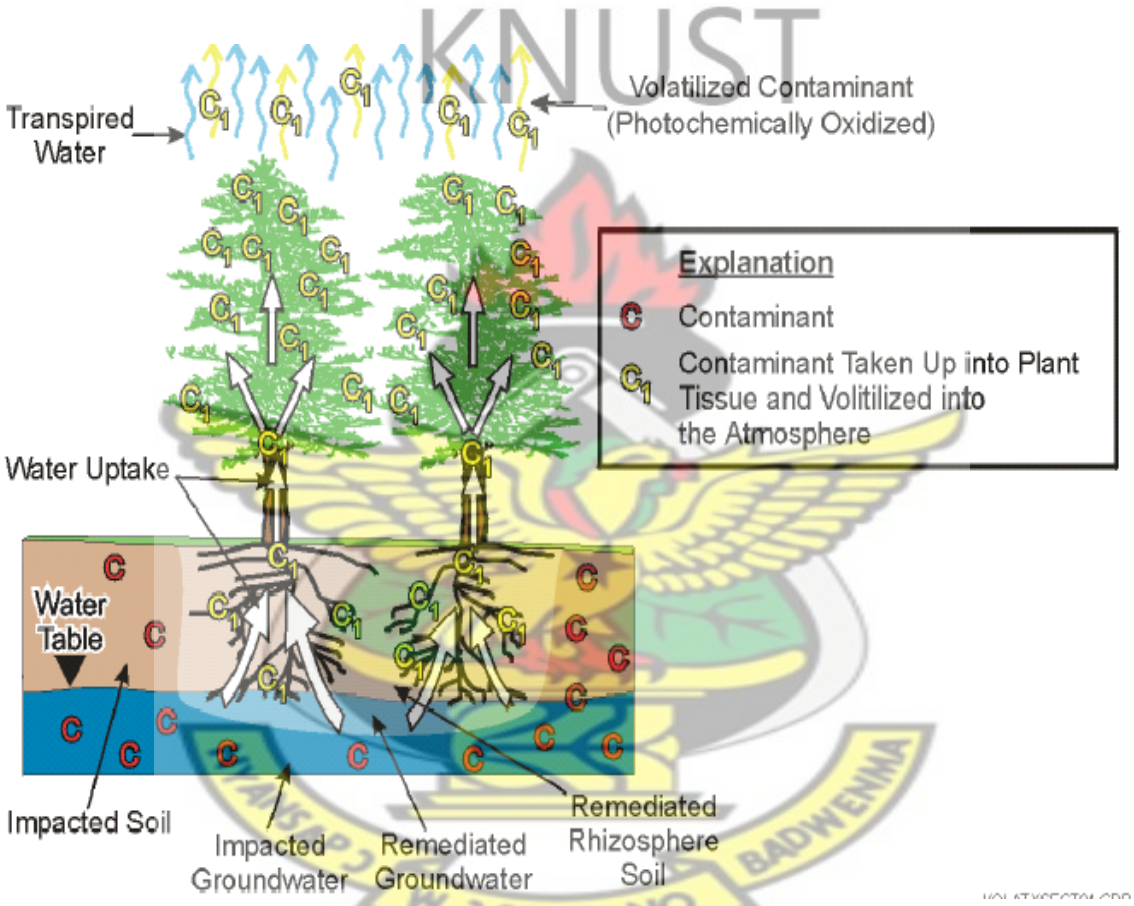

Figure 3: Phytovolatilization (U.S. EPA, 2000)

2.5.3 Phytodegradation

When the phytodegradation mechanism is at work, contaminants are broken down after they have been taken up by the plant. As with phytoextraction and phytovolatilization, plant uptake generally occurs only when the contaminants' solubility and hydrophobicity fall into a certain acceptable range. Phytodegradation has been observed to remediate some organic contaminants, such as chlorinated solvents, herbicides, and munitions, and it can address contaminants in soil, sediments, or groundwater (U.S. EPA, 2000b). Figure 4 shows organic contaminants being taken up into plant tissue with the formation of an intermediate compound and finally the incorporation of the organic pollutant into biomass resulting in the degradation of the original pollutant.

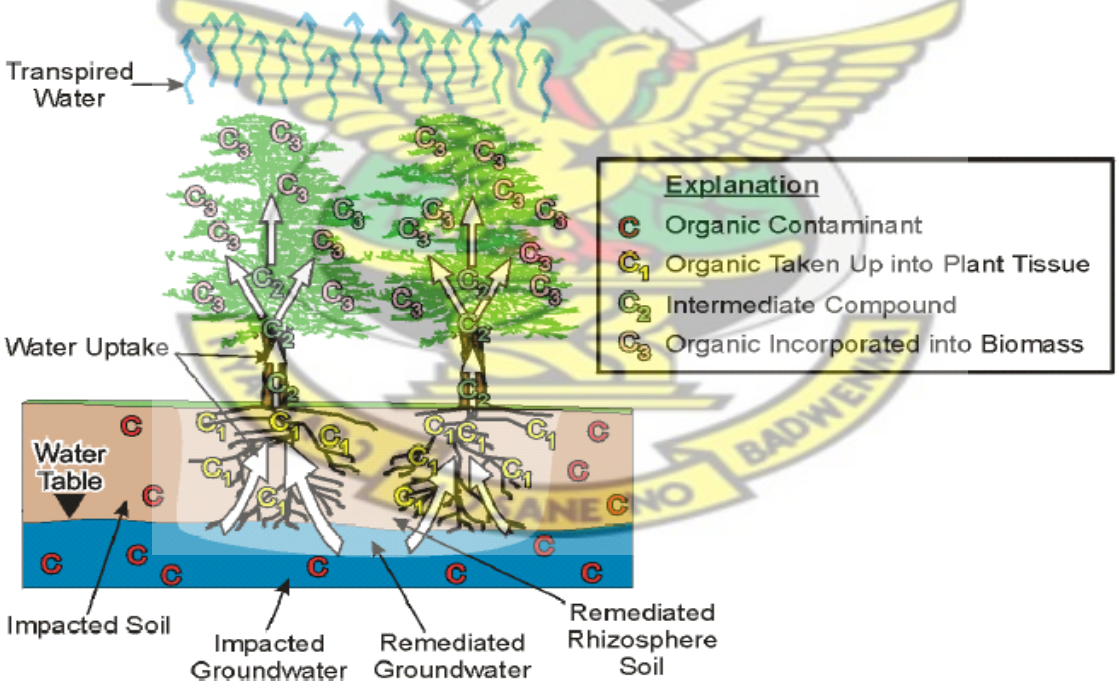

Figure 4: Phytodegradation (U.S. EPA, 2000)

2.5.4 Rhizodegradation

Rhizodegradation refers to the breakdown of pollutants within the plant root zone, or rhizosphere. Rhizodegradation is believed to be carried out by bacteria or other microorganisms whose numbers typically flourish in the rhizosphere. Studies have documented up to 100 times as many microorganisms in rhizosphere soil as in soil outside the rhizosphere (McCutcheon and Schnoor, 2003). Microorganisms may be so prevalent in the rhizosphere because the plant exudes sugars, amino acids, enzymes, and other compounds that can stimulate bacterial growth. The roots also provide additional surface area for microbes to grow on and a pathway for oxygen transfer from the environment. The localized nature of rhizodegradation means that it is primarily useful in contaminated soil, and it has been investigated and found to have at least some success in treating a wide variety of mostly organic chemicals, including petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, pesticides, polychlorinated biphenyls (PCBs), and benzene, toluene, ethylbenzene, and xylenes (BTEX) (U.S. EPA, 2000b). Figure 5 shows hydrocarbon contaminants at the root zone acting as energy for microbes growth and thereby helping in the breakdown of contaminants.

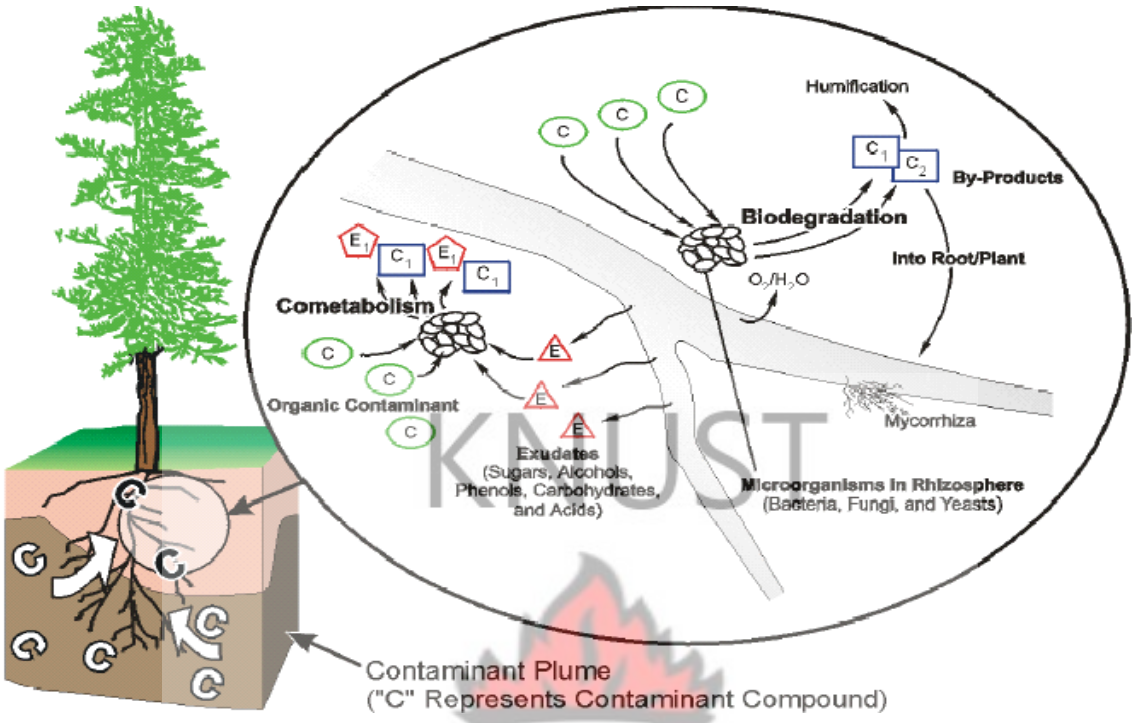

Figure 5: Rhizodegradation (McCutcheon & Schnoor, 2003)

2.5.5 Rhizofiltration

In the rhizofiltration process, contaminants are also taken up by the plant and removed from the site when the plant is harvested; however, in this case, the contaminant is removed from the dissolved phase and concentrated in the root system. Rhizofiltration is typically exploited in groundwater (either in- situ or extracted), surface water, or wastewater for removal of metals or other inorganic compounds (U.S. EPA, 2000b). Figure 6 shows contaminant being removed from the dissolved phase (C) and concentrated in the root system in a stabilized form (C_2)

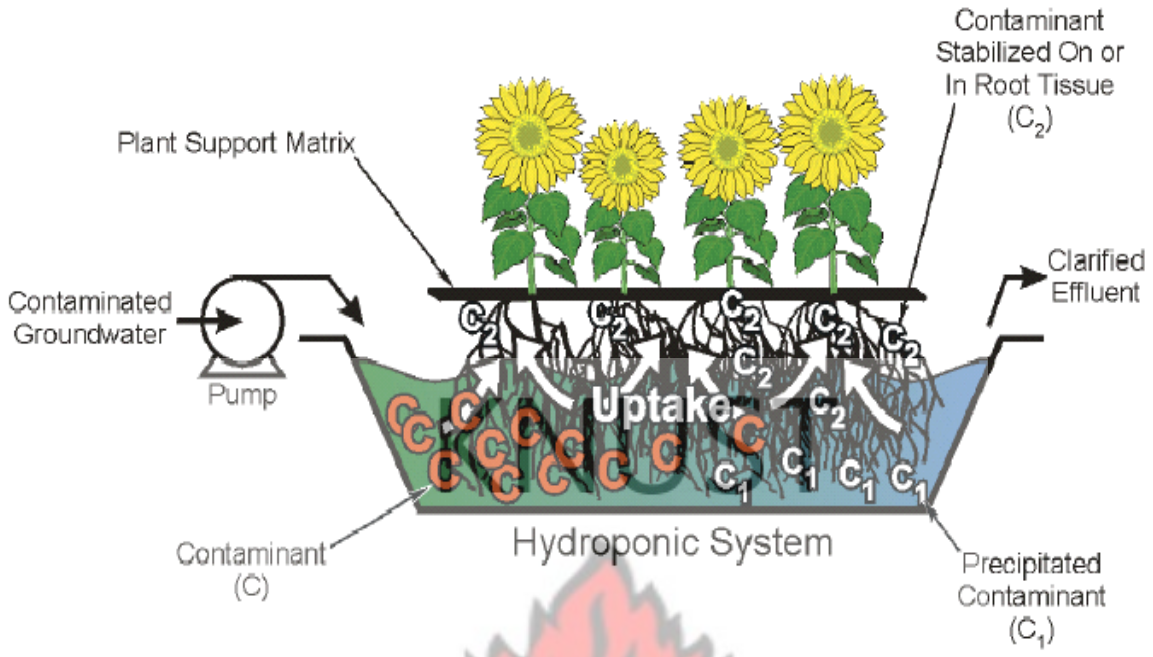

Figure 6: Rhizofiltration (U.S. EPA, 2000)

2.5.6 Phytostabilization

Phytostabilization takes advantage of the changes that the presence of the plant induces in soil chemistry and environment. These changes in soil chemistry may induce adsorption of contaminants onto the plant roots or soil or cause metals precipitation onto the plant root. The physical presence of the plants may also reduce contaminant mobility by reducing the potential for water and wind erosion. Phytostabilization has been successful in addressing metals and other inorganic contaminants in soil and sediment (U.S. EPA, 2000b). Figure 7 shows contaminant from soil stabilized around the root zone and thereby making it not readily available in the soil.

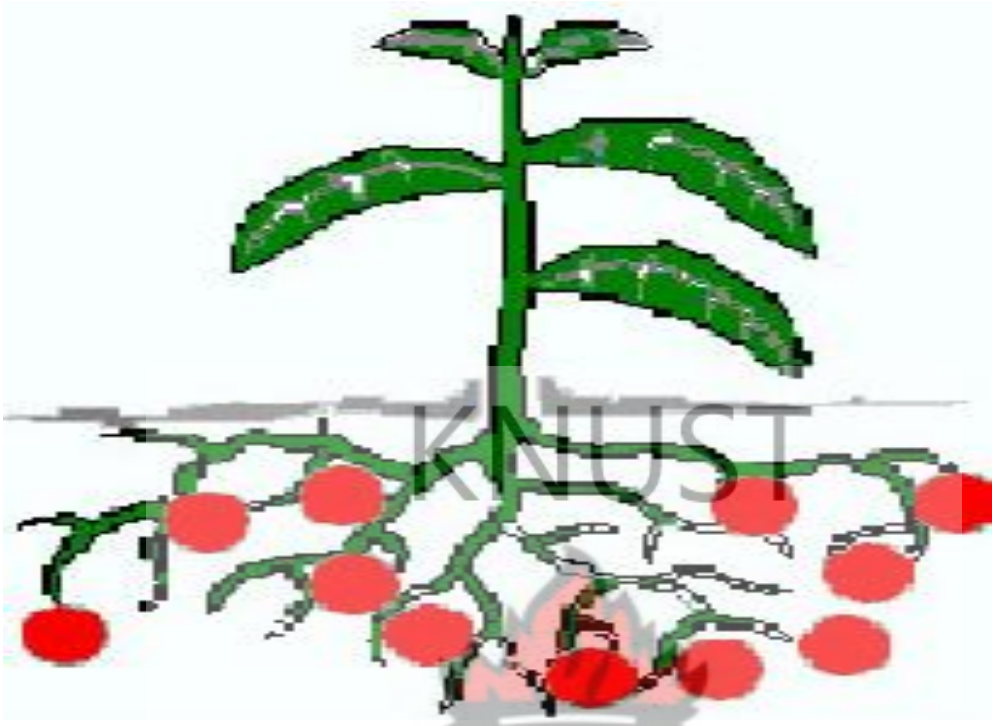

Figure 7: Phytostabilization (U.S. EPA, 2000)

The success of phytoremediation at a given site cannot always be attributable to just one of these mechanisms because a combination of mechanisms may be at work.

The different phytoremediation processes listed above can be grouped under those that can degrade organics and those that can degrade inorganics. Rhizodegradation, Phytodegradation and Phytovolatilization are mainly responsible for organics breakdown whiles Phytoextraction, Rhizofiltration and Phytostabilization takes care of inorganics. (U.S. EPA, 2000).

2.6 EVALUATING PHYTOREMEDIATION AS A POTENTIAL REMEDIATION TECHNOLOGY

In the traditional Superfund or similar remediation process, a risk assessment may be performed to evaluate what human health or ecological risks exist at a site and how potential remedial options may address those risks (Amanda, 2006). Remedial options such as physical and biological methods are compared to one another, and an innovative remediation technology, such as phytoremediation, must offer advantages in terms of either risk reduction or cost savings over excavation and landfilling of contaminated material or other traditional techniques to be implemented at a site (Amanda, 2006).

2.6.1 Benefits of Phytoremediation

Numerous benefits of phytoremediation have been established or hypothesized:

- Phytoremediation can be less invasive and destructive than other technologies.
- Studies have indicated that implementing phytoremediation may result in a cost savings of 50 to 80 percent over traditional technologies (U.S. EPA, 2000b).
- Phytoremediation may provide habitat to animals, promote biodiversity, and help speed the restoration of ecosystems that were previously disrupted by human activity at a site (U.S. EPA, 2000b; Wilson, 2004).
- Phytoremediation installations can improve the aesthetics of brownfields or other contaminated sites.
- Phytoremediation may promote better air or water quality in the vicinity of the site (Wilson, 2004).
- Vegetation may help reduce erosion by wind or water (Wilson, 2004).

- Planted trees may also provide shade to buildings, helping to decrease energy consumption (Nowak and Crane, 2002).
- The plants can be easily monitored
- It is potentially the least harmful method because it uses naturally occurring organisms and preserves the environment in a more natural state.

2.6.2 Limitations of Phytoremediation

Phytoremediation is not universally appropriate or successful; some important limitations must be noted:

- Extremely high contaminant concentrations may not allow plants to grow or survive; phytoremediation is likely to be more effective or reasonable for lower concentrations of contaminants (U.S. EPA, 2000b).
- For remediation to be successful, contamination must generally be shallow enough that plant roots can reach the contaminants, or contamination must be brought to the plant (U.S. EPA, 2000b).
- Phytoextraction techniques can cause contaminants to accumulate in plant tissues, which could cause ecological exposure issues and thus form part of the food chain (U.S. EPA, 2000b).
- Phytovolatilization may remove contaminants from the subsurface, but might then cause increased airborne exposure (U.S. EPA, 2000b).
- If non-native species are selected for phytoremediation, the consequences of introducing them to the ecosystem may be unknown or unexpected (U.S. EPA, 2000b).

- The time required to achieve the remedial goals may be longer with phytoremediation than with other treatment technologies (e.g., Bioremediation). Phytoremediation can require several growing seasons for a tree stand to be established and for contaminant concentrations to be reduced (U.S. EPA, 2000b).
- With plant-based systems of remediation, it is not possible to completely prevent the leaching of contaminants into the groundwater (without the complete removal of the contaminated ground, which in itself does not resolve the problem of contamination) (U.S. EPA, 2000b).

2.7 FACTORS AFFECTING PHYTOREMEDIATION

2.7.1 Weather

Phytoremediation might be best suited for tropical countries where plant growth occurs all year round (Kamath *et al.*, 2004). In temperate climates, the active contribution of phytoremediation is restricted to the growing period only. Winter operations may pose problems for phytoremediation when deciduous vegetation loses its leaves, transformation and uptake cease, and soil water is no longer transpired (Kamath *et al.*, 2004).

2.7.2 Time Scale of clean-up

Degradation of organics may be limited by mass transfer, i.e., desorption and mass transport of chemicals from soil particles to the aqueous phase may become the rate determining step (Schnoor, 1997). Therefore, phytoremediation may require more time to achieve clean-up standards than other more costly alternatives such as excavation or ex-

situ treatment, especially for hydrophobic pollutants that are tightly bound to soil particles (Schnoor, 1997).

In many cases, phytoremediation may serve as a final "polishing step" to close sites after more aggressive clean-up technologies have been used to treat the hot spots (Kamath *et al*., 2004).

The time it takes to clean up a site using phytoremediation depends on several factors:

Type and number of plants being used

Type and amounts of harmful chemicals present

Size and depth of the polluted area

Type of soil and conditions present

These factors vary from site to site. Plants may have to be replaced if they are destroyed by bad weather or animals. This adds time to the cleanup. Often it takes many years to clean up a site with phytoremediation.

2.7.3 Plant Density

Planting density depends on the application. For hybrid poplar trees, 1000-2000 trees per acre are typically planted with a conventional tree planter at 12-18 inches depth or in trenched rows 1-6 ft. deep. The poplars are planted simply as "sticks", long cuttings that will root and grow rapidly in the first season. Several phreatophytes in the *Salix* family, such as willow and cottonwood, can be planted in a similar manner. Poplars have the ability to root along the entire buried depth (Schnoor, 1997).

2.7.4 Agronomic Inputs

2.7.4.1 Irrigation

Results suggest that irrigation can enhance bioremediation of certain diesel components (Kamath *et al*., 2004). For terrestrial phytoremediation applications, it is often desirable to include irrigation costs on the order of 10-20 inches (convert inches to either mm or m) of water per year, in the design. Spray irrigation is less efficient than drip irrigation as it encourages the growth of weeds that compete for nutrients with plants and hinder their delivery to the contaminated zone (Kamath *et al.,* 2004). Irrigation of the plants is especially important during the start of the project.

2.7.4.2 Fertilizer addition

As both microbial activity and plant growth can be affected by addition of fertilizer, fertilizer addition is an important factor in affecting the efficiency of bioremediation process (Tang *et al*., 2010). Contaminated soils are usually deficient in macro- and micro-nutrients necessary for establishing healthy vigorously growing plants and stimulating microbial contaminant degradation (Kamath *et al*., 2004). Organic sources of nitrogen are better than inorganic sources. This is probably because organic nitrogen sources provides a low release source of nitrogen, and also help to improve soil structure and soil water relationships for plant growth. It was found that poultry manure increased the growth of corn in a soil containing 3 percent weight per volume crude oil more than an inorganic fertilizer containing nitrogen, phosphorus, and potassium (Amadi *et al*., 1993). The addition of sawdust alone improved germination by decreasing oil contact with seeds, but accentuated the adverse effect of the oil on later growth, apparently by further widening

the carbon-to-nitrogen ratio (Amadi *et al.*, 1993). With respect to TPH degradation, nutrient addition during phytoremediation has yielded mixed results (Hutchinson *et al*., 2003; Joner *et al*., 2001; Palmroth *et al*., 2006b). Better degradation of TPH was observed using grasses with N/P amendments than without inorganic amendments (Hutchinson *et al.*, 2001). Joner *et al*. (2002) reported improved degradation of 3 and 4 ringed PAHs with the addition of N/P, but diminished degradation of 5 and 6 ringed PAHs. Finally, no improved degradation of diesel fuel was observed with nutrient amendments during phytoremediation with pine, poplar, or grasses (Palmroth et al., 2002). Microbial bioremediation of TPH contaminants with nutrient addition also produced widely varying results.

2.7.5 Oxygen Requirements

Soil oxygen is required for optimal aerobic microbial degradation of petroleum hydrocarbon contaminants. Similar to nutrient deficiencies, oxygen depletion is caused by natural microbial respiration of contaminants. Within phytoremediation, plants may be a net positive or negative oxygen source (Lee *et al*., 2000). Plants may improve soil oxygen through two mechanisms. First, specially adapted plants use parenchyma, channels of reduced air resistance, to transport oxygen to the root zone, enhancing aerobic biological degradation (Shimp *et al*., 1993; Erickson *et al*., 1993). Secondly, soil dewatering and fracturing increases soil porosity, allowing increased diffusion of atmospheric oxygen (Rentz *et al*., 2003). Plant roots can also be a net oxygen sink within petroleum-contaminated soils. Rentz *et al*., (2003) observed stimulation of hybrid poplar growth and increased poplar root density with the addition of Oxygen Release Compound (ORC) when plants were grown in petroleum smear zone soils (Rentz *et al*., 2003).

2.7.6 Cost

Phytoremediation is usually less costly than competing alternatives such as soil excavation, pump-and-treat, soil washing, or enhanced extraction (Kamath *et al*., 2004). Apart from costs incurred during installation of vegetation at the site, a field-scale phytoremediation project involves expenditure on design, site preparation, reporting, monitoring, and operation and maintenance (Green and Hoffnagle, 2004). It would be prudent to include preliminary greenhouse experiments along with agronomic soil testing during the design phase to ensure vigorous plant growth at the field-site. Mathematical modeling may be necessary to demonstrate the effectiveness of the technology to regulatory agencies (Kamath *et al*., 2004).

2.8 FIELD APPLICATION OF PHYTOREMEDIATION

As it is a relatively new technology, phytoremediation is still mostly in its testing stages and as such has not been used in many places on a full scale (U.S. EPA, 2001). However, it has been tested successfully in many places around the world for many different contaminants. Not much work has been done and published as far as phytoremediation in Ghana is concerned. Table 1 shows some phytoremediation sites in the US, the type of application used, the plants and the medium being remediated.

Table 1: Some Phytoremediation Sites in the USA

LOCATION	APPLICATION	POLLUTANT	MEDIUM	PLANT(S)
Ogden, UT	Phytoextraction & Rhizodegradation	Petroleum & Hydrocarbons	Soil & Groundwater	Alfalfa, poplar, juniper, fescue
Anderson, ST	Phytostabilization	Heavy Metals	Soil	Hybrid poplar, grasses
Ashtabula, OH	Rhizofiltration	Radionuclides	Groundwater	Sunflowers
Upton, NY	Phytoextraction	Radionuclides	Soil	Indian mustard, cabbage
Milan, TN	Phytodegradation	Expolsives waste	Groundwater	Duckweed, parrotfeather
Amana, IA	Riparian corridor, phytodegradation	Nitrates	Groundwater	Hybrid poplar

SOURCE: (U.S. EPA, 2001).

2.8.1 Plant Selection Criteria

Plants should be selected according to the needs of the application, the contaminants of concern and their potential to thrive on contaminated soil (Kamath *et al.,* 2004). Design requirements should include the use of native plants to avoid introduction of invasive species. Apart from this, vegetation should be fast growing, hardy, easy to plant and maintain (Kamath *et al.,* 2004). The main aim is to ensure that roots expand throughout the entire contaminated zone. In temperate climates with shallow contaminated aquifers,

phreatophytes, such as *Populus* spp. (hybrid poplar, cottonwood, aspen) and *Salix* spp. (willow) are often selected because of fast growth, deep rooting ability down to the surface of groundwater, large transpiration rates, and the fact that they are native throughout most of the country (Kamath *et al.,* 2004). Grasses are often planted in tandem with trees at sites with organic contaminants as the primary remediation method (Mohebi and Dialami, 2011). They provide a tremendous amount of fine roots in the surface soil, which is effective at binding and transforming hydrophobic contaminants such as TPH and PAHs. Grasses are often planted between rows of trees to provide for soil stabilization and protection against wind-blown dust that can move contaminants off-site. Legumes such as alfalfa (*Medicago sativa*), alsike clover (*Trifolium hybridum*), and peas can be used to restore nitrogen to poor soils. Fescue (*Vulpia myuros*), rye (*Elymus* spp.), clover (*Trifolium* spp.) and reed canary grass (*Phalarisa rundinacea*) have been used successfully at several sites, especially petrochemical wastes. Once harvested, the grasses can be disposed of as compost or burned. Plant tolerance to high contaminant concentrations is also a very important factor for the process (Kamath *et al*., 2004). The phytotoxicity of petroleum hydrocarbons is a function of the specific contaminant composition, its concentration, and the plant species used (Kamath *et al*., 2004). Major adverse effects typically include reduced germination and growth if contaminant concentrations are sufficiently high (Kamath *et al.,* 2004).

In general, TPH values of 15 percent or greater can result in significant reductions in plant growth and in some cases mortality. Compared with uncontaminated soil, soils with 2 % TPH reduced alfalfa yields by 32 percent (Wiltse *et al.*, 1998). Production of biomass by ryegrass was reduced 46 percent at a soil concentration of 0.5 percent (5000

mg/kg) hydrocarbons (Gunther *et al*., 1996). It was found that plants pre-grown in clean soil and subsequently transplanted to the contaminated soil grew nearly as well as the control, showing that toxicity was associated with germination and/or early plant growth (Mohebi and Dialami, 2011).

Similarly, poor rooting of ryegrass compared to legumes appeared to adversely affect the removal of TPH from Gulf War-contaminated soils (Yateem *et al*., 1999). Although the germination of sunflower seeds and beans was greater than that of maize, vegetative growth was greater for maize than beans, demonstrating that germination and later plant growth may be affected differently (Chaineau *et al*., 1997).

Aged spills tend to be much less phototoxic than fresh ones, possibly because of the lower bioavailability of toxic compounds in the aged spills. However, the speciation of petroleum hydrocarbons is also very important in determining phytotoxicity (Kamath *et al.*, 2004).

Phytoremediation is more than just planting and letting the foliage grow; the site must be engineered to prevent erosion and flooding and maximize pollutant uptake. There are 3 main planting techniques for phytoremediation.

1. Growing plants on the land, like crops. This technique is most useful when the contaminant is within the plant root zone, typically 3 - 6 feet or the tree root zone, typically 10-15 feet (Belz, 1997).
2. Growing plants in water (aquaculture). Water from deeper aquifers can be pumped out of the ground and circulated through a "reactor" of plants and then used in an application where it is returned to the earth (e.g. irrigation).

3. Growing trees on the land and constructing wells through which tree roots can grow. This method can remediate deeper aquifers in-situ. The wells provide an artery for tree roots to grow toward the water and form a root system in the capillary fringe (Wagner, 1997).

2.9 PLANT CONSIDERATION

Chromolaena odorata (Siam weed) was used since it is very invasive, hardy and common around the Newmont mining site. Also, a publication by Belford *et al*. (2009) on potential candidates for phytoremediation, revealed that, *Chromolaena odorata* has high ash content thereby having high bioaccumulation and translocation potential. Harrison Ifeanyichuku Atagana of the institute of science and technology education of the University of South Africa published in the international journal of phytoremediation volume 13, issue 7, 2011, a paper on the potential of *Chromolaena odorata* to decontaminate used engine oil impacted soil under greenhouse conditions (Atagana, 2011). In Atagana's publication, residual TPH after 90 days showed that between 21% and 100% of oil was lost from the planted soil. Phanwimol Tanhan in Thailand also published a paper on effects of soil amendments and EDTA on lead uptake by *Chromolaena odorata*: greenhouse and field trial experiments (Tanhan, 2011). This was published in the international journal of phytoremediation volume 13, issue 9, 2011 and it indicated that *Chromolaena odorata* could be used for phytoextraction of lead contaminated soil. Based on these and the fact that *Chromolaena odorata* is an invasive weed in the Newmont catchment area, it was chosen for the exercise. But for time considerations, other tree/plant species that are known to be good bioaccumulators (e.g.

Willow, Poplar, Soybean, Sunflower, Indian mustard, Red clover etc.) would have been considered. Plate 1 shows some *Chromolaena odorata* plant cuttings used for the experiment.

Plate 1: ***Chromolaena odorata*** **Cuttings used for the Experiment**

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 STUDY AREA

The study site is located approximately 300 km northwest of the capital city of Ghana, Accra, 107 km northwest of Kumasi (the Ashanti Regional capital) and 40 km south of the Brong Ahafo regional capital, Sunyani. The Project is located along a mineralized zone that extends approximately 70 km in the central portion of Ghana. Plate 2 shows a section of a map of Ghana with Ahafo, the project site.

Plate 2: Location Map of Project in Ghana

3.2 VARIOUS TREATMENTS OF SOIL

For simplicity, codes from letters A to M were used to represent the various soil treatments used for the experiment. Table 2 shows the various soil treatments and their respective codes.

Table 2: Soil Treatments and their Codes

TREATMENTS	CODES
HCS (4kg) + Topsoil 0.2 % N	A
HCS (4kg) + Topsoil 0.4 % N	B
HCS (4kg) + Topsoil 0.6 % N	C
HCS (4kg) + Topsoil 0.8 % N	D
HCS (4kg) + Compost 0.2 % N	E
HCS (4kg) + Compost 0.4 % N	F
HCS (4kg) + Compost 0.6 % N	G
HCS (4kg) + Compost 0.8 % N	H
HCS (4kg) + Urea 0.2 % N	I
HCS (4kg) + Urea 0.4 % N	J
HCS (4kg) + Urea 0.6 % N	K
HCS (4kg) + Urea 0.8 % N	L
HCS Only (4kg) - Control	M

3.3 Contaminated Soil Collection Site

The volatilization pad was constructed using an impervious compacted soil covered with a high density polyethylene (HDPE) liner. It has a sump to collect runoff and it is fenced to avoid unauthorized entry. The Volatilization Pad is part of the Integrated Waste Management Facility on Newmont site where all forms of waste (e.g. hazardous, non-hazardous, inert, electronic, wood and activated sludge from the waste water treatment plant) are kept and managed. Plate 3 shows a section of the Volatilization Pad facility on Newmont site.

Plate 3: Volatilization Pad Facility at Newmont

3.4 SOIL COLLECTION AND SET UP

Three different sources of Nitrogen were used in this study namely; topsoil, compost and fertilizer (urea). Contaminated soil was sampled from the volatilization pad facility of Newmont Ghana Gold Limited by grab sampling method. Topsoil (0-15 cm) was collected from topsoil stock pile on NGGL site – a place that has no historical exposure of oil spills. Compost (200 kg) was obtained from a compost facility on site. Fertilizer of strength 46 % urea was bought from the local market. Plate 4 shows the shed under which the experiment was carried out.

Plate 4: Shed for Phytoremediation Experiment

The experiment was carried out under a wooden structure covered with plastic rubber. This setup basically prevented rain water from having direct contact with the plants and also to allow reduced amount of sunlight into the setup. This presented a major difference compared to the volatilization pad system, where samples are left in the open. The experiment was replicated three times in randomized complete block design. Each block contained 13 different treatments.

3.5 PROCEDURE FOR PHYTOREMEDIATION EXPERIMENT

- Three set ups involving mixings with portions of hydrocarbon contaminated soil and portions of fertilizer, compost and topsoil based on the N-P-K levels baseline situation of the contaminated soil was done.

- The fertilizer, compost and topsoil were used to adjust the N-P-K level to the optimum/desired soil condition suitable for plant growth.

- In the set-up, vegetative parts of *Chromolaena odorata* species were planted in four (4) different media.
- Media 1 - Hydrocarbon Contaminated soil + top soil
- Media 2 – Hydrocarbon contaminated soil + fertilizer. (Urea and Sulphate of Ammonia)
- Media 3- Hydrocarbon contaminated soil + Compost
- Media 4- For each media, *Chromolaena odorata* was planted on the contaminated soil without any treatment to serve as control.

The experiment was replicated three times in Randomized Complete Block Design (RCBD). Each block contained thirteen (13) different treatments (table 4.2). Six (6) vegetative parts of *Chromolaena odorata* was planted in each bowl.

3.6 AUGMENTATION

Ways were found to augment the levels of these nutrients to appreciable/optimum levels. Topsoil, compost and fertilizer from literature, have appreciable levels of N,P and K. Based on literature available and consultations with experts from the Soil Research Centre, calculations for the amounts of the various media to be added to the contaminated soil to support plant growth were done. Laboratory assay of the N- level was carried out to verify whether the levels were consistent with the calculated values.

Minimum percentage amount of Nitrogen in soil for plant growth from literature is 0.2%. Different variations of 0.2%, 0.4%, 0.6% and 0.8% nitrogen levels were therefore chosen for each media.

Baseline Nitrogen concentrations in topsoil, compost and fertilizer were 0.35%, 0.8% and 46% respectively. These concentrations far exceeded the nitrogen concentration in the contaminated soil i.e. 0.08%. Plate 5 shows some measurements of topsoil used for the experiment.

Plate 5: Measuring some quantities of Top soil for Augmentation

3.6.1 Preliminary Activities Performed

The initial levels of Total Petroleum Hydrocarbon (TPH) and Oil and Grease in the contaminated soil and plant were measured. The nutrients that are required in soils to support plant growth were also analyzed for the contaminated soil to know their initial levels.

Since the contaminants are mostly various forms of oils in vehicles used on Newmont site (diesel, brake fluid, engine oil etc.) the levels of TPH/Oil and Grease were very high, ranging from 37,000 ppm to above 50,000 ppm. The presence of these oils had drastically reduced the levels of Nitrogen, Phosphorus and Potassium. Moisture content was also very low.

3.6.2 Baseline Conditions of the Hydrocarbon Contaminated Soil Taken From Newmont's volatilization pad Facility

Initial analyses of Oil and Grease/ TPH were done to know the extent of hydrocarbon contamination of the soil samples at the Volatilization Pad facility. Other parameters such as Total Carbon, Total Nitrogen, Moisture Content, Temperature, Phosphorus and Potassium for the contaminated soil were also done. Table 3 shows some parameters of interest and their initial amounts.

Table 3: Mean Baseline Conditions of the Hydrocarbon Contaminated Soil

PARAMETER	VALUE
OIL & GREASE (mg/kg)	55278.00 ± 4028.00
TOTAL PETROLEUM HYDROCARBON (mg/kg)	37814.85 ± 1403.15
MOISTURE CONTENT (%)	19.00 ± 2.00
TEMPERATURE (^{o}C)	24.80 ± 0.7
TOTAL NITROGEN (%)	0.08 ± 0.04
AVAILABLE PHOSPHORUS (mg/kg)	5.20 ± 2.48
POTASSIUM (mol/kg)	0.20 ± 0.08
TOTAL CARBON (%)	5.05 ± 0.55

Based on the initial amounts above, quantities of the compost, topsoil and fertilizer to be added to the 4 kg contaminated soil were calculated. Laboratory assay of the N- level was carried out to verify whether the levels were consistent with the calculated values. For

example 600 g of Compost was added to 4000 g of the Contaminated Soil to achieve 0.2 % Nitrogen of the compost blend. Table 4 shows the quantities of the various media added to the contaminated soil.

TABLE 4: Quantities of Topsoil, Compost and Fertilizer added to 4 kg Contaminated soil.

NITROGEN SOURCE / LEVELS OF NITROGEN (%)	COMPOST/ (g)	TOPSOIL/ (g)	FERTILIZER/ (g)
0.2	600 ± 80	1371.4 ± 28.6	10.4 ± 0.3
0.4	1600 ± 130	3657.1 ± 137.1	12.8 ± 0.4
0.6	2600 ± 150	5942.9 ± 92.9	45.2 ± 0.5
0.8	3600 ± 120	8228.6 ± 72.6	62.6 ± 0.6

Growth of the plants were seen after some three weeks of planting. Plate 6 shows plant growth.

Plate 6: Signs of plant growth after three weeks of planting

3.7 MONITORING THE DEGRADATION PROCESS

The degradation process was monitored by analyzing the following parameters

- Total Petroleum Hydrocarbon (TPH) before the start of the process and thereafter at scheduled times using *Infra red spectroscopy method*
- Oil and Grease on weekly basis using *Gravimetric method*
- Total nitrogen by *the Kjeldahl Method.*
- Physical parameters such as pH, Temperature, Moisture content were monitored over time.
- pollutant concentrations in the plants were also monitored

3.8 LABORATORY ANALYSIS

The analysis performed include Total Petroleum Hydrocarbon (TPH), Oil and Grease (for the hydrocarbon contaminated soil, topsoil samples and the plants used for the experiment), Total Nitrogen and Moisture content analyses of the soil were also done.

3.8.1 TPH Analysis of Soil by Infra-Red method

Procedure for TPH analysis of soil by IR was carried out in accordance with standard methods for the examination of water and wastewater, (21st edition, 2005, method 5520-B) (Andrew *et al*., 2005).

Approximately 20 g of soil was weighed into a 16 oz. French square bottle with minimum exposure, along with 50 ml of distilled water and adjusted to a pH of 3 with hydrochloric acid (HCl). The bottle was capped tightly using a Teflon line cap and shaken mildly to disperse the soil for 1 to 2 min.

After shaking, 25 ml of Freon was pipetted into the bottle and shaken well again for 15 minutes using a paint or lateral shaker. Sample was allowed to stand to permit content of bottle to separate into distinct layers.

10 ml of Freon was pipetted from the appropriate layer and filtered through 5 g of activated silica gel and 1 g of sodium sulphate into a reference cell.

The TPH Analyzer was turned on and allowed to warm-up for 30 minutes.

The instrument was calibrated with working standards prepared from reference oil.

The analyzer was blanked with the extractant solvent and cell filled with sample inserted into the calibrated analyzer. The readings from the analyzer were then recorded. Plates 7 and 8 show some analysis being carried out at the NGGL Environment Laboratory.

Plate 7: TPH analyzer being used in the Laboratory

Plate 8: Sonication of soil in fume chamber

3.8.2 Determination of Oil and Grease in Soil by Gravimetric Method

Procedure for Oil and Grease analysis of soil by Gravimetry was carried out in accordance with standard methods for the examination of water and wastewater, (21st edition, 2005, method 5520-B) (Andrew *et al*., 2005).

Approximately 30 g soil sample was weighed into a 250 mL Schott bottle. 2 to 3 teaspoons of anhydrous Na_2S0_4 (more if the soil is very damp) was then put into the schott bottle. This was followed by measuring 30 mL of Freon Solvent and 2 mL concentrated Hydrochloric acid (HCl) to the Schott bottle. The Schott bottle was then coked and shaken vigorously to break up any aggregates. It was then sonicated for 10 minutes.

The supernatant liquid was poured off into a phase separator filter set in a glass funnel with approximately 10 g sodium sulphate and run into a pre-weighed beaker with 2 glass boiling chips added. 30 mL Freon Solvent was further added to the Schott bottle. The sonication and filtering process was repeated three times. The extracts were combined and evaporated to dryness on a hotplate at or below 70°C.

Sample was then cooled in a desiccator to constant weight. The weight was then recorded.

CALCULATION

$$\text{Oil and Grease (mg/kg, dry weight)} = \frac{B\text{-}A \times 10^6 \times F}{M}$$

Where:

B = final weight of beaker and residue, corrected for blank (g)

A = initial weight of beaker, corrected for blank (g)

M= weight of sample taken (g)

F = moisture factor

3.8.3 Determination of pH

Procedure for pH measurement of soil was carried out in accordance with standard methods for the examination of water and wastewater, (21st edition, 2005, method 5520-B) (Andrew *et al*., 2005).

The pH of the aqueous extract of all the contaminated soil, compost and topsoil were measured using the Orion-4-star pH-conductivity meter. The meter was first calibrated with pH buffers 4, 7 and 10 respectively. 25 g of the soil sample was weighed into a 1 L beaker. It was then mixed with 125 ml of distilled water and stirred for a period of 30 min. The pH of the supernatant water was then measured.

3.8.4 Moisture Content Analysis

Procedure for moisture content measurement of soil was carried out in accordance with standard methods for the examination of water and wastewater, (21st edition, 2005, method 5520-B) (Andrew *et al*., 2005).

A beaker was cleaned, dried and weighed (W1)

100 g of the soil sample was taken and weighed together with the beaker (W2). The sample was dried to constant temperature at 105 ^{0}C for a period of 24 hours. After drying, the sample was removed from the oven and cooled in a desiccator for 30 minutes. The final constant weight (W3) of the container with dried soil sample was recorded. The percentage moisture content in the soil is given by

$$W\ (\%) = [(W_2\text{-}W1)\text{-}(W_3\text{-}W1)/\ (W_2\text{-}W_1)]*100$$

Water was added to the various media on weekly basis to achieve the acceptable 40%-60% level range of moisture content

3.8.5 Determination of Total Nitrogen by Kjeldahl method

10 g of air dry soil was weighed into a 500 ml long – necked kjeldahl flask and followed by 10 ml distilled water. It was then allowed standing for 10 minutes to moisten. One spatula full of kjeldahl catalyst [mixture of l part Selenium + 10 parts $CuSO_4$ + 100 parts Na_2SO_4] and 20 ml conc. H_2SO_4 was then added. It was digested for a period of two hours until colorless or light greenish color was observed. It was further allowed to cool. The fluid was decanted into a 100 ml volumetric flask and make up to the mark with distilled water.

- DISTILLATION

An aliquot of 10 ml of fluid by means of pipette was transferred into the kjeldahl distillation apparatus provided. 20 ml of 40 % NaOH was dispensed. Distillate was collected over 10 ml of 4 % Boric acid and three (3) drops of mixed indicator in a 500 ml conical flask for 4 minutes. The presence of Nitrogen gave a light blue color.

- TITRATION

Collected distillate (about 100 ml) was titrated with 0.1 N HCl till blue color changes to grey and then suddenly flashes to pink. A blank determination was carried out without the soil sample.

- CALCULATION

The percentage of Nitrogen in the soil sample is,

$$\% N = \frac{14 \times (A - B) \times N \times 100}{1000 \times 1}$$

Where:

A = volume of standard HCl used in the sample titration

B = volume of standard HCl used in the blank titration

N = normality of standard HCl

3.8.6 Exchangeable cation determination (K)

Procedure for Exchangeable Cation measurement of soil was carried out in accordance with standard methods for the examination of water and wastewater, (21st edition, 2005, method 5520-B) (Andrew *et al*., 2005).

10 g of soil was weighed into extraction bottle. 100 ml of 1.0 N NH_4OAc solution was then added. Bottle with contents was placed in a mechanical shaker and shaken for 2 hours. The supernatant solution was filtered through No. 42 whatman filter paper.10 ml aliquot of it was taken and read for K or Na on a Flame Photometer after calibration of Photometer with prepared standards. Determination of the flame photometer reading for soil was done. Using the meter reading standard curve, the concentration of K in the soil extract was determined.

CHAPTER FOUR

4.0 RESULTS

4.1 BASELINE STUDIES ON THE CONTAMINATED SOIL

The baseline levels of TPH/Oil and Grease of the hydrocarbon contaminated soil from NGGL's volatilization pad and that of the compost and topsoil were determined. The rate of reduction of contaminants in the HCS as well as the increase in contaminants in the plants was also monitored. As the mean TPH levels in the soils decrease, the levels in the plants increased. This trend was similar to all the soil treatments. Table 5 shows the baseline concentrations of Oil & Grease / TPH for the contaminated soil, compost and topsoil.

Table 5: Mean Oil & Grease/TPH Baseline Concentrations in Media

Parameter / Sample ID	Oil and Grease Values (mg/kg)	TPH Values (mg/kg)
HCS	55278.00 ± 4028.00	37814.85 ± 1403.15
Topsoil	<10	<10
Compost	<10	<10

4.2 RESULTS OF OIL AND GREASE AND TPH FOR TOPSOIL, COMPOST AND FERTILIZER BLENDS

Mean Oil and Grease and TPH values of 55278.00 mg/kg and 37814.85 mg/kg respectively were the baseline concentrations of hydrocarbon contaminants in the soil. 0.2 % nitrogen level recorded the lowest reduction in contaminant concentration whiles 0.8 % nitrogen level recording the highest. Approximately 63.27 % reduction in Oil and Grease had occurred by the 26th week of the experiment in the 0.2 % topsoil blend. 83.06 % reduction had occurred by the same time in the 0.8 % nitrogen level. Statistically, there were differences ($p \leq 0.050$) in all four levels of nitrogen within the Topsoil blend. There were similarities in the degradation trends in the compost and fertilizer blends as compared to the topsoil blend. Table 6 shows some degradation trends in 0.2% and 0.8% nitrogen levels in the topsoil blend.

Table 6: Mean Oil and Grease Reduction Trends in 0.2% and 0.8% Topsoil Media

OIL AND GREASE REDUCTION TRENDS IN 0.2 % AND 0.8 % NITROGEN LEVELS OF THE TOPSOIL BLENDS (mg / kg)				
Sampling Period	**0.2 % N LEVEL**		**0.8 % N LEVEL**	
WEEKS	Concentration (mg / kg)	Reduction (%)	Concentration (mg / kg)	Reduction (%)
Week 0	55278.00 ± 4028.00	0	55278.00 ± 4028.00	0
Week 1	51255.66 ± 477.06	7.28	51290.10 ± 80.38	7.21
Week 2	48217.01 ± 209.32	12.78	45746.15 ± 73.96	17.24
Week 3	47807.31 ± 975.78	13.51	41808.65 ± 60.30	24.37
Week 4	45678.03 ± 320.77	17.37	38605.84 ± 158.00	30.16
Week 5	41740.05 ± 146.00	24.50	34445.64 ± 95.56	37.69
Week 9	36193.72 ± 210.07	34.52	29255.23 ± 44.75	47.08
Week 14	33058.29 ± 223.83	40.20	24447.17 ± 276.13	55.77
Week 17	30072.52 ± 254.40	45.60	15330.33 ± 164.04	72.27
Week 22	24548.25 ± 238.88	55.60	11997.32 ± 470.50	78.30
Week 26	20304.35 ± 919.92	63.27	9366.56 ± 759.19	83.06

4.3 TPH REDUCTION IN SOME SOIL BLENDS

Treatments J (0.4% Urea), K (0.6% Urea) and L (0.8% Urea) showed gradual TPH reduction over time. This reduction, however, was lower compared to those of the topsoil and compost blends. M (control sample) showed little reduction as stated earlier. Figure 8 shows TPH breakdown trends in some soil media.

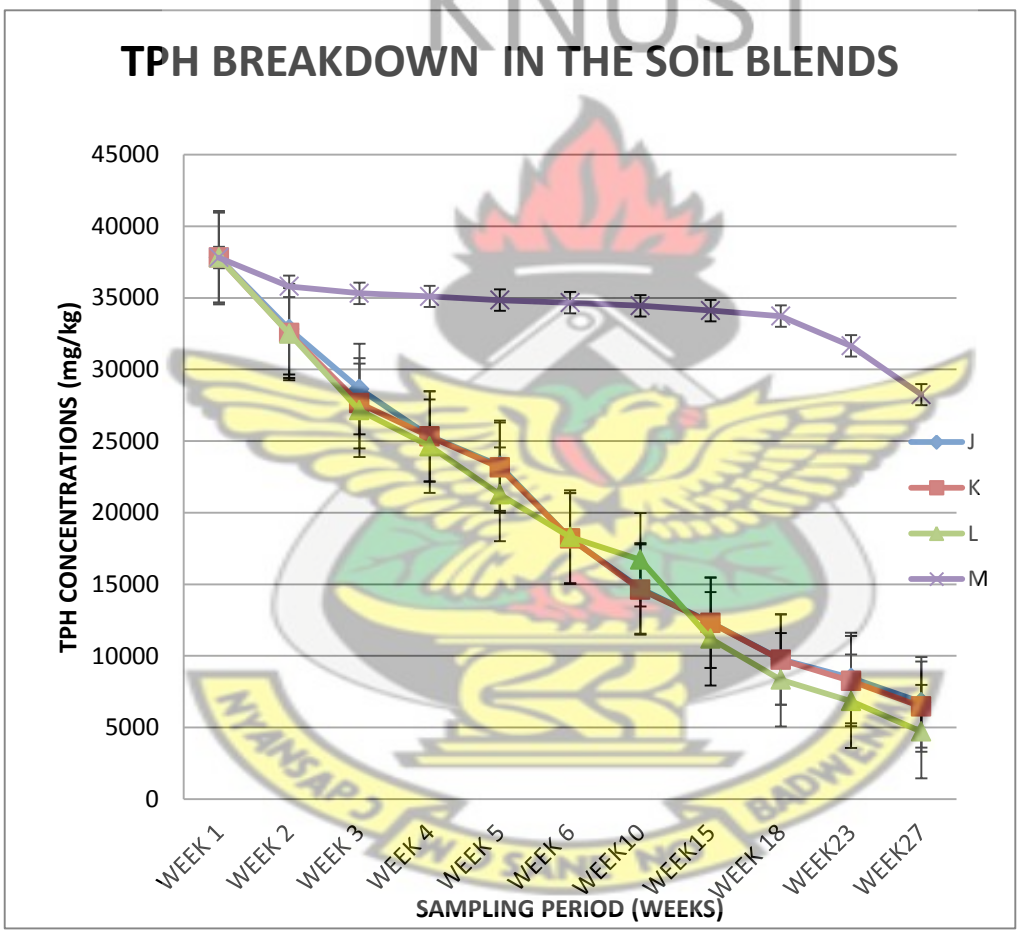

Figure 8: TPH Reduction Trends in some Soil Media

J- Contaminated Soil (4 kg) + Urea 0.4 % N	**K**- Contaminated Soil (4 kg) + Urea 0.6 % N	**L**- Contaminated Soil (4 kg) + Urea 0.8 % N	**M**- Contaminated Soil Only (4 kg) - Control

4.4 STATISTICAL ANALYSIS

The statistical software package used was Minitab with a follow up test using Tukey's Method. To determine whether there was significant breakdown in oil/grease and TPH, the analysis of variance approach was employed. The ANOVA at 95% confidence with a P value less than 5% showed that the treatment effects were not the same. The Tukey's Method (a multiple comparism test) further revealed that treatments D (HCS (4kg) + Topsoil 0.8%), B (HCS (4kg)+ Topsoil 0.4%), C (HCS (4kg) + Topsoil 0.6%), H (HCS (4kg) + Compost 0.8%) and K (HCS (4kg)+ Urea 0.6%) were significantly different from the other treatments in the absorption of oil/grease by the plants. Moreover, since their averages were higher than the others it implies that, it absorbed more oil/grease than the others. Similarly, that of TPH revealed that B, D, C were significantly different from the other treatments in the absorption of TPH by the plants. Moreover, since their mean averages were higher than the others, it implies it absorbed more TPH than the others.

4.5 DEGRADATION TRENDS

There was a gradual reduction in the concentrations of Oil and Grease / TPH in the various treatments. From a baseline situation of 0% reduction in the parameters, approximately 43.63% and 30.16% reduction had been recorded in TPH and Oil and Grease respectively by the 6th week of the experiment. There were, however higher percentage reduction in TPH than Oil and Grease for any particular week. Table 7 shows the percentage reductions in the contaminants from the start of the project to the 26th week in the 0.8% topsoil medium.

Table 7: Degradation Trend with Topsoil Blend (0.8% -Nitrogen)

PARAMETER / TIME (WEEKS)	MEAN OIL & GREASE VALUES (mg/l)	MEAN TPH VALUES (mg/l)	DECREASE IN OIL & GREASE (%)	DECREASE IN TPH (%)
week 0	55278.00 ± 4028.00	37814.85 ± 1403.15	0.00	0.00
week 1	51290.1 ± 80.38	32487.14± 175.14	7.21	14.10
week 2	45746.15 ± 73.96	27183.04 ± 165.91	17.24	28.12
week 3	41808.65 ± 60.29	24619.66 ± 137.55	24.37	34.90
week 4	38605.84 ± 157.99	21315.3 ± 91.01	30.16	43.63
week 5	34445.64 ± 95.56	18632.18 ± 617.97	37.69	50.73
week 9	29255.23 ± 44.75	16962.04 ± 197.78	47.08	55.14
week 14	24447.17 ± 276.13	11200.26 ± 185.34	55.77	70.38
week 17	15330.33 ± 164.04	8262.96 ± 191.57	72.27	78.15
week 22	11997.32 ± 570.49	6121.987 ± 18.84	78.30	83.81
week 26	9366.563 ± 759.19	4613.673 ± 987.13	83.06	87.80

By decommissioning stage, 83% to 88% reduction of the Oil and Grease / TPH contaminants had been achieved. This occurrence of breakdown of hydrocarbon was consistent with all the other different treatments. The rate of breakdown, however, differed from one treatment to the other.

4.6 RATE OF REDUCTION OF OIL & GREASE CONCENTRATION IN CONTROL SAMPLE (M)

The control sample i.e. the hydrocarbon contaminated soil without any augmentation, (as the case in NGGL), showed little reduction in mean Oil and Grease concentrations over time. Table 8 shows the slow rate of contaminant reduction in the control sample.

Table 8: Degradation Trend in Control Sample

Parameter / Sampling Period (Week)	MEAN OIL & GREASE CONCENTRATION (mg/kg)	REDUCTION IN CONCENTRATION (%)
0	55278.00 ± 4028.00	0
1	53714.43 ± 194.71	2.83
2	53255.75 ± 187.79	3.66
3	52340.40 ± 165.44	5.31
4	50805.02 ± 155.34	8.09
5	49331.63 ± 205.19	10.76
9	46183.96 ± 102.80	16.45
14	43212.67 ± 704.26	21.83

The Control sample performed poorly as far as degradation of the hydrocarbon contaminants are concerned.The mean values of Oil and Grease reduced steadily over time (refer to Table 5). As in the case of the volatilization pad at Newmont, the rate of degradation was slow. Plant's growth in the control sample was not encouraging. At a point some died because they lacked the basic nutrients needed for plant growth which the augmented soils provided. By the 14th week, approximately 22% reduction in Oil and Grease contaminants had been recorded as against the 0.8% topsoil blend's reduction of 56%. This phenomenon goes to buttress the point that optimum nutrient levels in soil is essential for plant growth and hence success of phytoremediation.

4.7 ABSORPTION OF CONTAMINANT BY PLANTS

As Oil and Grease / TPH mean concentrations reduced in the various media combinations, so did the plants record some levels of Oil and Grease / TPH. Oil and Grease mean concentrations of 1850.249 mg/kg, 2403.515 mg/kg and 1535.131 mg/kg were recorded on the 5th, 9th and 14th weeks respectively in plants picked at random on the 0.2% nitrogen level of the topsoil blend. Contaminant concentration in the plants increased as the plant matured.

4.8 CONTAMINANT DISTRIDUTION IN PLANTS

Some plants were selected at random and Oil and Grease analysis performed on them.The plants were separated into the root zone, the stem zone and the leaf zone. After analysis, it was realized that approximately 45% of the contaminants were stored in the root,18% in the stem and 37% in the leaf zone. Table 9 summarizes the contaminant distribution in the plants.

Table 9: Distribution of Contaminants in Plant

OIL & GREASE DISTRIBUTION IN PLANT			
	ROOT	STEM	LEAF
OIL & GREASE (mg / kg)	804.00 ± 17.79	320.00 ± 30.55	672.13 ± 55.65
PERCENTAGE (%)	45	18	37

The plants, however, could not account for all the contaminants that found their way out of the soil. Processes like volatilization and tranformation of hydrocarbons into other forms like water and carbon dioxide could account for that.

4.9 COMPARISON OF DIFFERENT LEVELS OF COMPOST, TOPSOIL AND FERTILIZER BLENDS

The 0.2% nitrogen level (mg/kg) in all three blends recorded the lowest oil and grease and TPH reduction. The residual Oil and Grease / TPH levels were thus higher in 0.2% compared to the 0.4%, 0.6% and the 0.8%. The higher the nitrogen augmentation in the various treatments, the higher the plant growth and thus the higher the reduction of the contaminants. 0.4% and 0.6% nitrogen levels performed almost the same in terms of Oil and Grease / TPH reduction. Table 10 shows the different nitrogen levels and their residual oil & grease concentrations by the 17th week of sampling in the Topsoil blend.

TABLE 10: Nitrogen Levels in Soil and Residual Oil & Grease Concentration

Nitrogen Levels (%) in Soil Blend	Mean Residual Oil & Grease Concentrations (mg/kg)
0.2	30072.52 ± 254.40
0.4	20546.26 ± 212.10
0.6	18832.35 ± 82.72
0.8	15330.33 ± 164.04

CHAPTER FIVE

5.0 DISCUSSION

5.1 LEVELS OF OIL & GREASE/TPH IN TOPSOIL, COMPOST, AND FERTILIZER BLENDS

Topsoil and compost samples used for the phytoremediation process did not show any initial concentrations of TPH and oil and grease contamination (Table 5). Topsoil and compost blends were similar in their ability to aid in plant growth. Their breakdown trends were comparable. Fertilizer blends had a slower rate of contaminant reduction. Though fertilizer (urea) enhances remediation of hydrocarbons in soils, not all phytoremediation processes respond to fertilizer augmentations as asserted by Venosa & *Zhu* (2003).

5.2 TOPSOIL / HYDROCARBON CONTAMINATED SOIL BLEND

Degradation of Oil and Grease / TPH in the topsoil blend for the various percentages of nitrogen levels, as seen in their mean values, was higher as compared to those of fertilizer. This is attributed to the fact that, the topsoil was rich in microorganisms and also had well stratified layers with air spaces. These helped in the growth of the plant and the subsequent bioaccumulation of the hydrocarbon contaminants. However, compost blends had higher degradation trends than topsoil. By the 26th week, residual concentrations of Oil and Grease in the 0.2% nitrogen levels were 15435.26 mg/kg, 19320.18 mg/kg and 23680.25 mg/kg for compost, topsoil and fertilizer respectively.

Percentage degradation for TPH followed the increasing order of 0.2 %< 0.4 %,< 0.6 %< 0.8%. Nitrogen is essential for plant growth and the higher the concentration the better it is for the plants to grow. At the Naval Air Station Reserve Base in the US, phytoremediation with particular emphasis on nitrogen augmentation of the soil gave a similar assertion of the need for higher nitrogen levels (Betts, 1997). The growth of the plant meant increase in the bioaccumulation. In both oil and grease and TPH, the lowest residual mean was recorded by 0.2% whereas 0.8% recorded the highest. (Refer to appendix C). The topsoil served the needs of the plant by providing water, air, nutrients and stability.

5.3 COMPOST / HYDROCARBON CONTAMINATED SOIL BLEND

Oil and Grease concentrations in the compost blend of soils had reduced from the initial mean value of 55278.00 mg/kg to 15435.26 mg/kg, 14800.10 mg/kg, 12301.11 mg/kg and 10540.33 mg/kg for the 0.2%, 0.4%, 0.6% and 0.8% nitrogen levels respectively. Growth of plant was evidently seen on the compost media as compared to the fertilizer media. 0.8% nitrogen level recorded the highest amount of Oil and Grease / TPH reduction with 0.2% recording the least. The rapid degradation of hydrocarbons in the compost system was expected since compost has the potential of improving soil structure, texture, and aeration capacity as was also asserted by Marx, (1999). A paper titled "Effect of compost in phytoremediation of diesel-contaminated soils" (Vouillamoz, 2001) asserts to the fact that the compost helps in phytoremediation of diesel-contaminated soil independent of the dilution effect that compost addition has. Several researchers have demonstrated that earthworm castings (vermicompost) have excellent aeration, porosity, structure, drainage, and moisture-holding capacity. The compost is a rich source of

beneficial microorganisms and nutrients and is used as a soil conditioner or fertilizer (Dickerson, 2004). Rapid increase in crop yield, soil nutrients status and nutrients uptake was reported due to application of compost, an assertion also made by Heenkende, (2011).

5.4 FERTILIZER / HYDROCARBON CONTAMINATED SOIL BLEND

A recent assessment found that about 40 to 60% of crop yields are attributable to commercial fertilizer use (Stewart *et al*., 2005). This formed the basis of the addition of fertilizer to the HCS prior to the commencement of the remediation process.

Surprisingly, fertilizer blends were the least performers compared to topsoil and compost. The poor performance can be explained by referring to some statements by Erv Evans, Consumer Horticulturist, NC State University, 2000 in a publication titled "A Gardener's Guide to Fertilizing Trees and Shrubs. He stated that "Many gardeners have the false impression that the more fertilizer they apply the more the plant will grow. Fertilizer is not plant food. Plants use water, carbon dioxide, elements from fertilizer, and energy from the sun to produce their own food". Also there is an assertion by Erv, (2000) that: fertilizer application to seeds planted is more effective for their growth than for already grown plants as in the case of this experiment. Also addition of excessive nitrogen fertilizer can result in an increase in soil salinity and thus will cause an increase in osmotic stress and suppresses the activity in hydrocarbon-degrading organisms (Walworth *et al*.,2003).

The stabilization after the mixing of the fertilizer with the contaminated soil took some time and thus whiles plants on the topsoil and compost started growing, that of the fertilizer delayed. By the second week, residual TPH levels in the 0.2%, 0.4%, 0.6% and 0.8% nitrogen levels in the fertilizer blend were 33990.50 mg/kg, 32702.43 mg/kg, 32592.47 mg/kg and 32400.90 mg/kg respectively.

5.5 ABSORPTION OF CONTAMINANTS BY *CHROMOLAENA ODORATA*

Several literature support the fact that plants can contribute to the removal of pollutants from soil. Gunther *et al.* (1996) asserts to the fact that direct interaction of plant roots with hydrocarbons in the soil by sorption, uptake and transport results in this. The *Chromolaena odorata* plants picked at random from the various bowls and subjected to analysis, recorded some contaminants levels in them. Further tests revealed storage of greater amounts of these contaminants at the root zone, as asserted by Gunther *et al*. (1996). The leaf zone recorded higher storage than the stem zone.

5.6 COMPARING DIFFERENT BLENDS: COMPOST, TOPSOIL AND FERTILIZER

Compost- hydrocarbon blend recorded the highest amounts of degradation, followed by the topsoil blend and then the fertilizer blend. This is evident in the results table of appendix C. The rapid degradation of hydrocarbons in the compost-hydrocarbon blend was expected since compost is rich in nutrients and has additional qualities such as improving soil structure, texture, and aeration capacity. The topsoil blend also did very well especially at the initial stages. The fertilizer took some time to mix well with the contaminated soil. This affected the early growth of the plants and thus their slowness in absorbing the contaminants.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSION

Phytoremediation, from the research has been recognized as a suitable tool to restore contaminated sites. The study showed that, *Chromolaena odorata* (Siam weed) has high bioaccumulation and translocation potential. This fact manifested in the plants being able to drastically reduce the high levels of hydrocarbon contaminants in the soils to very minimal levels over time. Augmentation of soil with topsoil, compost and fertilizer was also beneficial in creating the optimum conditions for the plants to grow, thereby making phytoremediation a success. There was significant degradation of hydrocarbon contaminated soil with the nutrient addition. Compost gave the best results with respect to hydrocarbon removal, followed by topsoil and fertilizer. Generally, there was a pattern of reduction of Oil and Grease/TPH concentrations within all the blends with the order of increasing performance as 0.2 %, < 0.4 %, < 0.6% and <0.8% of the three nitrogen sources (Compost, Topsoil and Fertilizer). It was also observed that the contaminants absorbed by the plants were distributed in the root, leaf and stem zones of the plant. After analysis,it was realized that,approximately 45% of the contaminants were stored in the root,18% in the stem and 37 % in the leaf zone. Soil media of nitrogen levels of 0.4 % topsoil, 0.6 % topsoil, 0.8 % topsoil, 0.8 % compost and 0.6 % Urea, from the analysis of the results, were the best performers i.e. they had high ability to degrade the contaminants. From the above, it can be concluded that phytoremediation using 0.8%

nitrogen level of the compost blend is highly recommended for Newmont's hydrocarbon degradation program.

6.2 RECOMMENDATIONS

- Newmont's topsoil deficiency situation for future reclamation activities, coupled with the fact that artificial fertilizer (urea) has adverse negative effect on microbial populations tend not to support the use of topsoil and fertilizer for this particular phytoremediation project. It is therefore recommended that the 0.8% nitrogen level of the compost blend be adopted for remedial purposes.
- Seeds of *Chromolaena odorata* could also be used in future works to compare to the cuttings that were used for this particular experiment.
- Further studies should be done using higher levels of nitrogen
- Aged soils are more difficult to phytoremediate than freshly contaminated ones. Therefore it is recommended that phytoremediation is done quickly on soils freshly contaminated than aged ones.

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6.4 APPENDICES

6.4.1 Appendix A

Calculations for the Quantities of Topsoil, Compost and Fertilizer added to the Contaminated Soil for Augmentation

4Kg of contaminated soil was put in each of the bowls for the experiment. Nitrogen percentages of **0.2 %, 0. 4%, 0.6% and 0.8%** were desired for all the three media

For Topsoil

Nitrogen level in topsoil	0.35%
Nitrogen level in H-C	0.08%
Weight of HC cont. soil used	4000g

For 0.2%

Weight of 0.2%N in H-C	3.2 g
Actual Weight of 0.2%N in H-C	8.0 g
Nitrogen Deficit /g	4.8 g

If 0.35 g = 100 g ,then 4.8 g = 1371.4 g

Quantity of Topsoil therefore to add to the H-C to obtain 0.2%N level is 1371.4 g

For 0.4%

Weight of 0.4%N in H-C	3.2 g
Actual Weight of 0.4%N in H-C	16 g
Nitrogen Deficit /g	12.8 g

If 0.35 g = 100 g ,then 12.8 g = 3657.1 g

Quantity of Topsoil therefore to add to the H-C to obtain 0.2%N level is 3657.1 g

Similar calculations were done for the 0.6% and 0.8% topsoil blends and also for the compost and fertilizer blends. The quantities obtained are shown below:

LEVELS OF NITROGEN (%)	COMPOST/ (g)	TOPSOIL/ (g)	FERTILIZER/ (g)
0.2	600	1371.4	10.4
0.4	1600	3657.1	12.8
0.6	2600	5942.9	45.2
0.8	3600	8228.6	62.6

6.4.2 Appendix B

STATISTICAL ANALYSIS

To determine whether there is significant breakdown in oil/grease and TPH the analysis of variance approach is employed. The following hypotheses are tested at 5% significant level using Minitab:

H_0: Treatment effects are the same

H_1: Treatment effects are all not the same

Analysis of Variance for OIL AND GREASE

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TREATMENT	12	6584594955	6584594955	548716246	89.69	0.000
TIME	10	61028163673	61028163673	6102816367	997.57	0.000
Error	380	2324723747	2324723747	6117694		
Total	402	69937482375				

S = 2473.40 R-Sq = 96.68%

Analysis of Variance for TPH

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TREATMENT	12	6614109173	6614109173	551175764	101.56	0.000
TIME	10	31633119687	31633119687	3163311969	582.87	0.000
Error	380	2062326489	2062326489	5427175		
Total	402	40309555349				

S = 2329.63 R-Sq = 94.88%

Analysis of variance for OIL AND GREASE

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TREATMENT	12	65980178	65980178	5498348	9.59	0.000
TIME	5	52310460	52310460	10462092	18.24	0.000
Error	216	123882090	123882090	573528		
Total	233	242172728				

Analysis of Variance for TPH

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TREATMENT	12	34082997	34082997	2840250	8.74	0.000
TIME	5	33906379	33906379	6781276	20.87	0.000
Error	216	70177543	70177543	324896		
Total	233	138166918				

Grouping Information Using Tukey Method for OIL AND GREASE

TREATMENT	N	Mean	Grouping
D	18	3216.3	A
B	18	3136.6	A
C	18	2569.2	A B
H	18	2466.5	A B C
G	18	2217.3	B C
F	18	2118.7	B C D
E	18	2082.4	B C D
L	18	1994.9	B C D
A	18	1898.7	B C D
K	18	1807.7	B C D
I	18	1738.0	B C D
J	18	1648.3	C D
M	18	1344.0	D

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method for TPH

TREATMENT	N	Mean	Grouping
B	18	2257.2	A
D	18	1837.2	A B
C	18	1657.5	A B
I	18	1517.6	B
F	18	1509.7	B
G	18	1490.4	B
A	18	1476.7	B
H	18	1466.2	B
E	18	1461.9	B
K	18	1252.0	B
L	18	1241.9	B
J	18	1238.6	B
M	18	495.5	C

Means that do not share a letter are significantly different.

6.4.3 Appendix C

Table of Results

Oil and Grease Concentrations in Soil (Replicate 1)

RI		OIL AND GREASE IN SOIL										
	DATE	13/09/10	20/09/10	27/09/10	4/10/2010	11/10/2010	18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
	WKS.	week 1	week 2	week 3	week 4	week 5	week 6	week 10	week 15	week 18	week 23	week 27
TREATMENT		BASELINE	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9	SD10
A		55278.00	51303.61	48223.12	47100.66	45812.00	41789.72	36200.15	33001.96	29978.50	24520.00	19320.18
B		55278.00	51321.60	47420.66	46850.00	42511.72	37500.10	33011.90	25480.50	20562.41	18783.90	14734.23
C		55278.00	51317.66	46550.10	42210.50	37500.10	33011.90	27480.50	23562.41	18740.30	15430.24	12458.14
D		55278.00	51290.65	45750.00	41805.00	38600.70	34441.44	29255.20	24480.50	15355.00	12573.38	9682.34
E		55278.00	50301.61	48000.10	46800.50	43812.44	40650.11	35700.43	28864.20	21770.40	18945.00	15435.26
F		55278.00	51285.60	48300.11	46900.54	42712.38	40600.11	35700.50	27462.20	22770.40	17540.13	14800.10
G		55278.00	50060.23	47680.11	46800.52	42812.44	38650.11	34700.43	27864.20	19570.40	16300.93	12301.11
H		55278.00	50000.50	49002.10	46500.55	44812.44	37650.11	33700.43	26864.20	17770.4	15690.56	10540.33
I		55278.00	52503.11	48817.10	47470.26	45982.99	42769.72	37290.05	34000.96	30798.52	25820.66	23680.25
J		55278.00	52312.64	47550.10	42210.50	37500.10	33011.90	27480.50	23562.41	20740.30	18568.90	16700.5
K		55278.00	52000.63	46550.10	42210.50	37500.10	33011.90	27480.50	23562.41	18740.30	16336.19	13130.99
L		55278.00	51807.24	45750.00	41805.00	38600.70	34441.44	29255.20	24480.50	15355.00	13468.32	11238.41
M		55278.00	53724.00	53340.50	52170.21	50978.32	49341.60	46082.11	43897.45	40705.00	36400.10	32524.23

Oil and Grease Concentrations in Soil (Replicate 2)

R2		OIL AND GREASE IN SOIL										
	DATE	13/09/10	20/09/10	27/09/10	4/10/2010	11/10/2010	18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
	WKS.	week 1	week 2	week 3	week 4	week 5	week 6	week 10	week 15	week 18	week 23	week 27
TREATMENT		BASELINE	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9	SD10
A1		55278.00	51706.94	48423.21	47400.62	45312.00	41854.73	35980.50	32868.00	29878.52	24324.76	20450.32
B1		55278.00	51550.72	47150.55	46920.44	42302.77	37850.24	32876.36	25734.00	20326.55	18916.11	15856.01
C1		55278.00	51120.34	46582.67	42265.45	37720.92	34026.32	27222.90	23654.01	18856.31	14817.40	11684.44
D1		55278.00	51209.45	45818.11	41750.26	38450.48	34543.23	29210.50	24705.12	15155.35	11432.57	9916.90
E1		55278.00	50120.50	48210.35	46625.13	42679.01	40210.90	35945.45	28755.36	21070.00	18992.39	15450.56
F1		55278.00	51205.45	48350.20	47200.38	42500.00	40740.26	35650.03	27517.35	21500.56	17500.00	14363.15
G1		55278.00	51300.45	47450.35	46876.89	42546.11	38715.90	34543.23	27950.36	20614.79	16150.15	13947.33
H1		55278.00	49860.22	49500.36	46250.00	44915.75	37502.67	33820.35	26608.22	17820.34	15540.69	12405.00
I1		55278.00	52814.16	48605.90	47548.28	45828.96	42618.32	37320.50	34037.51	30548.37	25628.16	21863.73
J1		55278.00	52620.19	47443.45	42367.86	37725.14	32950.17	27654.20	23225.35	20500.11	18421.56	15348.67
K1		55278.00	52200.16	46470.20	42156.11	37585.15	32960.44	27510.50	23300.17	18555.50	16407.90	13540.24
L1		55278.00	52042.18	45580.77	41968.28	38430.23	34250.60	29360.55	24401.64	15489.68	13260.60	11790.83
M1		55278.00	53904.17	53040.52	52350.35	50758.44	49121.63	46182.10	43250.15	40008.12	36540.61	33400.0

Oil and Grease Concentrations in Soil (Replicate 3)

R3		OIL AND GREASE IN SOIL										
	DATE	13/09/10	20/09/10	27/09/10	4/10/2010	11/10/2010	18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
	WKS.	week 1	week 2	week 3	week 4	week 5	week 6	week 10	week 15	week 18	week 23	week 27
TREATMENT		BASELINE	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9	SD10
A2		55278.00	50756.44	48004.71	48920.66	45910.10	41575.70	36400.50	33304.90	30360.55	24800.00	21142.56
B2		55278.00	51102.65	47722.56	46652.9	42719.30	37249.01	33220.65	25150.40	20749.82	18520.98	15740.57
C2		55278.00	51524.14	46539.69	42186.57	37260.22	33018.45	27618.66	23402.44	18900.45	15482.97	11263.22
D2		55278.00	51370.2	45670.35	41870.68	38766.33	34352.24	29300.00	24155.89	15480.63	11986.01	8500.45
E2		55278.00	50565.11	47855.20	46980.25	43782.16	40850.22	35602.89	28678.47	22344.29	18876.40	16056.98
F2		55278.00	51332.55	48252.42	46615.35	42895.48	40516.68	35689.00	27391.23	23750.11	17582.50	14155.20
G2		55278.00	51280.2	47840.44	46718.9	42950.19	38600.40	34933.62	27688.45	21055.10	16448.46	13300.06
H2		55278.00	51022.17	49246.83	46720.45	44730.23	37714.41	33622.40	26985.50	17618.12	15765.22	12900.28
I2		55278.00	52312.76	48954.39	47382.45	45916.24	42834.17	37160.43	34086.52	30874.18	25950.50	22714.34
J2		55278.00	52117.20	47655.61	42513.37	37322.38	33121.50	27301.10	23770.00	20901.28	17854.89	14540.12
K2		55278.00	52134.19	46670.77	42309.59	37432.17	33080.75	27345.32	23637.45	18840.66	16251.00	13548.55
L2		55278.00	51224.01	45903.32	41716.82	38768.47	34613.45	29191.35	24500.04	15225.30	13610.34	13035.47
M2		55278.00	53515.11	53386.22	52500.65	50678.31	49531.65	46287.67	42490.42	40925.01	36306.44	32690.66

TPH Concentrations in Soil (Replicate 1)

RI		TPH IN SOIL										
	DATE	13/09/10	20/09/10	27/09/10	4/10/2010	11/10/2010	18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
	WKS.	week 1	week 2	week 3	week 4	week 5	week 6	week 10	week 15	week 18	week 23	week 27
TREATMENT		BASELINE	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9	SD10
A		37814.85	33592.41	30134.30	29450.00	26845.21	24500.65	20046.90	16125.20	12204.65	9054.11	7200.38
B		37814.85	33291.50	29780.00	27665.21	25300.65	23146.90	18205.20	14604.65	10345.90	7076.00	5690.22
C		37814.85	32590.43	27665.21	25300.65	23146.90	18205.20	14604.65	12345.90	9780.20	6525.35	4300.50
D		37814.85	32305.83	27180.00	24665.21	21302.60	18300.77	16980.00	11210.11	8261.50	6135.50	3900.11
E		37814.85	32592.45	29135.66	28740.00	26500.60	22842.10	18290.22	12764.39	9680.45	8700.11	6450.45
F		37814.85	32502.76	30135.66	27740.00	26000.60	23842.10	17290.22	12764.39	9600.45	7220.50	5502.55
G		37814.85	32400.43	29135.66	27244.00	25500.60	22842.10	16295.22	12000.39	9450.45	6802.13	4730.70
H		37814.85	32305.21	29000.60	28740.00	24501.60	21315.10	17590.22	12764.39	9280.45	6005.46	4320.34
I		37814.85	33990.47	30234.30	29850.11	27805.26	25100.68	20646.94	16752.22	12454.65	9864.10	7650.68
J		37814.85	32702.44	28665.21	25300.65	23146.90	18205.20	14604.65	12345.90	9780.20	8458.66	6521.62
K		37814.85	32592.41	27665.21	25300.65	23146.90	18205.20	14604.65	12345.90	9780.20	8219.17	6600.90
L		37814.85	32400.41	27180.00	24665.21	21302.60	18300.77	16980.00	11210.11	8261.50	6849.16	4011.32
M		37814.85	35812.43	35352.41	35095.57	34914.00	34612.90	34321.45	34218.26	33827.60	31644.00	28500.30

TPH Concentrations in Soil (Replicate 2)

R2		TPH IN SOIL										
	DATE	13/09/10	20/09/10	27/09/10	4/10/2010	11/10/2010	18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
	WKS.	week 1	week 2	week 3	week 4	week 5	week 6	week 10	week 15	week 18	week 23	week 27
TREATMENT		BASELINE	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9	SD10
A1		37814.85	32820.48	30300.35	29250.25	26800.00	24604.65	20082.72	16187.50	12294.51	9112.20	7350.56
B1		37814.85	32320.34	29940.11	27516.65	25571.21	23285.00	18315.39	14440.13	10432.72	7034.12	6470.44
C1		37814.85	32450.65	28430.00	25560.11	23410.26	18100.00	14655.70	12417.25	9620.40	6630.00	4823.46
D1		37814.85	32500.22	27350.44	24465.11	21412.00	19345.16	16755.89	11010.20	8455.26	6100.46	4200.69
E1		37814.85	33817.61	29060.90	28831.56	26320.49	23021.00	18236.62	12855.00	9420.54	8805.16	7118.11
F1		37814.85	32686.45	30240.32	27700.81	26460.47	24100.21	18150.20	12700.36	9645.32	7216.10	6354.00
G1		37814.85	32350.22	29032.15	27285.20	25000.00	23014.34	17300.80	12100.76	9240.12	6880.13	5741.94
H1		37814.85	32150.34	29120.45	28550.90	24705.10	21180.22	17617.64	12550.45	9400.00	6145.20	5143.35
I1		37814.85	33540.32	30417.45	29623.33	27865.21	25341.16	21079.20	16846.90	12378.33	10002.56	8642.68
J1		37814.85	32750.23	28738.19	25205.15	23446.48	18317.14	15090.16	12143.89	9550.00	8250.12	8005.00
K1		37814.85	32320.68	27812.45	25250.01	23243.78	18115.80	14750.56	12155.23	9883.76	8500.00	7655.25
L1		37814.85	32746.35	27239.97	24430.46	21000.50	18155.15	16450.47	11084.19	8415.34	6802.11	5504.45
M1		37814.85	35702.68	35485.22	35195.64	34853.00	34718.44	34556.33	34006.22	33630.64	31845.45	28764.0

TPH Concentrations in Soil (Replicate 3)

R3		TPH IN SOIL										
	DATE	13/09/10	20/09/10	27/09/10	4/10/2010	11/10/2010	18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
	WKS.	week 1	week 2	week 3	week 4	week 5	week 6	week 10	week 15	week 18	week 23	week 27
TREATMENT		BASELINE	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9	SD10
A2		37814.85	32240.81	30010.52	29652.00	26882.11	24408.22	20010.10	16112.86	12179.20	9000.60	7110.56
B2		37814.85	32705.35	29480.26	27866.53	25138.58	23055.72	18123.22	14754.35	10212.00	7096.11	6420.68
C2		37814.85	32630.23	27352.10	25166.40	22867.80	18314.15	14482.31	12210.11	9824.66	6418.19	6056.00
D2		37814.85	32655.37	27018.67	24728.66	21231.31	18250.60	17150.24	11380.48	8072.12	6130.00	5740.22
E2		37814.85	32046.1	29170.42	28653.67	26654.30	22714.67	18315.90	12680.23	9802.31	8603.20	7430.25
F2		37814.85	32775.12	30049.30	27782.39	26225.00	23416.38	17069.00	12814.55	9565.58	7226.66	6439.86
G2		37814.85	32400.31	29242.50	27207.70	25815.66	22640.77	17459.22	12050.45	9635.10	6755.60	6228.12
H2		37814.85	32417.16	29210.36	28920.33	24355.30	21476.24	17420.11	12923.68	9055.01	6220.16	5450.55
I2		37814.85	33855.70	30100.19	29980.00	27742.45	25172.45	21139.20	16662.00	12600.12	9115.60	6417.32
J2		37814.85	32985.42	28524.65	25503.21	23250.60	18121.10	14434.78	12501.67	9930.34	8666.16	5771.90
K2		37814.85	32716.00	27456.11	25422.36	23065.45	18310.66	14550.30	12428.31	9560.48	8016.12	5118.64
L2		37814.85	32364.17	27053.37	24814.24	21542.69	18461.30	16712.67	11297.25	8345.25	6886.22	4656.00
M2		37814.85	35900.40	35117.44	35005.52	34765.90	34657.93	34456.45	34109.52	33720.68	31448.12	27450.22

Change in Oil and Grease Concentrations in Soil

Replicate 1

△ IN OIL AND GREASE IN SOIL					
18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/2011
SD5	SD6	SD7	SD8	SD9	SD10
4022.28	5589.57	3198.19	3023.46	5458.50	5199.82
5011.62	4488.20	7531.40	4918.09	1778.51	4049.67
4488.20	5531.40	3918.09	4822.11	3310.06	2972.10
4159.26	5186.24	4774.70	9125.50	2781.62	2891.04
3162.33	4949.68	6836.23	7093.80	2825.40	3509.74
2112.27	4899.61	8238.30	4691.80	5230.27	2740.03
4162.33	3949.68	6836.23	8293.80	3269.47	3999.82
7162.33	3949.68	6836.23	9093.80	2079.84	5150.23
3213.27	5479.67	3289.09	3202.44	4977.86	2140.41
4488.20	5531.40	3918.09	2822.11	2171.40	1868.40
4488.20	5531.40	3918.09	4822.11	2404.11	3205.20
4159.26	5186.24	4774.70	9125.50	1886.68	2229.91
1636.72	3259.49	2184.66	3192.45	4304.90	3875.87

Replicate 2

3457.27	5874.23	3112.50	2989.48	5553.76	3874.44
4452.53	4973.88	7142.36	5407.45	1410.44	3060.10
3694.60	6803.42	3568.89	4797.70	4038.91	3132.96
3907.25	5332.73	4505.38	9549.77	3722.78	1515.67
2468.11	4265.45	7190.09	7685.36	2077.61	3541.83
1759.74	5090.23	8132.68	6016.79	4000.56	3136.85
3830.21	4172.67	6592.87	7335.57	4464.64	2202.82
7413.08	3682.32	7212.13	8787.88	2279.65	3135.69
3210.64	5297.82	3282.99	3489.14	4920.21	3764.43
4774.97	5295.97	4428.85	2725.24	2078.55	3072.89
4624.71	5449.94	4210.33	4744.67	2147.60	2867.66
4179.63	4890.05	4958.91	8911.96	2229.08	1469.77
1636.81	2939.53	2931.95	3242.03	3467.51	3140.61

Replicate 3

4334.40	5175.20	3095.60	2944.35	5560.55	3657.44
5470.29	4028.36	8070.25	4400.58	2228.84	2780.41
4241.77	5399.79	4216.22	4501.99	3417.48	4219.75
4414.09	5052.24	5144.11	8675.26	3494.62	3485.56
2931.94	5247.33	6924.42	6334.18	3467.89	2819.42
2378.80	4827.68	8297.77	3641.12	6167.61	3427.30
4349.79	3666.78	7245.17	6633.35	4606.64	3148.40
7015.82	4092.01	6636.90	9367.38	1852.90	2864.94
3082.07	5673.74	3073.91	3212.34	4923.68	3236.16
4200.88	5820.40	3531.10	2868.72	3046.39	3314.77
4351.42	5735.43	3707.87	4796.79	2589.66	2702.45
4155.02	5422.10	4691.31	9274.74	1614.96	574.87
1146.66	3243.98	3797.25	1565.41	4618.57	3615.78

Oil and Grease Concentrations in plants

Replicate 1

OIL AND GREASE IN PLANT					
18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/2011
SD5	SD6	SD7	SD8	SD9	SD10
1850.249	2403.515	1535.131	1451.2608	2456.325	2339.919
3808.831	2917.33	5347.294	3245.9394	1244.957	2834.769
2692.92	3318.84	2350.854	2893.266	1986.036	1783.26
2745.112	3422.918	3151.302	6022.83	1835.869	1908.0864
1423.049	2227.356	3076.304	3192.21	1271.43	1579.383
950.5215	2204.825	3707.235	2111.31	2353.622	1233.0135
1873.049	1777.356	3076.304	3732.21	1471.262	1799.919
3223.049	1777.356	3076.304	4092.21	935.928	2317.6035
1445.972	2465.852	1480.091	1441.098	2240.037	963.1845
2019.69	2489.13	1763.141	1269.9495	977.13	840.78
2019.69	2489.13	1763.141	2169.9495	1081.85	1442.34
1871.667	2333.808	2148.615	4106.475	849.006	1003.4595
736.524	1466.771	983.097	1436.6025	1937.205	1744.1415

Replicate 2

1624.917	2349.692	1494	1405.0556	2332.579	1627.2648
3250.347	3233.022	5071.076	3514.8425	987.308	2142.07
2216.76	4082.052	2141.334	2878.62	2423.346	1879.776
2578.785	3519.602	2973.551	6302.8482	2457.035	1000.3422
1184.693	2047.416	3451.243	3688.9728	997.2528	1700.0784
844.6752	2443.31	3903.686	2888.0592	1920.269	1505.688
1838.501	2002.882	3164.578	3521.0736	2143.027	1057.3536
3558.278	1767.514	3461.822	4218.1824	1094.232	1505.1312
1541.107	2542.954	1575.835	1674.7872	2361.701	1806.9264
2291.986	2542.066	2125.848	1308.1152	997.704	1474.9872
2219.861	2615.971	2020.958	2277.4416	1030.848	1376.4768
2006.222	2347.224	2380.277	4277.7408	1069.958	705.4896
785.6688	1410.974	1407.336	1556.1744	1664.405	1507.4928

Replicate 3

1950.48	2277.088	1454.932	1383.8445	2557.853	1682.4224
4102.718	2618.434	5729.878	2904.3828	1560.188	1946.287
2545.062	3239.874	2529.732	2701.194	2050.488	2531.85
2913.299	3334.478	3395.113	5725.6716	2306.449	2300.4696
1231.415	2203.879	2908.256	2660.3556	1456.514	1184.1564
999.096	2027.626	3485.063	1529.2704	2590.396	1439.466
1826.912	1540.048	3042.971	2786.007	1934.789	1322.328
2946.644	1718.644	2787.498	3934.2996	778.218	1203.2748
1294.469	2382.971	1291.042	1349.1828	2067.946	1359.1872
1764.37	2444.568	1483.062	1204.8624	1279.484	1392.2034
1827.596	2408.881	1557.305	2014.6518	1087.657	1135.029
1745.108	2277.282	1970.35	3895.3908	678.2832	241.4454
481.5972	1362.472	1594.845	657.4722	1939.799	1518.6276

Change in TPH Concentrations in Soil

Replicate 1

Δ IN TPH IN SOIL					
18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
SD5	SD6	SD7	SD8	SD9	SD10
2344.56	4453.75	3921.70	3920.55	3150.54	1853.73
2153.75	4941.70	3600.55	4258.75	3269.90	1385.78
4941.70	3600.55	2258.75	2565.70	3254.85	2224.85
3001.83	1320.77	5769.89	2948.61	2126.00	2235.39
3658.50	4551.88	5525.83	3083.94	980.34	2249.66
2158.50	6551.88	4525.83	3163.94	2379.95	1717.95
2658.50	6546.88	4294.83	2549.94	2648.32	2071.43
3186.50	3724.88	4825.83	3483.94	3274.99	1685.12
2704.58	4453.74	3894.72	4297.57	2590.55	2213.42
4941.70	3600.55	2258.75	2565.70	1321.54	1937.04
4941.70	3600.55	2258.75	2565.70	1561.03	1618.27
3001.83	1320.77	5769.89	2948.61	1412.34	2837.84
301.10	291.45	103.19	390.66	2183.60	3143.70

Replicate 2

2195.35	4521.93	3895.22	3892.99	3182.31	1761.64
2286.21	4969.61	3875.26	4007.41	3398.60	563.68
5310.26	3444.30	2238.45	2796.85	2990.40	1806.54
2066.84	2589.27	5745.69	2554.94	2354.80	1899.77
3299.49	4784.38	5381.62	3434.46	615.38	1687.05
2360.26	5950.01	5449.84	3055.04	2429.22	862.10
1985.66	5713.54	5200.04	2860.64	2359.99	1138.19
3524.88	3562.58	5067.19	3150.45	3254.80	1001.85
2524.05	4261.96	4232.30	4468.57	2375.77	1359.88
5129.34	3226.98	2946.27	2593.89	1299.88	245.12
5127.98	3365.24	2595.33	2271.47	1383.76	844.75
2845.35	1704.68	5366.28	2668.85	1613.23	1297.66
134.56	162.11	550.11	375.58	1785.19	3081.45

Replicate 3

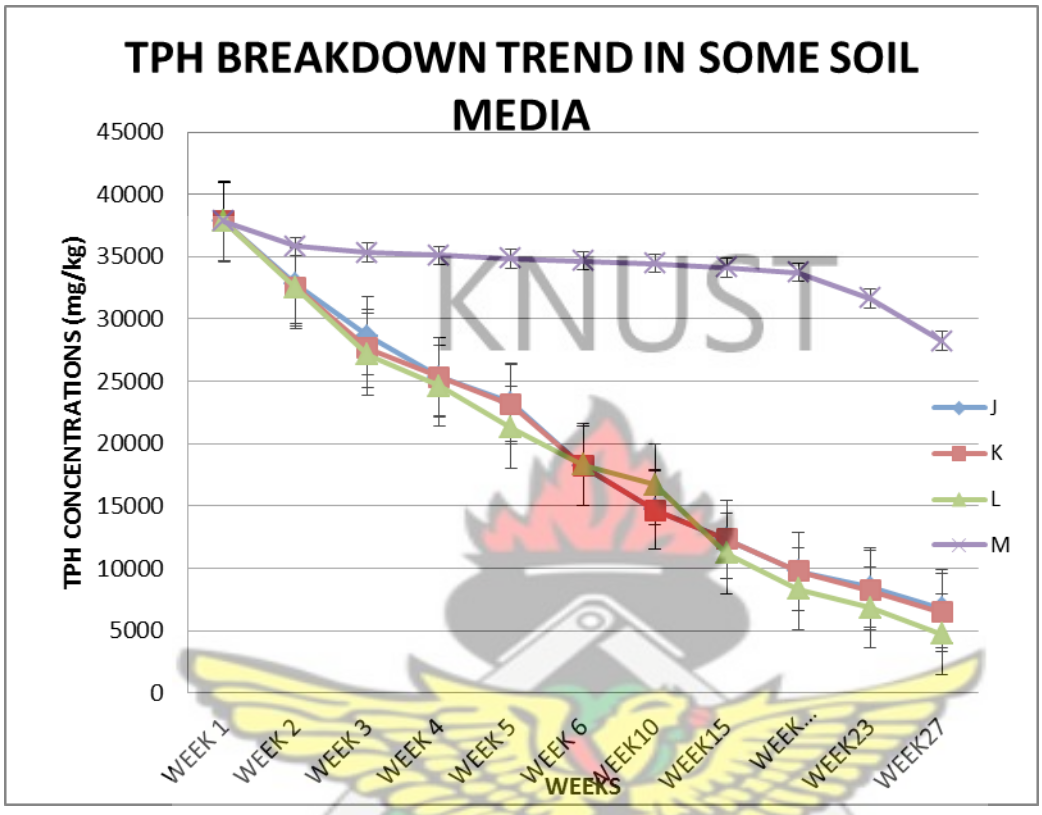
2473.89	4398.12	3897.24	3933.66	3178.60	1890.04
2082.86	4932.50	3368.87	4542.35	3115.89	675.43
4553.65	3831.84	2272.20	2385.45	3406.47	362.19
2980.71	1100.36	5769.76	3308.36	1942.12	389.78
3939.63	4398.77	5635.67	2877.92	1199.11	1172.95
2808.62	6347.38	4254.45	3248.97	2338.92	786.80
3174.89	5181.55	5408.77	2415.35	2879.50	527.48
2879.06	4056.13	4496.43	3868.67	2834.85	769.61
2570.00	4033.25	4477.20	4061.88	3484.52	2698.28
5129.50	3686.32	1933.11	2571.33	1264.18	2894.26
4754.79	3760.36	2121.99	2867.83	1544.36	2897.48
3081.39	1748.63	5415.42	2952.00	1459.03	2230.22
107.97	201.48	346.93	388.84	2272.56	3997.90

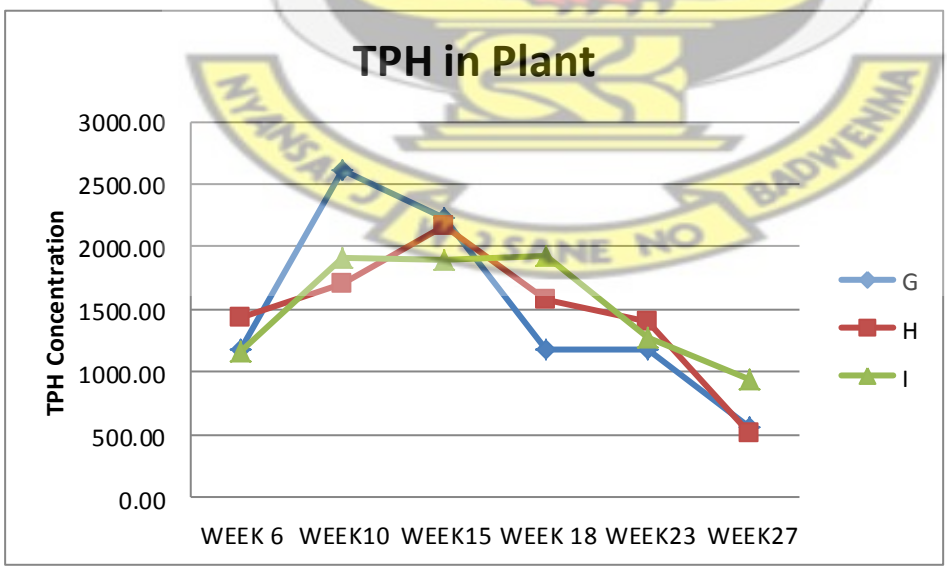
TPH IN PLANTS					
18/10/10	15/11/10	20/12/10	10/1/2011	14/02/11	14/03/11
SD5	SD6	SD7	SD8	SD9	SD10
1500.52	1692.425	1882.416	1646.631	1323.227	778.5666
1744.54	3162.688	2736.418	2981.125	2288.93	970.046
2717.94	1980.30	1242.31	1411.14	1790.17	1223.67
1981.21	871.71	3808.13	1946.08	1403.16	1475.36
1646.33	2048.35	2486.62	1387.77	441.15	1012.35
971.33	2948.35	2036.62	1423.77	1070.98	773.08
1196.33	2946.10	1932.67	1147.47	1191.74	932.14
1433.93	1676.20	2171.62	1567.77	1473.75	758.30
1217.06	2004.18	1752.62	1933.91	1165.75	996.04
2223.77	1620.25	1016.44	1154.57	594.69	871.67
2223.77	1620.25	1016.44	1154.57	702.46	728.22
1350.82	594.35	2596.45	1326.87	635.55	1277.03
135.49	131.15	46.44	175.80	982.62	1414.67

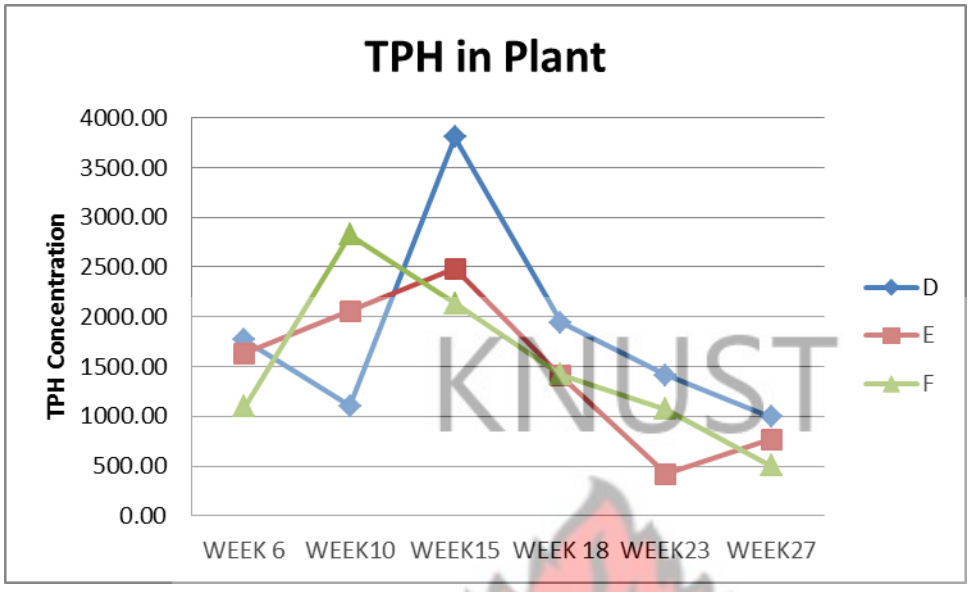
1426.98	1808.772	1869.7056	1557.196	1272.924	704.656
1828.97	3230.247	3061.4554	2765.1129	2345.034	388.9392
2920.64	1894.37	1231.15	1538.27	1644.72	993.60
1364.11	1708.92	3792.16	1686.26	1554.17	1253.85
1484.77	2152.97	2421.73	1545.51	276.92	759.17
1062.12	2677.50	2452.43	1374.77	1093.15	387.95
893.55	2571.09	2340.02	1287.29	1062.00	512.19
1586.20	1603.16	2280.24	1417.70	1464.66	450.83
1135.82	1917.88	1904.54	2010.86	1069.10	611.95
2308.20	1452.14	1325.82	1167.25	584.95	110.30
2307.59	1514.36	1167.90	1022.16	622.69	380.14
1280.41	767.11	2414.83	1200.98	725.95	583.95
60.55	72.95	247.55	169.01	803.34	1386.65

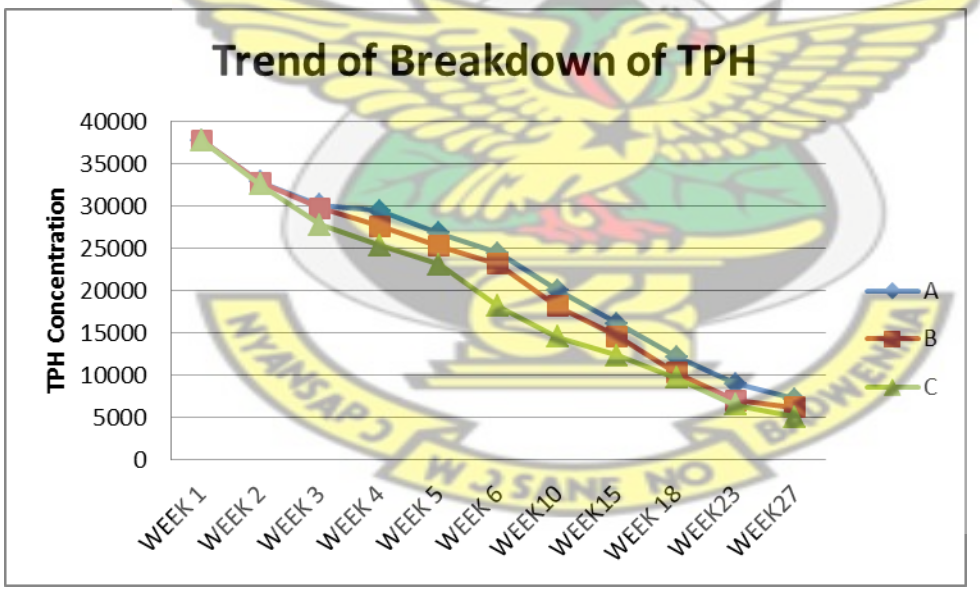
6.4.4 Appendix D

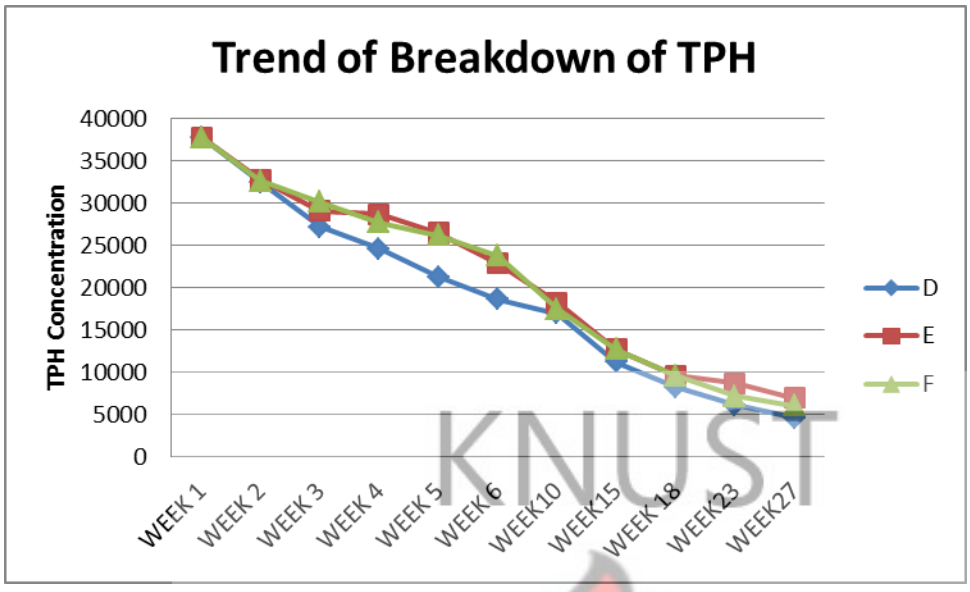
Some Trend Analysis

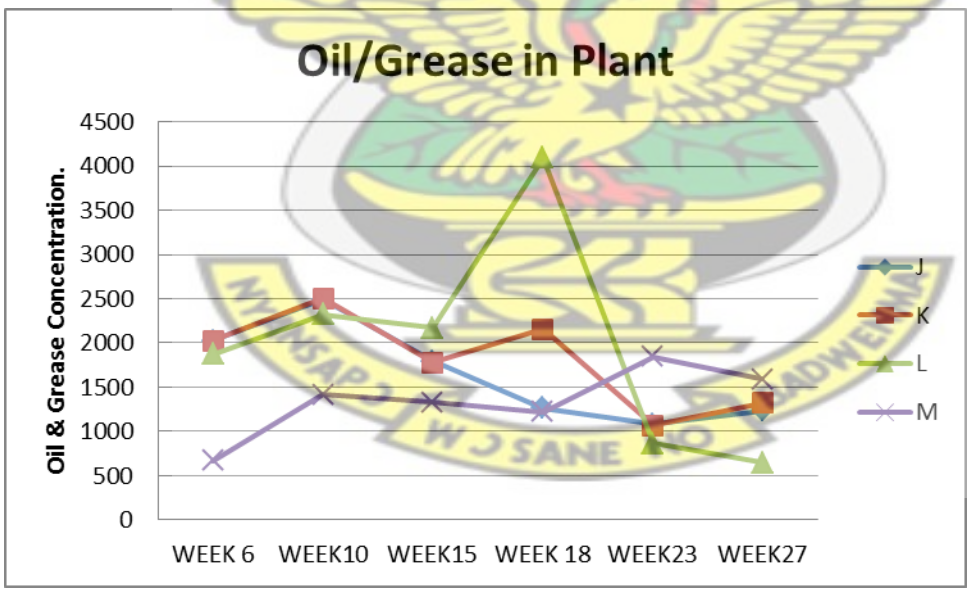


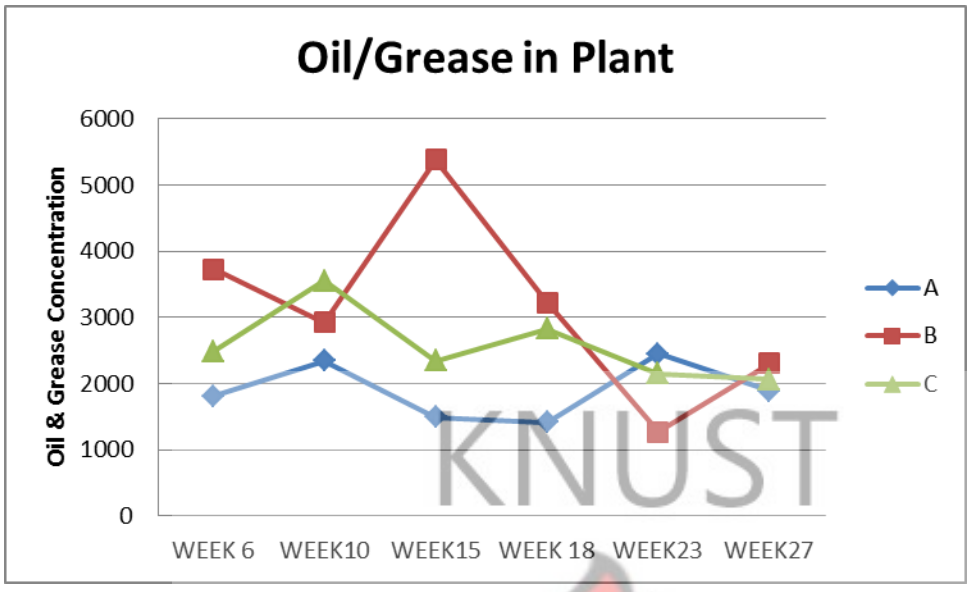


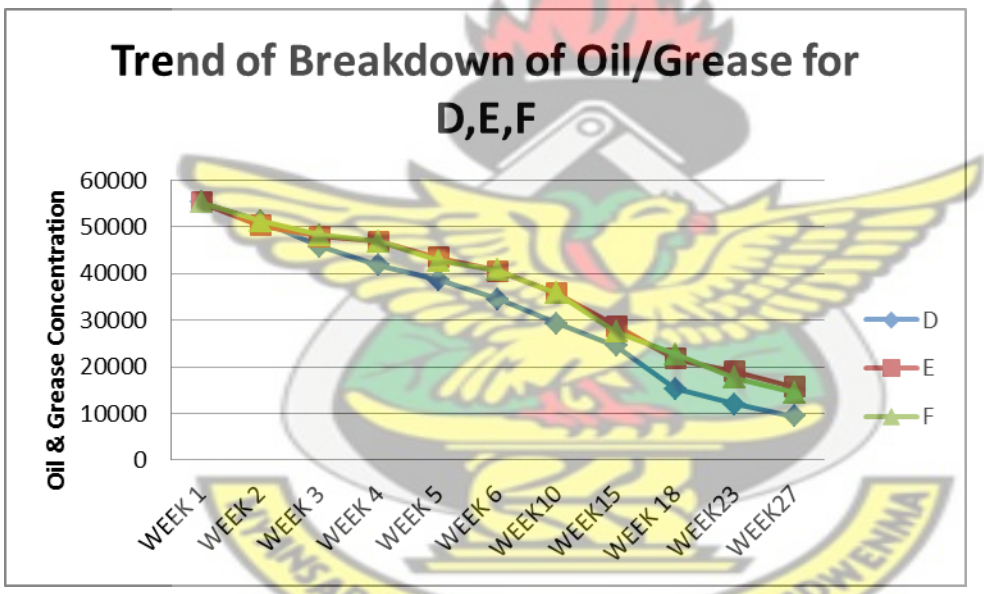

TPH in Plant
TPH Concentration
4000.00
3500.00
3000.00
2500.00
2000.00
1500.00
1000.00
500.00
0.00
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
D
E
F

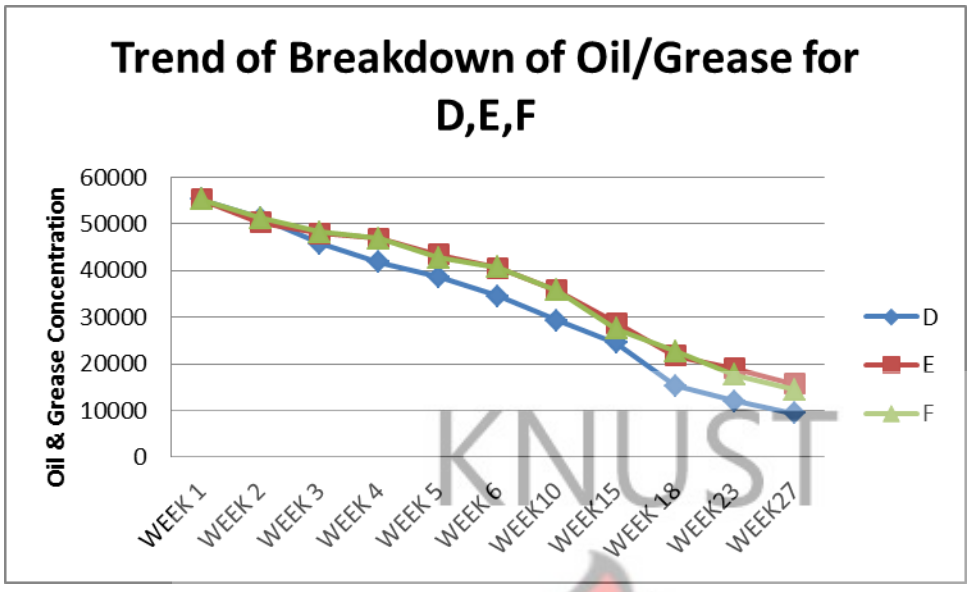

Trend of Breakdown of TPH
TPH Concentration
40000
35000
30000
25000
20000
15000
10000
5000
0
WEEK 1
WEEK 2
WEEK 3
WEEK 4
WEEK 5
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
A
B
C


Trend of Breakdown of TPH
TPH Concentration
40000
35000
30000
25000
20000
15000
10000
5000
0
WEEK 1
WEEK 2
WEEK 3
WEEK 4
WEEK 5
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
D
E
F


Oil/Grease in Plant
Oil & Grease Concentration.
4500
4000
3500
3000
2500
2000
1500
1000
500
0
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
J
K
L
M


Oil/Grease in Plant
Oil & Grease Concentration
6000
5000
4000
3000
2000
1000
0
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
A
B
C
KNUST


Trend of Breakdown of Oil/Grease for D,E,F
Oil & Grease Concentration
60000
50000
40000
30000
20000
10000
0
WEEK 1
WEEK 2
WEEK 3
WEEK 4
WEEK 5
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
D
E
F


Trend of Breakdown of Oil/Grease for D,E,F
Oil & Grease Concentration
60000
50000
40000
30000
20000
10000
0
WEEK 1
WEEK 2
WEEK 3
WEEK 4
WEEK 5
WEEK 6
WEEK10
WEEK15
WEEK 18
WEEK23
WEEK27
D
E
F