CHAPTER 1

INTRODUCTION

1.1 The Environment

The Environment consists of four segments—atmosphere, hydrosphere, lithosphere and biosphere. The soil is the most important part of the lithosphere (Anil, 1994). According to Section 2 of Environmental Protection Act, 1986 (E.P.A) “Environment” includes water, air and land and the interrelationship which exists among and between water, air and land, and human beings, other living creatures, plants, microorganisms and property” (Trivedy and Shastri, 1998).

At present there are many environmental issues, which have grown in size and complexity day by day. Of course, the issues are linked with ecological, social, political and economical questions which have also to be taken into account (Anil, 1994). The effects of industrialization have ruptured the equilibrium which by recycling, natural wastes had remained in balance over a long period of time. The sudden discharge of masses of toxic residues into the environment has gradually led to numerous new risks to the equilibrium of the environment and ecosystem, as well for man himself, the producer of these wastes and causative agent of this monumental disequilibrium. (Lecomte, 1998). Most frequently, problems occur by the release of substances into the environment which are naturally present, with the problem arising simply from an increase in concentration above the natural levels. It is the concentration of a pollutant which is of concern with respect to individual living organisms (Roger, 2002).

According to Section 2 of Environmental Protection Act, 1986 (E.P.A) “Environmental pollutant” means any solid, liquid or gaseous substance present in such concentration as may be or tend to be, injurious to environment. “Environmental pollution” means the presence in the environment of any environmental pollutant (Trivedy and Shastri, 1998).
In general, environmental pollutants can be categorized as follows:

(i) Primary polluting compounds are those emitted and discharged into the environment where they could be (a) degraded into harmless end products, such as water, carbon dioxide, etc., (b) transformed into resistant compounds, or (c) persistent during the physical, chemical and biological weathering processes.

(ii) Secondary polluting compounds are those breakdown, conversion products, which are produced during the environmental weathering of the primary polluting compounds; they might be more toxic than their parents, such as some photo-oxidation products, they are at least temporarily resistant to further degradation and they can affect the fate of other pollutants.

(iii) Tertiary polluting compounds are those primary and secondary pollutants which are buried, accumulated in the ecosystem in inactive, non-bio available form but become active, bio available as a result of the presence of primary and secondary polluting compounds or extreme change in the environmental conditions. Tertiary polluting compounds could be heavy metals, buried in sediment or soil, mobilised by complexing agents during oxidation of some petroleum compounds, or by other compounds.

Pollutants can also be classified broadly into two groups (Webber and Singh, 1995):
(i) Organic, which contain carbon, and
(ii) Inorganic, devoid of carbon.

A contaminated site may be defined as a space wherein the activity of production, transformation, transport or service etc. is carried out and which, due to negligence or defective design or improper maintenance, leads to the occurrence of damage and immediate or deferred risks for the users, the present and future inhabitants and for the environment (Ricour, 1993).
Contaminated sites can be classified according to various criteria: legal standards, mode of dispersion of pollutants, nature and number of pollutants, type of activity and so forth. Environmental diagnosis constitutes the first step in studying the contamination-remediation of a given site before embarking on the subsequent steps, namely evaluation of risks and implementation of operations of remediation. Evaluation of risk, i.e., “risk assessment” signifies a quantitative estimate of the risk faced by the population and the ecosystem when the initial environmental state of a site is impaired. The purpose is to estimate the potential hazard represented by a site, either for relative ranking of individual sites of an ensemble or proposing a scheme for rehabilitation of a particular site. After the diagnosis has been completed and the risk evaluated, before considering a plan of remediation, one ought to decide whether or not remediation and rehabilitation actions are needed. There are five groups of methods that form the basis of all remedial technologies. These are: (i) physical methods involving removal of pollutants, (ii) physical methods of trapping pollution, (iii) chemical methods, (iv) thermal methods and (v) biological methods (Lecomte, 1998).

Environmental protection has been made a fundamental duty for every citizen of India under article 51-A (g) of the constitution which reads as follows: “It shall be the duty of every citizen of India to protect and improve the natural environment including forests, lakes, rivers and wildlife and to have compassion for living creatures.”

Article 21 of the constitution is a fundamental right which reads as follows: “No person shall be deprived of his life or personal liberty except according to procedure established by law.” Right to life includes, right to a living environment congenial to human existence.

In recent years, major projects have encountered serious difficulties because insufficient account has been taken of their relationship with the surrounding environment. It is very risky to undertake finance, or approve a major project without first taking into account its environmental consequences. An Environmental Impact Assessment (EIA) predicts the environmental consequences of a proposed major development project, finds ways to reduce unacceptable impact and to shape the project so that it suits the local
environment and presents these predictions and options to decision-makers (Khan, 1998). The new awareness by society will bring about a quick change in attitude towards the need for respecting and protecting the environment, leading to better health and well-being of fellow citizens (Lecomte, 1998).

1.2 Soil Study

Soil is a natural body, having both mineral and organic components as well as physical, chemical and biological properties (Kabata-Pendias and Pendias, 2001). Soil is developed from the parent rocks. Several factors control the formation of soil from the parent material. Climate, organisms, parent material, relief and time are considered the five major factors in soil formation. Jenny [1941] reported that soil could be characterized by the formula: \( S = f (c_l, o, p, r, t) \). In this equation, \( S \) = soil, \( f \) = function, \( c_l \) = climate, \( o \) = organisms, \( p \) = parent material, \( r \) = relief and \( t \) = time.

Climate is the main factor in the formation of soil as it causes weathering of rocks. Bacteria, fungi, protozoa cause decay of plant and animal remains; some transform atmospheric nitrogen into soil nitrogen. Burrowing animals such as rodents, and insects and worms also loosen material and expose more rock surface to the action of other agents of weathering. Roots of higher plants penetrate the soil and help to make it porous. Deep-rooted plants bring mineral nutrients from the sub soil and build them into their tissues. When all these die and decay the minerals are added to the soil.

Of the several definitions of soil that can be found in the literature today, the definitions of Kellogg [1941] and the USDA Soil Survey [1951, 1990] perhaps most closely reflect the relationship of soils to the environment. According to these definitions: “Soils are considered as natural bodies, covering parts of the earth’s surface that support plant growth, and that have properties due to the integrated effect of climate and organisms acting upon the parent material, as conditioned by relief, over a period of time.”

On digging a trench into the soil down to the bedrock, various layers are seen. Fig.1.1 shows distinctive layers with increasing depth.
These layers called horizons. The top layer, several inches in thickness, is known as the top soil or “A-horizon”. The A-horizon contains weathered solid, mineral material and semi-decayed plant and animal material called humus. It is of considerable importance for vegetation cover and agricultural crops. When a soil is ploughed and cultivated, the natural state of the top soil is modified.

The sub soil or B-horizon comprised of those soil layers underneath the top soil. The B-horizon contains material removed from A-horizon. It is usually composed of fine particles and forms a more compact substance then the A-horizon. Crop production is affected by root penetration into the sub soil and by the reservoir of moisture and nutrients it represents. The sub soil, unlike the top soil is not normally subject to significant human alteration except by drainage.

The next layer C-horizon is composed of weathered parent rocks from which the soil originated. The C-horizon covers the solid rock.
There are differences in the viewpoint of different people towards the concept of soil. To the geologist and engineer, the soil is no more than finely divided rock materials. The hydrologist sees the soil as a storage reservoir affecting the water balance of the catchments, while the ecologist is interested in only those properties of soil that influence the growth of different plant species. The farmer looks upon the soil as a habitat for plants. The farmers make a living from the soil and thereby they are forced to pay more attention to its characteristics, although their interests will not extend below that depth of soil, which is not penetrated by the plough (20-25 cm) [Simonson 1968, Jenny 1980].

The earliest recorded history contains evidence that through trial and error, humans learned to distinguish the differences in soils. They also learned the value of treating soils with plants and animal wastes. More than 42 centuries ago, the Chinese used a schematic soil map as a basis for taxation. Homer, in his Odyssey, believed to have been written around 1000 B.C., made a reference to the use of manure on the land. Greek and Roman writers described a reasonably elaborate system of farming that involved leguminous plants and the use of ashes and sulphur for soil amendment. These evidences suggest that by the time of the early Roman civilization, many of the practical principles governing modern agriculture, including soil management had been discovered and put to use by farmers and livestock owners [Gates 1976].

From the seventeenth century until the middle of the twentieth century, the primary occupation of soil scientists was to increase the production of crop plants. Jan Baptista van Helmont, a Flemish chemist, in his famous five-year willow tree experiment concluded that 164 pounds of dry matter came primarily from the water supplied since the soil lost no weight while producing the tree. This concept was altered by John Woodward, an English researcher, who found that muddy water produced more plant growth than rainwater or river water, leading him to conclude that the fine earth was the "principle" of growth.
The eminent German chemist, Julius Von Liebig, from his experimental findings, reported that crop yield was directly related to the content of "minerals" or inorganic elements in the manures applied to the soil. He proposed that mineral elements in the soil and added manures and fertilizers are essential for plant growth. Liebig's work revolutionized agricultural theory. He stated what has since been called the law of the minimum, that "By the deficiency or absence of one necessary constituent, all the others being present, the soil is rendered barren for all those crops to the life of which that one constituent is indispensable" [Brady, 1988].

After Liebig, unravelling of the complexities of nitrogen transformations in soil, had to wait till the emergence of the soil bacteriologist, J.T. Way, who demonstrated in 1856 that nitrates are formed in soil from ammonia-containing fertilizers. In 1890, Winogradski isolated the two groups of bacteria responsible for the transformation of ammonia to nitrate.

1.3 Plant nutrients

Plants are the means of life, for they are the sources of food for man and all other animals. The soil in which they grow is therefore an important factor in the production of all forms of life. Plants are dependent on a favorable combination of some six environmental factors: viz., light, mechanical support, heat, air, water and nutrients.

With the exception of light, soils can supply each of these factors. But only when these are supplied in the right combination, best plant growth is obtained. Anything less will limit the growth. One of the principal reasons for studying soil is to ascertain which factor is the least optimum and how its limitation to plant growth can be removed.

For the satisfactory growth of plants, their entire nutritional requirement for the development and survival must be available where they grow. If a plant is to grow successfully all the life process mechanisms must work. This means that all necessary materials for its nutrition must be available to it, the physical environment must be suitable for a reasonable uptake, and no toxic materials should be present.
Sixteen chemical elements are known to be essential for the growth of crop plants. These plant nutrients are hydrogen, carbon and oxygen from air and water, phosphorous, potassium, calcium, magnesium, sulphur, iron, manganese, boron, molybdenum, copper, zinc and chlorine from the soil, and nitrogen from both air and soil [Russell 1973]. Thus, soil is the source of thirteen of the sixteen essential nutrients. The concentrations of these thirteen nutrients in soil and the conditions, making them available to plants are of fundamental importance to plant growth [Epstein 1972].

Out of the thirteen elements necessary for plant growth and obtained from soil, six (nitrogen, phosphorous, potassium, calcium, magnesium and sulphur) are used in relatively large amounts and are called macronutrients, while the other seven (iron, manganese, boron, molybdenum, copper, zinc and chlorine) are needed only in small amounts and are called micronutrients. Cobalt is also often considered as a micronutrient. Other minor elements, such as sodium, fluorine, iodine, silicon, strontium, barium, etc., do not seem to be universally essential although the soluble compounds of some might enhance the growth of specific plants.

All the nutrient elements, essential for plant growth, must be present in a specific concentration range for optimum plant growth. If the concentration of a given element in the plant root zone is too low, a deficiency of that element occurs and the plant growth is restricted. Likewise if the root zone concentration of that element is too high, toxicity develops and plant growth is severely limited. Deficiencies and toxicities in plants are usually manifested in reduced yield, abnormal coloration, and fruit deformities. Only in a specific range of concentrations, optimum plant growth is obtained. One of the principal objectives of the soil scientists is to maintain concentration of each element in the optimum range.

Physical properties of soil are as important as the chemical ones that influence the plant growth. The physical soil properties include soil pore sizes and the related problem of aeration and water content, soil stability, soil texture, soil structure, soil consistency and the hardness or cementation of soil layer. The pore spaces of the soil are occupied by gas and liquid phase. One of the most obvious biological effects of an imbalanced
oxygen and carbon dioxide content in soil air is its impact on plant growth. It is an established fact that improper cultural practices result in poor aeration, reduce plant growth. Water and nutrient uptake are also inhibited. Under normal field conditions, oxygen deficiency is considered more serious to root growth than excess CO$_2$ [Taylor and Ashcroft, 1972].

Water is held in the pore spaces by forces of attraction exerted by the soil matrix, by attraction of the ions and by surface tension of the capillaries. The water retained in the soil by these forces constitutes the reserve water supply for plant use. Micronutrients move in soil mainly by mass flow and diffusion. In both the processes, soil water is the medium through which the movement takes place.

Together with its dissolved salts, soil water makes the soil solution, which is so important as a medium for supplying nutrients to growing plants. Both the macro and micro nutrients are present in soil as ions and the ionic strength measurement of soil solutions gives an estimate of their total amount. Ionic strength is calculated by using the relationship,

\[ I = \frac{1}{2} \sum c_i z_i^2 \]

where $c_i$ and $z_i$ are respectively the concentration and the valence of the cations and the anions. Ionic strength is an important soil solution parameter in understanding surface charge characteristics of variable charge soils.

### 1.4 Petroleum and Petroleum Contaminated Sites

Crude oil or Petroleum is a black viscous liquid which occurs deep below the earth crust entrapped under rocky strata which is a mixture of tremendous complexity, containing hundreds of hydrocarbon and nonhydrocarbon components, many of them still unidentified and some of these very toxic towards microorganisms (Atlas and Bartha, 1973a). Crude oil is considered hazardous primarily because of the presence of carcinogenic compounds such as polynuclear aromatic hydrocarbons (PAHs).
Compounds in crude oil can be divided into three general classes consisting of saturated hydrocarbons, aromatic hydrocarbons, and polar organic compounds (Huesemann and Moore, 1993). Crude oil also contains a number of heavy metals such as nickel, vanadium, zinc, lead, and copper in the low parts per million range. Most crude oils contain the same type of compounds. Where they differ is in the concentration of these substances (Bestougeff, 1967).

Petroleum is a natural product which has very wide range of uses. In earlier days people obtained the liquid crude oil and the solid bitumen from seepages in some places and used them for various purposes. In about 200 BC, a well drilled in China for brine struck oil by accident at a depth of about 140m. This gave a clue to the possibility of finding oil at depth. So, to pump oil to the surface we have first to bore down to the rock to obtain an "oil well". An area having oil bearing deposits is called "oil field".

In 1556 AD, a German geologist Agricola described oil as a substance naturally occurring in the earth which can be recovered in a scientific manner. He also indicated a possibility of dividing crude oil into different fractions by heating.

The first scientific attempt at locating oil in the sub surface was done by Col. Edwin Lorentine Drake. The first oil well was drilled by Drake at Titusville, Pennsylvania, USA, on 27th August 1859. It struck oil at a depth of about 21m. Drake can thus be said to have laid down the foundation of modern oil industry.

In 1890 AD, the Assam Railway and Trading Company drilled an oil well in Digboi, Assam and drilling was completed at a depth of 662 feet. This Digboi oil well is the first oil well in India. The operational authority of Digboi oil field originally vested with AR&T Company passed on to Assam Oil Company since its formation on May 5, 1899 AD then as a follow up of the nationalization of the Assam Oil Company in October 1981 it was transferred to Oil India Limited (OIL) (Sarma, 2009).

The Assam oil fields have been operating ever since the discovery of oil at Digboi more than a century ago. Most of the oil wells are located in the districts of Sibsagar, Jorhat,
Dibrugarh, and Tinsukia. In Assam, the public sector petroleum company Oil and Natural Gas Corporation Limited (ONGCL) and Oil India Limited (OIL) have been engaged in exploration, production and transportation of crude oil.

The oil collected from the different oil wells in a particular area is taken to the gathering centres, where after some treatment to remove water etc. the oil is pumped to the different “refineries”. Refining of crude oil is done by dividing crude oil into different fractions with different boiling ranges. The refining processes should be suitable and adaptable for the preparation of large variety of products. India obtained its first refinery in Digboi in the year 1901 AD.

Presently the unrecoverable portion of natural gas from the oil wells in Assam is allowed to burn continuously. The flares are highly intense and rise up to 15-26 m in the sky. Such burning torches are a common site in the areas where the oil wells have been discovered (Rao, 1984).
Produced water is defined as the water brought up from the hydrocarbon bearing strata during the extraction of oil and/or gas and this may include; Formation water, Injection water, small volumes of condensed water and trace amount of treatment chemicals (Ayes and Parker, 2001). The water is separated from the oil as far as possible. Known as the produced water or sometime simply formation water, this contains oil and salts. The formation water is highly alkaline in nature (Sharma and Choudhury, 1992). The aromatic hydrocarbons and metals in produced water were reported by Neff and Anderson (1981) to be toxic to organisms.

The heavy metals encountered most frequently are lead, arsenic and chromium used as corrosion inhibitors in pipelines. Numerous toxic and caustic chemicals are used in drilling muds and fluids.

During the drilling operations and the work of collection, storage and transport of the crude oil, crude oil spill and leakage are quite likely to occur depending upon the extent of good housekeeping by the oil companies. A large number of contaminants including heavy metals enter into the nearby areas of a gathering centre through spills, leaks as well as through emissions from gas flaring and from effluents which are likely to pollute the environment. The waste products produced during these operations may pose disposal problem. All the waste products require adequate treatment and safe disposal in order to prevent environment from getting contaminated with the polluting substances present in the waste products.

If oil is spilled on the surface of soil during the drilling operation the hydrocarbons gradually penetrate into the soil system. Adsorption to soil organic matter plays a significant role in temporary immobilization of oil (Mackay, 1975; McGill et al 1981). The absorptive capacity of soils for oil-components varies but this is significantly less than their water holding capacity (Schwendinger, 1968). It has been found that the oil hydrocarbons can infiltrate up to a depth of 50-cm (Ilangoovan and Vivekanandan, 1992). However, it is known that rainfall prior to or during the spills reduces oil infiltration into the soil and washes petroleum components away to runoff waters (Francke and Clark, 1974).
Extent of underground soil pollution and surface soil pollution varies with spill size, spill time, soil type, oil type and weather conditions. On a porous surface, the radius of a spill will tend to be proportional to the 0.25 power of the time period of the spill as compared to the spill time raised to the power of 0.50 for spill on impermeable surface (Mackay and Mohtadi, 1975; Raisbeck and Mohtadi, 1974). Small and slow spills tend to contaminate a small surface area but relatively large underground area, while in the case of large and rapid spills, surface spreading predominates (Mackay and Mohtadi, 1975). The infiltration of oil through a porous surface is dependent on the average radius of the soil capillaries and the wettability of the soil by oil (Raisbeck and Mohtadi, 1974). Heavy crude or fuel oils, because of their high viscosity, tend to move horizontally, while gasoline and low viscosity fractions penetrate readily into deeper soil strata (McGill and Rowell, 1977).

Oil infiltration into the soil modifies the soil properties (Kalita et al., 2007). In general, due to crude oil spillage, inorganic ion concentrations of polluted soils and streams varied significantly from those of unpolluted soils and streams (Onyeike E N et al., 2002). Formation of nitrate in soil is reduced even by presence of small amount of oil. Murphy (1929) reported that one percent of oil, when mixed with soil practically checked nitrate formation. Beyond 3% concentration, oil has been reported to be increasingly deleterious to soil biota and crop growth (Baker, 1976). The spilled oil on site may also, sometimes, inform serious conflagration that may consume several acres of arable land (Nwankwo and Ifeadi, 1988).

In oil-producing states, the proximity of livestock to drilling operations and production sites often results in poisoning of animals from ingestion of crude oil, condensate, salt water, heavy metals, and caustic chemicals. Toxicity of carcinogenic and growth-inhibiting chemicals present in the crude oil to micro organisms and man is well known (Atlas and Bartha, 1973a, 1973b, 1973c; Odu, 1972, 1978, Okpokwasili and Odokuma, 1990). The identification and quantification of petroleum hydrocarbons, toxic chemicals and heavy metals in intestinal contents and tissues are diagnostically significant. The most difficult cases involve chronically ill and poor-doing animals following exposure.
to oil field wastes. Many of these cases could be prevented if livestock were prevented access to such sites by fencing or other means. The circumstantial evidence in many cases suggests the need for additional research on the toxicity of petroleum hydrocarbons, drilling muds and other oil field wastes (Edwards et al. 1979).

The oil production activities may affect vegetations in various ways. The flame and heat of the flare cause direct burning of various parts of the shoot of a nearby plant. In areas inundated by accidental oil spills, the herbaceous vegetation cover is quickly destroyed (Ellis and Adams, 1961; Odu, 1972). Effects of petroleum used as sprays on vegetation were studied by Young (1935). He found that the sprays produced varying degree of plant injury and the damage was proved to be due to two causes—suffocating effect and toxicity. The application of oily wastes (containing 1-5 % oil) to the soil in moderate amounts, in the upper 15 cm layer, usually has less deleterious effects on the plant community than do large scale accidental spills (Schwendinger, 1968; Raymond et al., 1976).

Metals supplied to the environment are transported by water and air, ultimately reaching the soil and sediment where they become bound. The composition of the soil at a contaminated site can be extremely diverse and the heavy metals present can exist as components of several fractions (Salt et al., 1995). Soil and sediment colloids roughly consist of inorganic clay minerals and organic substances. According to Mengel and Kirkby (1982), the presence of hydroxyl group and electron pairs of oxygen in the structure of inorganic clay minerals and carboxyl and phenolic groups of organic substances makes the soil and sediment colloids negatively charged. Positive metal ions are attracted to these ions. In general, higher the clay and organic matter, the more firmly bound are the metals.

Metal concentrations in media differ depending on different retention times of the metals in different media (Förstner and Wittman, 1979). Water and air function more or less as transport media for elements, and thus metals have a shorter retention time in those media. Soil and sediment are considered as sinks and metals are therefore accumulated in these media resulting in high concentration.
There is equilibrium in the interface between the metals in the water and the metals in the sediment in aquatic environment (Forstner, 1979). In the case of the air-soil interface, however, there is no such equilibrium like that found in the aquatic environment (Greger, 1999).

Plants are able to take up metals from air and water as well as from soil and sediment, depending on the growth environment. Heavy metals are primarily taken up by plants through roots. However, foliar absorption and stem uptake also represent potential mode of entry (Greger et al., 1993). Plants grown in metal-enriched substrates take up metal ions to varying degrees. This uptake is largely influenced by the bioavailability of the metals which is, in turn controlled by both external (soil-associated) and internal (plant-associated) factors (Saxena et al., 1999). The availability of metals from the soil is controlled by: (1) chemical (pH, Eh, CEC, metal speciation), (2) physical (size, texture, clay content, organic matter content,), and (3) biological processes (bacteria, fungi) and their interactions (Ernst, 1996). The uptake of metals by plants is affected by various factors such as type of the plant species, the metal species involved, metal concentration in the medium, presence of other cations and anions in the medium, pH of the medium, light, temperature, relative humidity etc.

In addition to uptake, there is also a release of metals back into the water and soil from plant tissue or to the air from the leaves. These cause a net accumulation of the metal in the plant (Greger, 1999).

When the formation water is discharged into the soil, it may create salinity problem to various degrees. Saline soils are characterised by low nutrient ion activities and extreme ratios of Na+/Ca2+, Na+/K+, Ca2+/Mg2+, and Cl-/NO3-. Plants acquire mineral nutrients from their native soil. Most of crop plants have developed mechanisms for absorbing mineral nutrients in non-saline soil. In saline environment, plants take up excessive amounts of Na at the cost of K and Ca (Kuiper, 1984). Salinity was observed to induce soil macro and micro nutrient deficiencies in an oil field located in East Central Wyoming (Rohman et al, 1993). Both Ca2+ and K+ are required in the external medium.
to maintain the selectivity and integrity of the cell membrane (Wyn Jones and Lunt, 1967; Fageria, 1983). The high Na⁺/Ca²⁺ and Na⁺/K⁺ ratios in saline growth medium may impair the selectivity of root membrane (Kramer et al, 1977). Under saline conditions nutritional disorders can develop and growth may be reduced (Grattan and Grieve, 1992).

Within a plant, in general, trace elements accumulate in different concentrations in different plant parts. Jarvis et al. (1976) examined the cadmium distribution in 23 species and found that cadmium concentration decreased in the following order: fibrous roots > storage roots > stems > leaves. Whether essential or non-essential, heavy metals in excess concentrations are toxic to both plants and animals. Heavy metal intake by human via consumption of fruits and vegetables grown on contaminated land is a matter of great concern.

The presence of petroleum in aquatic ecosystem is generally harmful because the water soluble fractions of the oil are toxic to the biota. Oil is most objectionable in a stream because it spreads to form a thin film on the surface and so tends to prevent diffusion of oxygen into the water. Oil in any considerable amount tends to coat the gills of fish, thus making the utilization of dissolved oxygen difficult or even impossible (Blumer, 1967). Majority of oil spills involve accidents at sea. With reference to aquatic ecosystems, it is the marine ecosystem that has received the greatest attention. Some fresh water systems have been seriously polluted with oil. The single largest source of oil discharge to the ocean is river run off. (NAS, 1975)

Petroleum products are remarkably stable in the marine environment (Blumer et al., 1970). There is no doubt that some bacteria can metabolise petroleum hydrocarbons, but no single bacteria is effective against all hydrocarbons in crude oil (EPA, 1972). The hydrocarbons that are ingested by the marine organisms can pass through the wall of digestive tract and can be retained for long term (Blumer, 1967). When the concentration of petroleum hydrocarbons in marine organism exceeds 200-300 ppm, the organism acquires a distinctly tainted taste and becomes unpalatable, there fore can not be eaten any way (NAS, 1975).
1.5 Biodegradation and Bioremediation

Biodegradation is the metabolic ability of microorganisms to transform or mineralize organic contaminants into less harmful, non-hazardous substances, which are then integrated into natural biogeochemical cycles (Margesin and Schinner, 2001). Biodegradation of oil is one of the most important processes for the eventual removal of petroleum from the environment, particularly for the non-volatile components of petroleum (Albert and Xueqiong, 2003). Considerable effort is being made to remediate soils contaminated with petroleum hydrocarbons heavy metals and other organic and inorganic compounds that have resulted from industrial activities, accidental spills and improper waste disposal practices (Saldaña et al., 2005). Microbial degradation of pollutants has been considered as an important way to clean up the contaminated sites (Díaz, 2008). The oil concentration in the soil of the contaminated field decreases with time. Initially the oil concentration is high in the upper 1 to 30-cm layer but after six months, the rapid decrease of oil in the upper layer reverses the situation. Biodegradation, evaporation and leaching could be considered as causes for the decrease but leaching has been shown to be not very significant (Raymond et al., 1976; Dibble and Bartha, 1979a and b). In nature, biodegradation of a crude oil typically involves a succession of species within the consortia of microbes present. Different oils vary in their degree of susceptibility to bacterial attack.

Degradation of the petroleum hydrocarbons usually proceeds via oxidation. For example, in the case of naphthalene, it is first oxidized to trans-1, 2-dihydroxy 1, 2 dihydronaphthalene by soil fungi before being degraded further (Ferris et al. 1976, Cerniglia and Gibson 1977, Cerniglia et al. 1979).

In general, lighter weight oils are more readily oxidised than heavier ones (Stone, 1941). Degradation of petroleum involves progressive or sequential reactions, in which certain organisms may carry out the initial attack on the petroleum constituent; this produces intermediate compounds that are subsequently utilized by a different group of organisms, in the process that results in further degradation. Micro-organisms classified
as non-hydrocarbon utilizers may also play an important role in the eventual removal of petroleum from the environment (Karrick, 1977).

The general degradation pathway for an alkane involves sequential formation of an alcohol, an aldehyde, and a fatty acid. The fatty acid is then cleaved releasing carbon dioxide (decarboxylated) and forming a new fatty acid two carbon units shorter than the parent molecule. This process is known as β-oxidation. The general pathway for degradation of an aromatic hydrocarbon involves cis-hydroxylation of the ring structure forming a diol. The ring is then cleaved forming a dicarboxylic acid. (Atlas, 1978).

Compared to saturates and aromatics, very little is known about biodegradation of asphaltenes; this is due to their complex structure which are difficult to analyze.

The concentration of a hydrocarbon can affect its biodegradability (USEPA, 1985). There would seem to be, for many hydrocarbons, an optimum concentration range for metabolism below which degradation is not stimulated (McCarty et al., 1981) and above which inhibition occurs (Alexander, 1985).

The oil surface area is important because growth of oil degraders occurs almost exclusively at the oil-water interface (Atlas and Bartha, 1992). Microbial degradation of hydrocarbons can occur at temperatures ranging from -2 to 70°C (Texas Research Institute, Inc., 1982). Although hydrocarbon degradation can occur over a wide range of temperatures, the rate of biodegradation generally decreases with decreasing temperature. Too high temperature is not beneficial for stimulating petroleum biodegradation (Phillips and Brown, 1975). Highest degradation rates generally occur in the range of 30-40 °C in soil environments, 20-30°C in some freshwater environments, and 15-20°C in marine environments (Bossart and Bartha, 1984; Cooney, 1984; Jordan and Pyne, 1980).

Aerobic conditions are generally considered necessary for extensive degradation of oil hydrocarbons in the environment since major degradative pathways for both saturates
and aromatics involve oxygenases (Atlas, 1981; NAS, 1985; Cerniglia, 1992). Anaerobic oil degradation has been shown in some studies to occur only at negligible rates, as reviewed by Atlas (1981). However recent studies have shown that anaerobic hydrocarbon metabolism may be an important process in certain conditions (Head and Swannell, 1999).

The provision of limiting nutrients has been shown to be effective in stimulating hydrocarbon degradation after oil spills. One possible explanation may be that the presence of nutrient stimulated the activity of indigenous bacterial populations sufficiently to enhance the degradation of the crude oil (Pitchard et al., 1992; Swannell et al., 1999). In theory, approximately 150mg of nitrogen and 30mg of phosphorus are utilised in the conversion of 1g of hydrocarbon to cell materials (Rosenberg and Ron, 1996). A potential limiting nutrient is iron, which was found to limit oil degradation in clean offshore sea water, but is not likely to be limiting in freshwater (Fought and Westlake, 1987).

When the formation water is discharged into the soil, it may create salinity problems to various degrees. Changes in salinity may affect oil biodegradation through alteration of the microbial population (Ward and Brock, 1978).

Generally, the saturated n-alkanes are the most readily degradable components in a petroleum mixture (Zobell, 1946; Atlas, 1981). Aromatics are generally more resistant to biodegradation. Some low molecular weight aromatics such as naphthalene may actually be oxidised before many saturates (Fought and Westlake, 1987). The degradation of lower molecular weight two- or three- ring PAH compounds is known to occur much more rapidly than degradation of four-, five- and six- ring PAH. (Wilson and Jones, 1993; Shuttleworth and Cerniglia, 1995; Jack et al, 1996). Resins and asphaltenes have previously been considered to be refractory to degradation. However, there was evidence of asphaltene degradation through co-metabolism (Leahy and Colwell, 1990). Some resins, particularly low-molecular-weight resin fractions, can also be biodegraded at low concentrations (NAS, 1985).
The natural recovery of crude oil from polluted soils is slow. Many of the hydrocarbons are resistant to degradation in the natural environment. Unless all the proper conditions are met for a given compound biodegradation is not likely to occur. Remediation can lead to quick recovery of the polluted soils (Gradi 1985, Alexander 1978).

Remediation has been defined as the management of a contaminant at a site so as to prevent, reduce or mitigate damage to human health, or the environment, which can also lead to quick recovery of the affected lands (Doelman, 1994). Irrespective of the technology used, three modes of application of remediation operations can be identified. These modes of treatment application are as follows:

(i) Application of treatment away from site,
(ii) Application of treatment in situ, and
(iii) Application of treatment on or near site.

Application away from site involves removing quantities from the natural medium by excavation or pumping the material to be remediated and transporting it from the site to a specialised centre where it will be treated and eventually brought back to the site for relaying, as in the case of soil.

For treatment 'in situ', the task is accomplished directly in the contaminated natural medium, without having first to separate the contaminated part. The remediation system on the site operates directly on the medium to be treated.

Application on or near site involves removing the material to be remediated from the natural medium as done in the 'away from site' mode but administering treatment on or near the site using a mobile remediation system.
The various remediation technologies are grouped into five major groups based on one methodological principle (Lecomte, 1998):

(i) Physical methods involving removal of pollutant whereby the pollutant is extracted by physical means, from where it is found in the medium,

(ii) Physical methods of trapping pollution whereby the pollution is physically immobilised on the spot, either by confinement or by stabilisation,

(iii) Chemical methods based on some reaction for removing or transforming the contamination,

(iv) Thermal methods treating the contaminated material to high temperature to destroy, extract or stabilise the contaminants, and

(v) Biological methods based on use of the metabolism and activity of living organisms (bacteria, fungi, higher vegetation) for degrading the contaminants.

Bioremediation process enhances the indigenous bacteria via the addition of oxygen and nutrients to degrade petroleum hydrocarbon to carbon dioxide and water. Bioremediation is dependent on an interdisciplinary approach involving such disciplines as microbiology, engineering, ecology, geology, and chemistry. Bioremediation can be coupled with other physical or chemical treatment methods. Some of the important bioremediation technologies available are: landfarming, composting, bioreactors, bioventing, biofilters, bioaugmentation, biostimulation etc.

The outcome of each degradation process depends on major factors such as microbial (biomass concentration, population diversity, enzyme activities), substrate (physicochemical characteristics, molecular structure, and concentration), and a range of environmental factors (pH, temperature, moisture content, Eh, availability of electron acceptor and carbon and energy sources). Several non-technical factors affect the development of bioremediation technologies. Some of the non-technical factors that affect bioremediation are ability to achieve the required clean-up target, acceptable cost
relative to other remediation options, acceptable risks in residual contaminants remaining after bioremediation, favourable public perception, ability to meet time limitations, and the ability to conform to space limitations (Boopathy, 2000).

The time required for degradation of petroleum hydrocarbons in soils depends on the chemical compositions of crude oil, the properties of soil and the climatic conditions. Unless all the proper conditions are met for a given compound, biodegradation is not likely to occur (Bitton and Gerba, 1985).

Soil conditions are often controlled to increase the rate of contaminant degradation (Odu, 1978, Gradi, 1985). Two of the most important soil factors that affect degradation are soil pH and available nutrients.

In the biodegradation process, pH of the soil plays a predominant role. This is because each type of microorganisms has a preferred pH range for optimal growth and activity. For example, Fungi predominate under acidic conditions (pH<7), Bacteria and actinomycetes near pH 7.0. A soil pH of 7.8 has been shown to be the optimum pH (Dibble and Bartha, 1979a) for microorganisms' growth. The soil pH regulates the solubility, mobility, and the availability of the ionized forms of contaminants (JRB Associates, Inc., 1984).

The microbial activity is controlled by the availability of nutrients, especially nitrogen and phosphorus (Margesin and Schinner, 1997). The use of lipophilic fertilizer to enhance microbial utilization of crude oil has also been investigated (Olivieri, et al., 1978, Abu and Ogiji, 1996) and it has been found that the efficiency of a fertilizer depends greatly on the environment and design of the treatment protocol (Riser-Roberts, 1998). At the same time, the activity may be limited by the presence of toxicants in the soil and, in such cases; the tolerance of the microorganisms towards the toxicants and other environmental factors, such as temperature determines their effectiveness for biodegradation.
There are several important limitations for application of conventional biological treatment methods (Boopathy, 2000; Brown et al., 1986). These are:

(i) Some chemicals are not amenable to biodegradation, for instance, heavy metals, radionuclides, and some chlorinated compounds.

(ii) For supporting microbial growth the environmental parameters like pH, temperature, redox state, and available nutrients must be appropriate.

(iii) By-products of biodegradation may be more toxic or persistent than the original compounds.

(iv) Substrate concentration may be too high (toxic) or too low (inadequate energy source).

(v) Complex organic mixture may include inhibitory compounds.

(vi) Bioremediation must be tailored to the site-specific conditions, which means one has to do treatability studies on a small scale before the actual clean-up of the sites.

Although cleanup measures are usually carried out as a part of the oil spill contingency programme, petroleum hydrocarbons have been found to persist in surface and subsurface soils long after such clean-up activities, thus impairing agricultural productivity (Osuji, 2001; Volkman et al., 1984; Williams et al., 1986).

1.6 Aims and Objectives of the present work

The present study was designed with an aim to investigate the damage done to the agricultural fields by the oil field activities. The study area taken up in this work is a part of the district of Sibsagar in Assam (India). Crude oil contaminated sites near the five well-known GGSs, i.e., Rudrasagar GGS1, Rudrasagar GGS2, Lakowa GGS1,
Lakowa GGS3 and Lakowa GGS9 operated by the Oil and Natural Gas Corporation Limited in Assam were selected as the study area.

In the present study elaborate discussion of damages to soil due to the above activities has been pointed out. Through the review of literature, important factors towards soil quality damages namely effects of gas flaring, effects of oil spill on soil, impacts of petroleum hydrocarbons on vegetations, degradation of petroleum hydrocarbons on soil, etc., were discussed. We also investigated heavy metal accumulation in plants at crude oil contaminated sites near the selected GGSs. The effect of pH, N, P and K on crude oil contaminated soil was also investigated by carrying out detailed laboratory scale study.

**Objectives of the study are:**

1. To determine the various physico-chemical parameters like pH, total organic carbon, soil texture, electrical conductivity, water holding capacity, major anion content (chloride, sulphate, phosphate), and major cation content (Na, K, Fe, Al) in the soil samples to establish a correlation between these parameters and the total petroleum hydrocarbon content.

2. To determine the heavy metal content (as may be present in the oil field soil or as may be introduced from the spill and leakage of crude oil to the nearby area) in the soil samples and to determine the input from the oil-fields by comparing with a control soil sample.

3. To determine the variation in total petroleum hydrocarbon content in the soil samples of two oil fields (Rudrasagar and Lakowa) with respect to distance and depth.

4. To determine the heavy metal contents of fruits, vegetables and rice paddy grown in the oil field area with respect to any possible impact from the oil field operations.

5. To carry out a laboratory scale study on the effects of pH and N-P-K fertilizer on remediation of soil spiked with petroleum hydrocarbons.