CHAPTER - 1

INTRODUCTION

1.1 A brief outline of the growth of Soil Science:

The environment consists of four segments, namely, atmosphere, hydrosphere, lithosphere, and biosphere.

The mutual interactions and energy flows among the four segments of the gross environment are shown in Fig. 1.1.
The soil is at the interface between the atmosphere and lithosphere (the mantle of rocks making up the earth's crust). It has an interface also with bodies of fresh and soft water (called the hydrosphere). The soil sustains the growth of many plants and animals and so forms part of the biosphere. Soil means different things to different users. To the geologist and engineer, the soil is no more than finely divided rock material. The hydrologist sees the soil as a storage reservoir affecting the water balance of the catchment, while the ecologist may be interested in only those soil properties that influence the growth and distribution of different plant species. The farmer is naturally concerned about the multiplicity of ways in which the soil can influence the growth of his crops and the health of his livestock, although frequently his interest will not extend below the depth of soil which is disturbed by the plough (20-25 cm) [Simonson 1968, Jenny 1980].

Man's exploitation of the soil for food production began some two or three thousand years after the close of the last Pleistocene ice age, which occurred about 11,000 years ago. Neolithic man and his primitive agriculture spread outwards from settlements in the fertile crescent embracing the ancient lands of Mesopotamia and Canaan and reached as far as China and the America within a few thousand years. In China, for example, the earliest records of soil survey (4,000 years ago) show how the fertility of the soil was used as a basis for levying taxes on the incumbent landholders. The study of the soil was a practical exercise of everyday life, and the knowledge of soil husbandry that had been acquired by Romans was faithfully passed on by peasants and landlords, until the early 18th century [Gates 1976].

From that time onwards, however, the rise in demand for agricultural products in Europe was dramatic. Condition of comparative peace and much improved living standards as a result of the industrial revolution, further stimulated this demand throughout the 19th century. This period was also one of great discoveries in the sciences of physics
and chemistry, the implications of which sometimes burst with shattering effect on the conservative world of agriculture. In 1840, von Liebig firmly debunked the ‘humus theory’ of plant nutrition, and established that plants absorbed nutrients as inorganic compounds from the soil. In the 1850s, Way discovered the process of cation exchange in soil and during the years from 1860 to 1890 eminent bacteriologists, including Pasteur, Warington and Winogradsky elucidated the role of microorganisms in the decomposition of plant residues and the conversion of ammonia to nitrate in the soil [Kellogg 1950, Russell 1957].

Over the same period, botanists such as Von Sachs and Knop, by careful experimentation in water culture, identified the major elements which were essential for healthy plant growth. Agricultural chemists drew up balance sheets of the quantities of these elements taken up by crops and by inference, the quantities which had to be returned to the soil in fertilizers or animal manure to sustain growth. This approach, whereby the soil is regarded as relatively inert medium providing water, mineral ions and physical support for plant growth, has been called the ‘nutrient bin’ concept.

The soil properties important to the growth of plants are used at several lower category levels in soil taxonomy. One of these factors is soil fertility, the plant nutrients available in the soil. 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, phosphorus, potassium, sulfur, calcium, iron, magnesium, boron, copper, manganese, zinc, molybdenum and chlorine from the soil and nitrogen from both air and soil [Russell 1973].

Soil is the source of 13 of the 16 essential plant nutrients. All of these 13 except nitrogen originate in the parent rocks from which the soil developed. The soil concentrations of these thirteen nutrients and the conditions making them available to
plants are of fundamental importance to plant growth. Plant nutrients found in the soil are chemical constituents of that soil [Epstein 1972].

As important as the chemical properties of the soil are to plants, the physical properties of soil may often be as critical to the growing plant. The physical soil properties include soil pore sizes and the related problems of aeration and water content, soil stability, soil texture, soil structure, soil consistency and the hardness or cementation of soil layers.

Water and air occupy the pore spaces in the soil. Some water will move downward in response to gravity and the large pores will be emptied of their water but refilled with air. For good plant growth there must be enough large pore spaces to hold air and enough small pore spaces to retain water to satisfy the needs of plant roots for oxygen and water between cycles of rainfall or irrigation.

The magnitude of plant growth reflects a composite of many favourable and unfavourable factors. Favourable growth factors include adequate aeration, water, nutrients, adequate soil depth, and proper soil temperature. Unfavourable growth factors are many, among which are toxic levels of certain elements, disease, harmful insects, adverse temperatures and inadequate or excess sunlight. Any accurate estimate of the plant productivity of a soil must include all favourable and unfavourable factors.

Plant's nutritional requirements to ensure its development and survival must be available where it grows. These essentials are normally obtained from the soil. If a plant is to grow successfully all the life process mechanisms must work. This means that all the necessary materials for its nutrition must be available to it, its environment must be suitable, and no toxic materials should be present. Satisfactory growth is not easy to define, it does not necessarily mean maximum growth. Plants growing under natural
conditions may often be stimulated to greater development by applying fertiliser, or by giving more water, or as a result of warmer weather [Epstein 1972].

1.2 Macro and Micronutrients

The inorganic elements known to be generally essential for plant development are K, P, S, Ca, Mg, Fe, Mn, B, Mo, Zn, Cu and Se. While the absence of any one of these elements will prevent proper plant growth, the quantitative requirements of each one differ quite considerably and this enables the list to be divided into two main groups.

In the first group are those elements required in significantly large quantities and which within certain limits, show a direct correlation between amount of growth and quantity of nutrient element available. These elements usually occur as constituent elements in organic compounds elaborated during growth, e.g. Magnesium is a constituent of chlorophyll; phosphorus and sulphur are constituent elements of certain proteins but they may also be concerned with the actual syntheses of such compounds during growth, e.g. phosphorus is involved in high energy chemical bonds which enable certain reactions to proceed in a forward direction; calcium can combine with surplus organic acids which might slow down metabolic processes and release them should there be a demand for any particular supply. The elements in this first group are K, P, S, Mg, Fe, and Ca and these are often referred to as macro nutrients.

In the second group are the elements which are only required in extremely small amounts for full and successful plant growth, and provided a minimal supply is available to the plant, growth proceeds to the maximum extent. These elements have been shown to be the activators of the enzymes which promote various metabolic processes in many enzyme systems, specific relationships exist although in some enzymes a certain degree of substitution of metal coenzyme can be tolerated. These trace
elements or micro nutrients include Mn, B, Mo, Zn, Cu and Se. Besides being useful as micro nutrients for plants, they also provide the essential elements required by the grazing animals which normally exist on plant products. The plants also supply a few additional elements like cobalt, iodine and fluorine, and in the agricultural production of crops it is important that these elements should be present in the plant in adequate amounts.

Some elements inhibit biological growth, and their absorption by plants can cause death or lack of perfect development. Arsenic, chromium, lead and nickel are in this category, but it is also important to note that several of the essential nutrient elements can also be toxic to the plant or to the grazing animal if they are absorbed by the plant in amounts in excess of normal requirements. Of particular importance here, are boron, copper, fluorine, molybdenum and selenium. All the other elements which may or may not be present in plant ash are there accidently. Their adventitious presence in the soils leads to absorption by the plant root and their inertness to biological reaction invokes no special mechanism on the part of the plant to reject them.

The following list gives the status of various elements in plant nutrition, including those elements essential for animal growth, which normally originate in plants. Elements of doubtful importance or of importance in a limited range of plants are placed in brackets.

<table>
<thead>
<tr>
<th>Macro-nutrient elements</th>
<th>Micro-nutrient elements</th>
<th>Harmful elements</th>
<th>Incidental elements</th>
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</thead>
<tbody>
<tr>
<td>C  Mg</td>
<td>B  (Ba)</td>
<td>As</td>
<td>Ag    Ge    Ti</td>
</tr>
<tr>
<td>H  S</td>
<td>Co  (Ga)</td>
<td>Cr</td>
<td>Au    Hf    Pt    Ti</td>
</tr>
<tr>
<td>O  Ca</td>
<td>Cu  (Li)</td>
<td>Ni</td>
<td>Be    Hg    Re    W</td>
</tr>
<tr>
<td>N  Fe</td>
<td>F  (Ra)</td>
<td>Pb</td>
<td>Bi    In    Ru    Y</td>
</tr>
<tr>
<td>P  (Si)</td>
<td>I  (Rb)</td>
<td>As</td>
<td>Cd    Ir    Sb    Yb</td>
</tr>
<tr>
<td>K  (Na)</td>
<td>Mn  (Sc)</td>
<td>Cr</td>
<td>Ce    La    Sm    Zr</td>
</tr>
<tr>
<td></td>
<td>Mo  (Sr)</td>
<td>Ni</td>
<td>Cs    Nb    Sn</td>
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<td></td>
<td>Se  (U)</td>
<td>Pb</td>
<td>Dy    Nd    Ta</td>
</tr>
<tr>
<td></td>
<td>Zn  (V)</td>
<td>As</td>
<td>Eu    Os    Te</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Ga    Pd    Th</td>
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</tbody>
</table>
Many of these nutrients may be present in soil as ions and the ionic strength measurements of soil solutions give an estimate of their total amount. Ionic strength has a linear relationship with electrical conductivity of soil solution [Alva et al. 1991]. Ionic strength calculated by using the relationship $I = \frac{1}{2} \sum c_i z_i^2$ where $c_i$ and $z_i$ are concentration and valence of the cations and anions respectively. Ionic strength is an important soil solution parameter in understanding surface charge characteristics of variable charge soils [Gillman and Bell 1978, Gillman 1981, Bolan et al. 1986, Gillman and Sumner 1987, Alva et al. 1990].

1.3. Impact of petroleum drilling

Lithosphere has been gradually degraded mainly due to human activities through expansion of habitat and industries. Of all the industrial activities, petroleum exploration, drilling, refining and production of petrochemicals could be held mainly responsible for polluting the lithosphere.

The word petroleum is derived from two Latin words petra - rock and oleum - oil. Petroleum is called rock-oil or crude oil. Petroleum was in use some 5000 years ago. The liquid crude oil and the solid bitumen, were first used by Sumerians, Assyrians, Babylonians, and Egyptians, who obtained it from natural seepages in some places. The solid form of oil asphalt or bitumen was first noticed on the shores of lake Asphaltite, which fact gives it the name. In ancient India, at Mohen-Jo-Daro, oil was used as a leak proofing material in bathrooms, the liquid oil was also used as a fuel for burning torches at night and later for cooking food.

At the end of 19th century, there was little progress in finding how oil was generated and where it could be located from the surface. The famous first well, drilled by Col. Edwin Lorentine Drake at Titusville, Pennsylvania U.S.A. on 27th August 1859
strode: oil at a depth of about 21m from the surface. The well blew out but, fortunately for Drake, the blow-out stopped by itself. This was the first scientific attempt at locating oil in the sub-surface. Drake can thus be said to have laid the foundation of the modern oil Industry. In November, 1890, the Assam Railway and Trading company drilled a well at Digboi. It struck oil and was completed as a produce at a depth of 662 feet (220 metres) with a production of 200 gallons (900 litres). The Digboi well No.1 is the real harbinger of oil in India.

Crude oil consists, for the most part, of an extremely complex mixture. The petroleum contain five main classes of hydrocarbons:

(i) Normal Paraffins  (ii) Branched Chain Paraffins  (iii) Cyclo Paraffins
(iv) Aromatics  (v) Asphalts

The crude oil also contains oxygen, nitrogen, sulphur, and varying amounts of heavy metals i.e. vanadium, nickel, iron, copper etc.

1.3.1 Damage to water bodies

During the exploration and exploitation of petroleum resources of an area, the surrounding environment gets polluted in a variety of ways. In course of seismic surveys for sub-surface petroliferrous structures, the seismic shot holes mode, may lead to a permanent damage to the fresh water aquifers in the area by allowing shallow polluted water and alkaline waters to enter deeper potable aquifers, defective caring and cementing programmes can lead to shallow aquifers getting mixed by cross formational flow.
Water bearing formations in the surrounding areas may also get spoiled by seepage of water containing dissolved salt and mud and chemicals from drilling. Mud stored in pits around drillsites, oil spills on land and on water may damage the ecology of the surrounding area and the waste products produced during these operations may pose disposal problem.

The major by-products of oil field operation are oil field brine, oil bearing water and oil drill mud. All these by-products require adequate treatment and safe disposal in order to prevent environment from getting contaminated with the offensive substances present in these by-products. In the early days of the oil industry oil field brines were allowed to flow by natural drainage into streams until it was noted that some of the once good fishing streams contained less fish, that fur bearing animals had disappeared in these areas and dead trees, and barren soil bordered these streams that once had luxurious vegetation. Because of increasing demand for fresh water and the adverse effect of brine and drill mud on the suitability of fresh water for domestic uses, it is no longer possible to dispose of these waste waters directly into rivers, streams and lakes.

The inorganic and organic additives that are currently in use in drilling mud, which include a number of friction reducers, additives for fluid loss control, varieties of inhibitors and additives added to control the properties of acidising fluid may find their way to the water environment, if these fluids are disposed without giving adequate treatment.

In a highly rural and agricultural society any spoilage of agricultural soils can be of major concern. Disposal of solid wastes and sludges on land is generally done in limited and planned areas and yet there are instances reported where washings or leachings from such dumped sludges and solid wastes have damaged fields.
Oil field brine with high dissolved solids, if allowed to flow freely over cultivated land, may ruin the vegetation and render the land completely useless for further cultivation.

Oil floating on the open sea is a threat to fish. Oil spills kill adult fish in open sea. Oil on the sea has, however, two visible well known effects. It reduces coastal amenities and kill sea birds. Birds are particularly vulnerable to oil pollution as oil is liable to trap birds in particular ways. If birds come in contact with liquid oil it soaks their plumage and destroys its water proofing and insulating properties so that the birds are killed and are liable to die of exposure and exhaustion. If they inhale or swallow toxic components of the oil while attempting to clean themselves, this may lead to internal damage to the respiratory, alimentary or excretory systems. Oil pollution is therefore likely to cause more damage to bird population than to any other form of wildlife if pollution is not controlled [Singh 1992].

1.3.2 Gas flares

In products operations, the management of oil wells needs to be looked into carefully. Presently, the unrecoverable portion of natural gas from the oil wells is allowed to burn continuously. The flares are highly intense and rise upto 15-26m in the sky. Such burning torches are a common sight in the landscape of Sibsagar District in Assam, as well as in other areas where the oil wells have been discovered [Rao 1984].

The flares generate tremendous heat and cause temperature build up vis-a-vis thermal imbalance in the area. During calm period the flame goes upwards vertically, making the air shed unstable, but during windy periods it has a lateral or horizontal transport. There is increase in temperature, decrease in density and decrease in humidity of the air mass around the flame. An area, having large number of flares, may experience
development of low pressure and incidence of frequent storms, especially during summer time.

1.3.3 Solid wastes

The source of solid waste starts from the moment the well has been spudded. The main solids during drilling are generated in terms of drill cuttings, sand and clay. In a well with a depth of about 4000 m, may produce cuttings volume to the tune of about 300 m³. Besides, the solid spills from the base drilling fluid material such as bentonite, baryte, polymers etc. may be between 10 and 15% of the total consumption of the materials. The chemical settleates from the chemical tank and solids from settling tanks add another 15-20 m³ of solids. In some rigs, where effluent treatment systems are available, solid wastes generated may be between 40 and 50 m³. By all fair estimates all the solids put together in a rig operating for a period of about 6 months the waste solids will be around 450 m³.

In the prevalent plan for drilling rigs while provisions exist for holding the generated waste water, inadequate plan for solids containment may result in creating an adverse environment.

Chemical Distribution and Solids Generation:

The scrutiny of the data over a period of time for different deepwells (3000-5000 m) in the eastern region indicates that bentonite and baryte put together account for 87% of the total chemical consumption in the drilling fluid system. The distribution of chemical consumption is illustrated in Fig. 1.2. The other chemicals such as lignosulfonate, lignite and caustic soda accounts for about 5% of the total volume of the chemical consumption. The other chemicals such as polymers, thinners and other additives (use
depends on the null condition) add to a volume of around 8%.

Solids generation and their distribution in the operation of a drilling rig are indicated in Fig.1.3. The drill cuttings and clays constitute the largest portion (65%) while the sludge (10%) can be very important from the point of polluting the soil where it is discharged.

Drill site Layout and Equipment Position

The efficient management of the solids generated in a drill site, to a great extent, depends on the drillsite layout and equipment position. The basic consideration of solid holding pit has to be invariably made at each drill site, independent of the nature of the well deep or shallow. Adopting to this criteria would solve a major part of the solids handling problem. The second stage to overcome the entangled problem, may come in the form of positioning of the equipments.

Solids Management

As has been indicated in the Fig.1.4 about 80% of the solid waste comes from the drill cutting or clay material, settleates from the settling tanks and solid spills from chemical stores and stock yards. Another 10% has been contributed by the treatment units. Wherever, the treatment unit is available as mobile, their positioning can be made according to the vantage requirement. The other 10% of the solid is generated from unknown sources, which need not cause undue concern. Therefore, when 90% of the solids generated from the operating location is taken care of, it can be assumed that the problem has been as good as contained. Therefore, as has been estimated, and the basis indicated earlier, the solids holding pit has to be made accordingly. The drilling rig can be broadly classified in terms of their derrick engine power and accordingly, the depth of
**Fig 1.2** Distribution and consumption rates of additives in drilling fluid.

**Fig 1.3** Solids generation and their distribution ratio.
Figure 1.4 Drilling Fluid circulation system and solid drilling mechanism.
the well to be drilled by a particular rig is decided. Therefore, the layout plan can be made in the maximum of their depth limit. However, the unique geographical location of a site, even otherwise need an isolated approach considering its critical location, climatic conditions, etc.

**Disposal Mechanism**

Having planned the solid management to the strategic advantage, the collected solids can be effectively used for land filling or wherever, it is required. These materials are not classified as hazardous in the conventional sense and they do not need any underground, sealed burial. If land filling is not possible, incineration may be an alternative way of disposal; however allowing the material to be biodegraded in landfills, is considered the best possible method, having also economic viability.

Effluent treatment units generate a sludge volume of 10% where the solid volume is no more than 1%. The remaining 9% is nothing but water. The entire 10% volume spreading on the earth can reduce the solid volume to a mere 1%. Alternatively, squeezers may be employed. However, considering the period of operation of the rig and the overall cost of the treatment, the squeezers may not be economical. Thus, adopting to the spreading practice, the reduction in the solid volume can be easily achieved to the tune of 75 m³, a significant volume considering the limited period of operation. The drill cuttings of the sand zone and other gravel piece materials can be made to be lifted by the local inhabitants through suitable encouragement, incentives and motivation.

**1.3.4 Oil Spill on Soil**

In an accidental spill the contaminated soil area will be determined by numerous factors. The volume of the spill, the viscosity of the oil at the prevailing environmental
temperature, the contours of the land, and the porosity of the soil are the primary
determinants, but surface roughness, litter, plant cover, and weather conditions other
than temperature can become major contributing factors to the distribution of spilled oil.
In environmental impact assessments for pipelines and other petroleum handling
facilities, attempts are made to estimate the frequency and size of accidental spills and
the area of land affected by them. Obviously, some of the above factors, such as spill
volume and oil viscosity, readily lend themselves to calculation, while others are more
elusive. Complex equations have been developed by several authors for calculating the
distribution of terrestrial oil spills [Raisbeck and Mohtadi 1974; Somers, 1974; Mackay
and Mohtadi 1975; Vanloocke et al. 1975; McGill et al. 1981] but the reliability of
predictions based on such equations is very limited. Essentially, two models can be
assumed.

The simpler model is based on soil that is impermeable to oil because of freezing,
water saturation or extreme compaction. On such a surface, assumed to be flat, Raisbeck
and Mohtadi (1974) described the spread of oil from a point source by the formula:

\[ r = \left( \frac{Q}{\pi h} \right)^{1/2} t^{1/2} \]

where
- \( r \) = radius of the oil spill at time \( t \)
- \( Q \) = rate of spillage
- \( h \) = thickness of the oil layer
- \( t \) = time

According to this equation the oil spill radius will be proportional to the spill time
raised to the power of 0.5. The thickness of the oil layer is assumed to be constant and
dependent on surface roughness and oil viscosity. In reality, oil viscosity will change
with time and distance from the spill source because of evaporation and temperature
change, thus also altering the thickness of the slick. Variations in surface roughness and
land contour also limit the predictive power of the equation.

The situation for a permeable surface is considerably more complex. The horizontal spread of the oil is reduced by the amount that infiltrates into the soil (vertical movement). The formula developed by Raisbeck and Mohtadi (1974) for the spread of oil on a porous surface is:

\[
 r = Q \left[ \frac{r_c \gamma (\cos \theta)}{2 \mu \pi} \right]^{1/2} t^{1/2}
\]

Where

- \( r_c = \) radius of soil capillaries
- \( \gamma = \) surface tension at oil air interface
- \( \theta = \) angle of contact between oil and solid, expressing the "wettability" of soil particles by the oil
- \( \mu = \) viscosity of the soil

In this formula infiltration is considered dependent on the average radius of soil capillaries, the surface tension, the "wettability" of the soil by oil, and the viscosity of the oil. The soil is considered to be completely dry, and the oil flow to be a single phase liquid system. This severely limits the usefulness of the equation. As discussed by Somers (1974), soils are partially saturated with water. The flow is that of a two phase liquid system. It needs to be considered, in addition, that the "wettability" of soil particles by oil will change with their hydration state. These practical considerations introduce complexities that preclude reliable calculations based on theoretically derived equation
like this. At best, it can be concluded that on a porous surface the radius of the spill will tend to be proportional to the 0.25 power of the time period of the spill as compared to the $t^{1/2}$ for spill on impermeable surface.

Because of the limitations of this theoretical approach, the calculations by Mackay and Mohtadi (1975), based on measurements derived from accidental and experimental spills, appear to be somewhat more useful. On the porous soils of the Mackenzie valley the following relationship between contaminated area and spill volume was established:

$$\text{Spill area (m}^2\text{)} = 53.5 \times [\text{Spill Volume (m}^3\text{)}]^{0.89}$$

Even in the above case, the authors caution that the actual spill area may differ from the calculated one by a factor of 3 and, in extreme cases, by a factor of 8.

The vertical and subsurface movement of oil was described by Vanlooocke et al. (1975) as follows:

$$D = KV/A$$

Where,

- $D =$ maximum depth of penetration (m)
- $V = \text{Volume of spill of oil (m}^3\text{)}$
- $A =$ area of infiltration
- $K =$ Constant based on oil retention capacity of the soil and on viscosity of the oil (values of $K$ for different soils and petroleum fractions range from 400 to 12)
If sufficient oil is spilled on porous soil, it tends to move down to the water table and spread at the surface of the water table into a "pancake". The area of the underground "pancake" was described by the same authors by the equation.

\[ S = \frac{1000}{F} (\frac{V}{d} - \frac{Ad}{K}) \]

Where \( S \) = maximum spread of oil (m²)

\( d \) = depth of ground water table (m)

\( F \) = thickness of oil "pancake" (mm) (values for \( F \), according to soil type, range from 5 to 400 m.)

Small quantities of oil dissolve in the ground water, and unfortunately, very small quantities are sufficient to taint it. According to Mckee et. al. (1972) and Vanloocke et al. (1975), concentrations as small as 1-5 ppm hydrocarbon will cause a foul taste and odour in the water. Displacement by rainwater and fluctuation of the water table will cause further migration and spreading of the underground oil. [Raisbeck and Mohtadi, 1974; Somers, 1974; Vanloocke et al. 1975; Mckendrick et al. 1981].

The relative importance of surface to underground pollution varies with spill size, soil type, and weather conditions. Small and slow spills tend to contaminate a small surface but relatively large underground area, while in the case of large and rapid spills, surface spreading predominates [Mackay and Mohtadi, 1975].

Rainfall prior to or during the spill will reduce oil infiltration into the soil and wash petroleum components away in runoff waters [Francke and Clark, 1974]. Heavy crude and fuel oils, because of their high viscosity, tend to move horizontally, while
gasoline and low-viscosity oils penetrate readily into deeper soil strata (McGill and Rowell, 1977).

The absorptive capacity of soils for oil varies but is considerably less than their water-holding capacity. Schwendinger (1968) reported that well-drained agricultural soils absorb up to one-third of their water-holding capacity. Adsorption to soil organic matter plays a significant role in temporary immobilization of oil [Mackay 1975; McGill et al. 1981].

The oil concentration in the soil of the contaminated field decreases with time. Initially oil concentration is higher in the upper 1 to 30 cm layer of soil, but after 6 months the more rapid decrease of oil in the upper layer reverses the situation. Biodegradation, evaporation and leaching could be considered as causes for this decrease, but leaching has been shown to be not the most significant factor [Raymond et al. 1976, Dibble and Bartha 1979(a) and 1979(b)].

If oil is spilled on the surface of soil during the drilling operations, it affects the soil system in various ways. When present in soil, oil may cause increase in organic carbon, immobilization of N and P and reduction in population size and biomass of soil microflora. It may also inhibit seed germination, possibly by checking the imbibition of water and diffusion of gases into the seed. In oil saturated soils, the root hair gets plasmolized and root system of plants get killed, leading to eventual death of plants.

If the oil covered surface of soil catches fire, there is wholesale destruction of ground cover and microbial flora as well as a decrease in soil moisture due to increased temperature.
Refining of crude oil also generates oil sludges as a major solid waste. Common sources of these sludges are storage tank bottoms, oil-water separators, effluent treatment plants, cleaning processing equipment and soil from occasional spills on refinery grounds. The quantity of sludges generated at refinery is so high that it needs proper treatment before disposal like incineration [Hitchcock 1979] and land spreading [Kincannon, 1972, Francke and Clark 1974; Dibble and Bartha 1979(a)].

In oil sludge, nitrogen content ranged between 0.1 and 0.4% [Trushell 1979, Janiyan et al. 1993]. The source of this nitrogen must be the nitrogenous compounds in crude petroleum, which are pyridine derivatives (including quinolines, and phenanthridines), indole derivatives (including pyrroles, carbazoles, and benzo carbazoles), and aromatic amides [Synder and Saunders 1979]. The oil sludge spread on land, may therefore add to the fertility of land, but impact of other harmful ingredients of the sludge has also to be considered, which might outweigh the nutritional quality of the sludge. Not much study appears to have been done on this regard.

1.3.5. Impact of oil on soil quality

The damaging of soils by crude oil and salt water is of common occurrence in petroleum producing regions. A study of the mechanism of injury to soil by petroleum and recommendations for the reclamation of the oil injured soils was undertaken by Plice (1948).

Baldwin (1922) found that increasing amounts of crude oil retarded nitrification in soil, but it began again in all instances within 2 weeks of incubation. Bacterial counts rose with increasing amounts of oil but bacterial “types” were reduced by the larger amounts. The numbers of anaerobes were little affected by the oil increments. Results in growing corn were not striking but the yields were highest on the plants receiving the
largest amount of crude oil. Murphy (1929) reported that nitrate formation in soil was reduced even by very small applications of oil. One percent of oil, when mixed with the soil practically checked nitrate formation.

In a study of soil bacteria which attacks crude petroleum, [Stone 1941] found that such organisms appeared to be present wherever soil samples were taken. He stated that there seemed to be no specialized group of organisms involved and that all of the common soil forms have the ability to adopt themselves to an infinite variety of organic compounds. He found, however, that different oils vary in their degree of susceptibility to bacterial attack. In general, lighter weight oils oxidize more readily than heavier ones and paraffinic oils more easily than asphaltic (aromatic or naphthenic) oils.

An oil spill has its influences on the soil microbial activities. It was observed by Albrechtsen (1991) that such an oil spill on Danish salt marsh resulted in an increase in the number of bacteria, yeast and fungi.

Soil that is accidentally contaminated by petroleum fuel spills is classified as hazardous waste [Bartha and Bossert, 1984]. When the amounts of contaminated soil are large, the currently accepted disposal methods of incineration or burial in secure chemical landfills can become prohibitively expensive. This often results in cleanup delays while the contaminated soil continues to pollute scarce ground water resources [Pye and Patrick, 1983]. Petroleum hydrocarbon disappearance rates were compared in contaminated but otherwise untreated soil, in bioremediation treated soil, and in soil poisoned in order to suppress biodegradation. [Pramer and Bartha 1972, Song et al. 1990].

A considerable work on effects of crude oil and petroleum pollutants on fresh water and ecosystem in respect of micro-organisms has been reported [Conney et al.
1968, Cooney and Walkar 1973, Cooney and Summers, 1976]. Oil exerts adverse effect on soil conditions [Rowell 1977] and only a few beneficial effects of well degraded oil on soil biota has been reported [McGill 1980]. Some investigators have examined the effectiveness of a few inorganic fertilizers [Atlas and Bartha 1973, Toogood et al. 1977, Amadi et al. 1993] and some organic nutrient supplements [Lehtomaki and Niemela, 1975] in oil polluted soils. It has also been found that the oil hydrocarbons can infiltrate up to a depth of 50 cm. [Ilangovan and Vivekanandan 1992].

The class of co-ordination compounds in soil comprises of compounds of sufficiently strong donor acceptor interaction. Its subclasses are mineral, organomineral and organic. They are divided into families according to co-ordination mechanisms such as complexes with and without charge transfer, molecular association complexes, $\sigma$ and $\pi$ complexes etc. [Karpukhin 1990].

Organic pollutant migration in soils is affected by soil organic matter. Molecular and mechanistic aspects have been studied to a considerable extent [Senesi 1993]. It is pointed out that various factors such as soil humic substances, organic pollutants in soils, adsorption mechanisms, ionic bonding (cation exchange), hydrogen bonding, electron transfer (electron donor - acceptor) etc. influence the migration and mobility of soil organic matter.

1.3.6 Fate of hydrocarbons on soil

Adsorption of selected petroleum hydrocarbons (benzene, o-xylene, toluene and n-hexadecane) on a series of Canadian soils was studied by Nathwani and Philips [1977]. It was found that at concentration between 1 and 100 ppm the equilibrium distribution of the hydrocarbons studied was described by the Freundlich Isotherm. Eltantwy and Arnold (1972) presented evidence of interlayer sorption of n-hexane and
n-dodecane by Ca-wyoming montmorillonite. n-Hexane was able to form a single layer complex with the clay to the extent of 110 mg n-hexane and n-dodecane per gram. n-alkanes can penetrate the interlayer space of montmorillonite but at a very slow rate. Theng (1974) pointed out that the intercalation of hydrocarbon species into the expanding layer silicates was essentially a process in which part of the interlayer water associated with the exchangeable cations was replaced by the organic species. In dehydrated systems, where the silicate layers of a clay crystal are fully collapsed, intercalation of hydrocarbons is either absent or proceeds only with difficulty.

Hydrocarbons within the saturated fraction of crude oil include n-alkanes, branched alkanes, and cycloalkanes (napthenes). The n-alkanes are generally considered the most readily degraded components in a petroleum mixture [Zo-Bell 1946, Mckenna and Kallio 1964, Treccani 1964, Davies and Hughes 1968, Katar et al. 1971]. The biodegradation of n-alkanes normally proceeds by a monoterminal attack; usually a primary alcohol is formed followed by an aldehyde and a monocarboxylic acid. [Miller and Johnson 1966, Ratledge 1978].

Highly branched isoprenoid alkanes, such as pristane, have been found to undergo omega oxidation, with formation of dicarboxylic acids as the major degradative pathway [Mckenna and Kallio, 1971, Pirnik, et al. 1974, Pirnik 1977]. Methyl branching generally increases the resistance of hydrocarbons to microbial attack [Fall, et al. 1979, Schaeffer, et al. 1979]. Schaeffer, et al. (1979) found that terminal branching inhibits biodegradation of hydrocarbons. Methyl biodegradation of the beta position (anteiso-terminus) blocks β - oxidation, requiring an additional strategy, such as alpha oxidation. (Beam and Perry 1973, Laugh 1973), omega oxidation (Pirnik 1977), or beta alkyl group removal [Seubert and Fass, 1964, Cantwell et al. 1978].

Cycloalkanes are particularly resistant to microbial attack [Ooyama and Foster
1965, Donoghue et al. 1976, Stirling et al. 1977, Trudgill 1978, Perry 1979]. Complex alicyclic compounds, such as hopanes (tri-penta cyclic compounds) are among the most persistent components of petroleum spillages in the environment [Atlas et al. 1981]. Upto six-membered condensed ring structures have been reported to be subject to microbial degradation. [Cobet and Guard 1973, Walker et al. 1975]. Several unsubstituted cycloalkanes, including condensed cycloalkanes, have been reported to be substrates for co-oxidation with formation of a ketone or alcohol [Beam and Perry 1973, Beam and Perry 1974(a) and 1974(b), Perry 1979]. Once oxygenated, degradation can proceed with ring cleavage. Degradation of substituted cycloalkanes appears to occur more readily than the degradation of the unsubstituted forms, particularly if there is an n-alkane substituent of adequate chain length [Soli 1973, Perry 1979]. Normally microbial attack occurs first on the substituted portion, leading to an intermediate product of cyclohexane carboxylic acid or a related compound. The degradation of cyclohexane carboxylic acid involves formation of an aromatic intermediate [Perry 1979] followed by cleavage of the aromatic ring structure.

The degradation of aromatic hydrocarbons has been studied by [Rogoff 1961, Gibson 1968, Gibson 1971, Gibson and Yeh 1973, Gibson 1976, Gibson 1977, Cripps and Watkinson 1978, Hopper 1978]. The bacterial degradation of aromatic compounds normally involves the formation of a diol followed by cleavage and formation of a diacid such as cis, cis-muconic acid. In contrast, oxidation of aromatic hydrocarbons in eucaryotic organisms has been found to form a trans diol. Fungi have been shown to oxidize napthalene to form trans 1,2 dihydroxy 1,2, dihydronaphthalene [Ferris et al. 1976, Cerniglia and Gibson 1977 and 1978, Cerniglia et al. 1978].

The metabolic pathways for the degradation of asphalitic components of petroleum are probably least well understood. These are complex structures which are difficult to analyze with current chemical methodology. The degradation of various sulfur
containing components of petroleum has been examined [Kodama et al. 1970, Hou and Laskin 1976, Walker et al. 1976] but no uniform degradative pathway, comparable to the pathways established for aliphatic and aromatic hydrocarbons, has yet emerged for the asphaltic petroleum components. Often, the benefits and good services derived from crude petroleum are put to question by the environmental hazards caused by oil spills. Crude oil contains toxic substances such as polycyclic aromatic compounds which can combine with common environmental materials to form carcinogens [Sewell 1975]. Therefore, the problem of petroleum pollution of ecosystems has resulted in intense investigations into the sources of and biological impacts of this major form of pollution [Amund and Igiri 1990].

1.3.7 Fate and impact of oil in water

The widespread use of petroleum and its by-products has inevitably resulted in...
the discharge of oil to the environment. With reference to aquatic systems, it is the marine ecosystems that has received the greatest attention, since the majority of the oil spills have involved accidents at sea. However, some freshwater systems have been seriously polluted with oil, and indeed the single largest source of oil discharge to the oceans is river runoff [NAS, 1975]. In other words, a study of marine oil pollution encompasses most, if not all, of the problems relevant to freshwater oil pollution as well.

The presence of petroleum or refined petroleum products in aquatic ecosystems is generally harmful for physical reason, i.e. coating, smothering etc. or because water soluble fractions of the oil are toxic to the biota. Crude oil causes more physical damage and fuel oil is generally more toxic.

Oil is most objectionable in a stream, not only from an aesthetic standpoint on account of the visible pollution it causes, but also because it spreads to form a thin film on the surface and so tends to prevent diffusion of oxygen into the water, thus interfering with re-aeration of the river water. Oil in any considerable amount tends to coat the gills of fish, thus making the utilization of dissolved oxygen difficult or even impossible. Often undegraded effluents from refinery and sewage are deposited as an oily sludge on the stream bed, thus impairing the quality of the water especially when there was a flush out after a period of low flow [Ludzack et al. 1957].

Petroleum products are remarkably stable in the marine environment. Although they are well protected when the sediments are anaerobic. For instance in a spill of fuel oil in 1969, at West Falmouth, U.S.A., oil was incorporated into the sediments of coastal waters, rivers, harbours and marshes but remained still present in the sediments one year after the accident, and transport of oil laden sediments contaminated area beyond those immediately affected by the spill [Blumer et al. 1970].
Hydrocarbons that are dissolved in the water column are eventually destroyed by bacterial attack. The analysis of the fat of oysters, polluted by a fuel oil spill showed that the amount and chemical composition of fuel oil hydrocarbons remained nearly unchanged even after six months in a clean aquarium [Blumer et al. 1970]. The hydrocarbons that are ingested by the marine organism can pass through the wall of digestive tract and can be retained for long term [Blumer, 1967].

The effect of oil discharge in ocean is determined by the nature of hydrocarbons involved. Although other factors, including weather conditions and the distance of the discharge from the shore, also play an important role in determining the extent of ecological damage [Kerr, 1977].

There is no doubt that some bacteria can metabolize petroleum hydrocarbons, but no single bacteria is effective against all hydrocarbons in crude oil [EPA, 1972].

There is also definite tendency for the toxicity per unit molecular weight to decrease as the molecular size of the hydrocarbons increases [Nelson-Smith 1972]. Aromatics and other toxic hydrocarbons apparently exert their effects by disruption of interior of cell membranes and cease to properly regulate the exchange of substances between the interior and exterior of the cell. In extreme cases the cell membrane may lyse, allowing the contents of the cell to spill out and obviously destroying the cell. Although the low molecular weight alkanes and cycloalkanes were once considered to be harmful to aquatic life, it is now known that these compounds can cause necrosis and anestheses in a variety of lower animals [Blumer, 1969].

The oil pollution of aquatic environment seems to have least concern with public health, because only a few large aromatic hydrocarbons are carcinogenic compounds but, they are present in very small amount in crude oil and can not be ingested by persons
eating oil contaminated fish or shell fish. When the concentration of petroleum hydrocarbons in marine organism exceeds 200-300 ppm, the organism acquires a distinctly tainted taste and becomes unpalatable, therefore can not be eaten any way [NAS, 1975]. Although the carcinogenecity is a matter of great concern, but at present there is no reason to ensure that oil pollution of aquatic resources is a significant public health problem.

1.3.8 Effects of petroleum hydrocarbons on vegetation

The oil production operations may affect vegetation in various ways, which may include effects of oil (liquid and vapour), flare heat, flare pollutants, photochemical pollutants and combination of different gaseous pollutants. It may be pointed out that all the primary (SO₂, NO₂, HC, SPM) and secondary (O₃, PAN) pollutants may effect singly as well as in combination with the others [Rao et al. 1988].

The flame and heat of the flare cause direct burning of leaves of plants nearby. The green leaf represents the energy production potential of the terrestrial ecosystem and thus the burning of bamboo forests in the oil well area of Sibsagar in Assam, represents a direct loss to the ecosystem, affecting the natural food chain and economic pattern of the area. The herbs and shrubs affected by the flare, show burning of leaves, buds, young branches and the entire shoot system. The area of vegetation damage from the proximity of the oil well, gradually enlarges with time. The flares, thus, have a continuing stress on the soil structure and influence the biological production of the ecosystem.

All the primary and photochemical pollutants, produced in the air environment around the flame zone are phytotoxic in nature and they certainly effect the health status of plants growing in the area. Though the effects of specific pollutants is hard to
decipher but the total effect of injury is clearly visible in the form of species extinction; asymmetrical canopy, folian necrosis, leaf size reduction, stunted growth, phenomenological changes, decreased life-span and reproductive potential, leaf senescence, defoliation and premature drops of flowers and fruits. All such stressed plants show reduction of chlorophyll pigment in their leaves [Rao et al. 1988]. It was also shown that the chemical composition of flare - components and emissions from an oil refinery are more or less similar.

Petroleum pollution of soil generally has strong negative effects on the plant community. The mode in which petroleum acts on plants is complex and involves both contact toxicity and indirect deleterious effects mediated by interactions of the petroleum with the abiotic and microbial components of soil. The low boiling components of petroleum exhibit a high degree of contact toxicity to the tender portions of plant shoots and roots, but they have little effect on the woody parts of trees and shrubs. Contact toxicity occurs primarily by the solvent effect of low boiling hydrocarbons on the lipid membrane structures of the cells. The order of toxicity is monoaromatics > olefins and naphthalenes > paraffins. Within each class toxicity is positively correlated to increasing polarity and inversely correlated to increasing molecular weight [McGill et al. 1981]. The low boiling petroleum components are readily removed from the biologically active surface layer in moist, well drained soils through evaporation and leaching [Hunt et al. 1973] and therefore, the effects of these components are of short duration. The direct effects of petroleum pollution include the plant growth regulatory effects of napthenic acids [Fattah and Wort, 1970]. Indirect effects of petroleum pollution in soil include oxygen deprivation of plant roots, because of exhaustion of soil oxygen by hydrocarbon degrading microorganisms. Such anaerobic conditions may bring about the microbial generation of phytotoxic compounds, such as H₂S. Oil degrading microorganisms compete with plants for mineral nutrients.
The oil also affects the physical structure of the soil, decreasing its capacity to store moisture and air [Dejong 1980]. All these negative effects manifest themselves either immediately or during the biodegradation of the polluting oil. Once the biodegradation process of a moderate size spill is complete the negative effects tend to disappear and the soil may actually show improvement in its ability to support plant growth, compared with its pre-spill status. Such improvement is due to the increased amount of organic matter and combined nitrogen in the soil after the biodegradation of the spill. The severity and duration of the effects of a petroleum spill on a plant community are highly dependent on the quantity and quality of the spilled petroleum and on the post-spill treatment and type of the contaminated soil. The effects of accidental or experimental petroleum spills on plants reported in the literature should be interpreted in the framework outlined above.

In areas inundated by accidental oil spills, the herbaceous vegetation cover is quickly killed [Ellis and Adams, 1961, Odu, 1972, Hunt, et al. 1973, Dibble and Bartha 1979(c), Dejong, 1980]. The full extent of the damage to trees and shrubs may not manifest itself until several months after the spill [Bartha, 1977], especially if the soil is cold and the trees dormant. Dibble and Bartha 1979 (c) reported on the case history of a winter wheat field inundated by a kerosine spill. Although the wheat stand was completely killed, the well-aerated, drained, and fertilized sandy soil showed almost total recovery after 10 months and was capable of supporting normal crops. In a less favourable environment the time needed to reestablish a stable plant cover may take more than 10 years. Hunt et al. 1973 reported that the vegetation on an Alaskan soil contaminated with jet fuel recovered only to 65% after 15 years.

The application of oily wastes to soil in moderate amounts (1-5% oil in the upper 15cm soil layer) usually has less deleterious effects on the plant community than do the
large scale accidental spills [Baldwin 1922, Schwendinger 1968, Raymond et al. 1976]. Very low hydrocarbon level (<1% oil) may actually stimulate plant growth and crop yield. This may be due in part to petroleum components acting as growth hormones [Fatah and Wort, 1970]. Delayed growth enhancement may also occur in response to the greater humus content and water holding capacity of soils that have recovered from an oil contamination incident.

The climate and nutritional status of a soil play an important role in the recovery of its vegetation. Arctic regions with short growing seasons and nitrogen-poor soils generally exhibit the most deleterious and prolonged effects of oil contamination on the plant community. Lower hydrocarbon biodegradation rates, decreased evaporation of toxic, volatile petroleum components and shorter growth seasons act to retard revegetation. Arctic plants contaminated with petroleum hydrocarbons loose frost hardiness and die during the winter; the resulting large input of dead plant matter, together with petroleum hydrocarbons, results in retardation of hydrocarbon, and sometimes cellulose, decomposition [Linkins et al. 1978]. An additional concern in Arctic and subarctic soils is the deterioration of the permafrost layer. Elevated amounts of organic matter from dead vegetation may increase thermokarst through greater solar absorption thereby disrupting the fragile ecological balance of an Arctic community [Hunt et al. 1973, Mckendrick et al. 1981].

Plant communities of soils in temperate regions are also affected by organic nutrient depletion following oil contamination. Limited nitrogen reserves are competitively utilized by both plants and hydrocarbon degrading microorganisms [Hoeks 1972, Odu 1972]. During revegetation, nitrogen limitation may select plants requiring little or no exogenous combined nitrogen. In a survey of 15 oil contaminated sites, Gudin and Syratt (1975) reported that leguminous plants were the dominant flora, indicating a selective advantage to plants with a symbiotic nitrogen fixing potential.
Baldwin (1922) demonstrated a significant decrease in nitrate concentrations of amended greenhouse soil to which crude oil was applied. Plant growth of corn, measured as dry shoot weight, proportionately declined with increasing amounts of crude oil added. Supplementary nitrate partially reversed the inhibitory effects of the oil on plant growth. Westlake et al. [1978] reported that N and P fertilization of oil contaminated soil enhanced the rate of revegetation. Inorganic nutrients applied to polluted soils relieve competition for limiting mineral nutrients between microorganisms and plants. In addition, heavy fertilization may overcome restricted mineral nutrient absorption, because of decreased water uptake of roots in a hydrophobic environment [Schwendinger, 1968]. Although petroleum biodegradation is crucial to the rehabilitation of the contaminated soil for plant growth, the process may temporarily increase petroleum toxicity not only by its oxygen and mineral nutrient demand, but also by its metabolic intermediates. Products of incomplete microbial oil degradation include fatty acids and terpenoid materials, which possess phyto-toxic properties [Stevenson 1966]. These and other hydrocarbon metabolites may amplify the phytotoxicity of polluted soils if not removed through leaching or humification processes.

The detrimental effects and subsequent revegetation of soils contaminated with petroleum ultimately rest on the type of flora indigenous to the affected area. As in the microbial community, a decrease in species diversity and a shift in dominant plant types occurs during the revegetation period of oil contaminated soils. Kinako (1981) noted that the lower stages of a Nigerian rain forest community were most adversely affected by crude oil application to soil. Herbaceous plants were most susceptible, whereas perennials became more easily reestablished. Odu (1972) observed that crop plants of a Nigerian agricultural soil polluted by an oil well blow out responded differentially during recovery. Tuberous crops, like yams and cassava, were most adversely affected, even in lightly contaminated areas, and only minimum regrowth occurred, even after six months.
Mango trees and rhizomatous plantation and banana trees appeared to be most adaptable and after initial defoliation, recovered quickly in moderately contaminated areas (6.6 - 7.2% oil), whereas palms did not become reestablished while trees specially conifer failed to reappear during the observation period. In a peat soil [McGill and Nyborg, 1975] revegetation after oil contamination was most successful when grasses were planted. Willow and dogwood seedlings exhibited moderate ability to become reestablished, whereas spruce and larch seedlings were most inhibited. Generally, the plant types most susceptible to oil pollution include seedlings, annual plants with a large surface area or shallow root systems, mosses and lichens [McGill and Nyborg, 1975, McGill et al. 1981].

Plant damage due to natural gas leaks was noted early [Scholloenberger, 1930]. Extensive damage to urban tree plantings in the Netherlands was reported due to underground leakage from natural gas distribution system [Adamse et al. 1971, Hoeks 1972]. Methane, the main component of natural gas, is not highly toxic to plants, the damage is caused indirectly by oxygen deprivation of the tree roots. Oxygen deprivation occurs in part because of physical displacement of air by methane in the soil pores and in part by the rapid use of the remaining oxygen by the methanotrophic bacteria. Processes common to amoxic soils, such as the formation of \( \text{H}_2\text{S} \) may aggravate the damage to the roots and eventually kill the trees. The problem became particularly widespread in the Netherlands when natural gas was distributed through old pipe system with gaskets that had dried out and shrunk, thus causing gas leaks at the pipe joints.

Some effects of petroleum and kerosene used as sprays on vegetation have been noted by Young (1935) who found that the sprays produced varying degree of plant injury, somewhat according to the amounts of sulphonatable fractions present in the oils. The sprays which were low in such fractions caused only slight injury to plants. The
damage proved to be due to two causes (a) “suffocating effect” and (b) toxicity, as su

1.3.9. Problems of salinity on Plants

Crude oil from wells, is always accompanied by water, sometimes, upto 20%. Known as the formation water, this contains oil and salts. The water is separated from the oil as far as possible, but its salt content remains unaltered during the treatment of oil field effluent. When this water is discharged into the soil, it may create salinity problems to various degrees.

Salinity was observed to induce soil macro and micro nutrient deficiencies in an oil field located in East Central Wyoming [Rohman et al. 1993]. Plants acquire mineral nutrients from their native soil environment. Most crop plants are glycophytes and have evolved under condition of low soil salinity. Consequently, they have developed mechanisms for absorbing mineral nutrients in non-saline soils. Under saline conditions, which are characterised by low nutrient ion activities and extreme ratios of Na+/Ca2+, Na+/K+, Ca2+/Mg2+ and Cl-/NO3-, nutritional disorders can develop and crop growth may be reduced [Grattan and Grieve, 1992].

Rice, a moderately salt-sensitive crop species [Mass and Hoffman, 1977], is generally grown during the reclamation of salt affected soils because it can grow well under flooded conditions. In saline environment, plants take up excessive amounts of Na at the cost of K and Ca [Kuiper 1984]. The accumulation of Cl parallels that of Na [Yeo and Flowers 1985]. Both Ca and K are required in the external medium to maintain the selectivity and integrity of the cell membrane [Fageria 1983, Wyn Jones and Lunt 1967]. Ca is also needed for selective transport of ions like K+ across membranes [Wyn Jones and Lunt 1967]. Therefore high Na/Ca and Na/K ratios in saline growth medium may impair the selectivity of root membrane and result in passive accumulation
of Na in the root and shoot [Kramer et al. 1977]. In addition, a low Na/K ratio is equally important for stomatal movement. Rice was grown on a transitional red brown earth for 3 consecutive seasons and irrigated with saline groundwater of salinities 0.25, 0.5, 1.0, 1.5 and 2.0 dS/m. Grain yield was only affected by the 4.0 dS/m treatment, where a 25% yield reduction occurred [Beecher 1991].

1.3.10 Role of Metals

Petroleum refining activities and the effluents generated contribute to the increasing metal content of the nearby soil. For example, Omgbu and Kokogho (1993) have shown that the refining has led to considerable accumulation of Pb, Zn, Hg and Cu in the soil near an oil refinery with an abundance order of Pb>Zn>Hg>Cu.

Heavy metals such as Cd, Cu, Ni, Cr, Pb, Zn are components of commercial fertilizers, pesticides, paints, pigments, mordants, electroplating effluents lubricants, vehicular emissions, mining etc. [Tiller 1989]. Of the global emission of 40 million metric tones of trace metal per annum; more than 70% reach the soil directly through industrial and sewage effluents [Nriagu 1988]. Current anthropogenic emissions have a exceeded the inputs from natural sources [Nriagu and Pacyna 1988] and the resultant heavy metal pollution in natural environment usually never arise from a single metal. Mineralization activities of heavy metals are attributed to soil properties, and there is good evidence that Cd, Ni, and Pb adsorption in soil are related to texture, clay content, pH, CEC, organic matter content, etc [Gadd and Griffiths 1978, Piccolo 1989]. Dar Hassan (1995) hase demonstrated that metals added together are more toxic to soil ecosystems than the additive toxicity of individual metals.

Metal toxicity was more in acidic pH than in alkaline pH ranges. Ca and Mg reduced the toxicity of low concentrations of metals but when metal concentrations were
high, Ca and Mg had very little effect on their toxicity. [Rao and Gowrinathan 1992].

Elkhatib et al. (1992) demonstrated that first order kinetics and parabolic diffusion equations modeled Pb desorption from the clay and sandy soils more accurately than the Elovich or modified Freundlich isotherms. Diffusion and desorption rate constants increased with time. In another study, it was shown that Pb reached depths of 10-15 cm on average and penetrated to 40 cm in heavily polluted roadside areas [Puchlt et al. 1993].

Friedland (1992) demonstrated the trace metal behaviour in organic soils, spatial temporal patterns in trace metal accumulation, vertical distribution of trace metals in the forest floor, and effects of metals on biological, processes in the forest floor.

The speciation and spatial distribution of trace metals in soils were shown to be closely related to their behaviour in multiphase and dynamic soil systems. The behaviour of trace metals in the soil environment depends to some extent on their origin. Lithogenic metals are associated mainly with primary minerals, and may be phyto available under specific conditions in the soil plant system. Anthropogenic metals show great diversity, but in most cases they are likely to be very mobile and easily available to plants [Kabuta - Pendias 1993].

A study of heavy metal contaminated [ Cd 1.1 - 2.7 mg/kg, Zn 234 - 571 mg/kg, Cu 310 - 751 mg/kg] paddy field showed that the no of actinomycetes and bacteria decreased significantly with increasing heavy metal content [Hiroki 1992].

The process of dynamic sorption and leaching of Zn\textsuperscript{2+}, Cu\textsuperscript{2+}, Cd\textsuperscript{2+} and Pb\textsuperscript{2+} cations in three kinds of mineral soils, sand, loess, and loam, with neutral and acid reactions were studied by Gaszczysk (1990). Soil liming caused changes in the
magnitude of sorption from 1.1 to 12.8 times for $\text{Zn}^{2+}$, an increase occurred in all the soil types for $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ and increase in sand and loess soils. Chemical transformation of heavy metals in heavy metal amended soils may occur over short or long periods. [Emmerich et al. 1982, Sposito et al. 1983, Miller et al. 1987]. Studies of $\text{CO}_2$ formation and organic C mineralization rates in soils contaminated with heavy metals showed that although soil respiration was negatively influenced by pollution level, this was not necessarily reflected in a corresponding decrease in $\text{CO}_2$ formation. With the assumption that C mineralization follows first order kinetics, a non linear dependence of mineralization rate on pollutant level was observed. [Benkert and Shindler 1992].

Baker (1970) and Delaune et al. (1979) demonstrated that some elements in oil exert adverse effects on plants. High levels of some elements in soil due to oil spill and leakage may be toxic to plants and animals or may affect the quality of food crops for human consumption. These potentially toxic elements include $\text{Cd, Pb, Se, Zn, Cu, Cr, B, Mn, V, F}$. In particular $\text{Pb}$ and $\text{Cr}$ have attracted the attention of researchers and several reports have been published on soil contaminated with these toxic elements [Cook 1977, Leep 1981, Ali 1982, Martin et al. 1982, Nasralla and Ali 1985 and 1986, Ali and Nasralla 1986]. Bogacz et al. (1991) found an especially large accumulation of $\text{Zn, Cu, Pb and Cd}$ in the soils and plants and a somewhat lesser one of $\text{Cr and Ni}$ in one of the city of Wroclaw quarters in which metallurgical works are situated. Uptake, distribution and effects of metal compounds on plants have been studied by Berrow et al. (1991). Heavy metals were determined in agricultural soils and plants in south-west Madrid. The sequence of heavy metal accumulation in plants with respect to soil content was $\text{Cd}>\text{Zn}>\text{Cu}$ [Moreno et al. 1992]. Walter et al. (1992) demonstrated that the uptake of $\text{Cd}$ and $\text{Ni}$ by plant tissues was dependent on metal concentration in the soil, plant species and soil characteristics.
Application of some by-products of the metal industry, which contain plant nutrients, to agricultural land could constitute resource recovery instead of costly disposal. Some industrial by-products contain appreciable concentration of heavy metal contaminants, such as Cd, Cr, Ni, and Pb. After land application, plant uptake of these heavy metals varies with plant species, soil pH, soil texture and the particular metal [Mortvedt 1992]. The antagonistic and synergistic interaction of plant nutrients such as K, Ca, P, Fe and Al and factors affecting their toxicity in plants and deficiency have been studied by Wang (1992).

The effect of zinc and iron applications on their uptake was studied in four varieties of rice [IR 20, Joya, Pusa 2-21 and IET 1444]. Zinc in increasing doses increased the uptake of the element by the plant. Iron in increasing doses, increased the uptake of iron while it had little effect on the uptake of Zinc, rather there was slight decrease in it [Tandon 1992]. Zn at 0.5 - 5 ppm enhanced rice growth, but high Zn concentration (20-200) ppm was toxic. Zn deficiency retarded rice growth. Rice root accumulated more Zn than the stem and leaves [Dong and Zhang 1992]. Widespread occurrence of Zn deficiency in low land rice has been reported from various countries including India [Giordano and Mortvedt 1972, Randhawa et al. 1978].