GENERAL INTRODUCTION
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Soil is a product, resulting from disintegration and decomposition of rocks, plants and animal materials. It possesses a distinct morphological, mineralogical and physicochemical properties, resulting from certain inheritance, from its unique position on the surface of the earth and from the environmental factors existing at that position. However, according to Joffe (1936) the soil may be defined as a natural body, differentiated into horizons of mineral and organic constituents, usually unconsolidated, of variable depth, which differs from the parent material below in morphology, physical properties and constitution, chemical properties and composition and biological characteristics.

COMPOSITION OF SOIL

Soil is very complex in nature and consists of mainly five important constituents namely mineral matter, organic matter, soil water, soil air and living organisms.

MINERAL MATTERS:

The mineral matter is a product of physical and chemical weathering of rocks consists of particles of varying sizes; those in the finer state of subdivision \( \leq 0.002 \text{ mm} \) form the clay fraction. The crystal structure of clay minerals have been discussed
in considerable detail by Grim, (1953); Marshall, (1964); Van Olphen, (1963). Extensive studies of X-ray diffraction patterns have revealed that clay is crystalline in nature and composed of few simple building units (Donahue, 1977). The first is a tetrahedron of four oxygen atoms surrounding a central cation (usually $\text{Si}^{4+}$ or $\text{Al}^{3+}$) and the second unit consists of octahedron of six oxygens (or hydroxyls) around a large cation which is most commonly $\text{Al}^{3+}$, $\text{Mg}^{2+}$, $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$ combination of these structural units gives rise to the structure of the clay minerals. Various types of clay minerals are made up of some basic arrangements of tetrahedra and octahedra namely, 1:1 and 2:1 arrangements. Some important and most frequently found clay minerals are: montmorillonite, illite, vermiculite, chlorite, kaolinite and amorphous clays. Structures of some important clay minerals are given in Figs. 1 and 2. The cation exchange, surface areas and basic unit arrangements of the clay minerals and amorphous materials are given in Table-I.

**Montmorillonite:**

Montmorillonites are swelling and sticky clays. They have 2:1 arrangement in which a single tetrahedral layer joined to each side of the octahedral layer in sandwich fashion by sharing of oxygen atoms. Some important references associated with the investigations on the montmorillonite are: Hofmann et al. (1933);
I(a) Diagrammatic edge view of kaolinite showing two complete layers. The respective crystal units are bound to each other tightly by an oxygen-hydroxyl linkage, thereby giving a restricted and non-expanding lattice. The adsorptive capacity is limited.

I(b) Diagrammatic edge view of montmorillonite showing two complete layers. The respective crystal units are loosely bound to one another by weak oxygen linkages which allow wide expansion of the lattice. There is high internal adsorption of water and cations.

I(c) Illite has the same general structural organization as montmorillonite except in respect to the linkages between the crystal units. Here K atoms supply additional connecting linkages between the crystal units, thus supplementing the oxygen bonding. The expansion is sharply lessened by K linkages, and adsorptive capacity of the clay lowered.
TETRAHEDRAL SILICON SHEET

OCTAHEDRAL GIBBSITE SHEET

HYDROGEN BONDING

6 (OH)  - 6
4 Al  +12
4 O + 2 (OH) -10
4 Si  +16
6 O  -12

NET CHARGE  0

C-axis

7.2 Å

OCTAHEDRAL SHEET

TETRAHEDRAL SHEET

OCTAHEDRAL SHEET

b-axis

EXCHANGEABLE CATIONS

H2O

14 Å

TETRAHEDRAL SHEET

OCTAHEDRAL SHEET

TETRAHEDRAL SHEET

2(c) ILLITE STRUCTURE IS SIMILAR TO 2(b)
EXCEPT THAT THE ELECTRICAL IMBALANCE IS SET RIGHT BY THE PRESENCE OF K IONS SITUATED BETWEEN ADJACENT LAYERS SO THAT THE NET CHARGE IS 0.

2(b) MONTMORILLONITE, A FREELY EXPANSIBLE 2:1 LAYER MINERAL.
THE INTER-LAYER CATIONS ARE FREELY EXCHANGEABLE.

FIG 2
Marshall (1935); Maegdefrau and Hofmann (1957); Hendricks (1942); Schramm and Kwak (1984); Keren (1979); Barshad (1960); and Brown and Miller (1971) etc. who contributed in ascertaining the physico-chemical behaviour of the clay mineral vis a vis its structure. Marshall (1935) and Hendricks (1947) showed that montmorillonite always differs from its theoretical formula \((\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}\cdot n\text{H}_2\text{O}\) because of substitution within the lattice of Al by Mg, Fe, Zn and Cr etc. and Si by Al giving a series of group minerals. X-ray studies have shown the stacking of silica-alumina-silica units in the \(c\)-direction, layer being continuous in \(a\)- and \(b\)- direction with the result that these exert a weak bond and an excellent cleavage between them. Water and other polar molecules can easily penetrate between the unit layers causing the lattice to expand in the \(c\)-direction. The dimension of \(c\) axis is, therefore, not fixed but varies from 9.6 \(\AA\) to substantially complete separation of the individual layers in some cases. The cation exchange capacity of this mineral is high and varies from 80-120 meq/100 g clay.

**Illite:**

It has been well established (Grim et al., 1937; Bolt et al., 1963) that illite has very similar structure to that of montmorillonite having 2:1 type of basic unit structural arrangement. However, it has large number of potassium ions between the
silica sheets of two successive units that act as a bridge in holding adjacent layers together so tightly that water cannot penetrate between these layers. The size of the unit cell is $10 \, \text{Å}$. Amorphous substitution is possible within the lattice resulting in a wide variation in their composition. Because of illite's close structural similarity to primary mica, it is considered to be a member of mica group. The cation exchange capacity of illite varies from 20–40 meq/100 g clay.

**Vermiculite:**

This mineral is similar to that of illite in its structure (Gruner, 1934; Hendricks and Jefferson, 1938) but the layers held more weakly together by hydrated magnesium (6 water molecules in octahedral coordination with Mg) rather than tightly bound together by $\text{K}^+$ ions. Vermiculite has more swelling property than illite but not as much as montmorillonite.

**Chlorite:**

It is often called 2:2 type clay (Donahue et al. 1977) because its layer has two silica tetrahedra, an alumina tetrahedron and a magnesium octahedron. It is similar to the unit lattice of vermiculite except that the hydrated magnesium in vermiculite, is a firmly bonded magnesium hydroxide octahedral sheet in chlorite. Chlorite do not swell when wetted with water and have low cation exchange capacity varying from 10–40 meq/100 g clays.
Kaolinite:

Kaolinite is a hydrous aluminium silicate of approximate composition $\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O}$. The structure of this mineral was suggested by Pauling (1930) and further work on the structure rapidly followed by Gruner (1932). Kaolinite, Nacrite, Hallocite and Dickite are the isomers of kaolin group. Kaolinite is 1:1 type clay having only one sheet of silica tetrahedra per sheet of alumina octahedra per layer. Almost no substitution of $\text{Al}^{3+}$ for $\text{Si}^{4+}$ or $\text{Mg}^{2+}$ for $\text{Al}^{3+}$ has occurred in kaolinite, so the net negative charge is zero and thus the cation exchange capacity is low. However each layer has one plane of oxygens replaced by hydroxyls which result in strong hydrogen bonding between the oxygen and hydroxyl layers of adjacent units. Because of such strong hydrogen bonding, kaolinite do not allow water to penetrate between the layers and have almost no swelling property. The size of unit cell is $7.2\text{Å}$. The cation exchange capacity of this mineral varies from 3-15 meq/100g clay.

Amorphous clays:

These are the mixture of crystalline and amorphous oxides and hydroxides of silica, iron, aluminium and other elements which are also exist in soils (Schwertmann and Fischer, 1973; Bigham et al., 1978; Koon et al., 1980; Adam and Kassim, 1984; Mehlich, 1962; Basila, 1962) in varying proportion. A very little research
**TABLE - I**

CATION EXCHANGE CAPACITY, SURFACE AREA, AND BASIC UNIT ARRANGEMENTS OF VARIOUS CLAY MINERALS AND AMORPHOUS MATERIALS.

<table>
<thead>
<tr>
<th>Mineral matter</th>
<th>Physical properties</th>
<th>Basic unit arrangement</th>
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<tbody>
<tr>
<td></td>
<td>Cation exchange</td>
<td></td>
</tr>
<tr>
<td></td>
<td>capacity (meq/100g)</td>
<td></td>
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<tr>
<td></td>
<td>Surface area</td>
<td></td>
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<tr>
<td></td>
<td>(sq. meter per gram)</td>
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</tr>
<tr>
<td>Kaolinite</td>
<td>3-15</td>
<td>7-30</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>80-150</td>
<td>600-800</td>
</tr>
<tr>
<td>Illite</td>
<td>10-40</td>
<td>65-100</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>100-150</td>
<td>600-800</td>
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<tr>
<td>Chlorite</td>
<td>10-40</td>
<td>25-40</td>
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<tr>
<td>Oxides and</td>
<td>2-6</td>
<td>100-800</td>
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<tr>
<td>hydroxides</td>
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* From Baily and White (1964).

**Difference with montmorillonite:**

a) A large number of K ions between silica sheets of two successive units and amorphous substitution is possible.

b) Similar to illite but has the layers held more weakly together by hydrated magnesium rather than K ions.
has been done on these materials regarding their physical and chemical properties and their contribution to soil characteristics. Hsu and Bates (1963) have reported that these amorphous clays have positive charge and may contribute significantly to anion exchange capacity of the soil that depends upon the pH of the soil solution.

**SOIL ORGANIC MATTER**

The soil organic matter (SOM) or humus may be defined as the organic residue left behind after microbial decomposition of plant and animal remains, frequently dark coloured and possessing certain characteristics physical and chemical properties (Waksman, 1936). Its synthesis and degradation constitutes a dynamic process and depends largely on soil environment. In general, humus may be divided into two main groups as follows:

1. **Humic Substances:** Transformed products bearing little or no resemblance to the anatomical structures from which they are derived.

2. **Nonhumic Substances:** Unaltered remains of plant and animal tissues and also organic compounds that have definite characteristics.

The humic substances can further be subdivided into three main subgroups (Banerjee, 1979) according to their solubility in alkali and acids, namely:
(i) **Humic acid:** Soluble in alkali and insoluble in acids.

(ii) **Fulvic acid:** Soluble in both alkali and acids.

(iii) **Humin:** Insoluble in both alkali and acids.

Accumulation patterns of humic and fulvic acid fractions have been studied by various workers (Goh et al., 1976; Schnitzer and Khan, 1972; Syers et al., 1970; Kilham and Alexander, 1984) to show that the humic acid concentrated principally in the surface or immediately below the surface horizon while fulvic acid fraction extends to much lower depth and is hardly precipitated from an alkaline extract by acid because of its more functional groups (Schnitzer and Khan, 1972; Stevenson and Goh, 1971).

The chemistry of humic substances has extensively been studied in recent years (Ghosh and Schnitzer, 1980; Wilson, 1981; Wilson and Goh, 1983; Wilson et al., 1983; Newman and Tate, 1984) to characterize their composition and properties in soil. The kind of soil and its environment and the method of extraction have been considered (Tan, 1978) as the conflicting factors to affect the nature and characteristics of the humic substances. The need to standardize the method of extraction is, therefore, stressed (Flaig et al., 1975; Burges, 1966) as it influence the chemical behaviour of these substances. For example, Tan (1978) extracted humic substance with $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH to study the changes in IR spectra. It was reported that $\text{Na}_4\text{P}_2\text{O}_7$ yield HA with better resolved spectra than NaOH, and allowed to observe
the difference in HA spectra between soil groups. The structure of humic materials extracted from marine environments are highly aliphatic and, from terratorial environments range highly aromatic to highly aliphatic (Wilson & Goh, 1983).

In general, humic acid molecules are composed of an aromatic and aliphatic parts which are linked together (Zunino and Martin, 1977). Humic acid consists of phenolic and other aromatic units with amino acids, peptides, polysacharides etc. The functional chemical analysis revealed that the major functional groups in humic acid are carboxylic, phenolic, alcoholic, conjugated ketonic, carbonyl, methoxy, amino (-NH$_2$), secondary amino (-NH-) and ring nitrogen. All these groups are electron donar, hence can coordinate metal ion which behave as electron acceptor. The presence of large concentration of oxygen containing groups (-COOH, -OH, and -C=O) in humic materials tend to make them hydrophilic. While the aromatic rings, fatty acids, esters and aliphatic carbons provide them a hydrophobic nature. Thus, the humic materials are considered to have a simultaneous hydrophilic as well as hydrophobic nature and hence capable of adsorption of hydrophobic and hydrophilic substances on its surfaces.

On the basis of numerous analysis made on humic and fulvic acids, the main differences between model HA and FA were reported (Schindler and Ghosh, 1979) as follows: Total acidity, alcoholic OH, and COOH content of the FA are appreciably higher than HA.
while the number of phenolic OH, total C=O and -OH groups
are approximately same in both the substances. The higher E_r/E_o
ratio of FA than that of hA indicates the lower particle size
of FA.

The macromolecular structure of humic and fulvic acids
has been studied by various workers (Mukherjee and Lahiri, 1958;
Visser, 1964; Flaig and BeutaloSpacher, 1968) and the concepts of
'Sphero-colloid' and 'Flexible linear configuration' put forward.
It was shown that the hA and FA behave like 'Sphero-colloid' at
high sample concentration, low pH, or in presence of sufficient
neutral salt concentration while they are 'Flexible linear colloid'
in normal conditions (Ghosh and Schnitzer, 1980) that are pre­
vailing in soils. The chemical structure and reactions of humic
substances have been a subject of researches of nearly two cen­
turies, yet much remains to understand about these substance.
Considering various aspects of reported literature, Schnitzer and
Ghosh (1979) proposed a model of partial chemical structure of FA
as shown in Fig. 3. The molecular arrangement may account for a
significant position of the fulvic acid structure. Besides the
Vander Waals interaction and π-π bonding, attraction between
the building blocks is also likely, mainly through hydrogen bond­
ing which makes the structure flexible permitting building blocks
to aggregate and disperse reversibly depending upon the environ­
ment, viz. pH, ionic strength and nature of metal ions present
etc.
Humin is a fraction of soil humus which is strongly bound to clay minerals after the usual alkali extraction of humic acids and is known to resist the extraction. Khan (1945) and Zyrin (1948) reported that a part of humic substance known as humin, consists of humic and fulvic acids, but the only difference is that the humic acid extracted from humin fraction contains lower percentage of oxygen and hydrogen than that extracted from the decalcified soil. Besides, the humic and fulvic acid content, hymatomelanic acid has also been reported to be present in humin fraction (Benerjee and Mukherjee, 1972).

**SOIL WATER**

Soil water is an important constituent of soil which helps to control soil air, soil temperature, evapotranspiration requirement and supply of nutrients to growing plants (Brady, 1974). The soil water content vary with the soil texture and vary from 5.1 to 11.9 percent (Donahue, 1977).

In a study of water retention in soils, Ali and Biswas (1968) determined the relationship between the nature and amount of clay in soil and water retention capacity. It was found that the water retention and release were maximum in bentonite clay followed by illite and then kaolinite. The amount of available water in soil was also found to be related with silt (Abrol and Bhumbla, 1966) and organic matter content (Ali, 1965).
Water movement in soils is an another important aspect of soil water relationship since it decides the amount of water stored in the root zone, or the depth to which applied water will move or whether the soil will percolate salt to prevent the development of soil salinity. The movement of water in soil is influenced by the location, extent, and physical characteristics of the different horizons. Since a major portion of water either from rainfall, or from irrigation moves under unsaturated conditions, it is important to determine the hydraulic conductivity under unsaturated conditions. The references associated with the work on the subject are Luxmoore et al. (1977); McNeal (1968); Lagerwerff (1969); Sojka et al. (1977); Clothier et al. (1977) and Nakano (1977) etc.

SOIL AIR

The soil air mainly consists of oxygen, carbon dioxide, nitrogen and nitrous oxide etc. It has been observed that the composition of soil air varied with the climate conditions (Russell and Appleyard, 1915) as well as with the nature of the soil (Jong, 1981).

Using various analytical methods i.e. IR spectroscopy, Gas chromatography etc., nitrogen and nitrous oxide gases have been measured in soils (Arnold, 1954; Dowdell and Smith, 1974) which may be a cause of nitrogen losses under an aerobic conditions due to denitrification processes. The other physiologically
active gases like ethylene, methane, hydrogen sulphide, volatile fatty acids, alcohols, ketones and aldehydes have been reported to be formed in water logged soils by microorganisms (Smith, 1977).

MICROBIALS AND THEIR ACTIVITIES IN SOIL

Small living things are biologically classified as plant (microflora) or animal (microfauna) and are considered to be present in the soil surface or in top few inches of the soil having their population in billions per gram of soil (Donahue, 1977). It is a universally known truism that these microorganisms affect and influence the properties of soil.

Soil microfaunae primarily comprises of:

(i) **Protozoa**

They are primitive, unicellular microscopic animals that feed mainly on bacteria and hence are believed as a controlling factor upon the abundance of bacteria. Thus influence microbiological populations and hastens the recycling of plant nutrients. The main protozoan groups are amoebae, flagellates and ciliates.

(ii) **Nematode**

Nematodes are microscopic, unsegmented, thread like worms and may be classified according to their feeding habits. Omnivo-
rous, prodaceous and parasitic nematodes are common in soils.

Soil microflora consists of bacteria, fungi, actinomycetes and algae which occur in almost all soil samples.

(i) **Bacteria**

Bacteria are most abundant groups usually present in soils. These are unicellular and include spore forming and nonspore-forming rods, cocci, vibro and spirills. They vary considerably in shape, size and in their energy requirements (aerobic and anaerobic), energy utilization (autotrophic and heterotrophic) and in relation to plants and animals (Saprophytic and parasitic). Some specific autotrophic soil bacteria can oxidize ammonia to nitrites and then to nitrates. Some other bacteria can also oxidize sulphur, iron, manganese, hydrogen and carbon monoxide. Another autotrophic bacteria may reduce the nitrates to inert nitrogen gas. While heterotrophic bacteria includes both nitrogen fixing and nonnitrogen fixing kinds. Clostridium (more abundant in poorly drained acid soils) and Azatobacter (more abundant in well drained neutral soil) could fix atmospheric nitrogen into soils.

(ii) **Fungi**

Fungi can be classified according to their nutritive process and are parasitic, saprophytic or symbiotic. Parasitic fungi decomposes resistant cellulose, lignins and gum resulting holes in
soil and cause plant diseases. Saprophytic fungi obtain their energy from decomposition of organic matter while symbiotic fungi live on the roots of certain plants in a dependent relationship in which both fungus and plant are mutually benefitted.

(iii) **Actinomycetes**

Actinomycetes are characterized by branched mycelia similar to fungi (Nocradia genera), and resembles bacteria when the mycelia break into fragments (genera streptomyces and micro-monospora). Actinomycetes vary greatly in their biochemical properties in relation to higher plants and animals and in their effects on soil bacteria.

(iv) **Algae**

Soil algae are microscopic, chlorophyll bearing organisms. The main groups are the green, blue green, yellow green and diatoms. They develop that in moist fertile soils. Certain blue green algae have demonstrated the ability to fix nitrogen from atmosphere. The species of these type of algae genera are nostoc, scytonema and anabaena (Cameron and Fuller, 1960; Mayland et al., 1966).

(v) **Viruses**

Viruses are noncellular organisms and are composed of specific nucleic acid surrounded by a coat of protein. They can multiply and grow only inside living cells.
The microbial activities in soil are largely responsible for the maintenance of soil fertility as well as soil properties (Russell, 1973). A number of biochemical transformation viz., ammonification, nitrification, denitrification, symbiotic and non-symbiotic $N_2$-fixation etc., soil respiration sulphur, phosphorus and other trace metal transformation have been reported to occur as a result of microbial activities in soil (Parr, 1974; Gowda et al. 1976; Bollag and Henninger, 1976; Vlassak, 1975; Gaur et al. 1977) etc. Microbials mineralize (Reich and Bartha, 1977); oxidize (Pepper and Miller, 1978) and reduce elements in soils and indirectly influence their solubilities. Pesticides are considered to alter the number of activities of microorganism in soils (Wainwright, 1978). Atmospheric pollution is also considered by Wainwright (1980) as a factor to effect the microbial activities.

Studies on the nitrogen fixation by root nodule bacteria and Rhizobium have been a subject of considerable research (Reddy and Patrick, 1979; Charyulu and Rao, 1979). The nodulating bacteria of various legumes are mostly those of the cowpea group which is very well represented in India and the tropics. The pea (R. Leguminosarum), and bean (R. Phaseoli) groups are represented by few legume hosts. Nitrogen fixation by root nodule bacteria is influenced by many factors, such as, nitrogen status of the soil, supply of nutrient elements like phosphorus and molybdenum etc.
ORGANIC COMPOUNDS IN SOIL

A number of organic chemicals are reported to exist in soils. The transformation of organic compounds occurs mostly through biochemical processes caused by the action of microorganisms, particularly of their enzyme systems. The organic compounds which are generally found in soils are:

(a) **Aliphatic acids**

A large number of organic acids are intermediates of metabolism of plants and microorganisms or can be derived from them. Some are products of oxidative degradation of organic substances (Yoshida and Nakadate, 1964). The amounts of formic and acetic acid depend upon the soil conditions in which they exist. The level of formic acid and acetic acid ranges from 0.5 to 0.9 and 0.7 to 1.0/g of soil respectively.

Many organic acids occur in the aqueous systems of both higher and lower forms of plant life. Aliphatic acids of common occurrence in plants include the lower members of the fatty acid series: formic, acetic, propionic, butyric. Of equally wide distribution are the following acids: oxalic, glycolic, lactic, tartaric.

Other acids are citric, succinic, malic acids are found in many fruits and leaves. In poorly drained soils the conditions for the formation of aliphatic acids by microorganisms are more favourable than in aerobic soils. For instance Takijima (1961) has reported the accumulation of acid in soils are in the order
acetic > butyric > formic > fumaric, propionic, valeric, succinic and lactic acids in some cases.

Some work has been reported on the influence of acids on the growth of plants and concluded both favourable and unfavourable effects. Organic acids are also involved in the solubilization, and transport of the mineral part of the soils. Schwartz et al. (1954) have been first to use modern chromatographic techniques for characterizing aliphatic organic acids in aerobic soils.

(b) Amino acids and Proteins

About 20 to 50 percent of the organic bound nitrogen is in the form of amino acids in soils (Bremner, 1965). The total amount does not exceed 2 µg per g soil. The composition of the amino acids from decomposing plant material, microbial synthesis or exudation by roots, seems to have no such influence on the composition of proteins in soil (Stevenson, 1956). But characteristic differences occur when organic substances are decomposed by selective groups of organisms (Cheshire et al., 1965). In soil hydrolysates, leucine and isoleucine, lysine, alanine, glycine, valine and sulphur containing amino acids are found mostly in larger quantities than the other amino acids.

(c) Carbohydrates

The dead vegetative material contributes the major part of carbohydrates to soil organic matter in the form of different
polymer saccharides, especially cellulose and hemicellulose. The microorganisms synthesize polysaccharides and other carbohydrates and furthermore they also decompose the polysaccharides from plant material. The approximate content of carbohydrates in soil organic matter is 5 to 16 percent isolated by various procedure (Cheshire and Hurdie, 1965; Dormaar, 1967; Gupta and Sowden, 1963).

Gupta (1967) listed some of the different carbohydrates which have been found in soils as:

(i) **Monosaccharides**

Hexoses: glucose, lactose, mannose, fructose.

Pentoses: arabinose, xylose, ribose, fucose, rhamnose.

(ii) **Disaccharides**

Sucrose, cellubiose, gentiobiose.

(iii) **Oligosaccharides**

Cellotriose.

(iv) **Polysaccharides**

Cellulose, hemicellulose.

(v) **Amino sugars**

Glucosamine, lactosamine, N-acetyl-D glucosamine.
(vi) **Sugar alcohols**

Manitol, inositol.

(vii) **Sugar acids**

Glacturonic, Glucoronic acid.

(viii) **Methylated sugars**

2,0-methyl-D-xylose, 2,0-methyl-D-arabinose, 2,0-methylrhamnose, 4,0-methyl lactose.

(d) **Monocyclic phenolic compounds**

Phenolic compounds in soils can be derived from phenolic plant constituents such as flavones, flavanols, catechines, phenolcarbonic acids and others formed by microbial synthesis.

(e) **Organic phosphates**

Soil organic matter contains a small portion of organic phosphates. The constitution of the compounds identified so far allows the assumption that they are derived from nucleic acids, inositol phosphates and the phospholipids. Some of them come into the soil by plant material, others are synthesized by microbes.
PESTICIDES

Pesticides are chemicals used for controlling the pests like fungi, insects, herbs or other animal pests that attack crop resources & other useful to man. The general definition for pesticides was given by Ware (1978) as "Any substance used for controlling, preventing, destroying, repelling or mitigating pests is known as pesticide ".

Pesticides can broadly be classified into various classes according to their use such as herbicides, fungicides and insecticides. There are also rodenticides, nematocides, molluscacides, acaricides, and weedicides etc.

Herbicides

Herbicides are those chemicals which are used to destroy or suppress the growth of unwanted herbaceous and weed plant without injuring others. Organic chemicals which exhibit herbicidal and plant growth regulator properties are numerous and varied from biological, physical and chemical standpoints. They can be subclassified into following groups:

(i) S-Triazines: These herbicides conform to the general formula:
where \( R_1 \) and \( R_2 \) refers to the N-substituted with lower alkyls and \( X \) to Cl, OCH\(_3\), and SCH\(_3\) etc. for extensively used S-triazine. Some of the commonly used S-triazine herbicides are: Simazine, Atrazine, Atratone, Prometone, Ametryne, Prometryne etc.

(ii) Substituted ureas: The substituted urea class of herbicides contain a number of widely used compounds such as fenuron, diuron, monuron, linuron, norea, chloroxuron, fluometuron and siduron etc. Various new herbicides of this group are being evaluated. These are used at high concentration rates as soil sterilants and at low rates as selective pre- and post-emergence herbicides in crop production.

(iii) Phenoxyalkanoic acid: The members of this class of herbicides are used primarily as foliar applied treatments. Some of the important phenoxy alkanoic acid herbicides are: 2,4,5-T; MCP; MCPA; Dichlorprop and Silvex etc. They are generally employed as pre-emergence treatment in conjunction with other herbicides because of their short residual life.
(iv) **Carbanilates**: Many types of carbanilates show herbicidal actions. Some of the most extensively used compounds of this group includes swep, propham, chloropropham and banban etc. Swep, propham and chloropropham are used as pre-emergence herbicides, while banban is used as post-emergence control of wild oat in cereals. These compounds are readily degradable by microorganisms. They are lost through volatilization if they are applied to wet soil.

(v) **Chlorinated Aliphatic acids**: Various chlorinated aliphatic acids such as 2,2-dichloropropionic acid (dalapan); trichloroacetic acid (TCA) and 2,2-dichloroisobutyric acid (FW-450) etc. have been used as herbicides.

(vi) **Amitrole**: It is a substituted triazole (3-amin0-1,2,4-triazole) herbicide which is used primarily due to its resistivity towards microorganism (Ashton, 1961). However, it was later observed that chemical as well as microbial degradation both may be experienced by this compound.

Besides the above most extensively used herbicides, there are many other compounds which are also used as herbicides. They include: Pyridine, N-aliphatic carbamates, Dipyridyls and many others.

**Fungicides**

Fungicides are those chemicals which are used to control
various fungi and fungus born diseases like mildew, blights, smuts, rusts, scab, spot, rot etc. Fungi are pathogenic organisms which may be present on foliage surface as powdery mildews, they may remify through plant tissues.

Fungicides are of two main types:

(i) **Surface fungicides:** These fungicides are used to apply to foliage as sprays or dusts. They do not enter the plant tissues but kill the fungus and the surface spores. They include: Bordeaux mixture, lime sulphur, preparations containing Cu, Zn, Mg, As, S and other natural plant extractions.

The organic surface fungicides are: organic mercury, alkyl mercury and phenyl mercury. They are appeared to cause widespread environmental hazards due to much toxic mercury metal (Dix, 1981). The organic thiocarbamates such as thiram, ziram, zineb and Maneb etc. and phenolic compounds such as dinitrophenol, dinocap and many others have been used as organic surface fungicides to replace organic mercury compounds.

(ii) **Systemic fungicides:** These fungicides are absorbed into the plant through leaves, roots and seeds and are translocated within the plant tissues. Consequently this group is more effective than the surface fungicides. However, newer systemic fungicides are continuing to be developed, benomyl, MBC, TBZ, thiophanates, dowco, triarimol, and carboxin etc. are in common use. All organic fungicides have low toxicity to plants, birds and mammals, so they are
not potentially hazardous in the short term. Some products containing metal that are known to accumulate in food chains, may pose some health hazards.

**Insecticides**

Insecticides are those chemicals which are used to kill or control various insects. They can be applied directly to soil or as sprays or dusts to foliage plants. Pests such as wire-worms, chafer grubs and root maggots in soil are extremely difficult to be controlled due to their relatively inactive nature. Volatile insecticides are more beneficial as they can permeate the soil crevices and reach the inactive stages of the pests such as eggs or pupae. In general, insecticidal chemicals may be classified into following groups:

(i) **Organochlorines:** Among various organochlorine insecticides, the most important and best known is DDT, it was followed by BHC (1942). Within a very short period, a range of these insecticides were developed as chlordane (1945), heptachlor (1945), toxaphene (1947), methoxychlor (1948), aldrin (1948), dieldrin (1948), endrin (1951), and endosulfan (1956) etc. and are used as insecticides. In general, these are wide spectrum insecticides used to kill a great variety of pests.

(ii) **Organophosphorus:** The organophosphorus insecticides includes: Parathion (1944), diazinon (1952), trichlorophon (1952),
phorate (1954), carbophenothion (1955), disulfoton (1956),
dimethoate (1956), fenthion (1957), thionazin (1959), menazone
(1961), diffonate (1966), chlorfen vinylphos (1963) and others like
malathion, phosphamidon, dichlorvos etc. The organophosphates
are much more soluble in water, but their volatility is nearly
equal to that of organochlorines. These insecticides are less
persistent in comparison to organochlorines.

(iii) Carbamates: Some carbamate compounds have also been used
as insecticides. They include CHyIC, carbofuron, bendiocarb,
aminocarb, metabol etc. Most of the carbamates act on insects in
a similar way to the organophosphorus compounds. They persist much
less than organochlorines but longer than organophosphorus compounds

With increasing use of pesticide in agriculture, these
chemicals are harmful for environment. Rachael Carson (1963) was
one of the first, who recognize the dangers of pesticide pollution.
She produced evidence of toxic effects upon wild life and potential
hazard to man. Since then, a number of workers have carried out
experiments on various aspects of environmental pollution caused
by pesticides (Heuper and Conway, 1964; Mellanby, 1972a,b).

Some pesticides are described as stable and persistent in
soil for varying period of time. Watter and Grussendorf (1969)
showed that organo-chlorine insecticide deposits on the walls of
stores might be a source of residue in grains. Few organochlorine
and organocarbamate insecticides are feebly systemic and are
adsorbed by roots or leaves, metabolized, and translocated in
noninsecticidal amounts to leave persistent and undesirable
residues at harvest. Duggan (1968) showed that oil containing
seeds may concentrate these to one tenth of the original content
in soil.

Menzie (1969) has classified the possible biotransfor-
mination of pesticides in plants and soils. These include; oxidation,
dehydration, dehydrohalogenation, reduction, conjugation, hydro-
lytic reaction, exchange reaction and isomerization. The factors
including the presence of residues may be artificial or natural.
The natural factors are more subtle in their effect on residues
in plants. They include the plants (Stoller, 1970); soil
(Harris and Sans, 1969); Weather (Linkson et al. 1965); penetra-
tion (Frank, 1967; Frank, 1970); absorption (Hulpke, 1970);
translocation (Nash and Beall, 1970) and diffusion. Animals and
humans absorb these chemicals from their food and accumulate them
in specific body organs until it reaches a lethal threshold dosage
for species. In general, the harmful effects of pesticides can
directly be related to their persistence and accumulation in the
environment, as well as within the body tissues of animals and
humans.

Various aspects of pesticide residues have been studied
by many workers. Some of those include; persistence (Robinson,
1970); pesticide in peoples (Wasserman et al., 1967); transloca-
tion (Helling, 1971; Wain and Carter, 1967); residues in feed,
food and fibre plants, and tobacco (Finlayson and MacCarty, 1965).
TRACE METALS

Sixteen elements are known to be essential for plant growth and microbial activities in soils. Of these some are needed by plants in larger amounts and are called major nutrients while others that are required in smaller amounts are known as micro or trace elements. These are iron, manganese, zinc, copper, boron, chlorine and molybdenum. Apart from these, some other elements such as Pb, Cd, Cr, Ni, Ag, Hg, As, Se, V and Ba etc. are also known to be present in soil in trace quantities. However, they are not essential for plant or animal growth and found to be toxic to man and animals and produce undesirable effects (Singh and Singh, 1977; Dijkshoorn et al., 1979; Lauwerys et al., 1979; Schmitt, et al., 1979 etc.). Forbes et al. (1974) have reported that the adsorption of heavy metal cations on solid solution interface, is not simply an electrostatic but consider (i) as a function of properties of the solid surface and the adsorbing species, (ii) the ability of the adsorbing metal ions to hydrolyse in solution in determining their affinities for the surface of soil minerals.

In recent years, man has utilized the sewage and industrial wastes as a source of micronutrients in most of the developing countries like India. Large population centres producing tremendous amount of sewage sludge and rapid industrialization
incorporating many heavy metals, however, aroused the concern over their possible use in agriculture. Composition of different sludge and industrial wastes has been studied by various workers (Stover et al., 1976; Anderson and Nilson, 1972). It was found that heavy metals constitute a major part of its composition. They are accumulated in soils because of their excessive use and causes a hazardous problem to plant and animal life.

In most of the studies, it has been shown that the metals added to soil remain in the upper few inches (Williams et al., 1980; Page and Chang, 1975) because of various immobilizing mechanisms like precipitation of specific adsorption on oxides, clay minerals and organic matter. Considering the sludge as a complex mixture of organic and inorganic species, various forms of trace metals in soil could be understood (Gregson and Alloway, 1984; Tills and Alloway, 1983).

The chemical behaviour of trace metals has extensively been studied in relation to soils and clays (Bowman et al., 1981; Hodgson, 1963; Tiller et al., 1979). It has been observed that Pb may form soluble inorganic complexes with anionic groups like hydroxyl, chloride, sulphide, phosphate and carbonate according to soil pH, and acidity of interacting ions. Richard and Nriagu (1978) observed that Pb remains as carbonate species, particularly, Pb\((\text{CO}_3)_{2}\)^2- at pH in between 6 and 8, while at pH < 6 and in absence of carbonate, Pb\(^2+\), PbCl\(^+\), and PbCl\(_2\) were predominant inorganic
species. Santillan-Medrano and Jurinak (1975) reported the formation of PbCO$_3$, Pb(OH)$_2$, Pb$_3$(PO$_4$)$_2$, Pb$_5$(PO$_4$)$_3$OH, and/or Pb$_4$O(PO$_4$)$_2$ species at pH in between 7.5 and 8.0. Pb has also been observed to complex with sulphur based amino acid, cysteine and fulvic acid (Sillen and Hartell, 1964; Schnitzer and Skinner, 1967). Gregson and Alloway (1984) studying the Pb speciation in heavily polluted soil, reported that Pb occurs as both high and low molecular weight organo-Pb-complex depending upon the initial pH. In a potentiometric study of metal-HA complexes, Stevenson (1977) reported that there are two or more binding sites in Pb-HA complex formation. Thus, 2:1 and 1:1 Pb-HA complex are formed to give a chain like structure by displacing H ions from exchange sites or by releasing proton from hydration water of metal ion. In comparison to other heavy metals, the order of stability constant for metal-HA complex is as follows:

$$\text{Cu} > \text{Pb} \gg \text{Cd} > \text{Zn}$$

Bittel and Miller (1974) studied the adsorption behaviour of Pb on montmorillonite, kaolinite and illite to show that the adsorption sites were all alike and there was little or no interaction between adsorbed ions. On goethite, Pb was reported to be specifically adsorbed and its distribution between solid and liquid phase is pH dependent (Forbes et al., 1974). It was reported (Forbes et al., 1976) that for each Pb ion adsorption, nearly two moles of H$^+$ ions are displaced from interface which was in the
direct contrast of the mass action approach of Grimme (1968). Again, the Pb$^{2+}$ has hydrolysable nature, its adsorption could be considered to occur via the adsorption of PbOH$^+$ and Pb(OH)$_2^0$ species at higher pl values (James and Healy, 1972).

Cadmium is accumulated in soils mainly through continuous application of sewage sludge; (Anderson and Nilsson, 1972) on the soil colloids is a major factor influencing the distribution of Cd between aqueous and solid phase in soil water system. Lagerwerff and Brower (1972) investigated the exchange behaviour of cadmium with Al and Ca treated soils. It was found that cadmium adsorption decreased with increasing AlCl$_3$ or CaCl$_2$ and decreasing NaCl concentration in soil solution. The effect of exchangeable cations on the Cd sorption by montmorillonite was studied by Garcia-Miragaya and Page (1977) who observed the following decreasing order:

Na$\rightarrow$K$\rightarrow$Ca$\rightarrow$Al-montmorillonite.

Jarvis and Jones (1980) found that the cadmium strongly sorbed by soils when added in the amount comparable to that added through sewage sludge or phosphatic fertilizers. They also observed that various cations are capable of disorbing Cd from soil in the order:

Pb$>$Zn$>$Cu$>$Mn$>$Ca

Nickel is another phytotoxic (Foronghi et al., 1976; Ormrod, 1977) and zootoxic element, especially to marine life (NRC, 1975; Toth,
1968). It causes carcinogenesis (NRC, 1975). Nickel is generally accumulated in soils through industrial and municipal wastes. It is introduced into human and animal food chain mainly through water and food plants via soils. Thus, the availability of Ni in soil solution and its absorption by plants is an important process which is governed by its chemistry in soils. Sadiq and Enfield (1984) studied the solid phase formation and chemistry of Ni in soils. It was observed that nickel behaves in several ways depending upon the pH of soil solution. In Fe dominated soils, nickel ferrite (NiFe$_{2}$O$_{4}$) and Ni(PO$_{4}$)$_{2}$ are precipitated depending upon the availability of Fe in soils. Nickel oxides and hydroxides have been identified in soils having pH greater than 9. Other species which are reported to precipitate are carbonate, sulphate, phosphate, chloride, hydroxy complexes like Ni(OH)$^{+}$, Ni$^{2+}$, NiSO$_{4}^{0}$, NiHPO$_{4}^{0}$ etc. Bromo-, chloro-, iodo- and nitrocomplexes etc.

In general, it has been pointed out that atmospheric fall out from ore smelter contributes significantly to soil contamination with heavy metals (Goodman and Roberts, 1972; Cartwright et al., 1977; Franzin et al., 1979). They exist in soil as bound species with carbonate, oxide, organic matter and as exchangeable or incorporated in crystal lattice (McLaren and Crawford, 1973; Gibbs, 1977). Mattigod and Sposito (1977) reported the sulphate complex species of these trace metals at low pH values, which decreased with increasing pH due to their complexation with organic matter.
Ginzburg (1960) reported that the preferential uptake of metal cations followed the order \( \text{Pb} > \text{Cu} > \text{Ca} > \text{Ba} > \text{Mg} > \text{Hg} \) on montmorillonite and that the capacity of the heavy metals to replace the Ca on Kaolinite is in the order \( \text{Pb} > \text{Cu} > \text{Hg} \).

**ADSORPTION**

The term adsorption was first used by Kayser (1881) at the suggestion of E-du Boise-Raymond and refers strictly to the existence of higher concentration of any particular component at the surface of liquid or solid phase than is present in the bulk.

In general, adsorption may be classified into two types namely physical and chemical. The physical adsorption occurs mainly due to weak forces, like ion-dipole, dipole-dipole, polarization or induced dipole, and Vander Waal's forces etc. It involves usually lesser heat changes of the order of 0.5 to 2 KCal or less (Adams, 1973; Glasstone, 1960). This phenomenon is more or less non-specific, reversible and temporary in character. While chemical adsorption is due to the formation of chemical bond between the adsorbent and adsorbate molecules. It is characterized by a large heat change as 5-20 KCal. In some cases, the value of the heat of adsorption has been reported to be in the range of 15 to 50 KCal per mole. (Adamson, 1960; Biggar and Cheung, 1973; Gregg and Singh, 1967). Thus, the chemical adsorption is a speci-
fic, non-reversible and permanent surface phenomenon.

Adsorption of inorganic and organic components have gained considerable importance in the field of soil chemistry. In recent years, Khan and Bansal (1980); Joshi (1986); Goodman (1986); Cline and Oconnor (1984); O'Connor et al. (1983); Kuo and Baker (1980); Ellicott and Huang (1979); Curtin et al. (1980); Reddy et al. (1987); Rick et al. (1987); and others have studied the adsorption phenomena in relation to soil and clays in various aspects.

The clay minerals as well as crystalline and amorphous oxides and hydroxides both having a capacity for adsorption due to coulombic, and/or physical forces. Organic pesticides adsorb on both organic and inorganic surfaces depending upon the chemical properties of adsorbent and adsorbate (Weber, 1972). The organic matter has been reported to have a highest cation exchange capacity (200 to 400 meq/100 g) and surface area (500 to 800 sq. m. per gram) which are comparable to montmorillonite and vermiculite (Bailey and White, 1964). Basic pesticides were reported to be adsorbed strongly on soil organic matter (Weber et al., 1969) and expanding lattice clay minerals (Weber, 1966; Weber, 1970). Acidic pesticides were adsorbed in moderate amounts on organic matter and relatively low amounts on clay minerals and hydrous metallic oxides (Carringer & Weber, 1974; Scott & Weber, 1966; Weber, 1972). While non-ionic pesticides were considered to adsorb in greatest amount by organic matter but their adsorption by clay mineral was
also important for organophosphate and several other pesticide families (Weber, 1972). In addition, it has been reported that carbamate and organophosphate insecticides were adsorbed by soil organic matter (Leenheer and Ahlrichs, 1971). The physico-chemical nature of adsorbate which controls the role of the molecules may be summarized as follows: (i) Chemical character, shape and configuration, (ii) Acidity or basicity of the molecule, (iii) Water solubility, (iv) Charge distribution on the organic cations, (v) Polarity, (vi) Molecular size and (vii) Polarizability.

Adsorption of inorganic cations with soils has extensively studied by a number of workers as Curtin (1980); Kuo and Baker (1980); Graffin and Au (1977) etc. and generally found in the following order,

\[ H^+ > Al^{3+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+ > Li^+ \]

The property of adsorption plays an important role in holding water and plant nutrients and keeps them available for the use of growing plants. Fertilizers in the form of soluble substances, are retained on the surface of the soil colloid due to their adsorption and indurate for leaching.

**Adsorption equations**

An adsorption isotherm represents the functional relationship between adsorbed phase concentration \( (X/m) \) and solution concentration \( (Ce) \) at constant temperature. Generally, two types of
isotherm equation namely Freundlich and Langmuir equations, have most frequently been used to describe the adsorption behaviour of various species in soils.

(a) **Freundlich equation:** In Freundlich type of adsorption isotherm, the concentration of solute species in adsorbed phase is given by the equation:

\[
\frac{x}{m} = K \frac{1}{n} C_e
\]

or

\[
\ln\left(\frac{x}{m}\right) = \ln K + \frac{1}{n} \ln C_e
\]

where, \(\frac{x}{m}\) is the amount of solute adsorbed \((x)\) per mass of adsorbent \((m)\), the constants \(K\) and \(\frac{1}{n}\) represents the adsorption capacity and intensity, respectively, \(C_e\) is the equilibrium concentration of solute in solution.

If \(\ln\left(\frac{x}{m}\right)\) is plotted against \(\ln C_e\), a straight line is obtained whose intercept and slope represents the constant \(K\) and \(\frac{1}{n}\) respectively. Using the value of \(K\) as a measure of adsorption, the adsorption capacity of various adsorbent may be compared while \(\frac{1}{n}\) measure the non-linearity of the process. If \(\frac{1}{n}\) is unity, the process is said to be linear.

(b) **Langmuir equation:** The Langmuir equation may be written as:

\[
\frac{x}{m} = \frac{A B C_e}{1 + B C_e}
\]
where, \( A = \text{adsorption maxima (}\mu\text{g/g)}; B = \text{coefficient that reflects the relative rates of adsorption and desorption at equilibrium and, thus, an affinity term (ml/}\mu\text{g)}; \frac{x}{m} \) and \( C_e \) are the same as in Freundlich equation.

The linear transformation of the above equation can be written as:

\[
\frac{C_e}{x/m} = \frac{C_e}{A} + \frac{1}{BA}
\]

The slope and intercept of the plot \((C_e/x/m \text{ vs. } C_e)\) gives the value of constants, \(1/A\) and \(1/BA\) respectively. The adsorption capacity of adsorbent \((A)\), depends upon the specific surface area, surface charge characteristic etc. The constant \(B\) is a measure of the adsorption energy.

**Classification of Adsorption isotherm**

Giles et al. (1960) studied the adsorption from aqueous solution of a variety of solutes and developed a classification of adsorption isotherms into S,L,H & C types depending upon the initial slope.

**S-Type:**

The S-type isotherms are common when solid had a high affinity for the solvent. This type of isotherm indicates a tendency for large adsorbed molecules to associate rather than to
remain as isolated units. In the S-type curve the slope initially increased with increase in concentration due to cooperative adsorption. At the saturation point where no site remained vacant slope fill. Such type of isotherms occurred when the activation energy for desorption of solute was concentration dependent and or was markedly reduced by large negative contribution of the solvent.

**L-Type:**

The L-type of isotherm was formed when the solid had a high affinity for the solute, or the adsorbed solute molecule were not vertically oriented. This curve showed that as more sites in the substrate were filled up it became increasingly difficult for a bombarding solute molecule to find a vacant site. In L-type curve, the solid possessed few sites which were widely separated and had large hydrophobic region. This type of isotherms was reported by Weber (1966) and Bailey et al. (1968) in studying the adsorption of triazine pesticides.

**H-Type:**

The H-type curve was rare and obtained when the solute has a very high affinity for substrate or there was no measurable amount of solute left in the solution. The initial part of H-type isotherm was vertical. This type of curve along with a plateau was obtained in case of chemisorption of fatty acids,
(Smith and Fuzek, 1946), nematocides such as telome (Singhal and Kumar, 1976) and ionic micelles or polymeric molecules. The length of plateau indicated the difficulty of formation of second layer.

C-Type:

The C-type isotherm, was obtained when new sites became available as the solute molecules were adsorbed from the solution. It represented penetration of substrate micropores by solute with or without solvent. The small solute molecules were found to be accompanied by water while the larger were with or without water. Such type of isotherms were found by Greenland et al. (1962) and Singhal et al. (1976) in case of amino acid and nematocide adsorption respectively.

MOBILITY OF PESTICIDES AND TRACE METALS IN SOILS

The movement of chemical substance in soil may influence both its effectiveness and potential as a contaminant in adjacent soil, water or air. The substance moves predominantly in vertical direction in the zone of aeration above the water label (Jordan et al. 1970). The chemical substance in soil may translocate due to two general processes namely, mass transfer and diffusion. Any movement to a considerable distance is said to be occurred by mass transfer i.e. flow or convection. It is caused by water percolat-
ing downward or absorption upward through soil pores. Furthermore, the soils have pores of various sizes, therefore, the mobility of a particular substance in soils varies with the particle size. The movement through diffusion may be described by Fick's law which is:

\[ J = -D \frac{\partial C}{\partial X} \quad \text{and} \quad \frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial X^2} \right) \]

It shows that the rate of movement \( J \) of a chemical substance over a distance of \( X \) at time \( t \) is directly proportional to its diffusion coefficient, \( D \) and concentration, \( C \). The diffusion coefficient, \( D \) determines whether the chemical diffuse through air or water. According to Goring (1967), the chemicals with water/air ratios under \( 1 \times 10^{-4} \) diffuse primarily through air while those with their ratios higher than this diffuse through water. It is also observed that most of the pesticidal chemicals have their water/air ratio more than \( 3 \times 10^{-4} \) and hence, their movement in soil occurs in aqueous solutions (Helling, 1970).

Interaction with the soil itself is a highly significant factor which retards the movement of chemicals in soil. Various other factors which affect the mobility have been reported by Bailey and White (1964) and others (Rhodes et al., 1970; Schreiber et al., 1971). Some important parameters influencing the movement of chemical substances includes their adsorption, formulation and their solubility in water, flow rate, amount of wetting events,
rise of their application and degradation etc. Some other factors like nature of chemical substance and soil colloids, soil pH, exchangeable cations and anions etc. have also been reported (Singhal and Bansal, 1978; Khan and Khan, 1986; Grover, 1973; Singhal et al., 1977) etc. to affect the translocation process in soil.

To evaluate the movement of chemical substance in soil, various methods have been used. In which column chromatographic methods and soil thin layer are considered as powerful tools. Various conventional columns have been used by various workers e.g. aluminium rings (Harris, 1967), sectioned monel metal pipes (Upchurch and Pierce, 1957), stove pipe sections (Rodgers, 1968), staked time cans (Sheets, 1958), perforated teflon (Kay and Elrick, 1967), rectangular plastic paper (Horowitz, 1968) etc. The chemical substance is analysed in various sections of the column. Direct analysis of column effluent (Davidson and Santelmann, 1968; Rodgers, 1968) has been carried out for highly mobile substances.

**Soil Thin Layer Chromatography:** Thin layer chromatography is an inexpensive, sensitive, selective and rapid tool of analytical chemistry used for the separation and identification of inorganic and organic compounds (Ludwick et al., 1977; Pribyl et al., 1977; Krahne et al., 1977). Soil thin layer chromatography is an adsorption chromatography using a thin layer of soil as adsorbent or stationary phase. While the mobile phase being liquid (generally
water) percolate through the stationary phase. This technique was first successfully used by Helling and Turner (1968). It is analogous to conventional TLC with substitution of soil as the adsorbent phase. Later, this technique was successfully applied to study the movement of various pesticides (Rhodes et al., 1970; Helling, 1971a,b,c; Abdel-Kader et al., 1984; Dedek et al., 1985); organics (Singhal and Bansal, 1978; Krishnamurthy, 1983; Shannon et al., 1985); and tracemetals (Singhal et al., 1977; Singh et al., 1985).

The preparation of soil TLC plates is carried out by spreading a uniform thin layer of aqueous soil slurry with the help of an applicator. It is then allowed to stand overnight for horizontal drying in position (Bremner et al., 1961). The thickness of the layer on soil TLC plates in the range of 0.15 to 2.0 mm, is unimportant with respect to \( R_f \) for diagnostic or qualitative work (Helling, 1971).

The amount of substance applied, depends upon the layer thickness and the visualization method which are inversely proportional to each other. The substance to be studied is normally applied by touching the tip of a filled capillary, micropipette or microburette to the adsorbent layer. The sample is placed or spotted about 3 cm above the bottom end of the plate so that the solvent level will be at least one centimeter below the centre of the spot. The diameter of the spot should not exceed 0.5 cm and should be as small as possible. These plates were then developed
in developing solution (usually water), air dried, and the spot is detected by various methods like chemical reagents, fluorescence and iodine vapours etc., but the substance with which the component reacts chemically must not be used. The mobility is then estimated as $R_f$-values which is the ratio of the distance travelled by the substance under study to the distance travelled by the solvent (Helling, 1971). The substance detection on the developed plate is an important step of this technique and must be made very clear as it characterizes the adsorption behaviour of that substance and adsorption capacity of the soil. It was observed (Helling, 1970) that highly mobile compound without any significant tailing, is adsorbed linearly on to the soil surface. While in the case of compounds with lesser mobility exhibiting tailing, shown a non-linear adsorption. Thus, soil thin layer chromatography provides a very large field of application for investigating problems in various applied or non-applied fields.

**THE PROBLEM**

The application of pesticides, sewage and industrial waste to soil are finding a great importance in modern agricultural practices. Their presence in soils may influence the growth of plants and soil microorganisms. They are also posing some undesirable effects on our flora and found due to the indiscriminate use of pesticides and heavy metals. In India, various food plants have
been studied to analyse the presence of pesticides and heavy metals such as Pb, Cd, Ni, Hg, Ag and many others. It has been observed that their concentration exceeds the maximum permissible limit in food plants.

Pesticide residues in soil may originate from accidental or incidental contamination, as from spoilage, from pesticides in adhering particles of treated soil, by volatilization of pesticides from treated soil or from dusts or sprays drifted by wind. While sewage sludge and industrial wastes and many other processes like atmospheric fallout, auto exhaust, fertilizer impurities, have produced the heavy metal contamination of soils and plants.

Due to the great importance attached with the heavy metals and pesticides, it was considered worthwhile to undertake investigations along the following lines which constitute the subject matter of this thesis entitled, "Adsorption and mobility of pesticides and trace metals with soils and clays".

1. Studies on the mobility of some heavy metals through soil by thin layer chromatography as influenced by organic acids and bases.

2. Studies on the mobility of some pesticides as affected by their chemical characteristics and some soil properties.

3. Adsorption of Cu$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ with Ca-saturated illite.

4. Studies on the adsorption of methyl, 2-benzimidazole carbamate (MBC) with clays as affected by various soil parameters.
REFERENCES


FINLAYSON, D.G. and MacCARTY, H.R.; Res. Rev. 9, 114 (1965).


GRUNER, J.W.; Am. Miner., 19, 557 (1934).


HARRIS, C.I.; Weeds, 15, 214 (1967).


HENDRICKS, S.B.; J. Geol., 50, 276 (1942).


HENDRICKS, S.B.; J. Geol., 50, 276 (1947).


MELLANBY, K.; 'Pesticides and Pollution Collins' (1972).


MUKHERJEE, P.N. and LAHIRI, A.; Fuel, 37, 220 (1958).


WAINWRIGHT, M.; Plant Soil, 55, 199 (1980).


