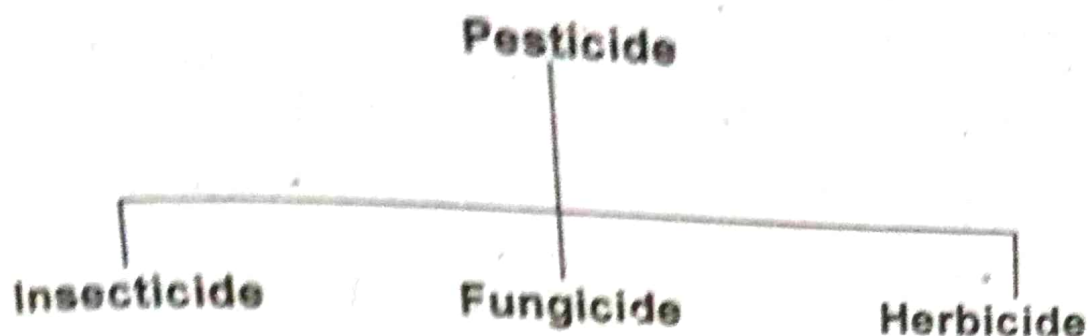
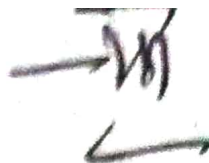


# Pesticides



The history of man is replete with (quite full of) stories of his battles with pests. More than 10,000 species, of insects, 600 weed species, 500 plant diseases and 1500 species of nematodes (round worms) are known to be injurious at least to some degree to man, plants and animals.

The use of chemicals to control pests has been practised for centuries. For example, Greeks are said to have used sulphur to control certain plant diseases. In the early 19th century Pasteur discovered that microbes were the cause of certain plant and animal diseases. Copper - containing Bordeaux mixture, lime and sulphur mixtures and arsenic sprays have been used for the prevention of disease and insect damage. Naturally occurring insecticides such as rotenone and pyrethring were also extensively used. It was the discovery of the insecticidal properties of D.D.T. in 1939 and the herbicidal effect of 2.4D in 1941 that truly began the chemical revolution in agriculture. Modern pesticides are a boon to the world impoverished by the ravages of an overwhelming number of insects rats, mice and other pests. In a tropical country like, India, which promotes optimal growth and multiplication of pests their control has always been a problem. World - wide losses from pests and plant - diseases have been estimated between 15 and 35% of all agricultural production.

## Definition

A pesticide may be defined as any substance or mixture of substances, intended for preventing, destroying, repelling or mitigating any pest such as insects, rodents, nematodes, fungi, weeds or other forms of objectionable plant or animal life. Pesticide is the term used to

describe any toxic chemical used for controlling various kinds of pests. Large number of pesticides have been developed in recent years for the control of pests which destroy crops and stored food grains.

### Classification of pesticides (insecticides fungicides and herbicides)

Pesticides may be classified in three different ways.

#### 1. On the basis of mode of action

Low

- a. **Fumigants :**  
Chemicals used in enclosed spaces for giving out fumes or vapours with lethal effects. e.g., BHC, HCN,  $CS_2$ , nicotine, etc.,
- b. **Contact Poisons :**  
Chemicals which kill by actual contact with the body of the pest e.g., DDT, pyrethrins, lime sulphur, oil emulsions, para hion etc.,
- c. **Stomach Poisons :**  
Chemicals which kill on ingestion by pests, e.g., lead arsenate, paris green, etc.,
- d. **Systemics :**  
Chemicals which are absorbed by roots or leaves and get translocated to other parts of the plant and there by render the plants toxic to certain species of insect. e.g. nicotine preparations.
- e. **Repellents :**  
Chemicals which repel the pests. e.g., dimethyl and dibutyl phthalates.
- f. **Desiccants :**  
Chemicals which kill by dehydration e.g. calcium phosphate, activated clays etc.

This classification is useful, as it serves to give some idea of how pesticides act and therefore how they should be used.

#### 2. On the basis of chemical nature

- a. **Inorganic :**  
Arsenicals, mercurials, borates, fluorides.
- b. **Natural organic :**  
Nicotine, pyrethrum, rotenone, petrolieum oils.



**Synthetic Organic :**

- i. Chlorinated hydrocarbons : e.g. DDT, BHC, chlordane methoxychlor.
- ii. Organo phosphorus compounds : E.g. malathion, parathion.
- iii. Carbamates : e.g. carbaryl, propoxur.
- iv. Miscellaneous : e.g. thanite.

**On the basis of the type of Pests against which they are used****Insecticides :**

Used against insects : e.g. DDT, BHC, pyrethrins.

**Fungicides :**

Used against fungi or moulds e.g., sulphur, copperoxychloride.

**Harbicides (or weedicides) :**

Used against weeds e.g., alachlor 2, 4 -D compounds.

**d. Acaricides :**

Used against ticks and mites belonging to the class acarina e.g., malathion.

**e. Rodenticides :**

Used against rodents (rats, mice, etc.) e.g., zinc phosphide.

**General methods of preparation and application :**

Only small concentrations of pesticides are required for any situation and no pesticide can be used in its pure form generally. Hence it is necessary to provide them in a variety of effective formulations. A wide range of formulations is now available for most of the pesticides. The common types of formulations are dusts, emulsions, solutions, wetttable powders and aerosols.

**Dusts :**

Dusts are usually made by diluting the toxicant with finely divided, ground plant materials, such as wheat or walnut shell flours or with minerals such as talc, clays and sulphur. Coarse or granular formulations of dusts are also made to be used by aircraft and for ground applications.

**Emulsions :**

An emulsion is one liquid dispersed in another liquid, each maintaining its original identity. Emulsions are made by dissolving the

toxicant and an emulsifying agent in an organic solvent thus making emulsifiable concentrates. These are diluted with water and applied as sprays.

### **Solutions :**

Solutions consist of molecular mixtures of the toxicant with a solvent such as water, or with petroleum distillates such as kerosene. They may be applied by spraying by dipping or impregnating or by brushing. Oil solutions are phytotoxic and often constitute a fire hazard.

### **Wettable powders :**

Wettable powders are toxicants adsorbed or absorbed on powders that can be readily mixed with water because a wetting or conditioning agent has been added. These form suspension type sprays and must be constantly agitated to give uniform coverage.

### **Aerosols :**

Aerosols are suspensions of solid or liquid particles of ultramicroscopic size which remain suspended for long periods. They may be the liquefied gas type utilizing the propelling agents Freon - 12 or methyl chloride or mechanically generated oil clouds or fogs (mechanical fogging).

### **Insecticide mixture :**

Often the spraying or dusting operation is designed to control, by one application several insect pests and often some plant diseases as well ; thus a mixture of materials can be used advantageously. If no deleterious effects are produced when different insecticides and fungicides are combined and applied simultaneously, they are said to be compatible. If the combination, causes any kind of injury to the host or lowered the effectiveness of the components, or results in any other adverse effects, it is said to be non - compatible. e.g. ; a combination of calcium arsenate and cryolite is said to be non - compatible.

### **Toxicity :** *am*

Toxicity of pesticide refers to the poisonous nature. The toxicity studies are made on test animals, usually white rats. The toxicity of different pesticides has been measured separately for two routes of administration - through food and through the skin. These are expressed "oral" and "dermal" toxicity in terms of LD<sub>50</sub> values (Table 16). These values are statistical estimates of the dosages in milligram of the poison



per kilogram of body weight, required to kill 50 percent of a very large population of the test animal under specified condition. (Lethal Dose).

The  $LD_{50}$  values serve as a basis for the classification of pesticides, according to their relative toxicities. The values represent pesticide toxicity in test animals when the compound concerned is administered to the animal in one single dose. These values can give no indication of the actual hazards involved when a pesticide is used under various conditions.

Table - 16

Actual Oral and Dermal  $LD_{50}$  values of some pesticides for Female white rats

Compound	type oral	$LD_{50}$ (mg/Kg)	Dermal $LD_{50}$ (mg/kg)
Chlordane	CH	430	690
DDT	CH	118	2510
Lindane	OH	91	990
Malathion	OP	1000	> 4444
Methoxychlor	CH	6000	> 6000
Parathion	OP	3.0	6.8
Pyrethrins	B	584	> 1500

OH - Chlorinated Hydrocarbon

OP - Organo Phosphorus Compound

B - Botanical.

The following hazards have come to light as a result of the routine use of pesticides:

1. Direct toxic effects (both immediate and delayed) on man and animals.
2. Disturbance of ecological equilibria, giving rise to uninhibited growth of certain pests.
3. Environmental pollution, with resultant deterioration in the quality of food, water, soil and air.
4. Development of pest resistance to pesticides leading to loss of property and disease.

These are two types of poisoning - acute or immediate and chronic or cumulative.

- i. In the acute type, the effects are immediate and there will be clinical symptoms needing prompt medical attention. Both organophosphorus and carbamate of pesticides cause this type of poisoning.
- ii. Chronic toxicity does not manifest itself immediately. It is the result of a gradual accumulation of pesticides in the human system, following exposure to the chemicals over a long period. Organo chlorine pesticides such as DDT and aldrin generally cause this type of poisoning.

All pesticides are toxic in one way or the other and almost every country in the world has imposed restriction and regulations in regard to their production, storage and use.

### ~~Handwritten mark~~ Safety measures when using pesticides <sup>10/10</sup>

Pesticides being toxic to human beings and domestic animals should be handled with utmost care the following precautions should be observed:

1. The pesticides should always be stored in their original containers and kept in locked cupboards. (They should not be placed within the reach of the children and domestic animals).
2. They should be kept away from food or food stuffs and medicine.
3. Bags and containers of pesticides should be cut open with a separate knife.
4. The empty containers should be destroyed and should not be put into some other use.
5. Inhaling of pesticides sprays or dusts and smoking, chewing, eating or drinking while mixing or applying the chemicals should be avoided.
6. Particles or drops of pesticides, which may accidentally get into eyes, should be flushed out immediately with large volumes of clean water.
7. Protective clothings and devices should be used while handling poisonous chemicals to avoid exposure to sprays or drifts.
8. Dusting or spraying should never be done against, the wind and it is preferable to have them in cool and clam weath. r.
9. After handling pesticides hands, face and body should be washed and clothing changed.
10. Persons engaged in handling pesticides should under go regular medical check - up.



# Insecticides

## Definition :

An insecticide is defined as any substance intended for killing insects.

Insects are the most abundant form of animal life on earth. They are found nearly everywhere in the world except in the open seas and some parts of the polar regions. Whether they are considered helpful or harmful or neutral to man depends on whether man is co-operating, competing or indifferent to their presence.

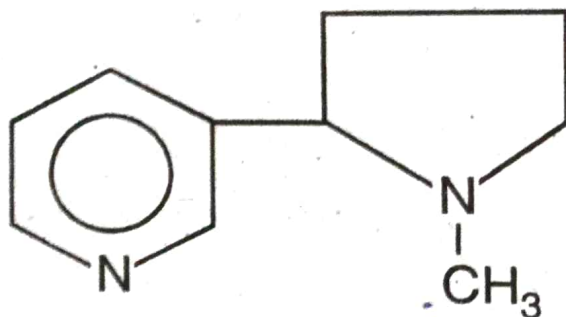
Insects may be helpful to man by producing materials of economic value, such as silk, honey, beeswax, shellac etc., and by aiding in the production of flowers, fruits, vegetables and seeds because of pollinating activity. Insects may be harmful to man and cause great economic loss by damaging or destroying agricultural crops and other valuable plants that produce diseases of plants ; by annoying man or other animals in various ways ; and by destroying stored foods, other products and possessions. For example, insects such as beetles, weevils and borers make short work of stored food, especially cereals, pulses and their flours. Insects preferentially consume the starchy endosperm and other nutritive parts, leaving the food depleted of much of its vitamins and other essential nutrients.

## Organic Insecticides - Plant products

Natural plant chemicals such as nicotine and pyrethrum have been in use as insecticides for a very long time. Rotenone and oils such as petroleum and tar oils are ; perhaps later additions. Kerosene oil has been in use since its introduction as an illuminant. Highly refined oils (white oils) came into use only by 1924.

### 1. Nicotine $C_{10}N_2H_{14}$

Nicotine is the chief alkaloid of tobacco plant (*Nicotiana glauca*). It occurs in the plant leaves as salts of malic acid and citric acid to the extent of 4 to 5%. Nicotine is the trivial name for (S)-3-(1-methylpyrrolidin-2-yl)pyridine, marketed as crude nicotine (95 - 98% alkaloids) and nicotine sulphate (40% alkaloids). They are prepared commercially from waste tobacco by steam distillation in the presence of alkali. The predominant component of the crude alkaloid is (-) nicotine.



Nicotine

Nicotine is a mobile colourless liquid (b.p.  $247^{\circ}\text{C}$ ) turning brown and finally black becoming more viscous. It is a well defined base. (In the tobacco plant it is combined with malic and citric acids).

#### i. Action :

It is a non - persistent contact poison. It is toxic not only to insects but to higher animals also. It is readily absorbed through the skin and mucous membranes causing paralysis of nerves. However, it may be safely used to fumigate green houses as it volatilises quickly and its effect is purely temporary. Fumigation may also be done by burning nicotine shreds.

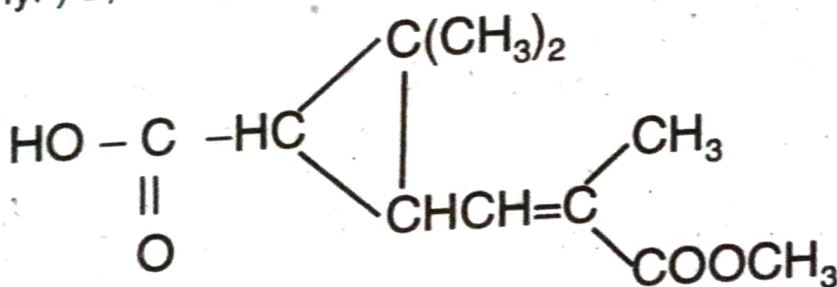
#### ii. Pyrethrum

Pyrethrum powder is obtained by crushing the flowerheads of *pyrethrum cinerariae folium* (originally known as Dalmatian insect flowers) and two other species, grown mainly in Japan, Kenya and East Africa. Good quality pyrethrum flowers usually contain 0.5 to 1.5% of the active



ingredients, pyrethrins. During drying, a part of the active ingredients may be lost. The powder formed by grinding the dried flowers is called pyrethrum. It retains its insecticidal property for varying periods of time; the loss of potency depends on the fineness of the powder and the period of exposure to sunlight and heat. Anti oxidants such as tannic acid, hydroquinone, and resorcinol have been used to retard this loss of activity.

The powder is usually extracted with kerosene and the extract is concentrated. The extract contains all the insecticidal ingredients of Pyrethrum. All the active ingredients are esters; the pyrethrins (pyrethin I and II) and the cinerins (Cinerin I and II). These are the esters of two ketonic alcohols (e.g. pyrethrolone) and two acids (e.g. pyrethic acid). The dicarboxylic acid present in pyrethrum as the monomethyl ester is known as pyrethic acid. It is (1 - R) - trans - 3 - [(E) - 2 methoxy carbonyl prop - 1 - enyl ) 2,2 dimethyl cyclo propane carboxylic acid.



The general term pyrethrins includes the cinerins as well. They are all unstable to sunlight and quickly hydrolysed by alkalis with loss of insecticidal properties.

### Action :

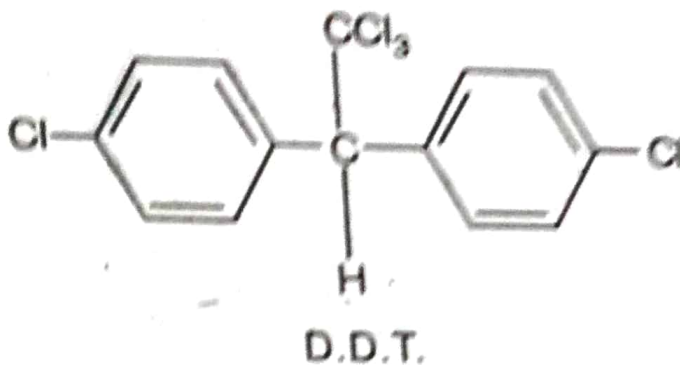
Most insects are killed by sprays having 0.002-0.004% pyrethrins. The pyrethrins are powerful contact poisons causing a rapid paralysis or 'knock-down' effect on insects owing to their effect on the nervous system. They have the unique quality of being toxic to insects but not appreciably so to plants and higher animals. Pyrethrum is especially useful in control of cockroaches and mosquitoes. Also the insects do not usually develop physiological resistance to it. However, pyrethrum powder can cause dermatitis in some people and the pyrethrins can be dangerously toxic when introduced intravenously. When inhaled or ingested or brought in contact they are relatively non-toxic to man.

### iii. Rotenone : $\text{C}_{23}\text{H}_{22}\text{O}_6$

Rotenone is the trival name given to the insecticide isolated from

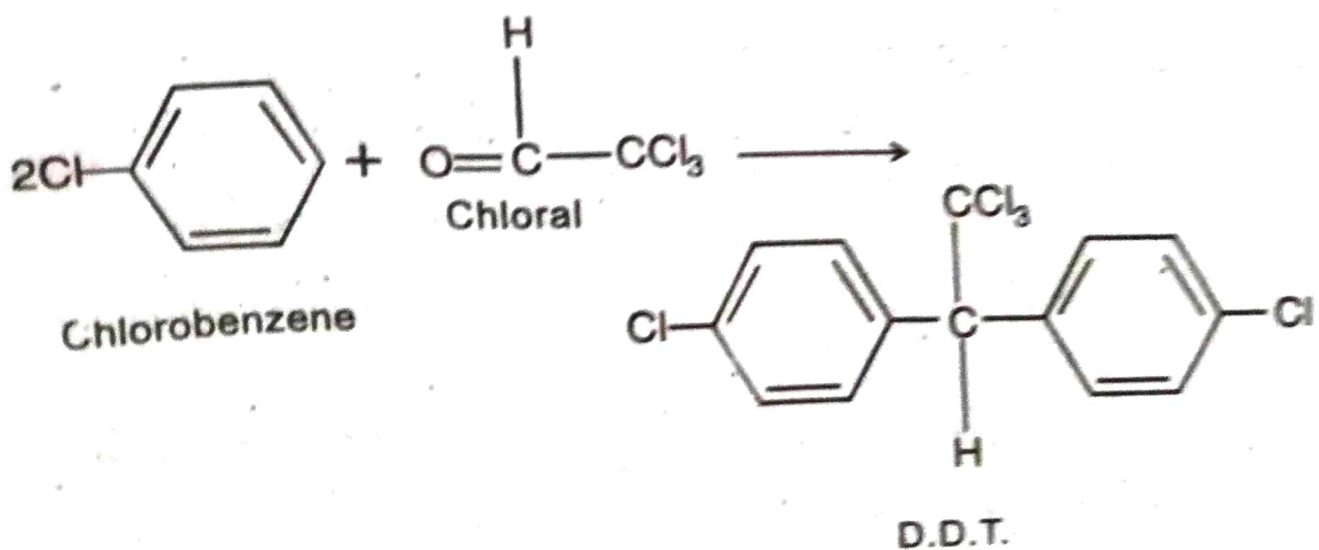
proving resistant to them. In developing countries like India, these are still used because of their low cost, easy availability and continued effectiveness for long periods. (The average daily diet of an Indian contains 0.27 mg of D.D.T.)

1. ~~D.D.T~~ ( $C_{14}H_9Cl_5$ ) SM  
 The initials D.D.T come from the compound's commercial name Dichloro Diphenyl Trichloro ethane. The compound is 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane.



The insecticidal properties of D.D.T. were first discovered in 1944 by P. Muller. It became popular during the last war and has remained so, as it is cheap and has proved immensely useful in the control of flies, mosquitoes and other disease-bearing insects.

D.D.T. is prepared by heating chlorobenzene with chloral  $CCl_3CHO$ , in presence of conc. sulphuric acid (2 molecules of chlorobenzene condense with 1 molecule of chloral).



D.D.T is a waxy solid, insoluble in water, and in most aromatic and chlorinated solvents. The compound is stable in air and is not attacked



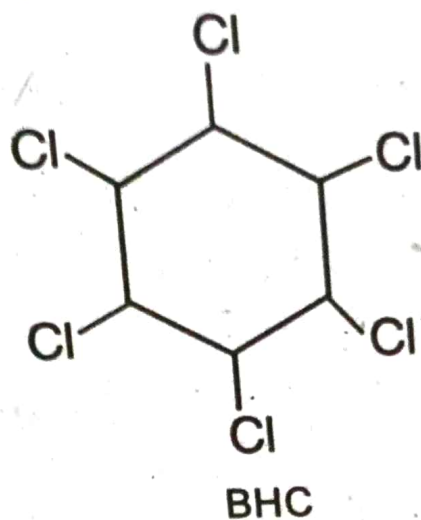
by aqueous acids and alkalies. On heating the soiled compounds evolves HCl gas, forming ethylene, with loss of insecticidal properties. It has a high and specific toxicity for various insects such as the house fly mosquito.

**Action :**

It is a powerful stomach and contact insecticide and larvicide. It has little action on carpet beetles, red spiders, cotton be weevils, some species of ants and the common cockroach. Poured on stagnant water, it quickly destroys mosquito larvae. It could eliminate, with rapidity and efficiency, flies, mosquitoes, bugs, lice, caterpillars, leaf hoppers, cloth moths and their larve. But with continued use, these insects are becoming immune to it. It is not ordinarily toxic to man in small concentrations but tends to build up in body fats. When dissolved in vegetable oil, it is more readily absorbed through the skin and hence can become doubly toxic.

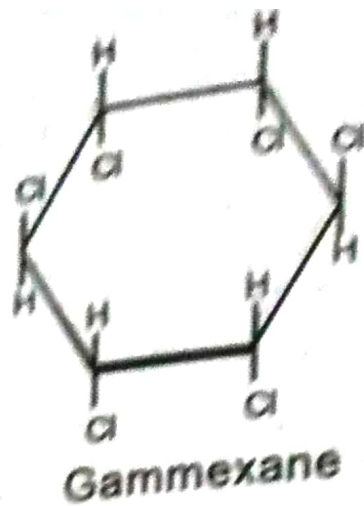
**Benzene hexa chloride, (B.H.C)  $C_6H_6Cl_6$**

The compound was discovered by Faraday in 1825, but its insecticidal activity was first evaluated only in 1942. It is known by the commercial name BHC or 666 derived from its formula  $C_6H_6Cl_6$ . It is 1,2,3,4,5,6 Hexa chloro cyclo hexane (HCH).

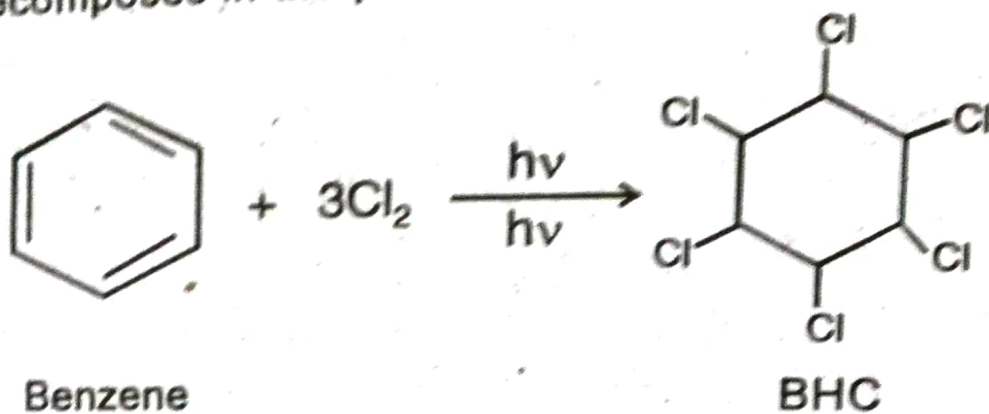


It can exist in 16 isomeric forms, of which only 6 have been isolated and studied so far. Of these the alpha form is the major constituent of technical BHC (65 - 70%) but it has no toxicity. The beta isomer (5 - 6%) is highly toxic to higher animals, while the delta isomer (6%) is known to irritate eyes and mucous membranes. The gamma form is called Gamexane and it constitutes roughly 13% of BHC. It is this isomer which is the insecticide.

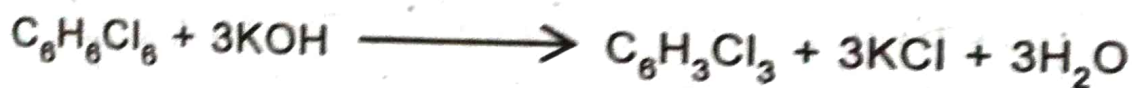




BHC is obtained as an addition product when benzene is treated with chlorine in the presence of sunlight. It is an amorphous buff coloured substance with a characteristic musky odour. It is insoluble in water, but soluble in benzene and kerosene. It is stable towards light, air, heat and acids, but decomposes in the presence of alkalis.



The property of one molecule of BHC to liberate 3 atoms of chlorine on reacting with alcoholic-potash is made use of in the determination of the compound.



#### Action :

BHC is a persistent stomach and contact poison. It is effective against soil insects, grasshoppers, cotton pests, storage and household pests, in the form of smoke, sprays, aerosols or dusting powders. At higher concentrations, it can cause root deformation and also taints certain crops seriously (e.g., potato)

#### Formulations :

1. Dusting powders containing 5 and 10% active ingredients.
2. Water dispersible powder containing 50% active ingredients.
3. Granules having 6 and 10% active ingredients.

## **Lindane :**

151

It is 99% pure gamma BHC. The compound was introduced under the trade name Grammexane. It is prepared by the selective crystallization of crude BHC. It forms colourless crystal, sparingly soluble in water and in petroleum oils, but readily soluble in acetone. It is stable to air, light, heat and carbon dioxide, and is not attacked by strong acids but is dehydrochlorinated BHC or DDT since it is more readily excreted by the human body.



# Fungicides and Herbicides

## Fungicides

Fungicides are chemicals used for killing fungi which are responsible for producing many plant diseases. Fungicides are used primarily to control the field diseases of fruits and vegetables. They are also used to counteract seed diseases of common crops and protect harvested fruits and vegetables from decay and rot.

2m.

## Inorganic fungicides

### Sulphur compounds

#### i. Sulphur :

It is primarily a fungicide and acaricide, but may serve as a diluent for insecticidal dusts. It is usually formulated as a fine dust 95% with 10% inert material. The flow of the dust is also made more free by the addition of 3% tricalcium phosphate. It is also formulated as a wettable powder. Effectiveness increases with the fineness of sulphur particles. It is generally non-toxic, but irritating to eyes.

#### ii. Lime sulphur :

It is the aqueous solution of calcium polysulphides. It is prepared by sulphur solution in calcium hydroxide suspensions preferably under pressure in the absence of air. Calcium pentasulphide and calcium tetrasulphide present in the mixture are responsible for the insecticidal activity. Lime sulphur is still extensively applied as a fungicide for orchards.

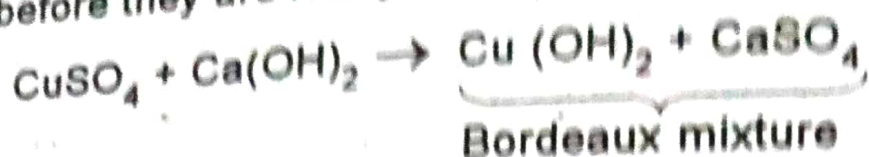
## Copper compounds :

#### i. Bordeaux mixture :

It is a complex compound containing copper and calcium that has been used for many years in the control of foliage diseases. It is essentially a mixture of lime (CaO) and copper sulphate. Standard 5-5-50 Bordeaux mixtures are made up by dissolving 5 pounds of copper sulphate in 25 gallons of water ; 5 pounds of fresh hydrated lime are pasted in water and made up to 25 gallons. The two solutions are poured together while stirring. These mixtures are used as fungicides by spraying



on potatoes, tomatoes and vines. On fruits, the ratio is always 3 of slaked lime to every 2 of copper sulphate, i.e., 4:6:100. Today there exists many substitutes, for Bordeaux mixtures that only require stirring into water before they are ready for application.



Dry Bordeaux contain 26% copper and is usually marketed as fine powder. Leaf spot of beans, beet, carrots, peas, potatoes and tomatoes has been controlled by applications of sprays containing 5 pounds to dry Bordeaux per 100 gallons of water.

#### ii. Copper Oxychloride :

This is another fungicidal material that has been developed with success as a substitute for Bordeaux mixture. Blister blight of tea, Hemeleia of coffee, late blight of potatoes and leaf spot of bananas and tobacco are among the foliage diseases that have been controlled by applications of this material.

#### iii. Cuprous Oxide :

Potato blight, sugarbeet leaf spot and downy mildew of onions are some of the diseases which have been controlled by applications of this material. It is usually marketed either as dusts (containing 6 - 25% copper) or as wettable powders (containing 50% copper)

#### iv. Organic Copper Compounds :

During the past few years, experiments have been taking place with several organic copper fungicides. Copper oxinate is the copper salt of oxine (8 - hydroxy quinoline). It has been used as a wettable powder for control of many diseases, including apple and pear scab, certain soft fruit diseases, and also on vegetables and flowers.



# HERBICIDES

## Introduction :

A weed is a plant growing where it is not desired or a plant out of place. Herbicides may be defined as substances or mixture of substances used to destroy the unwanted weeds which compete with the main crop for food and light. Starting with 2,4 - D (Chlorinated phenoxy acetic acid), dozens of other chemicals in literally hundreds of formulations have been placed on the market. These include triazines, phenyl ureas, aliphatic acids, carbamates, dinitroanilines and dipyridyl. Herbicides are biodegradable and most of them are relatively low in mammalian toxicity. Some are quite toxic to fish and perhaps to other wildlife.

Herbicides are often best applied when the weeds are young since weeds are most susceptible at this stage, particularly in the tropics where they acquire tolerance to chemicals more quickly than corresponding weed, do in temperate regions. Further less chemical is required at this stage and less damage is caused to the crop by spraying equipment. Herbicides are therefore most commonly applied either in the early stages of growth (post - emergence spraying) or prior to the emergence of the crops above the ground (pre - emergence spraying). The latter technique is of particular advantage for really early weed control. For example, pre - emergence application of 2,4 D or simazine is the most effective method for weed control in maize.

Relatively little is known about the tolerance of different crops to various herbicides. Some crops are so highly susceptible to damage from certain types of herbicides. For example, cotton is speciacularly damaged by the majority of the weed killers. All cereals are to some

extent susceptible to 2,4 D, and MPCA. But rice can be sprayed with these chemicals at concentrations adequate to kill weeds if this is done at tillering stage, some weeks after planting. Earlier spraying cause damage and reduce yields. On the other hand, maize which is more susceptible than the small cereals, can only be sprayed by the pre-emergence technique, Its is, therefore, of the first importance to know for each crop the chemicals that can be used and at what stage of growth and at what concentration they can be safely applied. (The herbicides are not so much used in India because the labour is cheap here).

**Classification :** Herbicides may be classified

1. according to their chemical nature
  - a. Inorganic herbicides and
  - b. Organic herbicides.
2. according to their mode of action.
  - a. Selective, comprising compounds which kill weeds only, without damaging the crop.
  - b. non-selective comprising compounds which kill all vegetation with which they come into contact.

Selectivity is depedent upon many factors such as growth stage, species and variety and formulation of the herbicide.

Post - emergence treatments are made overall to crop and weeds. These treatments may be subdivided into

- i. contact herbicides and
- ii. translocated herbicides.

Contact herbicides are those that kill plant tissues only in the vicinity of the point of contact. Translocated herbicides, however, may be moved within the plant to distrub metabolic processes in other parts of the plant. They tend to act more slowly than contact herbicides.

## **INORGANIC HERBICIDES**

### **a. Arsenic compounds**

Sodium arsenite has been used for many years as a non selective herbicide. It is solid as an aqueous solution containing about 10lb arsenious oxide ( $AS_2O_3$ ) equivalent per gallon, or as a water - soluble



## Acaricides

Acaricides are the chemicals used against the ticks and mites belonging to the class acarina. They kill the insects which bite the leaves of the plants. Diphenyl sulphone, chlorofenson, dicofol are some of the important compounds of this class.

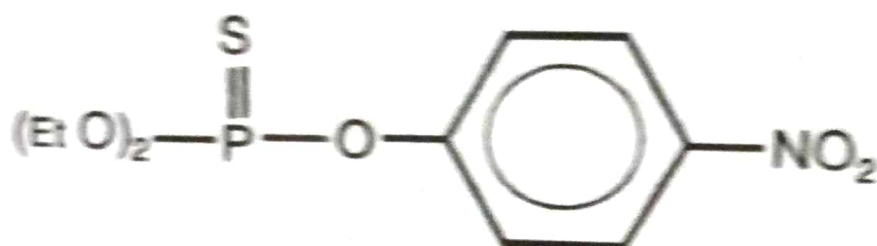
### i. Fenson :

Fenson is the common name for 4-chlorophenyl benzene sulphonate. It has recently shown itself to be of value in the control of red spider and other mites. It is particularly toxic to the eggs. Mites on beans, cotton, melon and grapes have been controlled by applications of 5% fenson.

### ii. Azobenzene :

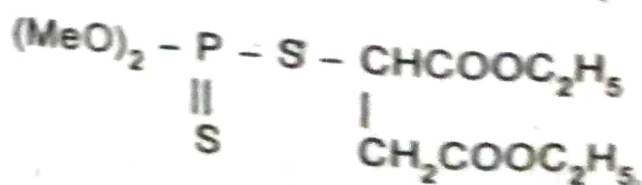
Azobenzene is an organic compound which volatilizes readily when heated. It has been used to control red spider in greenhouses. It is usually marketed in the form of a powder that can be heated on steam pipes or as smoke generators.

### iii. Parathion



Parathion is O,O-diethyl O-(4-nitro-phenyl) phosphorothioate. It is a yellow to deep-brown oily liquid with a garlic-like odour. It is sparingly soluble in water, but is readily soluble in alcohol, ether, ester, oils and fats. It is a contact and stomach insecticide and acaricide. Being cheap, powerful and effective in small concentrations against a variety of pests, it is widely used in agriculture.

### iv. Malathion



Malathion is S-1, di(ethoxy carbonyl) ethyl O-O-dimethyl phosphoro dithioate. (or) S (.1, 1-dicarbethoxy ethy O, O-dimethyl dithio phosphate. It is a brownish liquid with an obnoxious odour. It is an

insecticide and acaricide of low mammalian toxicity. Because it is both effective and safe, the U.S. Department of Agriculture has sanctioned its use for controlling more than 100 pests occurring in 90 field, vegetable and fruit crops. In India malathion has proved to be a popular rat repellent. A drawback of malathion is that it is highly toxic to bees.

One of the most important methods of controlling insects is by means of chemicals. Application of chemicals for killing insects implies the use of insecticides. The word "insecticide" means insect-killer materials which kill insects are called insecticides, and these may be inorganic or organic compounds. Chemicals for insect control are classified in various ways. e.g., stomach poisons, contact poisons, fumigants, repellents and attractants.

## 1. Rodenticides 14 (b)

Rodenticides are chemicals which are used against rodents like rats, mice, etc. Several inorganic compounds are used as rodenticides. e.g., Zinc phosphide, Barium carbonate. Thallium sulphate (i) Barium Carbonate  $\text{BaCO}_3$ , causes haemorrhage of gastro-intestinal tract and kidneys and muscular paralysis (ii) Thallium sulphate.  $\text{Ti}_2(\text{SO}_4)$  is a slow-acting rodenticide as well as an ant poison. (iii) Zinc phosphide,  $\text{Zn}_3\text{P}_2$ , has been in long use as a rat poison, It is a grey powder with garlic odour. Though a stable compound, it decomposes slowly in moist air. It is used as a 2% bait for the control of field rats. Zinc phosphide ingested along with the bait reacts with the hydrochloric acid of the rodent stomach and releases phosphine gas which is extremely reactive and poisonous.  $\text{LD}_{50}$  for rats; oral 45.7.

## 2. Attractants :

Chemical substances which attract insects towards their source are called attractants. Many substances attract insects by olfactory stimulation. The insects are attracted by the odours emanating from the food or from the opposite sex and from prey. Attractants are useful in luring insects into traps or to poisons.

A mixture of geraniol and eugenol (1:1) serves as food lure and attracts beetle adults. Moths and butterflies are attracted by fermenting syrups and sugars and molasses. The hornworm moths of tomato and tobacco are lured by isoamyl salicylate. Ammonia attracts the walnut



husk fly. Protein hydrolysates are used in baits for attracting fruitflies. In poison baits for snails and slugs metaldehyde is used as an attractant.

### 3. Repellents:

Materials which prevent migration, oviposition (laying of eggs) or feeding of insects are described as being repellent or having repellent properties. This effect is made manifest by the negative response of insects to the physical and chemical properties of these various substances when applied to plants. Many of the better repellents are chemicals producing lethal effects, if the concentration is high enough and if the insects are unable to move away rapidly.

Bordeaux mixture is very repellent to potato flea beetles and leaf hoppers; sulphur applied to the body is a chigger repellent; cattle fly sprays prevent live stock from annoyance and loss of blood; coal tar creosote repels chinch bug, termites, powder post beetles and wood borers; paradichlorobenzene and mothballs are repellent to carpet beetles, clothes moth and other fabric pests; hydrated lime and aluminium sulphate applied to foliage (leafage) act as repellents for adult Japanese beetles; oil of citronella, indalone, dibutyl phthalate, dimethyl phthalate (DMP) and benzyl benzoate are repellents for mosquitoes, flies, ticks and chiggers. Many of the stomach, contact and fumigant materials also possess some repellent properties.

## Properties of Soil

Agricultural chemistry or agrochemistry, is the scientific discipline concerned with the interaction of plants, soil and fertilizers in the cultivation of crops. The objective of agrochemistry is to study the cycle of nutrients in agriculture and find ways to influence the chemical processes occurring in the soil and plants with a view to enhancing the yields of crops. Application of fertilizers is by far the most drastic way of altering this cycle.

Soils are the natural bodies on which plants grow. Man is dependent on soils; he enjoys and uses the plants because of their beauty and because of their ability to supply fibre and food for himself and his animals, Man's standard of living is often determined by the quality of soils, and the kinds and quality of plants and animals grown on them.

### Definition of soils : 2m

The terms 'soil' (derived from the Latin word 'solum') means floor or ground. The formulation of a simple definition of soil is made difficult by the great diversity of soils in the world. In general, soil refers to the loose surface of earth as distinguished from solid rock. 2m (2)

Soil may be defined as the superficial loose covering of the earth's surface; the soil layer has been formed by the weathering of the rocks in the distant past.

Soil has been defined (by Allee, Parn and Park) as the shallow upper layers of earth that are formed by weathering of underlying rocks in association with organic matter and with living organisms and has become a suitable habitat for plants and animals.

Treshow (1970) defined the soil as a complex physical biological system providing support, water nutrients and oxygen for the plants.

Soil is often referred to as a complex and highly heterogeneous colloidal system.



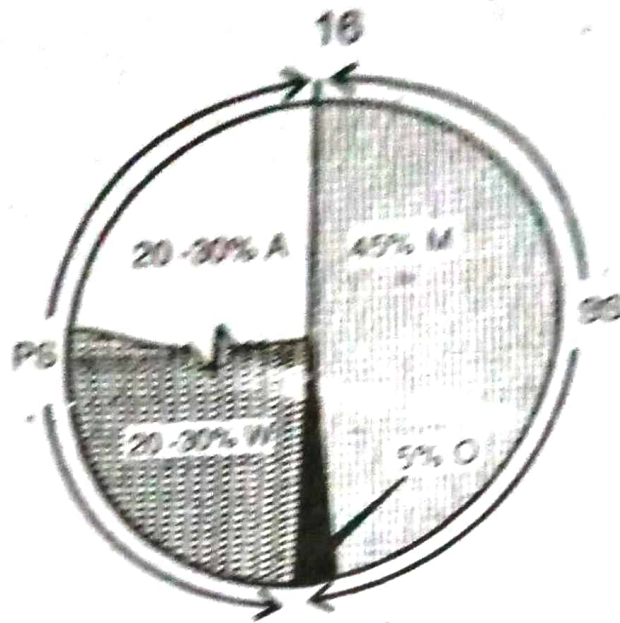


Figure 1

### Volume Composition of Mineral Soils

- |                    |                    |
|--------------------|--------------------|
| A = Air            | O = Organic matter |
| W = Water          | P.S. = Pore Space  |
| M = Mineral matter | S.S. = Soil solids |

The approximate volume composition of the four major components of soil is as follows.

- |                    |       |     |
|--------------------|-------|-----|
| i) Mineral matter  | about | 45% |
| ii) Organic matter | "     | 5%  |
| iii) Soil water    | "     | 25% |
| iv) Soil air       | "     | 25% |

It is interesting to note that about half the volume is pore space viz. air and water (Figure 1). The four major components of the normal soil exist in an intimately mixed condition. This encourages both simple and complex reactions within the groups and permits an ideal environment for the growth of plants.

Proportions of the components vary from time to time and from place to place. The volume of water and air bear a direct reciprocal relationship with each other. Entrance of water into the soil excludes air. As water is removed by drainage, evaporation or plant growth, pore space which was occupied by water becomes filled with air once again. Sub soils contain less organic matter than surface soils.

4. **Soil water :** 2m(3)

[All soils contain water. Even the "dry soil" contains a certain amount of water. However, the amount of water present in soils varies considerably. Different soils absorb and retain different quantities of water.]

**Importance of soil water :**

Soil water plays an important role in the growth of plant. Water serves as a solvent and carrier of food nutrients; it self acts a nutrient. Plants transpire large quantities of water, which they continuously absorb through their roots and give out from the leaf surface. Thus a growing plant requires large quantities of water. It is necessary for a plant to



have optimum moisture conditions in the soil during the growth period. Water supply is the most important factor affecting the plant growth. The yield is more often determined by the amount of water available than by the deficiency of other food elements.

Soil obtains its water from rain, snow dew or irrigation. A part of the water soaks into the ground; the rest of it runs over the surface of the ground and is carried away in streams. The water that soaks into the ground travels down into the lower layers, wetting the soil through which it passes. A part of this water is drained away and the rest is retained by the soil particles. Of the total amount of water that reaches the soil, a very small fraction is actually retained in the soil and made available to the growing plant.

The processes of weathering and soil formation depend on water. The downward movement of substances from the surface layer and their accumulation in the lower layers take place through the agency of water. The micro-organisms in the soil also require water for their metabolic activities. Thus water indirectly affects plant growth through its effects on soil and micro-organisms.

### **Retention of water by soil :**

Soil particles, like almost all substances, possess the power to absorb moisture (water vapour) from the atmosphere. If a dry soil is exposed to moist atmosphere, it absorbs a certain amount of water. The absorption of moisture is due to the condensation of water vapour on the surface of the soil particles. The soil goes on absorbing moisture till the moisture so absorbed is in equilibrium with moisture in the atmosphere. It is mainly the clay or colloidal particles that are responsible for absorbing water. Silt and sand particles do not absorb water.

Soil water is subjected to two physical forces as a result of which it is retained in the soil. The soil particles try to hold the water on their surfaces due to the forces of absorption (or attraction) while the force of gravity tries to pull it downwards. The surface force is far greater than the force of gravity. Depending on the magnitude of the resultant force acting on it, the water may remain attached to the soil particle or move downwards into the lower layers.



Soil water may be divided into three categories depending upon the physical forces at play and the mode of retention ; i) Hygroscopic water ii) Capillary water and iii) gravitational water.

### i. **Hygroscopic water :**

The water held on the surface of clay (colloidal) particles by the dipole orientation of its molecules is known as hygroscopic water. The layer of hygroscopic water so formed is extremely thin (thickness varies from 8A to 28 A and is made up of three to ten layers of water molecules. On account of the great force (about 10,000 atmosphere) with which it is held in the soil, it is incapable of any movement. It is held so strongly by soil particles that plants cannot make use of it. Plant roots are unable to draw up this water from the soil. Hygroscopic water cannot be separated from the soil unless it is heated. ( $105^{\circ}$  to  $110^{\circ}\text{C}$ )

The amount of hygroscopic water absorbed by soil depends on i) its texture, ii) the amount and nature of colloidal material iii) the humidity and, iv) the temperature of atmosphere. The amount of water varies inversely with the size of soil particles ; the smaller the particle the greater the amount of hygroscopic water it adsorbs. Fine-textured soils like clays contain more hygroscopic water than coarse textured soils.

The presence of humus which is a colloidal material also increases the amount of hygroscopic water in a soil; the greater the amount of organic matter, the greater is hygroscopic moisture.

When the humidity of air increases, the amount of hygroscopic moisture adsorbed by a soil also increases. On the other hand, an increase in temperature decreases the amount of water adsorbed and vice versa.

**Hygroscopic Coefficient** is the maximum amount of hygroscopic water adsorbed by 100 gm of dry soil under standard conditions of humidity and temperature.

### ii. **Capillary water :**

If more water is supplied to a soil that has reached its maximum hygroscopic capacity, it begins to adhere to the



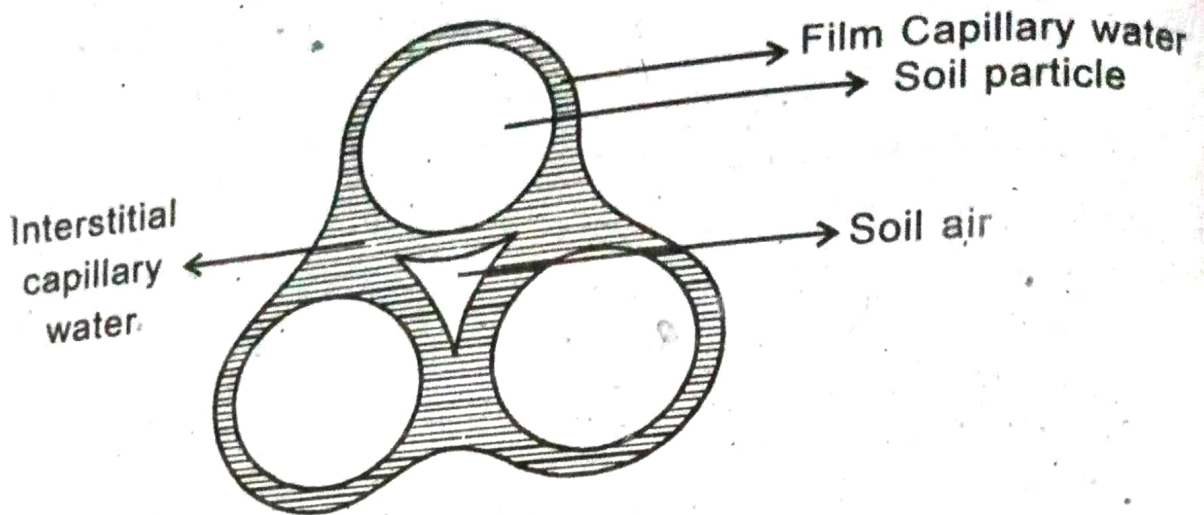


Figure - 4

surface of the soil particles as liquid water in the form of a thin film. This film of water is known as *capillary water*. At first the films occur as thin rings around the soil particles. As the moisture content is increased, the rings become thicker and the films around adjacent particles join up and become continuous. When the films around three or more adjoining particles join up a part of the soil pore-space occupied by water and the rest remains full of air (Fig 4). A part of the capillary water exists as film round these soil particles and the rest as interstitial water in the interstitial spaces between them; a major bulk of the capillary water is present in the interstices.

The capillary water is not held as firmly as hygroscopic water. However it is held so strongly that gravity cannot separate it from the soil particles. The molecules of capillary water are free and mobile and are present in the liquid state. Due to this reason it evaporates easily at ordinary temperature unlike hygroscopic water. Plant roots are able to absorb it and capillary water is, therefore, known as *available water*.

The amount of capillary water held by a soil mainly depends upon four factors; 1) Surface tension of the water film; ii) soil texture iii) soil structure, and iv) organic matter. An increase in surface tension increases the amount of capillary water. A rise in temperature lowers the surface tension and thus causes a fall in the amount of capillary water. The finer the texture of soil, the greater the amount of capillary water it holds; this is mainly due to the great surface area and a large number of interstitial



spaces. A clay soil, therefore, carries a greater amount of capillary water than a sandy soil.

Structure also affects the amount of capillary water. A clayey soil having a granulated structure has more interstitial space than one having a single - grain structure; hence it contains more capillary water. The presence of organic matter helps to increase the capillary capacity of a soil. Undecomposed organic matter is generally porous having a large internal surface area which helps to hold more capillary water. The humus that is formed on decomposition has a great capacity for absorbing and holding water.

The capacity of a soil to hold the maximum amount of capillary water is known as its **maximum capillary capacity**. It represents the maximum amount of capillary water that a soil can hold. Soils having a fine texture have a high maximum capillary capacity.

#### **Water-holding capacity :**

The capacity of a soil to hold the maximum amount of **total water** is known as its **water-holding capacity**. It represents the maximum amount of water that the soil can hold against the gravitational pull. The water-holding capacity varies with the size of the soil particle. Finely-textured soils have a higher holding capacity than coarse-textured soils.

#### **iii. Gravitational water :**

When the amount of water in a soil is increased beyond its maximum capillary capacity, the additional water appears as free by soil particles and therefore, comes under the influence of gravity. Hence this water is called *gravitational water*. The water moves downward through the soil due to the force of gravity and this downward movement is known as **percolation**. A part of this water moves through cracks formed in (clayey) soils due to shrinkage or through channels and cavities formed by decaying plant roots, burrowing animals, insects and worms. This water is known as **seepage water**.

If the soil is pervious (penetrable), the gravitational water percolates down into the lower layers and drains away. However, if the soil has an impervious layer through which water cannot penetrate, the water collects over it. If this process continues, the gravitational water begins to accumulate. The soil above the impervious water begins to accumulate.



The soil above the impervious layer contains free water and is said to be saturated. The entire pore space in the saturated soil mass is full of water. The upper level of water in the saturated area is known as water table. As more water percolates down, the level of water-table rises and this causes water-logging. When the watertable rises right up to the surface, the whole soil gets water logged and the plants growing in such soils suffer from want of aeration. It also leads to the development of salt and alkaline lands.

Texture and structure play a great part in controlling the rate of movement of gravitational water. The flow of water is proportional to the size of the particles. Because of the bigger size of pore tubes water percolates more rapidly in sandy soils than in clay soils; The structure is also an important factor in percolation. Because of closer arrangement water percolates much more slowly in clayey soils than in sandy soils.

### **Soil moisture constants :**

The whole range of soil moisture is divided into three broad classes, viz, hygroscopic water, capillary water, and gravitational water. The hygroscopic and capillary waters are in equilibrium with the soil under given conditions. The hygroscopic coefficient and the maximum capillary capacity are the two equilibrium points when the soil contains the maximum amount of hygroscopic and capillary waters respectively. The amount of water that a soil contains at each of these equilibrium points known as a **soil moisture constant**. Two more soil constants viz, field capacity and wilting coefficient, have been introduced to express the soil-plant-water relation as it found to exist under field conditions.

### **Field capacity :**

When water is applied to a dry field, it moves down rapidly and wets the soil mass. The distribution of moisture in the wet soil is not uniform. The surface layer usually contains some gravitational water which slowly moves down into the lower layers. After sometime (usually 2-4 days) when all the gravitational water has drained away and the rate of downward movement has ceased, the wet soil is almost uniformly moist. The amount of water (*percentage of moisture*) held by the soil after the drainage has ceased is known as the *field capacity* of that soil.

It is not easy to determine accurately the exact field capacity under field conditions. A laboratory method of measuring the power of different



soils to hold moisture has been devised by submitting a thin layer of the soil to a centrifugal force of 1000 times the force of gravity in a suitable machine. The amount (percentage) of water retained by a soil when submitted to this treatment is known as *moisture equivalent*. The moisture equivalent so determined is practically the same as field capacity for all normal soils. Both field capacity and moisture equivalent vary with the texture the greater the moisture equivalent. Addition of organic matter increases the moisture equivalent.

### **Wilting coefficient :**

A growing plant requires water for its growth and development. It takes water from the soil through its roots by the process of osmosis. As long as the soil contains sufficient moisture it supplies water to the plant to meet its needs. When the water is so firmly held by the soil particles that plant roots are unable to draw water. The loss by transpiration can no longer be met. The plant is unable to keep up its turgor and begins to wilt (wither). At this stage even if the plant is kept in a saturated atmosphere, it does not regain its stage at which this occurs is called the wilting point, and the percentage amount of water held by the soil at this stage is known as the wilting coefficient. The wilting point represents the point at which the soil is unable to supply water to the plant.

The wilting coefficient is influenced by the texture of the soil and the type of plant grown in it. Fine-textured soils have a higher wilting coefficient than coarse soils. Generally soil that have a higher water-holding capacity also have a higher wilting coefficient.

### **Available and unavailable water :**

It is evident that all the water present in a soil is not available for the use of plants. The total amount of water that a soil absorbs gives no indication of its crop-producing power. Even all the capillary water, that is considered to be loosely held by the soil particles, is not utilised by the plants; only a part of it is actually available for the use of plants.

According to state of availability, the whole range of soil moisture can be divided into three parts: (1) The unavailable water includes the whole of hygroscopic water plus a part of the capillary water below the wilting point. Though the latter is free liquid water, it is held so firmly by the soil particles that it can not be absorbed by plant roots. 2) The available water is that water which lies between wilting coefficient



and field capacity. It is obtained by subtracting wilting coefficient and field capacity. It is obtained by subtracting wilting coefficient from moisture equivalent. 3) The water beyond the field capacity stage is said to be super-available (super-fluous). It includes gravitatonal water plus a part of capillary water removed from larger interstices. This water is also unavailable for the use of plants.

In addition to three forms of water, soil particles contain water of crystallisation which forms a parts of the clay minerals. Water exists in the soil also in the gaseous phase as water vapour which always saturates the soil air except when it is dry.

6. Soil temperature : 2m (3) (4)

The soil derives its heat directly from the sun and loses much of it by radiation back in the sky. The sun has an effective radiation surface temperature of 6000K. The temperature of the surface layer of a bare soil on a clear sunny day is controlled by the rate at which it is absorbing solar energy. Only a part of the incoming radiation received by the soil is absorbed.

The movement or transfer of heat in soil takes place mainly by conduction. The heat absorbed by the surface soil penetrates into the lower layers, and thus heats up the soil profile. During the day, the heat moves downwards as the temperature at the surface is greater than in the lower layers. At night it moves upwards towards the surface.



30

soil development are accelerated when there is an increase in soil temperature.

The maximum absorption of water by the roots and the maximum metabolic activities of the plants take place usually between 20° and 30° C. Lowering of temperature below 20°C causes an appreciable reduction in the rate of absorption and transport of water and nutrients. The absorption of water is almost nil at *freezing* temperature. Cold soils; therefore, causes poor vegetation and the plants tend to be dwarf. Warm soils of the tropics, on the other hand, support tall trees. The prevailing soil temperature in South India is very favourable for plant growth and microbial activity.

### Factors Controlling Soil Temperature :

The temperature of soil is affected by a number of factors : nature of soil, soil moisture, plant cover, topography and climate.

#### 1. Nature of soil :

The capacity of the soil to absorb heat varies with the relative proportions of the constituents - mineral and organic matter. The specific heat of mineral substances (iron, copper, quartz, kaolin, marble, etc.,) is less than that organic materials (like wood ; peat ; humus) and their heat conductivity is very high. Hence mineral soils get heated more readily than organic soils such as peat.

Soil temperature is also influenced by soil texture. Sandy soils warm up quicker than clayey or fine-grained soils. Soil structure also affects soil temperature by controlling the pore space or the amount of air in soils. Soils having good structural condition warm up more rapidly than when the structure is impaired.

The temperature of the soil is influenced by soil colour. Dark coloured soils usually warm up more readily than light coloured soils. Hence black and brown soils are warmer than grey and white soils. Red and yellow soils are intermediate in this respect.

#### 2. Soil moisture :

Moist soils have a high specific heat than dry ones. So a moist soil gets heated more slowly and has a lower temperature than dry soil.

### 3. Plant Cover :

Soils that are covered with vegetation absorb less heat than those that are bare. Vegetation absorbs the incident radiation and thus acts as an insulating agent and retards the warming of the soil surface.

### 4. Topography :

The direction and position of ground slope in relation to the sun has considerable effect on soil temperature. This is due to the angle of incidence of the sun's rays. The absorption of heat is the greatest when the rays are at right angles to the surface.

### 5. Climate :

Soils in temperate and cool arctic regions are cooler than those in tropical and semi-tropical regions. There is an increase in soil temperature as one proceeds from the arctics to the equator.

### Measurement of soil Temperature :

For measuring the soil temperature a thermometer known as soil thermometer is being used. Soil thermometer is nothing but the ordinary thermometer with divisions in celsius ( $^{\circ}\text{C}$ ) and the thermometer is enclosed in a hard tubular container. We have to just insert the bulb of the soil thermometer to the required depth into the soil wait for minutes and record the temperature. (Soil thermometers are available with Messers Istruments and Equipments Co., Madras).

### University Questions

1. Define soil. Mention (three) important properties of soil
2. How does soil water differ from ordinary water? ... tested?



## Soil Acidity and Buffer Action 15 (b)

a. Soil acidity : 5m (2)

Soil acidity is primarily a function of the colloidal fraction of soils, but soluble acids may also contribute to the condition. It has been estimated that 95% of the acidity of mineral soils is due to the exchangeable hydrogen and / or aluminium associated with the colloidal material.

Traces of inorganic acids such as  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  may be present.  $\text{CO}_2$  is present in moist soils and with water produces a slightly acid reaction:  $\text{CO}_2 + \text{HOH} \rightarrow \text{HCO}_3 + \text{H}^+$ . Other organic acids

such as acetic, oxalic and citric acids are liberated during decay of fresh plants and may exist in the soil for a short period. However, acids of this kind are readily decomposed by soil micro-organisms in well-aerated soils and have only a temporary existence in soils.

### Reserve and active acidity :

For a soil to give an acid reaction, there must be an excess of  $H^+$  ions over  $OH^-$  ions in the solution surrounding the colloidal complex. In the case of an acid clay, in which the clay is saturated with  $H^+$  ions, the concentration of  $H^+$  ions in the diffuse double layer is greater than in the true solution.

The  $H^+$  ions present in the diffuse layer (on the colloidal nucleus) constitute what is known as reserve or potential (or exchangeable) acidity, while those present in the soil solution (surrounding the colloidal complex) give rise to active acidity of the soil. The pH values express the active acidity of the soil. The pH values express the active acidity or intensity of the soil. The two groups of  $H^+$  ions are in dynamic equilibrium, the adsorbed ions being greater in number than those in the soil solution. When the  $H^+$  ions in soil solution which are responsible for active acidity, are removed by neutralisation or lost in drainage or depleted in any other way, the adsorbed ions move outward into the solutions and thus restore the original active acidity in the soil solution. If an alkali solution is added to the clay suspension just sufficient to neutralise the active acidity, no change in pH takes place. Excess additions of the alkali solutions, equivalent quantities of adsorbed  $H^+$  ions progressively move out into the true solution to replenish (make good) those which have been neutralized, keeping the pH unchanged. A definite change in pH will take place only after all the adsorbed  $H^+$  ions (i.e., the reserve acidity) are neutralised and  $OH^-$  ions begin to appear in soil solutions.

In a medium - textured soils there may be much as 50,000 times more reserve acidity than acidity. Clayey soils usually carry a much larger amount of reserve acidity than sandy soils. Organic soils carry still a larger amount of reserved acidity. Hence clayey soil rich in organic matter has a very large reservoir of reserve or potential acidity.



## Micro nutrients

In general, the availability of B, Cu and Zn is reduced in alkaline soils, and that of Mo in acid soils.

There are two general sources of readily available nutrients in the soil: (i) nutrients adsorbed on the colloids and (ii) salts in the soil solution. In both cases, the essential elements are present as ions, such as  $K^+$ ,  $Ca^{++}$ ,  $Cl^-$ ,  $SO_4^{--}$ . The cations such as  $K^+$  are mostly adsorbed by colloids, whereas, the anions and a small fraction of the cations are found in the soil solution. The more important ions present in the soil solution or on the soil colloids are given in Table 7.

Table - 7

## Important ions present in the soil

Nitrogen	$\text{NH}_4^+$ , $\text{NO}_2^-$ , $\text{NO}_3^-$	Iron	$\text{Fe}^{2+}$ , $\text{Fe}^{3+}$
Phosphorus	$\text{HPO}_4^{2-}$ , $\text{H}_2\text{PO}_4^-$	Manganese	$\text{Mn}^{2+}$ , $\text{Mn}^{4+}$
Potassium	$\text{K}^+$	Molybdenum	$\text{MoO}_4^{2-}$
Calcium	$\text{Ca}^{++}$	Boron	$\text{BO}_3^{3-}$
Magnesium	$\text{Mg}^{++}$	Chlorine	$\text{Cl}^-$
Sulphur	$\text{SO}_3^{2-}$ , $\text{SO}_4^{2-}$	Water	$\text{H}^+$ , $\text{OH}^-$