

01. Manures – types, composition and value – sources

There are many ways of classifying the fertilizers and manures, the classification being based on one or two properties of the materials.

Nature of source

1. Natural manures
2. Artificial manures
3. Mineral manures

Nutrient content

1. Single manures
2. Compound manures

Nutrient element present

1. Complete manures
2. Incomplete manures

Nature of the materials

1. Organic manures
2. Inorganic manures
3. Indirect manures

Nature of action

1. General manures
2. Special manures
3. Stimulative substances
4. Soil amendments or soil conditioners

Critical consideration of the above-mentioned classification reveals that none of the classification is satisfactory. Each of the classification is based on only one property and may not be suitable to cover wide range of materials.

They are generally classified into Bulky organic manure and concentrated organic manures

ORGANIC MANURES

The word manure derived from the French "Manoeuvrer", means to manipulate, to work, to produce crop. In general manure means excreta of animals. The term bulky organic manure generally includes those materials of natural origin, organic in composition having greater volume per unit content of nutrients and being used to

increase the nutrient status of the soils as well as organic matter content of soils. They are obtained mainly as natural products. The materials included in this group are farmyard manure, compost, sewage sludge and green manure. Of these FYM, compost and green manure are the most important and widely used bulky organic manures.

Farm Yard Manure (FYM)

The FYM refers to the refuse from farm animals, mainly sheep, cattle and poultry. This is one of the oldest manure known and is highly valued for its many of the beneficial properties that are said to be produced when this manure is added to the soil. It not only adds the constituents to the soil but also adds organic matter to the soil.

Composition of farm manure

Several factors influence the composition of farm manure and they are the following

1. Source of manure
2. Feed of the animals
3. Age of the animals
4. Condition of the animals
5. Manner of storage and handling
6. Litter use etc.,

On an average the composition of FYM is usually 0.5 % N, .25 % P_2O_5 and 0.5 % K_2O .

Methods of collection

Many methods of collecting the cattle manure are in vogue and this include,

1. Use of ordinary cattle shed with kacha floor
2. Use of cattle shed with impermeable floor and provision for collecting urine in separate urine pit
3. Dry earth system
4. Loose box system
5. Other special methods

The method of collection and storage is the most important factor which decides the final composition of the manure. The following are recognized methods of storing FYM

1. The heap method

2. The pit method

Various losses during collection and storage of FYM can be prevented or atleast minimized by adopting the following procedures

1. Better methods of collection
2. Better methods of storage
3. Use of cow dung gas plant
4. Use of chemical preservatives like gypsum, superphosphate etc

Organic Wastes :

Organic wastes are the wastes of biological / animal / agro-industry origin and can be converted to valuable manure by composting. The various organic wastes can be classified as follows,

Sources of Organic Wastes			
<i>Agriculture</i>	<i>Animal Husbandry</i>	<i>Agro-industries</i>	<i>Municipal Activities</i>
* Crop residues (paddy straw, sugacane trash etc) * Weeds	* Dairy * Goat / Sheep * Poultry * Piggery	* Sugar Indutry (Pressmud) * Coir Industry (Ciorpith) * Fruits / vegetables processing industries * Sago Industry	* Household / municipal solid waste * Market waste (Vegetable/ fruit / flower market)

02. Green manures-Oilcakes-Sewage sludge-Biogas plant slurry-Plant and animal refuges

GREEN MANURES

Green manure:

Growing the plants *in-situ* and incorporation in the field.

Green leaf manure

Addition of green or plant tissues obtained from elsewhere *viz.*, trees, herbs, shrubs pruning and unwanted weeds.

Benefit of Green manure or Green leaf manures

- Addition of organic matter.
- Adds Nutrient – Macro, Secondary and micro nutrients.
- It improves physical condition of soil.
- Act as a soil amendment to reclamation of problem soils.
- It act as a cover or catch crop to prevent soil erosion, conserve moisture, prevent nutrient leaching.
- Leguminous crops fix the atmospheric – N by the roots and improves N status of the soil.

Characteristics of Green manure

- It should have rapid growth and shorter duration so that can be fitted in a crop rotation
- It should yield abundant biomass and should be succulent to have rapid decomposition
- It should have the ability to grow on poor soils.

Nutrient content of agricultural wastes

Agricultural wastes	N	P ₂ O ₅	K ₂ O
Sugarcane Begasse	0.25	0.12	0.20
Sugarcane Begasse compost	1.40	0.45	0.60
Sugarcane Begasse Press mud	1 – 1.5	2.0	-

Press mud – compost	1.5	1.5	-
Saw dust	Traces	0.2 0.25	-
Tobacco waste	0.5 – 1.0	0.8	1.0
Tobacco seed cake	4 – 4.5	7 – 15	5 – 5.5
Tea waste	2.8 – 3.6	03. – 0.4	1 – 2
Cotton dust	1 – 1.5	-	-
Textile waste	1 – 1.5	-	-

Nutrient content of Commonly used Concentrated manures

Oil cake	N	P2O5	K2O
Groundnut cake (Decordicated)	7.8	1.5 – 1.9	1.4
Lin seed cake	5.5	1.4	1.2
Mustard cake	4.5	1.5	1.0
Neem cake	5.2	1.0	1.4
Niger cake	4.8	1.8	1.0
Pungam cake	2.5	1.0	1.0
Safflower (decordicated)	7.8	2.2	2.0
Sesamum	6.2	2.0	1.2
Castor	5.8	1.8	1.0
Coconut	3.2	1.8	1.7

Slaughter House wastes

Wastes	N	P2O5	K2O
Blood meal	10 – 12	1.2	1.0
Meat meal	10.5	2.5	0.5
Fish meal	4 -10	3 – 9	0.3 – 1.5
Horn – Hoff meal	13	-	-

Leather - waste	7	0.1	0.2
Hair and wool waste	12.3	0.1	0.3
Sewage water	25ppm	5 ppm	15 ppm
Sludge	1.5 – 3.5	0.75 – 4	0.3 – 0.6

Nutrients content of Commonly used Green manures

Green manure	N %	P2O5%	K2O %
Sunhemp	0.5	0.1	0.4
Danicha	1.1	0.2	0.4
Sesbania	0.7	0.1	0.6
Pelli pesera	0.7	0.2	0.4
Cluster bean	0.3	0.1	0.3
Cow pea	0.7	0.2	0.6
Green leaf manure			
Kolungi	0.7	0.1	0.4
Calotropis	0.3	0.1	0.6
Pungam	1.2	0.2	0.8
Glyricidia	0.8	0.1	0.7
Puvarasu	0.8	0.2	0.9

Guano - Birds Excreta or bat Dung

Guano	2.6	4.2	0.6
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03. Composting of organic wastes – composting technologies

COMPOSTING OF ORGANIC WASTES

Composting is a process of allowing organic materials to decompose more or less controlled conditions to produce stabilized product that can be used as a manure or soil amendment. Composting is basically a microbial process, which change the property of the organic material or mixtures.

Compost is the material resulting from the decomposition of plant residues under the action of bacteria and fungi. Composting is simply an acceleration of natural process or organic matter mineralization. The final product is dark brown in colour and resembles FYM in its properties and appearance.

Essential requirements for composting

- A bulky organic manure
- A suitable starter
- Addition of enough water
- Aeration

Main systems of composting

- ADCO process (Hutchinson and Richards of England)
- Activated compost process (Fowler and Rege)
- The Indore process (Howard and Wad)
- The Bangalore process (C.N.Acharya)
- The coimbatore method

Benefits of composting:

- * Enables clean environment
- * Absorbs odors, degrade toxic substances and heavy metals
- * Avoids un-necessary dumping of wastes
- * Supply valuable organic manure

Composting technologies

1. Crop residue composting

- Collect the available crop residues and weeds
- Shred them to a size of 2 to 2.5 cm length
- Mix these wastes with green residues (freshly collected), if available
- Form the compost heap (4 feet height)
- Add the bio-inoculants (2 kg of bio-mineralizer or 40 kg of cowdung for 1 tonne of waste)

- Properly aerate the compost either by providing perforated PVC pipes or by mechanical turning
- Maintain the moisture at 60 % by regular watering
- The compost will mature in 60 days

2. Vermi-composting

Vermicomposting is a process of degradation of organic wastes by earthworms. The species like *Eisenia foetida* and *Eudrilus eugeniae* are effective in converting the agricultural wastes into compost. The various steps involved in making vermicompost are as follows

Methods followed:

Heap method
 Pit method – aboveground and belowground
 Belowground method pit size : 10 X 1 X 0.3 m
 Each layer : 6-7cm thick
 Sprinkle water once in 8-10 days
 Release : 2-2.5 kg worms / pit

Steps:

Collect the predigested wastes and mix cattle dung @ 30 %.
 Place it in the pit/container layer by layer
 Moist the residues at 60 % moisture
 Allow the verms in to the feed material / residues @ 1 kg/ tonne of residue
 Protect the pit or container from ants and rats (which are the enemies of verms)
 The residue will be composted in 30 to 40 days
 Remove the composted materials layer by layer at a weekly interval so as
 To avoid any damage /disturbance to the feeding verms.

Nutritive value of vermicompost

The nutrients content in vermicompost vary depending on the waste materials that is being used for compost preparation. If the waste materials are heterogeneous one, there will be wide range of nutrients available in the compost. If the waste materials are homogenous one, there will be only certain nutrients are available. The common available nutrients in vermicompost is as follows

Organic carbon = 9.5 – 17.98%
 Nitrogen = 0.5 – 1.50%

Phosphorous = 0.1 – 0.30%

Potassium = 0.15 – 0.56%

Sodium = 0.06 – 0.30%

Calcium and Magnesium = 22.67 to 47.60 meq/100g

Copper = 2 – 9.50 mg kg⁻¹

Iron = 2 – 9.30 mg kg⁻¹

Zinc = 5.70 – 11.50 mg kg⁻¹

Sulphur = 128 – 548 mg kg⁻¹

3. Coirpith composting

Coirpith is an agricultural waste produced from the coir industry. Approximately 180 grams of coirpith is obtained from the husk of one coconut. Coirpith contains Carbon : Nitrogen in the ratio of 112:1 and contains 75 per cent lignin which does not permit natural composting as in other agricultural wastes.

Mushroom *Pleurotus* has the capacity to degrade part of the lignin present in coirpith by production of enzymes like cellulases and lactases. The carbon: nitrogen ratio of coirpith is reduced from 112:1 to 24:1 as a result of composting.

Composting method

Select a shaded place of 5 x 3 m dimension and level it after removing weeds. Spread 100 kg of coirpith uniformly. Spread 100 g of *Pleurotus* spawn on this and cover with a second layer of 100 kg of coirpith. On the surface of the second layer, spread one kg of urea uniformly.

Repeat this sandwiching of one layer of coirpith with spawn followed by another layer of coirpith with urea up to one metre height.

Sprinkle water to keep the heap moist. Allow the heap to decompose for one month.

Manure conversion

The coirpith is converted into good manure after 30 to 40 days and the lignin content is reduced from 40 per cent to 30 per cent. The nitrogen content is increased from 0.20 per cent to 1.06 per cent. Coirpith compost contains macronutrients and micronutrients. It can absorb water up to eight times its weight. Coirpith, when added to sandy soil at 2 per cent increases the water holding capacity up to 40 per cent. It can be applied to a wide variety of crops and can be used to prepare potting mixture and can be applied as organic manure in kitchen gardens.

4. Composting of crop residues and weeds:

Composting is one of the useful ways for utilizing the some of the weeds and noncommercial plants like *Parthenium*, Water hyacinth, *Ipomoea* etc. instead of their eradication. The plants can be composted using *Trichoderma viridi* and *Pleurotus sajor-caju* as a microbial consortium with supplementation of urea. Select an elevated shady area of a thatched shed and mark an area of 5x1.5 meter. Cut the composting materials into 10 – 15 cm size. Spread 100 kg of these materials over the marked area. Sprinkle 1 bottle of microbial consortia over this layer. Again spread another 100 kg of composting materials over this layer. Spread 1 kg of urea uniformly over this layer. Likewise repeat these processes of spreading composting materials, then microbial consortia, again composting materials followed by urea application until a minimum of 1-meter height is reached. Sprinkle water to attain a moisture level of 50% to 60%. The surface of the heap is covered with a thin layer of soil. Water should be sprinkled depending upon the necessity to maintain the moisture around 50%. A turning is given at the end 20 days to give a thorough mixing of outside material with that of the inside ones. The bio-converted compost will be ready in about 40 days time.

5. Method of composting the Municipal Solid Wastes

Biodegradable municipal solid waste should be separated and collected for composting. Five hundred kg of material should be heaped in the compost yard. In that heaped waste, 1 kg of TNAU microbial consortium should be applied in the form of slurry to cover the full waste material. This 1 kg microbial consortium can be mixed with 5 litres of water to make slurry. This slurry is sufficient to cover 0.5 tonne of material. Then, 50 kg of cowdung should be mixed with 30 litre of water to form cowdung slurry. This cowdung slurry should be sprayed over the heap of municipal solid waste. Then, 1 kg of urea should be mixed with solid waste. 60% moisture should be maintained through out the period of composting. Compost should be turned up once in 15 days to create good aeration, and for thorough mixing. Because of this practice, a uniform composted material will be obtained. Solid waste can be composted with in 90 days by this method with the indication of reduction in the volume, appearance of dark coloured materials and a small of earthy odour. After the completion of composting, compost should be sieved through normal mesh to separate unwanted and partially composted material.

6. Value addition of poultry waste compost

A known quantity of poultry droppings and coir pith @ 4:5 ratio should be mixed well to attain a C/N ratio of 25:1 to 30:1 which is considered to be the optimum C/N ratio

for composting. *Pleurotus sajor-caju*, a lignocellulolytic organism, should be inoculated into the mix @ 2 packets per tonne of waste in order to speed up the composting process. The mix should be heaped under the shade. The moisture content of the mix should be maintained within 40 – 50%. Periodical turning should be given on 21st, 28th and 35th day of composting. Another two packets of *Pleurotus sajor – caju* is to be added when turning is given on the 28th day of composting. A good quality compost will be obtained in 45 days, which contains 2.08% N, 1.93 % P and 1.41 % K with C/N ratio of 10-16

7. Enriched Farm Yard Manure (EFYM)/ Reinforced FYM

Phosphorus content in FYM is relatively low and complete utilization of nitrogen and potassium in the manure is seldom realized. Hence, heavy quantities intended to supply the needed quantity of phosphorus will result in wastage of nitrogen in most soils. To overcome this P insufficiency, addition of superphosphate to the manure is recommended and the process is called reinforcing / enriching and the resultant material is called “enriched farmyard manure”. The Single Super Phosphate (SSP) can be sprinkled either in the cattle shed or on the manure heap. Rock phosphate can also be recommended for this purpose.

Factors affecting the Composting Process:

- I. The Type and Composition of the Organic Waste
- II. The Availability Of Microorganism
- III. Aeration
- IV. The C, N and P Ratios
- V. Moisture Content
- VI. Temperature
- VII. pH
- VIII. Time

Preparation of Coir Waste Compost Using Yeast Sludge:

Yeast sludge is a waste product by alcohol distilleries @ 2t/day. This waste contain 6% N, 0.3% P and 0.9% K with other micronutrients, vitamins and growth promoting substances. The coir waste should be sieved so as to remove all the fibrous materials. For one tone of coir waste 200 kg of yeast sludge and 10 kg of rock phosphate should be added and mixed thoroughly. Moisture should be maintained at 60%. After mixing the material should be formed as heap. Within 4-5 days the temperature of the heap will be raised to 50-60° C. Within 40 to 50 days the coir waste and yeast sludge will become as mature compost. The matured compost will turn from

brown to black. There will not be any odor. The volume of the compost heap will be reduced to 1/3. The temperature of the heap will be 25-30°C and it should be constant. The compost will be very light and fine textured. The compost prepared by this means of above method contains N-1.09%, P-1.35%, K-1.95% besides copper, manganese, iron and zinc. This compost doesn't have any phytotoxicity and used for all agricultural crops.

C. Preparation of sugarcane trash compost using yeast sludge:

sugarcane trash collected from sugarcane field has to be cut into small bits using chaff cutter or shredder to a size of 1-2cm. for every tone of sugarcane trash 200 kg of yeast sludge and 10kg of rock phosphate are added and mixed thoroughly. Moisture is maintained at 60%. the heap is formed to a height of 1-1½ m. within 45-50 days sugarcane trash compost will be ready for application to crops. The sugarcane trash compost consists of N-1.2%, P-0.7%, K-1.5% and considerable quantities of micronutrients. This compost can be applied at the rate of 5t/ha.

d. Japanese method of composting:

Instead of pits in conventional composting system, vats of 18-30' in length, 3-4' in width and 2.5-3.0' height are made of bamboo stakes of 2.5-3.0' width. For growth a non-leaky surface is prepared with broken stone stable or brick and plastered with cement. About 2 feet space is kept free on one side of the vat to facilitate turning the residues regularly. Sliced and broken pieces of coconut, shells, leaves, fibrous materials, tender tree barks or pieces form the bottom 10-15 cm layer. Second layer of dry leaves, grass residues, groundnut haulms are of 10-15 cm height. Cow dung, urine, biogas slurry are sprinkled over and this layer of soil and ash is spread over. Nitrogen rich green leaves of pongamia, albizzia, daincha, sesbania and crop residues forms third layer of 10-15 cm. Fourth layer of 10-15cm contains organic wastes rich in phosphorous and potash. Over these 2-3 buckets of cow dung and biogas slurry are sprinkled. Fifth layer contains paddy or ragi straw that is rich in carbon and provides energy for microorganisms. Sixth layer contains exclusively of dried and powdered cow dung of 20-30cm. Over these small quantities of old compost, tank silt and ash are sprinkled. For rapid degradation *Aspergillus*, *Penicillium*, *Trichoderma* should be inoculated. *Pleurotus* and *Polyporus* should be inoculated for degradation of high lignin contained residues. *Azotobacter* and Phosphobacteria can be mixed for enriching the composts.

General Properties Of Commercially Accepted Compost.:

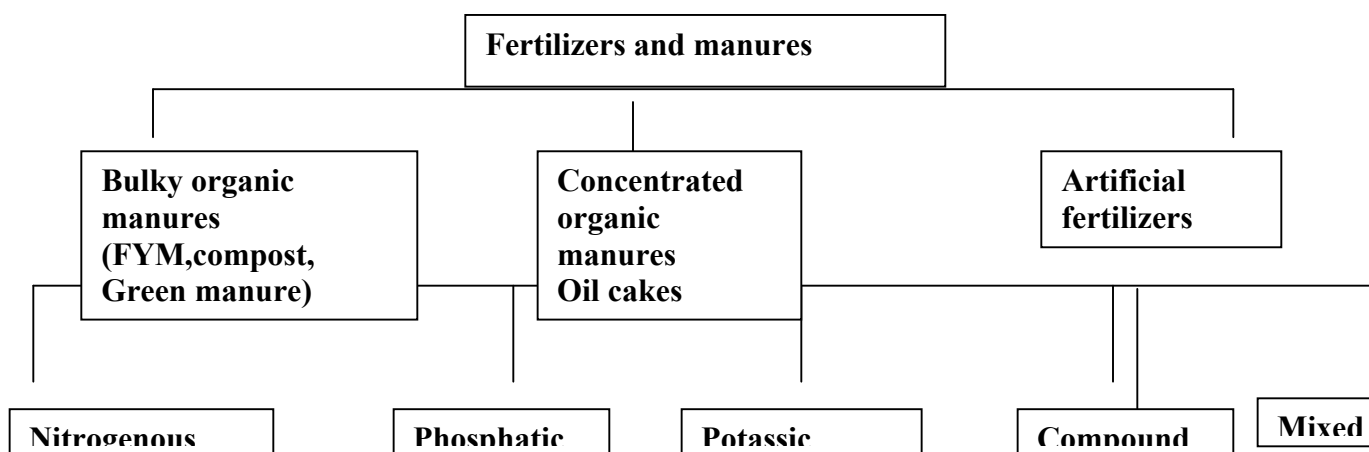
N %	>2	Color	Brown Black
C: N	<20	Odor	Earthy
Ash %	10-20	Water Holding Capacity (%)	150-200

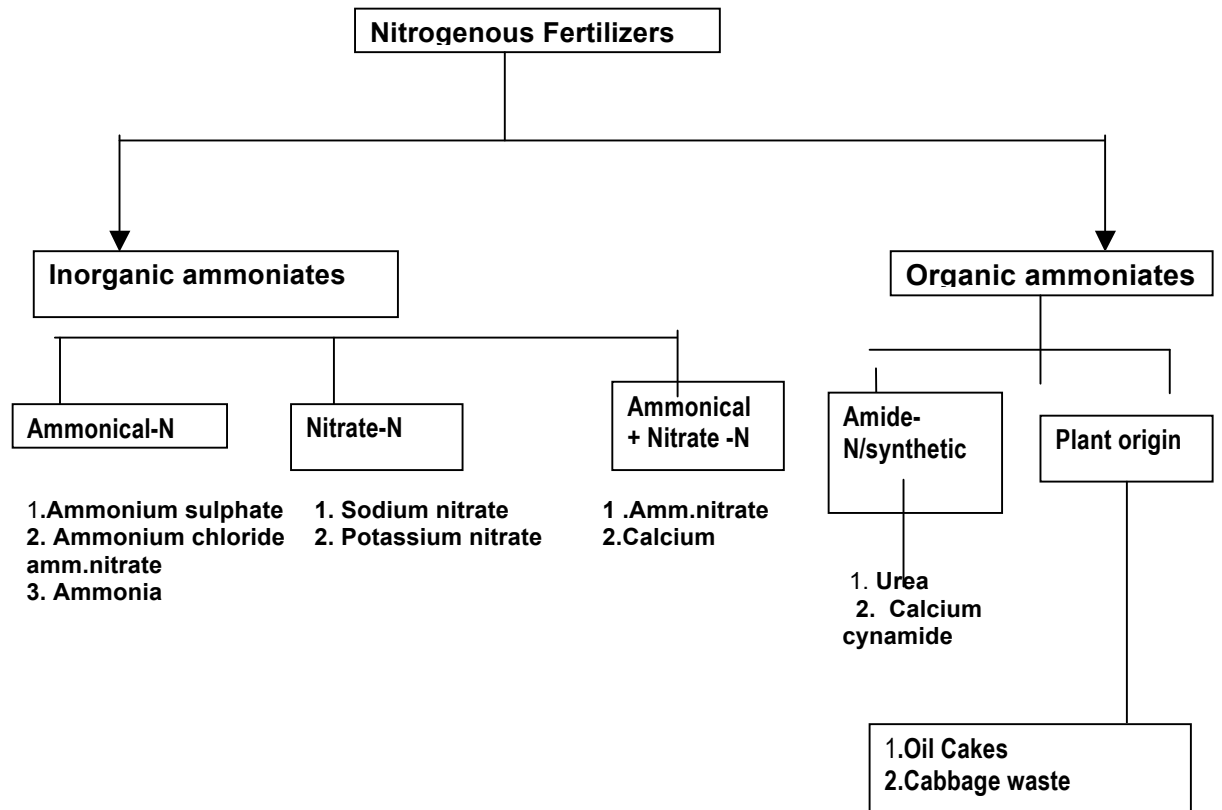
Moisture %	10-20	CEC (Meq 100 g ⁻¹)	75-100
P %	0.15-1.5	Reducing Sugar (%)	<35%

04. Classification of fertilizers – N, P and K fertilizers

Classification of fertilizers

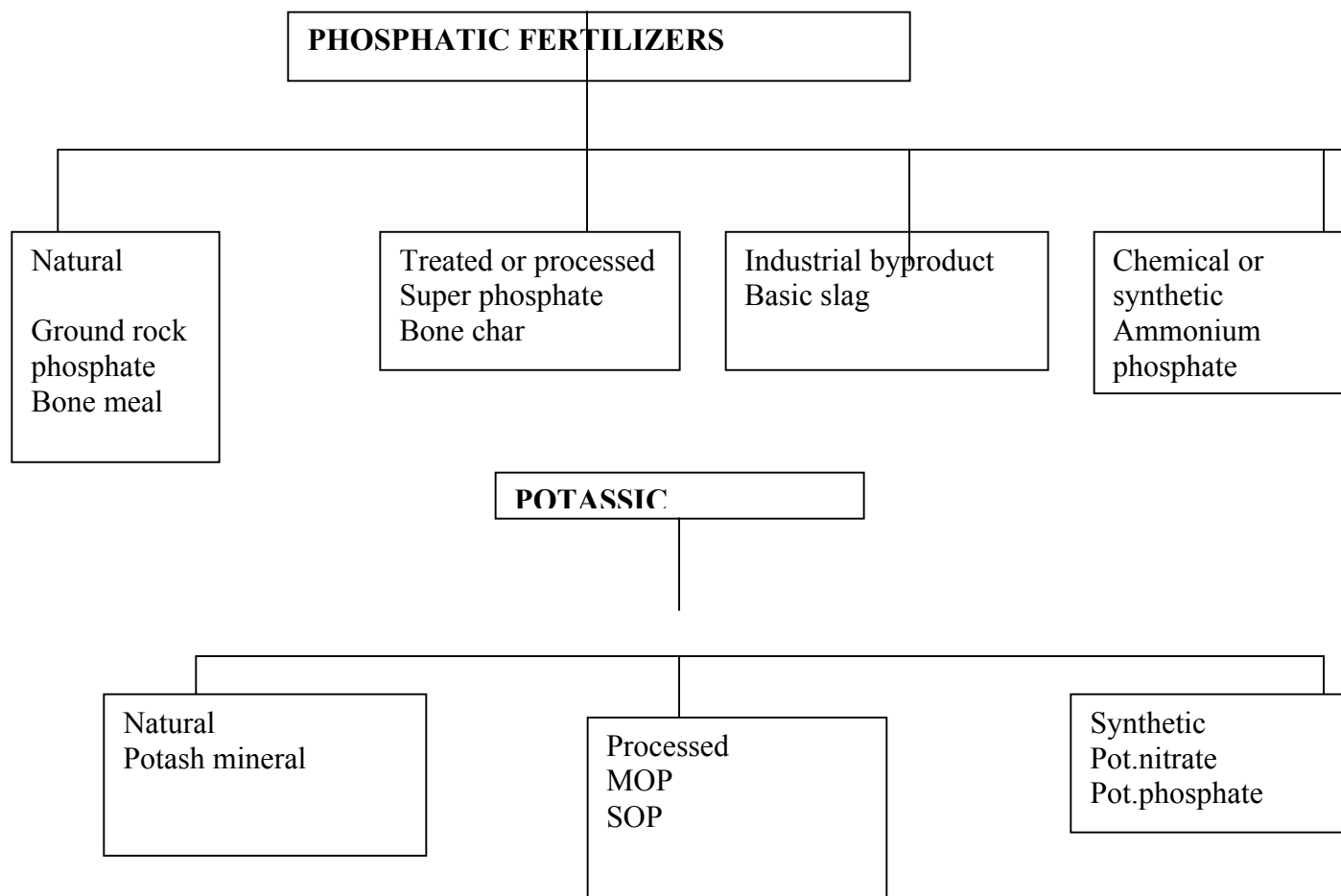
Commercial N, both organic and inorganic is desired from a wide variety of materials which are found to differ very widely in their sources, properties, method of preparation and their reactions in the soil. Classification based on chemical form seems to be more satisfactory as indicated below.





The nitrogen content of different nitrogenous fertilizers is given below

Sl.No	Name of the fertilizer	N content (%)	Form of N
1	Sodium nitrate (NaNO_3)	16.0	Nitrate (NO_3)
2	Potassium nitrate (KNO_3)	12.5-13.5	Nitrate
3.	Ammonium sulphate (NH_4) ₂ SO_4	20.6	NH ₄ (Ammonia)
4.	Ammonium chloride (NH_4 Cl)	26.0	NH ₄
5.	Ammophos - A	11.0	NH ₄
6.	Ammophos – B	16.0	NH ₄
7.	Ammonium Nitrate (NH_4)	33.0	NH ₄ – 16.5 NO ₃ – 16.5
8.	Ammonium sulphate nitrate	25.6	NH ₄ – 19.5 NO ₃ – 6.6
9.	Urea ($\text{CO (NH}_2)_2$)	46.0	Amide
10.	Calcium cyan amide (CaCN_2)	20.6	Amide
11.	Dried blood	3-14	Protein(organic)
12.	Groundnut cake	8.0	Protein(organic)
13.	Meat meal	09.0-11.	Protein (organic)
14.	Guano	10.0	Protein (organic)



05. Nitrogenous fertilizers – sources – fundamental processes involved in manufacturing procedures for ammonia, sulphuric acid, nitric acid and phosphoric acid

NITROGENOUS FERTILIZERS

Elemental Nitrogen, recognized by Rutherford in 1772 as a colorless, odorless and inert gas, is the main constituent of air (approximately 79 percent by volume). Hence one might naturally expect that plants may not have any deficiency for this nutrient element and that there may be large deposits of mineral compounds of N on the surface of the earth. But actually this is not so. Though in the air over an acre of land there is a N supply of over 35,000 tons (an abundant supply) the plants, except the legumes, are incapable of utilizing this elemental N for their growth. Most of important mineral deposits are the Chile saltpeter (NaNO_3), or Chilean niter and Niter (KNO_3) or Bengal saltpeter.

Sources of N

1. Mineral deposits: Chile saltpeter (NaNO_3) in Northern Chile, Peru, Bolivia, California and Nevada.

Niter (KNO_3) or Bengal saltpeter: present in Spain, Egypt, Persia, India and U.S.A. and ammonium sulphate in various “volcanic regions of the world”.

2. Addition through rain-water

A small amount of about 10 to 12 kg of N per year per acre is added to the soil during thunderstorms in these process discharges of atmospheric electricity produce nitrous oxide and rain carries this to the soil as HNO_3 where it is quickly converted into nitrates.

3. Soil organic matter

This is the main sources of N in the soil and the N content of any soil will depend upon the quality and quantity of organic matter of that soil.

4. N fixing organisms

The free living, Non-symbiotic E.g. *Azotobacter* and *Clostridium* and symbiotic E.g.: *Rhizobium* sp. Bacteria are found to fix considerable amounts of the elemental N in a combined form. For example the non- symbiotic bacteria are found to fix 50 – 55 kg of N per year per acre while the symbiotic organisms fix about 300-350 kg of N per year per acre.

5. Industrial source

N is obtained from the industries in a combined form by the following processes.

- a. Arc process
- b. Cyanamid process and
- c. Direct synthetic ammonia process.

Classification of Nitrogenous fertilizers and manners

Commercial N, both organic and inorganic is desired from a wide variety of materials which are found to differ very widely in their sources, properties, method of preparation and their reactions in the soil. Classification based on chemical form seems to be more satisfactory as indicated below.

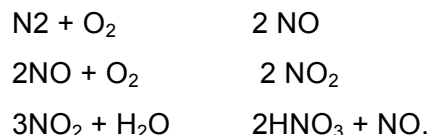
Industrial or synthetic fixation of nitrogen

For the commercial manufacture of the various nitrogenous fertilizers, the elemental N has to be converted into a combined form either as NH_3 or HNO_3 which may serve as the basic material for the synthesis of other materials. There are three main processes of synthetic fixation of N,

1. Direct oxidation process (Arc process): The final product is dilute HNO_3 .
2. Calcium cyan amide process: Final product is CaCN_2 .
3. Synthetic ammonia or Haber –Bosch process: Final product is anhydrous or aqueous NH_3 .

I. Direct oxidation process

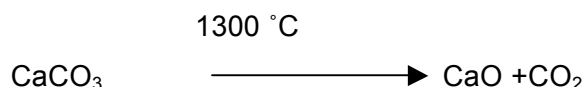
This method was demonstrated by Cavendish in 1766 on a laboratory scale. This is the most simple process of synthetic N fixation and it was first to be commercially utilized. The basic reaction of this process involved the union of N and O by means of an electric arc, the process being similar to that which is known to take place between N and O in the atmosphere in the presence of electricity produced during thunderstorms and lighting. In this commercial process, the reaction is secured by blowing air through a flaming electric arc which has a temperature of about 3500°C . Only about 2 percent of the air is heated and combined. The nitric oxide produced is converted to nitric acid (HNO_3) by the action of water and atmospheric oxygen.



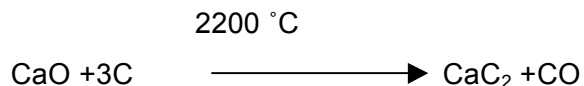
But this process requires high amount of electric power and high capital cost. It requires about five times as much electricity to fix a ton of N as is required by the cyanamide process. But this method is found to be suitable for countries like Scandinavia and Norway where the electricity is very cheap.

II. Cyanamide process

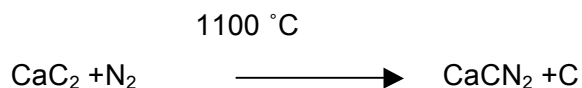
This process was developed in Germany and is said to have been invented by two Chemists Frank and Caro in 1898. At present, this process is probably the only commercial method used for synthetic fixation of N other than the ammonia synthesis process. Calcium cyanamide was first tried as a fertilizer in 1901. The first step or stage involving burning of limestone in a vertical furnace or kiln at about 1300°C where the limestone decomposes to CaO.



The CaO obtained is reacted with coke in a continuous type electric furnace at 2200°C to form fused calcium carbide (CaC₂) which is withdrawn and solidified.



In the third stage the air is liquefied by compressing and cooling from which the CO₂ and moisture are removed. The N is purified by fractional distillation. In the final stage, the purified N is caused to permeate a mass of finely ground CaC₂ in ovens under slight pressure at 1100°C.



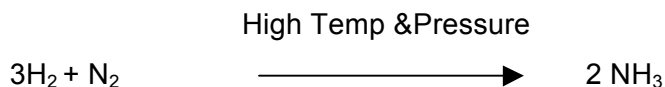
Ninety per cent of the CaC₂ is found to be reacted completely. The crude cyanamide is ground and treated with water to destroy residual CaC₂ and is brought into convenient physical condition. This method is not suitable where the coal supply is limited.

III. Direct or synthetic ammonia process

This was developed between 1900 and 1910 by a team of German scientists, Haber, Nernst, Bosch and others. The main principle of this method is when 3 moles of

H and one mole of N are brought into contact with a suitable catalytic surface at elevated temperature and pressure, ammonia is formed. High pressure and temperature are necessary, because at high temperature and pressure alone the reaction is irreversible.

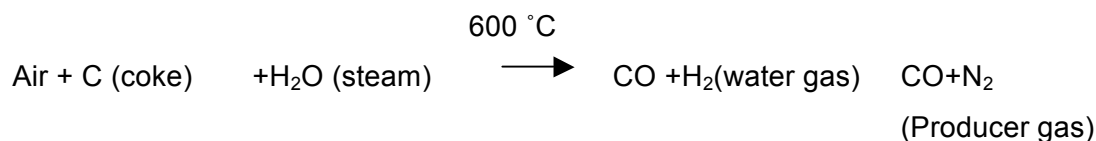
High temperature



This process consists of the following three main steps.

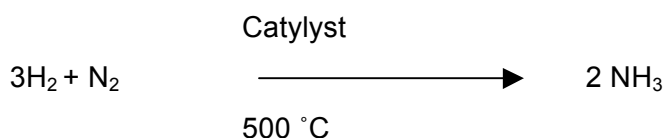
1. Preparation of H and N.
2. Purification and compression of three gases.
3. Catalytic conversion to ammonia.

To prepare H and N, the most famous water gas and producer gas procedures are followed. The method consists of passing air and steam over red-hot coke to produce a mixture of water gas ($\text{CO} + \text{H}_2$) and producer gas ($\text{CO} + \text{N}_2$). The coke is blasted with air at 600°C and superheated steam is passed through the coke.



After the formation of the CO_2 , pressure is raised to 50 atm for dissolving the CO_2 in water, which is removed and solidified for use in the later stages. The gas mixture is now adjusted to one volume of N to three volumes of H and compressed to 250 atm and the last traces of CO and CO_2 are removed by an ammoniacal solution of cuprous formate.

In the final stage, the temperature is raised to 500°C and the gas mixture is passed through special steel tower, capable of with standing high temperature and in the presence of catalyst, either platinized asbestos or iron, the N and H will react to form ammonia.



The prepared ammonia can be used as anhydrous or aqueous or it can be converted to HNO_3 and used.

Ammonia

Pure NH_3 is made up of 82.25 % N and 17.75% H. It is the most concentrated form and the lowest priced N fertilizer so far used either in the production of mixed fertilizer or for direct application. As described earlier, NH_3 can be obtained, either as a by product during the destructive distillation of coal in coke oven, or from other coal industries, or by synthetic process. For fertilizer are these are two forms available.

1. Anhydrous NH_3 and 2. Aqua or aqueous NH_3 . Both the forms are extensively used in ammoniation of superphosphate, in the preparation of mixed fertilizers and for direct application.

Anhydrous ammonia is produced by compressing dry NH_3 gas to form a liquid. The fertilizer grade of anhydrous NH_3 contains 99.5% NH_3 equivalent to 82.0 per cent N. It is an acid forming fertilizer and has a potential acidity equivalent to 148 lb of CaCO_3 per 100 lb of ammonia. Aqueous ammonia is formed by dissolving NH_3 gas in water. Commercial grades are found to have 30% NH_3 which is widely used for ammoniation of superphosphate and mixed fertilizers and produce the same activity. Application of liquid NH_3 through irrigation water is called '**Nitrogation**' and application of gaseous NH_3 directly to the field by using special devices is called '**Nitrojection**'.

NITRIC ACID MANUFACTURE

About 75% of the HNO_3 produced is consumed in the fertilizer manufacture, while about 15% of the production goes into the manufacture of explosives. The remainder is used in a wide variety of outlets, the more important ones being synthetic fibers, dyes and plastics.

Production capacity

HNO_3 is produced in about 50 factories in India. Out of these, 18 factories are producing above 100 t p a.

Raw materials: NH_3 and air are required for the manufacture of HNO_3

Manufacture

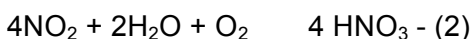
Nitric acid is produced by NH_3 oxidation process. The liquid NH_3 is evaporated, superheated and sent with compressed air to the converter, containing platinum –rhodium catalyst. In the converter, NH_3 is converted to nitric oxide, which is

then converted to nitrogen dioxide in oxidation vessel with the help of secondary air. In the process, water absorbs nitrogen dioxide to form HNO_3 while running in counter flow to the raising nitrogen dioxide in absorption column.

The various processes used can be classified as medium pressure, high pressure and combination of medium and high pressure, i.e, dual process. For fertilizer industry HNO_3 of concentration from 58 to 60% is used.



Nitrogen dioxide



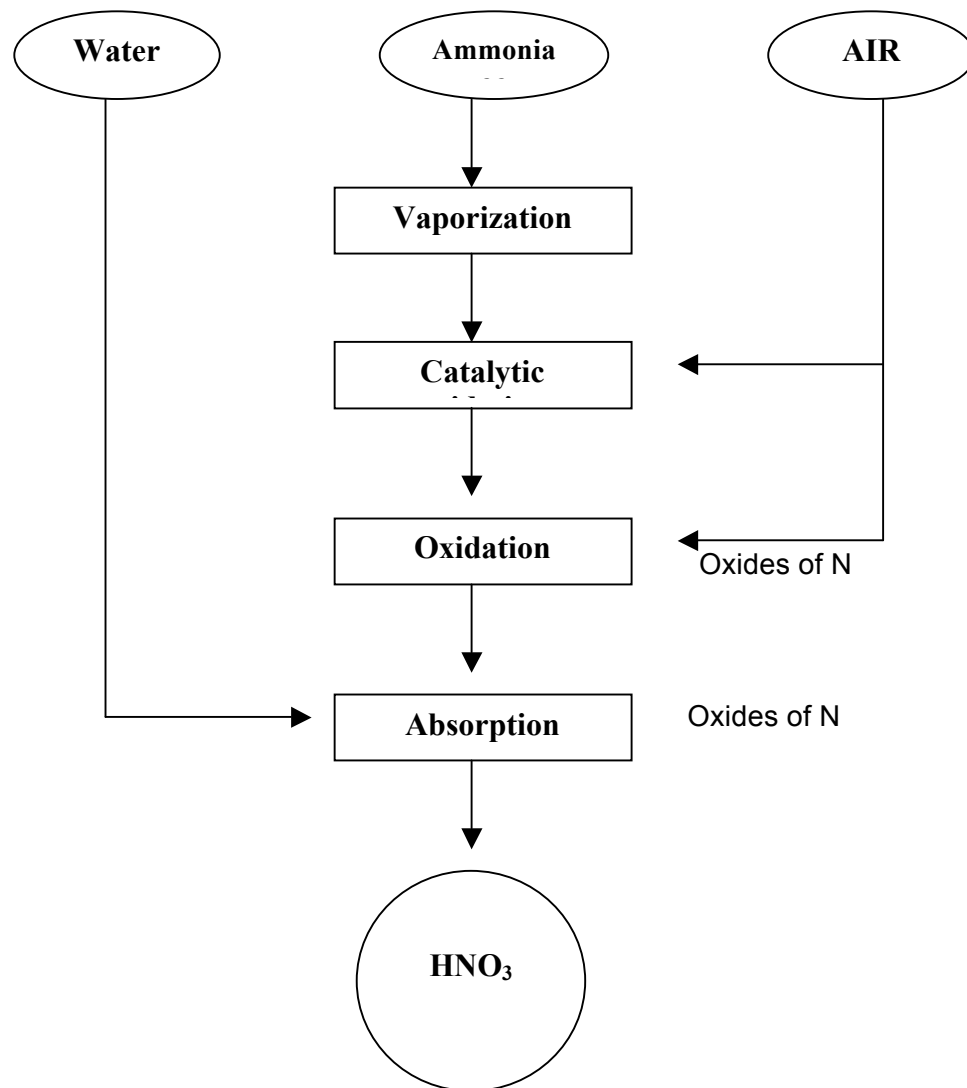
Concentrated nitric acid

Nitric acid / water form a constant boiling mixture at around 68% and cannot therefore be separated by conventional distillation. The HNO_3 can be further concentrated by extractive distillation with concentrated H_2SO_4 or $\text{Mg}(\text{NO}_3)_2$. The method involves high temperature reconcentration equipment operated under highly corrosive conditions.

Handling, storage and packing

HNO_3 is stored in stainless steel vessels. It is transported (large quantity) in stainless steel tankers or (small quantity) in stoneware bottles and glass carboys. Bottles and carboys shall be placed in an upright position on one layer of sand or ash free from cinders and the empty surrounding space shall also be filled with the same material to prevent movement.

Flow chart for manufacture of HNO_3



SULPHURIC ACID

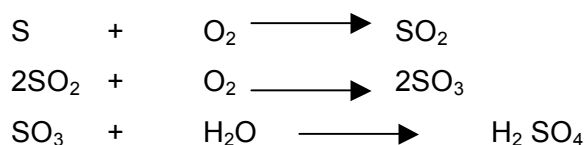
H_2SO_4 is one of the most important heavy chemicals produced in India. It has a wider variety of industrial uses than any other chemical. Per capita consumption of H_2SO_4 often has been used as an index of the industrial development of a country. The fertilizer industries, by far, the greatest consumer of H_2SO_4 for acidulation of RP and for the manufacture of $(\text{NH}_4)_2\text{SO}_4$. other important fields of its use are steel works, rayon and staple fiber, alum and other inorganic chemicals and petroleum refining etc.

Raw materials/ sources

H_2SO_4 may be produced from elemental sulphur, pyrites (Sulphides of iron, copper, zinc and lead), hydrogen sulphide as contained in sour gas and petroleum, waste gases from the burning of fuel and smelting operations and sulphate salts such as anhydrite, gypsum and iron sulphates. Elemental S, pyrites and sulphates are the true basic raw materials. H_2SO_4 produced by burning of fuel and smelting operation is called by products H_2SO_4 . H_2SO_4 production from metallic sulphates is not economical. Thus for H_2SO_4 production elemental S and pyrites are the only two important raw materials. In India, all the factories are based on elemental S except for Hindustan copper Ltd., Khetri and Hindustan Zinc Ltd., Udaipur which are based on flue gases from copper and Zinc smelters respectively. Also, one plant at Sindri is producing acid based on iron pyrite and a similar plant of larger capacity is under construction by the Sindri unit of FCI.

Methods of manufacture

S is burnt to sulphur dioxide and pyrites are roasted to oxidize the sulphide content to SO_2 . SO_2 after catalytic conversion to Sulphur trioxide is absorbed in water to give H_2SO_4 . the differences in H_2SO_4 processes are in the manner in which SO_2 is converted to SO_3 and absorbed in H_2O to produce H_2SO_4 .



(i) Chamber/tower process

The oldest process is the chamber process, so called because the reactions which produce SO_3 and H_2SO_4 take place within a lead chamber. The conversion to

SO₃ and then to H₂SO₄ in the chamber is made possible by the use of nitrogen oxides as oxygen carrying catalysts. The need to attain greater output of acid resulted in the development of the so-called tower process in which packed towers are substituted for the lead chamber.

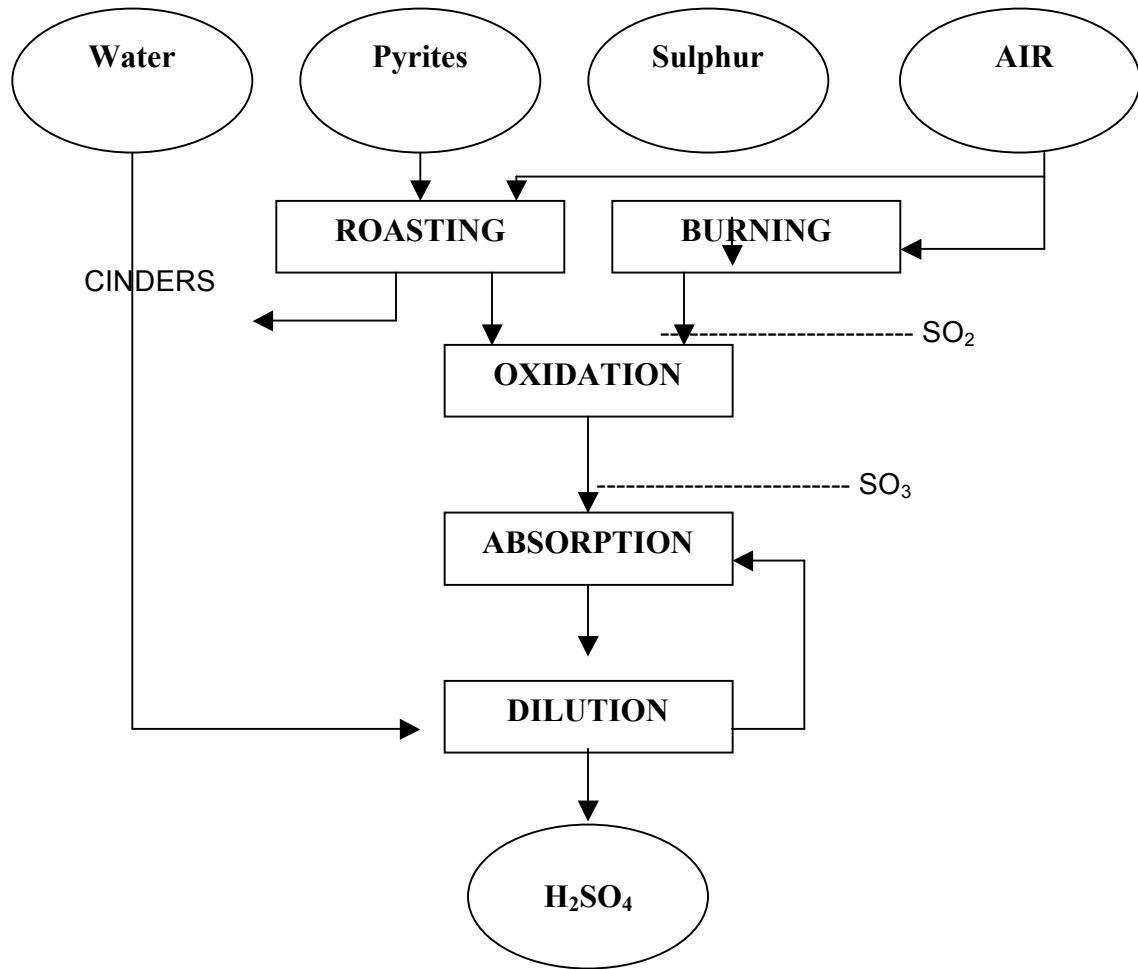
(ii) Contact process

In this process, SO₂ is converted to SO₃ by the use of a metal or metal oxide catalyst. The more common catalysts are platinum, iron oxide and vanadium pent oxide, although never plants use the latter almost exclusively. SO₃ is passed to a tower where it is absorbed in recycling con.H₂SO₄.

Properties

- | | |
|---------------------------------|----------------------------------|
| i) Chemical formula | - H ₂ SO ₄ |
| ii) Molecular weight | - 98.08 |
| iii) Appearance | - Colorless, viscous liquid |
| iv) Specific gravity (18°C/4°C) | - 1.834 |
| v) Boiling point | - Decomposes at 340°C |
| vi) Solubility in water | - Miscible in all proportions. |

Flowchart for H₂SO₄ manufacture



06. Manufacturing of ammonium sulphate, ammonium nitrate and ammonium chloride

Ammonium sulphate

$(\text{NH}_4)_2\text{SO}_4$ is one of the important fertilizers produced in India. It contains about 21% N and 24% S and has been traditionally been very popular in various parts of the country. It is a white crystalline salt having good keeping quality in dry conditions.

Production capacity

The total installed capacity in the country is about one million tones of $(\text{NH}_4)_2\text{SO}_4$

Raw materials / sources

The raw materials required to produce $(\text{NH}_4)_2\text{SO}_4$ are

- H_2SO_4 for its recovery from coke oven plants.
- NH_3 and H_2SO_4 for neutralization process.
- Gypsum (natural or by product from H_3PO_4 plants) and NH_3 for process using gypsum route.

Method of manufacture

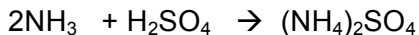
The following methods are used for producing $(\text{NH}_4)_2\text{SO}_4$.

(i) Recovery from coke-ovens

The coke-oven gas (obtained when coal is heated to make coke) contains about 1% NH_3 by volume. The gas is cooled and passed into saturators containing weak H_2SO_4 so as to form $(\text{NH}_4)_2\text{SO}_4$ crystals which is then recovered, centrifuged, washed and dried. This process is used in the steel plants where large coke- oven batteries are in operation.

(ii) Direct neutralization

Gaseous ammonia is directly neutralized with H_2SO_4 to produce $(\text{NH}_4)_2\text{SO}_4$.



The neutralizer reactor and the crystallizer are interconnected so that the heat released during neutralization is used to evaporate water in the slurry. The crystallizer is designed to produce uniformly sized crystals.

Amorphous $(\text{NH}_4)_2\text{SO}_4$ is prepared by reacting gaseous NH_3 and H_2SO_4 in spray towers. The heat of reaction removes all the water present and the dry, fine product is continuously removed from the base of the tower. This product is suitable for making dry-mixed and granular fertilizers, FCI (Sindri), FACT (Alwaye) use the direct neutralization process.

In the manufacture of some granular NPK fertilizers, $(\text{NH}_4)_2\text{SO}_4$ is formed directly with other ammonium salts. E.g. in the 16 – 20 – 0 grade product made by FACT, a

mixture of H_3PO_4 and H_2SO_4 is neutralized with NH_3 to form a slurry of $(\text{NH}_4)\text{PO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, which is then granulated.

(iii) Gypsum process

NH_3 gas is absorbed in water and then converted to $(\text{NH}_4)_2\text{CO}_3$ by absorbing CO_2 . The $(\text{NH}_4)_2\text{CO}_3$ is reacted with gypsum ($\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$) to produce $(\text{NH}_4)_2\text{SO}_4$ and CaCO_3 .



CaCO_3 is removed by filtration $(\text{NH}_4)_2\text{SO}_4$ solution is evaporated, crystallized, centrifuged and dried. Naturally occurring gypsum, or by product gypsum from H_3PO_4 plants can be used for this process. CaCO_3 produced can be used for cement manufacture FCI (Sindri), FACT (Alwaye), EID-parry (Ennore), and GSFC (Baroda), produce $(\text{NH}_4)_2\text{SO}_4$ from CaSO_4 .

(iv) Byproduct

$(\text{NH}_4)_2\text{SO}_4$ from caprolactum plants $(\text{NH}_4)_2\text{SO}_4$ solution is formed during the manufacture of caprolactum (the starting material for Nylon- 6). The solution is concentrated and $(\text{NH}_4)_2\text{SO}_4$ is recovered by crystallization, centrifuging and drying. GSFC (Baroda) has commissioned a 20,000 t p a caprolactum plant which will produce about 80,000 tonnes of $(\text{NH}_4)_2\text{SO}_4$ per year.

Specification as per FCO

- | | |
|---|-------|
| - Moisture % by weight. Max | 1.0 |
| - $\text{NH}_4 - \text{N}$ % by weight Min | 20.6 |
| - Free acidity as H_2SO_4 % by weight max | 0.025 |
| - Arsenic (As_2O_3) % by weight max | 0.01 |

Handling storage and packing

Crystalline $(\text{NH}_4)_2\text{SO}_4$ is free flowing and does not normally pose any problem in handling and storage. However, it generally contains some powdered material which causes caking especially under high humidity.

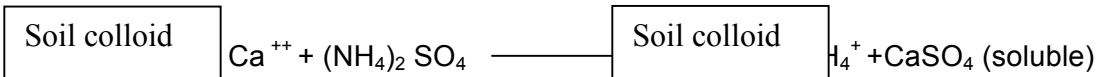
Due to its susceptibility to caking and slight acidity $(\text{NH}_4)_2\text{SO}_4$ is normally bagged in polyethylene lined gunny bags or high density polyethylene (HDPE) woven sacks.

Properties

- It is a white crystalline salt and to some extent hygroscopic
- It has good storage quality
- It is very soluble in water and so called as quick acting fertiliser
- It should not be used along with alkaline materials

- It is physiologically acidic in nature

Reactions in soil



Ammonia gas is evolved when ammonium sulphate reacts with alkaline materials

When lime and ammonium sulphate is used together in the soil, ammonia gas is produced

Ammonium chloride (NH₄ Cl) 26% N

This is sometimes called nitrate of ammonia. It is commercially prepared by combining ammonia with HCl and the resultant product, NH₄Cl is found to have very good physical condition. Though this fertilizer has not been used extensively as straight fertilizer, it is preferred in preparing many fertilizer mixtures because of its good physical properties. This fertilizer is also obtained as a by product of the Solvay process of making (Na)₂ CO₃.

The commercial sample is a white, crystalline salt containing 26% N in the NH₄ form. The fertilizer is suitable for many crops except for those, which are sensitive to high chlorine content. This is physiologically acidic fertilizer.

Manufacture

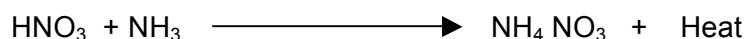
Sodium chloride is treated with ammonia and carbon dioxide to form ammonium chloride and sodium bicarbonate. The resulting ammonium chloride is then separated



Ammonium chloride is also obtained as a byproduct of soda ash (Na₂CO₃) and manufactured as Solvays process. It is prepared by reacting calcium chloride with ammonium carbonate. Ammonium chloride is obtained by double decomposition between ammonium sulphate and sodium chloride at 1300⁰ C

Ammonium nitrate (NH₄ NO₃) – 33% N

This is mainly manufactured by passing NH₃ gas into HNO₃ and then isolating the product in a solid form suitable for use as fertilizer. The equipment should be stainless steel or other special alloys.



NH₄ NO₃ is continuously produced with the aid of a neutralization tower. NH₃ gas is introduced near the bottom of the tower, while air is added at a higher point to cool the

solution and carry off the water vapor. The solution containing about 80% of NH_4NO_3 is with drawn and converted to crystals or pellets as the case may be.

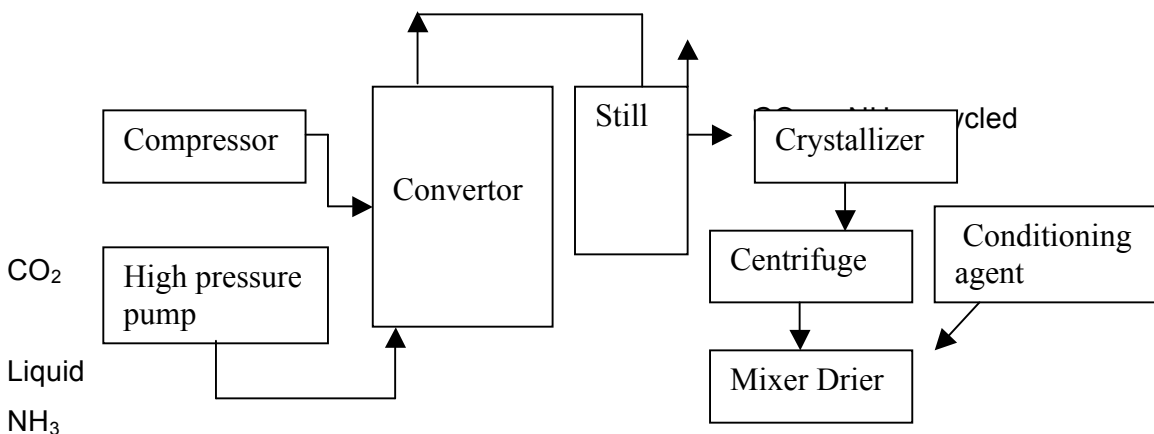
Pure NH_4NO_3 is a white crystalline salt having 33% of N, one half of which is in the NH_4 form and the other half in the NO_3 form. It is readily soluble in water and completely utilized by crops and hence no residues are left in the soil. It is highly hygroscopic and cakes up very soon. But, when the crystal is coated with about 5% of a conditioning agent like clay etc, it is found to have good physical properties. It is an excellent fertilizer both for direct application to the soil and for use in mixtures. It is an economical source of fertilizer N, suited to a wide range of crops, soils and climatic conditions. Its NO_3 content contributes to rapid crop response while the NH_4 - N makes it more resistant to leaching losses than other materials carrying their entire N in the NO_3 form.

07.Manufacturing of urea

Urea: $\text{CO}(\text{NH}_2)_2$ (42 to 46% N)

The main principle involved in the process of manufacture is combining pure ammonia with pure CO_2 and removing one molecule of H_2O from the resulting NH_4CO_3 to form Urea. The CO_2 and NH_3 are allowed to react in the liquid phase under greatly elevated pressure and temperature and this process requires highly specialized equipment. The CO_2 and NH_3 are compressed and heated as they enter the converter where urea is formed. A large excess of NH_3 is used in order to increase the conversion rate. The un reacted NH_3 and CO_2 are removed by means of an evaporator still and are then recycled. The urea solution is pumped to the crystallizer where cooling and crystallization take place. The urea crystals are centrifuged and dried.

FLOW CHART FOR UREA MANUFACTURE



08. Slow release N fertilizers – coated fertilizers – types of coating – lac coated-neem cake blended and coal tar coated urea- chemically modified forms-urea formaldehyde, IBDU, CDU

Slow-release fertilizers are excellent alternatives to soluble fertilizers. Because nutrients are released at a slower rate throughout the season, plants are able to take up most of the nutrients without waste by leaching. A slow-release fertilizer is more convenient, since less frequent application is required. Fertilizer burn is not a problem with slow-release fertilizers even at high rates of application; however, it is still important to follow application recommendations. Slow-release fertilizers may be more expensive than soluble types, but their benefits outweigh their disadvantages.

Slow-release fertilizers are generally categorized into one of several groups based on the process by which the nutrients are released. Application rates vary with the different types and brands, with recommendations listed on the fertilizer label.

Pelletized:

One type of slow-release fertilizer consists of relatively insoluble nutrients in pelletized form. As the pellet size is increased, the time it takes for the fertilizer to breakdown by microbial action is also increased. An example of this type is MagAmp, a 7-40-0 fertilizer that is available in a coarse grade lasting two years and a medium grade lasting one year. MagAmp is used commercially for container plants, but is appropriate for use on turf, tree seedlings, ornamentals, vegetables, and flower borders.

Chemically Altered:

A fertilizer may be chemically altered to render a portion of it water insoluble. For instance, urea is chemically modified to make Ureaform (ureaformaldehyde) -- a fertilizer that is 38 percent nitrogen, 70 percent of which is water-insoluble. This percentage is often listed on fertilizer labels as the Percent W.I.N., or the percent of water-insoluble nitrogen. This form of nitrogen is released gradually by microbial activity in the soil. Because microbial activity is greatly affected by soil temperature, pH, aeration, and texture, these variables can affect the release of nitrogen from Ureaform. For example, there will be less fertilizer breakdown in acid soils with poor aeration -- an environment unfavorable to soil microorganisms. Ureaform is used for turfgrass; landscaping; ornamental, horticulture, and greenhouse crops.

IBDU (isobutylidene diurea) is similar to Ureaform, but contains 32 percent nitrogen, 90 percent of which is insoluble. However, IBDU is less dependent on microbial activity than Ureaform. Nitrogen is released when soil moisture is adequate. Breakdown is increased in acid soils. IBDU is used most widely as a lawn fertilizer.

Coated fertilisers

Controlled- or slow-release fertilizers are broadly divided into uncoated and coated products. Uncoated products rely on inherent physical characteristics, such as low solubility, for their slow release. Coated products mostly consist of quick-release N sources surrounded by a barrier that prevents the N from releasing rapidly into the environment. Different mechanisms, but similar (though not identical) end results.

The terms “controlled-release” and “slow-release” can mean different things to different people, but for purposes of this discussion, the two terms are synonymous. Except for a few slow-release K sources, almost all slow-release fertilizers are N sources. They represent a relatively small segment of the total fertilizer industry (3 to 4 percent), but their use is growing faster than soluble (quick-release) materials. This is primarily because they reduce the overall environmental impact of N fertilizers, as now mandated in BMPs.

Coated:

Water-soluble fertilizers may be coated or encapsulated in membranes to slow the release of nutrients. For example, **Osmocote**, a controlled-release fertilizer is composed of a semipermeable membrane surrounding water-soluble nitrogen and other nutrients. Water passes through the membrane, eventually causing enough internal pressure to disrupt the membrane and release the enclosed nutrients. Because the thickness of the coating varies from one pellet, or prill, to another, nutrients are released at different times from separate prills. Release rate of these fertilizers is dependent on temperature, moisture, and thickness of the coating. Osmocote is recommended for turf, floriculture, nursery stock, and high-value row crops.

Another type of coated fertilizer is **sulfur-coated urea** (SCU), which is manufactured by coating hot urea with molten sulfur and sealing with a polyethylene oil or a microcrystalline wax. Nitrogen is released when the sealant is broken or by diffusion through pores in the coating. Thus, the rate of release is dependent on the thickness of the coating or the sealant weight. SCU is broken down by microorganisms, and chemical

and mechanical action. The nitrogen in SCU is released more readily in warm temperatures and dry soils. SCU appears to be more effective when applied to the soil surface, rather than mixed into the soil. Any method of application that crushes the granules will increase the release rate to some extent.

SCU is best used where multiple fertilizer applications are normally necessary, such as on sandy soils or in areas of high rainfall or irrigation. SCU is used on grass forages, turf, ornamentals, and strawberries.

Nutricote is characterized by coating nitrate compound fertilizers with a special resin. The duration of nutrient release is controlled by the porosity of the resin coating. A more porous coating results in quicker release. This technology ensures consistency and precision of nutrient release from Nutricote controlled release fertilizers.

When Nutricote is applied to the soil, the water in the soil enters the granule through micropores which dissolves the nutrient elements. The nutrient elements will then be released steadily through the same pores. Most Nutricote granules are 3 to 4 mm in diameter and the nutrient content are NPK: 14-14-14 and NPK: 20-7-10.

Nutricote's release rate is influenced by soil temperature, the higher the soil temperature, the greater the release rate. Absorption of nutrients and water by plants is generally increased with increasing temperature and plant growth will become more vigorous as a result. Nutrient supply through Nutricote nicely matches the physiology of plant response to temperature.

The release rate of Nutricote is not significantly influenced by soil moisture levels nor by soil type or pH. Nutricote does not depend upon microbiological decomposition for its action.

2.Polymer-coated fertilizers

Polymer-coated fertilizers (PCF) represent the most technically advanced state of the art in terms of controlling product longevity and nutrient efficiency. Most PCFs release nutrients by diffusion through a semipermeable polymer membrane, and the release rate can be controlled by varying the composition and thickness of the coating. The type of fertilizer substrate also may influence the rate of N release.

Meister products : Meister products are produced by using thermoplastic resins as coating materials. The coatings are applied to a variety of substrates including urea, diammonium phosphate, potassium sulfate, potassium chloride and ammonium nitrate. Release-controlling agents such as ethylene-vinyl acetate and surfactants are added to the coating to obtain the desired diffusion characteristics, while coating thicknesses remain similar for most products. Release rates can also be altered by blending talc resin into the coating.

Reactive Layer Coating: A relatively new coating technology known as reactive layer coating (RLC) combines two reactive monomers as they are simultaneously applied to the fertilizer substrate. These reactions create an ultra-thin membrane coating, which controls nutrient release by osmotic diffusion. RLC products include coated basic fertilizer materials such as urea, potassium nitrate, potassium sulfate, potassium chloride, ammonium sulfate, ammonium phosphate and iron sulfate, in various particle sizes. Coating weights on urea vary from 1.5 to 15 percent, depending on the release duration desired.

Multicote products: In the production of multicote products, fertilizer granules are heated in a rotating pan and treated with materials that create multiple layers of a fatty acid salt. This is followed by the application of a paraffin topcoat. Coating weights are relatively large compared to other technologies, but this is offset by the comparatively low cost of the coating materials. Substrates include potassium nitrate, urea and triple superphosphate. The various coated components are blended together into different grades.

Coated N Fertilizers;

1.Ureaformaldehyde reaction products

Ureaformaldehyde (UF) reaction products represent one of the oldest controlled-release N technologies, having been first produced in 1936 and commercialized in 1955. Urea and formaldehyde are reacted together to various extents to produce polymer-chain molecules of varying lengths. The more these products are reacted, the longer the chains tend to be. Chain length, in turn, affects release characteristics.

Ureaform is the oldest class of UF reaction products. It is sparingly soluble, and contains at least 35 percent total N, with at least 60 percent of the total N as cold-water-insoluble N (CWIN). Ureaform is composed largely of longer-chained molecules of UF polymers. The unreacted (and, therefore, quick-release) urea N content in UF is usually less than 15 percent of the total N.

Methylene ureas are a class of sparingly soluble products that evolved during the 1960s and 1970s. These products predominantly contain intermediate-chain-length polymers. The total N content of these polymers is 39 to 40 percent, with between 25 and 60 percent of the N present as CWIN. The unreacted urea N content generally is in the range of 15 to 30 percent of the total N.

UF solutions are clear water solutions. They contain only very-low-molecular-weight, water-soluble UF reaction products, plus unreacted urea. Various combinations of the UF solutions are produced. They contain a maximum of 55 percent unreacted urea with the remainder as one or more of methylolureas, methylolurea ethers, MDU, DMTU or triazone.

Isobutylidene diurea (IBDU) : Unlike the reaction of urea and formaldehyde, which forms a distribution of different UF polymer chain lengths, the reaction of urea with isobutyraldehyde forms a single type of molecule. Although similar in chemical structure to methylene diurea (MDU), its physical properties are quite different. IBDU is a white crystalline solid available in fine (0.5 to 1.0 mm), coarse (.7 to 2.5 mm) and chunk (2.0 to 3.0 mm) particle sizes. The product contains a minimum of 30 percent N with 90 percent of the N in water-insoluble form. The typical commercialized product contains about 31 percent N.

Crotonylidene Diurea (CDU) : This slow acting nitrogen compound is formed by reaction with crotonaldehyde or acetaldehyde. Powdered CDU containing 30 percent N has been directly used as a fertilizer. The microbial decomposition of the chemically bound CDU is temperature dependant

Agronomic properties and nutrient release mechanisms of UF materials

The conversion of UF reaction products to plant-available N is a multi-step process, involving dissolution first, and then microbial decomposition. Once in the soil solution, UF reaction products are converted to plant-available N through either microbial

decomposition or hydrolysis. Microbial decomposition is the primary mechanism of N release. Environmental factors such as soil temperature, moisture, pH and aeration affect microbial activity and, therefore, the rate of N release.

The rate of N release from UF reaction products is directly affected by polymer chain length. The longer the methylene urea polymer, the longer it takes for the N to become available. For ureaform and methylene urea products, the rate of mineralization is reflected by the CWIN content and its Activity Index. The higher the AI value, the more rapidly the N will become available. It is questionable if the very long methylene urea polymers (HWIN) are effectively used by the plant.

Agronomic properties and nutrient release mechanisms of IBDU: Nitrogen from IBDU becomes available to plants through hydrolysis. In the presence of water, the compound will hydrolyze (break down) to urea and isobutyraldehyde. The rate of hydrolysis is accelerated by low pH and high temperature. Unlike UF polymers that rely on soil microbial populations to make the N available, IBDU is primarily dependent on water as the critical element in N availability. Its low water solubility controls the transport of the product into the soil solution.

Agronomic properties and nutrient release mechanisms of SCU: The mechanism of N release from SCU is by water penetration through micropores and imperfections (i.e., cracks) or incomplete sulfur coverage in the coating. This is followed by a rapid release of the dissolved urea from the core of the particle. When wax sealants are used, a dual release mechanism is created. Microbes in the soil environment must attack the sealant to reveal the imperfections in the sulfur coating. Because microbial activity varies with temperature, the release properties of the wax-sealed SCUs are also temperature dependent.during the cool-season growth period.

09. Controlled release fertilizers and reaction in soil - nitrification inhibitors – criteria and advantages

Controlled-Release Fertilizers Using Zeolites

The U.S. Geological Survey (USGS) has experimented with zeolites to help control the release of fertilizer nutrients in soil. The use of soluble fertilizers can lead to water pollution and to wasted nutrients. Nitrogen, for example, can leach into ground and surface waters, especially in sandy soils, and phosphate may become fixed and unavailable to plants, especially in tropical soils. Zeolites are porous minerals with high cation-exchange capacity that can help control the release of plant nutrients in agricultural systems. Zeolites can free soluble plant nutrients already in soil, and may improve soil fertility and water retention. Because zeolites are common, these unique minerals could be useful on a large-scale in agriculture.

Controlled-Release Nitrogen Fertilizer

Urea is one of the most common nitrogen fertilizers. It is very soluble in water, and can be leached through the root zone. In addition, urea is converted into ammonium ions by an enzyme found in most soils. Soil bacteria then convert these ammonium ions into readily leachable nitrate ions. Using zeolitic rocks in fertilizer can help prevent these nutrient losses.

Controlled-Release Phosphorous Fertilizers

Phosphate (H_2PO_4) can be released to plants from phosphate rock (P-rock) composed largely of the calcium phosphate mineral apatite by mixing the rock with zeolite having an exchange ion such as ammonium. The approximate reaction in soil solution is as follows: $(\text{P-rock}) + (\text{NH}_4\text{-zeolite}) = (\text{Ca-zeolite}) + (\text{NH}_4^+) + (\text{H}_2\text{PO}_4^-)$.

The zeolite takes up Ca^{2+} from the phosphate rock, thereby releasing both phosphate and ammonium ions.

Growth responses to controlled-release fertilizers

Most controlled-release fertilizers are N-based, and most of the research involving them has evaluated plant responses to N application. Additionally, because most

controlled-release N sources cost several times more per pound of N than the soluble sources, most of the evaluation has been conducted on higher-cash-value crops such as ornamentals, vegetables, citrus and turfgrasses. Little research has been conducted on agronomic crops because their use in this sector is not considered economically feasible. Technologies currently under development may reduce the cost of controlled-release products to the point that they can be used on agronomic crops, but such is not yet the case.

Nitrification inhibitors

It should be non-toxic plants, soil microorganisms, animals, fish and mammals

It should block the conversion of NH_3 to NO_3 by inhibiting Nitrosomonas activity

It should not interfere with the transformation of NO_3 (nitrite) by Nitrobacter

It should be able to move with the fertilizer so that it will be distributed uniformly through the soil zone contacted by nitrogen fertilizer

It should be stable for the inhibitory action to last for an adequate period of time

It should be relatively inexpensive, so that it can be used on a commercial scale

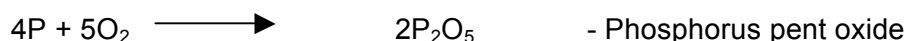
There are various nitrification inhibitors, of which N-Serve or nitrapyrin and AM are most important.

N-Serve- It is 2-chloro-6(trichloromethyl) pyridine and also referred to as nitrapyrin

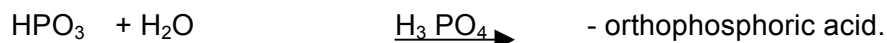
AM- Chemically it is a substituted pyrimidine (2-amino-4-chloro-6-methyl pyrimidine)

10. P fertilizers – rock phosphate – bone meal – basic slag

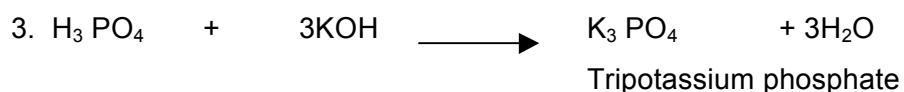
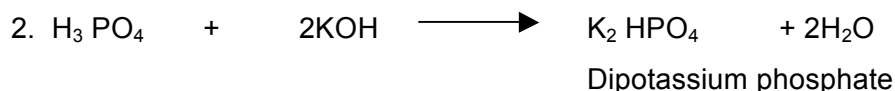
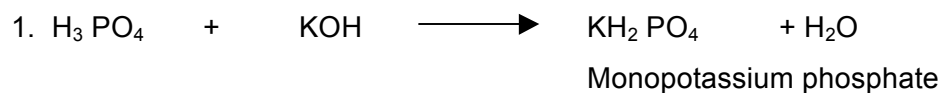
The element was discovered in 1669 and was found to be widely distributed in the lithosphere as phosphates. It is found to occur mostly as calcium phosphate (Tricalcium phosphate). The $\text{Ca}_3(\text{HPO}_4)_2$ is considered to be the basic material for the manufacture of very many phosphatic fertilizers. More than 50 countries produce phosphatic fertilizer. The top five fertilizer producing countries were United States, China, Russia, India and Brazil. Phosphorus when heated in an abundant supply of O_2 , it burns and forms P_2O_5 which, when dissolved in waters, forms metaphosphoric acid.



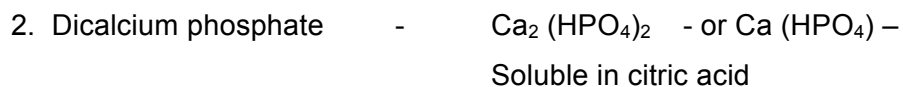
When this meta phosphoric acid is heated with water, it forms orthophosphoric acid which is commonly called as phosphoric acid.



This orthophosphoric acid has three replaceable H^+ atoms and hence it forms three classes of salts replacing one or two, or all the three H^+ atoms. The neutralization is said to occur in stages as follows.



The corresponding calcium salts are



This monocalcium phosphate is an acid salt having a solubility of 100 g L^{-1} of water. The di and tricalcium phosphates are almost neutral salts having the solubility of 0.25 g and 0.005g per liter of water respectively.

Sources of phosphorus

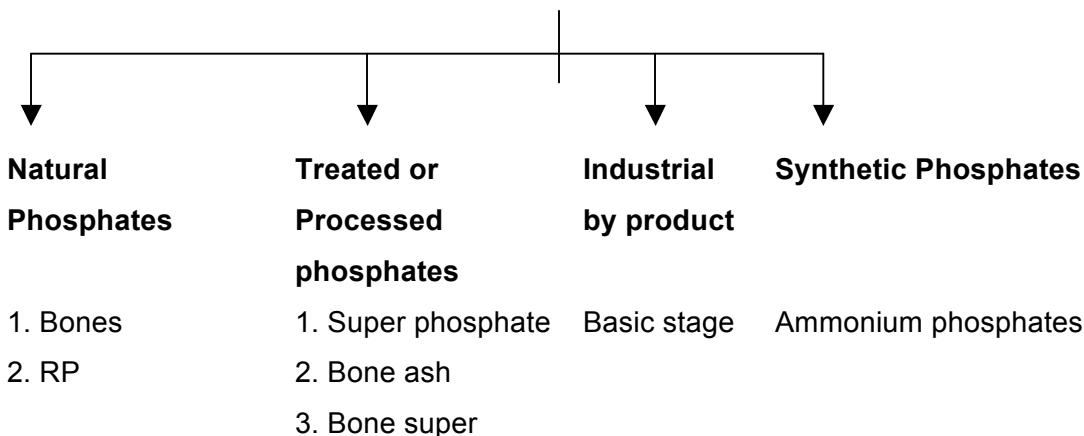
1. Mineral deposit

It occurs naturally, as mineral deposits consisting mainly of $\text{Ca}_3(\text{PO}_4)_2$ combined with either CaF_2 , CaCO_3 , $\text{Ca}(\text{OH})_2$ or CaCl_2 . The naturally occurring mineral is called “Apatite” or “Phosphorite” or “Phosphate rock” having the general formula $(\text{Ca}_3(\text{PO}_4)_2)$

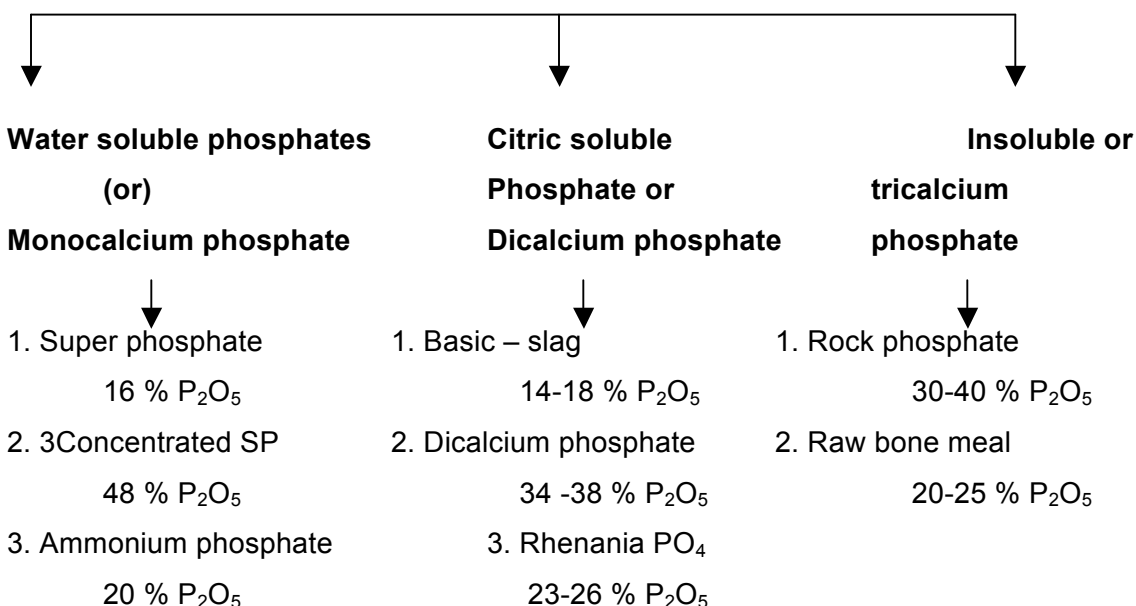
Ca X. These natural deposits serve as the basic material for the synthesis of all other phosphoric fertilizers.

Classification of phosphatic fertilizers

1. Based on nature of source or manufacture Phosphatic materials



2. Based on the solubility of the phosphate



As in the case of N, the P is incapable of being utilized in the elemental form, but only in the combined form as acid ions (anions). All plants absorb P either in the monovalent (H_2PO_4) or divalent (HPO_4) ions.

1. Water soluble phosphate

These include either monocalcium phosphate $Ca(H_2PO_4)$ or other water soluble phosphates like ammonium phosphates. These fertilizers are readily soluble in water which can be observed quickly, as plants absorb P as monovalent phosphate ion H_2PO_4 . But, when applied to the soil, the water – soluble form is converted to water insoluble

forms resulting in the reduced availability, though there may not be any total loss to the applied P. The fertilizers included in this group are found to be suitable for neutral and alkaline soils but not for acid soils.

2.Citric –soluble phosphates

The materials, having water – insoluble phosphates, but soluble in one percent citric acid, are included in this group. The availability of P is not as quick as in the case of water – soluble P, but adequate quantities are found to be released in the available form as divalent phosphates (HPO_4) for plant utilization. This group is found to be useful for acid soils, as under low pH of the soil the citrate soluble phosphates does not easily get converted into monocalcium phosphates or water soluble phosphates, and there are less chances of phosphate getting fixed up as iron and aluminum phosphates. Moreover, due to their basic reaction and high Ca content, they act particularly well on acidic soils and as such, this group is well suited for **lateritic** and acidic soils.

3.Insoluble phosphates

This group includes those materials having water and citric acid insoluble phosphates. The phosphates are being present mainly as tricalcium phosphate. The availability is very low and the phosphates will be converted to available form very slowly through various chemical reactions. Though the solubility of phosphates is low, the phosphates will be available for prolonged period of time.

These fertilizers are well suited for strongly acidic soils or organic soils which require large quantities of phosphatic materials to raise the soil P status.

The following table illustrated the phosphate (P_2O_5) content and the form of phosphate.

Sl. No.	Fertilizers	Total P_2O_5 (%)	Form of PO_4	Avail. P_2O_5
1.	Ordinary super phosphate	16	Water soluble	16.5 - 17.0
2.	Concentrate super phosphate	46 – 48	-do-	
3.	Monoammonium phosphate	48 (11 N)	-do-	
4.	Diammonium phosphate	53 (21 N)	-do-	46 (18N)
5.	Ammophos – A	48 (11 N)	-do-	
6.	Ammophos – B	20 (20 N)	-do-	
7.	Basic slag	14 – 18	Citric soluble	

8.	Dicalcium phosphate	34 – 38	-do-	34.0
9.	Fused tricalcium phosphate	28	-do-	
10.	Rhenania phosphate	23 – 26	-do-	
11.	Raw bone meal	20 – 25	Insoluble	NA
12.	Steamed bone meal	22 – 25	-do-	NA
13.	Rock phosphate	30 – 40	-do-	NA

1. Rock phosphate

The phosphate mineral in soil is found to occur as tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ in combination with either CaCO_3 , CaF_2 , Ca(OH)_2 or CaCl_2 . The primary mineral is called 'apatite' and its massive form is sometimes called as 'Phosphorite'. The apatite is of igneous origin found as a constituent of granites, gneisses and basalt. The apatite is usually found as crystals having a clear and transparent colour. There are five important forms of apatite that are found to occur and they are called according to the other components contained in the molecules.

Apatite General formula $(\text{Ca}_3(\text{PO}_4)_2)_3 \text{Ca}_x$ or $\text{Ca}_{10}(\text{PO}_4)_5 \text{X}$ where
 $x = \text{CO}_3, \text{Cl}_2, \text{F}_2, \text{SO}_4$ or $(\text{OH})_2$.

1. Carbonato apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaCO}_3$
2. Fluor apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaF}_2$
3. Chlor apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaCl}_2$
4. Hydroxy apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{Ca(OH)}_2$
5. Sulphate apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaSO}_4$

All the above five apatite are primary minerals, of which the fluor apatite is the most commonly occurring one. In some acid soils the phosphate may be found in combination with titanium and iron in varying quantities and there when present in the soil are classified as secondary mineral. The apatite as such is found to occur in the amorphous form and it may be in the compact, concretionary or earthy form and these forms are commonly referred as rock or boulder phosphate, pebble phosphate and soft phosphate respectively. The apatite deposits are classified into residual deposit, replacement deposit and sedimentary deposit.

Deposits of apatite of economic importance have been found in every continent and in many islands of the world. In India, the phosphoric deposits are found in Trichy district of Tamil Nadu, Udaipur of Rajasthan and Singbhum of Bihar. The deposits in Trichy are found in the form of nodules in a bed of clay and hence are called Trichy phosphatic nodules. The exact locality is Uttalur about 30km from Trichy and the deposit

is found to spread over an area of 11 to 12 square miles. The Trichy phosphatic nodule analyses as follows

P_2O_5	-	24 – 27%
$CaCO_3$	-	42 – 47 %
F	-	2 – 3 %
Fe_2O_3 & Al_2O_3	-	4 – 9 %

As compared to the phosphatic deposits found in other countries, this phosphate deposit contains a high content of F (2-3%), high content of sesquioxides (4-9%) and low content of phosphate. The high contents of F and R_2O_3 made the RP unsuitable for the manufacture of other phosphatic fertilizers at a lower cost. Larger quantities of acids are required to eliminate the F and R_2O_3 which will thus increase the cost of production. Moreover, the Trichy deposit is not suitable for direct use as fertilizer because of high F and R_2O_3 contents. The deposit is mainly in the form of carbonate apatite and fluor apatite. The fertilizing value is nil unless the F and R_2O_3 are removed. The ground RP is marketed, which passes through 200 mesh sieve.

Bone meal

Bone meal contains tri calcium carbonate or hydrated tri-calcium phosphate. This also contain sodium, magnesium and carbonate. Bone meal is prepared by crushing bones and availability of phosphorus in bone meal increases as material is crushed to a finer size.

Raw bone meal

It is prepared by grinding the bones as such without any treatment. The bones are collected, dried before grinding. The protein present in the form of remaining flesh provides nitrogen ranging between 2 to 4%. This contains fat of glue which prevents the decomposition of bone when applied in the soil.

Total P_2O_5 on dry weight basis (Max.)	: 20 %
Available P_2O_5 soluble in 2% citric acid (Min.)	: 8 %
Total nitrogen, % by weight (Min.)	: 3 %

Steamed bone meal

Steamed bone meal is obtained by the boiling the bones under steam pressure. Under this process the fat and some other materials are removed so that decomposition can take place readily in the soil after it is applied. However this process reduces the nitrogen content but phosphate content is increased. The bones are then ground and

sold as fertilizer material in the market. The steamed bone meal should have the following standard according to fertilizer quality control order (1957) if Government of India:

Free moisture percentage by weight (Max.) : 7.0

Total phosphates as P_2O_5 percentage by weight (Min) : 22.0

Available phosphates as P_2O_5 soluble in 2 %

Citric acid solution % by weight (Min.) : 16.0

Bone meal consists of P_2O_5 in citric acid soluble form hence it should always be applied as basal. The bone meal sources are limited and hardly 30,000 to 35,000 tonnes of bone meal is produced and consumed annually in the country. Now-a-days it is also used as feed to the animals in the form of concentrate hence the materials, as fertilizers, is further reduced.

Basic slag

It is a by-product from the steel industry. During the steel manufacture, the P in the iron ore is removed to get a high quality steel as the steel containing more than 2% of P is brittle. The basic slag is obtained by the various processes of steel manufacture.

1. Thomas and Gilchrist method

The method was introduced as a modification to the old Bessemer process in 1877. In this, molten pig iron containing the various impurities like Ca, SiO_2 and P is introduced into a limed converter with air blast arrangements. At a particular temperature, lime melts and combines with the acid forming impurities and the resulting product, which are lighter, rise to the surface of the molten mass. The floating solids are poured off as slag, cooled, powdered and marketed. This is containing 17 or 20% P_2O_5 .

2. Open Hearth method (Modern Method)

Here the impurities are oxidized by means of the iron ore (Iron oxide) itself. Iron ore and lime are heated in an open heater and molten pig iron is then added. This carries not more than 15% P_2O_5 and not less than 8% P_2O_5 .

Properties

The name 'basic slag' is derived from metallurgy. Any flux that is added to remove the impurities is recovered mixed with the impurities as a slag. The flux that is added to remove basic impurities produces acid slag and the one that is added to remove acid impurities forms basic slag. The basic slag is a heavy dark powder and is alkaline to litmus. The availability of P is found to increase with the fineness of the product as well as with silica content and decrease as the F content increase. Basic

slag should not be used as an ingredient in manure mixtures. The phosphate is found to be present in a double silicate form with lime $[(\text{CaO})_5 \text{P}_2\text{O}_5 \text{SiO}_2]$ but some consider it as tetra calcium phosphate $(\text{Ca}_4 \text{P}_2\text{O}_5)$ and still others consider it is a basic silicon oxy apatite. It is only a slow acting fertilizer. This more useful for acid soils and in addition to the phosphate it is valued for the magnesium and Mn content. Following is the average composition of basic slag.

Phosphate (P_2O_5)	-	12 - 20 %
Lime (CaO)	-	40 - 50 %
Silica (SiO_2)	-	5 - 16 %
Sesquioxides (R_2O_3)	-	12 - 16 %
Manganese oxide (MnO)	-	5 – 10 %
Magnesium Oxide (MgO)	-	2 – 3 %

Artificial Basic slag

When PR is fused with Mg containing minerals like serpentine and olivine, the resultant product is called as artificial basic slag. The fertilizing value of basic slag is influenced by the fineness of the fertilizer and material passing through a 100 mesh sieve is found to be better. It is more suitable for acid soils because of high lime content. The presence of Mg and Mn corrects the deficiency of these elements in the soil.

11. Single and triple super phosphates – thermophosphates – method of manufacturing Super phosphate

The term super phosphate is generally applied to phosphates which are present in a readily available form to plants. After the resolution passed in the meeting of the first world International congress on chemical fertilizers, 1938, the term super phosphate is restricted to refer those phosphates having less than 25% of P_2O_5 and the term concentrated SSP for all those phosphates containing more than 25% P_2O_5 .

The super phosphates are generally manufactured from phosphate rock, but bones and phosphatic guanoes are also extensively used for the manufacture. The super phosphates prepared from organic sources (bones & guano) are said to be having good physical condition, but with a lower P_2O_5 content. In recent times only the phosphate rock is being utilized for the manufacture of various super phosphate.

Phosphate rock containing less than 50% of tricalcium phosphate are not suitable for manufacture of phosphatic fertilizers and are not used in the industry. Phosphate rocks containing $> 4\%$ total R_2O_3 are considered unsuitable and the phosphate rock should not contain $> 2\%$ iron oxide.

The following method are commonly followed to convert the insoluble phosphate found in RP into more soluble forms.

1. Acid treatment method.
2. Phosphorus volatilization method
3. Decomposition with an alkali or silicate, and
4. Method followed in steel industry.

a. Ordinary super phosphate

This is also called as Den super phosphate. Often the term 'super' is used to refer only to this product. This is the most extensively used fertilizers among the farmers.

Manufacture

The principle involved in the process is the treatment of RP with acids, mainly H_2SO_4 to convert the insoluble and unavailable tricalcium phosphate to available dicalcium and monocalcium phosphates. Concentrated HNO_3 , HCl , H_3PO_4 and H_2SO_4 can be used, but sulphuric acid is found to be more suitable because of the fact that when it reacts with the RP, $CaSO_4$ is formed, which is a dehydrating agent and improves the physical condition of the final product to a better condition.

The method consisted of mixing equal quantities of RP with H_2SO_4 in open tanks and then powdering the resultant product after the reactions are over. The calculated

quantity of H_2SO_4 and ground phosphate rock (material passing through a four-mesh sieve only has to be used) are introduced and mixed very thoroughly and then dropped in a pit or den. The process is also called Den method. Sufficient time of 24 to 36 hrs is allowed for the completion of the reaction. Temperature rises to 100°C and there is a loss of volume by 10% due to evaporation of water, CO_2 and F. The CaSO_4 act as a dehydrating agent and artificial drying is also done wherever necessary. Then the product is ground to a very fine powder and stored for sufficient time for the curing of the material.



Precautions

1. An excess quantity of H_2SO_4 should not be used.
2. The quality of the RP must be pre decided.

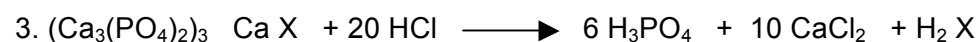
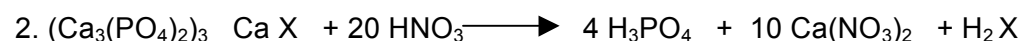
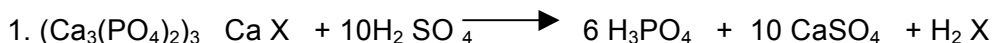
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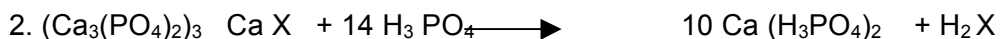
The commercial super phosphate is grey in colour and it is only partly soluble in water. It has an acid odour and acid reactions due to the presence of some free acids and the acid salt monocalcium phosphate. It addition to the presence of phosphate, it contains gypsum, silica and aluminum sulphate, CaF etc. It contains about 20% Ca and 12% Sulphur which are the secondary nutrient elements required for the plants.

b. Concentrated super phosphate

The main principle involved in the preparation is to first manufacture, phosphoric acid (H_3PO_4) by treating the RP with excess quantity of HCl or HNO_3 or H_2SO_4 and secondly the H_3PO_4 so obtained is used for the treatment of another quantity of phosphate rock to get this fertilizer. Hence, there are two acid treatments involved and so the product is called double super phosphate (double insulation). Following are the main steps in the manufacturer of concentrated super phosphate.

1. Preparation of H_3PO_4 using RP and one of the mineral acids.
2. Preparation of the concentrated super phosphate by treating fresh quantity of RP with the prepared H_3PO_4 .





PR is ground and allowed to pass through a constant weight feeder to which a measured flow of H_3PO_4 under pressure enters. All the mixing is done in the funnel like mixer and the mixture is allowed to stand for sufficient time for the reaction to take place. The slurry is conveyed to a troughed belt conveyor where the product sets in a few seconds to plastic mass. To get a dried material, sufficient retention time is allowed and at the end of the belt- conveyor, a rotary disintegrator reduces the lumps to less than 2" size. The disintegrated super phosphate is stored for curing at least for a period of 15 weeks.

Properties

This fertilizer resembles in all respects the ordinary super phosphate. It is grey in color, a major portion being soluble in water. It contains 45 to 48% water soluble P_2O_5 . It contains lesser quantity of other ingredients.

Thermophosphates

These are manufactured by heating phosphate rock in varying temperatures.

The main drawbacks in thermal phosphates are

They are generally more expensive than acid derived phosphates. It contains no water soluble P. They do not have any value in the manufacture of NPK fertilizers

Polyphosphates

Differ slightly from the more common orthophosphate fertilizers. Nearly all of the liquid fertilizers containing P are of the polyphosphate type. Polyphosphates are composed of a series of orthophosphate molecules connected by the process of dehydration (removal of water). Commercial ammonium polyphosphates are usually a mixture of ortho- and polyphosphate. With prolonged storage, polyphosphates will hydrolyze to orthophosphates. Solutions of ammonium polyphosphate most commonly made are 10-34-0 and 11-37-0. The most common dry polyphosphate is 13-52-0.

12. Potassic fertilizers – manufacturing of KCl, K₂SO₄ and Schoenite

Potassium found to occur very commonly in the combined form as naturally occurring minerals. Common soil forming rocks like granite and gneiss are found to have about 3% K. For many years, K has been considered as important plant nutrient element. The Chinese were the pioneers among the various farmers who used K for agricultural purposes. The mineral deposits were not discovered and used as fertilizers until eighteenth century. The first product to be used as K manure was the wood ash and the practice of using wood ash existed for centuries.

In olden days, the wood ash was primarily used to get the potassium salts. The wood was burnt and the resultant ash was leached in mud pots to get the salt mixture containing chlorides, SO₄ and CO₃ of K, Ca and Mg. (Pot + ash = Potash). It would be advantageous and more correct to use P and K to refer to P and K, instead of P₂O₅ and K₂O in the fertilizer technology i.e.,

$$\% K = \% K_2O \times 0.83 \text{ and } \% \text{ of } K_2O = \% K \times 1.2)$$

Source of potassium

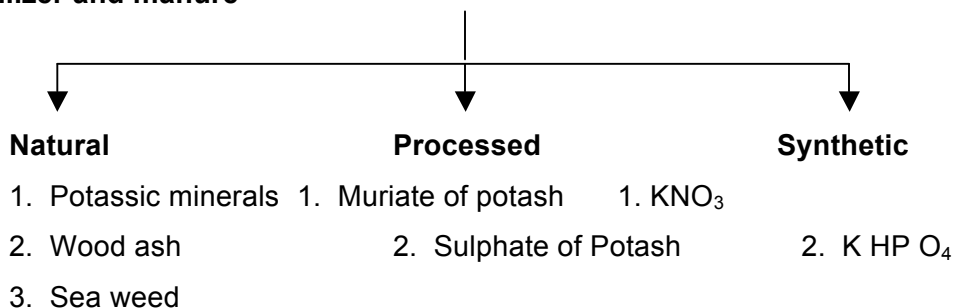
The following are the main sources of K.

1. Mineral deposits
2. Industrial by products
- and 3. Synthetic K salts

Classification of potassic fertilizers

Potassic fertilizer are classified broadly into chlorides and non- chlorides. The following are the most important K containing materials. Wood ash, tobacco stems, wool waste, flue dust, by products from sugar and alcohol industry. Sea weed, sea water, K minerals, processed fertilizer like muriate and SO₄ of potash and synthetic fertilizers.

K Fertilizer and manure



A. Organic K fertilizer Sources

1.Wood ash

Use of wood ash as K fertilizer has been there for centuries. Wood twigs and branches are burnt to get the ash. Sawdust is also used. The burnt material will contain

varying amounts at K_2O from 5 to 25%. Since wood ash is highly alkaline it should not be applied to germinating crops.

2.Tobacco stem

In the manufacture of cigarette, cigar and chewing tobacco, there results considerable wastes consisting of mainly the stems and midribs of the leaves. This waste material is collected, ground and sold as manure. Tobacco stem contains 4 to 10% K_2O and 2 to 3% N. It is found to be a valuable conditioner and adds bulk to the fertilizer mixtures.

3.Wool waste

Before the raw wool could be used for spinning, it must be treated for the removal of 'suint' which is the dried sweat of sheep. This 'suint' consists largely of K salts and contains 1.5 to 5.0 % K_2O .

4.Flue dust

It is a by product from the steel and cement industry. For melting the iron a mixture of iron ore, coal, coke and limestone are introduced into a blast furnace. When ignited, due to tremendous heat, the K contained in the iron ore volatilizes and when the gases containing volatilized K are burnt, the K dust will settle in the flue through which the gases pass and from time to time the dust accumulated will be collected and used. This will have 3 to 18% K_2O as Cl , SO_4 and CO_3 of K.

In the same way in cement manufacture also the raw materials used are found to have appreciable amount of K and this volatilized during the cement manufacture. The flue dust obtained from this is found to have 3 to 13% K_2O . The dust can be used as a straight fertilizer.

5.Sea weeds

This is referred to as the poor mans manure. It contains a high amount of K_2O varying with species of weeds. Out of many varieties 'kelp' is found to occur extensively throughout the world. The Sea weeds ash is found to have more than 25% K_2O .

6. Sea water

It contains an inexhaustible amount of K. It contains 0.04 % K, 0.14% Mg, 0.05 % Ca and 1.14 % Na.

B. Potassic minerals

There are as many as 50 minerals that are found to contain K but all of them are not economically important. The K containing minerals are roughly classified into

1. Minerals highly soluble in water occurring in brines or salt deposit

Sylvinite	-	KCl (Sylvite)
Carnallite	—	KCl. MgCl ₂ . 6 H ₂ O
Langbeinite	-	K ₂ SO ₄ . MgSO ₄
Kainite	-	KCl. MgSO ₄ . 3 H ₂ O

2. Minerals less soluble in water.

Polyhalite	-	K ₂ SO ₄ . Mg SO ₄ . 2 CaSO ₄ . 2 H ₂ O
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3. Minerals insoluble in water

Glauconite	-	KFeSi ₂ O ₆ . 2 H ₂ O
Feldspars	-	orthoclase - KAlSi ₃ O ₈
Micas	-	Muscovite and biotite.

The following are commercially used for the manufacture of potassic fertilizers.

1. Sylvinite - KCl - contains 63.1 % K₂O
2. Carnallite — KCl. MgCl₂. 6 H₂O - contains 17% K₂O
3. Kainite - KCl. MgSO₄. 3H₂O - contains 18.9% K₂O
4. Langbeinite - K₂SO₄. 2MgSO₄ – contains 26.6% K₂O
5. Polyhalite - K₂SO₄. MgSO₄. 2CaSO₄. 2H₂O – contains 15% K₂O

The deposits are found to occur at a depth of 650 to 2,500 feet below the earth's surface.

Processed K Fertilizers

1. Muriate of potash (KCl)

KCl is commercially manufactured using any one of the minerals; 1. Sylvinite or sylvite and 2. Carnallite . There are two main steps involved in the manufacture of this fertilizer.

1. Mining of the K mineral
2. Separation of the main ingredient and purifying.

Mining

The deposits are found to occur usually from 650 to 2,500 feet below the earth's surface. Many methods of mining are employed out of which the room and pillar method of mining is found to be familiar. After a mine shaft is sunk to a point slightly below the level of the ore body a large tunnel is driven on both sides of the shaft. At right angles to this tunnel the ore is mined in larger rooms about 25 to 50 feet wide and 300 feet long. The ore is brought over to the surface by electrically operating elevators and machineries.

Purification

This involves the following process: 1. Grinding 2. Lixiviation or converting the ore into solution form 3. Crystallization 4. Separation, drying etc.

Grinding

The potassic ore, after mining and bringing over to the factory site, is ground to fine size and screened to get only the ore of required size.

Solutioning

The ore is dissolved in hot water and to that is added the NaCl solution (brine) for obtaining a mixture of KCl + NaCl. The temperature of the mixture is increased by which more and more of sylvinite will dissolve and the solubility of NaCl will stop after a stage. This is continued till a saturated solution of KCl is obtained.

Crystallization

The saturated solution containing both KCl and NaCl is suddenly cooled in a vacuum and the KCl separates out as crystals while NaCl remains in the solution.

Separation

Crystallized KCl can be separated out by mechanical means and it is dried, powdered and used. The above process is called the crystallization method and the principle involved is the differential solubility of KCl and NaCl in cold and hot solution. When KCl is mixed with NaCl it is much more soluble in hot water than in cold water, whereas NaCl is somewhat more soluble in cold water than in hot water. By increasing the temperature, therefore, the solubility of KCl increases while that of NaCl remains virtually constant.

Floatation method

Floatation is a metallurgical process in which small quantities of special reagents are added to the pulp to coat or film some of the minerals selectively with respect to other minerals present. When the reagent added pulp is agitated in a mechanical cell in such a manner that air is drawn into the pulp to create a frothing action or condition, the finely divided air bubbles attach themselves to the reagent filmed particles and float them to the surface of the cell, where the froth rich with the selected mineral may be skimmed off. Some are found to be very effective to NaCl that is present in sylvinite.

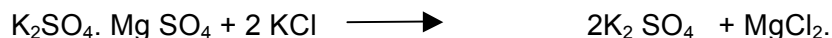
First, after grinding and passing through the screen, the desired sized sylvinite mineral is dissolved in water to get a pulp and the reagent is added to the pulp. The reagent will form a coating or film round the NaCl molecules and this reagent added pulp is allowed to pass through a series of floatation cells in which air is introduced at the

bottom in such a manner as to form a small bubble froth that attaches to NaCl. The commonly used reagents are (1) Sulphonated aliphatic alcohols of KCl and (2) 20% of mono-n-octadecyl- amines neutralized with acetic acid and a 0.5% solution of this is used for NaCl.

It is found that at least 90% of the potassic fertilizers consumed is in the form of muriate of potash. It contains 48 to 62% K₂O and 35 to 47% Cl. The commercial product is either granular or powdery having white or red colour.

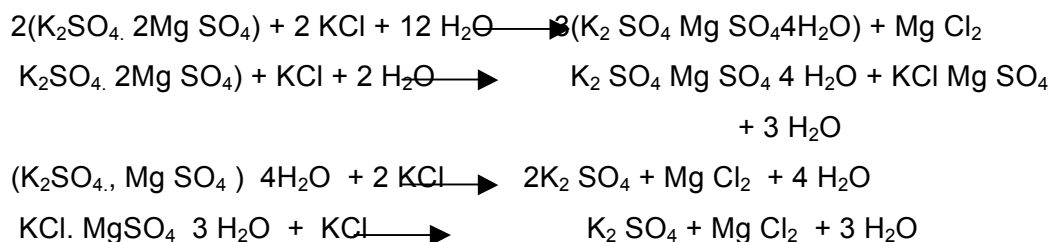
2. Potassium sulphate – K₂SO₄

This is manufactured from kainite (KCl. Mg SO₄. 3H₂O) or langbeinite (K₂ SO₄. Mg SO₄), the latter being commonly used. The raw materials required are the mineral langbeinite and KCl



The MgCl₂ is rejected. The KCl is used in the form of a mother liquor obtained from KCl manufacturing process.

The method is found to be efficient only in the presence of a proper ratio between K₂SO₄ and MgSO₄ of the raw material and to maintain a proper ratio, KCl or Kainite is added. The reactions are found to take place in different ways

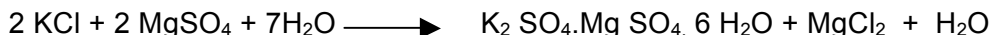


Langbeinite, ground to pass through a 200 mesh sieve and the mother liquor from the KCl process is mixed and then the salts are recycled with water and fresh quantity of langbeinite. The reactions are allowed to take place in interconnected tanks and the crystallized K₂SO₄ is separated out by means of centrifuge. The used K₂SO₄ is separated out by means of centrifuge. The wet K₂SO₄ is dried and conveyed to storage place. It contains 48% K₂O. Only limited quantities of K₂SO₄ are manufactured, as the cost of manufacture is more, but is preferred for those crops where quality is desired or where chlorine toxicity will result when K Cl is used.

3. Potassium Magnesium sulphate

In U.S.A. it is manufactured by mere washing of langbeinite (K₂SO₄. Mg SO₄) to remove the impurities and is sold under the name sulphate of potassium and magnesium. It contains 18.5% MgO and 22.6% K₂O. Since, the langbeinite is soluble in

water; the washing is done very easily. In Germany, it is prepared by dissolving MgSO_4 and adding KCl to it.



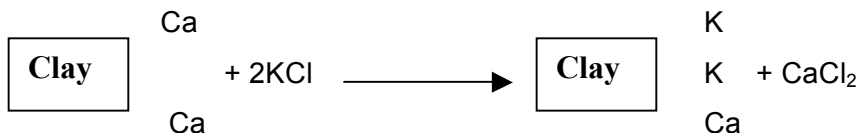
Manure salts

The ground and partially processed potassium mineral is sold under the name manure salt or mine run potassium salt. Various grades are available in different counties; Carnalite of 9-12 % K_2O and other salts of 12-15 % K_2O , 18-22% K_2O , 28-32 % K_2O , 38-42 % K_2O are also marketed and used on a limited scale.

The muck, peat, sandy, lateritic and laterite soils are deficient in K and response will be more in these soils for K fertilizers. Clayey soils are found to give poor response for K fertilizers. Potassic fertilizers can be added to these soils in which heavy feeders of K are grown such as tuber crops, coconut, arecanut, banana etc. The vegetables are found to respond well to K application.

Reactions of potassic fertilizers in the soil

Application of any potassic fertilizer does not change the pH of the soil. When a potassium salt is applied to a soil it is immediately dissolved and undergoes ionization. A portion of K^+ ions remains in the soil solution, another portion gets adsorbed to clay complex by CEC reactions and a third portion is converted into unavailable form.



Hence, in the soil the K will be in the solution, exchangeable and fixed forms. The solution form is readily available and the exchangeable form is slowly and steadily available to plants. The fixed K is unavailable but always in any soil there is a constant equilibrium among these three forms and hence mostly exists no deficiency of K. A small quantity of K is fixed by clays like illite, and this fixation of K depends upon the type of clay, temperature, wetting and drying and soil pH. In this case the fixation is beneficial as it reduces leaching loss and the availability of K will be there for a long time.

Factor affecting K fixation in soils

1. Nature of Colloids

The ability of various soil colloids to fix K varies widely. Kaolinite fixes little, while montmorillonite and illite fix more.

2. Wetting and Drying

When soils containing exchangeable K are alternatively wetted and dried, a large portion of exchangeable K is converted to the less available form.

This has been explained by assuming an entrapment of K ions between contracting structural units when the soil dries some release of the ions thus held occurs upon rewetting but the liberation is slow.

3. Influence of lime

Soils with high degree of base saturation lose less of their exchangeable K by leaching than the soils with a low degree of base saturation. Liming is the common means by which the base saturation of soils is increased and so liming decreased the loss of exchangeable K. The K ions are more readily replaced by calcium.

Application

The K fertilizers are usually applied before the crop is planted or sown, that is the basal dressing. Since the applied K is not lost from the soil either by leaching or by fixation, K fertilizers can be applied well in advance but it is preferable to apply only just before planting. Top dressing with K fertilizers can also be done for vegetables and other crop.

13. SECONDARY AND MICRONUTRIENT FERTILIZERS-Manufacturing of Zinc sulphate and Ferrous sulphate

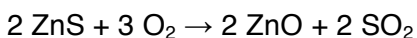
Zinc

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper with an annual production of about 12 million tonnes.[14] The world's largest zinc producer is [Nyrstar](#), a merger of the Australian [OZ Minerals](#) and the Belgian [Umicore](#). [74] About 70% of the world's zinc originates from mining, while the remaining 30% comes from recycling secondary zinc.[] Commercially pure zinc is known as Special High Grade, often abbreviated *SHG*, and is 99.995% pure.

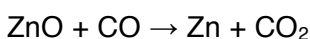
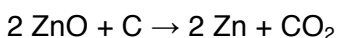
Worldwide, 95% of the zinc is mined from [sulfidic](#) ore deposits, in which sphalerite ZnS is nearly always mixed with the sulfides of copper, lead and iron.[77] There are zinc mines throughout the world, with the main mining areas being China, Australia and Peru. China produced 29% of the global zinc output in 2010.

Zinc metal is produced using [extractive metallurgy](#). [78] After grinding the ore, [froth flotation](#), which selectively separates minerals from [gangue](#) by taking advantage of differences in their [hydrophobicity](#), is used to get an ore concentrate.[78] A final concentration of zinc of about 50% is reached by this process with the remainder of the concentrate being sulfur (32%), iron (13%), and SiO_2 (5%).[78]

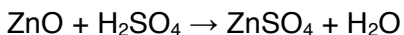
[Roasting](#) converts the zinc sulfide concentrate produced during processing to zinc oxide:[77]



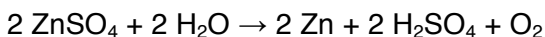
The sulfur dioxide is used for the production of sulfuric acid, which is necessary for the leaching process. If deposits of zinc carbonate, zinc silicate or zinc spinel, like the [Skorpion Deposit](#) in Namibia are used for zinc production the roasting can be omitted. For further processing two basic methods are used: [pyrometallurgy](#) or [electrowinning](#). Pyrometallurgy processing reduces zinc oxide with [carbon](#) or [carbon monoxide](#) at 950°C ($1,740^\circ\text{F}$) into the metal, which is distilled as zinc vapor.[80] The zinc vapor is collected in a condenser.[77] The below set of equations demonstrate this process



Electrowinning processing leaches zinc from the ore concentrate by [sulfuric acid](#)



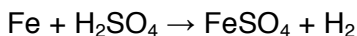
After this step [electrolysis](#) is used to produce zinc metal.[\[77\]](#)



The sulfuric acid regenerated is recycled to the leaching step.

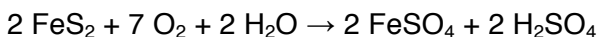
Ferrous Sulfate

In the finishing of [steel](#) prior to plating or coating, the steel sheet or rod is passed through [pickling baths](#) of sulfuric acid. This treatment produces large quantities of iron(II) sulfate as a by-product.[\[2\]](#)



Another source of large amounts results from the production of [titanium dioxide](#) from [ilmenite](#) via the sulfate process.

Ferrous sulfate is also prepared commercially by oxidation of pyrite:



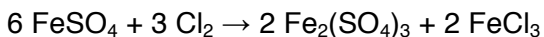
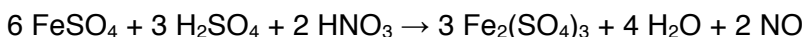
[\[edit\]](#)

Reactions

On heating, iron(II) sulfate first loses its [water of crystallization](#) and the original green crystals are converted into a dirty-yellow anhydrous solid. When further heated, the anhydrous material releases [sulfur dioxide](#) and white fumes of [sulfur trioxide](#), leaving a reddish-brown iron(III) oxide. Decomposition of iron(II) sulfate begins at about 480 °C.

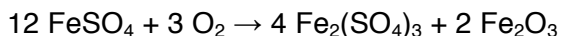


Like all iron(II) salts, iron(II) sulfate is a reducing agent. For example, it reduces nitric acid to nitrogen oxide and chlorine to chloride:



Ferrous sulfate outside [titanium dioxide](#) factory in Kaanaa, [Pori](#).

Upon exposure to air, it oxidizes to form a corrosive brown-yellow coating of basic ferric sulfate, which is an adduct of [ferric oxide](#) and [ferric sulfate](#):



14. Complex fertilizers – manufacturing ammonium phosphates – nitrophosphates and NPK complexes

COMPLEX FERTILIZERS

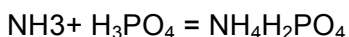
Complex fertilizers is defined as a material containing all three primary, nutrients (N,P and K) and it is also designated as complete complex fertilizers while a fertilizer material containing one or two of the primary nutrient elements (N and P or P and K etc) are known as incomplete complex fertilizers. They are produced by a process of chemical reaction. Most important complex fertilizers are Nitro phosphates & polyphosphate based fertilizers etc

Nitro phosphates

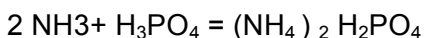
It is a granular fertilizer containing stabilizer which prevents reversion of citrate soluble phosphates to insoluble phosphate. Being granulated it maintains excellent physical condition during storage and handling. Nitrophosphate contains nitrogen and phosphorus in different proportions depending upon the process of manufacture. It also contains easily soluble and readily available $\text{NO}_3\text{-N}$ as well as $\text{NH}_4\text{-N}$. Phosphorus is also present as water soluble as well as citrate soluble forms. All nitrophosphates have less acidic effect on soil compared to other fertilizers.

Ammonium Phosphate

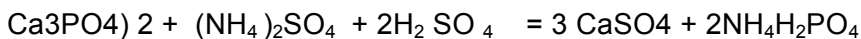
Ammonium phosphate is an incomplete complex fertilizer and both monoammonium and diammonium phosphates are manufactured by the combination of ammonia with H_3PO_4 and also by treating with rock phosphate with H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ as follows:



(Mono-ammonium phosphate)



(Diammonium phosphate)



(Rock phosphate)

The resulting solution contains both nitrogen and phosphorus. The liquid is turned into a granular product in the granulator. The granular product is dried and screened. Product that is too small or too large is recycled to the granulator.

In India, different types of nitrophosphates are manufactured with different chemical reactions and mixing process by different fertilizer company. They marketed the complex fertilizers as their different grades and commercial names. Most important grades of nitrophosphate is 20: 20 : 0 and it means that nitrophosphate contains 20 percent nitrogen. 20 per cent phosphorus and no potassium. Besides these there are various other commercially produced complex fertilizers such as of different grades e.g. 15: 15 : 15: 20: 20 : 20 etc.

Polyphosphate based fertilizers

Ammonium polyphosphate. potassium polyphosphate. zincated poly phosphates etc. are the most popular complex fertilizers that have been recently developed.

Ammonium polyphosphate

It is a complex fertilizer. Although it contains N and P but it contains chiefly phosphorus because polyphosphate is a compound derived from the condensation of two or more phosphoric acids.

Ammonium polyphosphates may be granular and liquid. Different grades of polyphosphates are marketed like 15-62-0; 12-53-0, 15-60-0; etc. as solid or granular and 10-54-0, 11-37-0 as liquid. In addition to these there are Sulphated and Zincated ammonium polyphosphates which are also available in the market to supply secondary and micronutrient to the plant along with nitrogen and phosphorus. So the polyphosphate based different micronutrient fertilizers which acts as slow-release micronutrient are going to be developed recently.

Zincated polyphosphates can also be manufactured with the rock-phosphate containing Zn and polyphosphates and that is also soluble in water and available to plants.

A potassium polyphosphate solution of grade 0-26-26 was produced and this was made by reacting superphosphoric acid and potassium hydroxide and contained a mixture of ortho- pyro-and higher polyphosphates. Solid potassium polyphosphates of grades 0-42-42 to 0-47-47 are also available

When polyphosphatic fertilizers are applied to soils, these are hydrolysed step by step either chemically or biologically to form orthophosphate.

Diammonium phosphate (DAP) (chemical formula $(\text{NH}_4)_2\text{HPO}_4$)

It is one of a series of water-soluble ammonium phosphate salts which can be produced when ammonia reacts with phosphoric acid. DAP is used as a fertilizer and a fire retardant. When applied as plant food, it temporarily increases the soil pH (more basic), but over a long term the treated ground becomes more acidic than before upon nitrification of the ammonium. It is incompatible with alkaline chemicals because its ammonium ion is more likely to convert to ammonia in a high-pH environment.

Product containing diammonium phosphate as essential ingredient with small amount of mono ammonium phosphate

Total nitrogen: x (18-21)%

P₂O₅ soluble in neutral ammonium citrate and water: y (45-53)%

15. Mixed fertilizers – sources – preparations- their compatibility – advantages

Mixed fertilizers

For over hundred years the mixed fertilizers are in use besides straight fertilizers. Many fertilizer mixtures are made available now and this account for a major portion of the consumption of N, P and K. Present day statistics show that numerous grades of fertilizers mixtures are manufactured and the fertilizer mixing industry is being considered as one of the major agro- industry.

The following are some of the common term frequently used in the mixed fertilizer industry.

Fertilizer : The substance which is used for the supply of plant nutrients

Mixed fertilizer : A mixture of more than one straight fertilizer which can supply more than one plant nutrient element

Complete fertilizer : A single fertilizer material containing the entire three major plant nutrients viz, N, P and K

Fertilizer grade : This refers to the minimum guarantee with regard to the nutrient content of the fertilizer mixture in terms of N, P and K.

Fertilizer formula : This related to the quantitative expression of the analysis of the different ingredients included in the mixed fertilizer in terms of N, P and K.

Fertilizer ratio : This indicates the relative percentage of N, P_2O_5 and K_2O in the manure mixture.

Acidic fertilizer : Fertilizer capable of increasing the acidity of the soil by continued applications.

Basic fertilizer : Fertilizers which increase the pH and the soil on continued use by leaving a basic residue in the soil.

Neutral fertilizer : Materials which are neither increasing nor decreasing the pH of the soil

Filler : It is called as the 'make-weight' material added to the fertilizer mixtures. Filler materials are inert materials like sand, saw dust etc, are added to make up the difference between weight of ingredients added to supply the plant nutrients in a tonne and the final weight viz., 1,000 kg.

Advantages

All the three major plant nutrients are made available in one and the same material. There is saving of time and labour. The residual effects will not be there. The fertilizer mixtures are usually prepared taking into account the acidic or alkaline nature of the ingredients, and other chemical reactions. Hence, some of the residual effects like acidity

will not be there. Usually mixed fertilizer are prepared to suit a group of crops and soils.

Disadvantages

- Specific needs of crops and deficiency of individual nutrient elements cannot be satisfied by using mixed fertilizers as efficiently as in the case of straight fertilizers.
- The use of mixed fertilizer in such cases of specific needs will be a waste as other nutrients are also added to the soil.
- Unit cost of the various nutrients contained in the mixed fertilizer will always be higher when compared to the unity cost of nutrients contained in the straight fertilizers.

Improper mixing and storage of fertilizers can result in large nutrient losses. Some important aspects to consider in fertilizer mixing and storage include the following:

- Urea should not be mixed with ammonium calcium nitrate (CAN), KCl, SSP or TSP.
- Urea can be mixed with most other fertilizers but fertilizer mixtures containing urea should be applied immediately after mixing. Do not store fertilizer mixtures containing urea.
- Ammonium phosphates and super phosphates should not be mixed with lime, slag, rock phosphate or CAN.
- Potassium chloride and sulfate of potash can be mixed with most fertilizers, but mixtures of these fertilizers with urea and calcium ammonium nitrate should not be stored.
- CAN should not be mixed with basic slag but can be mixed with urea, single superphosphate, and ammonium phosphates immediately prior to application.

Do not store fertilizers in damp or dirty places. Make sure that bags of fertilizer in the store do not absorb moisture from leaky roofs or water seepage through walls and floors.

Preparation of mixed fertilizers

Many kinds of materials are used in the manufacture of fertilizer mixtures. The materials are found to be highly varying in their properties. However, only a limited number of materials are being used like $(\text{NH}_4)_2\text{SO}_4$, $\text{CO}(\text{NH}_2)_2$, Super phosphate, ammonium phosphate, muriate of potash, limestone, gypsum and some fillers.

The manufacture of fertilizer mixtures usually involves the weighing and proportioning of ingredients that are used, sieving and sizing of the various ingredients, mixing the different materials and packing. All the above operations are done both mechanically and by hand operation. Different kinds of machineries are being used.

Guide for mixing

To determine the amount of individual fertilizer in a mixture, the quantity is calculated as follows.

$$\text{Quantity} = \frac{(\text{Percentage of plant nutrient desired} \times (\text{Weight of final mixture in the mixture}))}{(\text{The Percentage of the plant nutrient in the straight fertilizer})}$$

$$A = \frac{R \times T}{P}$$

R = Percentage in the mixture
 T = Final weight of the mixture
 P = Percentage in the straight fertilizer.

To prepare a mixture of 10: 5: 10 using $(\text{NH}_4)_2\text{SO}_4$, (20% N), Super phosphate (16% P_2O_5) and muriate of potash (60% K_2O), the following quantities will be required per tonne (1,000 kg).

$$1. \text{ Ammonium sulphate} = \frac{10 \times 1000}{20} = 500 \text{ Kg.}$$

$$5 \times 1000$$

$$2. \text{ Super phosphate} = \frac{\quad}{16} = 312.5 \text{ Kg.}$$

$$3. \text{ Muriate of potash} = \frac{10 \times 1000}{60} = 166.5 \text{ Kg.}$$

$$\text{Total} = \underline{979.0 \text{ Kg.}}$$

$$\text{Filler} = 1000 - 979 = 21 \text{ Kg.}$$

If the total calculated weight exceeds the final weight, a mixture of that ratio can not be prepared.

Changes that occur while manufacturing mixed fertilizer

The ingredients used in fertilizer mixtures vary widely in their physical and chemical characteristics. When such widely varying materials in physical and chemical properties are mixed together, naturally many changes are expected to take place during or after the mixing. Some changes will be of physical nature and some will be of chemical nature. The following are the most important physical changes that will take place during or after the mixing of fertilizers.

Hygroscopicity

It is a property of any substance which absorbs from air and gets converted to semi- solid or liquid condition. Fertilizer like $\text{Ca}(\text{NO}_3)_2$, NH_4NO_3 , NaNO_3 and $\text{CO}(\text{NH}_2)_2$ are capable of absorbing moisture from air and become hygroscopic. In such cases handling will be very difficult for such mixtures.

Caking up

Moisture present in some of the ingredients is responsible for caking up. Moisture dissolves some of the easily soluble ingredients and forms a saturated solution. This saturated solution on evaporation gives out crystals which knit together forming larger lumps.

The caking up can be prevented by the use of certain kind of materials called as 'conditioners'. The commonly used conditioners are groundnut hulls, lime, clay etc. Another way of preventing the caking up is manufacture of granulated fertilizer mixture.

The granulation aims at preparation of uniform sized particles with reasonable stability, which presents caking up.

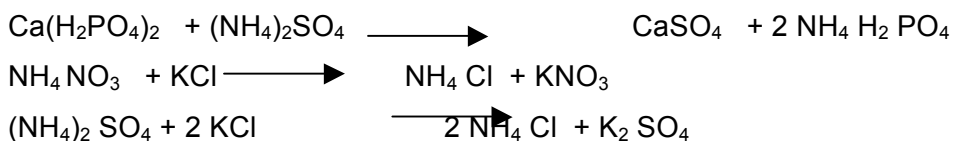
Segregation

This relates to separation of different sized particles individually. When ingredients of different sizes and densities are included there will be the tendency for the segregation (sorting out to different sizes) to take place. To prevent this bad effect, granulation is conveniently followed.

The following are some of the most important chemical changes that take place either during or after the manufacture of fertilizers mixtures. These changes are found to be influenced by temperature, moisture content and particle size of the ingredients.

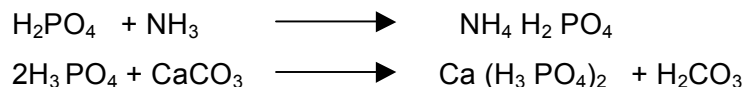
(a) Double decomposition

The reaction is between two compounds without a common ion in the presence of moisture. New compounds are formed which may have different physical and chemical properties.



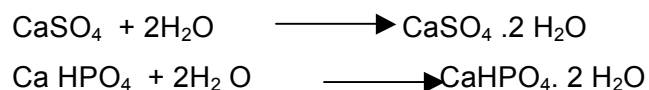
(b) Neutralization

This reaction takes place when free acids present in some of the fertilizers are neutralized by alkalis or Ca containing salts included in the mixture.



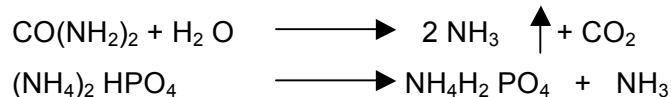
(c) Hydration

The process of tying up of water by the anhydrous form of salts is called hydration. Some of the fertilizers are found to have this property.



(d) Decomposition

Under certain conditions of moisture and temperature, there will be break down in the composition of molecules forming new compounds.



However, the following important principles must be taken into consideration while preparing mixed fertilizers.

1. All fertilizers containing ammonia are not mixed directly with the basic fertilizers (e.g. RP, limestone, basic slag, CaCN_2) as reaction will take place resulting in the loss of gaseous NH_3 .
2. The water – soluble phosphates are not mixed with those materials which contain free lime (e.g) lime stone, CaCN_2) as there will be reaction towards the reversing of water – soluble phosphate to water – insoluble phosphates.
3. Hygroscopic fertilizers are not included as they will facilitate caking up.
4. The acidic fertilizers are likely to produce some free acids which may damage the container or packing materials.

Manufacturing process

The principal steps in the manufacture of solid mixed fertilizers are calculating, weighing, sieving, sizing, mixing the materials and packing the product.

Calculating and weighing

With a good weighing device the calculated quantities of the various ingredients are weighed accurately for preparing mixtures.

(1) Sieving and sizing

If the raw materials have undergone too much of caking in the storage piles, it may be necessary to subject them to preliminary grinding, sieving and sizing. The raw materials must be converted into uniform sized particles to have effective making and to avoid segregation during subsequent handling.

(2) Mixing

Many kinds of fertilizer mixing machines have been proposed and used at present. Rotary drum type is found to be more common than the vertical cylinder type. Weighed quantities of different materials are introduced into the mixer and mixed thoroughly.

(3) Packing

Equipments for packing fertilizer mixture range from the simplest types of hand operated facilities to highly sophisticated automatic machines.

Granular mixtures

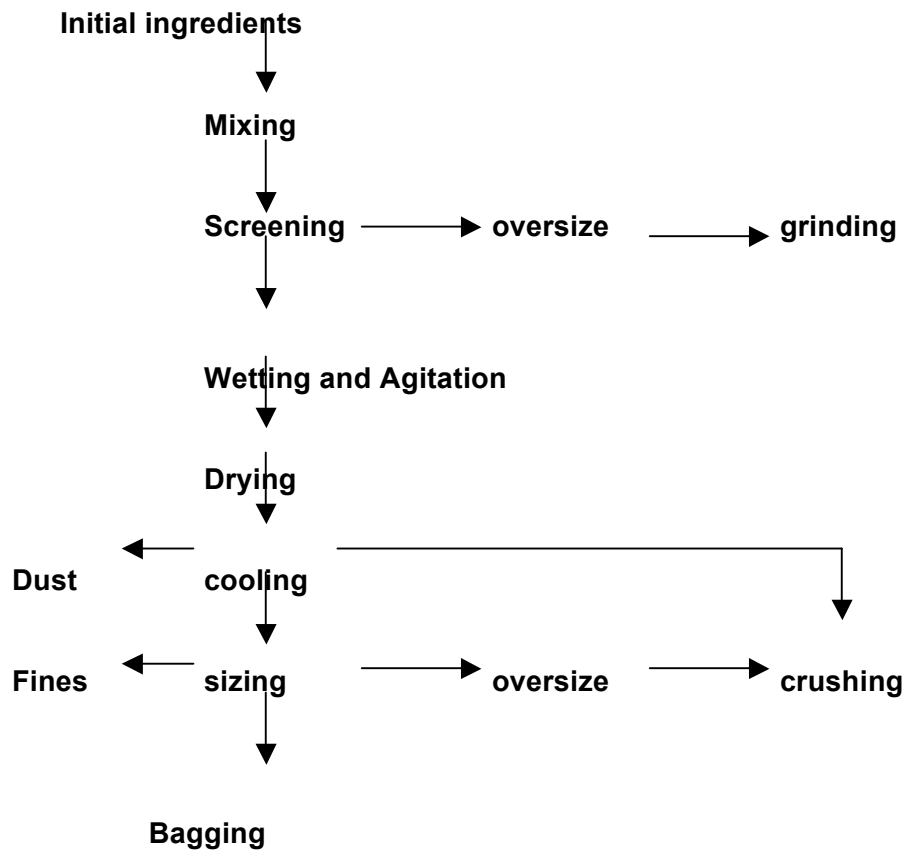
Compared to pulverized or powdered mixture, the advantages of granular mixtures are reduced caking up tendency, less dusting loss and easy handling. Of late, attention is found in the manufacture of only granular mixtures.

Ingredients used in mixtures

Different types of materials are used for the manufacture and they can be roughly classified according to the main functions they serve in the fertilizer mixture.

(i) Supplier of plant nutrients

Various sources supplying the plant nutrients used according to the requirement and availability of the raw materials. The selection of the different materials will be based mainly on the prices of the various fertilizers.



(ii) Conditioners

To avoid caking up and other bad physical changes during or after mixing, some materials are added to have a better physical condition. Usually low – grade organic materials are added to reduce the caking up property, tobacco stem, groundnut hull; paddy husk and peat are commonly used as conditioners. A maximum of 50kg/ tonne is used as conditioner.

(iii) Neutralizer

If acidic fertilizer likes $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and urea are used, the mixture may be acidic or the acidity may be formed due to the interaction between the various fertilizers used. To neutralize this acidity a basic material like dolomitic limestone is added. The material is designated as neutralizers of residual acidity in the fertilizer mixture.

(iv) Filler

A filler is a 'make –weight' material added to a fertilizer mixture. It is added to make up the difference between the weight of the added fertilizer required to supply the plant nutrients and the desired quantity of fertilizer mixture usually, the filler are inert materials like sand and sawdust which are commonly used. This must be usually less than 50 kg per tonne of mixture.

Unit value

The unit value of a fertilizer or manure is the cost of that quantity of material capable of supplying one per cent of the plant food ingredient in one tonne of the material. The cost per unit is arrived at by dividing the cost per tonne by the percentage of nutrient contained in it. For example, if the cost of a tonne of ammonium sulphate is Rs.300/- then the unit value is $300/20 = \text{Rs.}15/-$. From the unit value it is possible to evaluate the relative value of any fertilizer or mixture.

BIOFERTILIZERS

Biofertilizers are defined as preparations containing living cells or latent cells of efficient strains of microorganisms that help crop plants uptake of nutrients by their interactions in the rhizosphere when applied through seed or soil. They accelerate certain microbial processes in the soil which augment the extent of availability of nutrients in a form easily assimilated by plants.

Use of biofertilizers is one of the important components of integrated nutrient management, as they are cost effective and renewable source of plant nutrients to supplement the chemical fertilizers for sustainable agriculture. Several microorganisms and their association with crop plants are being exploited in the production of biofertilizers. They can be grouped in different ways based on their nature and function.

I. N₂ fixers

- a. Free living : Aerobic – *Azotobacter*, *Beijerinckia*, *Anabaena*
Anaerobic – *Clostridium*
Faultative anaerobic – *Klebsiella*
- b. Symbiotic : *Rhizobium*, *Frankia*, *Anabaena azollae*
- c. Associative symbiotic : *Azospirillum*
- d. Endophytic : *Gluconacetobacter*
Burkholdria

II. Phosphorus solubilizers

- Bacteria : *Bacillus megaterium* var. *phosphaticum*
B. subtilis, *B. circulans*
Pseudomonas striata
- Fungi : *Penicillium* sp.
Aspergillus awamori

III. P mobilizers

- a) AM fungi
 - b) Ectomycorrhizal fungi
 - c) Ericoid Mycorrhiza
 - d) Orchid mycorrhiza
- IV. Silicate and Zinc solubilizers: *Bacillus* sp,
- V. Plant growth promoting Rhizobacteria: *Pseudomans spp.*, and many more

Importance of Biofertilizers

Biofertilizers are known to make a number of positive contributions in agriculture.

- Supplement fertilizer supplies for meeting the nutrient needs of crops.
- Add 20 – 200 kg N/ha (by fixation) under optimum conditions and solubilise/mobilise 30-50 kg P₂O₅/ha.
- They liberate growth promoting substances and vitamins and help to maintain soil fertility.
- They suppress the incidence of pathogens and control diseases.
- Increase the crop yield by 10-50%. N₂ fixers reduce depletion of soil nutrients and provide sustainability to the farming system.
- Cheaper, pollution free and based on renewable energy sources.
- They improve soil physical properties, tilth and soil health.

1. Rhizobium

Rhizobia are soil bacteria, live freely in soil and in the root region of both leguminous and non-leguminous plants. However they enter into symbiosis only with leguminous plants, by infesting their roots and forming nodules on them. Non legume nodulated by Rhizobia is *Trema* or *Parasponia* sp.

The nodulated legumes contribute a good deal to the amount of N₂ fixed in the biosphere, (50-200 kg N/ha) varied with crops.

Clover - 130 kg N/ha

Cowpea - 62 – 128 kg N/ha

Beijerinck first isolated and cultivate a microorganism from the roots of legumes in 1888 and he named this as *Bacillus radicola* and latter modified as *Rhizobium*.

Legume plants fix and utilise this N by working symbiotically with *Rhizobium* in nodules on their roots. The host plants provide a home for bacteria and energy to fix atmospheric N₂ and in turn the plant receives fixed N₂ (as protein).

Cross inoculation group (CGI)

It refers the group of leguminous plant that will develop nodules when inoculated with the rhizobia obtained from the nodules from any member of that legume group.

Genera/species	Principal and other reported hosts
<i>Rhizobium</i>	
<i>R. etli</i>	<i>Phaseolus vulgaris</i> , <i>Mimosa affinis</i>

<i>R.galegae</i>	<i>Galega orientalis, G.officinalis</i>
<i>R.gallicum</i>	<i>Phaseolus vulgaris, Leucaena, Macroptilium, Onobrychis</i>
<i>R.giardini</i>	<i>Phaseolus vulgaris, Leucaena, Macroptilium</i>
<i>R.hainanense</i>	<i>Desmodium sinuatum, Stylosanthes, Vigna, Arachis, Centrosema</i>
<i>R.huautlense</i>	<i>Sesbania herbacea</i>
<i>R.indigoferae</i>	<i>Indigofera</i>
<i>R.leguminosarum</i> <i>bv trifolii</i> <i>bv viciae</i> <i>bv.phaseoli</i>	<i>Trifolium</i> <i>Lathyrus, Lens, Pisum, and Vicia,</i> <i>Phaseolus vulgaris</i>
<i>R.mongolense</i>	<i>Medicago ruthenica, Phaseolus vulgaris</i>
<i>R.sullae</i>	<i>Hedysarum coronarium</i>
<i>R.tropici</i>	<i>Phaseolus vulgaris, Dalea, Leucaena, Macroptilium, Onobrychis</i>
Mesorhizobium	
<i>M.amorphae</i>	<i>Amorpha fruticosa</i>
<i>M.chacoense</i>	<i>Prosopis alba</i>
<i>M.ciceri</i>	<i>Cicer arietinum</i>
<i>M.huakuui</i>	<i>Astragalus sinicus, Acacia</i>
<i>M.loti</i>	<i>Lotus corniculatus</i>
<i>M. mediterraneum</i>	<i>Cicer arietinum</i>
<i>M.plurifarium</i>	<i>Acacia senegal, Prosopis juliflora, Leucaena</i>
<i>M.tianshanense</i>	<i>Glycyrrhiza pallidiflora, Swansonia, Glycine, Caragana, Sophora</i>
Sinorhizobium	
<i>S.abri</i>	<i>Abrus precatorius</i>
<i>S.americanus</i>	<i>Acacia spp.</i>
<i>S.arboris</i>	<i>Acacia senegal, Prosopis chilensis</i>
<i>S.fredi</i>	<i>Glycine max</i>
<i>S.indiaense</i>	<i>Sesbania rostrata</i>
<i>S.kostiense</i>	<i>Acacia senegal, Prosopis chilensis</i>
<i>S.kummerowiae</i>	<i>Kummerowia stipulacea</i>
<i>S.meliloti</i>	<i>Medicago, Melilotus, Trigonella</i>

<i>S.medicae</i>	<i>Medicago truncatula, M. polymorpha, M.orbicularis</i>
<i>S.morelense</i>	<i>Leucaena leucocephala</i>
<i>S.sahelense</i>	<i>Acacia, Sesbania</i>
<i>S.terangae</i>	<i>Acacia, Sesbania</i>
Azorhizobium	
<i>A.caulinodans</i>	<i>Sesbania rostrata</i>
Allorhizobium	
<i>A.undicola</i>	<i>Neptunia natans, Acacia, Faidherbia, Lotus</i>
Bradyrhizobium	
<i>B.elkanii</i>	<i>Glycine max</i>
<i>B.japonicum</i>	<i>Glycine max</i>
<i>B.liaoningense</i>	<i>Glycine max</i>
<i>B.yuanmingense</i>	<i>Lespedeza, Medicago, Melilotus</i>

Description and characteristics

Classification

1. Family : Rhizobiaceae
2. Genus : *Azorhizobium*-for stem nodulation
Bradyrhizobium
Rhizobium
Sinorhizobium

Morphology

1. Unicellular, cell size less than 2µ wide, short to medium rod, pleomorphic.
2. Motile with Peritrichous flagella
3. Gram negative
4. Accumulate PHB granules.

Physiology

1. Nature : Chemoheterotrophic, symbiotic with legume
2. C source : Supplied by legume through photosynthates, monosaccharides, disaccharide
3. N source : Fixed atmospheric N₂

4. Respiration : Aerobic
5. Growth : Fast (*Rhizobium*), slow (Bradyrhizobium)
6. Doubling time : Fast growers – 2-4 hrs
Slow growers – 6-12 hrs
7. Growth media : YEMA

Contribution

1. Direct contribution of N symbiotically with legumes.
2. Residual nitrogen benefit for the succeeding crop.
3. Yield increase is by 10-35%.
4. Improve soil structure.
5. Produces exopolysaccharides.
6. Produces plant growth hormone.

Recommended for legumes (Pulses, oilseeds, fodders)

Promising strains: NGR 6, NC 92, CC 1, CRR 6, CRU 14, COBE 13.

2. Azotobacter

It is a free living N_2 fixer, the cells are not present on the rhizoplane, but are abundant in the rhizosphere region. It is classified under the family Azotobacteriaceae. It requires more of organic matter and depend on the energy derived from the degradation of plant residues. Beijerinck was the first to isolate and describe *Azotobacter*.

Species

Cell size, flagellation, pigmentation and production of extracellular slime are considered as diagnostic features of these bacteria in distinguishing species.

- A. chroococcum* : Black to brown insoluble pigment.
- A. vinelandii*, *A. paspali*, *A. agilis* : Green fluorescent and soluble pigments
- A. beijerinckii* : Yellow to light brown insoluble pigments
- A. macrocytogenes* : Pink soluble pigments
- A. insignis* : Yellow brown pigments

Azotobacter cells are polymorphic, gram negative, form cyst and accumulate Poly Beta hydroxy butyric acid and produces abundant gum.

Morphology

Cell size	:	Large ovoid cells, size 2.0 – 7.0 x 1.0 – 2.5 μ
Cell character	:	Polymorphic
Gram character	:	Negative

Physiology

1. Nature	:	Chemoheterotrophic, free living
2. C source	:	Mono, di saccharides, organic acids
3. N source	:	N ₂ through fixation, amino acids, NH ₄ ⁺ , NO ₃ ⁻
4. Respiration	:	Aerobic
5. Growth	:	Ashby / Jensen's medium
6. Doubling time	:	3 hours

Benefits

- Ability to fix atmospheric N₂ – 20-40 mg BNF/g of C source in laboratory equivalent to 20-40 kg N/ha.
- Production of growth promoting substances like vitamin B, Indole acetic acid, GA.
- Ability to produce thiamine, riboflavin, pyridoxin, cyanogobalanine, nicotinic acid, pantothenic acid, etc.
- Biological control of plant diseases by suppressing *Aspergillus*, *Fusarium*.
 - Recommended for Rice, wheat, millets, cereals, cotton, vegetables, sunflower, mustard and flowers.

3. Azospirillum

Azospirillum was I isolated by Beijerinck (1922) in Brazil from the roots of *Paspalum* and named it as *Azotobacter paspali* and later named as *Spirillum lipoferum*. Dobereiner and Day (1976) reported the nitrogen fixing potential of some forage grasses due to the activity of *S. lipoferum* in their roots. Dobereiner coined the term "**Associative symbiosis**" to denote the occurrence of N₂ fixing *spirillum* in plants. Taxonomy was re-examined and Tarrand *et al.* (1978) designated this organism as *Azospirillum*.

It is an aerobic or micro aerophilic, motile, gram negative bacterium. Non spore former and spiral shaped bacterium, inhabiting the plant roots both externally and internally. Being a micro aerophilic organism, it can be isolated on a semi solid malate medium by enrichment procedures.

Classification

Species: (7) Family – *Spirillaceae*

1. *A. brasilense*
2. *A. lipoferum*
3. *A. amazonense*
4. *A. halopraeferens*
5. *A. irkense*
6. *A. dobereineriae*
7. *A. largimobilis*

Morphology

1. Cell size : Curved rods, 1 mm dia, size and shape vary
2. Accumulate : PHB
3. Gram reaction : Negative
4. Development of white pellicles : 2-4 mm below the surface of NFB medium

Physiology

1. Nature : Chemoheterotrophic, associative
2. Sole carbon source : Organic acids, L-arabinose, D-gluconate, D-fructose, D-glucose, sucrose, Pectin
3. N source : N_2 through fixation, amino acids, N_2 , NH_4^+ , NO_3^-
4. Respiration : Aerobic, Microaerophilic
5. Growth media : NFBTB (NFB) medium
6. Doubling time : 1 hr in ammonia containing medium
5.5 – 7.0 hrs in malate containing semisolid medium

Mechanism of Action

1. Contribution by BNF
2. Production of PGP substances by bacteria
 - Increases root hair development, biomass.

3. Production of PGP substances by plant
 - Morphological changes in root cells.
 - Increased activity of IAA oxidase
 - Increase in endogenous IAA
 - Increased mineral and water uptake, root development, vegetative growth and crop yield.
4. Competition in the rhizosphere with other harmful microorganism.
5. Polyamines and amino acids production.
6. Increased extrusion of protons and organic acids in plants.

Benefits

1. Promotes plant growth.
2. Increased mineral and water uptake, root development, vegetative growth and crop yield.
3. Inoculation reduced the use of chemical fertilizers (20-50%, 20-40 kg N/ha)
4. Increases cost benefit ratio.
5. Reduces pathogen damage.
6. Inhibit germination of parasitic weeds.
7. Restoration of arid zone, margine mangrove ecosystem.
8. Reduces humic acid toxicity in compost.
 - Recommended for rice, millets, maize, wheat, sorghum, sugarcane and co-inoculant for legumes.

4. *Gluconacetobacter diazotrophicus*

It is an endophytic N₂ fixer and form to occur on large numbers in roots, stem and leaf of sugarcane and other sugar rich crops. It was first isolated from sugarcane. Cavalcanti and Dobereiner (1988) reported this new endophytic N₂ fixer and recently called as from *G. diazotrophicus*. It can tolerate upto 30% sucrose concentration and pH upto 3.0. Optimum sucrose concentration is 10-15%.

Produce surface yellow pellicle on semisolid medium. Does not grow at pH 7.0. Optimum is 5.5.

Benefits

- Fixes atmospheric N₂
- Production of PG hormones (GA, DAA is double than *Azospirillum*).
- Suitable for sugar rich crops with acidic pH.

5. Azorhizobium

These genera can produce stem nodules. Stem nodulation has been reported in 3 genera of legumes: *Aeschynomene*, *Neptunia* and *Sesbania*.

Stem nodulating *Rhizobium* comprises both fast and slow growing types having the generation time of 3-4 hr and 10 hrs respectively. Those nodulate *Aeschynomene* can cross inoculate with *S. rostrata* strains *Azorhizobium caulinodans*.

- fix N_2 in free living conditions without differentiating into bacteroids.
- have O_2 protection mechanisms, to fix N_2 under free living conditions.
- Mode of entry is through lateral root cracks. No infection thread is formed during colonization.
- Form both stem and root nodules in *S. rostrata*.
- Gram negative, motile rods.
- Produces root nodules in rice, wheat.

6. Algal Biofertilizers

The agronomic potential of cyanobacterial N_2 fixation in rice fields was recognised in India during 1939 by De who attributed the natural fertility of tropical rice fields to N_2 fixing blue green algae. The rice field ecosystem provides an environment favourable for the growth of blue green algae with respect to their requirements for light, water, high temperature and nutrient availability.

Algal biofertilizers constitutes a perpetual source of nutrients and they do not contaminate ground water and deplete the resources. In addition to contributing 25-30 kg N ha^{-1} of biologically fixed N_2 , they can also add organic matter to the soil, excrete growth promoting substances, solubilises insoluble phosphates and amend the physical and chemical properties of the soil.

Blue green algae are a group of prokaryotic, photo synthetic microscopic plants, vigorously named as Myxophyceae, Cyanophyceae and Cyanobacteria. They show striking morphological and physiological similarities like bacteria and hence called as cyanobacteria.

Cyanobacteria

They are the photosynthetic bacteria and some of them are able to fix N_2 . They can be divided into two major groups based on growth habit.

- a) Unicellular forms and
- b) Filamentous forms.

N_2 fixing species are from both groups, found in paddy fields, but the predominant ones are the heterocystous filamentous forms.

Cyanobacteria are not restricted to permanently wet habitats, as they are resistant to desiccation and hot temperatures, and can be abundant in upland soils. However wet paddy soils and overlying flood waters provide an ideal environment for them to grow and fix N₂.

Natural distribution

BGA are cosmopolitan in distribution and more widely distributed in tropical zone. Free living cyanobacteria can grow epiphytically on aquatic and emergent plant as well as in flood water or on the soil surface. Heterocystous cyanobacteria formed less than 10% of the population of eukaryotic green algae and the abundance increased with the amount of available phosphorus and with the pH value over the range 4 – 6.5. In rice soil, population ranges from 10 – 10⁷ cfu g⁻¹ soil.

The main taxa of N₂ fixing cyanobacteria

Group	Genera	DNA (mol % GC)
Group-I. Unicellular: single cells or cell aggregates	<i>Gloeotheca</i> , <i>Gloeobacter</i> , <i>Synechococcus</i> , <i>Cyanothece</i> , <i>Gloeocapsa</i> , <i>Synechocystis</i> , <i>Chamaesiphon</i> , <i>Merismopedia</i>	35-71
Group-II. Pleurocapsalean: reproduce by formation of small spherical cells called baeocytes produced through multiple fission .	<i>Dermocarpa</i> , <i>Xenococcus</i> , <i>Dermocarpella</i> , <i>Pleurocapsa</i> , <i>Myxosarcina</i> , <i>Chroococcidiopsis</i>	40-46
Group-III. Oscillatorian: filamentous cells that divide by binary fission in a single plane.	<i>Oscillatoria</i> , <i>Spirulina</i> , <i>Arthrospira</i> , <i>Lyngbya</i> , <i>Microcoleus</i> , <i>Pseudanabaena</i> .	40-67
Group-IV. Nostocalean: filamentous cells that produce heterocysts	<i>Anabaena</i> , <i>Nostoc</i> , <i>Calothrix</i> , <i>Nodularia</i> , <i>Cylinodrosperum</i> , <i>Scytonema</i>	38-46
Group-V. Branching: cells divide to form branches	<i>Fischerella</i> , <i>Stigonema</i> , <i>Chlorogloeopsis</i> , <i>Hapalosiphon</i>	42-46

The N₂ fixing forms generally have a specialized structure known as heterocyst. The BGA have minimum growth requirement needing only diffused light, simple inorganic

nutrients and moisture. The heterocysts which are modified vegetative cells, because of their thick walls and absence of photosystem II in photosynthesis, act as ideal sites for N_2 fixation under aerobic conditions. Although the nitrogenase is present in vegetative cells, it remains inactive because of the presence of oxygenic photosynthesis. They built up natural fertility (C, N) in soil.

N_2 fixing BGA: *Anabaena*, *Nostoc*, *Cylindrospermum*, *Tolypothrix*, *Calothrix*, *Scytonema*, *Westiellopsis* belonging to orders Nostocales and Stignematales. Many non-heterocystous forms are also fix N_2 . eg: But need microaerobic or anaerobic conditions. *Gleocapsa* fix in aerobic condition.

The species of BGA, known to fix atmospheric N_2 are grouped as 3 groups.

- (i) Heterocystous – aerobic forms
- (ii) Aerobic unicellular forms
- (iii) Non-heterocystous, filamentous, micro aerophilic forms.

The blue green algal culture's composite inoculum consists of *Nostoc*, *Anabaena*, *Calothrix*, *Tolypothrix*, *Plectonema*, *Aphanotleca*, *Gleocapsa*, *Oscillatoria*, *Cylindrospermum*, *Aulosira* and *Scytonema*.

Contributions of algal biofertilizer

- Important component organic farming.
- Contribute 20 – 25 kg N ha⁻¹.
- Add organic matter to the soil.
- Excrete growth promoting substances.
- Solubilize insoluble phosphates.
- Improve fertilizer use efficiency of crop plants.
- Improve physical and chemical properties of soil.
- Reduce C:N ratio.
- Increase the rice yield by 25-30%.
- Cyanobacteria are more compatible with nitrate N than ammonium N.

It increases FUE of the crop plants through exudation of growth promoting substances and preventing a part of applied fertilizer N from being lost.

Phosphobacteria and Mycorrhizae

I. Phosphate solubilising Microorganisms

Introduction

Though most soils contain appreciable amounts of inorganic P, most of it being insoluble forms, cannot be utilized by crops unless they are solubilized. Soils also contain organic P that could not be utilized by plants only when it is mineralized. Phosphate solubilizing microorganisms not only able to solubilize insoluble forms of inorganic P but are also capable to mineralize organic forms of P, thus improving the availability of native soil P making their P available to plants. PSM can also solubilize P from rock phosphate (RP), slag or bone meal making their P available to plants.

Thus PSM biofertilizer being economical and environmentally safe offers a viable alternative to chemical fertilizers.

Microorganisms involved

Many microorganisms can solubilize inorganic phosphates, which are largely unavailable to plants. Microbial involvement in solubilization of inorganic phosphate was first shown by Stalstron (1903) and Sacket *et al.* (1908) gave conclusive evidence for bacterial solubilization of RP, bonemeal and TCP.

Various bacteria and fungi reported to solubilize different types of insoluble phosphates. Not only solubilizes but also mineralize organic P compounds and release orthophosphates.

In general PSM constitute 0.5 – 1.0% of soil microbial population with bacteria and out numbers the fungi by 2 – 150 folds. But bacteria may lose the P solubilizing ability while sub culturing and fungi do not lose. Among bacteria, aerobic spore forming bacteria are more effective P solubilizers.

Mechanism of PO_4 solubilization

Different mechanisms were suggested for the solubilization of inorganic phosphates.

- Production of organic acids
- Chelating effect
- Production of inorganic acids
- Hydrogen sulphide production (H_2S)
- Effect of carbon dioxide
- Proton extrusion
- Siderophore production

Siderophores, bind iron tightly to prohibit its reaction with soluble phosphate and rather help release PO_4 fixed as ferric phosphate. It is important in acid soils, where ferric PO_4 is one of the major forms.

The extent of PO_4 solubilization depends on the type of organisms involved. The genus *Bacillus* showed maximum activity followed by *Penicillium* and *Aspergillus*. *Streptomyces* was least effective.

A. awamori & *A. niger*, *Bacillus polymixa* & *Penicillium striata* are effective in solubilization of phosphate solubilization

II. Mycorrhizae

Mycorrhiza (fungus root) is the mutualistic association between plant roots and fungal mycelia. Frank (1885) gave the name "*mycorrhiza*" to the peculiar association between tree roots and ectomycorrhizal fungi. 95% of the plant species form mycorrhizae. It can act as a critical linkage between plant roots and soil. This association is characterized by the movement of plant produced carbon to fungus and fungal acquired nutrients to plants. Mycorrhizal fungi are the key components of the rhizosphere are considered to have important roles in natural and managed ecosystems.

Types of mycorrhiza

Mycorrhizal associations vary widely in structure and function. Two main groups of mycorrhizae are recognized; the ectomycorrhizae and endomycorrhizae, although the rare group with intermediate properties, the ectendotrophic mycorrhizae.

1. Ectomycorrhiza

The fungal hyphae form a mantle both outside the root and within the root in the intercellular spaces of the epidermis and cortex. No intracellular penetration into epidermal or cortical cells occurs, but an extensive network called the Hartignet is formed between these cells. Sheath or Mantle increases the surface area of absorbing roots and offers protection to the roots. Hartignet can act as storage and transport organ for P.

Ectomycorrhizae are common on trees, including members of the families pinaceae (Pin, Fir, Spruce, Larch, Semlock), Fagaceae (Willow, Poplar, Chesnut), Betulaceae (Birch, Alder), Salicaceae (Willow, Poplar) and Myrtaceae.

The fungi forming Ectomycorrhizal association are coming under Basidiomycotina and Ascomycotina. eg: *Laccaria laccata*, *Suillus*, *Rhizopogan*, *Amanita*

2. Endomycorrhizae

Endomycorrhizae consist of three sub groups, but by far the most common are the Arbuscular Mycorrhizal fungi. Fungi under AM are the members of Endogonaceae and they produce an internal network of hyphae between cortical cells that extends out into the soil,

where the hyphae absorb mineral salts and water. This fungus do not form an external mantle but lives within the root. In all forms, hyphae runs between and inside the root cells which includes,

- Ericoid mycorrhiza - Associated with some species of Ericaceous plants
- Orchid mycorrhiza - associated with orchid plants
- Arbuscular mycorrhiza - associated with most of the plant families

Arbuscular Mycorrhizal fungi

The most important one is AM

AM, an endomorphie mycorrhizae formed by the aseptate phycomycetous fungi are associated with majority of agricultural crops, growing under broad ecological range.

Class : Zygomycotina

Order : Endogonales

Family : Endogonaceae

150 species of AMF are known.

Colonization Process

Roots do not show visual morphological changes due to AM colonization. AM fungal infection into a host occurs by germination of spore, hyphal growth through soil to host roots, penetration of host roots and spread of infection inter and intracellularly in the root cortex. Colonization occurs under two phases: (1) Extra matrical phase and (2) Intra radical phase.

Extra matrical phase: Events occurring outside the root after the germination of chlamydospores. Mycelium explores larger soil volume. Fungal growth can be 80-130 times the length of root. Extra matrical hyphae (EMH) are larger in diameter than inner hyphae. Once the fungus recognises the plant, appresorium is formed in the host roots and penetration occurs via the appresorium. EMH ends with resting spores in soil.

Intra radical phase: Events occurring inside the root cortex. After penetrating the cortex, the fungus may produce intercellular as well as intracellular hyphae in the cortical cells. Forms two morphological structures namely arbuscules and vesicles inside the cortical cells.

Arbuscules: are the first formed structures after the hyphal entry into the cortical cells. Arbuscules are the fine dichotomously branched hyphal filaments look like little trees. Arbuscules start to form approximately 2 days after penetration. They are considered as the

major site of exchange between the fungus and host root. They are short lived (4-13 days) and degenerate.

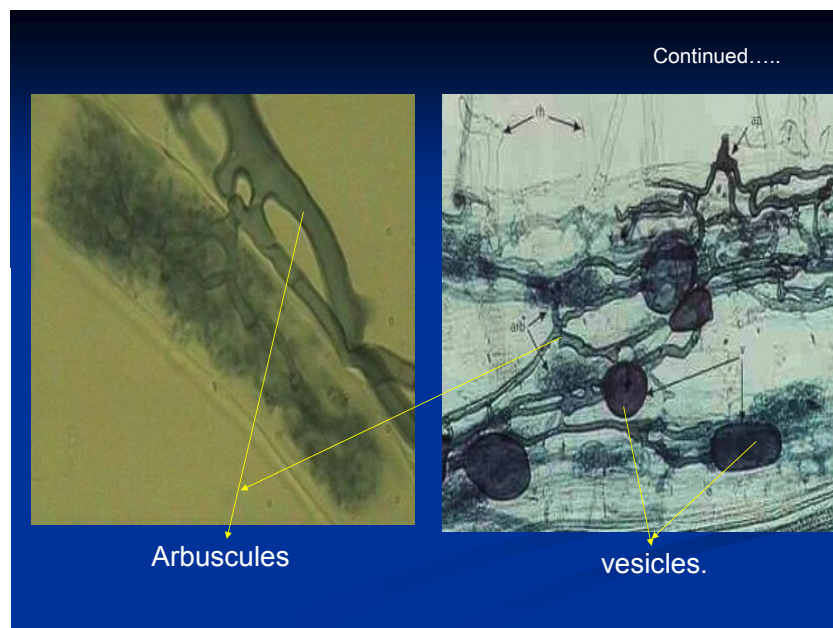
Vesicles: Following the formation of arbuscules, some species of fungi also form vesicles in the roots. Terminal or intercalary hyphal swellings of the hyphae called vesicles. Vesicles contain lipids and cytoplasm. They act as P storage organ and they ever be present in the root. Size of the vesicles is about 30-100 μm . In vesicles P can be accumulated as polyphosphates.

EMH, vesicles and Arbuscules play a key role in nutrient transfer particularly in mobilisation of phosphorus.

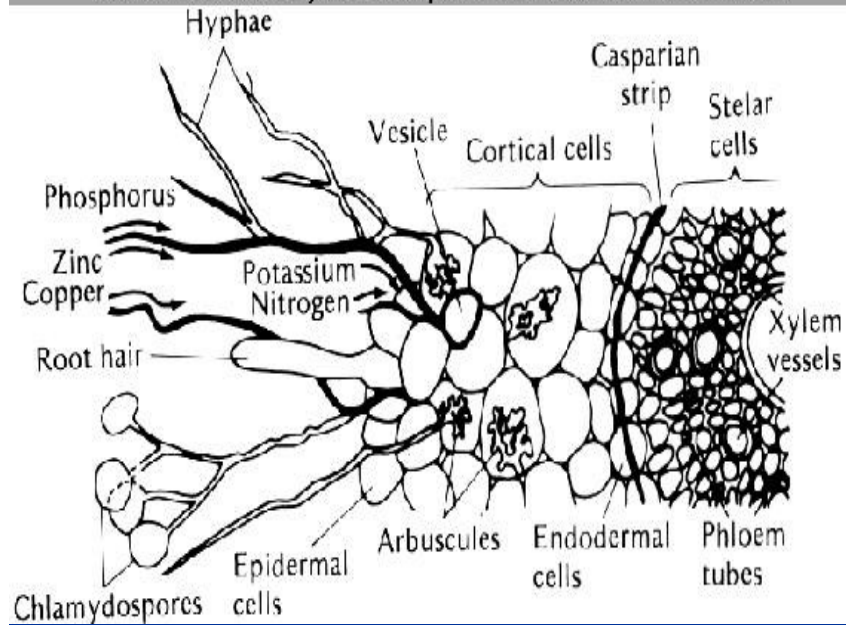
Mechanism of action

The beneficial effect on plant growth and yields following inoculation with VAM is attributed to

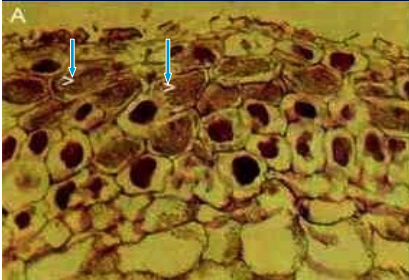
- (i) improved mineral nutrition, especially P (P, Zn, Cu, K, S, NH_4)
- (ii) Mobilization of nutrients through greater soil exploration.
- (iii) Protection of host roots against pathogen infection.
- (iv) Improved water relation
- (v) Better tolerance to stress like salinity, heavy metal pollution
- (vi) Protection against transplantation shock.



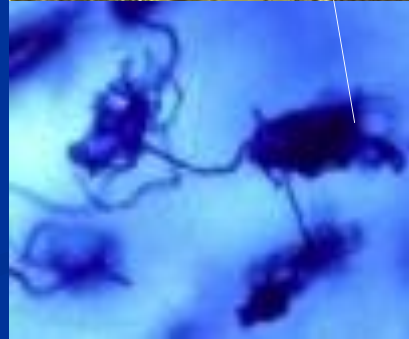
Vesicular arbuscular mycorrhizae - penetrate between cells and into cells

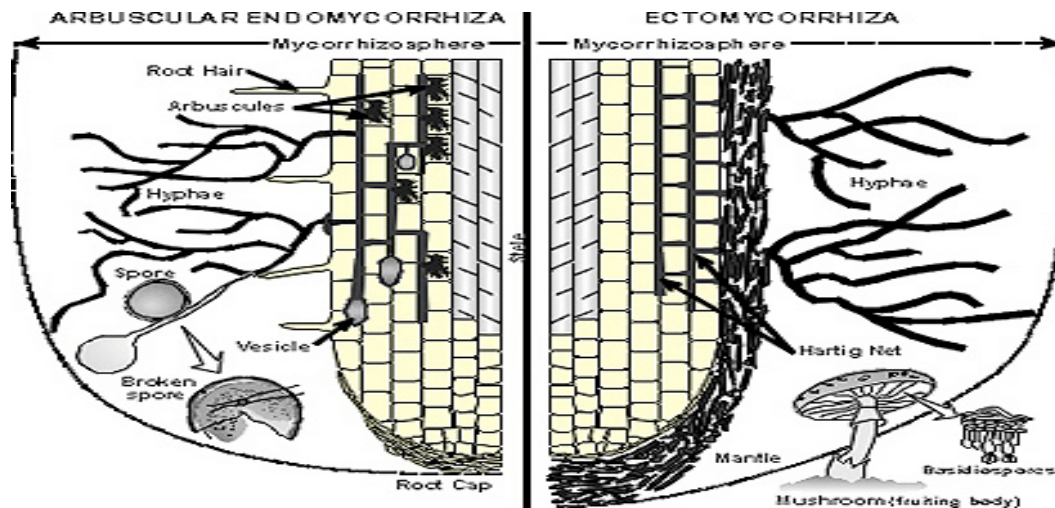


stained masses of fungal hyphae (arrowheads).



cells of the orchid are filled with coils of fungal hyphae





Reasons for Enhanced P uptake by AM Fungi

- Physical exploration of soil.
- Higher affinity towards P
- Lower threshold concentration
- Rhizosphere modification
- Differences in anion and cation absorption due to exudation pattern.
- Siderophore production.
- Selective stimulation of microorganisms in the rhizosphere.
- Increased hyphal area for absorption (EMH).
- Absorb and transport P beyond the depletion zone around the root.
- P absorption by EMH is 1000 times faster than normal hyphae and 3-4 times greater.

Disease resistance

- Resist the parasitic invasion and minimises the loss.
- Mycorrhizal roots harbour more actinomycetes.
- Mycorrhizal roots have elevated levels of phenols, while offers resistance to fungal hydrolytic enzymes.
- Mycorrhizal infection stimulates biosynthesis of phytoalexins.

18. IMPACT OF FERTILIZERS ON THE ENVIRONMENT

Fertilizer is one of the major contributors to increased crop production. Recently, concern has been expressed that over-reliance on mineral fertilizers may cause unsustainable environmental penalties like eutrophication of surface water, nitrate (NO_3^-) pollution of groundwater, heavy metal pollution of soil, atmospheric pollution due to emission of nitrous oxide and ammonia, acid rain, etc. Though there are incidences of these problems in several parts of the world, very few of such problems in India can be linked to fertilizer use.

India has to produce 380 million tonnes against the present production of 206 million tonnes of food grain per annum in order to feed a population of 4 billion by 2025.. As there is no scope for horizontal expansion of our agricultural land additional amount of food grain has to be harnessed vertically in which fertilizer takes the lead role. Where there is no doubt on the yield propelling effect concerns have been expressed about the environmental impact of fertilizer use. There are some claims of dire consequences with fertilizer use and more particularly against N fertilizers. This makes some sense as fertilizer recovery efficiency of N " seldom exceeds 50 per cent. A major portion of the applied fertilizer is lost from soil-plant system by leaching, runoff, denitrification and volatilization and pollutes the soil, water and air; the vital resources of nature..

At present the country consumes about 17.8 million tones of fertilizer per annum and more than 65 per cent of it is nitrogenous fertilizer. The consumption of fertilizer has registered a spectacular growth during the last 3 decades and a very good correlation has been seen between food grain production and fertilizer consumption. Average consumption of fertilizer (N+P+K) in the country in 1999-2000 is about $106 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Though, this is much less in comparison to many other countries like China, Japan, United Kingdom, Korea, and Netherlands, where the consumption of N+P+K are 271, 295, 343, 459, and $50 \text{ kg ha}^{-1} \text{ yr}^{-1}$. respectively. Fertilizer consumption even in the neighbouring countries like Bangladesh and Pakistan are higher i.e., 154 and $129 \text{ kg ha}^{-1} \text{ yr}^{-1}$, respectively, than that of India. Moreover there is regional disparity in terms of fertilizer consumption. Farmers of Punjab use nearly $250 \text{ kg fertilizer ha}^{-1} \text{ yr}^{-1}$, whereas in North East Regions it is only $5\text{-}10 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

Environmental Consequences of NPK Fertilizer Use

Fertilizer N, P and K, after their application in soil undergo various transformation

processes. A host of physical, chemical and biological processes are involved in such turn over. For example, dynamics of N in the soil-plant-atmosphere system includes the various soil processes like mineralization, immobilization, urea hydrolysis, nitrification, volatilization and, denitrification. Phosphorus after its application in soil is either removed by crop or gets converted into various insoluble forms (Fe and Al phosphate in acid soil and Ca-phosphate in alkaline soils) and gets fixed in soil -clays or organic matter. The use efficiency of P does not exceed 20%. Significant amount of P is lost from the soil through surface runoff and erosion resulting in eutrophication of water bodies. Potassium is the most abundant plant nutrient in soil. It is more mobile than phosphate and is susceptible to loss by leaching, runoff and erosion. The use efficiency of fertilizer K is about 70%. Loss of K is a waste but carries no environmental concern.

Major environmental' consequences related to fertilizer use

Nitrate Pollution of Groundwater

Pollution of groundwater from fertilizer N is caused by leaching. The magnitude of loss depends upon soil conditions, agricultural practices, agro-climatic conditions, and type of fertilizers and methods of application. The time taken by nitrate "to move from the root zone to the water table, therefore, varies considerably. In sandy soils with high water table and high rate of fertilizer application, it may reach the water table in matter of days whereas in heavy soils, low rainfall and low rate of application' with deep water table, it may take years.

Two main alleged health hazards are blue baby disease of young babies and cancer due to nitrate ingestion in food and water. World Health Organization (WHO) recommends that drinking water should not more than 10mg NO₃-N L⁻¹ (50mg ,NO₃]' Lot). However, nitrate is non-toxic, the concern is with its microbial reduction to nitrite. The nitrate is converted into nitrite in the intestine and then absorbed in the blood stream. Young babies cannot detoxify this nitrite, which combine with hemoglobin to form inactive form methaemoglobin thus reducing the capacity of blood to carry oxygen. When the conversion of nitrate to nitrite exceeds 10% blood is incapable of carrying oxygen and clinical symptoms such as gray or blue skin develop known as "methaemoglobinaemia" or "blue baby syndrome".

Tamil Nadu in the south, Orissa (Ganjam district) and Bihar in the east and Gujarat on the west high average nitrate and high N fertilizer consumption. But there were several exceptions. For example, in West Bengal, where the average nitrate level was low inspite of high dosage of N fertilizers. There are very few cases of high nitrate content in groundwater in India that can be related to fertilizer use. We argue that the

stray incidence of high nitrate levels in groundwater in certain pockets cannot be attributed to mineral fertilizer consumption but to dumping of animal wastes and extensive use of farmyard manure

Eutrophication

Another major problem associated with excess fertilizer use is the eutrophication of surface water causing several diseases. Arable soils leak considerable amounts of nitrate, phosphate, potassium and other nutrients mainly through run-off and erosion, which enrich the water body in terms of nutrients leading to luxurious growth of algae and other organisms and resultant eutrophication problems in ponds

Ammonia Volatilization

Volatilization of NH_3 is not only a major loss of N but also a cause of environmental pollution. From the atmosphere NH_3 , is washed out by clouds and redeposit' on the terrestrial ecosystem In the atmosphere it is oxidized to N_2O , which acts as a greenhouse gas and is responsible for the destruction of ozone layer. It also forms salts with acidic gases and these salt particles can be transported long distances especially in the absence of clouds. The deposition close to the source is substantial, but hard to estimate due to interaction with other pollutants. In northern Europe, it has been estimated that 94% of the NH_3 , released from agricultural sources is redeposited into surrounding ecosystems

Acid Rain

The effect of acid rain on ecosystems is gradually being documented, particularly in temperate region Nitrogenous fertilizers contribute substantially towards emissions of ammonia, one of the agents causing acid rain. A high atmospheric concentration of ammonia can result in acidification of land and water surfaces, cause plant damage and reduce plant bio-diversity in natural systems. Excess of ammonia deposited causes eutrophication effect of N. Deposition of NH_3 contributes to acidification of soils if nitrified.

Greenhouse Gases

Greenhouse gases (GHGs) are atmospheric compounds that store energy, thus influencing the climate. Each of the GHGs has a different global warming potential that takes into account the effectiveness of each gas in trapping heat radiation and its

longevity in the atmosphere. For instance, one kilogram of methane (CH_4) is estimated to have the same warming potential as 21 kilograms of carbon dioxide (CO_2), and one kilogram of nitrous oxide (N_2O) has an equivalent impact to approximately 310 kilograms of CO_2 .

According to the Organization for Economic Cooperation and Development (OECD), CO_2 , CH_4 and N_2O emissions in agriculture at global level are estimated to account for 14 per cent of the total emission of GHGs. However, estimates of both absorption and emission of these three gases are subject to significant uncertainties.

Nitrogen Gas (N_2)

Large amounts of nitrogen gas are emitted to the atmosphere via denitrification, including that of nitrogen fertilizers. Nitrogen gas constitutes 78 per cent of the atmosphere and it has no direct greenhouse effect. Release of N_2 reduces nitrogen (N) available to crops, but is not otherwise detrimental to the environment.

Nitrogen Oxides (NO and NO_2)

Nitrogen oxides are not GHGs. Nitrogen fertilizer input accounts for only 0.5 per cent of NO emissions. Both nitric oxide (NO) and nitrogen dioxide (NO_2) react in sunlight with volatile organic compounds to form tropospheric ozone (O_3). Ozone is toxic to crops, even at low concentrations, and detrimental to the health of sensitive individuals.

Nitrous Oxide (N_2O)

Nitrous oxide has a greenhouse effect and is considered to be detrimental to the ozone layer. According to experts of the Intergovernmental Panel on Climate Change (IPCC), N_2O is responsible for 7.5 per cent of the calculated greenhouse effect caused by human activity. The concentration in the atmosphere is increasing at a rate of about 0.2 per cent per year. Although nitrogen fertilizers can be a direct or indirect source, they account for only 0.8 per cent of the N_2O emissions. Moreover, new, more efficient nitrogen fertilizers coupled with site-specific fertilization practices reduce N_2O emissions.

Methane (CH_4)

Methane is a GHG. Within agriculture, CH_4 is emitted mostly by ruminant digestive process and from livestock wastes. Rice paddy fields are also a major source of CH_4 that is formed by the anaerobic decomposition of organic matter. The addition of readily

decomposable organic matter significantly increases CH₄ emissions. The impact of mineral fertilizers on CH₄ emissions is not clear, but seems minor.

Fertilizers and Gas Emissions

The use of phosphate and potash fertilizers does not contribute directly to GHG emissions, but all forms of nitrogen fertilizers may lead to N₂O emissions. Since there is no significant uptake mechanism for N₂O in agricultural systems, mitigation focuses on emission reduction. In general, agricultural practices that increase nutrient use efficiency and diminish nitrogen leaching are also appropriate for minimizing N₂O emissions. Best management practices, which match the nitrogen supply to crop requirements and integrate animal manure and crop residue management into crop production, result in a net reduction in N₂O emissions. The proper balance of nutrients optimizes the efficiency of applied and residual soil nitrogen. Other agricultural practices that minimize nitrogen losses include the adoption of reduced tillage practices, the prevention of water-logging through improved drainage and the treatment of sodic soils.

Replacing plant nutrients removed during harvests, and minimizing nutrient losses to the environment are the goals of effective fertilization. This involves both efficient and balanced fertilization to ensure adequate plant nutrition while maintaining optimum soil fertility levels.

Trace Element and Heavy Metals Contamination

There is an increasing concern about the occurrence of trace elements in the environment in concentrations which can be harmful for animal health. Many fertilizers, phosphatic fertilizers in particular, contain varying amounts of trace elements such as F, As, Cd, Co, Cr, Hg, Mo, Ni and Pb (Table). The main issues concerning these potentially harmful elements are i) soil accumulation and possibility of the long-term effects on crop yields and quality, ii) plant uptake and the content of the element in animal feed and human diet, iii) potentially damage to the soil micro flora, and iv) direct exposure to humans through contact and ingestion. The famous incidences of "itai-itai" and "minamata" diseases due to Cd and Hg toxicity, respectively are the examples of potential threat of heavy metal pollution. In Japan excessive use of sulphate containing fertilizers in paddy soils resulted in As toxicity, which was attributed to the displacement of arsenate ions from soil particles by sulphate ions. Such situations may be observed in

the Deccan plateau of India, which are of volcanic origin.

Heavy metal contents (average) in fertilizers

Fertilizer	Heavy metal (mg kg ⁻¹ fertilizer)			
	Cu	Zn	Mn	Mo
Single super phosphate	26	115	150	3.3
Diammonium phosphate				109
Muriate of potash	3	3	8	0.2
Ca-ammonium nitrate	0.2	6	11	
Urea	0.4	0.5	0.5	0.2
Ammonium sulphate	0.5	0.5	70	0.1
Triple super phosphate	7	75	200	0.1
Ammonium phosphate	3	80	160	2
Complex fertilizer	22	276		
Rock phosphate	100	200	0.5	-

Quality of Environment due to Fertilizer Use

While explaining the negative impacts of fertilizer application one should look into the benefits the world is harvesting from fertilizer use. Fertilizer is an indispensable input of intensive agriculture. The success of green revolution also goes to fertilizer use as **Dr. N.E. Borlaugh said, "If the high yielding varieties were the catalysts that ignited the green revolution, the chemical fertilizers were the fuel that powered its forward thrust"**. It improves soil-health and the deteriorating health of soil due to excess mining of nutrients. Availability of organic manures would not be sufficient to replenish the whole of harvested nutrients. Even it were possible to supply the entire amount of N needed by organic sources, the pollution problem would be greater. It is reported that

losses of N from organic sources were more than that of inorganic sources. Fertilizer also improves farming efficiency. The extensive-intensive type of farming would be impossible without fertilizers. Moreover, the mineral, protein and vitamin content of crops may be improved as judicious fertilization corrects the inadequate level of nutrient

availability.

Fertilizer application also retards erosion as the better developed canopy and extensive root system of fertilized crop protects the soil against wind and water erosion, The residual effects of the greater organic production are significant in the improved soil aggregation imparted by the larger quantity of fresh organic return. It also conserves water because only well nourished crops use water efficiently thereby producing more yields per unit amount of water. Use of fertilizer promotes air purification by stimulating vegetative production absorbing more CO₂ from atmosphere and purifies the air. Fertilizer, by increasing productivity reduces the encroachment of farming onto marginal, erodible and forest land.

19.FERTILIZERS CONTROL ORDER (FCO) 1985

ORDER

Under the Essential Commodities Act, 1955 (10 of 1955), the Central Government makes the Fertilizers (Control) Order, 1985. It shall come into force on the date of its publication in the Official Gazette. In this Order, some of the definitions are used

Act means the Essential Commodities Act, 1955 (10 of 1955).

"certificate of source" means a certificate given by a State Government, Commodity Board, manufacturer, + importer, pool handling agency

Commodity Board means the Coffee Board constituted under section 4 of the Coffee Act, 1942 (7 of 1942) or the Rubber Board constituted under section 4 of the Rubber Act, 1947 (24 of 1947)

compound or complex fertilizers means a fertilizers containing two or more nutrients during the production of which chemical reaction takes place

controller means the person appointed as Controller of Fertilizers by the Central Government and includes any other person empowered by the Central Government to exercise or perform all or any of the powers, of the Controller under this Order.

"dealer" means a person carrying on the business of selling fertilizers whether wholesale or retail or industrial use* and includes a manufacturer, +Importer, and a pool handling agency carrying on such business and the agents of such person, manufacturer, +importer or pool handling agency.

fertilizer means any substance used or intended to be used as a fertilizer of the soil and/or crop and specified in Part A of Schedule I and includes a mixture of fertilizers and special mixture of fertilizers.

"grade" means the nutrient element contents in the fertilizer expressed in percentage

"granulated mixture" means a mixture of fertilizers made by intimately mixing two or more fertilizers with or without inert material, and granulating them together, without involving any chemical reaction.

"importer" means a person who imports fertilizers in accordance with the Export and Import Policy of the Central Government, as amended from time to time.

inspector" means an Inspector of Fertilizers appointed under clause 27.

"manufacturer" means a person who produces fertilizers or mixtures of fertilizers and the expression "manufacture" with its grammatical variations shall be construed accordingly.

"mixture of fertilizers" ***means a mixture of fertilizers made by physical mixing two or more fertilizers with or without inert material in physical or granular form and includes a mixture of NPK fertilizers, a mixture of micronutrient fertilizers and a mixture of NPK with micronutrient fertilizers.

"physical mixture" means a mixture of fertilizers made by physically mixing two or more fertilizers with or without inert material necessary to make a required grade, without involving any chemical reaction.

"prescribed standard" means-in relation to a fertilizers included in column 1 of Part A of Schedule-I, the standard set out in the corresponding entry in column 2, subject to the limits of permissible variation as specified in Part B of that Schedule

PRICE CONTROL-Fixation of prices of fertilizers

The Central Government may, with a view to regulate equitable distribution of fertilizers and making fertilizers available at fair prices, by notification in the Official Gazette, fix the maximum prices or rates at which any fertilizers may be sold by a dealer, manufacturer, +importer or a pool handling agency. The Central Government may consider the local conditions of any area, the period of storage of fertilizers and other relevant circumstances, fix different prices or rates for fertilizers having different periods of storage or for different areas or for different classes of consumers. No dealer, manufacturer +importer or pool handling agency shall sell or offer for sale any fertilizers at a price exceeding the maximum price or rate fixed under this clause.

Display of stock position and price list of fertilizers

Every dealer, who makes or offers to make a retail sale of any fertilizers, shall prominently display in his place of business:-**the quantities of opening stock of different fertilizers** held by him on each day & a list of prices or rates of such fertilizers fixed under clause 3 and for the time being in force.

Issue of cash/credit memorandum

Every dealer shall issue a cash or credit memorandum to a purchaser of a fertilizers in FormM*

CONTROL ON DISTRIBUTION OF FERTILIZERS BY MANUFACTURER/ IMPORTER

Allocation of fertilizers to various States

The Central Government may, with a view to secure equitable distribution and availability of fertilizers to the farmers in time, by notification in the Official Gazette, direct any manufacturer/importer to sell the fertilizers produced by him in such quantities and in such State or States and within such period as may be specified in the said notification.

AUTHORISATION OR REGISTRATION OF DEALERS”

Registration of Industrial dealers and authorization of other dealers

No person shall sell, offer for sale or carry on the business of selling of fertilizer at any place as wholesale dealer or retail dealer except under and in accordance with clause 8:

Application for intimation or registration

Every person intending to sell or offer for sale or carrying on the business of selling of fertilizer as Industrial Dealer shall obtain a certificate of registration from the controller by making an application in Form A together with the fee prescribed While, a manufacturer, an importer, a pool handling agency, wholesaler and a retail dealer intending to sell or offer for sale shall make a Memorandum of Intimation to the Notified Authority, in Form A1 duly filled in, in duplicate, together with the fee prescribed under clause 36 and certificate of _____ source _____ in _____ Form _____ O. On receipt of a Memorandum of Intimation, complete in all respects, the Notified Authority shall issue an acknowledgement of receipt in Form A2 and it shall be deemed to be an authorization letter granted and the concerned person as authorised dealer for the purposes of this Order.

A certificate of registration granted before the commencement of the Fertilizers (Control) Amendment Order, 2003, shall be deemed to be an authorization letter granted under the provisions of this Order: when the applicant is a State Government, a manufacturer or an importer or a pool-handling agency, it shall not be necessary for it or him to submit Form O.

Grant or refusal of certificate of registration

The Controller, shall grant a certificate of registration in Form 'B' within thirty days of the receipt of application to any person who applies for it under clause 8; no certificate of registration shall be granted to a person: -if his previous certificate of registration is under suspension; or
it has been cancelled within a period of one year immediately preceding the date of application; or if he has been convicted of an offence under the Act, or if he fails to enclose with the application a certificate of source ; or
if the application is incomplete in any respect;

Period of validity of certificate of registration and letter of authorization

Every certificate of registration granted, **be valid for a period of three years from the date of its issue.**

Renewal of certificates of registration and authorization letters

Every holder of a certificate of registration granted make an application for renewal to the Controller, in Form C, or to the Notified Authority in Form A1, respectively, in duplicate, together with the fee prescribed under clause 36 for such renewal and a certificate of source as required under clause 8.

Manufacture of Mixtures of Fertilizers - Restriction on preparation of mixtures of fertilizer

No person shall carry on the business of preparing any mixture of fertilizers. or special mixture of fertilizers except under and in accordance with the terms and conditions of a certificate of manufacture granted to him under clauses 15 or 16.

Standards of mixtures of Fertilizers

Subject to the other provisions of the order, no person shall manufacture any *mixture of fertilizers whether of solid or liquid fertilizers unless such mixture conforms to the standards set out in the notification to be issued by the Central Government in the Official Gazette;

Application for certificate of manufacture of mixtures of fertilizers

Every person desiring to obtain a certificate of manufacture for preparation of any mixture of fertilizers or special mixture of fertilizers shall possess such mixture, *and possess the minimum laboratory facility as specified in clause 21A of this Order. An applicant shall make an application to the registering authority if he is an applicant for a certificate of **manufacture for any mixture of fertilizers** in Form D, in duplicate, together with the fee prescribed there for under clause 36; or, if he is an applicant for a certificate of manufacture for any **special mixture, in Form E, in duplicate**, together with the fee prescribed there for under the said clause 36 and an attested copy of the requisition of the purchaser.

Grant or refusal of certificate of manufacture for preparation of mixtures of fertilizers

On receipt of an application under clause 14, the registering authority shall, by order in writing, grant or refuse **within forty-five days from the date of receipt of the application, furnish to the applicant a copy of the order so passed;** to the applicant in Form G

Period of validity of a certificate of manufacture for preparation of mixtures of fertilizers

Every certificate of manufacture granted under clause 15 for preparation of a mixture of fertilizers shall, unless suspended or cancelled, be valid for a period of three years from the date of issue.

Renewal of certificate of manufacture for preparation of mixtures of fertilizers

Every holder of a certificate of manufacture for preparation of a mixture of fertilizers desiring to renew the certificate, shall, before the date of expiry of the said certificate of manufacture make an application to the registering authority in Form D in duplicate, together with the fee prescribed for this purpose under clause 36.

Manufacturers/Importers pool handling agencies to comply with certain requirements in regard to packing and marking, etc.2

Every manufacturer/importer and pool handling agency shall, in regard to packing and marking of containers of fertilizers, comply with the following requirements, namely:-Every container in which any fertilizers is packed shall conspicuously be Superscribed with the word "FERTILIZERS" and shall bear only such particulars in case of containers the gross weight of which is 5 kg or less, no such printing of superscription and other particular shall be necessary

if such super superscription and other particulars are printed on a separate label which is securely affixed to such container. in case fertilizer bags are in cut, torn or damaged condition during transportation or is handling during loading or unloading operation, the manufacturer of such fertilizer may, under intimation to the State Government and the Central Government, repack the fertilizer in new bags or restandardise the quantity in terms of declared weight. Every fertilizers bag in which any fertilizers is packed for sale shall be of such weight and size as may be specified by the Central Government from time to time in this behalf

Manufacturers to comply with certain requirements for laboratory facilities:-

Every manufacturer shall, in order to ensure quality of their product, possess minimum laboratory facility, as may be specified from time to time by the Controller.

Disposal of non-standard fertilizers

Notwithstanding anything contained In this Order, a person may sell, offer for sale, stock or exhibit for sale or distribute, [any fertillser except any fertillser imported by the Central Government] which, not being an adulterated fertilizers, does not conform to the prescribed standard (hereinafter in this Order referred to as non-standard fertilizers) subject to the conditions that:- the container of such non-standard fertilizers is conspicuously super scribed in red colour with the words "non-standard" and also with the sign "X"; and an application for the disposal of non-standard fertilizers in Form H is submitted to the [Notified authority] to grant a certificate of authorization for sale of such fertilizers and a certificate of authorization with regard to their disposal and price is obtained in Form such non-standard fertilizers shall be sold only to the manufacturers of mixtures of fertilizers or special mixtures of fertilizers or research farms of Government or Universities or such bodies. The price per unit of the non-standard fertilizers shall be fixed by the notified authority If a manufacture or importer detects or as reasonable doubt about the standard of the fertilizer manufactured or imported by him, and dispatched for sale as deteriorated in quality during transit due to natural calamity and is not of the prescribed standards, he may, within fifteen days from the date of dispatch from factory or port, apply with detailed justifications to the Central Government for obtaining permission for reprocessing the same in a factory to meet the prescribed standards and the Central Government may, after considering the facts, permit the re-processing of such fertilizer on the terms and conditions as may be notified by the Central Government in this behalf.

ENFORCEMENT AUTHORITIES

Appointment of registering authority The State Government may, appoint such number of persons, as it thinks necessary, to be registering authorities for the purpose of this Order for industrial dealers, and may, define the limits of local area within which each such registering authority shall exercise his jurisdiction.

Notified Authority- The State Government may, appoint such number of persons, to be Notified Authorities for the purpose of this Order and define the local limits within which each such Notified Authority shall exercise his jurisdiction.

Appointment of inspectors-The State Government, or the Central Government may, by notification in the Official Gazette appoint such number of persons, to be inspectors of fertilizers for the purpose of this Order, and may, in any such notification, define the limits of local area within which each such inspector shall exercise his jurisdictions.

Qualifications for appointment of fertilizers Inspectors

No person shall be eligible for appointment as Fertilizers Inspector under this Order unless he possesses the following qualifications, namely:-Graduate In agriculture or science with chemistry as one of the subjects, from a recognized university; and Training or experience in the quality control of fertilizers and working in the State or Central Government Department of Agriculture.

Powers of Inspectors

An inspector may, with a view to securing compliance with this Order:- require any manufacturer, +importer, pool handling agency, wholesale dealer or retail dealer to give any information in his possession with respect to the manufacture, storage and disposal of any fertilizer manufactured or, in any manner handled by him draw samples of any fertilizers in accordance with the procedure of drawal of samples laid down in Schedule II. Provided that the inspector shall prepare the sampling details in duplicate In Form J, and hand over one copy of the same to the dealer or his representative from whom the sample has been drawn; enter upon and search any premises where any fertilizers is manufactured/ Imported or stored or exhibited for sale,; seize any books of accounts or documents relating to manufacture, storage or sale of fertilizers, etc. in respect of which he has reason to believe that any contravention of this

Order has been or is being or is about to be committed; Where any fertilizers is seized by an inspector under this clause, he shall forthwith report the fact of such seizure to the collector whereupon the provisions of sections 6A, 6B, 6C, 6D and 6E of the Act, shall apply to the custody, disposal and confiscation of such fertilizers. Every person, if so required by an inspector, shall be bound to afford all necessary facilities to him for the purpose of enabling him to exercise his powers under sub-clause (1).

ANALYSIS OF SAMPLES

Laboratory for analysis

A fertilizer sample, drawn by an inspector, shall be analyzed in accordance with the instructions contained in Schedule II in the **-Central Fertilizers Quality Control and Training Institute, **Faridabad or Regional Fertilizers Control Laboratories at Bombay, Madras or Kalyani (Calcutta)** or in any other laboratory notified for this purpose by the State Government [with the prior approval of the Central Government. Every laboratory in order to ensure accurate analysis, of fertilizers samples, possess minimum equipment and other laboratory facilities, as may be specified from time to time by the Controller in this behalf

Qualifications for appointment of fertilizers analyst in the fertilizer control laboratories

No person shall be eligible for appointment as fertilizers analyst for analysis of fertilizers samples in the laboratories notified under clause 29 of the Order, unless he possesses the following qualifications, namely:-graduate in Agriculture or Science with chemistry as one of the subjects from a recognized university; and training In fertilizers quality control and analysis at **Central Fertillzer Quality Control and Training Institute, Faridabad.** Provided that the fertilizers analysts appointed before the commencement of this Order, who do not possess the requisite training, shall undergo prescribed training, within a period of three years, in the Central Fertilizers Quality Control " and Training Institute, Faridabad from the date of commencement of this Order.

Laboratories for referee analysis

Every laboratory referred to in sub-clause (1) of clause 29 shall be designated as referee laboratory for the purpose of analysis of any sample of fertilizers : Provided that no such laboratory which carried out the first analysis of the fertilizers sample shall be so designated in respect of that sample: Further in respect of any sample the analysis of which has been challenged, may be sent for referee analysis to any one of the other laboratories except those which are located in the State or where the first analysis has been done. Central Fertilizers Quality Control and Training Institute and Regional laboratories shall be considered as one group of laboratories and a sample first analysed by any one of them, shall not be sent for referee analysis to any other in that group, but only to any other laboratory notified by a State Government.

Time limit for analysis, and communication of result

Where sample of a fertilizer has been drawn, the same shall be dispatched along with a memorandum in Form K to the laboratory for analysis within a period of seven days from the date of its drawl. The laboratory shall analyze the sample and forward the analysis report in Form L within [30 days] from the date of receipt of the sample in the laboratory to the authority specified in the said memorandum. The authority to whom the analysis report is sent under sub-clause (2) shall communicate the result of the analysis to the dealer/manufacturer/Importer/pool handling agency from whom the sample was drawn within [15 days] from the date of receipt of the analysis report of the laboratory.

Maintenance of records and submission of returns, etc.

The controller may by an order made in writing direct the dealers. manufacturers/ importers, and pool handling agencies:- to maintain such books of accounts, records, etc. relating to their business in Form 'N'. and to submit to such authority, returns and statements in such form and containing such information relating to their business and within such time as may be specified in that order. Where a person holds certificates of registration for retail sale and wholesale sale of fertilizers, he shall maintain separate books of accounts for these two types of sales made by him.

Fees

The fees payable for grant, amendment or renewal of an authorization letter or certificate of registration or certificate of manufacture a duplicate of such certificates or, renewal thereof

under this Order shall be such as the State Government may, from time to time fix, subject to the maximum fees fixed for different purposes by the Central Government and different fees may be fixed for different purposes or for different classes of dealers or for different types of mixtures of fertilizers or special mixture. Any fee paid under sub-clause (1) shall not be refundable unless the grant or renewal of any certificate of registration or certificate of manufacture or duplicate copy of such certificate or renewal under this Order has been refused.

The fees payable for grant, amendment, renewal or duplicate copy of certificate of registration for industrial dealer and the authority to whom and the manner in which such fee shall be paid, shall be such as may be specified by the Controller from time to time by notification in the Official Gazette*

20.ORGANIC CHEMISTRY AS PRELUDE TO AGROCHEMICALS - DIVERSE TYPE OF AGROCHEMICALS

“Agrochemicals” - include chemicals, which enhance growth and yield of crops apart from chemicals that destroys pests and diseases. Pesticides are chemicals designed to combat attacks of various pests on agricultural & horticultural crops.

Classification of pesticides:

- + Insecticides (for the control of insects)
- + Fungicides (for the control of fungal pathogens)
- + Herbicides (for the control of weeds)
- + Rodenticides (for the control of vertebrate pests)
- + Nematicides (to kill microscopic worms),
- + Molluscides (to kill slugs and snails)
- + Acaricides (to kill mites).
- + Antifeedant,- inhibit feeding
- + Repellent - to prevent the pest species from attacking its hosts.
- + Chemosterilant- induces sterility.
- + Algicides (for the control of algae)
- + Aphicides (for the control of aphids)

Besides there are other classes viz., Antibiotics, Carcinogen, Dessicants, Defoliants, Ovicide, Pheromone and Plant growth regulators

Predominant classes of pesticides used in India are **insecticides**, which accounted for about 57 per cent of total pesticide consumption followed by **fungicides** (29%) and **herbicides**, which constituted about 14 per cent.

21. PESTICIDE FORMULATIONS

Pesticides are formulated to make their application easier and to improve their effectiveness under field conditions. Formulation also improves the properties, storage, handling and safety.

Formulation is the process by which the active ingredients are made ready to be used by mixing with liquid or dry diluents by grinding or by addition of emulsifiers, stabilizers and other formulation adjuvants to form a commercial product.

Classification of Formulations

a) Dry formulations

Dusts

Wettable Powders

Crannels

Seed disinfections

Others

b) Liquid Formulations

1. Emulsion concentrates

2. Oil concentrates

3. Others

c) Others

A) DUSTS

Dusts consist of a mechanical mixture of the active ingredients with or without an inert diluent pulverized to a particle size of 3 to 30 μ . Dusts can be classified as follows:

1. Undiluted toxic agent (sodium fluoride)
2. Toxic agent with an active diluent (rotenone with sulphur)
3. Toxic agent with an inert diluent (DDT with pyrophyllite)
4. Inert dusts (silica)

Insecticides like calcium arsenate, sodium fluoride ground pyrethrum flowers may be applied as dusts with diluent.

Others like rotenone can be mixed with insecticides like sulphur and applied. Others may be diluted with inert materials like talc in order to cover more area and also to reduce the phytotoxicity of the chemical or to improve the chemical or physical properties.

When inert materials like silica, saw dust, ash are used they may cause abrasions on the pest surface or absorb moisture and desiccate them.

Method of Manufacture

Two methods are employed

1. Ball Mill Method
2. Solvent Mix Method / Toxicity Spray Method

1. Ball Mix Method

In this method the ingredients *viz.*, the active ingredients and fillers like soap stones, talc or pyrophyllite are intimately ground in a Ball Mill and mixed together by the blending operations of a mechanical mixture. In the grinding process, heat develops and increase the temperature, which melts the pesticide and thus gives a fine coating on the inert material. Also in the grinding process the pesticide particles get distributed among the diluents. Consequently grinding of the active ingredient together with the diluent gives a more efficient formulation than separate grinding of the ingredients with subsequent mixing. The finer the grinding more effective is the dust. However lumps may be formed in this process and these lumps are broken into fine particles by means of a powerful jet of air introduced from the sides. Particles of certain size alone are taken upstream by the jet of air and those heavier than the limit prescribed fall back in the ball mill to be ground again.

2. Solvent Mix Method/Toxicant Spray method

The toxicant in the form of a liquid is sprayed into the dust mixture during the blending the blending process. The solvent may be allowed to evaporate or it may be a higher boiling solvent of a petroleum fraction.

3. Bulk Density

It depends upon particle size, shape and actual density. It is an indication of fluffiness. A good diluent is one which weights 300-450 kg/m³ (0.3 g/cc). Lighter materials have low carrying power and remain in the air for a longer time. Heavier materials fall rapidly.

4. Particle Density

Particle density is the actual density of the solid materials, only as if there were no air spaces between them. It affects the feeding in the duster. Carrying power segregation and settling of dust depend upon particle density.

5. Electrostatic Charge

It is produced due to the friction between particles and the dusting equipment. Materials with high silica give type charge to the blower and recharge to the dust steam.

Electrostatic charges on particles affect the attraction of dusts to the plant surfaces and dust distribution.

6. Flowability

It indicates the feed rate of dusting equipment. The angle of slope which is a measure of flowability is measured by allowing the dust to fall through a funnel upon disc. Greater the angle poorer is the flowability. Dust with fibrous or needle shaped particles have a slower feed rate than dusts with spherical particles.

7. Other Properties

- a) Hardness -causes abrasion of the equipment
- b) Absorption -affects caking
- c) Adsorption -tendency to form lumps

Though dusting is less effective compared to spraying it is suitable in areas of water scarcity. Usually 10-50 kg is applied.

22. PESTICIDES FORMULATION

A) GRANULES

Granulated formulations are widely used for the control of soil inhabiting pests and also for making plants poisonous to the sucking pests. They are more convenient to handle and leave a smaller residue on the plants.

Granules can be prepared by several methods

1. By impregnation of prepared granules or minerals like perlite or vermiculite with liquid pesticides or their solutions.
2. By granulating the powder formulation on a suitable diluent with subsequent screening.

The most widely used granular formulations are of 0.2 to 1 mm size. For the treatment of plants, granules of low strength are used. While for the control of weeds in water reservoirs, granules of high strength are used. Granulated formulations of pesticides with fertilizers are also being prepared on a limited scale since many of the pesticides degrade when mixed with fertilizers.

B) FUMIGANTS

Fumigants are substances sufficiently volatile to produce toxic concentration of vapour in closed space. Diffusion is faster with gases of lower molecular weights. Fumigant concentration is expressed in weight volume, eg. mg/l or lbs/1000 c. ft. of fumigated space. Adsorption and leakage as well as settling and actual layering of the initially heavy vapour of most fumigants interfere with diffusion to such an extent that artificial means of stirring the gas mixture are usually employed.

Insect control of fumigation is practised in a number of fields like building fumigation, product fumigation, crop fumigation and soil fumigation.

INSECTICIDE CLASSIFICATION – ORGANOCHLORINES – MODE OF ACTION – LINDANE, ENDOSULFAN – CHARACTERISTICS AND USE

LINDANE

Lindane is a contact, stomach and respiratory poison. It is lethal to chewing and sucking insects but not to spider mites. The vapour pressure and good water solubility (~10 ppm) make lindane an excellent soil insecticide.

The method of use permits effective control of economically important soil pests (eg. Beetle larvae, wireworms, white grubs, flea beetles, cutworms, fruit fly). The tainting property even of highly pure lindane prevents use on fruit and vegetable crops, but

application in forest crops and cotton is wide. Under the name of lacutin it serves in veterinary medicine for control of ectoparasites such as ticks and mange mites.

Toxicology. The acute mammalian toxicity of lindane is somewhat greater than that of DDT (LD₅₀ rat 76-200 mg/kg). After administration, lindane is found in the milk, body fat and kidneys, but is excreted quickly. The danger of accumulation is very slight. In the technical product, hexachlorocyclohexane, the high chronic and cumulative toxicity of β -hexachlorocyclohexane (present to about 5-14%) make the use of the technical product very undesirable.

Lindane has a similar insecticidal spectrum to DDT but its physical properties are more suitable than DDT for use as soil insecticides because of its greater volatility and water solubility.

Mode of Action of Lindane

Lindane, like DDT, rapidly penetrates the insect cuticle and can exert a significant fungicidal action in a dry atmosphere.

Uses

It is stable to heat and is useful as a soil dressing against soil insects. As sprays lindane is valuable against many sucking and chewing pests and as smokes for control of pests in grain stores.

The crude material has an unpleasant musty odour and taste which tends to taint foodstuffs. This is due to the presence of other isomers because γ -HCH has no smell, but is more expensive.

The symptoms of insect poisoning superficially resemble those of DDT and γ -HCH is known to be a neurotoxicant. A concentration of 10 μ m increase the frequency of spontaneous discharges in the cockroach nerve cord and extends the synaptic cleft after discharge. Lindane rapidly penetrates the cuticle of cockroaches and accumulates in the peripheral regions of the central nervous system quickly causing tremors, loss of bodily co-ordination, convulsions and prostration. Like DDT, lindane probably kills insects by bringing about sodium potassium imbalance in nerve membranes.

One of the initial products of metabolism of lindane in houseflies was the monodehydrochlorinated compound pentachlorocyclohexane, isolated from lindane – resistant houseflies and the resistance to γ -HCH observed in houseflies is due to this.

B) ENDOSULFAN

(6, 7, 8, 9, 10, 10-hexachloro-1, 5, 5a, 6, 9, 9a-hexahydro-6, 9, methano-2, 4, 3, benzodioxathiepin-3-oxide).

Other Names

Thiodan, Mallx, Cyclodan, Thimul, Thifur.

The insecticidal properties were first described by W. Finkenbrink. Since 1950 endosulfan has been on the market under the name Thiodan.

Synthesis

Thiodandiol (obtained by saponification of the Diels-Alder adduct from HCCP and Cisl-4-diacetoxybutene) is converted into technical Endosulfan by heating with thionyl chloride in xylene.

Technical material is a brownish solid (m.p. 70-100°C). It is a mixture of two isomers differing in the position of the sulfite group. α -endosulfan (70%) and β - endosulfan (30%). Both isomers yield the corresponding cyclic sulfate upon oxidation.

The α - endosulfan is slowly converted to more stable isomer at high temperature. Both the isoemers are slowly oxidized in air and biological systems by provides or permanganate to endosulfan sulfate. Endosulfan is slowly hydrolysed back to the thiodandiol by the action of aqueous acid or base.

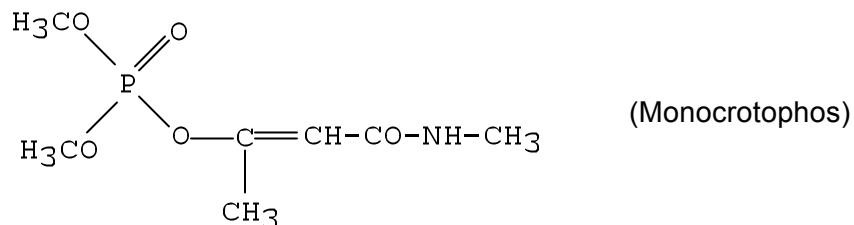
Endosulfan has a similar spectrum of insecticidal activity to aldrin, except that it is also acaricidal. Endosulfan, unlike most organochlorines is degraded in the environment and does not accumulate. It is the only organochlorine insecticide permitted in USA.

23. ORGANOPHOSPHATES – CHARACTERISTICS, PREPARATION AND USE OF MONOCROTOPHOS, PHOSPHAMIDAN, MALATHION AND CHLORPYRIPHOS

a) Monocrotophos (Azodrin)

Derivative of phosphoric acid

Monocrotophos (Dimethyl-1 methyl-2-methyl carbamoyl-venyl phosphate)



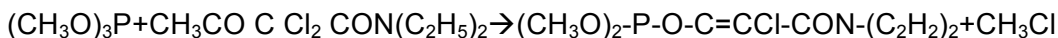
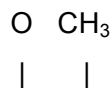
LD₅₀: 21 mg/g

b) Phosphamidon (Dimecron)

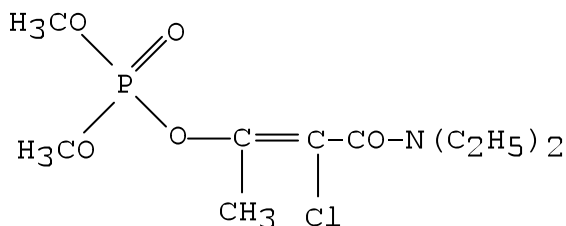
(2-chloro-2diethyl carbamyl-1-methylvinyl dimethyl phosphate)

1. Derivative of Phosphoric Acid

Phosphamidon is produced by reacting equimolecular quantities of trimethyl phosphite with boiling solution of diethylamide of dichloroacetic acid in chlorobenzene.



Phosphamidon is very similar to mevinphos in toxicity has a broad spectrum of activity against biting and sucking pests and spider mites.



LD₅₀: 10 mg

Pure phosphamidon is colourless. Commercial product is bright violet due to the presence of a dye. B.P. 70°C, with a faint pleasant odour.

Highly soluble in water, alcohol, acetone, slightly soluble in saturated hydrocarbons like hexane and insoluble in kerosene. Does not clog the nozzles and hence suited to ultra low volume and low volume sprays.

- Phosphamidon is stable in neutral and weak acidic aqueous solutions.
- It is rapidly hydrolysed in alkaline medium.
- Stable for 2 years when stored in closed containers.
- It is compatible with most pesticides except alkaline ones.
- When mixed with captan it is synergistic. Toxicity is reduced when mixed with copper oxychloride.
- When insects feed on this, the choline esterase is inhibited and the insect gets killed.
- Used as a systemic to control sucking pests in cotton.

c) Malathion

(0, 0-dimethyl S-(1, 2, dicarbethoxy) ethyl phosphorus dithioate)

Derivatives of Dithiophosphoric acid

Dithiophosphoric acid + Maleic acid → Malathion

Malathion is obtained by addition of dimethyl dithiophosphoric acid to maleic acid ester in the presence of basic catalysts.

Malathion was introduced in 1950 by the American Cyanamid company. It is an important and widely used contact insecticide and acaricide for the control of aphids, red spider mites, leafhoppers and thrips on a wide range of vegetable and other crops. It was important in the history of development of OP insecticides since it was the first member with a broad spectrum of contact insecticidal activity combined with the remarkably low mammalian toxicity (LD₅₀: 1300 mg/kg rats). Malathion is also valuable to control insect vectors eg. Mosquitoes and can be used as a substitute for organochlorine insecticides.

Pure malathion is a colourless liquid boiling at 120°C. It is sparingly soluble in water but highly soluble in most of the organic solvents except in saturated hydrocarbons.

Malathion on prolonged heating at 150°C is isomerised and goes over to thiol isomers.

d) Chlorpyrifos (Dursban)

(O, O-diethyl O-(3, 5, 6 trichlorophyridine-2 yl phosphorothioate)

Derivative of Thiophosphoric acid

Chlorpyrifos is used for mosquito control but may also be employed against ectoparasites on domestic animals.

LD₅₀: 135-163 mg/kg rat oral.

Metallic ions in soils often interact with organophosphorus insecticides; the cupric ion is a very effective catalyst for the degradation of some organophosphorus esters, such as diazinon and chlorpyrifos.

Chlorpyrifos has low acute mammalian toxicity in the 2000-5000 mg/kg range. Many organophosphorus insecticides contain heterocyclic moieties with nitrogen heterocycles. The only important pyridine derivatives are chlorpyrifos and chlorpyrifos methyl. Chlorpyrifos is a very valuable contact insecticide some 3500 tonnes were used in USA in 1982. It has a wide spectrum of activity, by contact, ingestion and vapour action. It is moderately persistent and retains its activity in soil for 2-4 months and is valuable against mosquito and fly larvae, cabbage root fly, aphids and codling and winter moths on fruit trees.

Chlorpyrifos has become one of the most widely applied insecticides in homes and restaurants against cockroaches, and other domestic pests. It is a comparatively safe insecticide. Chlorpyrifos methyl (R=CH₃) is quite volatile and is used to control insects in grain stores.

24. ORGANOPHOSPHATES – CHARACTERISTICS, PREPARATION AND USE OF PHORATE, PHOSALONE, DIMETHOATE AND QUINALPHOS

a) Phorate (Thimet)

(O, O-diethyl-S-2-ethylthiomethyl phosphoro dithioate)

Derivative of Dithiophosphoric acid.

Phorate is produced by reacting dimethyl dithiophosphoric acid with formaldehyde and ethyl mercaptan at room temperature.

The second method is by condensation of chloromethyl sulphide with sodium dithiophosphoric acid.

Phorate is a clear liquid. B.P. 100°C, highly soluble in most organic solvents. It is unstable to hydrolysis. In acid medium it is more stable. It is easily oxidized to the corresponding sulfoxide which is resistant to hydrolysis and hence persists on plants for long time providing insecticidal action.

Phorate has both systemic and contact insecticidal action and is a very toxic compound. Phorate is absorbed and translocated in plants. It is oxidatively metabolized. Phorate is employed for control of aphids, carrot fly, fruit fly and wire worm in potatoes.

b) Phosalone (Zolone)

(O, O-diethyl-S-(6-chloro-2, 3-dihydro-2 oxobenzoxazol-3-yl) methyl phosphorodithioate).

Derivative of Dithiophosphoric acid

Phosalone is a systemic insecticide and acaricide used in citrus and orchard fruits. It is also used to control aphids in cereals, oilseed, rape and brassicas. It is also used for testing seeds to protect the seedling from insect damage. LD₅₀: 135 mg/kg.

Phosalone is produced by condensation of sodium or ammonium diethyldithiophosphoate with 6-chloro-3 chloromethyl benzoxazolone.

It is practically insoluble in water. It is a white crystalline substance, m.p. 45-17°C. It is relatively stable in acid medium but in alkaline medium it is rapidly hydrolyzed to the 6-chloro-benzenehexazolone diethyl thiophosphoric acid and formaldehyde.

c) Dimethoate (Rogor, phosphamide, cygon)

(O, O-dimethyl-S-methyl carbamoylmethyl phosphoro dithioate).

Derivative of Dithiophosphoric acid

Dimethoate is a systemic and contact insecticides and acaricide, produced by reacting salts of dimethyldithiophosphoric acid with N-methylchloroacetamide in aqueous medium in the presence of some organic solvents.

It is also produced by reacting dithiophosphate with aqueous methylamine at low temperature.

Pure dimethoate is a white crystalline substance with camphor like odour. The technical material is a yellowish brown (amber) coloured oily liquid with sulphurous acid smell. It is highly soluble in water and most organic solvents. Dimethoate is thermally unstable and on heating it decomposes.

d) Quinalphos (Ekalux) or (Bayrusil)

Derivative of Thiophosphoric acid.

Quinalphos (O, O-diethyl-O- (2-quinoxaliny) phosphorothioate) is obtained by condensation of O-phenylenediamine with the hemi-acetal of glyoxylate.

The compound is highly active against biting and sucking insects and has an LD₅₀: 70 mg/kg rat (oral).

Quinalphos developed by Bayer AG (1969) is prepared by reaction of O-phenylenediamine, chloroacetic acid and O, O-diethyl phosphorochloride thioate.

Quinalphos is a broad-spectrum contact and systemic insecticides, applied as spray to control pests in cereals, brassicas and other vegetables. The mammalian toxicity is quite high (LD₅₀: 70 mg/kg) but the compound is degraded in plants within a few days of application.

25.CARBAMATES – CHARACTERISTICS, PREPARATION AND USE OF – CARBARYL, CARBOFURAN, CARBOSULFAN AND ALDICARB

Carbamates

Mode of action – carbaryl, carbofuran, methomyl, aldicarb and bendiocarb characteristics and use persistence in plant, soil and water.

Carbamates are derivatives (esters) of carbamic acid. Several carbamates are systemic, transported in the xylem. It is possible to control pests on shoots and roots which are otherwise difficult to reach. Hence, they are used as soil insecticides and nematicides (aldicarb, carbofuran, oxamyl etc.). Commercial products available are grouped into three groups.

1. N, N-dimethyl carbamates of enols and hydroxy heterocycles
2. Phosphocarbomates
3. Oxinecarbomate

Mechanism of action

The mechanism of action of the insecticidal carbamates is identical to that of the organophosphates, viz., inhibition of the enzyme cholinesterase. This enzyme has the function of hydrolyzing the post synaptic effector, acetylcholine into choline and acetic acid.

Inhibition of acetylcholinesterase (ACHE) leads to a buildup of acetylcholine in the post synaptic membrane and hence to a permanent nerve stimulation with lethal results. This stimulation of insects manifests itself in uncontrolled movements and paralysis.

A) Carbaryl (Sevin, Hexavin, Ravyon)

(Naphthyl carbamate, 1-Naphthyl-N-methyl carbamate)

LD₅₀: 850 mg.

Broad spectrum contact insecticide, non-systemic used in cotton, fruits, vegetables, forage crops etc. Also to control of earth worms.

Carbaryl, introduced by American Union Carbide Company in 1956 was the first successful commercial carbamate. Carbaryl is produced by any of the general methods of preparation of carbamates, like reacting 1-naphthol with methyl carbamoyl chloride at room temperature.

The rate of reaction is increased by removing the HCl that is formed with a stream of air or nitrogen.

Pure compound of carbaryl is obtained by reacting 1-naphthol with methyl isocyanate.

Carbaryl is also synthesized by reacting 1-naphthylchlorocarbonate with methylamine in the presence of HCl acceptors.

Carbaryl is a white crystalline compound with M.P. 142° C. it is highly soluble in organic solvents; resistant to the action of water at room temperature and also to light and oxygen of air.

In alkaline medium, it is rapidly hydrolysed and so it is not compatible with compounds of alkaline nature like Brodeaux Mixture.

B) Carbofuran (Furadan)

(2, 3, dihydro 2, 2 dimethyl 7, benzofuranyl)

Broad spectrum insecticide, nematocide and miticide.

LD₅₀: 8-14 mg/kg rat.

Can be incorporated in soil at 6-10 kg/ha for control of soil insects and nematodes. It has high mammalian toxicity but is rapidly metabolized to non-toxic products in plants and animals.

It is a systemic carbamate, broad spectrum insecticide. It is stable in acid and neutral media but unstable in alkaline medium. Sparingly soluble in water; but soluble in organic solvents. It is compatible with non-alkaline pesticides and fertilizers. It is not phytotoxic to rice. Carbofuran when applied to soil is absorbed by plant roots and distributed to stems and leaves and metabolized to non-toxic compounds in 30 days. Carbofuran present in soil is degraded by hydrolysis depending on soil pH and clay content. Toxic residues do not remain in the soil for long.

C) Carbosulfan

Carbosulfan, a sulphonylated derivative of carbofuran acts as a contact and systemic insecticide. It can be applied to the foliage or soil as a nematocide. It has a lower mammalian toxicity.

LD₅₀: 209 mg

The carbomates, carbofuran, carbosulfan and aidicarb are valuable nematocidesss. Carbosulfan formulated as granules is used in vegetables. eg. brassicas, carrots and turnips.

D) Aldicarb (Temik)

2-Methyl-2-(methylthio) propanol 0-Methylamino carbonyl oxime)

Systemic insecticide, acaricide, nematocide for soil use; only available as granules to reduce handling hazards.

LD₅₀: 0.93 mg/kg rat.

Used for cotton, sugarbeet and ornamentals. Aldicarb is extremely toxic and is absorbed through skin. It is therefore marketed as a granular formulation.

White crystalline substance m.p. 100°C. Sparingly soluble in water prepared by reacting corresponding oxime with methyl isocyanate.

Aldicarb is a carbamate of carbamoyl oxime group. It is effective for control of aphids, nematodes, flies beetles, leaf miners, thrips and white flies on a wide range of crops. Aldicarb is readily translocated in plants after soil application where it is metabolized to the sulfoxide and the sulphore which are also active.

26.BOTANICALS – CHARACTERISTICS, PREPARATION AND USE OF NEEM PRODUCTS, NICOTINE AND PYRETHRUM

Botanical insecticides

Toxicants derived from plants are used in insect control and among them neem products, nicotine and pyrethrum are well known.

Insecticidal butylamides

Several members of the Compositae and Rutaceae groups of plants contain insecticidal unsaturated butylamides. Example: Pellitorine and Fagaramide. These compounds like several of the pyrethrins, have a rapid knock down effect of flying insects; their practical application as insecticides is unfortunately, limited by chemical instability. However a number of synthetic analogues have been examined and several show promise as insecticides.

Azadirachtin

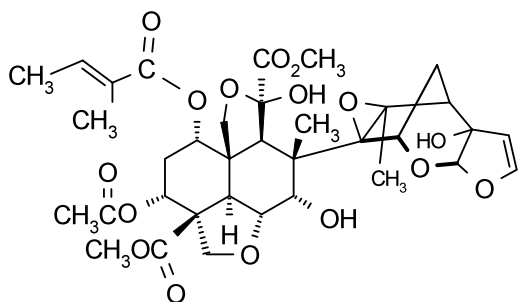
Neem – derived from Persian word Asad-dilakt-I-hind, which means free tree of India - *Azadirachta indica* A. Juss.

In India 14 million trees (1959 survey) of which 50 % in UP. Though not a forest tree it grows wild in the forests of AP, Tamil Nadu and Karnataka. Full-grown neem tree yields 50 kg fruit annually and 350 kg of leaves. India probably produces 0.7 million tones of fruits and 5 million tones of leaves every year.

Almost every part of the tree is bitter and finds its application in indigenous medicine. Oil and cosmetic industries are the users of neem. The refined and purified neem seed oil has many therapeutic properties. Considerable quantities of oil are used in cosmetic preparations. The neem cake after oil recovery is used for slow release of nitrogenous fertilizers.

Neem oil contains limonoids, a class of compounds that act as antifeedants or growth regulators in insects. They do not kill instantly but wipe out a whole generation of insects by preventing the young ones from maturing and the adults from reproducing.

The most effective of the limonoids is a compound called azadirachtin.



It is similar to the insect hormone ecdysone, which is needed for moulting during insect development. It works at a concentration of 1-10 ppm by blocking ecdysone's action, thereby preventing the larvae from shedding their external skeletons and maturing. It also prevents feeding in about 200 insects at a concentration of 10-100 ppm.

The knowledge about neem in India is at least a few centuries ago. Indian scientists had been studying neem for about 70 years and isolated some active compounds by 1960's.

A number of neem formulations are being produced by small-scale formulators and marketed as insecticides. (Neemguard, Margocode, Nimbicidine, Neemplus, Sukrina, Achook etc.).

Neem oil has some of the less known antifeedants like., salanin, nimbin and epoxyazadiradione.(4 International conferences were held discussing regarding production, structure elucidation, isolation of ai, residue analysis).

Nicotine (C₁₀ H₁₄ N₂).

Its chemical name is 1-methyl-2,3 (pyridyl) pyrrolidine. It is the principal alkaloid in tobacco (An alkaloid may be defined in general as a naturally occurring heterocyclic, optically active nitrogenous base of relatively high molecular weight and having marked physiological activity). Nicotine is found in the leaves of *Nicotiana tabacum* and *N. glauca* in the range of 2 to 14 per cent. Among the twelve alkaloids present in tobacco nicotine is the most important one contributing about 97 per cent and the other two of insecticidal value are (i) Nornicotine (C₉ H₁₂ N₂) 2-(3-pyridyl pyrrolidine) (ii) Anabasin (Neonicotine, 3-(2-piperidyl) pyridine).

Pyrethrum

The insecticidal principle in pyrethrum is found in the flower heads of certain plants of chrysanthemum genus, family compositeae. Only a few species like *C. roseum*,

C. cinerariaefolium, *C. marshalli* and *C. tamruti* have been found to be valuable sources of this insecticide. It is used as dusts and sprays.

The flowers are dried at 54.4°C. These flowers are ground to a fine powder and extracted with the solvents. The solvent is repeatedly percolated through the ground flowers and the weak extracts are evaporated in a vacuum still to recover the solvent. The extracted powder (pyrethrum) containing traces of pyrethrins is sometimes used as carriers in dust preparations. Dust concentrates are made from concentrated pyrethrum extracts with a non-volatile solvent and a suitable absorbent carrier and then diluted before use with an inert diluent. Antioxidants such as tannic acid or hydroquinone are used to stabilise the pyrethrins in dust preparations. Concentrated extracts of pyrethrum in acetone, alcohol or a hydrocarbon solvent together with an emulsifier is sold in the market.

Miscellaneous compounds

Picrotoxinin (PTX) has been isolated from the seeds of *Anamirta cocculus* and is moderately toxic to insects. E.g. Cockroaches, but is more toxic to mice. PTX, like avermectins act on GABA regulated chloride ion channels and functions as a GABA receptor antagonist.

Other compounds with a similar mode of action include the trioxabicyclooctanes. Eg. The phosphorus ester and bicycloorthocarboxylates: all are nerve poisons, which are not cholinesterase inhibitors. The compounds were generally more toxic to mammals than insects; the bicycloorthocarboxylates, however, can sometimes show selective activity to house flies and cockroaches and consequently, have potential for development as novel insecticides.

Insect neuropeptides (INPs) generally containing 5 – 10 amino acid residues play a vital role as circulating neurohormones and neurotransmitters. They control many aspects of insect's growth, development and reproduction together with important physiological and metabolic processes. Twenty five such processes are thought to be mediated via these neuropeptides. By 1988, some 27 INPs have been identified and their structures elucidated. For instance, in the locust, the adipokinetic hormones AKH I and II, stimulate lipid metabolism during periods of sustained activity. Eg. Migratory flight. Increased knowledge of the structures and physiology of INPs should provide new potential target

sites for the design of novel insecticides. Peptide synthesis is one possible area of exploitation – if certain physiologically active peptides were introduced to the insect at the wrong time. Severe disruptive effects would result.

If the gene coding for INPs could be introduced into crop plants, then insects attacking the crop could be killed. Another promising line of research would be the design of novel peptides and other molecules to block the INP receptors.

27. CHARACTERISTICS, PREPARATION AND USE OF SYNTHETIC PYRETHROIDS-FENVALERATE AND CYPERMETHRIN

Synthetic pyrethroids

Pyrethrum is derived from the dried flowers of the plant *Chrysanthemum cinerariaefolium*. The name given to the active insecticidal components of the dried flowers is known as pyrethrins. Chemically pyrethrins are organic esters formed by the combination of two carboxylic acids and three keto alcohols.

The synthesis of chrysanthemic acids and of cyclopentenolones opened up the possibility of obtaining synthetic pyrethroids, a remarkable class of insecticides.

The outstanding properties of pyrethrins are

- ✓ Rapid action
- ✓ Low mammalian toxicity
- ✓ Broad spectrum activity
- ✓ Lack of persistence
- ✓ Repellency

Allethrin is the first of its kind prepared by esterification of synthetic chrysanthemic acid with the alcohol allethrolone.

Allethrin had strong insecticidal activity (0.1 µg / insect) and removal of keto group gave another synthetic pyrethroid known as bioallethrin (0.02 µg / insect).

Bioresmethrin is an extremely active insecticide (0.005 µg / insect). This is photosensitive and consequently was not persistent. However when the isobutenyl group of bioresmethrin was replaced by the dichlorovinyl group, the resultant compound is NRDC134 which was more toxic to house flies and mustard beetles than the most known insecticides.

Permethrin was active against houseflies and mustard beetles and showed much greater photostability and consequently was a moderately persistent insecticide. It was the first synthetic pyrethroid effective as a seed treatment against wheat bulb fly.

Decamethrin was prepared by replacement of chlorine atoms by bromine and the introduction of α cyano group from permethrin. This was discovered in 1974 is a potent insecticide known. (0.0003 µg / insect) 50

times more active than Pyrethrin I. This has reasonable photostability and very low mammalian toxicity.

The corresponding chloro derivative as the cis – trans mixture is known as **cypermethrin** which is a broad spectrum insecticide (dose 20-80 g /ha) with good residual activity on plants.

A survey of the esters of furylmethanol led to the discovery of insecticidal activity in a group of phenyl acetic acid esters and Japanese chemists at Sumitoma company introduced **fenvalerate** in 1974. Fenvalerate is a mixture of 4 isomers and is used at 20-150 g ai/ha against a wide range of pests and relatively stable in light.

American Cynamid introduced another phenyl acetic acid esters viz., **flucythrinate and fluvalinate**.

Bromination of the double bonds on decamethrin and cypermethrin gave tralomethrin and tralocythrin. Both are highly active – activity may be due to the *in vivo* conversion in to parent compounds.

Lambda Cyhalothrin has a comparatively high mammalian toxicity (LD 50 (Oral) 60 mg /kg). It is effective at very low doses (5-30 g ai/ha) against major insect pests in many crops. Little hazard to honey bees and this represents an important advantage over OP insecticides which are highly toxic to honey bees. At normal rates cyhalothrin shows low toxicity to birds with no accumulation in eggs or tissues and no effect on earthworms. The half life in soil is 3-12 weeks; in aerobic soils it undergoes extensive mineralization to CO₂. In flooded soil degradation was slower and only hydrolysis products were detected. No phytotoxicity towards major crops and controls a wide spectrum of lepidopteran pests. This is valuable for the control of plant virus vectors.

Tefluthrin is the first pyrethroid effective as a soil insecticide at doses of 12-150 g ai/ha. It is formulated as granules and may also be applied as foliar spray or seed dressing. Tefluthrin kills insects that are resistant to OP and carbamate insecticides. Low mam. toxicity LD₅₀ =1500mg/kg. Little hazard to earthworms and birds but highly toxic to fish. Half life in soil is 4-12 weeks and there is no danger of residue accumulation.

Mode of action of pyrethroids

- ✓ The symptoms of insects poisoned by pyrethroids clearly show that the chemical attacks the insect's nervous systems.
- ✓ Pyrethroids cause hyper excitation followed by convulsions and death in arthropods.
- ✓ The rate and mechanism of metabolism has a major influence on the toxicology of a compound.
- ✓ In (rats) mammals pyrethroids are very rapidly metabolized by ester cleavage, oxidation hydroxylation.
- ✓ The synthetic pyrethroids are very expensive to prepare on a tonnage basis.
- ✓ The high insecticidal activity and low mammalian toxicity of pyrethroids are especially significant now that compounds stable to light and oxygen are potentially available.
- ✓ Their toxicity to fish is high. They are rapidly degraded in soil and have no detectable effects on soil microflora and microfauna. They are not active against mites.
- ✓ The major symptoms of pyrethroid poisoning in insects may be accounted by effects on the kinetics of nerve membrane sodium channels.
- ✓ The mean open times of these channels are prolonged with consequent hyperactivity of nerves.
- ✓ The synthetic pyrethroids have been found to be useful as early season sprays to control the variety of insects that occur on cotton including boll worms, leaf worms, jassids, thrips and whitefly. They are used in combination with an organo phosphorus insecticide as an ultra-low volume spray.
- ✓ They are non toxic to humans and animals. LD₅₀ to rats is around 8000 mg/kg. They are used at only 50 g/ha. The cost/of treatment per hectare is low.

28. HERBICIDES – MODE OF ACTION – CLASSIFICATION OF ORGANIC HERBICIDES CHARACTERISTICS –

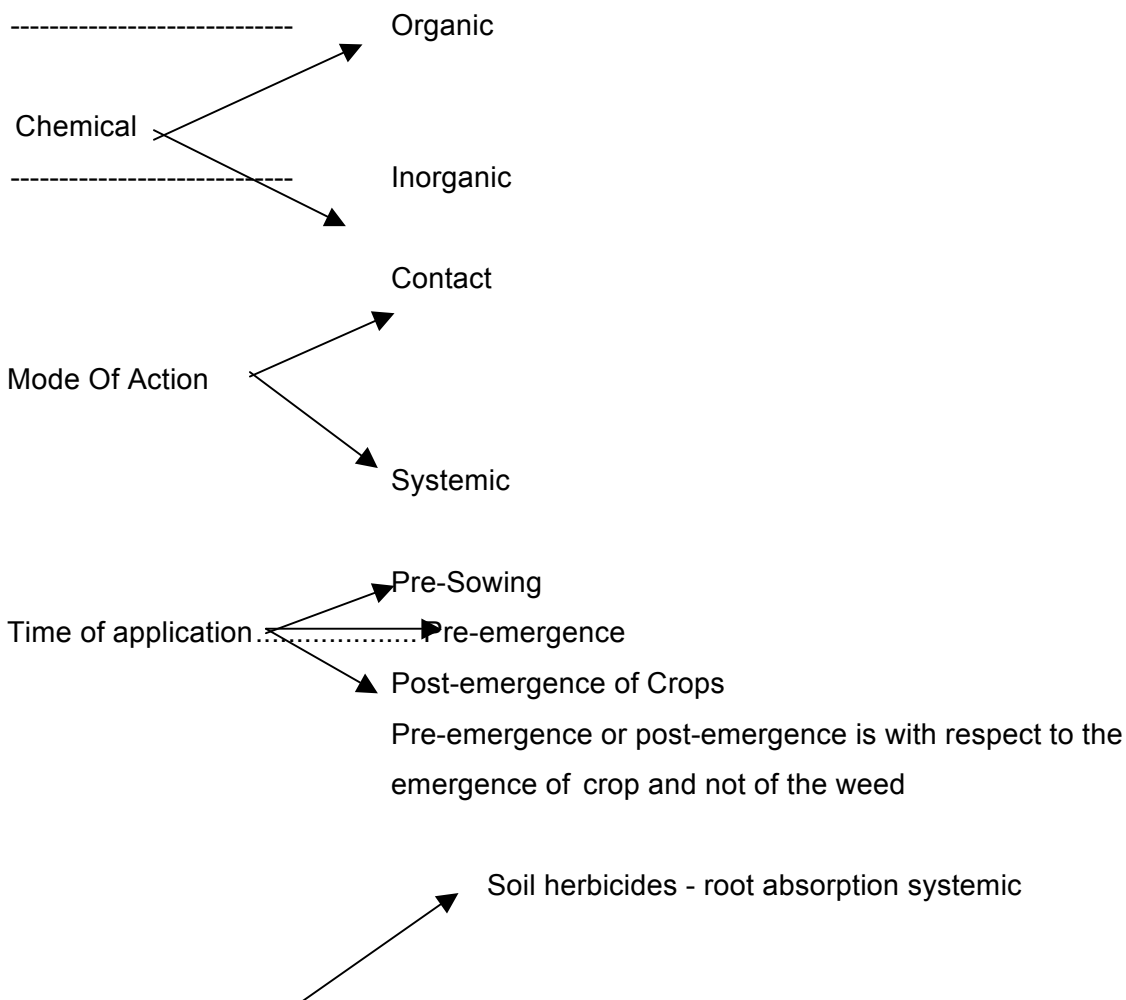
Introduction

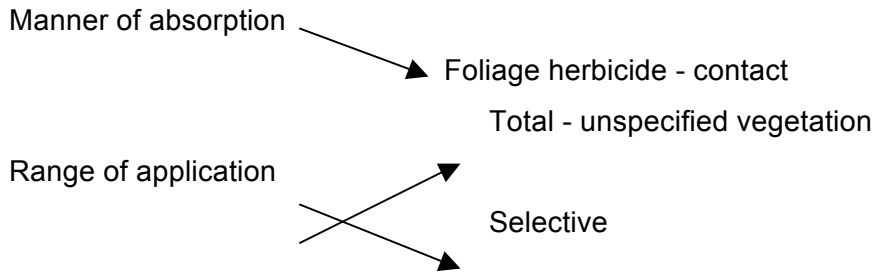
A herbicide in the broadest sense is any compound that is capable of killing or severely injuring plants and may be used for elimination of plant growth.

A weed is an plant, wild or cultivated that is undesired in that particular place. In Agriculture and horticulture weeds are thus any ant other than the specific crop being grown. On railway tracks, industrial sites, air port paths, open spaces and the like the entire vegetation can be regarded as weeds.

Weeds are conveniently divided into dicotyledonous plants, termed broad leaf weeds and monocotyledonous plants, termed grass weeds. Weeds completed with plants for water, light, food and above and below the surface. The yield loss due to weeds is estimated to be 9-10%. Also herbicide economies or helps in crop production by reducing the cultural operations.

Herbicides may be classified based on one or more common characteristics such as chemical composition or mode of action or time of application etc.





Aromatic-Carboxylic

a) 2, 4-D : 2,4-Dichlorophenoxy acetic acid

LD₅₀: 375

2, 4-D can be used for destruction of dictotyledonous plants and it is well tolerated by many monocotyledonous crop plants.

2, 4-D is used as a selective herbicide particularly in cereals. The great advantages are cheap manufacture and relatively low mammalian toxicity. It is a systemic herbicide.

b) 2,4,5, T : 2,4,5, Trichlorophenoxy acetic acid

LD₅₀: 500

2,4,5, T has particularly high activity against woody plants and usually used in combination with other herbicides for control of trees, shrubs and control of otherwise intractable broad leaf weeds.

Structural analogues of IAA such as NAA or 2,4-D promote growth in lower doses but have a herbeidal effect at higher concentrations. 2,4,5, T is more persistent in soil than 2,4-D or MCP A (2-methyl-4-chlorophenoxy acetic acid).

Mode of Action

- Interference with nucleic acid metabolism
- Disruption of translocation system

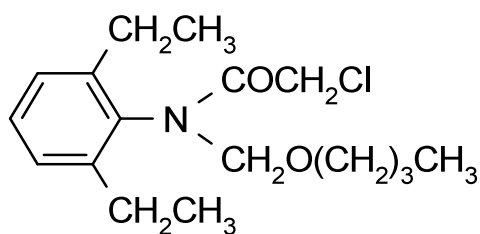
Anilides

The type of activity and the range of weed control vary greatly within this group some being used post-emergence while others are active through the soil.

In 1965, 1966 and 1969 Monsanto introduced three anilides for pre-emergence control of annual weeds.

- (1) (α -chloro-N-isopropyl acetanilide) as 'Ramrod' which shows a high degree of specificity for annual grass weeds and certain

broad- leaved weeds in maize, soybeans, sugarcane, peanuts and certain vegetables. (ii) **Alachlor** (α -chloro-2',6'-diethyl-Nimethoxy methyl acetamide) as 'Lasso' for use in maize, cotton, soybeans, sugarcane, peanuts and certain vegetable crops where it shows very good activity against annual grasses, particularly *Echinochloa crus-galli*, *Setaria* Spp. and *Digitaria* Spp. (iii) **Butachlor** (N-[butoxymethyl]-chloro-2',6'-diethyl acetanilide) as 'Machete' for the control of most annual grasses, certain broad-leaved species in transplanted rice. In 1974, Ciba Geigy introduced **metolachlor** (2-chloro-6'-ethyl-N- [2-methoxy-1-methylethyl] acet-o-toluidide) as 'Dual', a pre- emergence germination inhibitor, active mainly on grasses for use in maize, soybeans and groundnut.



Butachlor

oxyfluorfen

Thiocarbamates

EPTC (S-ethyl-N,N-dipropylthiocarbamate). 'Eptam', was introduced by Stauffer in 1954. It kills germinating seeds, a number of annuals and inhibits bud development in the underground organs of perennial weeds such as couch grass (*Agropyron repens*) and sedges (*Cyperus* Sp.). It may be used soil incorporated 3 weeks before planting potatoes, field beans, sugar beet and others. Monsanto introduced **di-allate** as 'Avadex' (S-2,3-dichloroallyl-N,N-di-isopropyl (thiocarbamate)), a volatile herbicide for pre-plant control of *Avena fatua* and *Alopecurus myosuroides* in brassica and beet crops in 1960; and **tri-allate** (S-[2,3,3'- trichloroallyl]-di-

isopropyl (thiocarbamate)) in for the control of these grasses and others in cereals and peas.

In 1970 **thiobencarb** (S-4-chlorobenzyl diethyl thiocarbamate) was introduced. It is an important herbicide for the control of weeds in rice showing very high selectivity between rice and barnyard grass (*Echinochloa crus-galli*). In addition it controls many other grass cyperaceous and broadleaved weeds.

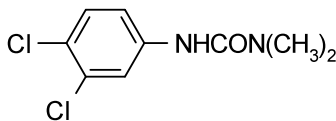
Thiobencarb



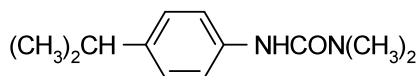
Substituted Ureas

Diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) as 'Karmex', was introduced by Du Pont in 1954 and **Fenuron** (I,I-dimethyl-3-phenyl urea) as 'Dybar' was introduced in 1957 and is used for the control of woody plants by basal application.

Fluometuron (1, I –dimethyl-3-[α-trifluoro-m-tolyl]urea) as 'Cotoran'. was introduced by Ciba Geigy and is used for the control of weeds in cotton. Another very important herbicide for the control of annual, grasses including *Alopecurus myosuroides*, *Avena fatua* and *Poa annua* and many annual broadleaved weeds in cereals was **isoproturon** (3-[4-isopropyl-phenyl]- 1, I –dimethyl urea) marketed by three companies - Hoechst (as 'Arelon'), Ciba Geigy (as 'Graminon') and Rhone-Poulenc (as 'Tolkan') in 1972.



Diuron

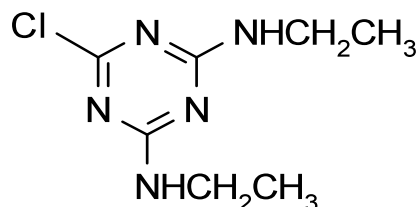


Isoproturon

Heterocyclic Nitrogen Compounds

Triazines

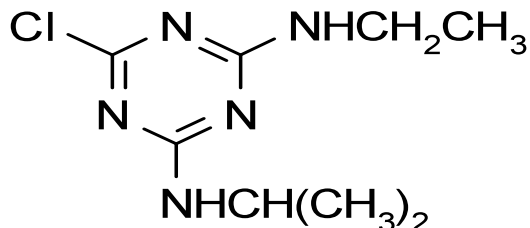
In general triazines have little effect on germination and they are taken up by the roots or leaves. Due to an inhibition of the Hill reaction of photosynthesis, affected plants turn yellow and necrotic symptoms develop. With a few exceptions, the symmetrical triazines have got substituted amino groups at two of the carbon atoms while the third carbon has a chloro, a thioether or a methoxy function. The chloro compounds (CI) end in azine, the thioethers (-S-) end in tryne (e) and the methoxy ones (CH₃O) in ton. In the list of herbicides which follows all were introduced by Ciba Geigy unless stated otherwise. The first commercial triazine, *simazine* (2-chloro-4,6-bis[ethyl-amino]-1,3,5-triazine) was introduced as 'Gesatop' in 1956 for the selective residual pre-emergence control of a great many annual grass and broadleaved weeds in a variety of deep-rooted crops (including citrus fruits, coffee, tea and cocoa), due to its low solubility in water (3.5 mg l⁻¹ at 20°C). It is also used for the control of most annual and perennial weeds in non-crop areas. It is remarkably selective for use on maize because of the ability of this crop to degrade it non-enzymically to the non-active hydroxy derivative.



Simazine

The second introduction *atrazine* (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), introduced as 'Gesaprin' and 'Primatol' in 1958, is both foliar and soil acting being taken up both by leaves of emerged weeds and by the roots of weed seedlings emerging after spraying. In maize, where it is also degraded in, a manner similar to

simazine, it is preferred to the latter especially in dry years. Being more water soluble (30mg l^{-1} at 20°C) it is more suitable for the dry soils on which this crop is grown where it will effectively control couch grass (*Agropyron repens*) and other perennial grasses. It is also used in roses, for selective use in coniferous forests and for non-selective use on non-crop land and industrial sites.

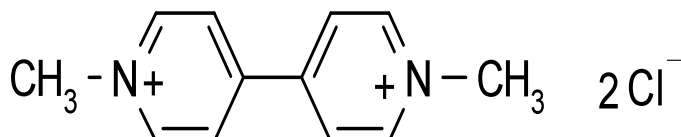
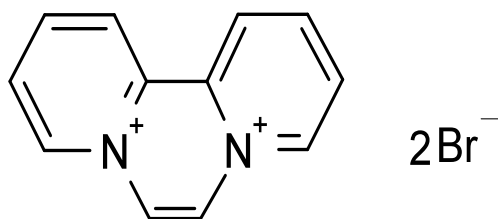


Atrazine

Pyridines

In 1957 and 1958 I.C.I. introduced two very important bipyridillium quaternary herbicides. Both are broad spectrum, rapidly acting causing wilt and desiccation, and are translocated to a certain extent. **Diquat** (1,1'-ethylene-2,2'-bipyridillium ion formulated as dibromide) under various trade names 'Reglone', 'Weedol', 'Path clear' is used for potato haulm desiccation, for seed crop desiccation and for aquatic weed control. The Chapman Chemical markets it as 'Aquacide'. **Paraquat** (1,1'-dimethyl-4,4'-bipyridilium ion formulated as dichloride) as 'Gramoxone' destroys photosynthetic tissues and is used for a variety of purposes including stubble cleaning, inter-row weed control, desiccation of various crops and killing out of old pastures which can then be resown without ploughing.

It is very fast acting, the first effects being noticeable after a few hours and kill is usually completed in 3-4 days. It is quickly absorbed on to soil (particularly clay) particles so that sowing can follow soon after application.



Diquat

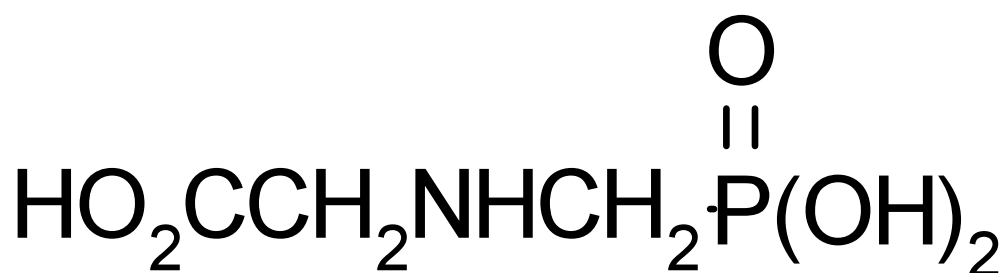
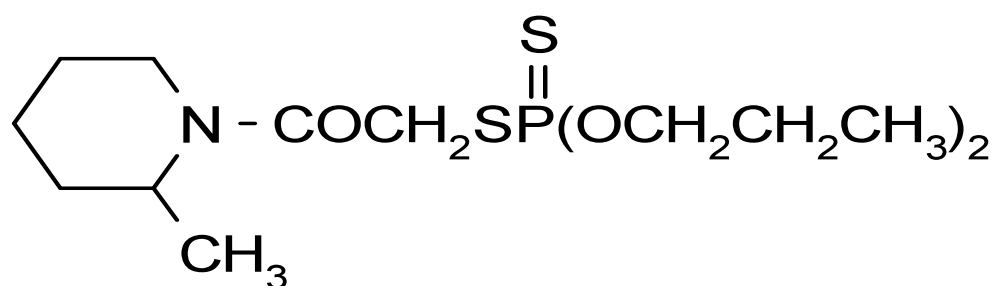
Paraquat

The Dow chemical has Introduced three foliar-applied, selective, growth-regulatory herbicides which produce symptoms on susceptible plants very similar to those produced by the auxin type herbicides, namely tissue proliferation, epinasty, leaf curling and production of adventitious roots.

Organophosphorus Compounds

The organophosphorus compounds include: (1) ***bensulide*** (0,0-diisopropyl-S-2-phenyl-sulphanylaminoethyl phosphorodithioate) which was introduced by Stauffer in 1964 as 'Prefair' for pre-plant pre-emergence use on cucurbits, brassicas, lettuce and cotton, and as 'Betasan' for pre-emergence control of annual grasses and broad-leaved weeds in lawns. (2) ***Piperophos*** (S-2-methylpiperidino-carbonyl methyl-0,0-dipropyl phosphorodithioate) was introduced by Ciba Geigy in 1969. It can be used pre-emergence in rice, maize, cotton, soybeans and groundnuts for the control of many monocotyledonous weeds including *Cyperus* Sp., *Echinochloa* Sp., *Trianthema portulacastrum* and *Monochoria vaginallis*. ***Glyphosate*** (N-[phosphonomethyl] glycine) a derivative of the amino acid, glycine, was introduced by Monsanto as 'roundup' in 1971. It is used post-emergence and is rapidly absorbed by the leaves and translocated from vegetative parts to underground parts, rhizomes or

stolens of perennial grass and broad-leaved weed species giving good control of both above-ground and underground organs *Agropyron repens* is very sensitive. Glyphosate is inactivated on contact with the soil. It provides excellent weed control in pre-tillage of post-harvest treatments of annual crops or when applied as a direct spray in woody crops such as vineyards, deciduous fruit, rubber, coffee, citrus, tea and oil palm. It can also be used in non-agricultural areas and for bush control in forestry.



Piperophos

Glyphosate

29. Fungicides - Classification - Inorganics - characteristics, preparation and use of sulfur and copper - Mode of action - Bordeaux mixture and copper oxychloride

Fungicides are chemicals that have the ability to reduce or prevent the damage caused by fungi in plants and their products. Fungicides are classified based on mode of action as protective, curative and eradicant fungicides.

Protective fungicides prevent fungal infection by sporicidal activity. These arrest the germination of spores or kill the fungal hyphae as they penetrate the leaf or prevent their penetration. **E.g. Sulphur**

Curative fungicides penetrate cuticle and kill young fungal mycelium growing in the epidermis and this prevents further development of fungal growth. E.g. **Organomercurials**.

Eradicant fungicides are agents that make control of fungus even after the symptoms become visible and that kill both newly developed spores and the mycelium. E.g. **Systemic fungicides**.

The early fungicides were inorganic materials like sulphur, lime sulphur, copper and mercury compounds.

Sulphur compounds

Elemental Sulphur is available in dust, wettable powder and colloidal forms. The efficiency of S dust increases with fineness of the particle size. A high proportion should pass through 200 – 300 mesh sieve. Colloidal sulphur is formulated with kaolin (diluent) with 40 per cent S and a particle size of $< 6 \mu$. Sulphur is a contact and protectant fungicide used to control powdery mildew in fruits, vegetables, flowers and tobacco. It is also effective against apple scab and rust of field crops. *Lime sulphur*: It is aqueous solution of calcium polysulphides. It is prepared by sulphur solution in calcium hydroxide suspensions under pressure in the presence of air. Calcium pentasulphide and calcium tetrasulphide found in the mixture are the active materials of fungicidal value which on exposure to air release elemental S.

Mode of action: At first it was observed that S could not be the toxic agent. Sempio (1932) reported that the action was due to the production of various S derivatives. Another theory was that the fungal spores reduce S to H_2S which has shown to be toxic to the spores. However in 1953 this

theory was disproved as colloidal S was more effective than H_2S . Another hypothesis ascribed to various oxidation products such as SO_2 , H_2SO_4 and thiosulphuric acid. Then no S derivative is responsible and came to Sempio and finally that S itself is fungi toxic.

Among the heavy metals only Cu and Hg have been widely used as fungicides although silver is most toxic metal cation. The relative toxicity is in the order of

$\text{Ag} > \text{Hg} > \text{Cu} > \text{Cd} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Fe} > \text{Ca}$

Copper compounds

Copper sulphate has been used since 18th century as seed treatment against cereal bunt later replaced by organomercurials. Cu ions in solution are toxic to all plant life. Selective fungicidal action can therefore be achieved by application of insoluble Cu compound on the foliage.

E.g. COC, Copper carbonate, Copper hydroxide, Bordeaux mixture etc.

Bordeaux mixture

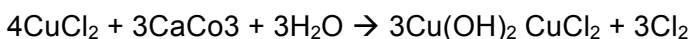
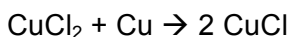
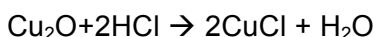
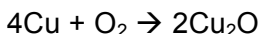
Millardet in 1882 discovered the Bordeaux mixture effective against powdery mildew. A mixture of copper sulphate and lime was initially applied as a paste and thus gained wide recognition as “Bovillie Bordelaise” (Bordeaux Mixture). As the initial mixture containing 8 kg of blue stone dissolved in 100 litres of water and 30 litres of lime suspension prepared with 15 kg lime was found to cause foliar injury. Various combinations were tried. Now a 4-4-50 mixture (copper sulphate in 1 b; lime in 1 b; water in gallons), is used but the concentration of the ingredients is varied depending on the purpose. However, the proportion of copper sulphate to lime usually remains constant. In India Bordeaux mixture is being made by preparing a solution of copper sulphate and quick lime (or hydrated lime) in finely ground form in separate containers and then mixing them simultaneously into a third container with copper sulphate like copper, wooden and earthen vessels. Wide variation in the composition of the resulting mixture will be observed due to chemical reactions between calcium hydroxide and copper sulphate in solution when the ratio between the components is changed. Bordeaux mixture named from the locality of its origin consists of Cu SO_4 (4.5 kg) and Ca (OH)_2 (5.5 kg) in 454 litres of water. It is prepared under a wide range of formulae. Once the mixture has been prepared it should be sprayed immediately on the crop since the toxicity decreases on standing. It is rather difficult to apply because the precipitate tends to block the nozzles. Jaggery or sugar is added to prevent crystallisation.

Mode of action is complex. The ai is probably not $\text{Cu}(\text{OH})_2$ but rather basic Cu SO_4 approximately to the formula $[\text{Cu SO}_4 \cdot 3 \text{ Cu}(\text{OH})_2]$. Bordeaux mixture is almost insoluble in water. So how is Cu mobilized in plants to kill the fungus? The exudates both from the surface of leaf and from the fungal spores can dissolve sufficient quantities of Cu from the dried deposits due to the presence of certain compounds like amino and hydroxy acids which can form chelates with copper.

B) Copper oxychloride

(Blue copper 50: Fytolan) Cupramar, Blimix 4%, Blitox 50%.

Copper oxychloride is one of the low soluble copper fungicides produced by the action of air on cupric chloride solution or scrap copper.



It is marketed in the form of wettable powder containing 50 and 90% copper oxychloride and dusts containing 4 to 12% metallic copper. The 50% formulation contains a diluent (Kaolin) and a surface active agent.

Burgandy mixture

This was introduced by Mason in 1887 by mixing copper sulphate (1 part) with sodium carbonate crystals (1 part) and is less effective than Bordeaux mixture.

Cheshnut compound

This is suggested by Bewley in 1921 consists of 2 parts of Cu SO_4 and 11 parts of $(\text{NH}_4)_2 \text{CO}_3$. The two compounds are well powdered thoroughly mixed and stored in air tight containers for 24 hours before use.

Chaubattia paste

This was developed at Government Fruit Research Station, Chaubattia, Almora district, UP. It is prepared by mixing copper carbonate (800 g) and red lead (800 g) in 1 litre of linolin or raw linseed oil. It is used as wound dressing agent on pruned parts.

Copper oxy chloride approximately $\text{Cu Cl}_2 \cdot 3 \text{ Cu}(\text{OH})_2$ is marketed as colloid and wettable powder. It is a protective fungicide used to control

potato blight, several leaf spots and effective against several diseases of horticultural crops.

***COPPER HYDROXIDE* Cu (OH)_2 IS A NEW FORMULATION INTRODUCED.**

Mode of action is the denature of proteins by free copper ions. Since enzymes are made up of proteins, the Cu inactivates the enzymes. The Cu kills the fungal spores by combining with the sulphohydril groups of certain enzymes.

30. Organic fungicides – Mode of action-. Dithiocarbamates- characteristics and use of Zineb and Maneb

Dithiocarbamates (Organic sulphur compounds)

Investigations of the DuPont Company (USA) showed that some of the derivatives of dithiocarbamic acid $\text{H}_2\text{N}-\text{CSH}$ had insecticidal and fungicidal properties. However dithiocarbamic acid itself is not known to exist in the free state. When the primary and secondary aliphatic and aromatic amines are treated with carbon-di-sulphide in alcoholic solutions, dithiocarbamates are produced.

The hydrogen attached to S dissociates and may be replaced by a metal or other radicals producing a variety of derivatives. The group $> \text{NCS}$ is considered to be essential for insecticidal and fungicidal action. By reacting dimethylamine and CS_2 under alkaline conditions, Thiram and salts of Na, Fe and Cd were prepared. Nabam was produced by reacting ethylene diamine and CS_2 . Subsequently the heavy metal complexes of dithiocarbamates like Ziram and Ferbam and complexes of bisdithiocarbamates like maneb and zineb were developed.

A large number of derivatives of dithiocarbamic acid possess fungicidal properties. They can be classified as follows.

1. Metallic dithiocarbamates – Ziram and Ferbam
2. Thiuram disulphide (Thiram) –S-S linkage
3. Bis dithiocarbamates – Maneb, Nabam, Zineb

A) Zineb (Dithane-A 78)

Dithane-Z 78 is a white crystalline substance insoluble in water and most organic solvents; moderately soluble in pyridine. It is unstable in the presence of moisture, heat, light and alkali. Moist compound under unfavourable storage conditions may decompose to 50% in a year. To reduce the chance of explosive evolution of CS_2 , Zineb has to be stored in a well ventilated place at low temperatures. It is compatible with most insecticides like Ferbam.

It is formulated as wettable powder. Its residual effect depends on weather and season. Zineb can be of great use on Zn deficient soils.

B) Maneb (Dithane-M 45, Manzate)

It is the manganese salt of ethylene bisdithiocarbamic acid; is similar to zineb, in most physical and chemical properties. Decomposes rapidly under high temperature and moisture. It is a yellow crystalline substance insoluble in water and organic solvents. Compatibility is similar to Ferbam. When stored in bulk, Maneb is capable of

spontaneous decomposition with charring which can be avoided by diluting with an inert material. Other analogues are Dithane C-31, Propineb, Thioneb (carbathene).

Thiram as tetra methyl thiuram disulphide was the first compound to be applied as a fungicide and is still used, especially against moulds and as a seed dressing against soil fungi causing damping off. Thiram is prepared by the interaction of carbon disulphide and dimethylamine in the presence of NaOH which is subsequently oxidized to thiram.

Later work resulted in the discovery of the fungicidal activity of zinc and ferric salts of dimethyl dithiocarbamates known as ziram and ferbam respectively. Disodium ethylene bis dithiocarbamate or nabum is also fungicidal and is used to control stem rots. **Nabum** is the insoluble zinc and manganese salts known as zineb and maneb which are produced by reaction with an aqueous solution of zinc and manganese sulphate have largely replaced water soluble. These are used as protectant fungicides and are applied for the control of wide range of phyto pathogenic fungi such as downy mildews. They have very low mammalian toxicities ($LD_{50} > 7000 \text{ mg kg}^{-1}$).

Metham-sodium (N- methyl dithiocarbamate) is a valuable soil sterilant for the control of damping off diseases.

Mancozeb, a coordinated complex of zinc and manganous salts was introduced in 1962. Maneb and mancozeb are formulated with synthetic fungicides to reduce development of resistance.

The dithiocarbamates owe their fungicidal activity due to their ability to chelate with metal cations such as copper. The dithiocarbamates get metabolized to isothio cyanates which react with vital thiol compounds with in the fungal cell.

Heterocyclic N compounds

Captan (N-(trichloromethylthio)-4-cyclohexane-1,2-dicarboximide) is a very effective and persistent foliage fungicide against many soil and seed borne diseases. Analogues that have been subsequently developed as foliar fungicides include folpet and difolatan, which are most active against potato blight. These are some of the safest fungicides ($LD_{50} > 10000 \text{ mg kg}^{-1}$).

Captan interacts with cellular thiols to produce thiophosgene which poison the fungus.

Dichlofluanid, introduced by Bayer is a broad spectrum protective fungicide which is less sensitive than captan.

Phenols

The majority of phenols, especially those containing chlorine, are toxic to microorganisms, their bacterial action has been known for along time and many phenols are also fungicidal. However many are phytotoxic.

Shirlan or salicylanilide is used to inhibit the growth of moulds on cotton and against a number of laef diseases as tomato mould.

Dinocap is a non systemic aphicide and contact fungicide which is effective for the control of powdery of mildew on many horticultural crops. Low mammalian toxicity $LD_{50} > 980 \text{ mg kg}^{-1}$.

Binapacryl is closely related to dinocap and is used for the control of powdery mildew on apples.

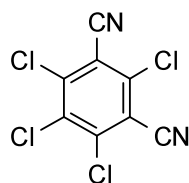
Oxine α -hydroxy quinoline is a protectant fungicide, when suitably formulated, appears to possess limited systemic action. Oxine has a striking capacity to form chelates with metals (Cu) which is effective against a range of phytopathogenic fungi.

Chlorobenzenes and related compounds

2,6-dichloro-4-nitro aniline was marketed in 1959 by Boots Ltd. Especially valuable for the control of Botrytis in tomatoes and against fungal organisms causing post harvest decay of fruits.

Penta chloro nitro benzene (PCNB) called quintazene is a widely used soil fungicide for damping off diseases. Chloroneb is used to control soil borne fungi as seed dressings or by soil application.

Chlorothalonil is a broad spectrum foliar or soil applied fungicide used in many crops. Sandoz kavach.



Chlorothalonil

Quinones

A number of quinines occur in plants and are also products of fungal metabolism.

Dichlone is more stable in light has been used as a seed dressing agent and a foliage spray against powdery mildew.

Dodine (N-dodecyl guanidine acetate) has been known as a bactericide (1941) and more recently has been shown to have fungicidal activity. Dodine is a cationic surfactant is generally formulated as wettable powder. Low mammalian Toxicity ($LD_{50} > 1500 \text{ mg kg}^{-1}$).

Guazatine is mainly used as seed dressing agent for cereals at $0.6 - 0.8 \text{ g ai kg}^{-1}$ of seed and against post harvest diseases. ($LD_{50} > 500 \text{ mg kg}^{-1}$). The fungicidal activity of these compounds probably depend on their ability to alter the permeability of the fungal cell wall, causing loss of vital cellular components such as amino acids and P compounds.

Dicarboximides

All members contain the 3,5-dichlorophenyl moiety and the fungicidal activity depends on the presence of the two chlorine atoms in 3, 5 positions.

Procymidone, hydantoin, iporodione and **vinclozolin** have been extensively used for the control of *Botrytis* and *Scelrotinia* sp in cereals, fruits and vegetables but their use is restricted due to the development of resistance.

More recently **metomedan, chlozolate** and **myclozoline** have been introduced.

Drazoxolon (ICI,1960) is a valuable seed dressing agent against damping off diseases.

The dicarboximides have low mammalian toxicities ($LD_{50} > 3500 \text{ mg kg}^{-1}$).

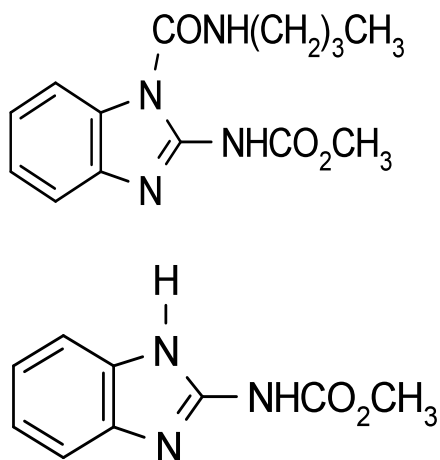
31. SYSTEMIC FUNGICIDES – Benomyl, carboxin, oxycarboxin, Metalaxyl, Carbendazim,- characteristics and use

The idea is earlier but 1960 only commercial systemic fungicides have come to market. A systemic fungicide is a compound that is taken up by a plant and is then translocated within the plant, thus protecting the plant from attack by pathogenic fungi or limiting an established fungal infection.

If a candidate chemical is to be an effective systemic fungicide the following criteria must be satisfied. It must be fungicidal or to be converted into an active fungitoxicant within the host plant. It must possess very low phytotoxicity. It must be capable of being absorbed by the roots, seeds or leaves of the plant and then translocated, at least locally, within the plant. The earlier protectant fungicides applied as foliar sprays formed dried deposits on the leaves of the host plant, protecting it from fungal attack. However the deposits are of course gradually removed by the effects of weathering and cannot protect new plant growth formed after spraying or any part of the plant not covered by spraying. These disadvantages can be overcome by the use of systemic fungicides which since penetrate the plant cuticle. They also offer the possibility of controlling an established fungal infection. Therefore systemic fungicides should exhibit both protectant and eradicant activity.

Benzimidazoles

These represent a new era in fungicide use when they were introduced in late 1960s.



Benomyl

Carbendazim

The most important members of this group are **benomyl** [methyl –1-(butyl carbamoyl) benzimidazole-2- carbamates] TN: Benlate and **thiobendazole**. Both are wide spectrum systemic fungicides effective against many pathogenic fungi including powdery mildews and soil borne pathogens. These fungicides may persist in plants for several months.

Benomyl was introduced in 1967. It was synthesized from cyanide and methylchloroformate. Benomyl and thiabendazole are both wide spectrum systemic fungicides active against many pathogenic fungi including powdery mildews and soil-borne pathogens, *Verticillium albo-atrum* on cotton and black spot on roses.

Du-pont; Benlate LD₅₀: > 9590

Foliar fungicide in wine grape fruits, vegetables, citrus, cereal seed dressing.

Benomyl is the more active compound and is widely applied as a foliar spray, seed dressing or to the soil for control of grey mould (*Botrytis cinerea*), apple scab (*Venturia inaequalis*) canker and powdery mildew (*Podosphaera leucotricha*), leaf spot (*Cercospora beticola*), major fungal diseases of soft fruits and some pathogens of tomato and cucumber. In aqueous solution benomyl is rapidly hydrolysed to methyl benzimidazole – 2 – carbamate and this is probably the active fungitoxicant **carbendazim** which is used as a wide spectrum systemic fungicide formulated as 50 per cent WP.

Metalaxyl

Metalaxyl is included in the phenylamides group of systemic fungicides.

The compounds of this group show protective and systemic activity against Oomycetes causing foliar, root and crown diseases in wide range of crops eg. downy mildews and late blight. The first members of this group Metalaxyl and Furalaxyl were introduced by Ciba-Geigy in 1977 (Metalaxyl = Ridomil). With a high activity at low rates of foliar or soil application metalaxyl controls diseases caused by air or soil borne oomycetes in crops like potatoes, grapes, tobacco, cereals, hops and vegetables.

A wettable powder formulation with mancozeb, (a complex of Zn and Mn salts fungicides) is widely used as a foliar spray against blight on potatoes. Metalaxyl has the broadest spectrum of fungicidal activity of this group of fungicides; it is good against downy mildew on vines, lettuce, maize and Pythium diseases and can be formulated as a seed dressing.

E) Carbendazim (Bavistin, Derosol)

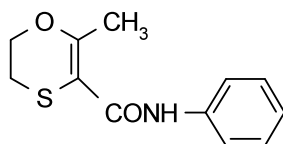
Foliar fungicide in grapes, fruits, vegetables, cereals, cereal seed dressing

LD₅₀: 15.000 Carbenda in methylbenzimidazole-2-carbamate is used as a wide spectrum systemic fungicide and may be formulated as a 50% w.p. for control of *Botrytis*, *Gloeosporium* rots, powdery mildews and apple scab. Carbendazim is absorbed by the roots and foliage of plants and is quicker acting than Benomyl.

The activity of the benzimidazole fungicides (Benomyl, thiabendazole and carbendazim) is due to the inhibition of nuclear division due to their action on the microtubule assembly and the resistance developed in fungi is the result of mutant strains possessing an altered microtubule assembly.

Carboxin and related compounds (Oxathiins)

Oxathiins are another group of heterocyclic compounds with interesting systemic fungicidal properties. **Carboxin** and the sulphone analogue known as **oxycarboxin** are primarily effective against basidiomycetes class of fungi which includes such economically important group of fungal pathogens rusts, smuts and bunts of cereals and the soil fungus *Rhizactonia solani*.



The fungitoxicity is due to inhibition of glucose and acetate oxidative metabolism and RNA and DNA synthesis.

Carboxin and Oxycarboxin

Oxathiins are another group of heterocyclic compounds with systemic fungicidal properties. Examples are Carboxin (5,6-dihydro-2-methyl-1,4-oxathin-3-carboxanilide) (Vitavax) and the sulphone analogue known as Oxycarboxin (Plantvax).

LD₅₀: 3820

LD₅₀: 2000

Seed dressing: cereals, cotton
smuts & Rests

Sol and foliar fungicide
Rusts

Carboxin is prepared by reaction of α -chloroacetoacetanilide and 2-thioethanol followed by cyclization. Oxycarboxin is obtained by subsequent oxidation of carboxin with hydrogen peroxide. Both are fairly water soluble and are not phytotoxic. They are active against Basidiomycetes class of fungi causing rusts, smuts and bunts of cereals and soil fungi *Rhizoctonia solani*. Carboxin can be formulated with other fungicides like thiram, copper oxine.

C) Oxycarboxin

Oxycarboxin has systemic action against rusts of cereals, and vegetables and seed treatment or soil application can be done. Carboxin is absorbed and translocated by plant roots. In water, soil and plants; the compound is oxidised to sulphoxide but further oxidation to sulphone was not observed. The sulphoxide is much less fungicidal and so oxidation causes loss of activity. The primary mode of action of carboxin and related compounds probably involves the blocking of succinate oxidation in the mitochondria of sensitive fungi.

Antibiotics

Antibiotics are chemicals produced by living organisms that are selectively toxic to other organisms. The first successful antibiotic against human diseases was penicillin discovered by Fleming (1929) but it has never achieved commercial significance as a systemic fungicide.

Glitoxin, an antifungal antibiotic produced by the soil fungus *Trichoderma viride* inhibited the growth of *Botrytis* and *Fusarium* spores at 2-4 ppm concentration but the compound was too unstable for use as a soil fungicide.

Streptomycin and **cycloheximide** are antibiotics obtained from the culture filtrates of *Streptomyces griseus* is used for the control of bacterial pathogens of plants.

Griseofulvin isolated in 1939 from *Penicillium griseofulvum* is an important antifungal antibiotic showing a wide spectrum of activity especially against *Botrytis* in lettuce and *Alternaria solani* on tomato.

Blasticidin, a pyrimidine derivative isolated from *Streptomyces griseochromogenes* give excellent control of rice blast and also inhibits certain bacteria. The antibiotic **polyoxin D** is another pyrimidine derivative which is toxic towards several fungi including rice blast. The fungi toxicity is due to interference with chitin synthesis.

Melanin Biosynthesis Inhibitors (MBIs) act on the pathogen to prevent it penetrating the plant epidermis; these compounds block melanin synthesis in a variety of Ascomycetes and fungi imperfecti. They provide practical control of rice blast and experimental control of some *Colletotricum* species. Tricyclozole prevents the rigidity of penetration by *Pyricularia oryzae*. **Validamycin** is an aminoglucoside antibiotic active mainly against *Rhizactonia* diseases and has been widely used to control rice sheath blight. **Probenazole** related to saccharin is effective by root application against rice blast and bacterial leaf disease *Xanthomonas oryzae*. It is not fungi toxic *Invitro* and probably acts indirectly by enhancing the resistance response of the host plant.

Aminopyrimidines

Some 30 years ago there is a series of 2-amino-4-hydroxypyrimidines had specific systemic activity against powdery mildews. These structure activity studies led to development of **dimethrinol** and **ethrinol**. Dimethrinol discovered in 1965, showed outstanding systemic activity by root application against certain powdery mildews in vegetables and some ornamentals.

Piperazine, pyridine, pyrimidine, imidazole and triazole fungicides

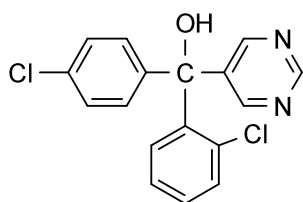
These fungicides are considered together because they all show a common biochemical target, namely synthesis of ergosterol; they are methylation inhibitors.

Triforine is the only piperazine derivative showing systemic activity against powdery mildews on cereals and vegetables.

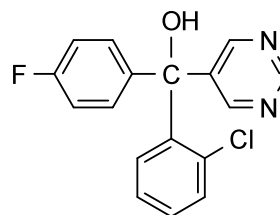


Buthiobate and **pyrifenox** are pyridine fungicides. Buthiobate is used mainly in Japan against powdery mildews while pyrifenox controls a wide range of leaf spot pathogens of fruits and vegetables.

Triarimol, **fenarimol** and **nunarimol** are pyrimidine derivatives introduced by Eli Lilly in the late 1960s. Triarimol has been withdrawn due to its undesirable toxicological properties. Fenarimol, a systemic and protective fungicide is used as a foliar spray to control a broad spectrum of powdery mildews, scabs, rusts and leaf spots. Nuarimol is used against powdery mildews in cereals.

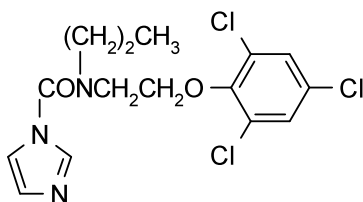


Fenarimol

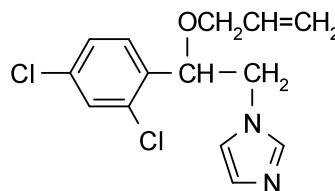


Nunarimol

Imazalil, the first imidazole agricultural fungicide (1960) is now used as seed dressing in cereals.



Prochloraz

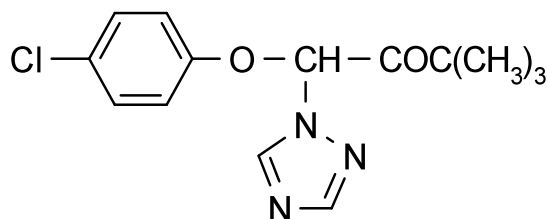


Imazalil

Prochloraz (Boots, 1973) is a broad spectrum fungicide with good activity against ascomycetes and fungi imperfecti but rather less activity against basidiomycetes.

Triflumizole controls a wide range of pathogens Viz., powdery mildews and scabs.

Triadimefon [(1-(4-chlorophenoxy) 3,3-dimethyl -1-(1,2-triazol -1yl) butan-1-one)] TN: Bayleton has systemic activity against a broad range of plant pathogens effective at rates of 0.1 – 2.0 ppm. This discovery led to the introduction of several 1,2,4- triazole fungicides.

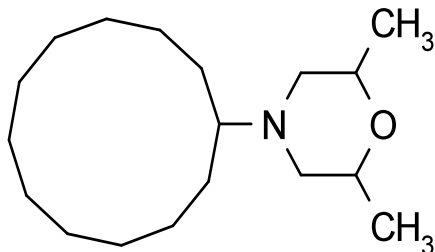


Triadimefon

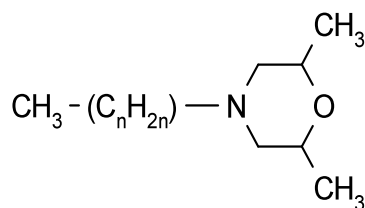
These fungicides owe their fungitoxicity due to their ability to inhibit ergosterol biosynthesis. Ergosterol is a major sterol in many fungi where it plays a major role in membrane structure and function.

Morpholine fungicides

Dodemorph (roses) and **tridemorph** (cereals) are systemic foliar fungicides effective against powdery mildews at 0.75 litres ha⁻¹.



Dodemorph



n = 10, 11, 12 (60 – 70%) or 13

Tridemorph

Organo phosphorus fungicides

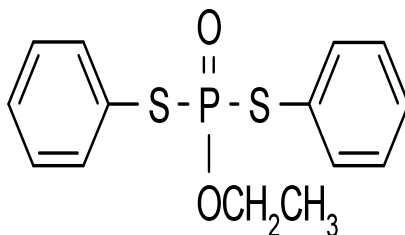
Today more than 100 OP compounds show fungicidal action. However relatively few compounds are of practical use as fungicides, Many are phytotoxic and very specific against fungal species.

One of the first Op fungicides was **triamphos** claimed to be the first systemic commercial fungicide. Since then many compounds were derived. **Pyrazophos** TN: Afugan is a foliar systemic fungicide effective against apple powdery mildew.

Triclophos – methyl is effective against Rhizactonia and other soil borne diseases as a drench in vegetables and against black scarf and canker in seed potatoes.

Iprofenfos TN: Kitazin P introduced in 1968, is a systemic rice fungicide applied as granules in paddy water to control rice blast and it inhibits mycelial growth in tissues.

Edifenphos is also very effective against rice blast.



OP fungicides have shown to block the synthesis of phospholipids. The reduction in phospholipids alters the membrane structure, increasing the permeability and consequent loss of vital cellular components and eventually killing the fungus.

Phenyamides and related compounds

- ***Metaloxy*** – broad spectrum
- ***Furalaxy*** – soil drenching
- ***Benalaxy*** – potato blight
- ***Oxadixyl*** –with mancozeb to control potato blight

Carbamates

- ***Prothiocarb*** – ornamentals
- ***Propamocarb*** – Fruits and vegetables
- ***Cymaxanil*** – Potatoes and vines

Miscellaneous compounds

Isoprothiolane – systemic fungicide against rice blast

Dithiolane

Formaldehyde (Formalin 40 %) is used as seed dressing and soil sterilant

Substituted

azepenes – systemic fungicidal activity against leaf spot, powdery mildew and rust diseases.

Recent potent fungicides for future use

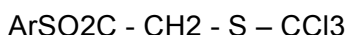
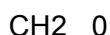
Chlorooximes

Very effective broad spectrum fungicide. Substituent in the oxime moiety plays a key role in the biological activity.

Cyano-oximes : The most active compound in this group is Cymoxanil which controls grape vine downy mildew disease. The analogous compound a propargyl derivative, is

equally effective. After isosteric replacement of the acetylenic triple bond by the cyanide triple bond the resulting compound showed enhanced activity against downy mildew

Aryl sulfonylallyl trichloromethyl sulfoxides : A series of 2-aryl sulfonylallyl trichloromethyl sulfoxides, have been found effective as broad spectrum fungicides with residual activity against grape downy mildew



β methoxyacrylates with oxime ether side chain:

Azoxystrobin, is a well known broad spectrum fungicide which facilitates the control of a wide range of major plant pathogens. If the central pyrimidine ring is replaced with an oxime ether moiety, it yields a highly effective fungicide. Analogous compounds containing a heterocyclic moiety instead of phenyl ring were also prepared to ascertain the fungicidal activity.

Pyrimidine derivatives: A series of novel 2-anilinopyrimidine compounds, based on lead compound were synthesized and introduced to the market in 1994. The synthetic compound mepanipyrim, exhibited excellent activity against grey mould of vine and vegetables, scab of apple and pear and brown rot of peach.

Biofungicides

These comprise of antibiotics and a few microbes such as *Pseudomonas cepacia*, *Peniophora gigantea* and *Trichoderma viride* which control a number of fungi associated with major crops

Mode of action of fungicides

Non systemic

The toxic action of sulphur in the cell is still not clear, however, several theories have been proposed from time to time. The theory accepted at present is that sulphur acts as hydrogen acceptor in metabolic systems to form H_2S , and in doing so disrupts the normal hydrogenation and dehydrogenation reactions in the cell. But in case of Cu-fungicides, the Cu ions precipitate or inactivate the proteins (enzymes of sulphhydryl group) and thus kill the spores.

The mercury fungicides also act either as vapour or in ionic form and destroy

sulphydryl group of (.SH) enzymes. Organomercurials are more toxic than the inorganic mercuric ones due to enhanced lipid solubility facilitating diffusion through the spore membrane to the site of action.

The mode of action of quinone derivatives may be due to binding of the quinone nucleus to .SH and -NH₂ groups in the cell leading to disturbance in the electronic transport systems. The activity of captan and related analogues may thus involve the role of Cl and S atoms of the molecule leading to inactivation of sulphydryl group of enzymes.

b) Systemic

The general mode of action of systemic fungicides is associated with a) interference with the electron transport chain influencing the energy budget of the cell, b) reduction in the biosynthesis of new cell material required for growth and development of the organism, and c) disruption of cell structure and permeability of cell membrane.

Benomyl and its related compounds interfere with mitosis in cell division in angiosperms and fungi. Benzimidazoles, thiophanates, oxathins, phenylamides (metalaxyl derivatives) influence DNA synthesis and are also mitosis inhibitors. The triazole group of fungicides interfere with the biosynthesis of fungal steroids and ergosterol which are important constituents of the cell wall. Pyrimidine derivatives inhibit purine biosynthesis and several pyridoxal dependent enzymes. The mode of

R₄Sn - R₃SnX - R₂SnX₂ - RSnX₃ - SnX.

action of morpho lines is still not well understood but appears to be inhibition of sterol biosynthesis. The mode of action of organ phosphorus fungicides is different from insecticides due to the absence of cholinesterase enzyme in fungi. The widely accepted theory is that it inhibits permeation through cytoplasmic membrane of the substrates for chitin synthesis.

The thiono compounds appear to be inactive against fungi and this may be due to fungus being unable to activate the thiono group to the ox on form by oxidation. The effect of penetration into the fungal hyphae depends on the polarity of the P=O group and needs to be balanced by a larger lipophilic group such as, the second thiophenyl group in case of edifenphos, cyclohexyl group in case of cerezin, benzyl mercaptan in case of kitazin or kitazin-P and the phenyl radical in the case of inezin.

Metabolism

The stability of fungicides in soil depends on chemical structure, nature of soil and climatic conditions. In general, the fungicides are not as stable as organochlorine

insecticides. The most versatile dithiocarbamate group of compounds, decompose in acidic soils to give non-toxic amines and carbon disulfide. Metabolism of alkyltin compounds in liver microsomal monooxygenase system and in mammals leads to the following sequence of detannylation (carbon-tin cleavage) reaction

The first step reaction product possessed increased toxicity and potency as inhibitors to mitochondrial respiration whereas in the subsequent steps the reaction product possesses less potency and has altered nature of biocidal activity.

The carboximides such as captan, folpet, captafol are hydrolysed under neutral and alkaline conditions. Chloroneb degrades to the phenolic derivative but reconversion to parent molecule is a microbial process and this might be the probable reason for long term effectiveness of chloroneb in soil.

Benzimidazole systemic fungicides like benomyl, thiabendazole and thiophanate methyl are first converted to carbendazim, an active ingredient at the site of action. These are finally degraded to non toxic compounds such as aniline, phenyl diamine and cyanoaniline. The breakdown of benomyl into MBC occurs by intramolecular process in slightly acidic or neutral media. A hydrogen bond is formed between the free electron pair of the N atom of the benzimidazole ring and hydrogen on the nitrogen of the butylcarbamoil side chain, forming an unstable four membered ring which opens up to yield MBC and butylisocyanate. The cyanate rapidly forms butylcarbamic acid with water which in turn decomposes into CO₂ and butylamine. The major metabolites of dimethirimol are ethirimol and 2-amino derivative.

Benomyl and thiophanate-methyl, in plants decomposes first to MBC which then gives photoproducts) like carbomethoxyguanidine (i), carbomethoxyurea (ii) and guanidine (iii) other minor compounds depending on the nature of the solvents used. Piperazine, a metabolite of the fungicide triforine in barley degraded to non toxic products such as iminodiacetic acid, glycine, and oxalic acid on the surface of the plants by photodecomposition. Chlorthalonil, 2,4,5,6-tetrachloroisophthalonitrile, in benzene solvent was photodegraded to a monophenyl adduct 3,5,6-trichlorobiphenyl-2, 4-dicarbonitrile, (i) as major photoproduct and disulfides. chlorophenyl methyl carbonate and an unknown product.

32. Insecticide act-Compatibility of pesticides with fertilizers and other Agrochemicals.

Agrochemicals combinations and their significance

Fertilizer-herbicide combinations are extremely popular because they combine two operations. Combinations with pre emergence chemicals are generally effective since both fertilizer and herbicide action are dependent on contact with the soil (requiring rainfall or irrigation). Post emergence herbicide action depends more on absorption by leaves, and granules in such combinations do not adhere well to smooth-surfaced leaves. They will stick better if applied when weed leaves are damp, perhaps with morning dew. "Weed and feed" materials present a conflict in desirable actions. Proper time for weed control often does not coincide with the most desirable time and rates for fertilizing. If used for follow-up fertilizations, there is danger of herbicide overdose.

HERBICIDE - INSECTICIDE COMBINATIONS

Emulsifiable concentrate formulations of insecticides can act like oil adjuvants when applied in combination with a herbicide. Past research has demonstrated that Lorsban in combination with Betanex or Betamix can cause more sugar beet injury than Betanex or Betamix alone. Lorsban should not be applied in combination with normal rates of Betanex, Betamix or Betamix Progress in situations where sugarbeet injury is a concern. The micro rate of Betanex or Betamix + UpBeet + Stinger + methylated seed oil at 0.5 pt/A + 1/8 oz/A + 1.3 fl oz/A + 1.5% v/v already has an oil adjuvant as a part of the system. Therefore, the addition of Lorsban to the micro rate would not be expected to cause an increase in sugarbeet injury.

While Lorsban act like oil adjuvants, the insecticides are not as effective as commercial oil adjuvants and the insecticides should not be substituted for oil adjuvants in herbicide treatments where oil adjuvants are needed for optimum weed control.

Adjuvants for enhancing herbicide performance

An adjuvant is any substance in a herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics.

Adjuvant selection: should be primarily based on herbicide label._ should consider percent active ingredient as well as cost.

Adjuvants are commonly used in agriculture to improve the performance of pesticides. Broadly defined, “an adjuvant is an ingredient that aids or modifies the action of the principal active ingredient.” The use of adjuvants with agricultural chemicals generally falls into two categories: (1) formulation adjuvants are present in the container when purchased by the dealer or grower; and (2) spray adjuvants are added along with the formulated product to a carrier such as water. The liquid that is sprayed over the top of a crop, weeds, or insect pest often will contain both formulation and spray adjuvants.

Formulation adjuvants are added to the active ingredient for a number of reasons including better mixing and handling, increased effectiveness and safety, better distribution, and drift reduction. These traits are accomplished by altering the solubility, volatility, specific gravity, corrosiveness, shelflife, compatibility, or spreading and penetration characteristics. With the large number of formulation options available (solutions, emulsions, wettable powders, flowables, granules, and encapsulated materials), adjuvants become even more important in assuring consistent performance.

Spray adjuvants are added to the tank to improve pesticide performance. Literally hundreds of chemical additives are now available that fall into this category. Spray additives can be grouped into two broad categories:

Activator Adjuvants include surfactants, wetting agents, stickers-spreaders, and penetrants; *special purpose* or utility modifiers such as emulsifiers, dispersants, stabilizing agents, coupling agents, co-solvents, compatibility agents, buffering agents, antifoam agents, drift control agents, and nutritionals.

SPECIAL PURPOSE ADJUVANTS

Compatibility agents allow simultaneous application of two or more ingredients. They are most often used when herbicides are applied in liquid fertilizer solutions. Unless the pesticide label states that it can be mixed with liquid fertilizers, a compatibility agent should be included.

Buffering agents usually contain a phosphate salt or more recently citric acid, which maintains a slightly acid pH when added to alkaline waters. These are added to higher pH solutions to prevent alkaline hydrolysis (a chemical reaction) of some organophosphate (OP) and carbamate insecticides. Some acidifying agents are also sold to enhance herbicide uptake and performance. However, there is little evidence to support the need for these acidifying agents for this purpose with most herbicides. Some buffering agents are also “water softening” agents that are used to

reduce problems with hardwater. In particular, calcium and magnesium salts may interfere with the performance of certain pesticides. Ammonium sulfate (AMS) is sometimes added to reduce hard water problems. Examine the specific pesticide and water source to determine the need for a buffering agent.

Antifoam agents usually are added to suppress surface foam and minimize air entrapment that can cause pump and spray problems. Defoamers often contain silicone.

Drift control agents (thickeners) modify spray characteristics to reduce spray drift, usually by minimizing small droplet formation. Drift inhibitors are generally polyacrylamide or polyvinyl polymers to increase droplet size.

Surfactants

The primary purpose of a surfactant or “surface active agent” is to reduce the surface tension of the spray solution to allow more intimate contact between the spray droplet and the plant surface. Any substance that brings a pesticide into closer contact with the leaf surface has the potential to aid absorption. Surface tension is a measure of the surface

energy in terms of force measured in dynes/cm. Water has a surface tension of 73 dynes/cm. Surfactants lower the surface tension of water to that of an oil or solvent, which spreads more readily than water on plant surfaces. Surfactants typically lower the surface tension of a solution to between 30 and 50 dynes/cm. The interaction between surfactant, herbicide, and plant surface is far more complex than simply lowering the surface tension of the pesticide solution. Surfactant molecules may also alter the permeability of the cuticle. Surfactants form a bridge between unlike chemicals such as oil and water or

water and the wax on a leaf surface. Although there are many different types of surfactants, in general, they are constructed of a long chain hydrocarbon group on one end that is considered lipophilic (fat loving) and a more hydrophilic (water loving) group of atoms on the other end.

Surfactants are classified as **nonionic, anionic, or cationic**.

Nonionic surfactants have no electrical charge and are generally compatible with most pesticides. Nonionic surfactants are most commonly used because of their universal fit. An anionic surfactant possesses a negatively charged functional group and is most often used with acids or salts. Anionic surfactants are more specialized and

sometimes used as dispersants or compatibility agents.

Cationic surfactants are used less frequently, but one group (ethoxylated fatty amines) has been frequently used with the herbicide Roundup.

The **organosilicone**-based materials are another group of surfactants more recently introduced. These surfactants are used in place of or in addition to more traditional nonionic surfactants. Proponents of these surfactants stress low surface tension, greater rain fastness, and possible stomatal penetration characteristics. Several silicone-based products are currently available for use with postemergence herbicides

Oils

Adjuvants that are primarily oil based are very popular with pesticide applicators. Crop oils are probably the oldest group within this category. *Crop oil* is a misnomer because the material actually is from petroleum (paraffin or naphtha base, not vegetable derivative), a phytobland (nonphytotoxic). Crop oils are believed to promote the penetration of pesticide spray through waxy cuticle or the tough chitinous shell of insects. Traditional crop oils are more commonly used in insect and disease control than with herbicides. Crop oils are typically used at 1 to 2 gallons per acre.

Crop oil concentrate contains 80 to 85 percent phytobland emulsifiable crop oil (petroleum based) plus 15 to 20 percent nonionic surfactant. The purpose of the surfactant in this mixture is to emulsify the oil in the spray solution and lower the surface tension of the overall spray solution. Crop oil concentrates attempt to provide the penetration characteristics of the oil, while capturing the surface tension reduction qualities of a surfactant. Crop oil concentrates are also important in helping solubilize less water-soluble herbicides such as Assure, Poast, Fusilade, Select, and atrazine on the leaf surface.

Vegetable oil concentrates have performed less consistently than their petroleum-based counterparts. However, manufacturers are attempting to improve plant or vegetable-based oils by increasing their non polar or lipophilic characteristics. The most common method has been through esterification of common seed oils such as methylated sunflower, soybean, cotton, and linseed oils. The methylated forms of these seed oil concentrates are comparable in performance to traditional (petroleum) crop oil concentrates so their importance has increased. In taking it one step further, organosilicone-based methylated vegetable oil concentrates are also available. These adjuvants boast the surface tension-reducing properties

of silicone but have the advantages of a methylated vegetable oil concentrate.

Nitrogen Fertilizer

Within the last 15 years, nitrogen fertilizers have been more frequently added to the spray solution as an adjuvant to increase herbicide activity. Ammonium salts (NH_4^+) appear to be the active component of these fertilizer solutions and have improved the performance consistency on some weeds. It is still unclear how ammonium salts improve herbicide performance. Herbicides that appear to benefit from the addition of ammonium are the relatively polar, weak acid herbicides such as Basagran, the sulfonylureas (Accent, Beacon, Classic, and Pinnacle, etc.), and the imidazolinones (Pursuit and Raptor). Nitrogen fertilizers may replace surfactant or crop oil concentrate with some of the contact type herbicides, but are usually added in addition to surfactant or crop oil concentrate with systemic products. Velvetleaf and some grassy annual weeds in particular have been responsive to the addition of nitrogen fertilizer in the spray mix. In general, velvetleaf control has improved by as much as 10 to 25 percent by the addition of an ammonium based fluid fertilizer compared to crop oil concentrate or surfactant. Some broadleaves and grasses show little or no response with the inclusion of ammonium fertilizer solutions. Ammonium-based fertilizers and, in particular, ammonium sulfate (AMS) are also being promoted to reduce potential antagonism with hard water or antagonism with other pesticides. Both hard water antagonism and pesticide antagonism can occur with some herbicides. Roundup (glyphosate) is one product that specifically recommends omits label the addition of ammonium sulfate (or a higher rate of Roundup) for hard water, cool air temperatures, or drought conditions. Examine the specific pesticide label, water source, and environmental conditions to determine the need for AMS or other adjuvants.

Foliar fertilizers

Many of these products are being used extensively in combination with herbicides. It is important to know the facts before mixing them unregistered with herbicides.

- Certain fertilisers do work effectively with certain herbicides for very specific reasons. It is however highly improbable that it is as a result of more actively growing plants.

- Foliar fertilisers could sometimes even be antagonistic to herbicide activity! Certain companies even warn farmers not to mix these products with their herbicides.
- If you mix unregistered combinations, please keep in mind that it becomes your problem and that the herbicide company will not take responsibility for poor weed control or crop damage. Unregistered combinations are a risk that you take. We don't think it worthwhile to take such a risk.

Tank mixtures

Unregistered tank mixtures are one of the main reasons for poor herbicide efficacy. It is important to keep the following in mind.

- Always stick to label recommendations
- If in doubt, contact the manufacturer for advice

Conditions during and just after spraying

Climatic conditions during application could make or break a herbicide.

- Remember that once the spray solution droplet hits the target, it is exposed to the forces of nature. Try to protect it in every way possible.
- Try to avoid herbicide-limiting factors such as low humidity and other environmental constraints.
- Always include the registered adjuvant as it can compensate somewhat for lower humidity and other environmental limitations.

Retention and absorption

It is important for spray solution droplets to firstly be retained on the leaf surface and then to be absorbed in adequate amounts.

- Remember that both retention and absorption are equally as important. Good wetting and spreading is useless if conditions for absorption are unfavourable.
- Try to avoid herbicide-limiting factors such as low humidity and other environmental constraints as this could detrimentally influence both retention and absorption.

- Always include the registered adjuvant as it ensures adequate retention and absorption.
- Don't follow unregistered practices as this could decrease both retention and absorption.

HERBICIDE MIXTURES AND PROBLEMS IN MIXING HERBICIDES

The use of herbicide combinations is not new, but it has not received the attention and input that is necessary to fully understand and implement the practice. Although the number of herbicides available is continually increasing, we have to realize that in most cases herbicides are quite specific in their activity toward either grass or broadleaf weeds and even other species within these broad categories. Excellent herbicides have limitations that might be alleviated with the proper addition of another herbicide.

There are several advantages that may be gained from the combination of herbicides over a single herbicide.

Some of these are:

1. Control of a broader spectrum of weeds.
2. More consistent control over a wide range of climatic conditions.
3. Reduced potential of herbicide residue in crops and soils.
4. Lower rates of application resulting in decreased crop injury and lower costs.
5. Unexpected synergistic effects (increased herbicidal effectiveness beyond that expected).

There have been limitations and concern in the past concerning the legal use of herbicide combinations. At no time has the University of Wyoming recommended chemical mixtures unless the herbicides, herbicide-fertilizer mixtures, and other pesticides were registered by the Environmental Protection Agency (EPA) and the state of Wyoming.

EPA's policy on herbicides and herbicide-fertilizer mixtures is as follows:

1. An herbicide or mixture of herbicides may be mixed

with other pesticides and/or with fertilizers if the mixture is not prohibited by the labeling.

2. Two or more herbicides and/or pesticides may be mixed if all the dosages are at or below the recommended label rate.

When making such mixtures it must be kept in mind that these pesticide mixtures are applied at the applicator's own risk with respect to effects on crops, application equipment, applicator safety, environmental effects and residue tolerance.

MIXING HERBICIDES

Always be sure the sprayer has been properly calibrated. Calculate the amount herbicide to add to the sprayer tank based on the active material in each gallon of herbicide concentrate, or the percentage of active ingredient of dry herbicide formulation. Always read and follow the instructions on the manufacturer's label pertaining to personal hazards in handling.

The following steps should be taken when mixing herbicides:

1. Fill the sprayer tank with at least half the volume of water or fertilizer solution you will ultimately need.
 2. Start continuous moderate agitation.
 3. Add compatibility agents if needed. For maximum benefit, they must be in solution before herbicides are added.
 4. Add, mix, and disperse dry herbicides (wetable powders, dry flowables, or water dispersible granules). These formulations contain wetting and dispersing agents that aid in mixing.
 5. Add liquid flowables and allow thorough mixing. These also contain wetting and dispersing agents.
 6. Add emulsifiable concentrates (EC's) and allow thorough mixing.
 7. Finish by adding water soluble formulations (2,4-D amine, etc.).
 8. Add any surfactants, crop oil concentrates, etc. last.
- Crop oils, especially, do not mix and disperse well if added first.

9. Add remainder of water or liquid fertilizer and maintain agitation while spraying until tank is empty.

Never pour concentrated herbicides into an empty tank.

Never allow a sprayer containing mixed chemicals to stand without agitation, as heavy wettable powders may clog nozzles or settle into corners of the spray tank. Wettable powder herbicides should be pre-slurried before addition to a spray tank. Adding the wettable powder directly to the spray tank can result in globs or unwetted material in the tank where it can clog spray equipment. This is particularly a problem with the more finely ground wettable powders.

Tank mixtures of a wettable powder and an emulsifiable concentrate can cause problems if not properly mixed. The proper procedure is to first pre-slurry the wettable powder and add it to the tank 3/4 full of water.

The emulsifiable concentrate should then be added followed by the necessary water to fill the tank. If the sequence is reversed with the wettable powder added last, problems can arise.

FERTILIZER AND HERBICIDE MIXTURES

The mixing of liquid fertilizers and pesticides and applying at the same time has several advantages. The mixture can save time, labor, fuel, and may help reduce soil compaction.

There could be mixtures of a herbicide + fertilizer = "weed + feed"; fertilizer + insecticide = "feed and worm"; herbicide + insecticide = "weed + worm". The following material will only be concerned with the "weed + feed" concept of mixing herbicides with liquid fertilizers.

Even before checking the compatibility of herbicide + fertilizer mixtures, other factors of importance must be taken into consideration.

1. Do you have the right equipment for application?

Fertilizer application is not as exacting as for applying herbicides.

Uniform application covering every square inch is essential for the effectiveness of herbicides.

The equipment ordinarily used for applying fertilizers does not give the uniform distribution pattern that equipment used for herbicide application provides.

Some fertilizer application equipment does not have the agitation necessary to keep herbicides uniformly dispersed.

Herbicide application equipment may not be able to withstand the weight and corrosiveness of liquid fertilizers nor apply the necessary volume of liquid fertilizer.

2. Are mixtures of herbicides and fertilizer practical? The applicator must determine if the timing of application, placement and distribution of each component in the mixture are similar enough to be applied as a mixture. Several herbicides and fertilizers can be applied at the same time. For example, AAtrex (atrazine) can be tank mixed with liquid fertilizer and applied to corn either preplant incorporated or broadcast on the soil surface after the corn is planted but before the crop emerges. Placement of the mixture may raise a question of practicality. Suppose a farm operator sprays the herbicide and fertilizer mix over the corn row, in a band, at planting time. By using a nitrogen solution as a carrier for the herbicide the nitrate form of nitrogen will be incorporated by rainfall. If the ammonium (NH_4) form of nitrogen is used as a carrier and soil surface applied, it will react with the soil particles and be held in the top 1/4 inch of soil. This nitrogen will move downward only after being converted to the nitrate form. If the fertilizer carrier for the herbicide is a solution containing nitrogen and phosphorus it will have to be positioned in the soil near the roots for plants to adequately utilize it as phosphorus does not move readily in most soils. If the nitrogen and phosphorus fertilizer solution is banded over the corn at planting time, the corn will not benefit from the phosphorus as a starter in early plant growth. Thus, this combination would not be practical from a placement standpoint.

3. Distribution of the mixture. Liquid fertilizers are usually broadcast over the entire field. Applying the herbicide in

with the fertilizer means broadcasting of the herbicide also.

Many herbicides can be band applied, a practice which reduces the total cost of the herbicide per acre in proportion to the row-spacing and width of the band treated.

Therefore, the total benefits and economics of mixing should be taken into consideration.

4. Is the fertilizer-herbicide mixture compatible?

Herbicides may not always mix evenly throughout the liquid fertilizer or the components may separate making their use impractical. A simple test should be used before mixing large quantities.

COMPATIBILITY

Even though guidelines have been presented with respect to tank mixes there still remains the question of compatibility when mixing two or more chemicals, especially, when directions for mixing and application are not included on the label.

Both chemical and physical incompatibility are possible. With chemical incompatibility the chemical maybe completely deactivated, resulting in no weed control, or the chemical might be made highly phytotoxic resulting in damage to the crop. It is also possible to change the mammalian toxicity making a normally safe chemical highly toxic.

Physical incompatibility is most commonly evidenced by precipitation in the spray solution which takes the form of crystalline solids, formation of a gelatinous mass, or separation of components which takes the form of layering.

Lack of compatibility may only result in the formation of a substance that plugs up screens and nozzles, however, extreme incompatibility may produce a settling out of material that can harden like concrete in the bottom of a tank and in hoses, pumps, and other internal parts of the sprayer. The result may be total loss of the pesticide and use of the sprayer.

Chemical compatibility of a mixture is impossible to determine without extensive research being conducted, whereas physical compatibility can easily be checked. You should use only labeled tank mixtures or mixtures recommended by experienced scientists whose

recommendations are backed by research. For all unlabeled tank mixtures, a jar test is strongly recommended to test for the compatibility of herbicide-herbicide mixtures, herbicide-insecticide mixtures, herbicide -fertilizer mixtures, or any combinations involving pesticides and/or fertilizers.

In some cases, adding a compatibility agent (Complex, Unite, or comparable surfactants) may aid in maintaining component dispersion.

JAR TEST FOR COMPATIBILITY

The jar test may be used to test the compatibility of herbicides with each other or herbicides and other pesticides with liquid fertilizers.

1. Add 1 pint of carrier (water, liquid fertilizer) each to two quart jars. Mark the jars with an identifiable letter, number or other means. Usually "with" and "without" is the most practical (representing with and without compatibility agent).
2. Add 1/4 teaspoon or 1.2 ml of compatibility agent to one jar (equivalent to 2 pints per 100 gallons of spray solution).
3. To each jar add the required amount of pesticide in the order suggested in the section on mixing herbicides. Shake well after each pesticide addition to simulate continuous agitation.
4. When all ingredients are added, shake both jars for 15 seconds and let stand for 30 minutes or longer. Then inspect the mixture for flakes, sludge, gels, or non dispersible oils, all of which may indicate incompatibility.

If, after standing 30 minutes, the components in the jar with no compatibility agent are dispersed, the herbicides are compatible and no compatibility agent is needed.

If the components are dispersed only in the jar containing the compatibility agent, the herbicide is compatible only if a compatibility agent is added.

If the components are not dispersed in either jar, the herbicide-carrier mixture is not compatible and should not be used.

33. Fate of pesticides in soil and plant.

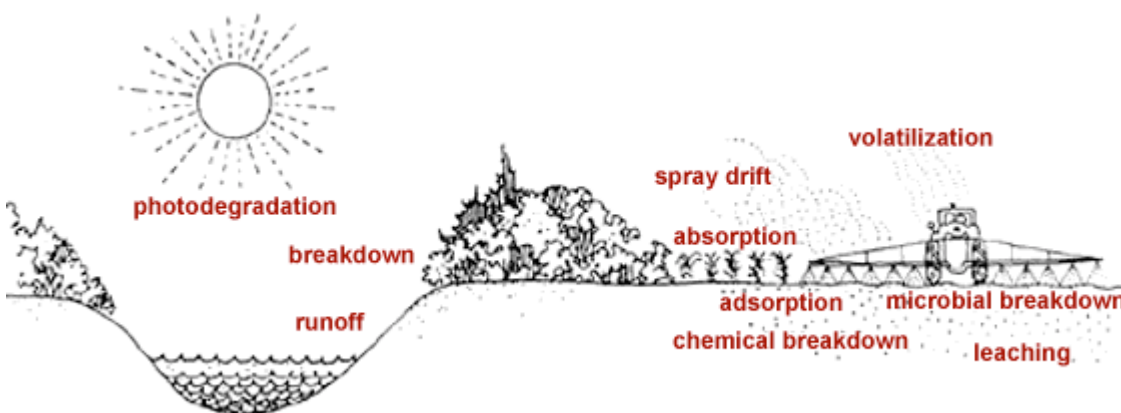
What Happens to Pesticides

When a pesticide is released into the environment many things happen to it. Sometimes what happens is beneficial. For example, the leaching of some herbicides into the root zone can give you better weed control.

Sometimes, releasing pesticides into the environment can be harmful, as not all of the applied chemical reaches the target site. For example, runoff can move a herbicide away from target weeds. The chemical is wasted, weed control is reduced, and there is more chance of damaging other plants and polluting soil and water. Or some of the pesticide may drift downwind and outside of the intended application site.

Many processes affect what happens to pesticides in the environment. These processes include adsorption, transfer, breakdown and degradation. Transfer includes processes that move the pesticide away from the target site. These include volatilization, spray drift, runoff, leaching, absorption and crop removal.

Each of these processes is explained in the following sections.



Transfer Processes

Adsorption is the binding of pesticides to soil particles. The amount a pesticide is adsorbed to the soil varies with the type of pesticide, soil, moisture, soil pH, and soil texture. Pesticides are strongly adsorbed to soils that are high in clay or organic matter. They are not as strongly adsorbed to sandy soils.

Most soil-bound pesticides are less likely to give off vapours or leach through the soil. They are also less easily taken up by plants. For this reason you may require the higher rate listed on the pesticide label for soils high in clay or organic matter.

Volatilization is the process of solids or liquids converting into a gas, which can move away from the initial application site. This movement is called vapour drift. Vapour drift from some herbicides can damage nearby crops.

Pesticides volatilize most readily from sandy and wet soils. Hot, dry, or windy weather and small spray drops increase volatilization.

Where recommended, incorporating the pesticide into the soil can help reduce volatilization.

Spray Drift is the airborne movement of spray droplets away from a treatment site during application.

Spray drift is affected by:

- spray droplet size - the smaller the droplets, the more likely they will drift
- wind speed - the stronger the wind, the more pesticide spray will drift
- distance between nozzle and target plant or ground - the greater the distance, the more the wind can affect the spray

Drift can damage nearby sensitive crops or can contaminate crops ready to harvest. Drift may also be a hazard to people, domestic animals, or pollinating insects. Drift can contaminate water in ponds, streams, and ditches and harm fish or other aquatic plants and animals. Excessive drift also reduces the pesticide applied to the target and can reduce the effectiveness of a treatment.

Runoff is the movement of pesticides in water over a sloping surface. The pesticides are either mixed in the water or bound to eroding soil. Runoff can also occur when water is added to a field faster than it can be absorbed into the soil. Pesticides may move with runoff as compounds dissolved in the water or attached to soil particles.

The amount of pesticide runoff depends on:

- the slope
- the texture of the soil
- the soil moisture content
- the amount and timing of a rain-event (irrigation or rainfall)
- the type of pesticide used

Runoff from areas treated with pesticides can pollute streams, ponds, lakes, and wells. Pesticide residues in surface water can harm plants and animals and contaminate groundwater. Water contamination can affect livestock and crops downstream.

Pesticide runoff can be reduced by:

- using minimum tillage techniques to reduce soil erosion
- grading surface to reduce slopes
- diking to contain runoff
- leaving border vegetation and plant cover to contain runoff

Pesticide losses from runoff are greatest when it rains heavily right after you spray. Reduce the chances of runoff by watching the weather forecast. If heavy rain is expected, delay spraying to avoid runoff. Irrigate according to label instructions.

Leaching is the movement of pesticides in water through the soil. Leaching occurs downward, upward, or sideways. The factors influencing whether pesticides will be leached into groundwater include characteristics of the soil and pesticide, and their interaction with water from a rain-event such as irrigation or rainfall. These factors are summarized in the table below.

Leaching can be increased when:

- the pesticide is water soluble
- the soil is sandy
- a rain-event occurs shortly after spraying
- the pesticide is not strongly adsorbed to the soil

Groundwater may be contaminated if pesticides leach from treated fields, mixing sites, washing sites, or waste disposal areas.

Summary of Groundwater Contamination Potential as Influenced by Water, Pesticide and Soil Characteristics		
	Risk of Groundwater Contamination	
	Low risk	High risk
Pesticide characteristics		
Water solubility	low	high
Soil adsorption	high	low
Persistence	low	high
Soil characteristics		
Texture	fine clay	coarse sand
Organic matter	high	low

Macropores	few, small	many, large
Depth to groundwater	deep (100 ft or more)	shallow (20 ft or less)
Water volume		
Rain/irrigation	small volumes at infrequent intervals	large volumes at frequent intervals
Based on: McBride, D. K. 1989. Managing pesticides to prevent groundwater contamination. North Dakota State University Extension Service, Publication E-979.		

Similar factors influence pesticide movement in surface runoff, except that pesticides with low water solubility may move with surface runoff if they are strongly adsorbed to soil particles and have some degree of persistence.

Soil characteristics are important to pesticide movement. Clay soils have a high capacity to adsorb many chemicals including pesticides and soil nutrients. Sandy soils have a much lower capacity to adsorb pesticides. Organic matter in the soil also can adsorb pesticides. Soil structure influences the movement of water and pesticides. Coarse textured sandy soils with large air spaces allow more rapid movement of water than fine textured or compacted soils with fewer air spaces. Other characteristics of the site, such as depth to groundwater, or distance to surface water, are important. Finally, the pattern of water falling on the soil through irrigation or rainfall is significant. Small volumes of water at infrequent intervals are less likely to move pesticides than large volumes of water at more frequent intervals.

Absorption is the uptake of pesticides and other chemicals into plants or microorganisms. Most pesticides break down once they are absorbed. Pesticide residues may be broken down or remain inside the plant or animal and be released back into the environment when the animal dies or as the plant decays.

Some pesticides stay in the soil long enough to be absorbed by plants grown in a field years later. They may damage or leave residues in future crops.

Crop Removal through harvest or grazing may remove pesticide residues.

Degradation or Breakdown Processes

Degradation is the process of pesticide breakdown after application. Pesticides are broken down by microbes, chemical reactions, and light or photodegradation. This process may take anywhere from hours or days to years, depending on environmental conditions and the chemical characteristics of the pesticide. Pesticides that break down quickly generally do not persist in the environment or on the crop. However pesticides that break down too rapidly may only provide short-term control.

Microbial breakdown is the breakdown of chemicals by microorganisms such as fungi and bacteria.

Microbial breakdown tends to increase when:

- temperatures are warm
- soil pH is favourable
- soil moisture and oxygen are adequate
- soil fertility is good

Chemical breakdown is the breakdown of pesticides by chemical reactions in the soil. The rate and type of chemical reactions that occur are influenced by:

- the binding of pesticides to the soil
- soil temperatures
- pH levels - Many pesticides, especially the organophosphate insecticides, break down more rapidly in alkaline soils or in spray tank water with a high pH level.
- moisture

Photodegradation is the breakdown of pesticides by sunlight. All pesticides are susceptible to photodegradation to some extent. The rate of breakdown is influenced by the intensity and spectrum of sunlight, length of exposure, and the properties of the pesticide. Pesticides applied to foliage are more exposed to sunlight than pesticides that are incorporated into the soil. Pesticides may break down faster inside plastic-covered greenhouses than inside glass greenhouses, since glass filters out much of the ultraviolet light that degrades pesticides.



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Pesticide Characteristics

From University of Nebraska NebGuide G1182

Pesticide characteristics are also important in determining the fate of the chemicals in the environment. These characteristics include:

1. solubility in water (water solubility)
2. tendency to adsorb to the soil (soil adsorption)
3. pesticide persistence in the environment (half-life)

Pesticides with high water solubility, low tendency to adsorb to soil particles and long persistence or half-life have the highest potential to move into water. These three factors, soil adsorption, water solubility and persistence, are commonly used to rate pesticides for their potential to leach or move with surface runoff after application.

Soil adsorption is measured by K_{oc} , which is the tendency of pesticides to be attached to soil particles. Higher values (greater than 1000) indicate a pesticide that is very strongly attached to soil and is less likely to move unless soil erosion occurs. Lower values (less than 300-500) indicate pesticides that tend to move with water and have the potential to leach or move with surface runoff.

Water solubility is measured in parts per million (ppm) and measures how easily a pesticide may be washed off the crop, leach into the soil or move with surface runoff. Pesticides with solubilities of less than 1 ppm tend to remain on the soil surface. They tend not to be leached, but may move with soil sediment in surface runoff if soil erosion occurs. Pesticides with solubilities greater than 30 ppm are more likely to move with water.

Pesticide persistence is measured in terms of the half-life, or the time in days required for a pesticide to degrade in soil to one-half its original amount. For example, if a pesticide has a half-life of 15 days, 50 percent of the pesticide applied will still be present 15 days after application and half of that amount (25 percent of the original) will be present after 30 days. In general, the longer the half-life, the greater the potential for pesticide movement. A pesticide with a half-life greater than 21 days may persist long enough to leach or move with surface runoff before it degrades.

No one factor--adsorption, water solubility, or persistence--can be used to predict pesticide behavior. It is the interaction of these factors and their interaction with the particular soil type and environmental conditions that determines pesticide behavior in the field.

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Ways to Minimize Pesticide Impact

The following are several practices which reduce the potential for pesticides to cause environmental damage or water contamination. Consider applying these practices to your farm.

Integrated Pest Management

Follow integrated pest management (IPM) principals. IPM doesn't rely solely on chemicals for pest control. Biological control, cultural practices, and timely chemical applications are used to obtain the necessary level of control. Pesticides are the last line of defense and are used only when pest levels are causing sufficient damage to offset the expense of the application. IPM also requires the following actions:

- Scout or monitor crops regularly to check the levels of pest populations and their damage.
- Implement available non-chemical control practices, including mechanical, cultural and biological controls, sanitation, and plant resistance. For example, use crop rotation to manage corn rootworms and cut alfalfa early to manage weevils (cultural controls); select resistant varieties (plant

resistance); thoroughly clean combines between fields to reduce weed seed introductions (sanitation); and use cultivation to control weeds (mechanical control).

- Maximize the benefits of naturally occurring biological controls by using pesticides only when necessary and selecting pesticides which are the least harmful to beneficials. For example, some insecticides and fungicides kill predatory mites, which can cause a mite outbreaks later in the season.

Prevent backsiphoning and spills

Never allow a hose used for filling a spray tank to extend below the level of the water in the tank. Contain all spills as quickly as possible and handle according to label directions. Use anti-siphon devices in the water line. They are inexpensive and effective. (See the [Emergencies section](#) of this website for further spill information.)

Consider weather and irrigation plans

Application just before rainfall or irrigation may result in reduced efficacy if the pesticide is washed off the target crop, resulting in the need to reapply the pesticide.

Heavy rainfall may also cause pesticide-contaminated runoff at the application site.

Pesticide use and storage

Always read and follow the label directions on the pesticide container. Use pesticides only when economic thresholds are reached and buy only what you need. Use appropriate protective equipment and clothing according to label instructions. Avoid mixing pesticides near wells or other sources of water. Store all pesticides safely, and according to legal requirements (see the [Storage and Shelf Life section](#) of this website).

Dispose of pesticide and chemical wastes safely

Dispose of excess chemical and pesticide containers in accordance with label directions. Triple-rinse empty pesticide containers (use this water in the spray tank), punch holes in containers, and dispose of them at approved waste disposal sites. (See the [Pesticide and Container Disposal section](#) of this website for further information).

Leave buffer zones around sensitive areas

Read the pesticide label for guidance on required buffer zones around water, buildings, wetlands, wildlife habitats and other sensitive areas.

Reduce off-target drift

Never begin an application when wind or temperature favors pesticide drift to an off target area. Use appropriate spray pressure and nozzle selection to minimize drift.

Application equipment

Maintain all application equipment in good working order and calibrate it regularly.

[Top](#) **Summary**

Many pesticides have the potential to cause harm to the environment if they are not used safely. Minimize the potential for environmental issues by following label directions, storing pesticides safely, and using them properly. Help keep groundwater free of contaminants; safeguard the health of your family, neighbors, and livestock; and ensure a clean, healthy environment by:

- Practicing Integrated Pest Management (IPM).
- Only using pesticides that are labeled for the intended crop and pest.
- Considering application site characteristics (soil texture, slope, organic matter).
- Considering the location of wells, ponds and other water bodies.
- Measuring accurately.
- Maintaining application equipment and calibrating accurately.
- Mixing and loading carefully.
- Preventing backsiphoning and spills.
- Considering the impact of weather and irrigation.
- Storing pesticides safely and securely.
- Disposing of wastes safely.
- Leaving buffer zones around sensitive areas.
- Reducing off-target drift.

34. Plant growth regulators

Plant hormones (phytohormones) are physiological intercellular messengers that are needed to control the complete plant lifecycle, including germination, rooting, growth, flowering, fruit ripening, foliage and death. In addition, plant hormones are secreted in response to environmental factors such as abundance of nutrients, drought conditions, light, temperature, chemical or physical stress. Hence, levels of hormones will change over the lifespan of a plant and are dependent upon season and environment.

The term “plant growth factor” is usually employed for plant hormones or substances of similar effect that are administered to plants. Growth factors are widely used in industrialized agriculture to improve productivity. The application of growth factors allows synchronization of plant development to occur. For instance, ripening tomatoes can be controlled by setting desired atmospheric ethylene levels. Using this method, fruits that are separated from their parent plant will still respond to growth factors; allowing commercial plants to be ripened in storage during and after transportation. This way the process of harvesting can be run much more efficiently. Other applications include rooting of seedlings or the suppression of rooting with the simultaneous promotion of cell division as required by plant cell cultures. Just like with animal hormones, plant growth factors come in a wide variety, producing different and often antagonistic effects. In short, the right combination of hormones is vital to achieve the desired behavioral characteristics of cells and the productive development of plants as a whole.

Traditionally five major classes of plant hormones are listed: auxins, cytokinins, gibberellins, abscisic acid and ethylene. However as research progresses, more active molecules are being found and new families of regulators are emerging; one example being polyamines such as putrescine or spermidine.

Note that this classification is based partially on the chemical structure and partially on the commonalities of plant physiological effects that certain substances exhibit. Members of one class may not relate from a structural point of view to another. Auxins for instance include not only many indole 3-carboxylic acid derivatives but numerous phenylacetic acids as well. Most cytokinins (such as zeatins) are derivatives from adenine but still differ widely in their chemical structure. Hence, the mechanism driving action may be different in each case and likewise each specific activity will differ also.

This is demonstrated by the range of optimal concentrations required for different factors which spans many decimals (0.001 – 100 mg/L).

Auxins

Auxin is the active ingredient in most rooting mixtures. These products help the vegetative propagation of plants. On a cellular level auxins influence cell elongation, cell division and the formation of adventitious roots. Some auxins are active at extremely low concentrations. Typical auxin concentration range from 0.01 to 10 mg/L.

Cytokinins

Cytokinins promote cell division, stimulate shoot proliferation, activate gene expression and metabolic activity in general. At the same time, cytokinins inhibit root formation. This makes cytokinins useful in culturing plant cell tissue where strong growth without root formation is desirable. Natural cytokinin hormone levels are high during maximum growth periods of mature plants. In addition, cytokinins slow the aging process in plants. Concentrations of cytokinin used for horticulture vary between 0.1 to 10 mg/L

Gibberellins

Gibberellins are derivatives of gibberellic acid. They are natural plant hormones and promote flowering, stem elongation and break dormancy of seeds. There are about 100 different gibberellins, but gibberellic acid (GA₃) is the most commonly used form. Gibberellins are fundamental to plant development especially with respect to the growth of stems. Low levels of gibberellins will prevent plants from reaching their natural height. Gibberellin synthesis inhibitors are extensively used in grain production to keep stems artificially short: shorter and thicker stems provide better support and resist weather conditions better too.

Gibberellins are particularly effective at breaking seed dormancy and at speeding up germination. Seeds that are difficult to germinate are frequently treated with gibberellic acid solutions

Abscisic Acid

Abscisic acid (ABA) is a plant growth inhibitor and an antagonist of gibberellins: it induces dormancy, prevents seeds from germinating and causes abscission of leaves, fruits, and flowers. High concentrations of abscisic acid can be induced by environmental

stress such as drought. Elevated levels of abscisic acid will eventually induce dormancy, when all non-essential processes are shut down and only the essential metabolism is maintained in guard cells

Ethylene

Ethylene is unique in that it is found only in gaseous form. It induces ripening, causes leaves to abscise and promotes senescence. Plants often increase ethylene production in response to stress and before death. Ethylene concentrations fluctuate with the seasons while playing a role in inducing foliage and ripening of fruit.

Polyamines

Polyamines are unique as they are effective (and are applied) in relatively high concentrations. Typical concentrations range from 5 to 500 mg/L. Polyamines influence flowering and promote plant regeneration

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