MAROTRAO WADAFALE COLLAGE OF AGRICULTURE, YAVATMAL

B.Sc. Hons (Agri)

Semester : VI

Course No : ELE-SSAC-364

Course Title : AGROCHEMICALS

COURSE TEACHER

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Teaching schedule

B.Sc. Hons (Agri.) **Semester: VI**

Course no. : ELE-SSAC-364 **Credit : 2+1=3**

Course title : Agro-chemicals

Lesson No.	Title	Weightage
1,	Introduction to agrochemicals. their types and role in agriculture	2
2	Effect of agrochemicals on environment, soil, human and animal health. Merits and demerits of their uses in agriculture, management of agrochemicals for sustainable agriculture	4
3	Fertilizers and their classification;	3
4 & 5	N fertilizers: classification, manufacturing process and properties their fate and reaction in soils.	4
6 & 7	Phosphatic fertilizers, Manufacturing process and properties	4
8	Potassic and complex fertilizers their fate and reaction in the soil	3
9 & 10	Secondary nutrients and fertilizers their types, composition, reaction in soil and effect on crop growth.	4
11	Micronutrient fertilizers their types, composition, reaction in soil and effect on crop growth	4
12	. Liquid fertilizers	3
13	Handling and storage of fertilizers	3
14	. Biofertilizers and their role in crop production.	4
15	Fertilizer control order and Insecticides Act	2
16	Introduction and classification of Insecticide. Different types of classification of insecticide.(Based on toxicity, mode of entry, mode of action, chemical nature)	4
17 & 18	Inorganic and organic insecticides, orgaochlorine, organophosphates, carbamates, synthetic pyrethroid, Neonitinoid, Biorationals	5
19	Insecticide act. and rules. Insecticide banned withdrawn and restricted. Criteria for banned, withdrawn and restricted use.	2
20	IGRs and Biopesticide ,reduced reisk insecticide	2
21	Botanical plant and animal systemic insecticides charecterstics & use (neem) pyrethrum, synthetic pyrethroids,.	3
22	Mode of action of insecticides (Pyrethroids,organophosphate carbamate and chitin synthesis inhibitors	4
23	Fate of insecticide in soil and plant. Degradation –Microbial degradation ,enzymatic degradation, conjunction of insecticide with clay/organic colloids(soil related properties	3
24	Insecticide resistance and its management	3
25	Pesticide residue Definition, steps involved in determination	3

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	of residue (collection, separation, cleaning, processing and cleanup, extraction)	
26 & 27	Copper fungicide. formation of Bordeaux mixture and Bordeaux paste, Chemical reaction involved merits and demerits of Bordeaux mixture, Mode of action of copper fungicide.	5
28	Sulfur fungicide: Organic and inorganic sulfur fungicide their classification and mode of action. Preparation of lime sulfur mixture and chemical reaction involved.	4
29	Benzimideazle fungicide, their chemical nature, mode of action and their use	3
30	Introduction to new generation fungicides. Viz. Metalaxyl, fosetyl A, Triazoles and shawbilirin fungicide	4
31	Herbicide- Classification, Formulations, Methods of application.	3
32	Mode of action of herbicide-Translocation and absorption	3
33	Persistence and fate of herbicide. Residual effect of herbicide	3
34	Introduction to selectivity of herbicide	2
35	Compatibility of herbicide with other Agrochemicals	2
36	Introduction to adjuvant and their use in herbicides	2

Lesson: 1

INTRODUCTION TO AGROCHEMICALS THEIR TYPES AND ROLE IN AGRICULTURE

Definition

The science of chemical compositions and changes involved in the production, protection and use of crops and livestock. Agrochemicals or agrichemicals, is a common name given to chemicals which are used in agriculture, to aid plants and crops growth and safety. Agrochemicals were manufactured to protect agricultural crops from pests and for augmenting crop yields. Agrochemical also includes fertilizers and soil conditioners.

Types of agrochemicals

Agrochemicals. They are the generic name given to chemicals (fertilizers, pesticides, insecticides, etc.) use in agricultural to facilitate plant growth and protection. Agro Chemicals in the Farm Ecosystem. Many farmers choose to use chemicals to keep weeds and pests from destroying their crops and to add more nutrients to the soil. There are three different kinds of pesticides; herbicides, insecticides and fungicides. ... Insects such as worms and beetles can infest a crop and destroy it.

Role in agriculture

Agrochemicals (agricultural chemicals, agrichemicals) are the various chemical products that are used in agriculture. In most cases, the term *agrochemical* refers to the broad range of pesticide chemicals, including insecticide chemicals, herbicide chemicals, fungicide chemicals, and nematicides chemicals (chemicals used to kill round worms). The term may also include synthetic fertilizers, hormones, and other chemical growth agents, as well as concentrated stores of raw animal manure. Typically, agrochemicals are toxic and when stored in bulk storage systems may pose significant environmental risks, particularly in the event of accidental spills. As a result, in many countries, the use of agrochemicals has become highly regulated and government-issued permits for purchase and use of approved agrichemicals may be required. Significant penalties can result from misuse, including improper storage

resulting in chemical leaks, chemical leaching, and chemical spills. Wherever these chemicals are used, proper storage facilities and labeling; emergency cleanup equipment; emergency cleanup procedures; safety equipment; as well as safety procedures for handling, application, and disposal are often subject to mandatory standards and regulations.While agrochemicals increase plant and animal crop production, they can also damage the environment. Excessive use of fertilizers has led to the contamination of groundwater with nitrate, a chemical compound that in large concentrations is poisonous to humans and animals. In addition, the runoff (or leaching from the soil) of fertilizers into streams, lakes, and other surface waters (the aquasphere) can increase the growth of algae, which can have an adverse effect on the life-cycle of fish and other aquatic animals.

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Lesson: 2

EFFECT OF AGROCHEMICALS ON ENVIRONMENT, SOIL, HUMAN AND ANIMAL HEALTH. MERITS AND DEMERITS OF THEIR USES IN AGRICULTURE, MANAGEMENT OF AGROCHEMICALS FOR SUSTAINABLE AGRICULTURE.

Agrochemicals. They are the generic name given to chemicals (fertilizers, pesticides, insecticides, etc.) use in agricultural to facilitate plant growth and protection. In short, they are agricultural chemicals. Environmental effects of the use of Agrochemicals. Many important benefits are achieved by the use of agrochemicals. These are largely associated with increased yields of plant and animal crops, and less spoilage during storage. Farmers apply nutrients on their fields in the form of chemical fertilizers and animal manure, which provide crops with the nitrogen and phosphorus necessary to grow and produce the food we eat. High levels of nitrogen and phosphorus can cause eutrophication of water bodies.

Excessive use of fertilizers, for example, can lead to the contamination of groundwater with nitrate, rendering it unfit for consumption by humans or livestock. Water containing large concentrations of nitrate can poison animals by immobilizing some of the hemoglobin in blood, reducing the ability to transport oxygen. In

addition, the run-off of agricultural fertilizer into streams, lakes, and other surface waters can cause an increased productivity of those aquatic ecosystems, a problem known as eutrophication. The ecological effects of eutrophication can include an extensive mortality of fish and other aquatic animals, along with excessive growth of nuisance algae, and an off-taste of drinking water. The use of pesticides can also result in environmental problems. As was previously noted, pesticides are used in agriculture to reduce the abundance of species of pests (that is the "targets") to below a level of acceptable damage, which is economically determined. Unfortunately, during many uses of pesticides in agriculture, the exposure of other organisms, including humans, is not well controlled. This is especially true when entire fields are sprayed, for example, when using application equipment drawn by a tractor, or mounted on an airplane or helicopter. During these sorts of broadcast applications, many non-target organisms are exposed to the pesticide. This occurs on the treated site, and also on nearby off-sites as a result of "drift" of the sprayed agrochemical. These non-target exposures cause many unnecessary poisonings and deaths of organisms that are not agricultural pests. In addition, there is a widespread, even global contamination of the environment with some types of persistent pesticides, especially with organochlorines such as DDT, dieldrin, and aldrin. This contamination involves the widespread presence of pesticide residues in virtually all wildlife, well water, food, and even in humans. Residues of some of the chemicals used in animal husbandry are also believed by some people to be a problem, for example, when traces of antibiotics and bovine growth hormones occur in consumer products such as meat or milk.

Some of the worst examples of environmental damage caused by pesticides have been associated with the use of relatively persistent chemicals, such as DDT. Most modern usage of pesticides involves chemicals that are less persistent than DDT and related chlorinated hydrocarbons. However, severe damages are still caused by the use of some newer pesticides. In North America, for example, millions of wild birds have been killed each year as a non-target effect of the routine use of carbofuran, an agricultural insecticide. This is a substantial ecological price to pay for the benefits associated with the use of that agrochemical. The use of some pesticides is also risky for humans. About one million pesticide poisonings occur globally every year,

resulting in 20,000 fatalities. About one-half of the human poisonings occur in poorer, less-developed countries, even though these places account for only 20% of the world's use of pesticides. This disproportionate risk is due to greater rates of illiteracy in poorer countries, and to lax enforcement of regulations concerning the use of pesticides.

There have been a few examples of pesticides causing extensive toxicity to humans. The most famous case occurred at Bhopal, India, in 1984, in the vicinity of a factory that was manufacturing an agricultural insecticide. In that case, there was an accidental release of about 45 tons (40 tonnes) of deadly methyl isocyanate vapor to the atmosphere. This agrochemical-related emission caused the deaths of about 3,000 people, and more than 20,000 others were seriously injured. These and other environmental effects of the use of some agrochemicals are unfortunate consequences of the application of these chemical tools to deal with agricultural problems. Researchers are constantly searching for non-chemical ways of dealing with many of these agricultural needs. Much attention is being paid, for example, to developing "organic" methods of enhancing soil fertility and dealing with pests. Unfortunately, economically effective alternatives to most uses of agrochemicals have not yet been discovered. Consequently, modern agricultural industries will continue to rely heavily on the use of agrochemicals to manage their problems of fertility, soil quality, and pest.

Reference:

Plimmer, Jack R. *Encyclopedia of Agrochemicals.* New York: John Wiley & Sons, 2002.

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Lesson: 3

FERTILIZERS AND THEIR CLASSIFICATION

Fertiliilzers

Any organic or inorganic material of natural or synthetic origin added to a soil to supply certain element essential for the growth of plants.

Fertilizers are classified on the basis of major nutrient content.

1. Nitrogenous fertilizers

2. Phosphatic fertilizers

3. Potassic fertilizers

1. Nitrogenous fertilizers

a) Ammonical N fertilizers (NH_3, $(NH_4)_2SO_4$)
b) Nitrate N fertilizer (KNO_3, $NaNO_3$)
c) Ammonical nitrate ($CaCO_3.NH_4NO_3$)
d) Amide N fertilizers (NH_2CONH_2, $CaCN_2$)
e) Slow release N fertilizer (urea coated, urea form,IBDU)

2. Phosphatic fertilizers

a) Water soluble - P SSP, DSP& TSP
b) Citrate soluble - P DCP, Basic slag
c) Citrate insoluble - P Rock phosphate , Bone meal

3. Potassic fertilizers

a) Muriate of Potash (Potassium chloride)
b) Sulphate of Potash (Potassium sulphate)

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Lesson No: 4 & 5

CLASSIFICATION, MANUFACTURING PROCESS AND PROPERTIES THEIR FATE AND REACTION IN SOILS. N FERTILIZERS: CLASSIFICATION, MANUFACTURING PROCESS AND PROPERTIES, THEIR FATE AND REACTION IN SOILS

Classification of nitrogenous fertilizers:

Nitrogenous fertilizers are classified into four groups on the basis of chemical form in which nitrogen is combined with other elements.

1. Nitrate fertilizers: Nitrogen is in. oxidised form i.e. NO_3

e. g. a) Sodium nitrate ($NaNO_3$) 16 % N

b) Calcium nitrate [($Ca(NO_3)_2$)] 15.5 % N

2. Ammoniacal fertilizers: Nitrogen is in reduced form i.e. NH_4-N

e.g. i) Ammonium sulphate [$(NH_4)2SO_4$] 20 % N

ii) Ammonium chloride (NH_4CI) 26 % N

iii) Anhydrous ammonia 82 % N

iv) Ammonium phosphate ($NH_4H_2PO_4$) - 20% N + 20 % P_2O_5 16 % N + 20 % P_2O_5

3. Nitrate and ammonium fertilizers : Nitrogen is in the form of NO_3-N + NH_4-N e.g.

i) Ammonium nitrate (NH_4NO_3) 34% N

ii) Calcium ammonium nitrate 26 %N

iii) Ammonium sulphate nitrate 26 % N

4. Amide fertilizers: Organic nitrogenous fertilizers nitrogen, in amide (NH_2) form e.g.

i) Urea [$CO(NH_2)_2$] 46 % N

ii) Calcium cynamide ($CaCN_2$) 21 %

Sources of nitrogen :

Mineral deposits, rain water, soil organic matter, atmospheric N and industrial source.

Management of nitrogenous fertilizers:

1. For paddy ammonical and ammonia forming fertilizers should be used.
2. For all other field crops, a II nitrogenous fertilizers are equally effective.
3. On acid soils *or* soils low in lime/calcium, continued use of ammonium sulphate, urea, ammonium chloride and ammonium sulphate nitrate should be avoided.
4. A nitrate fertilizer like sodium nitrate is suited for top dressing and side dressing when growing crops need nitrogen immediately.
5. Since nitrate fertilizers are easily leached, they should not be applied in Large quantities in Light sandy soils or during the rainy season. In sandy soils, the entire recommended dose of nitrogen should be applied in split doses.
6. In the winter or rabi season, the nitrogenous fertilizer should be selected on the basis of cheapness per unit kg of nitrogen; as all nitrogenous fertilizers are equally effective and loss of nitrogen due to leaching does not usually occur.

Reference:

1. Yawalkar K.S. & et al. Manures and fertilizers: 1992 (7th edition Agri. Horticultural publishing House, Nagpur pp. 164 to 189.

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Lesson No: 6 & 7

Phosphatic fertilizers, Manufacturing process and properties

Phosphatic fertilizers :

Manufacturing process and properties of single super phosphate, enriched super phosphate, ammonium phosphate, ammonium polyphosphate

Classification of phosphatic fertilizers :

Phosphatic fertilizers are classified into three groups, depending *on* the *form* in .which orthophosphoric acid/phosphoric acid is combined with calcium.

1. **Water soluble/Monocalcium phosphate: $Ca(H_2PO_4)_2$**

   i) Single super-phosphate - 16% P_2O_5

   ii) Double super-phosphate - 32 % P_2O_5

   iii) Triple super-phosphate - 48 % P_2O_5

   iv) Ammonium phosphate - 11 %N + 52% P_2O_5

2. Citric acid soluble/Dicalcium phosphate ($CaHP0_4$)

i) Basic slag - 14 to 18 % P_2O_5

ii) Tricalcium phosphate - 34% to 39 % P_2O_5

iii) Rhenania phosphate - 23 to 26% P_2O_5

3. Insoluble/Tricalcium phosphate - $Ca_3(PO_4)_2$ Acid soluble

i) Rock-phosphate - 20 to 40 % P_2O_5

ii) Raw bonemeal - 20 to 25 %10 P_2O_5

iii) Steamed bonemeal - 22 % P_2O_5

General characteristics of phosphatic fertilizers :

1. Water soluble/Monocalcium phosphate
2. Citric acid soluble/Dicalcium phosphate
3. Insoluble/Dicalcium phosphate

Reactions of single super-phosphate in soils:

a) Neutral soils

$Ca(H_2PO_4)_2 + Ca(HCO_3)_2 \rightarrow 2CaHPO_4 + 2H_2CO_3$

b) Alkaline soils

1) $Ca(H_2PO_4)_2 + Ca(HCO_3)_2 = 2CaHPO_4 + 2H_2CO_3$

2) $Ca(H_2PO_4)_2 + 2Ca(HCO_3)_2 = Ca(PO_4)_2 + 4H_3CO_3$

c) Acidic soils:

$2Ca\ (H_2PO_4)_2 + Fe\ _2O_3 = 2\ Fe\ PO_4 + 2\ CaHPO_4 + 3\ H_2O$

Reactions of Rock-Phosphate in soils :

a) Acidic soils

i) $[Ca_3(PO_4)\ _2]\ 3CaCO_3 + 6H_2CO_3 = 3Ca(H2PO_4)_2 + 7CaCO_3$

ii) $[Ca_3(PO_4)_2]\ 3CaCO_3 + 14HNO_3 = 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + H_2CO_3$

Management of phosphatic fertilizers:

1. Water soluble phosphatic fertilizers are suitable for slightly acidic, neutral or alkaline soils.
2. W.S.P. fertilizers are applied to soils when crop requires a quick start.
3. W.S.P. fertilizers are suitable for short duration crops like paddy, wheat, jowar, ragi, maize, soybeans, cabbage, cauliflower, potato, gram & Vegetable crops.
4. Citrate soluble phosphatic fertilizers are suitable for moderately acidic soils, long duration crops like sugarcane, tapioca, tea, coffee, legume & pastures.
5. Insoluble phosphatic fertilizers are suitable for the soil which is strongly to extremely acidic & long duration fruits crops.
6. SSP should be applied to the soil just before sowing in single dose.
7. SSP is unsuitable for top-dressing due to slow mobility for short duration crops and it should not be used in acidic soils.

Reference:

Yawalkar K.S. & et al. Manures and fertilizers: 1992 (7th edition Agri. Horticultural publishing House, Nagpur pp. 164 to 189.

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Lesson: 8

POTASSIC AND COMPLEX FERTILIZERS THEIR FATE AND REACTION IN THE SOIL

Classification of potassic fertilizers

1) Fertilizers having K in the chloride form e.g. KCl
2) Fertilizers having K in non-chloride form e.g. K_2SO_4 and KNO_3

Source of potassic fertilizers :

Mainly from water soluble potash minerals, and small extent from brine. The potash containing soluble minerals are:

1) Sylvite KCl 63.1 % K_2O
2) Carnallite KCl. $6H_2O$ 17.0 % K_2O

3) Kainite KCl. $MgSI_4.3H_2O$ 18.9 % K_2O

4) Langbeinite $K_2SO_42MgSO_4$ 22.6 % K_2O

5) Sylvinite (mixture) 20.3 % K_2O

Classification and properties of potassic fertilizers:

1) Potassium chloride / muriate of potash (KCl)

- K with Cl as anion chloride containing fertilizer.
- K_2O content 55 - 50 %
- Mineral used sylvite and carnalite

2) Potassium sulphate (K_2SO_4)

- Non chloride fertilizer
- Pure salt content 54 % K2O
- Commercial salt content 48 % K2O
- Mineral used kainite and longbeinite

3) Shoenite : K_2SO_4. $MgSO_4.6H_2O$

- It is double salt of SO_4 with K and Mg
- It is by product of marine salt works
- K_2O 25-30 %
- MgO 10-12 %

4) Reaction in soils

$KCl = K^+ + Cl^-$

$K_2SO_4 = 2K+ + SO_4^{2-}$

Management of potassic fertilizers :

KCl is cheaper fertilizer and extensively used by the cultivators for all crops except where no chloride is desired in the fertilizer, e.g. Tabacco.

K_2SO_4 is some what costlier on the basis of per unit of K as compared to KCl and used for the crops like potato, tobacco and tomato.

Complex fertilizers:

The commercial fertilizers containing atleast two or more of the primary essential plant nutrients (N, P, K) are called complex fertilizers. When the fertilizer contains only two of the primary nutrients it is designated as incomplete complex fertilizer, while one containing all three primary major nutrients (N, P and K) is designated as complete complex fertilizer.

Characteristics of complex fertilizer:

1. High analysis fertilizers
2. Have Uniform grain size
3. Cheaper on the basis of nutrient content per Kg.
4. Transport and distribution cost is less
5. Safe for storage
6. Desirable as these contain balanced nutrients *for* applications.
7. Non caking and non hygroscopic.

Advantages of complex fertilizers :

1. Easy application
2. Balanced crop nutrition.
3. High fertilizer efficiency
4. Even distribution of nutrients
5. Saving of labour and time
6. Safe for storage.

High analysis fertilizer :

Fertilizers have a high content of total plant nutrients more than 30 kg per 100 kg of fertilizer.

Complex fertilizer :

Give the manufacture, properties and nutrient content of following complex fertilizers.

Nitrophosphate Manufacture :

1. Nitro carbonic process
2. Nitro-separation process
3. Process involving nitric acid & phosphoric acid
4. Process involving nitric acid.

Properties of nitrophosphates :

1. Granulated fertilizer containing stabilizer
2. Contains Nitrogen as well as phosphorus
3. Excellent physical conditions during storage and handling

RCF (Trombay) manufactures three types of nitrophosphates:

1) Suphala (20:20:0) 2) Suphala 3) Suphala (15:15:15)

Ammonium phosphate :

Manufactured by combing ammonia with phosphoric acid. Monoamonium phosphate. (MAP). Diaimmonium phosphate (DAP) is popular having 11 :52:0 and 18:46:0 grades respectively.

Characteristics of Ammonium Phosphates:

1. Slightly grey material
2. Slightly acidic to neutral
3. Produce acidity in soil if used continuously and require 80 Kg of $CaCO_3$ to counteract its acidity
4. It is least hygroscopic

Various grades of ammonium phosphates are manufactured. NPK Complex fertilizers: Complex fertilizers containing various composition of N, P and K. These are manufactured for application to various crops.

Value of complex fertilizers :

1. Their content of individual nutrients and ratio of N, P, K.
2. Form in which individual nutrients are present
3. The resultant basic or acidic residual effect.
4. These contain trace elements and contamination substances viz. chlorides, sulphates etc.

Reference books :

Yawalkar *et al* (1976) Manures and Fertilizers.

ICAR Handbook of manures and fertilizers (1971) publication.

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Lesson: 9 & 10

SECONDARY FERTILIZERS THEIR TYPES, COMPOSITION, REACTION IN SOIL AND EFFECT ON CROP GROWTH

Secondary nutrients fertilizers:

Gypsum, magnesium sulphate, dolomite, elemental sulphur are used as secondary nutrients fertilizers. Calcium, magnesium, and sulphur are essential plant nutrients. They are called secondary nutrients because plants require them in smaller quantities than nitrogen, phosphorus, and potassium. On the other hand, plants require these nutrients in larger quantities than the micronutrients such as boron and molybdenum.

Calcium, magnesium, and sulphur are generally adequate in most soils with favourable pH and organic matter levels. They affect pH when applied to the soil. Calcium and magnesium both increase soil pH, but sulphur from some sources reduces soil pH. Compounds containing one or more of these nutrients are often used as soil amendments rather than strictly as suppliers of plant nutrition.

Calcium:

The primary function of calcium in plant growth is to provide structural support to cell walls. Calcium also serves as a secondary messenger when plants are physically or biochemically stressed. Soils with favourable pH levels are normally not deficient in calcium. Acid soils with calcium contents of 500 pounds per acre or less are deficient for legumes, especially peanuts, alfalfa, clovers, and soybeans. At this level, limited root system crops such as tomatoes, peppers, and cucurbit would also need additional calcium. Soluble calcium is available as the Ca^{2+} ion and is needed for peanuts at pegging time and for peppers and tomatoes to prevent blossom end rot. Available calcium can be lost from the soil when it is (a) dissolved and removed in drainage water, (b) removed by plants, (c) absorbed by soil organisms, (d) leached from the soil in rain water, or (e) absorbed by clay particles. Deficiency symptoms include death at the growing point, abnormally dark green foliage, weakened stems, shedding flowers, and any combination of these. Limestone is the primary source of calcium. Other common sources include basic slag, gypsum, hydrated lime, and burned lime. These sources are recommended for peanuts, peppers, and tomatoes. In

peanuts, they prevent pops and encourage pegging. In tomatoes and peppers, they prevent pops and blossom end rot. Hydrated lime and burned lime contain more readily available calcium than do basic slag and gypsum. Gypsum does not affect soil pH even though it contains calcium.

Average percentage of chemical content of major sources of calcium.

Calcium				
Material	**Calcium**	**Magnesium**	**Sulfur**	**Other**
Calcite lime	31.7	3.4	0.1	0
Dolomitic lime	21.5	11.4	0.3	0
Gypsum	22.5	0.4	16.8	0
Basic slag	29.0	3.4	0.3	No longer a P source

Magnesium:

Magnesium is adequate for crop production in most soils except the coarse sandy soils of the Coastal Plains and the heavy dark clays. Magnesium is absorbed as the Mg^{2+} ion and is mobile in plants, moving from the older to the younger leaves. It leaches from the soil like calcium and potassium.

Magnesium is the central atom amid four nitrogen atoms in the chlorophyll molecule, so it is involved in photosynthesis. It serves as an activator for many enzymes required in plant growth processes and stabilizes the nucleic acids. Interveinal chlorosis is a deficiency symptom in crops such as legumes, corn, sorghum, cotton, and certain leafy vegetables. (Interveinal chlorosis is a yellowing between the veins while the veins remain green.) The leaves may become pink to light red and may curl upward along the margins. To correct magnesium deficiency in soil, use dolomitic lime when lime is needed; use soluble sources of magnesium when lime is not needed.

Cattle are often affected by grass tetany when forage magnesium content is low. Other factors include nitrogen, calcium, and potassium levels, stage of growth (usually in spring), whether or not cattle are lactating, and seasonal conditions. Dolomitic limestone is recommended as a liming material where grass tetany has been a problem. Give grazing animals supplemental magnesium and calcium when grass tetany is an issue. The most common soluble sources of magnesium to use as fertilizer are magnesium sulfate (containing 10% Mg and 14% S, also known as Epsom salt), sulphate of potash magnesia (containing 11.2% Mg, 22% S, and 22% K2O, commercially sold as K-Mag), and magnesium oxide (containing 55% Mg, also known as magnesia).

Average percentage of chemical content of major sources of magnesium

Material	Calcium	Magnesium	Sulfur	Other
Magnesium sulfate	2.2	10.5	14.0	0
Sulfate of potash magnesium	0	11.2	22.7	22 K_2O
Magnesium oxide	0	55	0	0

Sulphur:

Sulphur is needed in fairly large quantities by most crops. It is an essential building block in chlorophyll development and protein synthesis. Sulphur is required by the rhizobia bacteria in legumes for nitrogen fixation. In general, crops remove about as much sulphur as they do phosphorus. Grasses remove sulphur more efficiently than legumes, and clovers often disappear from pasture mixtures when sulphur is low.

The sulphate ion, SO_4, is the form primarily absorbed by plants. Sulphate is soluble and is easily lost from soils by leaching. As sulphate is leached down into soil, it accumulates in heavier (higher clay content) subsoils. For this reason, testing for sulphur in topsoil is unreliable for predicting sulphur availability during a long growing season. Many coarse-textured, sandy soils and low organic matter, silty soils are sulphur deficient for crop production. Many acid soils contain metallic sulphides

that release sulphur as weathering occurs. Sulphur deficiency symptoms show on young leaves first. The leaves appear pale green to yellow. The plants are spindly and small with retarded growth and delayed fruiting. For a rapid correction of a deficiency, use one of the readily available sulphate sources. There are many sources of fertilizer sulphur available. Organic matter is the source of organic sulphur compounds and is the main source of soil sulphur. Other sources of sulphur are rainfall and fertilizers that contain sulphur. Some readily available sources include ammonium sulphate (21 % N and 24 % S), potassium sulphate (50 % K_20 and 17.6 % S), gypsum (32.6% CaO and 16.8 % S), and zinc sulphate (36.4 % Zn and 17.8 % S). There are several other sulphate sources as well as less available sources of sulphur in the elemental or sulphide form.

Average percentage of chemical content of major sources of sulphur

Material	Calcium	Magnesium	Sulfur	Other
Ammonium sulfate	0.3	0	23.7	21 nitrogen
Potassium sulfate	0	1.2	17.6	50 % K_2O
Gypsum	22.5	0.4	16.8	0
Magnesium sulfate	2.2	10.5	14.0	0
Zinc sulfate	0	0	17.8	36.4 % zinc
Prilled sulfur	0	0	33-99	0

Reference

Maathuis F.J.M. (2009) Physiological functions of mineral macronutrients. Current Opinion in Plant Biology 12:250-258.

McCauley A., Jones C., Jacobsen J. (2009) Plant nutrient functions and deficiency and toxicity symptoms, Montana State University Extension Service, Bozeman, MT. pp. 16.

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Lesson: 11

MICRONUTRIENT FERTILIZERS THEIR TYPES, COMPOSITION, REACTION IN SOIL AND EFFECT ON CROP GROWTH

Micronutrient :

Micronutrient is a chemical element necessary only in extremely small amounts (usually less than 50 ppm in plants) for growth of plants. Fe, Mn, Zn, Cu, Mo, B and Cl are essential micronutrients.

Micronutrient fertilizers : The carriers used as fertilizers to supply, micronutrients are called as micronutrient fertilizers.

Classification of micronutrient fertilizers

1. Straight inorganic salts
2. Natural and synthetic chelates as carriers of micronutrients .

1. Straight inorganic salts :

Micro Nutrients	Name of salt	Nutrient	Rate of application	
			Soil	Spray
Iron (Fe)	Ferrous sulphate $FeSO_4.7H_2O$	20 % Fe	10 kg/ha $FeSO_4$	0.4 % + 0.2 %lime
Zinc (Zn)	Zinc, sulphate $ZnSO_4.7H_2O$	22 to 35 % Zn	40 to 50 kg/ha $ZnSO_4$	0.5 % + 0.2 % lime
Copper (Cu)	Copper sulphate $CuSO_4.\ 5H_2O$	25 to 35 % Cu	10 to 50 kg/ha $CuSO_4$	0.1% to 0.5 % lime

Boron (B)	Borax (Sodium Borate) $Na_2B_4O_7$ 10 H_2O	10.6 % B	5-20 kg/ha Borax	0.2 % Boric acid
Molybdenum (Mo)	Ammonium molybdate $(NH_4)_6 Mo_7 O24, 4H_2O$	52 % Mo	0.14 kg/ha Mo or 1.12 kg/ha amino Molybdate (0.0) to 2.37	0.05 % Ammo. Molybdate

2. Synthetic and natural chelates :

Chelates : It is a term applied to compounds which tightly hold certain cations that are attracted towards them and release them slowly for utilisation by plants.

Chelates are generally organic compounds that combine with cations like Fe, Mn, Zn, Cu in complex ring structure.

Chelating compounds or agents :

EDTA, DTPA, EDDHA, CDTA, NTA

Natural chelates :

FYM and other organic manures contain the organic substances which acts as chelating compound. Therefore micronutrient salts applied through FYM and manures are slowly released and made available to plants.

Effects on crop growth :

1. Essential nutrients for life & growth of plants
2. Help to form enzymes or vitamins
3. Aid in keeping another element reduced or oxidised.
4. Increase the resistance to diseases
5. Interact with secondary and major plant nutrients.

6. Directly influence the activity of micro organisms.
7. Excess of micronutrients may create toxicity in plants.

Reactions of micronutrient / fertilizers in soil:

The different soil conditions influence the availability of micronutrients. The soil acidity, alkalinity, organic matter content, temporary water logging conditions, application of phosphotic and potassic fertilizers in soil are important factors which reduce or increase the availability of applied micronutrients.

When soil contains more lime, there is a iron deficiency. Excess phosphate fertilization induced iron chlorosis and Zn deficiency and favors molybdenum availability (Antagonistic effect). High potassium application creates manganese deficiency. Boron does not normally occur in toxic quantities on most arable soils. Decrease in acidity generally reduces the availability of copper. An increase in pH brings about a conversion of bivalent Mn compound to unavailable MnO.

Reactions of micronutrients in soil:

1. Micronutrient cations interact with silicate in two ways
   a) They may be involved in cation exchange reaction Ca of H
   b) They may be more tightly bound or fixed to certain silicate clays (2:1 type).
2. Zn, Co, Mn & Fe ions are found as elements in crystals of silicate clay.
3. Depending on the conditions they may be released from the clays or fixed.
4. The fixation may be serious in the case of cobalt and sometimes Zn.
5. The uptake of Fe & Zn may be reduced in the presume of excess P.
6. Micronutrient cations may be held in the Organic Cemlimation (Protein, aminoacids, Humus, citric and tartaric acid).
7. When an. inorganic iron salt such as $FeSO_4$ is added to calcareous soil most of the Fe is quickly rendered unavailable by reaction with hydroxide.

   $Fe^{3+} + 3OH^- \longrightarrow \_FeOOH + H_2O$

Available ←---------- Unavailable

8. If iron is added in the form of Fe chelate the iron remains in the chelate form which is available to plant.

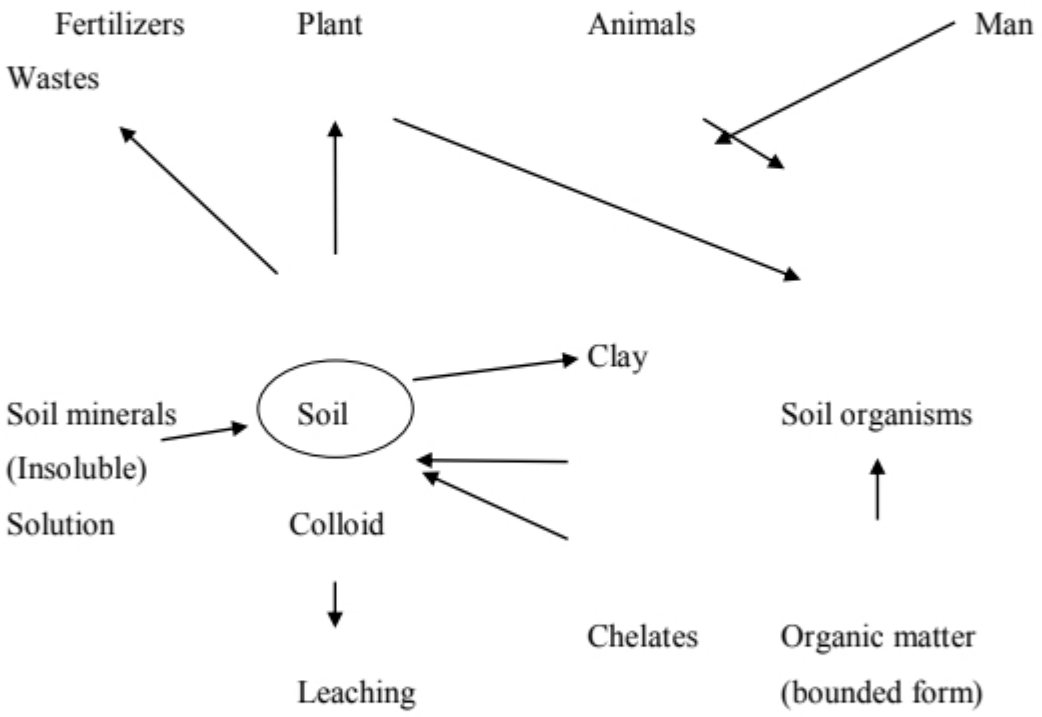
FeEDDHA+ 3 OH ------→ FeOOH + EDDHA-3 +

Available ←----- Ethyl Diomine Dihydroxy pheylactic acid. H_2O.

9. In chelate is added to a soil with significant quantities of available Iron.

Zn Chelate + Fe -----→ Fe chelate + Zn

←------



Reference:

1. N.C. Brady: Nature and properties of soil. 1985 : 10th edition.
2. Yawalkar K.S. Manures & fertilizer: (1992). pp. 200-214.

Lesson: 12

LIQUID FERTILIZERS

Some of the fertilizers are in liquid form for applying with irrigation water or for direct application.

Benefits of liquid fertilizers

- Less labour requirement and Ease of handling
- Possibility of mixing with herbicides have made the liquid fertilizers more acceptable to farmers.
- Liquid fertilizers has low price as compare to solid fertilizers.
- It allows accurate and even distribution.
- Higher efficiency than solid fertilizers, less leaching due to split application.
- It can be mixed with pesticides.
- By adding liquid fertilizers the droplet evaporation can be reduced and limits atmospheric pollution.

Liquid fertilizers are of two types

(1) Clear liquid fertilizers -

When the nitrogenous, phosphatic, potassic and other fertilizer materials are completely dissolved in water, these are called clear liquid fertilizers.

(2) Suspension liquid fertilizers-

Suspension liquid fertilizers are those in which some of the fertilizer materials are suspended as fine particles. Fertilizers are grouped based on the nutrient present in the fertilizers namely, nitrogenous fertilizer, phosphatic fertilizer, potassic fertilizer, boron fertilizer etc.

Application of fertilizers in liquid form

a. Starter solutions

b. Foliar application or spray fertilization

c. Direct application to the soil

d. Application through irrigation water (Fertigation)

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Lesson: 13

HANDLING AND STORAGE OF FERTILIZERS

Fertilizers differ in their ability to become moist or hygroscopic, as such they have to be handled during rainy season.

Main features from storage point of view are as below

Name of fertilizer	Easy storage and handling
i. Ammonium chloride	Excellent, no difficulty in storage and handling
ii. Ammonium nitrate fertilizer is	Storage prqperties satisfactory but hygroscopic. So bags are firmly tied. As it is fire hazardous handle carefully. It is bagged in polythene lined jute bags as it is hygroscopic.
iii. Urea	Storage properties satisfactory. Hygroscopic, store in polythene lined jute bags in dry place.
iv. Ammonium sulphate & sodium nitrate.	Storage properties good, no difficulties in handling & storage.

Phosphatic fertilizers:

1) **Single super phosphate:**

   i) It contains small amount of acid. which deteriorate gunny bags, hence it should be stored in polythelene lined gunny bags.

   ii) Cakes formation in moist condition.

2) **Dicalcium phosphate -** Excellent physical condition.

Potassic fertilizers:

Potassium sulphate	}	Excellent physical condition for
Potassium chloride		storage and handling.

Protect all fertilizer bags from moisture, water and rains. Protect bags against excessive sunshine .and heat by making use to shade of trees structures & covers.

Reference:

1) Yawalkar et.al. (1981) Manures and fertilizer, pp. 115-117.

2) FAT (1980) Hand book on Fertilizer Technology.

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Lesson: 14

BIOFERTILIZERS AND THEIR ROLE IN CROP PRODUCTION.

Biofertilizers :

These are also called as microbial inoculants which are biological material used as a source of supply of nutrients through various biological reactions in soil/plants.

Definition :

Generally they are defined as the preparations containing live or latent cells of efficient strains of nitrogen fixing phosphate solubilising or cellulolytic microorganisms used for the application to seed, soil or composting areas with an objective of increasing numbers of such micro-organisms and to accelerate certain microbial processes to augment the extent of availability of nutrients in a form which can be easily assimilated by plants.

Types of biofertilizers :

Rhiozobium, Azotobacter, Azospirillum, Blue green algae, Azolla, mycorrhiza, sulphur oxidising and, phosphate solubalizing microorganisms.

Azotobacter : Inoculation of seed or soil with Azotobactor culture is effective in increasing yields of crops. These bacteria fix nitrogen in the range of 3-15 N kg/ha^{-1} yr-1 under normal agricultural conditions.

1. Azotobacter chroococum - in neutral to alkaline soils

2 Azotobacter agilis - is an aquatic species

3. Azotobacter Bejerinka - is found Acidic soils.

Blue green algae : Utilization of blue green alagae for rice is very promising. The BGA possesses the twin properties. It is recommended that algal preparations are applied at the rate of 10 kg/ha^{-1} in rice fields after one week of transplantation.

Mycorrhizae : Mycorrhizae is the symbiotic association of fungi with roots of vasicular plants.

Vascular-arbuscular mycorhizae have (VAM) been observed in fruit crops like citrus, papaya and litchi with beneficial effects. These fungi assist in the uptake of phosphate also.

Azospirillum : Certain micro-organisms colonize the root zones and fix nitrogen in loose association with plants. A very important category of this bacterium is Azospirillum. The crops which respond to azospirillum application are maize, oat, barley, sorghum, pearl millet and forge crops.

Sulphur oxidising micro-organisms : The bulk of soil sulphur is in organic form which is metabolised by soil-microorganism to make it available in an inorganic form for plant nutrition. This conversion is termed as sulphur mineralisation. In the absence of Oxygen certain microorganisms produce H_2S from organic sulphur substrates.

eg. Bacteria: (Thiobacillus, Thithrix thioploca and Beggiatoa)

Actinomycetes - (Aspergillus, penicillum) fungi.

Thiobacillus produce H_2SO_4 when elemental sulphur is added to soil. Thiobacillus is used for manufacture of Siosuper organic fertilizer which is mixture of rock-phosphat and inoculated with Thiobacillus Thiooxidants.

Phosphate solubilizing organism : Phosphates exists in soil in both organic and inorganic forms. seed or soil is inoculated with P dissolving microorganisms alongwith P fertilizers. Solubilisation of P depends on pH of soil. 'In neutral to alkaline soils having high cone of Ca, which is precipitated as Ca-p, microorganisms dissolve such phosphates and render them easily available to plants. eg. Bacteria.Bacillus (B.Megaterium, B. Pulvifaciens) Pesudomonas (P. Putide, P. rathonia)

Fungi : Azospirullum (A. niger, A flavas).

Penicillium (P.digitatum P.oxysponim).

Reference :

1. N.S. Subba Rao : Biofertilizers in Agriculture (1986). Oxford & IBH PUB.CO. New Delhi.

2. A. K. Dohama : Organic farming for sustainable agriculture : 1977 : 2nd edition. Agrobotamic. Bikaner pp. 139-146. ,

3. ICAR : Hand book of manures and fertilizers: 1971 : Revised edition pp. 22.

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Lesson: 15

FERTILIZER CONTROL ORDER AND INSECTICIDES ACT

Fertilizer control order:

An order issued by the Government of India under powers conferred by Section 3 of the Essential Commodities Act 1955, under the powers, the Government controls the production, marketing, price and quality of fertilizers. There are 39 Clauses of this order covering definitions, prices, registration of dealers and fertilizer mixtures, regulation on manufacture cell packing requirement, disposal of non-slandered fertilizers, enforcement authority, analysis of samples, etc. The schedule I of the order includes detailed specifications of fertilizers covered by it. In schedule II detailed procedure regarding sampling technique and methods of analysis is given.

Insecticide Act :

The main objective of the Insecticide Act is to regulate the import, manufacture, safe transport, distribution and use of insecticides with a view to prevent risk to human beings, animals and for matter connected herewith. All the praisions of the Insecticide Act were brought into force with effect from 1st August, 1971, which was passed in 1968. Due to legal reasons, the act was called Insecticide Act and not pesticide Act under Section 93 (C) the word insecticide means. (1) Any substance specified in the schedule. (2) Any other such substances including fungicide and weedicides may be included after consolation with the board and central Government. (3) Any preparation containing one or more of such substances. Salient features of the Insecticide Act Functions of Central Institute Board Registration Committee, Registration Procedure, Provisional Registration under Section 9(3B), Regular Registration under Section 9(3) of the Act Date requirement for repeat registration under section 9(4).

Lesson: 16

INTRODUCTION AND CLASSIFICATION OF INSECTICIDE. DIFFERENT TYPES OF CLASSIFICATION OF INSECTICIDE. (BASED ON TOXICITY, MODE OF ENTRY, MODE OF ACTION, CHEMICAL NATURE)

PESTICIDES

Any substance or mixture of substances used to prevent, destroy, repell or mitigating any insects, rodent, namelodey, fungi, weed or any other form of terrestrial or aquatic plant or animal life or microorganisms. Pesticides is a general term which includes all the chemicals used as insecticides, fungicides, herbicides etc. Pesticides means any substance intended for preventing, destroying, attracting, repelling or controlling any pest including unwanted species of plants or animals during production storage, transport, distribution and processing of food agricultural commodities or animal feeds or which may be administered to the animals for the control of ectoparasites.

Insecticides : substances that prevent, destroy kill, mitigate insects.

Fungicides : Substances that prevent, destroy, or inhibit the growth of fungil diseases of crops.

Herbicides : Substances which are used for preventing or inhibiting growth of plant or for killing weeds.

Rodemticides : Substances that inhibit growth, destroy or kill rodents.

Nematicides : Substances that prevent, destroy repel or inhibit the nematodes.

Classification of pesticides

1. Acaricides - ticks and mites Ex. Sulphur and lime sulphur
2. Algicides - Algae and other aquatic vegetation Ex. Copper sulphate
3. Antiseptics- Non metals from microorganisms
   Ex. Phenol, mercuric chlorosis
4. Arboricides- Undesirable arborell (Vegetative part) and bushy
   vegetation. Ex. Sulphuric acid, copper sulphate.
5. Bactericides- Bacteria and bacterial diseases
   Ex. Penicillin, streptomacin.
6. Fungicides - Plant diseases caused by various fungi.
   Ex. Bordeax mixture
7. Herbicides - Control of weeds Ex 2-4-D, 2-4-5-T, Diurea.

8. Insecticides- Harmful insect Ex Endosulphan, carbaryl.
9. Molluscides - Climacides – soft bodjed insects like snails and slug
   Ex. Metal dehyde.
10. Nematicides - Control of nematode
   Ex. Methyle bromide and other fumigants.
11. Zoocides - Control of rodents
   (Rodenticides) Ex. Zinc phosphate, vartarin.
12. Pesticides - to kill the fish Ex. Rotenoue.

Adjutants and others

1. Chemosterilants - Used to reduce or completely suppress the reproductive ability of insects Ex. Abholate, Treatamine.

2. Plant growth regulators- used for regulate the growth of plant or supress the growth, rooting, ripening of fruits etc. Ex. G.A., IAA, IBA, Cycocel, Ethapon.

3. Defoliants -Removal of leaves. Ex. Sodium chlorate, Magnesium chlorate, sodium polyborate and folex.

4. Repellants -For repelling insects Ex. Delphone, Indalone.

5. Attractant -For attracting insects Ex. Muscalure, Disparlure.

Nomenclature of pesticide

It involves learning about their structure and name.

1. Common name

2. Propriety name / Trade name / Brand name

3. Chemical name

4. Structural formula

5. Molecular formula.

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Lesson: 17 & 18

INORGANIC AND ORGANIC INSECTICIDES, ORGAOCHLORINE, ORGANOPHOSPHATES, CARBAMATES, SYNTHETIC PYRETHROID, NEONITINOID, BIORATIONALS

Insecticides

Definitions –

Chemicals used for the control of harmful insects.

I) **Arsenic compounds**

II) **1.Paris green :** One of the arsenic compound containing copper (II) acelate arsenate $Cu(CH_3COO)_2{:}3Cu(ASO_2)$

Acid salt: $CaHASO_4,H_2O$,

Natural salt : $Ca_{3(}ASO_4)_2$: H_2O

Basic salt : $Ca_{3(}ASO_4)_2$ $Ca(OH)_2$: H_2O

Classification of insecticides

A) On the basis of chemical nature

a. Inorganic -Ex arsenates, fluorides compounds.

b. Organic insecticides.

i) Oils and soaps -Petroleum products

ii) Plant origine - Nicotine, Geraniol, pyrethrum and Rotenon.

iii) Synthetic

a) Chlorinated hydrocarbons – DDT, HCH, Heptachlor, aldrin etc. (CH & Cl)

b) Organophosphorus (C, H, O &, P, S) Malathion, parathion and Dematphosphamidon.

c) Carbonate insecticides – Carboryl, carbofuran.

d) Pyrethoids – Allethrin, permethrin, Deltametrin.

e) Miscellaneous Insecticides – Karathane, DNOC.

Plant Originated Insecticides

Nicotine – 3 (1-Methyl –2 pyrrolidyl) pyridine) Alkaloid present in the leaves of Nicotiana sp.

Nicotine ($C_{10}H_{14}N_2$) – (N-methyl-2, 3 (Pyridyl) Pyrollidine ring give structure of Nicotine.

Occurrence – occurs from solanaceous genera plant i.e. Tobacco propperties – Give properties.

Mode of action – contact insecticides and also fumigant. It enters in insect through spiracle in the tracheal system. Nicstice is highly toxic by injection, inhalation and skin absorption. It is an automatic blocking agent and acts like acetyl choline but only at gunglia and neuro muscular junctions, initially stimulating then depressing then symptoms are ercitation conclusion paralysis and death.

II) Pyrethrum :

a) Structure : $C_{21}H_{28}O_3$

b) Occurrence : Flower heads of chrysanthemum genera. Active material is pyrethrin

c) Mode of action : Quick knock down action of induction of temporary paralysis. The symptoms follow the typical pattern of nerve poison. Pyrethrum affect central nervous system interfering the Na^+ and K^+ ionic potential.

Pyrethrins - occurs in the roots of Derris elliptica pyrethrins derived from dried flowers of chrysanthemum. Chemically pyrethnins are organic esters formed by the combination of two carboxylic acids and three keto alcohols.

Botanical insecticides (neem) pyrethrum, synthetic pyrethroids, major classes & use.

Synthetic pyrethroids.

Pyrethroids are essentially ester compouonds Attempt to replace the ester with other linkages had reduced the inescticidal activity.

Type I – Pyrethrins, allethnins, resmethrin, phenothin, permethrin and oxime others.

Type II - Expermethrin, fenvalerate, deltamethrin.

Synthetic organic insecticides, major classes and properties

Chlorinated hydrocarbons - Aldrin chlordane, heptachlor, DBCP.

Organophosphates – Diazinon, disulfton, malathion, methyl parathion.

Carbamates – Carbayl, carbofuran, methomyl, aldicatb, dithiocarb, oxamyl,

Pyresthrin – Permethrin

Chemosterilants : Substances that stenlize pest.

Molluscicides : substances that prevent, repel, destray or inhibit the growth of phyllum mollusca.

Steps in development of pesticides

1. Synthesis
2. The preliminary screening
3. Formulation
4. Toxicity studies
5. Metabolism studies
6. Residue studies
7. Registration
8. Promotion
9. Plot plant studies
10. Commercial.

The synthetic organic group of insecticide is

1. Organochlorine insecticides

It includes substances which vary in their chemical structure but because of their common properties in high insecticidal activity and chemical and biological persistence, these are groped in to one. Chemical these can be further subdivided in to four major groups.

Classification of organochloride insecticides

a)	DDT and relatives	-	DDT, Perthane, Rothane (DDD)
b)	Benzene derivatives	-	BHC, Lindane
c)	Cyclodiencs	-	Aldrin, dieldrin, Endrin, Chlordane, Budosulfan, Heptachlore.
d)	Polychloroterpenes	-	Toxaphene, storbane.

General Properties of organochlorine insecticide

1. Organochlorine insecticide contains C,H,O and Cl-
2. They are haing chlorinated carbon cycle ring.
3. Chemically stable

4. Polarity and lipophilicity-low soluble in water but they have strong lipophidic character hence accumulated in biolipid and produce ill effect on kideney and liver.

5. Basically hydrogenated acarbon

6. donot cause immediate toxicity(cronic toxicity)

7. Long residue toxicity

8. Act as stimulants of central nerves system.

i) DDT – (Dichlorodiphenyl trichlorocthane)

a) Structure – Give structure – 1, 1, 1-trichloro –2, 2-bits (P-chlorophenyl) ethane. First synthesised by 'Zeidler in 1874.

b) Propertics – Give properties.

ii) BHC – Benzene hexachloride, $C_6H_6C_{l6}$. Hexachloro cyclohexane, 1, 2, 3, 4, 5, 6 – Hexchlorocyclohexane. Also called as HCH (Hexachloro cyclohexane).

First synthesized by Micheal Faraday in 1825.

Give properties.

iii) Cyclodienes – Insecticides having cyclic structure containing two double bonds. Prepared by Diels – Alder reaction.

a) Endosulpan (Thiodan) (5,H_6 $C_{l6}SO_3$.

(6, 7, 8, 9, 10, 10 – hexachloro – 1, 5, 59, 6, 9, 99 hexahydro 6, 9

Give structure and properites of Endosulfan

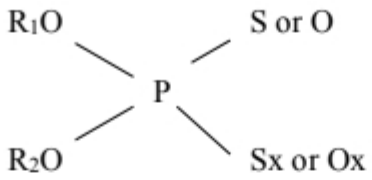
Mode of action of organochlorides

Chlorinated hydrocarbons are all neurotoxicants. Their application cause inhibition or inactivation or inter ferous in the functioning of Na-K. ATPase and Ca-ATPase enzymes which are required for proper a balance of Na and K in axon. The imbalance of these enzymes results in prevention of normal transmission of nerve imbalse in insects and mannuals. Eventually the neutrons five imbalses spontaneously causing muscles to twitch this may lead to convulsion and death.

2) Organophosphate insecticides –

They are the esters of different alcohols and phosphorus acid. They econtain C, H, O, P, S, N and Cl molecule in their structure.

The general formula of the compound is



Compounds of this group possessing insecticidal action can be classified on the basis of following acid derivatives.

a) Phosphoric acid - Dichlorovas, phosphamidon.

b) Phosphoric acid - EPN

c) Thiophosphoric acid - Parathion, Methyl demetan.

d) Dithiophosphoric acid - Malathion, Thimet, Dimethoate.

e) Pyrophosphotic acid - TEPP, Schradden

f) Others - Jsopestox

i) Phosphamidon – (Dimecron) C_{10} H_{19} O_5 NPCl)

a) Structure – Give structure (O, 0-dimethyl – 0- (2 – chloro – Al- N diethylcarbamyl)- methyl vinyl phosphate).

b) Properties – Give properties.

ii) Parathion – (Thiophos) ($10H_{14}$ NO_5S)

Give structure and properties.

iii) Malathion O C_{10} H_{19} O_6 PS_2.

O, O-dimethyl – S-1, 2 – dicarboethoxy –ethyl dithiophosphate give structure and properties.

iv) Rogor (Dimethoate) – 65 $H_{12}PS_2O_3N$.

O, O –dimethyl – S – (N methyl carbamyl) dithiophosphate Give structure and properties.

Mode of action of organophosphates :

Organophosphate insecticides affect the enzyme choline esterase (ChE) which is responsible for removal of acetyl choline (Ach) present in synapse (gap between nerve cell). This results in to continuous transmission of nerve impulses and loss of coordination of nerves and other organs giving rise to rapid twitching of voluntary muscles and finally paralysis of vital organs including langs. Thus failure of

respiration due to paralysis of lungs is the main cause of death. The reaction of inhibition of choline – esterase is irresersible so OPS are more total compared to carbomates.

3) Carbamate insecticides

Carbamate insecticides are esters of carbamic acid (HO-C – NH_2). They have an OCON = group in the molecule. They are esters of methyl and dimethyl carbamic acids. They are classified in to 3 groups as

a) A-methyl carbomate - carboryl, carbofuran

b) N-N-dimethyl carbomate – Isolan and Dimetelan

c) Oxime carbamate – Aldicarb, methomyl

1) Carbaryl (Sevin) – $C_{12}H_{11}O_2N$ – 1-Naphyl-N methyl carbamate give structure and properties.

2) Carbofuran (Furadan) - $C_{12}H_{18}NO_3^-$

2, 3 dihydro 2, 2-dimethyl – 7 – benzoturanyl – N methyl carbamate Give structure and properties.

3) Aldicarb (Temik) $C_7H_{14}SN_2O_2$

2-methyl-2 (methylthio) propionaldehyde 0-(methyl carbamate) Oxime

Mode of action – Similar to organophosphorus insectides.

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Lesson: 19

INSECTICIDE ACT AND RULES, INSECTICIDE BANNED WITHDRAWN AND RESTRICTED. CRITERIA FOR BANNED, WITHDRAWN AND RESTRICTED USE

Insecticides Act- 1968 and Insecticide Rules -1971

The Insecticides Act, 1968 was brought into force with effect from August 1971 with a view of regulating the import, manufacture, sale, transport, distribution and use of insecticides in order to prevent risk to human beings and animals. During the last 38 years, various provisions of this Act were amended. Many lacunae were found by the functionaries appointed under the Act during the implementation and endorsement of its provisions. Courts Lave reviewed various provisions of this Act and a few of them have even suggested for amendment of this Act substantially with a view to carry out the functions for implementation and enforcement thereof to fulfil the objectives of this Act.

The Central Government, therefore, made certain amendments in the Insecticides Act, 1968 and Rules 1971 through the Insecticides (Amendment) Act 1999. This covers almost the whole 1968 Act including the Preamble.

Exports are now explicitly included within the ambit of the Act. The classification of misbranded insecticides as given in Section 3 (K) has been modified and divided into five categories viz; (a) misbranded, (b) substandard, (c) spurious, and (d) duplicate. These clarifications have been fixed according to the severity of the offence and it appears to be more conducive and reasonable.

In Section 4 (3), some more members have been added in the constitution of the Board. In Section 9 (3), the Certificate of Registration is valid for a period of 5 years only and subject to re-registration after 5 years. The main objective of this amendment is to generate more revenue in the country. According to the new amendment, the Licensing Officer can refuse or grant license, as the case may be. As per amendment, the payment of the price of samples by the Insecticide Inspector has been deferred and the price is to be paid only if a sample after analysis is found misbranded, sub-standard, adulterated or spurious and that too only for two samples.

In the amendment, the time limit for replying the show cause notice has been reduced from 28 days to 10 days only. A new provision has been introduced by the Central Government under Section 24 (7) that since the test report of the Central Insecticides Laboratory is stated to be the conclusive evidence; the Director of Central Insecticides Laboratory need not be summoned by the court to prove the documents. The amended Rule 9A (3) (vi) is for compulsory use of I.S.I. Mark for every insecticide. In Rule 10(2), the applicant for grant of renewal of a license to sell insecticide should have a minimum qualification of 10+2 with science or agriculture as one of his subjects.

For an offence deemed to be misbranded, there is provision for issuing administrative warning of the offence which may be compounded by imposing fine up to Rs. 2,000. An offence deemed to be sub-standard, shall be punishable for first offence with fine up to Rs. 5,000 and for subsequent offence with imprisonment for a term which may extend to 6 months or fine up to Rs. 10,000 or both. Similarly, for an offence deemed to be adulterated, shall be punishable with imprisonment for a term which may extend to one year or fine up to Rs. 20,000 or both for the first offence and for second and subsequent offences with imprisonment for a term which may extend to two years or fine up to Rs. 50,000 or both.

List of pesticides which are banned, Refused registration and restricted in use:

(As on 19.03.2019)

I. Pesticides / Formulations Banned In India

	Pesticides Banned for manufacture, import and use.
1.	Aldicarb (vide S.O. 682 (E) dated 17th July 2001)
2.	Aldrin
3.	Benzene Hexachloride
4.	Benomyl (vide S.O 3951(E) dated 8th August, 2018)
5.	Calcium Cyanide
6.	Carbaryl (vide S.O 3951(E) dated 8th August, 2018)
7.	Chlorbenzilate (vide S.O. 682 (E) dated 17th July 2001)
8.	Chlordane
9.	Chlorofenvinphos
10.	Copper Acetoarsenite
11.	Diazinon (vide S.O 3951(E) dated 8th August, 2018)
12.	Dibromochloropropane (DBCP) (vide S.O. 569 (E) dated 25th July 1989)
13.	Dieldrin (vide S.O. 682 (E) dated 17th July 2001)
14.	Endosulfron (vide ad-Interim order of the Supreme Court of India in the Writ Petition (Civil) No. 213 of 2011 dated 13th May, 2011 and finally disposed of dated 10th January, 2017)
15.	Endrin
16.	Ethyl Mercury Chloride
17.	Ethyl Parathion
18.	Ethylene Dibromide (EDB) (vide S.O. 682 (E) dated 17th July 2001)
19.	Fenarimol (vide S.O 3951(E) dated 8th August, 2018)
20.	Fenthion (vide S.O 3951(E) dated 8th August, 2018)
21.	Heptachlor
22.	Lindane (Gamma-HCH)
23.	Linuron (vide S.O 3951(E) dated 8th August, 2018)
24.	Maleic Hydrazide (vide S.O. 682 (E) dated 17th July 2001)
25.	Menazon
26.	Methoxy Ethyl Mercury Chloride (vide S.O 3951(E) dated 8th August, 2018)
27.	Methyl Parathion (vide S.O 3951(E) dated 8th August, 2018)

	28.	Metoxuron
	29.	Nitrofen
	30.	Paraquat Dimethyl Sulphate
	31.	Pentachloro Nitrobenzene (PCNB) (vide S.O. 569 (E) dated 25th July 1989)
	32.	Pentachlorophenol
	33.	Phenyl Mercury Acetate
	34.	Sodium Cyanide (banned for Insecticidal purpose only vide S.O 3951(E) dated 8th August, 2018)*
	35.	Sodium Methane Arsonate
	36.	Tetradifon
	37	Thiometon (vide S.O 3951(E) dated 8th August, 2018)
	38.	Toxaphene(Camphechlor) (vide S.O. 569 (E) dated 25th July 1989)
	39.	Tridemorph (vide S.O 3951(E) dated 8th August, 2018)
	40.	Trichloro acetic acid (TCA) (vide S.O. 682 (E) dated 17th July 2001)
B.	**Pesticide formulations banned for import, manufacture and use**	
	1.	Carbofuron 50% SP (vide S.O. 678 (E) dated 17th July 2001)
	2.	Methomyl 12.5% L
	3.	Methomyl 24% formulation
	4.	Phosphamidon 85% SL
C.	**Pesticide / Pesticide formulations banned for use but continued to manufacture for export**	
	1.	Captafol 80% Powder (vide S.O. 679 (E) dated 17th July 2001)
	2.	Nicotin Sulfate
D.	**Pesticides Withdrawn (Withdrawal may become inoperative as soon as required complete data as per the guidelines is generated and submitted by the Pesticides Industry to the Government and accepted by the Registration Committee. (S.O 915(E) dated 15th Jun,2006)**	
	1.	Dalapon
	2.	Ferbam
	3.	Formothion
	4.	Nickel Chloride
	5.	Paradichlorobenzene (PDCB)
	6.	Simazine
	7.	Sirmate (S.O. 2485 (E) dated 24th September 2014)

	8.	Warfarin (vide S.O. 915 (E) dated 15th June 2006)

* Regulation to be continued in the extant manner for non-insecticidal uses

II. Pesticides Refused Registration

S.No.	Name of Pesticides
1.	2,4, 5-T
2.	Ammonium Sulphamate
3.	Azinphos Ethyl
4.	Azinphos Methyl
5.	Binapacryl
6.	Calcium Arsenate
7.	Carbophenothion
8.	Chinomethionate (Morestan)
9.	Dicrotophos
10.	EPN
11.	Fentin Acetate
12.	Fentin Hydroxide
13.	Lead Arsenate
14.	Leptophos (Phosvel)
15.	Mephosfolan
16.	Mevinphos (Phosdrin)
17.	Thiodemeton / Disulfoton
18.	Vamidothion

II. Pesticides Restricted For Use in the Country

S.No.	Name of Pesticides	Details of Restrictions
1.	Aluminium Phosphide	The Pest Control Operations with Aluminium Phosphide may be undertaken only by Govt./Govt. undertakings / Govt. Organizations / pest control operators under the strict supervision of Govt. Experts or experts whose expertise is approved by the Plant Protection Advisor to Govt. of India except [1]Aluminium Phosphide 15 % 12 g tablet and [2]Aluminum Phosphide 6 % tablet. [RC decision circular F No. 14-11(2)-CIR-II (Vol. II) dated 21-09-1984 and G.S.R. 371(E) dated 20th may 1999]. [1]Decision of 282nd RC held on 02-11-2007 and, [2]Decision of 326th RC held on 15-02-2012. The production, marketing and use of Aluminium Phosphide tube packs with a capacity of 10 and 20 tablets of 3 g each of Aluminium Phosphide are banned completely. (S.O.677 (E) dated 17thJuly, 2001)
2.	Captafol	The use of Captafol as foliar spray is banned. Captafol shall be used only as seed dresser. (S.O.569 (E) dated 25thJuly, 1989) The manufacture of Captafol 80 % powder for dry seed treatment (DS) is banned for use in the country except manufacture for export. (S.O.679 (E) dated 17thJuly, 2001)
3.	Cypermethrin	Cypermethrin 3 % Smoke Generator is to be used only through Pest Control Operators and not allowed to be used by the General Public. [Order of Hon,ble High Court of Delhi in WP(C) 10052 of 2009 dated 1407-2009 and LPA-429/2009 dated 08-09-2009]
4.	Dazomet	The use of Dazomet is not permitted on Tea. (S.O.3006 (E) dated 31st Dec, 2008)
5.	Dichloro Diphenyl Trichloroethane (DDT)	The use of DDT for the domestic Public Health Programme is restricted up to 10,000 Metric Tonnes per annum, except in case of any major outbreak of epidemic. M/s Hindustan Insecticides Ltd., the sole manufacturer of DDT in the country may manufactureDDT for export to other countries for use in

		vector control for public health purpose. The export of DDT to Parties and State non-Parties shall be strictly in accordance with the paragraph 2(b) article 3 of the Stockholm Convention on Persistent Organic Pollutants (POPs). (S.O.295 (E) dated 8th March, 2006) Use of DDT in Agriculture is withdrawn. In very special circumstances warranting the use of DDT for plant protection work, the state or central Govt. may purchase it directly from M/s Hindustan Insecticides Ltd. to be used under expert Governmental supervision. (S.O.378 (E) dated 26thMay, 1989)
6.	Fenitrothion	The use of Fenitrothion is banned in Agriculture except for locust control in scheduled desert area and public health. (S.O.706 (E) dated 03rdMay, 2007)
7.	Methyl Bromide	Methyl Bromide may be used only by Govt./Govt. undertakings/Govt. Organizations / Pest control operators under the strict supervision of Govt. Experts or Experts whose expertise is approved by the Plant Protection Advisor to Govt. of India. [G.S.R.371 (E) dated 20thMay, 1999 and earlier RC decision]
8.	Monocrotophos	Monocrotophos is banned for use on vegetables. (S.O.1482 (E) dated 10thOct, 2005)
9.	Trifluralin	(vide S.O 3951(E) dated 8th August, 2018) (i) The Registration, import, manufacture, formulation, transport, sell and its all uses except use in wheat shall be prohibited and completely banned from date of publication of this Order. (ii) (ii) A cautionary statement has to be incorporated in the label and leaflet that it is toxic to aquatic organism, hence should not be used near water bodies, aquaculture or pisciculture area.

Pesticides which shall be phased out vide gazette notification No. S.o. 3951 (e).

S. No.	Name of the pesticide	Insecticides to be phase out by 31st December, 2020
1	**Alachlor**	(i) No new certificate of registration to manufacture shall be issued after publication of this Order. (ii) No person shall import, manufacture or formulate Alachlor with effect from the 1st January, 2019. (iii) The use of Alachlor shall be completely banned with effect from the 31st December, 2020. (iv) It is toxic to aquatic organism, hence a cautionary statement should be incorporatedon label and leaflets " toxic to aquatic organism hence should not be used near water bodies, aquaculture or pisciculture area.
2	**Dichlorovos**	(i) No new certificate of registration to manufacture shall be issued after publication of this Order. (ii) No person shall import, manufacture or formulate dichlorvos with effect from the January, 2019. (iii)The use of dichlorvos shall be completely banned with effect from the 31st December, 2020. (iv)It is very toxic to aquatic organism, hence a cautionary statement should be incorporated on label and leaflets that it is toxic to aquatic organism, hence should not be used near water bodies, aquaculture or pisciculture area. (v) A warning may be incorporated in the label and leaflet stating that this product is toxic to honey bees so do not spray during active honey bees foraging period of the day.
3	**Phorate**	(i) No new certificate of registration to manufacture shall be issued after publication of this Order. (ii) No person shall import, manufacture or formulate Phorate with effect from the 1st January, 2019. (iii)The use of Phorate shall be completely banned with effect from the 31st December, 2020. (iv) It is very toxic to aquatic organism, hence a cautionary statement should be incorporated on label and leaflets that it is toxic to aquatic organism, hence should not be used near water bodies, aquaculture or pisciculture area. (v) A warning may be incorporated in the label and leaflet stating that this product is toxic to honey bees so do not spray during active honey bees foraging period of the day. (vi)A cautionary statement should incorporate in label and leaflet that this product is toxic to birds.
4	**Phosphamidon**	(i) No new certificate of registration to manufacture

		shall be issued after publication of this Order. (ii) No person shall import, manufacture or formulate Phosphamidon with effect from the 1st January, 2019. (iii) The use of Phosphamidon shall be completely banned with effect from the 31st December, 2020. (iv) It is very toxic to aquatic organism, hence a cautionary statement should be incorporated on label and leaflets that it is toxic to aquatic organism, hence should not be used near water bodies, aquaculture or pisciculture area. (v) A warning may be incorporated in the label and leaflet stating that this product is toxic to honey bees so do not spray during active honey bees foraging period of the day. (vi) A cautionary statement should incorporate in label and leaflet that this product is toxic to birds.
5	**Triazophos**	(i) No new certificate of registration to manufacture shall be issued after publication of this Order. (ii) No person shall import, manufacture or formulate Triazophos with effect from the 1 st January, 2019. (iii)The use of Triazophos shall be completely banned with effect from the 31st December, 2020. (iv) It is very toxic to aquatic organism, hence a cautionary statement should be incorporated on label and leaflets that it is toxic to aquatic organism, hence should not be used near water bodies, aquaculture or pisciculture area. (v) A warning may be incorporated in the label and leaflet stating that this product is toxic to honey bees so do not spray during active honey bees foraging period of the day (vi)A cautionary statement should incorporate in label and leaflet that this product is toxic to birds
6	**Trichlorfon**	(i) No new certificate of registration to manufacture shall be issued after publication of this Order. (ii) No person shall import, manufacture or formulate Trichlorfon with effect from the 1 st January, 2019. (iii)The use Trichlorfon shall be completely banned with effect from the 31st December, 2020. (iv)It is very toxic to aquatic organism, hence a cautionary statement should be incorporated on label and leaflets that it is toxic to aquatic organism, hence should not be used near water bodies, aquaculture or pisciculture area. (v) A cautionary statement should incorporate in label and leaflet that this product is toxic to birds.

Source http://ppqs.gov.in/divisions/cib-rc/registered-products

Criteria The FAO/WHO Joint Meeting on Pesticide Management [2008] recommended that highly hazardous pesticides should be defined as having one or more of the following characteristics:

- Criterion 1: Pesticide formulations that meet the criteria of classes Ia or Ib of the WHO Recommended Classification of Pesticides by Hazard; or

- Criterion 2: Pesticide active ingredients and their formulations that meet the criteria of carcinogenicity Categories 1A and 1B of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS); or

- Criterion 3: Pesticide active ingredients and their formulations that meet the criteria of mutagenicity Categories 1A and 1B of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS); or

- Criterion 4: Pesticide active ingredients and their formulations that meet the criteria of reproductive toxicity Categories 1A and 1B of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS); or

- Criterion 5: Pesticide active ingredients listed by the Stockholm Convention in its Annexes A and B, and those meeting all the criteria in paragraph 1 of Annex D of the Convention; or

- Criterion 6: Pesticide active ingredients and formulations listed by the Rotterdam Convention in its Annex III; or

- Criterion 7: Pesticides listed under the Montreal Protocol; or

- Criterion 8: Pesticide active ingredients and formulations that have shown a high incidence of severe or irreversible adverse effects on human health or the environment

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Lesson: 20

IGRS AND BIOPESTICIDE, REDUCED RISK INSECTICIDE

IGR

Insect growth regulators (IGRs) are insecticides that mimic hormones in young insects. They disrupt how insects grow and reproduce. IGRs can control many types of insects including fleas, cockroaches, and mosquitos. ... IGRs are generally low in toxicity to humans.

Nylar. The IGR Nylar is the active ingredient in NyGuard, Archer, Flea Fix and others. This material is photostable (can be used outdoors and indoors) and inhibits the growth of fleas and roaches. Nylar has a 3 to 6 month residual indoors and can last 30 days when used outdoors.

Martins IGR has a shelf life of about 3-5 years from the date of purchase. The product should be stored in a place where it is protected from over heating, freezing and direct sunlight to ensure the longest shelf life possible.

Insect growth regulators (IGRs) are pesticides that don't usually kill insects outright but instead affect the ability of insects to grow and mature normally. IGRs either block the insect's ability to turn into an adult or cause it to change into an adult before it is physically able to reproduce.

A biorational pesticide is a term used to define any pesticide material that relatively causes no harm to humans or animals, and does lit tle or no damage to the environment. An example of a biorational pesticide is citronella products.

Biopesticide It is define according to the US environmental protection Agency(USEPA) are pesticide derived from natural matrials such as animals ,.plants, bacteria and minerals and also include living organisms that destroy agricultural pests.

Biopesticides are certain types of pesticides derived from such natural materials as animals, plants, bacteria, and certain minerals. For example, canola oil and baking soda have pesticidal applications and are considered biopesticides.

Biopesticides tend to be highly targeted to specific pests. Because they are so targeted, they are generally considered to be more environmentally friendly than synthetic agrochemicals.

Homemade Organic Pesticides

- Neem. Ancient Indians highly revered neem oil as a powerful, all-natural plant for warding off pests. ...
- Salt Spray. Mineral Oil. Citrus Oil & Cayenne Pepper. Soap, Orange Citrus Oil, & Water. Eucalyptus Oil. Onion & Garlic Spray. Chrysanthemum Flower Tea.

Types of biopesticide:

In the past few years, there has been considerable mention of the development and use of "Reduced-risk" pesticides in agricultural crops. This should be of particular interest to local growers and PCA's because several new insecticides recently registered on vegetable and melons are considered Reduced-risk compounds. These new compounds are becoming increasingly important in our pest management programs and I would like to provide a brief overview of what reduced-risk insecticides are and how they fit within our desert cropping system.

Reduced-risk pesticides are newer classes of compounds that pose a lower health risk to humans and the environment. This new classification and registration process resulted when the EPA implemented the Reduced-Risk Pesticides Initiative in 1993 to provide incentives to encourage the development and registration of pesticides that present lower risks to public health and the environment, and to encourage the replacement of higher risk pesticides in the marketplace. Although FQPA was not passed until 1996, the Reduced-risk initiative began the process for the replacement of organophosphate pesticides. EPA technically defines a Reduced-risk pesticide use as one which "may reasonably be expected to accomplish one or more of the following": (1) reduces pesticide risks to human health; (2) reduces pesticide risks to non-target organisms; (3) reduces the potential for contamination of valued, environmental resources, or (4) broadens adoption of IPM or makes it more effective.

The agency has established criteria for each category by which a candidate compound must meet before reduced-risk status is granted.

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Lesson: 21

BOTANICAL PLANT AND ANIMAL SYSTEMIC INSECTICIDES CHARECTERSTICS & USE (NEEM) PYRETHRUM, SYNTHETIC PYRETHROIDS

Pyrethroids are essentially ester compouonds Attempt to replace the ester with other linkages had reduced the inescticidal activity.

Type I – Pyrethrins, allethnins, resmethrin, phenothin, permethrin and oxime others.

Type II - Expermethrin, fenvalerate, deltamethrin.

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Plant Originated Insecticides

Nicotine – 3 (1-Methyl –2 pyrrolidyl) pyridine) Alkaloid present in the leaves of Nicotiana sp.

Nicotine ($C_{10}H_{14}N_2$) – (N-methyl-2, 3 (Pyridyl) Pyrollidine ring give structure of Nicotine.

Occurrence – occurs from solanaceous genera plant i.e. Tobacco propperties – Give properties.

Mode of action – contact insecticides and also fumigant. It enters in insect through spiracle in the tracheal system. Nicstice is highly toxic by injection, inhalation and skin absorption. It is an automatic blocking agent and acts like acetyl choline but only at gunglia and neuro muscular junctions, initially stimulating then depressing then symptoms are ercitation conclusion paralysis and death.

II) Pyrethrum :

a) Structure : $C_{21}H_{28}O_3$

b) Occurrence : Flower heads of chrysanthemum genera. Active material is pyrethrin

c) Mode of action : Quick knock down action of induction of temporary paralysis. The symptoms follow the typical pattern of nerve poison. Pyrethrum affect central nervous system interfering the Na^+ and K^+ ionic potential.

Pyrethrins - occurs in the roots of Derris elliptica pyrethrins derived from dried flowers of chrysanthemum. Chemically pyrethnins are organic esters formed by the combination of two carboxylic acids and three keto alcohols.

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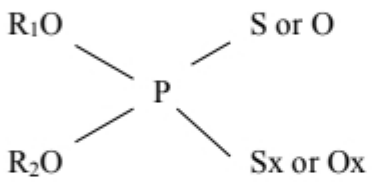
Lesson: 22

Mode of action of insecticides (Pyrethroids,organophosphate carbamate and chitin synthesis inhibitors)

Organophosphate insecticides

They are the esters of different alcohols and phosphorus acid. They econtain C, H, O, P, S, N and Cl molecule in their structure.

The general formula of the compound is



Compounds of this group possessing insecticidal action can be classified on the basis of following acid derivatives.

a) Phosphoric acid - Dichlorovas, phosphamidon.

b) Phosphoric acid - EPN

c) Thiophosphoric acid - Parathion, Methyl demetan.

d) Dithiophosphoric acid - Malathion, Thimet, Dimethoate.

e) Pyrophosphotic acid - TEPP, Schradden

f) Others - Jsopestox

v) Phosphamidon – (Dimecron) C_{10} H_{19} O_5 NPCl)

c) Structure – Give structure (O, 0-dimethyl – 0- (2 – chloro – Al- N diethylcarbamyl)- methyl vinyl phosphate).

d) Properties – Give properties.

vi) Parathion – (Thiophos) ($10H_{14}$ NO_5S)

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Mode of action – Similar to organophosphorus insectides.

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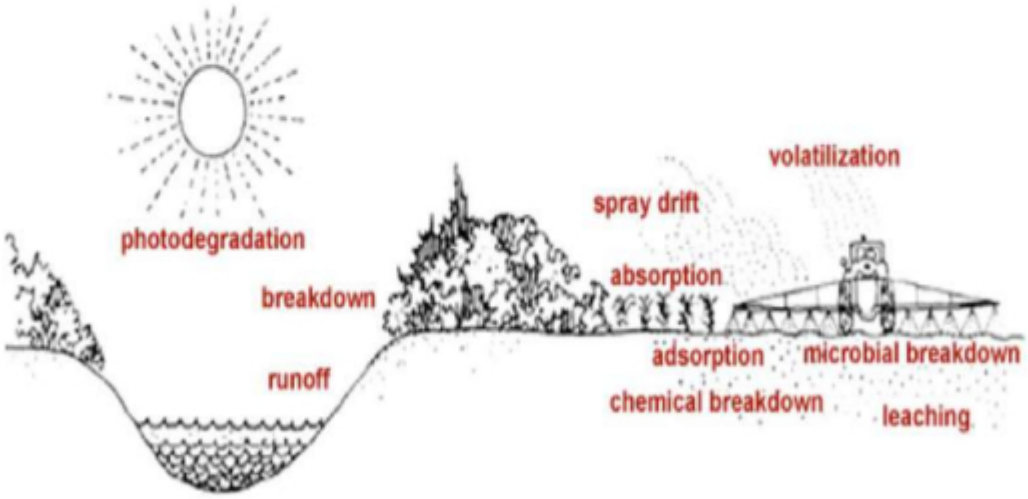
Lesson: 23

FATE OF INSECTICIDE IN SOIL AND PLANT. DEGRADATION –MICROBIAL DEGRADATION, ENZYMATIC DEGRADATION, CONJUNCTION OF INSECTICIDE WITH CLAY/ORGANIC COLLOIDS (SOIL RELATED PROPERTIES)

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 volatize 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

♣ 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.

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)

Ways to Minimize Pesticide Impact

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.

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.

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.

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.

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.

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Lesson: 24

INSECTICIDE RESISTANCE AND ITS MANAGEMENT

Resistance – A genetic change in an organism in response to selection by pesticides, which may impair control in the field.

Resistance mechanism – biological processes used by the pest to avoid the lethal action of the pesticide. Resistant organisms may have more than one resistance mechanism.

Behavioural resistance – any modification in pest behaviour that helps the pest to avoid the lethal effects of pesticides. The pest organism is still sensitive to the pesticide and will be killed if exposed to a lethal dose. Consequently, those individuals evading exposure survive and reproduce. This may lead to the development of a behaviourally resistant strain.

Cross-resistance – When resistance to one pesticide confers resistance to another pesticide, even where the pest has not been exposed to the latter product. Cross-resistance occurs because two or more compounds are acting on the same target site and/or are affected by the same resistance mechanism.

Multiple resistance – the simultaneous presence of several different resistance mechanisms in the same organism. The different resistance mechanisms may combine to provide resistance to multiple classes of pesticides.

Penetration resistance – a resistance mechanism essentially limited to insects, in which the cuticle slows the penetration of the pesticide into the body of the pest.

Resistance mechanisms

Agricultural pests use a variety of mechanisms to survive exposure to toxicants. Resistance can develop more easily when two or more of these mechanisms are used at the same time. The resistance mechanisms fall into the following general categories:

- ✓ Metabolic detoxification (enzymatic)
- ✓ Reduced sensitivity at the target site
- ✓ Reduced penetration
- ✓ Sequestration
- ✓ Behavioural resistance

Table Biological, genetic, and operational factors in resistance development.

Factor	Potential for resistance development	
	Lower	Higher
Biological factors		
Population size	Small	Large
Reproductive potential	Low	High
Generation turnover	One or less generations per year	Many generations per year
Type of reproduction	Sexual	Asexual
Dispersal	Little	Much
Seed bank	Large	Small or none
Pesticide metabolism	Difficult	Easy
Number of target sites of the pesticide	Multiple sites	Single, specific
Pest host range	Narrow	Wide
Genetic factors		
Occurrence of resistance genes	Absent	Present
Number of resistance mechanisms	One	Several
Gene frequency	Low	High
Dominance of resistance genes	Recessive	Dominant
Fitness of "R" individuals	Poor	Good
Protection provided by the "R" gene	Poor	Good
Cross resistance	Negative or none	Positive
Past selection	None	Significant
Modifying genes	Absent	Present
Operational factors		
Activity spectrum of the pesticide	Narrow spectrum	Broad spectrum
Pesticide application rate	Label rate: heterozygotes killed (If R gene is incompletely dominant)	Less than label rate: heterozygotes survive More than label rate: Only some homozygous resistant individuals survive and reproduce (especially if there is little immigration)
Application coverage	Good	Poor
Systemicity	Effect of factor is variable: may increase or decrease risk of resistance	
Treatment frequency	Low	High
Presence of secondary pests	Absent (only the target pest is treated)	Present (not targeted (potential) pests are also treated)
Life stages treated with related pesticides	Single	Multiple
Proportion of population treated	Effect of factor is variable: may increase or decrease risk of resistance	
Persistence	Short	Long
Number of crops treated	One	Many
Crop sequence	Crops separated by time or geography	Crops inter-planted: no break between planting: continuous
Pest control tactics	Multiple control tactics (chemical, biological, cultural)	Continuous use of single method or compound
Non target effects	Selective activity, no effect on natural enemies	Non selective, natural enemies also killed

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In managing insect resistance, it is important to keep in mind that the primary objective is to protect the crop or control the vector, not necessarily to kill all the insects. The overall strategy of avoiding overuse of a single insecticidal mode of action should be followed. Additional insecticide resistance management tactics are given below.

Crop-by-pest vs. regional tactics

"Crop-by-pest" resistance management tactics focus on a single crop-pest combination. They can be appropriate when the crop area is large and there is essentially one pest species (e.g. Helicoverpa on tomatoes) to be treated with an insecticide.

General practices

Use an integrated approach

Management of insecticide resistance requires a consideration of all aspects of crop production, including agronomic practices, physical and biological control methods, and insect pest biology. Simply complying with the concepts of integrated crop management can help prevent resistance from developing. For example, monitoring and adhering to recommended pest and/or damage thresholds, respecting the usefulness of natural enemies, carrying out simple sanitation measures, removing post-harvest residues in the field, using resistant crop varieties, and simply avoiding continuous year-round cultivation of a single crop can all help to slow and even prevent resistance development.

Protect beneficial organisms

Protect natural enemies of pests insofar as possible. The contribution of beneficial organisms to pest control can be significant in many cropping systems. Beneficial organisms can also play an important part in resistance management as they help control the target pests irrespective of the pests' degree of resistance or resistance mechanism, and thus can help slow down the resistance selection process. Natural enemies can be protected for instance by using selective insecticides, avoiding overdosing, or applying non-chemical control options.

Use recommended application rates

Use the recommended rates and treatment intervals as indicated on insecticide labels. Never apply more or less than the recommended rate, as this can result in resistance and/or unwanted effects on non-target organisms and the environment. Always make sure that spray equipment is in good condition, and that nozzles and filters are not blocked, which causes spraying of incorrect rates and can result in resistance development.

Rotate unrelated compounds

Use a variety of compounds registered for the use in question, from unrelated chemical classes that are not cross-resistant; never use a single compound or class.

Use mixtures with caution

Mixtures should be used with extreme caution and are not recommended except in very limited situations, as the incorrect use of mixtures can exacerbate resistance. In particular, mixtures should never be used if the target pest is already resistant to one of the modes of action in the mixture. If mixtures must be used, the active ingredients should be at their recommended application rates and should have similar residual activity to prevent selecting resistance to the component with the longest residual activity.

Use synergists with caution

The use of synergists, which block or delay the metabolic detoxification of insecticides, may improve their effectiveness and extend their useful lifetime if the synergists are applied at a non-toxic rate either before or at the same time as the insecticide (for example, in mixture with the insecticide).

Use non-specific products

Plant protection products such as oils and soaps that have a non-specific mode of action are good resistance management tools. Where possible they should be used in rotations or mixtures with conventional insecticides, provided they effectively control both susceptible and resistant target pest populations.

Apply products with care

Apply insecticides when the opportunity for control is optimum, i.e. the infestation has reached the action threshold but is not overwhelming. Ensure that coverage is good. Do not use the same compounds with the same mode of action to control a pest that has several generations in the growing season of the crop.

Monitor problematic pests

Monitor problematic pest infestations in order to detect first shifts in sensitivity. In many instances, baseline sensitivity data for representative field populations were established before the products became widely used. Re-examining the insecticide sensitivity of these populations at regular intervals can reveal possible changes in susceptibility. Resistance monitoring carried out at regular intervals is recommended to detect possible changes in pest sensitivity before serious control problems become evident.

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Lesson: 25

PESTICIDE RESIDUE DEFINITION, STEPS INVOLVED IN DETERMINATION OF RESIDUE (COLLECTION, SEPARATION, CLEANING, PROCESSING AND CLEANUP, EXTRACTION)

Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops.

Pesticide residue - Any substance or mixture of substances in food for man or animals resulting from the use of a pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance.

Steps involved in determination of residue

Collection

Collect a total sample approximating 10 kg by sampling a minimum of 10/ 1 kg subs selected at random from the lot. Small retail units may necessitate the collection of several units to total 1 kg per subdivision.

For large individual items (1 kg or more) such as fish, melons, cabbage heads, cauliflower, pineapple etc. collect a total composite of 10 subs taking only one unit from each of 10 different shipping containers or locations in the lot.

Collect a total composite sample of 10 kg by collecting 1 kg portions from each of 10 different bulk containers in the lot. The minimum amount of material to be submitted to the laboratory, is as follows;

COMMODITY	EXAMPLES	MINIMUM QUANTITY REQUIRED
Small or light products, unit barries weight upto about 25 g	Peas, olives parsley	1 kg
Medium sized products unit weight usually between	apples, oranges, carrots potatoes	1 kg (at least 10 units)
Large sized products unit weight over 250 g	cabbage, melons, cucumber	2 kg (at least 5 units)
Dairy products dairy products	Whole milk, cheese buffer, cream	0.5 kg
Egg (10 unit if whole) meat	Poultry, fat, fish and other fish and animal products	
Oils and fats	cottonseed oil margarine	0.5 kg
Cereals and cereal products		0.5kg- 1 kg
Spices	Chilies, cumin, coriander	0.25kg

The laboratory sample must be placed in a clean inert container offering adequate protection from external contamination and protection against damage to the sample in transit. The container must then be sealed in such a manner that unauthorized

of the food. This could be a quarter of a fruit, a piece of loin from a whole fish or other similar sectioning

Processing

The well equipped food analysis laboratory should have a variety of sample preparation equipment including mechanical choppers, mincers, grinders, blenders and a hammer or similar mill. Use of dry ice is recommended in case of volatile and unstable molecules during extraction.The type of mechanical processing equipment selected will depend on the food pro

duct to be treated. The analyst must also keep in mind that mechanical grinders, mills, etc. usually generate heat during the processing. This can possibly change the sample composition, such as for fatty foods where the heat may be sufficient to partially melt the fat. In such cases, hand chopping and mixing may be the best procedure. In other instances, the sample may have to be frozen before grinding. The moisture content of a food also plays an important role in determining the food processing procedure or equipment to use. Dry foods can generally be milled, while moist foods can be chopped, minced or ground. Very moist and liquid foods can be blended. The home food processors now available are very useful for many products. If no mechanical processing equipment is available, then of course hand processing must be done. The tools used include knives, granters and choppers. When a sample is processed by hand, it must be sufficiently finely divided to permit proper mixing and later sub-sampling of the mixture. The analyst must always keep in mind that proper sample preparation is not only to gain a representative portion for analysis, but is also to prevent change in the sample which may result in a biased analytical result.

Clean-up Techniques

Cleanup refers to a step or series of steps in the analytical procledure in which the bulk of the potentially interfering coextractives are removed by physical or chemical methods.

During extraction, the solvent comes in contact with the substrate matrix, to enable extraction of the pesticide along with some of the constituents of the substrate matrix also get solubilized. The extract not only contains pesticide residues but also other constituents, which are called co-extractives. The removal of interfering co-

extractives from extract is called clean up. The co-extractive generally extracted along with pesticide from various substrates are moisture, coloured pigment like chlorophyll, xanthophylls and anthocyanins, colourless compounds like oil, fat and waxes etc.

When dry substrate is extracted with water immiscible solvent, it contains traces of moisture, which can be removed by passing the extract through anhydrous sodium sulfate. High moisture containing substrate are extracted with water miscible solvent, the extract contains lot of water and water soluble compounds, the extract is concentrated to remove organic solvent, the aqueous phase is diluted with saturated sodium chloride solution and then extracted with water immiscible solvent just like water samples. After removal of moisture, the other coextractives are removed by using various separation techniques.

Extraction

Extraction means separation of pesticide residues from the matrix by using solvent. The extraction procedure should be such that it quantitatively removes pesticides form matrix (high efficiency), does not cause chemical change in pesticide and use inexpensive and easily cleaned apparatus. The extraction method and solvent type determine the extraction efficiency from substrates.

Solid Phase Extraction (SPE)

Solid phase extraction technique is based on the concept of selective retention by the device for the analyte, in this case the pesticide. SPE can be made to work on either the batch or column mode. This method has not become popular as there is loss of the pesticide as it tends to adhere to the surface of the beaker and tubes. The method is modified by the use of adsorbents contained in cartridges of various sizes usually made of plastic such as polyethylene or polypropylene of extremely high purity and is termed as column-liquid solid extraction (CLSE), however for simpliciaty it is referred to a SPE cartridges.

Solid Phase Micro-Extraction (SPME)

In this technique a droplet of extractant, or a fiber coated with the extractant is suspended in the solution to be extracted and then transferred to an analytical device.

Accelerated Solvent Extraction (ASE)

The extracting solvent is passed under amabient temperature or pressure through the matrix, removing the analyte using a smaller volume of the solvent.

Microwave-Assisted Solvent Extraction (MASE)

The technique employs the use of microwave energy and a suitable solvent to extract the analyte from the matrix, water is commonly preferred solvent in this procedure.

Supercriticial Fluid Extraction (SFE)

In the supercritical fluid extraction (SFE) method carbon dioxide gas is passed under supercritical temperature and pressure (liquefied carbon dioxide) through the matrix to extract the pesticide and then transferred to the analytical device for quantitation.

Stir-Bar Sorptive Extraction (SSE)

SBSE was introduced in 1999 by Pat Sandra's group to overcome some of the limits of the existing techniques, in particular in the recovery of medium-to-high volatility analytes when sampled in liquid phase with polydimethylsiloxane-open tubular traps (PDMS-OTT); further aim was to improve the limited recovery achievable in ultra trace analysis with solid-phase micro extraction (SPME), especially under un favourable phase ratios when working with small volumes of sorptive material (in general PDMS) coating the fused-silica fibre . SBSE was first developed for sampling in liquid phase and is based upon sorption of the investigated analytes or fraction onto a very thick film of PDMS coated onto a glass-coated magnetic stir bar (commercially known as Twister, Gerstel GmbH, and Mulheim, Germany). Sampling is done by directly introducing the SBSE device into the aqueous sample; in the original experiments, the analytes sampled for a given time were recovered by thermal desorption and then on-line transferred to a gas chromatography (GC) or GC–mass spectrometry (MS) system for analysis. Later, liquid desorption in combination with high performance liquid chromatography (HPLC) also was applied, mainly for analytes not analyzable by GC.

Reference:

http://www.old.fssai.gov.in/Portals/0/Pdf/Draft_Manuals/PESTICIDE_RESIDUE.pdf

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Constituents are ppt of tetra and penta sulpric

Reactions

$4CuSO_4 + 3\ Ca\ (OH)_2 – \underline{Cu(SO_4).\ 3\ Ca(OH)_2} + 3\ CuSO_4$

Basic copper sulphate Al

```
2 CuSO4 + Ca(OH)2 – Cu-OH                    Cu-OHHO-CaO.Cu
                      |                        |            |
                   SO4 + CaSO4 --→           SO4          SO4
                      |                        |
                   CuOH                     Cu-OH  HO.CuH-Cu

        Cu-O-Ca-OH + Ca (OH)2        Cu-O-Cu
            |                            |    |
CaSO4 +
            |                            |    |
        SO4                          SO4    SO4 + 2H2O
            |                            |    |
        Cu-O-Cu-OH                   CuO    Cu
```

Fresh solution is gelateneous, deep blue to sllightly greenish, on standing it looses fungicidal property.

Action – Copper kills spores by combining with sulph – hydryl (-H4) group of certain enzymes. Free copper ions precipitate or denature the proteins.

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Lesson: 28

SULFUR FUNGICIDE: ORGANIC AND INORGANIC SULFUR FUNGICIDE THEIR CLASSIFICATION AND MODE OF ACTION. PREPARATION OF LIME SULFUR MIXTURE AND CHEMICAL REACTION INVOLVED

Lime sulphur or calcium polysulphide CaS_2 to CaS_6

$Ca(OH)_2$ is boiled with sulphur, red orange coloured liquid 1.8 part of 5:1 part of lime : 10 part of water boiled for 1 hour filtered and filtered solution used as spray. Control – powdary mildew.

Action – Sulphur acts as hydrogen acceptor in metabolic system and disturbs normal hydrogenation and dehydrogenation reactions in cells, thus fungi are killed.

Organo sulphur fungicide – Thiram : TMTD, Thylate, Arasan, $C_6H_{12}N_2S_4$
Give structure and properties.

Action – Acts as strong chelating agent and forms complexes with heavy metals ions present in biological system, therefore depriving the cell of needed metal.

Organomercurial fungicide i) Phenyl mercuric acetate.

Give structure

Action – fungicidal activity of mercury either as sapour or ion is at –SH (Sulph hydryl group) of the succeptible proteins and enzymes.

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Miss P. R. Chaure
ELE-SSAC-364

Lesson: 29

BENZIMIDAZOLE FUNGICIDE, THEIR CHEMICAL NATURE, MODE OF ACTION AND THEIR USE

Benzimidazole fungicides are a class of fungicides including benomyl, carbendazim (MBC), thiophanate-methyl, thiabendazole and fuberidazole.

Chemical nature

The solubility of benzimidazole fungicides is low at physiological pH and becomes high at low pH. In plants, carbendazim, thiabendazole and fuberidazole are mobile, i.e. systemic, and benomyl and thiophanate-methyl are converted to carbendazim. This conversion also occurs in soils and animals.

In soil and water, carbendazim is mainly degraded by microbes. They are metabolized through hydrolysis and photolysis in plants. These fungicides kill cells during mitosis by distorting the mitotic spindle; β-tubulin, a protein important in forming the cytoskeleton, is targeted. They mostly inhibit polymerization of β-tubulin by interacting with it directly, but other interactions also exist.

Mode of action

Benzimidazoles are potent inhibitors of ß-tubulin polymerization in many species of fungi and have been used for plant disease control. Although direct interactions of inhibitors with ß-tubulin seem to be the predominant inhibitory processes for this chemical class, interactions with other forms of tubulin as well as differential interactions with tubulin in the free and polymerized states also have been reported.

Depending on their concentration, time of incubation and type of media, benzimidazoles appear to induce abnormalities in spore germination, germ tube elongation, cellular multiplication, and mycelial growth of sensitive fungi. The initial stages of spore germination often are not affected by benzimidazoles. Benzimidazoles prevent cell division, however, that is required for continued germ tube elongation and infection.

Benzimidazole fungicides control a remarkably broad spectrum of plant pathogenic fungi but they do not control Oomycetes like *Pythium, Phytophthora* and organisms that are responsible for downy mildew diseases of many crops. Interestingly, the

benzamide fungicide zoxamide introduced more recently has been reported to affect tubulin and microtubule interactions in Oomycetes as well as other fungi.

Use

They can control many ascomycetes and basidiomycetes, but not oomycetes. They are applied to cereals, fruits, vegetables and vines, and are also used in postharvest handling of crops.

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Lesson: 30

Introduction to new generation fungicides. Viz. Metalaxyl, fosetyl Al, Triazoles and Strobilurin fungicide

Phenylamide fungicides

Active ingredients and common/trade names: Metalaxyl (Apron), mefenoxam (Allegiance)

Residual on plant tissue: 2-3 weeks

Risk of fungicide resistance development: High

Mobility in plant: acropetal penetrant, xylem-mobile systemic movement from roots to shoots

Protection of plant tissues: Protective and suppressive for oomycetes (water molds).

Mode of action: Inhibits RNA synthesis, suppresses sporangial formation, mycelial growth, and establishment of new infections; does not inhibit zoospore release, zoospore encystment (a dormant stage), or initial penetration of the host.

Phenylamide fungicides are active exclusively on oomycetes including Pythium, Phytophthora, and downy mildew pathogens. They were first introduced on the market in 1977 and were very successful due to properties including high potency, curative and protective activity, excellent redistribution and protection of new plant growth, control of all oomycetes, and flexible application methods including seed treatments, soil drenches, and foliar sprays. Due to widespread use, resistance developed rapidly and future formulations included multiple modes of action to extend the life of the product. The risk of resistance development is high, and products must be used as part of a resistance management plan. Once resistance has developed in an oomycete population, the pathogen is cross-resistant to all chemicals in this class.

Demethylation Inhibitors fungicides, DMI, (Triazoles)

Active ingredients and common/trade names: imazalil (included in Raxil MD-Extra W); propiconazole (Tilt); prothioconazole (Proline); tebuconazole (Folicur); metconazole (Caramba, Quash); also available as blends with other MOAS.

Residual on plant tissue: Depends on the specific product; 10-30 days.

Risk of fungicide resistance development: Medium.

Mobility in plant: High systemic activity.

Protection of plant tissues: Protective and curative.

Mode of action: interfere with biosynthesis of sterols in fungal cell membrane; spore penetration and mycelial growth.

Demethylation inhibitors (DMI) fungicides, also called sterol biosynthesis inhibitors, were first introduced in the 70s. These products were a major breakthrough: they provide curative and protective activity at low application rates and have a high degree of systemic movement in the plant. They inhibit the formation of sterols, which are required for fungal cell wall formation, and thus are effective at preventing hyphal growth. The largest group of DMI fungicides, the triazoles, are commonly used on grain crops as curative and preventative products. They are particularly active against most rusts and have good preventative activity for Fusarium head blight on grains. They are also effective against powdery mildew and many foliar blights. Efficacy varies by active ingredient and disease combination. Mobility in the plant is much higher than the group 11 (QoI) fungicides: they are translaminar (move across leaf surfaces) and are transported by the transpiration stream (xylem, not phloem). Thus, they are active on the leaf to which they have been applied and new growing portions of the plant. Some may have limited downward movement in the plant (a few millimeters). Fungicides applied to leaves are highly unlikely to move (translocate) to the roots. Chemical that runs down between leaf sheaths may be transported into buds and possibly stems. Residual time and mobility varies by active ingredient. DMIs can have growth regulator effects, causing shortened internodes and smaller, greener leaves.

Resistance development is quantitative since there are multiple sites that need to be mutated in order to confer complete resistance. Dose of the fungicide will increase over time as the pathogen is exposed to DMI fungicides, but complete failures in a short time span are not as likely. Repeated use of these compounds has led to

resistance in diseases such as powdery mildew of grape and apple scab. This is of particular risk on diseases that cycle quickly during the season and require multiple applications. Cross-resistance is possible

Strobilurins fungicides

In the beginning of 90s a new class of fungicides, generated on the basis of the fungus Strobilurus tenacellus secondary metabolites was developed. Strobilurins, with a chemistry based on a natural product from a mushroom, are fungicide of new generation and proved to be quite effective, protective, eradicant and potential broad-spectrum substances against foliar diseases of winter wheat.

They have low mammalian toxicity and are environmentally safe. In addition to disease control, strobilurins have useful non-fungicidal physiological effects: they improve nitrogen metabolism and also inhibit ethylene biosynthesis. This latter effect is responsible for the greening effect which results in delayed senescence with higher amount of chlorophylls and index of photosynthesis. Strobilurins can act on delaying root water uptake, resulting in postponement of soil dehydration, which contributes to a slight increase of grain yield in some wheat genotypes in the field under water deficit conditions.

Fosetyl Al

Fosetyl-Al is phosphonate fungicide with the unique property of being phloem mobile.

Generic Names- fosetyl aluminum phosphonate

Chemical Group- phosphonates

Use- Fosetyl-Al, applied in granular formulations or applied as foliar spray, significantly reduced cankers on peach caused by Phytophtora cactorum

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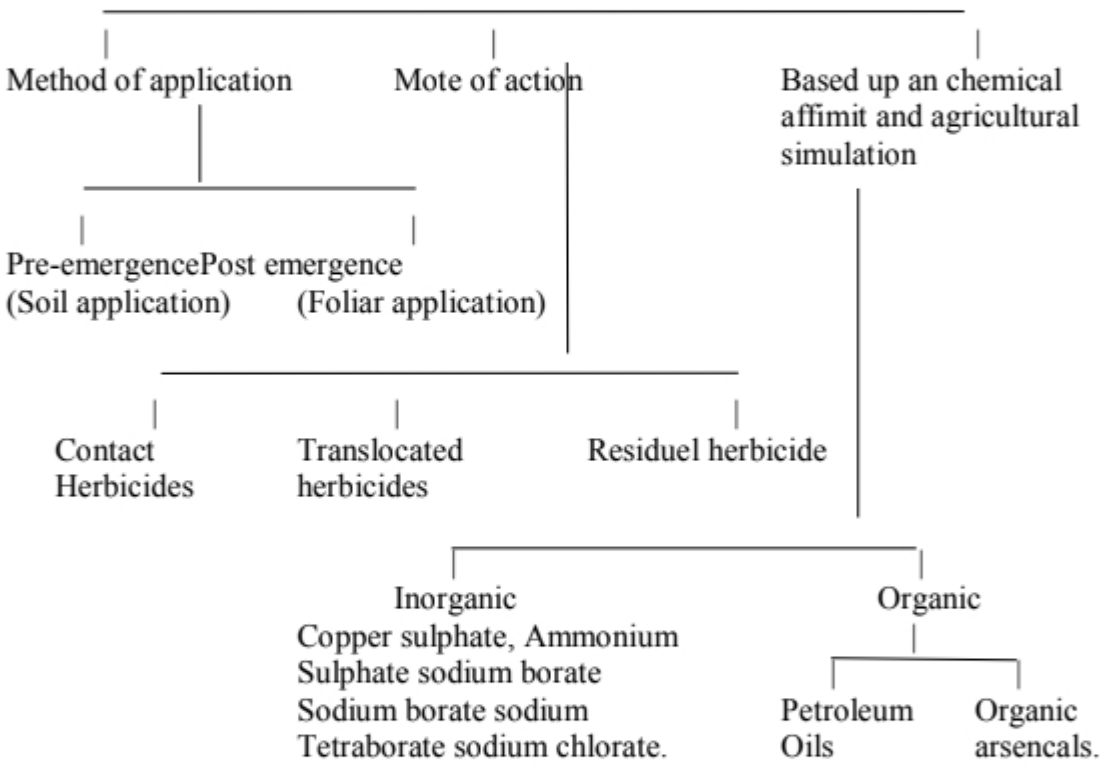
Lesson: 31

HERBICIDE-CLASSIFICATION, FORMULATIONS, METHODS OF APPLICATION

Herbicides - Major classes – properties and uses of 2-4 D, Attrozin, glyphosphate, butachlor, benthiocarb.

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

Classes of herbicides based as



Properties and use of some important insecticides under each class.

Properties and use of chlorinated hydrocarbon Aldrin, chlordane.

Organophosphates : Diazinon, disulfton, parathion, malathion.

Carbamates : Carbaryl, carbofuran, aldicarb.

Pyrethrin : Permethrin.

Herbicides: Chemicals employed for destruction of weeds.

Classification based on chemical nature

i) Inorganic – sodium arsenite, sodium and pot cyanate, Among, Borate, Sodium chlorate, sulphuric acid, cal. Cyanami.

a) Organic

1) Carboxylic – Aromatic compound

i) Acetic acid series – 2-4 D, 2-4-5T, MCPA

ii) Propionic acid series - 2-4-5 TP, MCPP

iii) Butyric acid series - 2,4 – DB, MCPB

iv) Decivative of phenyl acetic acid - Feriac.

2) Benzoic acid derivatives – 2, 3, 6 – Trichlorobenzoic acid Dicamba, Dinoben.

3) Benzo – nitriles - Diehlobenil, Ioxynil, Beomoxynil.

4) Pthalic acid derivatives – NPA

5) Aliphatic acid derivatives - Trichloroacetic acid (TCA), Dala.

6) Substituted phenols – Dinitrophenols, DNOC, DN6P, DINOSET.

7) Heterocylic i) Triozines – Simazine, Atrazine.

ii) Other heterocyclic – Amitrole, Mn, Pichloram paraquat, Diguant.

8) Substituted ureas – Fenuron, Monuron, Diuron, Linuron, Isoprot.

9) Carbonate -

i) Carbamate : Isopropyl, N-Phenylcarbamate (IPC), CIPC, Bar.

ii) Thiocarbamates : Eptam (EPTC), Vernam, Avadex.

iii) Dithiocarbametes – Vapam, Vegadex.

10) Anidex of aliphatic carboxylic acids – Diphanamide, Allidochlor, probamide.

11) Nitroanilines – Trifluralin, Nitralin, Fluchloratin.

12) Biphenyl ethers – Nitroten, fluroditen, oxythuroten.

13) Organo arsenicals – Cacodylic acid, Monosodium methyl arsonate (MSMA) DSMA.

14) Organophosphate – Glyphosate.

15) Substituted anilides – Propanil, Alachlor, Butachlor.

i) 2-4-D : (2, 4, Dichloraphenoxy acetic acid).

Give structure and properties.

Action – Simulatory herbicide in lower closes and inhibitory action in higher doses.

ii) Glyphosate : C3H8Nos-P

Action – systemic, nonselctive, post emergence herbicide with no soil activity or residual action. Absorbed in plant part and translocated in to roots and other plant parts. It interferes in formation of animo acids and other important derivatives in the plant enzyme systems.

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Lesson: 32

MODE OF ACTION OF HERBICIDE-TRANSLOCATION AND ABSORPTION

MODE OF ACTION OF HERBICIDE

Mode of action-

The term '**mode of action**' refers to the entire sequence of events from introduction of a herbicide into the environment to the death of plants.

'**Mechanism of action**' refers to the primary biochemical or biophysical lesion leading to death."

The following terms are concerned with how herbicides kill plants and are applied:

(1) **Herbicide**-a chemical that kills or inhibits growth of plants;

(2) **Contact herbicide**-a herbicide that causes injury only to tissue to which it is applied;

(3) **Mobile herbicide**-a herbicide that moves or translocates in a plant;

(4) **Simplest**-total living protoplasmic continuum of a plant; it is continuous throughout the plant, and there are no islands of living cells; the phloem is a component of the symplast, and long-distance symplastic transport is via the phloem;

(5) **Apoplast**- total nonliving cell-wall continuum of a plant; the xylem is a component of the apoplast, and long-distance apoplastic translocation is via the xylem;

(6) **Burndown**-refers to applying a foliage-active herbicide before planting to kill undesired vegetation;

(7) **Preplant incorporated**-refers to applying a herbicide to the soil before planting the crop and then mixing it with the soil;

(8) **Preplant**-refers to applying a herbicide to the soil surface before planting the crop;

(9) **Preemergence**-refers to applying a herbicide after planting but before the crops and weeds emerge;

(10) **Directed**-refers to applying a herbicide so contact with the crop is minimized;

(11) **Post emergence**-refers to applying a herbicide after emergence of the weeds or the crop, including broadcast and spot treatments.

Absorption of herbicide

Absorption of applied herbicides occurs through shoot and root tissue. To be effective in killing weeds, herbicides applied postemergence must move through the leaf surface to the living parts (symplast) of plant cells. Although leaves are the most important absorption site, absorption can occur through any aboveground plant part where the herbicide is present. After preemergence application, absorption is primarily through root tissue but can also occur through shoot tissue in contact with the treated soil. As with postemergence applications, herbicides applied preemergence must absorb into the plant and move to the symplasm for activity. Root absorption can be important after a postemergence herbicide application when the herbicide reaches the soil and moves in the soil to the root zone.

Absorption by Leaves and Stems

There are several factors that affect absorption by influencing the amount and distribution of herbicide on a plant surface, among which are the following:

1. The surface tension of the spray solution
2. The inherent wettability of the leaf surface
    a. The amount of cuticular wax and physical structure of the wax
    b. The hairiness (number of trichomes) on the leaf surface
3. Leaf orientation with respect to incoming spray droplets 4. The total leaf area per plant (probability of intercepting a spray droplet).

Most herbicide applications are made with water as the carrier. Water has a very high surface tension due to hydrogen bonding between water molecules. Thus, a water-based spray solution has difficulty wetting the waxy surface of weeds. The surface tension of water can be easily reduced by the addition of a surfactant.

The type of surface wax (epicuticular wax) and the surface topography can have a great influence on the ease with which a spray solution is able to wet the leaf surface and penetrate into the plant. Generally smooth leaf surfaces, devoid of crystalline epicuticular wax but containing amorphous wax (e.g., many dicot species), are relatively easy to wet. Leaf surfaces covered with crystalline epicuticular wax

(e.g., many grass species) are much more difficult to wet. Retention of spray solution on difficult-to-wet leaf surfaces increases with smaller droplet size and as the surface tension of the droplet at the moment of impact decreases. Large differences in absorption between species in some cases can account for herbicide selectivity between weed and crop. The most commonly cited examples of tolerant crop species are onion and *Brassica* species such as cabbage, because they absorb a minimal amount of a herbicide as a result of their thick leaf cuticles.

Once the herbicide has contacted the plant surface, five things can happen to the active ingredient it may

1. Volatilize and be lost to the atmosphere or be washed off by rain.
2. Remain on the outer surface in a viscous liquid or crystalline form.
3. Penetrate the cuticle but remain absorbed in the lipoid (wax) components of the cuticle.
4. Penetrate the cuticle, enter the cell walls, and then translocate prior to entering the symplasm. This is called apoplastic translocation, which includes movement in the xylem.
5. Penetrate the cuticle, enter the cell walls, and then move into the internal cellular system (through the plasmalemma) for symplastic translocation, which includes phloem movement.

Root absorption of herbicides from soil

With the exception of gaseous fumigants (e.g., methyl bromide), herbicides affect plants only after germination begins. Thus, entry of herbicides into ungerminated seeds during water imbibition may occur, but is not considered important to the ultimate death of the plant, importance is absorption of herbicides into roots as they begin to grow out from the seed.

Absorption of herbicides by roots is not as limited as absorption into leaves. The primary reason for this is that no significant wax layer or cuticle is present at the locations where most of the herbicide absorption occurs.

The most important pathway of entry is comigration of the herbicide with water being taken into the plant in the root hair zone (zone of differentiation) of the root tips. Root hairs greatly increase the surface area of roots available for uptake of water and herbicides. There is no known specialized "route of entry" for herbicides into root tissue; they go along with the mass flow of water because they are dissolved in the water. Even though the water solubility of some herbicides absorbed into roots is low

(0.3 ppm for trifluralin), the solubility is adequate to deliver the needed dose to the site of action.

Herbicide in the vapor phase in the soil may be important, but it will still have to diffuse through the film of water surrounding the root tissue at the root tip.

Shoot absorption of herbicides from soil

Shoot absorption is an important means of entry for many soil-applied herbicides that are active on germinating seeds or small seedlings (e.g. carbamothioates and chloroacetamides). Before emergence, a shoot has a poorly developed cuticle and probably no wax layers, making it more easily penetrated by herbicides.

In addition, the Casparian strip barrier is not present in shoot tissues. Shoot absorption is a particularly important route of herbicide entry in grass species, but less so for dicot weeds. Shoot zone entry is by diffusion, from herbicide dissolved in the soil solution in contact with the shoot tissue or, probably more important, diffusion from herbicide present in the vapor phase of the soil (e.g., EPTC). Herbicides known to have a major route of entry in the shoot zone are primarily growth inhibitors having their site of action in the shoot meristem as it emerges through the soil.

Absorption across plant membranes

All biochemical target sites for herbicide action are located within the living cell (symplast). For herbicides to reach their target site, they must cross the membrane located at the cell wall (plasma membrane; also termed the plasmalemma) and often an additional organelle membrane (e.g., chloroplast envelope).

Most herbicides cross membranes by simple diffusion, although a few have been shown to move with the help of specific carriers. In the case of herbicides crossing the plant membranes by simple diffusion, movement is related to the concentration difference (gradient) across the membrane. The herbicide moves from a region of higher concentration to a region of lower concentration. When the concentration is equal on both sides of the membrane, accumulation stops. The herbicide concentration gradient across the membrane is the driving force that moves the herbicide across the membrane.

The second important parameter for diffusion is the partition coefficient of the herbicide within the membrane, which represents its ability to "dissolve" in the membrane. Lipophilic (oil-soluble) herbicides are able to move more freely across the membrane than hydrophilic (water-soluble) herbicides.

Some herbicides can move across the plasma membrane against a concentration gradient. These herbicides have an ionizable group [e.g., carboxylic acid group (COOH)] as part of the molecule.

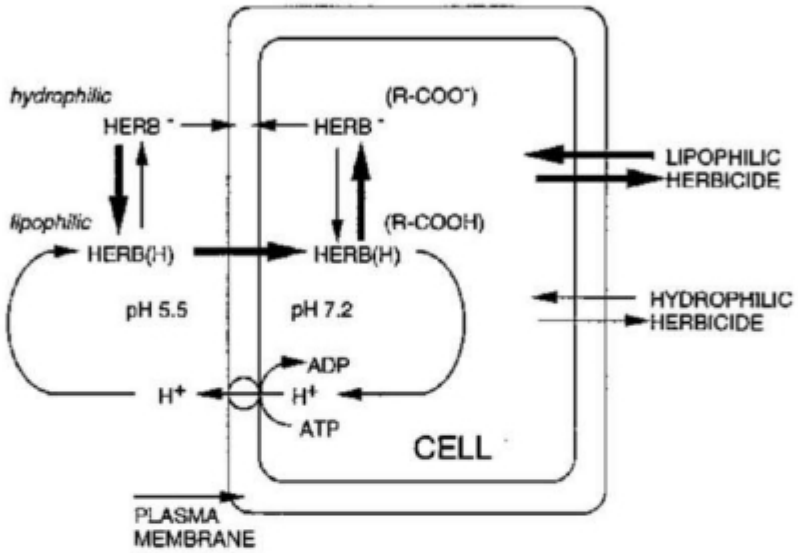

Figure 5-5. Movement of herbicides across plant membranes can occur by diffusion or by use of the H^+ gradient.

Translocation

Once a herbicide has penetrated the leaf or stem cuticle or the root epidermis, there are still many barriers that can affect movement to its site of action. The herbicide can be moved into a portion of the cell not containing a site of action (e.g., vacuole), resulting in the herbicide's becoming compartmentalized and no longer available for transport to its site of action.

A number of herbicides are conjugated (chemically bound) and adsorbed onto cellular components or in some way inactivated in the plant roots or leaves and do not move to other parts of the plant. A number of selectivity mechanisms that differ between weeds and crops are the result of differential compartmentation or inactivation by metabolism.

Short-distance herbicide movement across a few cell layers occurs by simple diffusion, ion trapping, or, for a few herbicides, carrier-mediated processes. Some herbicides (e.g., trifluralin applied preemergence and atrazine applied postemergence) require only diffusion to reach their target site of action.

Assuming the herbicide is not immobilized in some manner, it is available for long-distance movement in the plant through the xylem and phloem transport systems. In both systems herbicides dissolved in water move along with the mass flow of water.

Xylem

Herbicides that enter the plant roots may move upward in the xylem with the flow of water. The majority of preemergence herbicides transported in the xylem system enter the root near the root hair zone. This is because herbicide molecules dissolved in water move with the mass flow of water and most of the water transported in the xylem enters roots at the root hair zone.

Phloem

Movement of herbicides in the phloem follows the same path to the same locations as the products of photosynthesis (sugars). Translocation in the phloem system is from "source" (photosynthesizing mature leaves) to "sink" [plant parts using these sugars for growth (e.g., cellulose), maintaining metabolism (e.g., respiration) or storing the sugars for future use (e.g. starch)]. Examples of sinks are roots, underground storage organs (e.g. tubers and rhizomes), young developing leaves, all meristematic zones, flowers, and developing fruits.

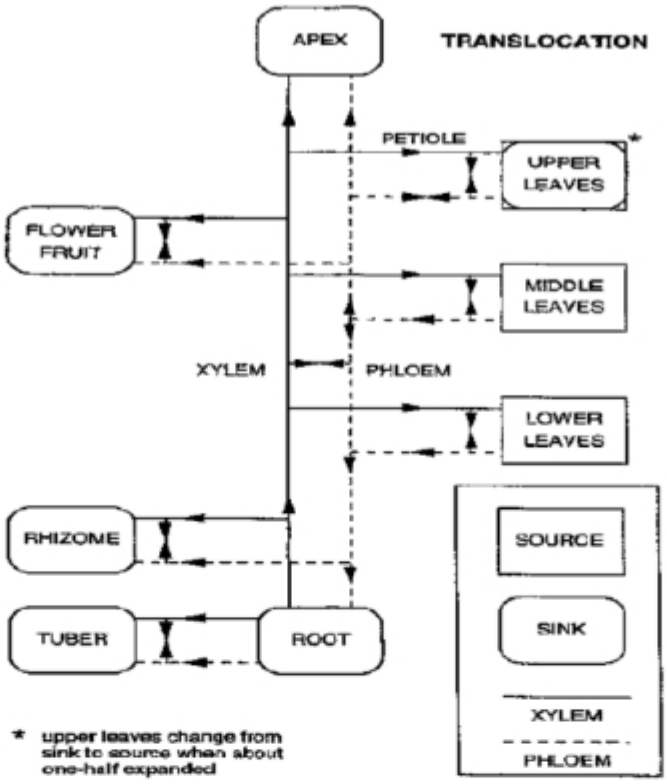

Fig.- Translocation of herbicides

General mode of action of herbicides.

1) Photosynthetic poisons

a) Interfere with Hill's reaction – In photolysis of water here is evolution of oxygen which is interfered by herbicides like triazines, carbamates, urea derivatives then interference will dead to no supply of oxygen.

b) Some interference in Electron transport chain – herbicides like paraquat, diquat, Bipyrillidium, after several stages …….

2) Those interfere with cellulor metabolisms – herbicides lil 2-4-D, phenoxy acids and benzoic acid series results in to an controlled growth leading to collapse of xylem, phloemce and plant die.

3) Interference in the protein metabolism – herbicid like butachlor interfere in protein metabolisum resulting in stunted root growth there by shortening of stem, etc and plant may die.

4) Uncoupling of oxidative phosphoralation – herbicides like DNOC, MSMA and even arsenic containing herebicides inter in the oxidative phosphorelation process and there is no format of ATP. Plant does not set emerge and it dies.

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Lesson: 33

PERSISTENCE AND FATE OF HERBICIDE. RESIDUAL EFFECT OF HERBICIDE

Persistence and fate of herbicides, residual effect of herbicides

Persistence of herbicides - The length of time that a herbicide remains active or persists in the soil is extremely important. Herbicide residues are important, as they relate to phytotoxic aftereffects *(carryover)* that may prove injurious to subsequent crops or plantings.

Factors that affect the persistence of herbicide in the soil are classified as either **degradation processes** or **transfer processes** and involve herbicide and soil characteristics, soil biota, and the environment.

Degradation processes that break down herbicides and change their chemical composition are

(1) Biological decomposition

i. Soil microbes

Soil is a mixture of inert and living materials. Sand, silt, clay, and organic matter make up the nonliving fraction. The living fraction is composed of bacteria, fungi, algae, nematodes, protozoa, worms, and hundreds of other organisms. The living portions of the soil force the turnover of nitrogen, phosphorus, sulfur, and iron, and partially control the final fate of soil-applied herbicides. Biological decomposition of herbicides includes detoxification by soil microorganisms and higher plants.

The primary microorganisms important for herbicide decomposition are bacteria and fungi. Herbicide may remain active in the soil for a considerable time if the soil is cold, dry, or poorly aerated or if other conditions are unfavorable to the microorganisms. The adsorption of herbicide into the soil can result in a reduced

ability of microorganisms to break it down, as the herbicide is less readily available (or accessible) in the soil solution.

The various atoms that make up the herbicide also affect microbial activity. Chemicals containing halogens (Cl, F, Br, or I) will decompose slowly. Another consideration in some fields where fumigation or sterilization has been used is that these processes kill most microorganisms. A lack of microorganism's results in no decomposition of any herbicide residue in the soil until a microbe population can reestablish. Soil pH also influences the growth of microorganisms. In general, the bacteria and actinomyces are favored by soils having a medium to high pH, and their activity is reduced below pH 4.5. Fungi tolerate all normal soil pH values. In normal agricultural soils, fungi predominate at low pH.

Higher Plant Decomposition

Herbicides absorbed from the soil by higher plants are generally changed or metabolized. A small amount can remain in its original form and can be stored or exuded.

(2) Abiotic decomposition

i. Chemical decomposition

Chemical decomposition is the breakdown of herbicide by a chemical process or reaction in the absence of a living organism. This may involve reactions such as oxidation, reduction, and hydrolysis. Ex. atrazine will slowly hydrolyze in the presence of water, rendering it ineffective as a herbicide, Hydrolysis of sulfonylurea herbicides in low pH or acidic soils.

In soil saturated with water, oxygen will likely become a limiting factor. Under such conditions, anaerobic degradation of organic compounds can be expected. Trifluralin, under standing water, was completely degraded in 7 days at 76°F in nonautoclaved soils, whereas only 20% had degraded at 38°F.

ii. Photodecomposition

Photodecomposition, is the breakdown of a herbicides by light. The process begins when the herbicide molecule absorbs light energy, which causes excitation of its electrons, and may result in breakage or formation of chemical bonds. Most herbicides are white, or nearly so, and have peak light absorption in the ultraviolet

range (220–324 nm), whereas yellow compounds such have absorption peaks at about 376 nm.

iii. Volatilization

Volatilization accentuated by high soil-surface temperatures, biological and chemical degradation, and adsorption are a few of the factors that should be considered in explaining the disappearance of herbicides from soils.

Shallow incorporation with a rotary hoe or harrow is recommended to prevent photodecomposition and volatilization if rainfall does not occur within 5 to 7 days of herbicide application.

Transfer processes important in determining what happens to herbicides in the soil are

(1) Adsorption by soil colloids

The interaction of herbicides with negatively charged soil colloids (clays, organic matter) is dependent on the chemical nature of the herbicides. Positively charged (cationic) herbicides such as diquat and paraquat (bipyrdilums) are held to soil by ionic bonds, much like potassium and calcium are held (cation exchange).

However, unlike potassium and calcium, paraquat and diquat bound to clays are not readily displaced through ion exchange. Basic herbicides, such as the triazines, can become cations in low-pH (acid) soils and adsorb to soil particles by changing from a net negative charge (nonionic sorption) to a net positive charge (ionic state). Thus the activity of s-triazine herbicides such as atrazine is greater in high pH (basic) soils than in acid soils. Weak acids such as 2,4-D (phenoxy), dicamba (benzoic), and picloram (pyridine) will lose a H^+ ion and go from a net zero (nonionic) to a net negative state that is not readily adsorbed, because they have the same negative charge as the soil particles. However, small amounts may be retained by organic matter and positively charged soil colloids such as iron and aluminum hydrous oxides. Small amounts of neutral or nonionic (molecular form) herbicides have no charge and little tendency to gain or lose H^+.

1. Soils high in organic matter require relatively large amounts of most soil-applied herbicides for weed control.

2. Soils high in clay content require more soil-applied herbicide than sandy soils for weed control.

3. Soils high in organic matter and clay content have a tendency to retain herbicides for a longer time than sand. The adsorbed herbicide may be released so slowly that the chemical is not effective as a herbicide.

(2) Leaching or movement through the soil

Leaching is the downward movement of a substance dissolved in water through soil. Leaching may determine herbicide effectiveness, may explain selectivity or crop injury, or may account for herbicide's removal from the soil. Pre emergence herbicides are frequently applied to the soil surface. Rain or irrigation moves the chemical into the upper soil layers, and weed seeds germinating in the presence of the herbicide are killed. Large-seeded crops such as corn, cotton, and peanuts planted below the area of high herbicidal concentration may not be injured. In addition to the protection offered by depth, crop tolerance to a herbicide through physiological processes is also desirable.

The extent to which herbicide is leached is determined principally by

1. Adsorptive relationships between the herbicide and the soil
2. Solubility of the herbicide in water
3. Amount of water passing downward through a soil

(3) Volatility

Herbicides may vaporize and be lost to the atmosphere as either phytotoxic or non-phytotoxic gases. The toxic volatile gases may drift to susceptible plants. The *ester* forms of 2,4-D are volatile, and the vapors or fumes can cause injury to susceptible crops such as cotton, tomatoes, and grapes. Certain herbicides may move in a porous soil as a gas.

(4) Surface runoff

Herbicides applied to the soil surface may dissolve in rainwater and leach into the soil. However, heavy rains may carry the dissolved herbicide away from the treated area. Severe runoff, which causes erosion, can also carry adsorbed herbicides on the eroding soil particles.

(5) Removal by higher plants

Herbicides may be absorbed by the crop or surviving weeds and stored or given off in their original form. Usually, however, the herbicide molecule is altered in the plant by metabolism, and the herbicide breakdown products are either used by the plant or

discharged back into soil solution. In some cases, herbicides are retained within the tissues of the plant, thereby delaying decomposition.

Herbicides may be removed from treated fields if the compounds are present in harvested plant parts, but the amounts removed are nearly always insignificant. For example, 1 ppm of a herbicide in a 10-ton hay crop amounts to only 0.02 lb/acre removed in the hay. However, plants can degrade sizable amounts of herbicide during a cropping season (Weber et al., 1973).

(6) Absorption and exudation by plants and animals

Herbicides that are absorbed by plants and microorganisms can also be *exuded* or discharged from inside the organism to the surrounding environment. The herbicide can be in an altered form or the original form. Generally, this does not represent a significant percentage of the amount the herbicide absorbed.

Herbicides persisting **30 days or less** may be used to control weeds present at the time of treatment. Those persisting **30 to 90 days** will protect the crop only during a short period early in the growing season. This is generally adequate for many annual row crops that produce a dense canopy and thereby suppress weed growth through shading. Those providing **90 to >144** days of control may protect the crop for the entire growing season and are useful in perennial crops. Those providing **more than 12 months** of control are used primarily for total vegetation control in noncrop situations where persistence is desirable.

Fate of herbicides

Both the physical nature of the herbicide and the structure of soil control the fate of herbicides. Most soil aggregates contain clay, organic matter, water, and microorganisms, with which the herbicide can interact. Overlaid on the complex soil structure are the three possible phases in which organic herbicides can exist. Chemicals can occur in one, two, or all three of the phases of vapor, solid, or liquid at any given time. The particular phase in which the chemical occurs will exert a significant impact on the fate of the herbicide.

Four major attributes of the herbicides are most important:

i. Water solubility- is a reflection of the polarity of the chemical and is determined by the maximum amount of chemical that will dissolve in pure water at a specified

temperature and pH. In general, the more polar a chemical, the higher its water solubility.

ii. Retention by organic matter or soil (KOD, which is the sorption coefficient)

Herbicide *sorption* is defined as the retention of a chemical on or in a solid phase (in this case, the soil).

iii. Vapor pressure (potential to volatilize)- The vapor pressure of a chemical is defined as the pressure of the gas that is in equilibrium with the solid/liquid phase at a given temperature; it gives an indication of the tendency of the chemical to escape from a surface as a gas. All chemicals have a vapor pressure.

iv. Soil half-life ($T_{1/2}$ or persistence).

Herbicide soil half-life ($T_{1/2}$) is the integrated result of all herbicide loss pathways that act upon the parent herbicide when it is in the soil environment. The $T_{1/2}$ is important because it affects the efficacy period, exposure to environmentally important transport processes, and potential carryover to the next crop.

TABLE 6-1. Herbicide Characteristics That Determine Their Effectiveness, Persistence, and Potential for Leaching[a]

Herbicide	Major Site of Uptake	Water Solubility[b]	Sorption Index[b] (KOC)	Soil Half-Life (days)	Leaching Potential[c] (ppm)
Alachlor	Shoot, some root	240	170	15	Medium
Atrazine	Root, some shoot	33	100	60	High
Benefin	Germinating seed, shoot	<1	9000	40	Low
Butylate	Germinating seed, shoot	44	400	13	Small
Clomazone	Root, some shoot	1100	300	24	Medium
Chlorimuron	Root, some shoot	1200	110	40	High
Chlorsulfuron	Root	7000	40	160	High
Cyanazine	Root, some shoot	170	190	14	Medium
Cycloate	Germinating seed, shoot	95	430	30	Medium
Dicamba	Root	400,000	2	14	High
Ethofumesate	Shoot, some root	50	340	30	Medium
Ethalfluralin	Shoot	<1	4,000	60	Low
EPTC	Germinating seed, shoot	344	200	6	Small
Imazaquin	Root, some shoot	160,000[E]	20[E]	60	High
Imazethapyr	Root, some shoot	200,000[E]	10[E]	90	High
Linuron	Root, some shoot	75	400	60	Medium
Metolachlor	Shoot, some root	530	200	90	High
Metribuzin	Root, some shoot	1220	60[E]	40	High
Metsulfuron	Root	9500	35	120	High
Pendimethalin	Shoot	<1	5000	90	Low
Picloram	Foliage	200,000[E]	16	90	High
Pronamide	Root	15	200	60	High
Propachlor	Shoot, some root	613	80	6	Low
Simazine	Root	6	130	60	High
Sulfometuron	Root	70	78	20	Medium
Terbacil	Root	710	55	120	High
Trifluralin	Shoot	<1	8000	60	Low

[a]Water solubility, sorption index, soil half-life, and leaching potential values are from the *Soil Conservation Service Pesticide Properties Database Technical Guide for Nebraska*, Section II-D-5.
[b]Water solubility and sorption index for these herbicides were measured at pH 7. $K_{oc} = K_D$/organic carbon.
[c]Soil texture and structure will affect leaching potential.
[E] = an estimate—a wide range of values have been reported.
Adapted from *Nebguide G92-1081-A*, by Moomaw et al. (1996).

Residual effect of herbicides

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ELE-SSAC-364

Environmental toxicity

Adjuvants, such as petroleum solvents (e.g. diesel fuel, deodorized kerosene, methanol), can be highly toxic. In addition, impurities resulting from the manufacturing process can be more toxic than the active ingredient itself.

Birds and Mammals

A herbicide's toxicity is described by its LD50, which is the dose received either orally (taken through the mouth) or dermally (absorbed through the skin) that kills half the population of study animals. The oral LD50s reported here were determined for adult male rats. The dermal LD50s were determined for rabbits. The LD50 is typically reported in grams of herbicide per kilogram of animal body weight. LD50s are determined under varying circumstances so comparisons between different herbicides may provide only a rough sense of their relative toxicities. Dermal LD50 values may be more meaningful to herbicide applicators because they are more likely to be exposed to herbicide through their skin rather than by oral ingestion. In any event, very few people, even among applicators, are exposed to herbicide doses as high as the LD50.

The LD50 does not provide any information about chronic, long-term toxic effects that may result from exposure to lesser doses. Sublethal doses can lead to skin or eye irritation, headache, nausea, and, in more extreme cases, birth defects, genetic disorders, paralysis, cancer, and even death. Impurities derived from the formulation of the herbicide and the adjuvants added to the formulation may be more toxic than the herbicide compound itself, making it difficult to attribute increased risks of cancer or other effects directly to a herbicide.

The most dramatic effects of herbicides on non-target plants and animals often result from the habitat alterations they cause by killing the targeted weeds. For example, loss of invasive riparian plants can cause changes in water temperature and clarity that can potentially impact the entire aquatic community, and the physical structure of the system through bank erosion. Removing a shrubby understory can make a habitat unsuitable for certain bird species and expose small mammals to predation.

Aquatic Species herbicide's toxicity to aquatic organisms is quantified with the LC50, which is the concentration of herbicide in water required to kill half of the study

animals. The LC50 is typically measured in micrograms of pesticide per liter of water.

In general, ester formulations are more dangerous for aquatic species than salt and acid formulations because ester formulations are lipophilic (fat-loving), and consequently, can pass through the skin and gills of aquatic species relatively easily. Ester formulations, additionally, are not water soluble, and are less likely to be diluted in aquatic systems. Soil Microbes Herbicides have varying effects on soil microbial populations depending on herbicide concentrations and the microbial species present. Low residue levels can enhance populations while higher levels can cause population declines. In many cases, studies are too short in duration to determine the true long-term impacts of herbicide use on soil microbes.

Human toxicology

When proper safety precautions are taken, human exposure to herbicides used in natural areas should be minimal. Properly fitted personal protection equipment and well-planned emergency response procedures will minimize exposure from normal use as well as emergency spill situations.

Exposure Agricultural workers are often exposed to herbicides when they unintentionally re-enter a treated area too soon following treatment. People who mix and apply herbicides are at the greatest risk of exposure. The most common routes of exposure are through the skin (dermal) or by inhalation (to the lungs). Accidental spills or splashing into the eyes is also possible and with some compounds, can result in severe eye damage and even blindness.

Agricultural herbicide applicators are typically exposed to herbicide levels ranging from micrograms to milligrams per cubic meter of air through inhalation, but exposures through the skin are thought to be much greater. Spilling concentrated herbicide on exposed skin can be the toxic equivalent of working all day in a treated field. Dermal exposure can occur to the hands (directly or through permeable gloves), splashes onto clothing or exposed skin, and anywhere you wipe your hands (e.g., thighs, brow). Some tests have found relatively high levels of dermal exposure to the crotch and seat of workers who got herbicide on their hands, and then touched or wiped the seat of their vehicles. Because adsorption through the skin is the most common route of exposure for applicators, the dermal LD50 may provide more

practical information on the relative toxicity of an herbicide rather than the oral LD50, which is based on oral ingestion.

Toxic Effects

A person's reaction to pesticide poisoning depends on the toxicity of the pesticide, the size of the dose, duration of exposure, route of absorption, and the efficiency with which the poison is metabolized and excreted by the person's body. Different individuals can have different reactions to the same dose of herbicide. Smaller people are, in general, more sensitive to a given dose than are larger people.

Herbicides can poison the body by blocking biochemical processes or dissolving or disrupting cell membranes. Small doses may produce no response while large doses can cause severe illness or death. The effects may be localized, such as irritation to the eyes, nose, or throat, or generalized, such as occurs when the compound is distributed through the body via the blood stream. Symptoms can occur immediately after exposure or develop gradually. Injuries are usually reversible, but in extreme cases can be permanently debilitating.

Common symptoms of low-level exposure (such as occurs when mixing or applying herbicides in water) to many herbicides include skin and eye irritation, headache, and nausea. Higher doses (which can occur when handling herbicide concentrates) can cause blurred vision, dizziness, heavy sweating, weakness, stomach pain, vomiting, diarrhea, extreme thirst, and blistered skin, as well as behavioral alterations such as apprehension, restlessness, and anxiety. Extreme cases may result in convulsions, unconsciousness, paralysis, and death.

Impurities produced during the manufacturing process and adjuvants added to the formulation may be more toxic than the herbicide compound itself. Consequently, LD50s determined for the technical grade of the herbicide may not be the same as that for the brand name formulation. Combinations of herbicides furthermore, can have additive and synergistic effects in which a formulation of two or more herbicides is two to 100 times as toxic as any one of the herbicides alone. Labels should be read carefully for manufacturer's warnings and safety precautions that may be required for a particular formulation.

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LESSON: 34

INTRODUCTION TO SELECTIVITY OF HERBICIDES

Selectivity is perhaps the most important concept of modern weed science. Because of this phenomenon weeds can be controlled in crops with herbicides. To be useful, the herbicide (or mixture of herbicides) must provide an acceptable level of weed control while not injuring the crop to the degree that yield loss occurs. A herbicide is selective to a particular crop only within certain limits. The limits are determined by a complex interaction between the plant, the herbicide, and the environment. There are numerous ways in which this is accomplished, some of which may be surprising.

The overall crop tolerance is often the result of a combination of two or more of the **selectivity mechanisms** described in the following sections.

1. Molecular Fate and Metabolism

The difference between herbicide's metabolism in the weed and in the crop is one of the main mechanisms for selectivity. The mechanism of metabolism varies significantly between different crop-herbicide combinations; thus, a simple table showing how each herbicide class is metabolized is not possible.

For example, Chlorimuron-ethyl undergoes ring hydroxylation in corn, and glutathione conjugation in soybean. However, there are two enzyme-based reaction types that dominate with respect to metabolism leading to selectivity in crop plants: **oxidation and conjugation**.

The overall metabolism of herbicides in plants can be divided into four phases.

Phase I is a direct change in the herbicide structure brought about by oxidation, reduction, or hydrolysis reactions.

Ex. Examples of oxidation reactions for herbicides include hydroxylation of aromatic rings (2,4-D, dicamba, primisulfuron, bentazon), hydroxylation of alkyl groups (chlortoluron, prosulfuron, chlorsulfuron).

Phase II is conjugation to cell constituents such as glucose, glutathione, or amino acids. Many herbicides undergo Phase I prior to Phase II; however, some

herbicides can be directly conjugated with no preoxidation. Ex. metribuzin and 2,4-D.

Phase III conjugates are transported across cell membranes into the vacuole or cell wall,

Phase IV where further processing can occur to yield insoluble and/or bound residues.

All these processes result in loss of herbicide activity.

2. Activation of herbicides through metabolism

The classic example of activation of a herbicide through metabolism is beta oxidation of 2,4-DB (which is not herbicidal) to 2,4-D.

In legume crops, beta-oxidation of 2,4-DB to 2,4-D does not occur; thus, they are protected from any herbicidal effects.

Other plant types, including many weeds, beta oxidize 2,4-DB to 2,4-D and are killed. Wild oat is killed by imazamethabenz as a result of rapid de-esterification of the inactive methyl ester to the phytotoxic acid, and wheat metabolizes imazamethabenz to an inactive form. Another example of plant metabolism activating herbicides is the carbamothioate herbicides that are activated by undergoing sulfoxidation to the more reactive sulfoxide form in susceptible weeds.

3. Placement of the Herbicide in Time or Space

In placement, the sensitivity of the crop to the herbicide must be considered, so the herbicide is kept away from the crop in **time or space**. This is accomplished by applying the herbicide weeks to months prior to when the crop is planted. Although the crop may have some tolerance to the herbicide, soil degradation of the herbicide that occurs prior to crop planting further reduces the risk of injury.

Another method is to apply postemergence herbicides to control emerged weeds before the crop emerges. **Timing** is critical, because if the crop has started to emerge, damage can occur. Contact non residual herbicides (e.g. paraquat, glyphosate, and glufosinate) are often used this way because the herbicide cannot damage the crop after moving into the soil.

Some herbicides not inherently selective may become selective when they are in specific **vertical positions** in the soil profile (Figure 5-8). Such selectivity depends on the different rooting habits of crop and weed. A herbicide that readily leaches below the rooting zone of a shallow-rooted crop can be used to control deep-rooted weeds

without injuring the crop. Conversely, a herbicide that remains near the soil surface can control shallow-rooted weeds in a deep-rooted crop. A residual preemergence herbicide absorbed by roots can be selective when it is placed on the soil surface (or incorporated shallow) and the roots of perennial crops or the seeds of annual crops remain below the herbicide zone. Examples include simazine, diuron, and terbacil on perennial crops such as sugar cane, asparagus, citrus, coffee, apples, peaches, and woody ornamentals. Certain herbicides applied on the **soil surface** over large-seeded crops planted deep (e.g., peanuts, beans, corn and cotton) are also selective, because roots rapidly grow away from the herbicide if contained in the upper zones of the soil. Shallow incorporation of trifluralin coupled with deep sowing of wheat is used to control green foxtail in spring wheat. For this "placement" mechanism to work, the herbicide must not be highly mobile in the soil. Examples include **contact herbicide** sprayed under tree crops, vineyards, cotton, soybeans, and corn. Often the stems of crop plants have more tolerance to the herbicide than leaves (perhaps due to reduced uptake); thus, if a small amount of herbicide is sprayed on the stem tissue, injury is minimal. This is accomplished in row crops by using drop nozzles and nozzles that minimize spray drift, carefully controlling the nozzle height and direction of the nozzles, and when the crop is taller than the weeds, (for example, 2,4-D in corn) (Figure 5-10).

Wick-wiper applicators are used where the weeds are higher than the crop. The herbicide solution is wiped on the weeds; very little, if any, herbicide contacts the crop.

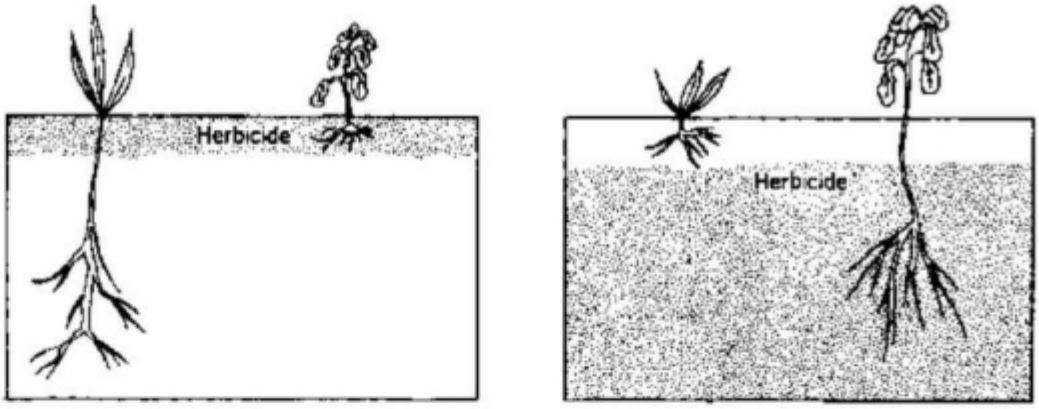

Figure 5-8. Differential leaching by herbicides alters selectivity. *Left*: A herbicide that remains near the soil surface can injure shallow-rooted weeds (*right*) and not injure the deep-rooted crop (*left*). *Right*: A herbicide that leaches from soil surface into the lower soil profile can injure deep-rooted weeds (*right*) and not injure a shallow-rooted crop (*left*).

A herbicide can be applied so that most of it covers the weed but little of it contacts the crop. This can be done by using **shielded or directed sprays** or wick-wiper applicators. Shielded sprays prevent the herbicidal spray from touching the crop while the weeds are covered with the spray. The spray nozzles are simply placed under a hood, or the crop is covered with a shield (Figure 5-9). Directed sprays are less cumbersome than shielded sprays and can be used when the crop can tolerate a small amount of the herbicide.

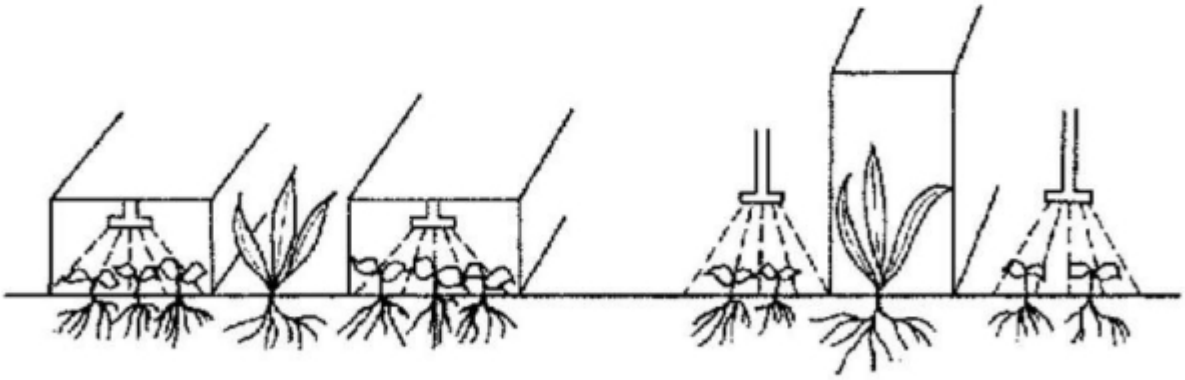

Figure 5-9. Shielded sprays protect crops from being sprayed with herbicides. *Left*: Spray confined within shields. *Right*: Crop covered with a shield.

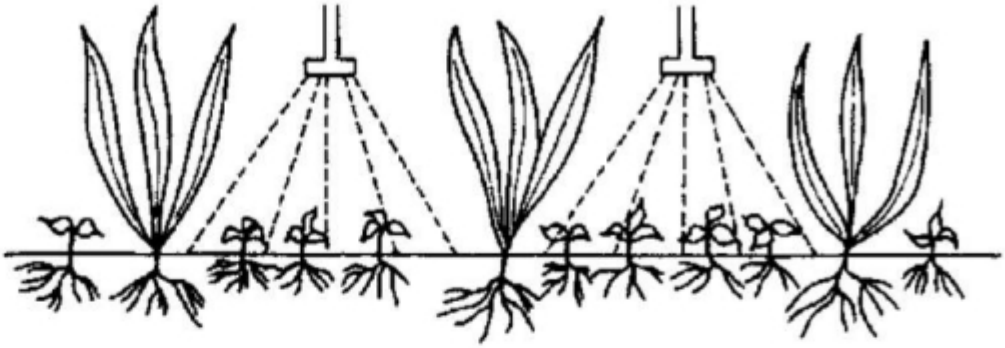

Figure 5-10. Directed sprays are aimed toward the base of the crop plant, favoring minimum coverage of the crop and maximum coverage of weeds.

4. Anatomical differences between crop and weed

The amount of **spray retention by foliage** after postemergence applications can affect selectivity. This selectivity is usually due to the crop plant's having a waxy cuticle that repels the spray solution. Examples include onions, peas, cereal grains, *Brassica* vegetable crops, and conifers. Medium to high spray volumes usually provide better selectivity, and adding an adjuvant can decrease selectivity as a result of enhanced adhesion of the spray droplets.

Differences in leaf shape, size, and orientation between weed and crop can provide some selectivity differences.

Postemergence selectivity can be due to the growing point of the crop being protected from direct contact by the herbicide while the growing point of the weed is exposed. The best example is dicot weed control in small grains.

Preemergence selectivity can be due to a difference in root morphology between the weed and the crop.

Morphology differences within stem tissue of grass plants can provide differences in selectivity. The growing point of many grass weeds (crabgrass and wild oat) are more exposed to herbicide-treated soil than wheat and barley where the growing point is protected inside the coleoptile.

5. Resistance at the site of action

Crop selectivity is due to resistance at the herbicide site of action in the cell. One example is the tolerance of carrots to dinitroanilines. Tolerance at the site of action may be due to the herbicide's being present as a proform where the metabolism

needed for changing the molecule to its active form does not occur in the crop. Perhaps the best-known example is the application of 2,4-DB to a legume and the deesterification of inactive imazamethabenz-methyl ester to the active acid, which is much more rapid and complete in weeds than in wheat.

Internal factors other than metabolism

6. Differences in the kind and/or quantity of food reserves in seeds

Differences in the kind and/or quantity of food reserves in seeds can be the basis for selectivity. Some crops with large food reserves in the seed are able to rapidly grow away from the location of the herbicide (cotton fields treated with trifluralin) or outlast the inhibition that occurs prior to the herbicide's being metabolized (corn fields treated with triazines).

7. Differences in crop and weed susceptibility at different stages of growth

There are herbicide applications in which selectivity is due to the crop's being dormant when small winter annual weeds are germinating and vigorously growing. An example is early application of herbicides to alfalfa during its dormant period in the early spring.

Selectivity may simply be due to a difference in age (development state) between the weed and the crop. For example, tomatoes are much more tolerant to metribuzin after they reach the 5 to 6 leaf stage.

8. Localized application of adsorbents

Activated charcoal is used to increase crop tolerance to certain herbicides. The charcoal is usually applied as a slurry to the roots during the transplanting process (e.g., strawberries) or in a narrow band over the row at time of seeding (e.g., some grass seed and vegetable crops). Any herbicide applied cannot reach the absorption region of the roots because of its being adsorbed by the charcoal.

9. Use of safeners to protect the crop

Otto Hoffman conceived the concept of using chemicals to achieve selectivity between weed and crop in the late 1940s. Application of the safener to the seed prior to planting and the other involves mixing the safener directly with the herbicide reduces crop injury without reducing weed control.

10. Role of herbicides relative to selectivity

The various aspects of herbicides relative to selectivity include **molecular configuration, concentration, formulation and chemical combinations**.

i. Molecular configuration

Variations in molecular configuration of herbicide changes its properties, which in turn modify its effect on plants. Chemical structures of herbicides are modified during discovery and development by chemical companies to alter phytotoxicity and selectivity.

ii. Concentration

Concentration may determine whether a herbicide inhibits or stimulates metabolism and growth of a plant. The endogenous plant growth regulator indole-3-acetic acid (IAA) inhibits respiration and growth at high concentrations but stimulates them at low concentrations. In many ways, herbicides like 2,4-D act similarly to IAA. In fact, 2,4-D at low concentrations is a common component of tissue culture growth media that stimulate cell division.

iii. Formulation

The formulation of herbicide is vital in determining whether it is selective or not with regard to a given species. A good example is the granular form that permits a herbicide to "bounce off" a crop and fall to the soil. In this instance, the crop may be susceptible to a spray application, yet tolerant to the herbicide if it can be kept off the foliage.

Substances known as adjuvants and surfactants are often added to improve the application properties of a liquid formulation; these additives may increase or decrease phytotoxicity. The addition of nonphytotoxic oils or surfactants to liquid atrazine or diuron formulations induces foliar contact activity in these normally soil-active herbicides. The addition of herbicide antidotes, safeners, or protectants (as discussed earlier) to formulations or as seed coatings is used to increase the crop tolerance to certain herbicides.

iv. Chemical combinations

Herbicides are often mixed with fertilizers, fungicides, insecticides, nematicides, or other herbicides to facilitate application. Occasionally, tank mixing of herbicides with other herbicides, pesticides, or fertilizers can alter selectivity. Therefore, it is advisable to use such combinations only when they are specifically recommended on the product label.

11. Role of the Environment

Dominant environmental factors that affect selectivity include soil type, rainfall or overhead irrigation, and soil-herbicide interactions.

Herbicide characteristics, soil type, and the amount of water received after herbicide application from rainfall or overhead irrigation determine the vertical position of a specific herbicide in the soil. Adsorption, the tenacity with which herbicide molecule is bound to soil particles, will strongly affect its movement in the soil. Low adsorption, high water solubility, high amounts of overhead water, and coarse soil types favor leaching of the herbicide into the soil profile. Some herbicides are extremely resistant to leaching, whereas others readily move with water. The movement is normally downward, but the herbicide may move upward as water evaporates from the soil surface.

The temperature of the environment in which a plant is growing has considerable influence on the rate of its physiological and biochemical processes. For example, the optimum temperature for the germination of seeds of different species varies greatly (e.g., spinach 41°F and cantaloupe 77°F). The selectivity of various plants to herbicides also varies as the temperature differentially affects their physiological and biochemical processes.

12. Growth and plant structure

Herbicides may induce abnormal plant growth through morphological, anatomical and cytological effects. However, these effects are generally specific for a given herbicide on a particular plant species. Among the abnormal responses induced by herbicides are (1) seed emergence failure, shoot inhibition, and root swelling after germination, (2) leaf chlorosis, (3) abnormal leaf form (Figure 5-12), (4) stem swelling, (5) cell division inhibition, (7) chloroplast destruction (Figure 5-13), and (8) membrane disruption followed by necrosis.

Reference

Weed Science: Principles and practices, Thomas J. Monaco, Stephen C. Weller and Floyd M. Ashton, 4th Ed., John Wiley and Sons, Inc. New York.

Lesson : 35

COMPATIBILITY OF HERBICIDE WITH OTHER AGROCHEMICALS

Simultaneous or sequential application of herbicides, insecticides, fungicides, antidotes, fertilizers etc., is followed in a single cropping season. These chemicals may undergo a change in physical and chemical characters, which could lead to enhancement or reduction in the efficacy of one or more compounds. The interaction effects were seen much later in the growing season or in the next season due to build-up of persistent chemicals or their residues in the soil. Knowledge on the interactions of various chemicals can be helpful in the formulation and adoption of a sound and effective plant protection programme. It can also help to exploit the synergistic and antagonistic interactions between various pesticides for an effective eradication of weed and other pest problems. When two or more chemicals accumulate in the plant, they may interact and bring out responses.

These responses are classified as additive, synergistic, antagonistic, independent and enhancement effects.

i) Additive effect: It is the total effect of a combination, which is equal to the sum of the effects of the components taken independently.

ii) Synergistic effect: The total effect of a combination is greater or more prolonged than the sum of the effects of the two taken independently e.g. The mixture of 2,4-D and Chlorpropham is synergistic on monocot species generally resistant to 2,4-D. Similarly, low rates of 2,4-D and Picloram have synergistic response on Convolvulus arvensis. Atrazine and Alachlor combination, which shows synergism is widely used for an effective control in corn.

iii) Antagonistic effect: The total effect of a combination is smaller than the effect of the most active component applied alone e.g. Combination of EPTC with 2,4-D, 2,4,5-T or dicamba have antagonistic responses in sorghum and giant foxtail. Similarly, chlorpropham and 2,4-D have antagonism. When simazine or atrazine is added to glyphosate solution and sprayed the glyphosate activity is reduced. This is due to the physical binding within the spray solution rather than from biological interactions within the plant.

iv) Independent effect: The total effect of a combination is equal to the effect of the

most active component applied alone

v) Enhancement effect: The effect of a herbicide and non-toxic adjuvant applied in combination on a plant is said to have an enhancement effect if the response is greater than that obtained when the herbicide is used at the same rates without the adjuvant e.g. Mixing Ammonium sulphate with Glyphosate.

Herbicide-moisture interaction

Soil applied herbicides fail when there is a dry spell of 10-15 days after their application. Pre-emergence herbicides may be lost by photo-decomposition, volatilization and wind blowing while some amount of water is desirable to activate the soil applied herbicides, excess of it may leach the herbicide to the crop seed and root zone. This may injure the crops and on other side, results in poor weed control. Heavy showers may wash down herbicides from the foliage. Continuous wet weather may induce herbicide injury in certain crops by turning them highly succulent e.g. Maize plants are normally tolerant to Atrazine but they become susceptible in wet weather, particularly when air temperature is low. Extra succulence has been found to increase atrazine absorption and low temperature decreases its metabolism inside the plants. Quality of water used may also determine herbicide action. Dusty water reduces action of paraquat. Calcium chloride rich water reduces glyphoste phytotoxicity.

Herbicide-insecticide interaction

These chemicals are usually not harmful at recommended rates. The tolerance of plants to herbicide may be altered in the presence of an insecticide and vice versa. The phyto-toxicity of monuron and diuron on cotton and oats is increased when applied with phorate. Phorate interacts antagonistically with trifluralin to increase cotton yield, by stimulating secondary roots in the zone of pesticide incorporation. Propanil interacts with certain carbamate and phosphate insecticides used as seed treatments on rice. But chlorinated hydrocarbon insecticides as seed treatment have not interacted with propanil. When propanil is applied at intervals between 7 and 56 days after carbofuron treatment, it results in greater injury to rice vegetatively.

Herbicide-pathogens / fungicides interaction

Herbicides interact with fungicides also. In sterilized soil, chloroxuron is not causing any apparent injury to pea plants, while in the presence of *Rhizoctonia solani i*n unsterilized soil it causes injury. Oxadiazon reduces the incidence of stem rot caused by the soil borne pathogen *Sclerotium rolfsii* L. in groundnut. Diuron and triazine which inhibit photosynthesis may make the plants more susceptible to tobacco mosaic virus. On the other hand, diuron may decrease the incidence of root rot in wheat.

Herbicide-fertilizer interaction

Herbicides have been found to interact with fertilizers in fields e.g., fast growing weeds that are getting ample nitrogen show great susceptibility to 2,4-D, glyphosate than slow growing weeds on poor fertility lands. The activity of glyphosate is increased when ammonium sulphate is tank mixed. Nitrogen invigorate (put life and energy in to) the meristamatic activity in crops so much that they susceptible to herbicides. High rates of atrazine are more toxic to maize and sorghum when applied with high rates of phosphorus.

Herbicide-microbes interaction

Microorganisms play a major role in the persistence behaviour of herbicides in the soil. The soil microorganisms have the capacity to detoxify and inactivate the herbicides present in the soil. Some groups of herbicides more easily degrade through microbes than others. The difference lies in the molecular configuration of the herbicide. The microorganisms involved in herbicide degradation include bacteria, fungi, algae, moulds etc. Of these, bacteria predominates and include the members of the genera *Agrobacterium, Arthrobacter, Achromobacterium. Bacillus, Pseudomonas, Streptomyces, Flavobacterium, Rhizobium* etc. The fungi include those of the genera *Fusarium, Penicillium* etc.

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Lesson: 36

INTRODUCTION TO ADJUVANTS AND THEIR USE IN HERBICIDES

Herbicides are formulated to facilitate their handling, storage, and application and to improve their effectiveness under field conditions. A formulation chemist can change the formulation of a chemical to affect its solubility, volatility, toxicity to plants, and numerous other characteristics. This is accomplished by changing the chemical form (e.g., acid to ester) or using adjuvants, including surfactants.

Adjuvants- An adjuvant is any substance in a herbicide formulation or added to the spray tank to modify herbicidal activity or application characteristics.

A surfactant (surface-active agent) is a material that improves the emulsifying, dispersing, spreading, wetting, or other properties of a liquid by modifying its surface characteristics. Adjuvants and surfactants are considered to be inactive ingredients even though they can have a pronounced effect on the performance of the product.Use of adjuvants, other than as formulation agents, is primarily restricted to postemergence herbicide applications. Adjuvants can be divided into two general categories: spray modifiers and activators.

The most common type of adjuvants are

(1) Activity enhancers, such as surfactants, oils, organosilicones, and fertilizers,

(2) Spray modifiers such as stickers and drift control agents, and

(3) Utility modifiers such as compatibility and antifoam agents.

However, not all adjuvants are always beneficial; some may have no effect or even decrease the desired effect. Therefore, adjuvants should not be placed in the spray mixture unless suggested on the label or recommended by knowledgeable authorities.

Classification of Adjuvants According to Use

Activity Enhancers

Surfactants derive their name from the term surface-active agents. Most surfactant molecules are composed of a lipophilic long-chain hydrocarbon (alkyl) group and a hydrophilic polar group.

Surfactants are generally classified according to the nature of the polar segment of the molecule. Among the types of surfactants are cationic (positive charge), anionic (negative charge), zwitter ionic (having both a positive and a negative charge, depending on the water pH), and nonionic (no charge).

Nonionic surfactants dissociate little in water, whereas the others are charged when dissolved in water. Because adjuvants contain both lipophilic (oil-like) and hydrophilic (waterlike) properties, they can interact with the lipophilic plant surfaces, lipophilic herbicides, hydrophilic herbicides, and water. The most common surfactants for use with herbicides are nonionic, and most emulsifiers are blends of anionic and nonionic types.

An important function of surfactants used as adjuvants is to reduce the surface tension of a spray solution. This allows increased wetting of leaves and spreading of the spray to achieve more intimate contact between the spray droplet and plant surface.

Any substance that will bring the herbicide into more intimate contact with the leaf surface and keep it in a soluble form has potential of aiding absorption. Surfactants achieve this by

1. Causing a more uniform spreading of the spray solution and a uniform wetting of the plant
2. Helping spray droplets to stick to the plant, resulting in less runoff
3. Ensuring that droplets do not remain suspended on hairs, scales, or other surface projections
4. Partially solubilizing the lipoidal plant cuticle substances (controversial)
5. Preventing crystallization of the active ingredient on the leaf surface by acting as a solvent
6. Slowing the drying of, and increasing the water retention in, spray droplets once on the leaf surface

Surfactants of the nonionic type are commonly used with contact herbicides such as paraquat and many postemergence grass and broadleaf specific herbicides to enhance activity at 0.1 to 0.5% by volume of the spray mixture. Surfactants are usually available at 50 to 100% active ingredient.

Oils used in agriculture are of two primary types: **refined oils** (petroleum-based) and **seed oils** (sometimes called vegetable oils). Petroleum (refined) oils are specific "cuts" from the distillation of petroleum, and crop oils and crop oil concentrates are

highly refined and purified paraffinic nonphytotoxic oils plus surfactants that are used to increase foliar activity of certain herbicides.

Organosilicone surfactants are often composed of a trisiloxane backbone (lipophilic or hydrophobic portion), with an ethylene oxide chain (hydrophilic portion) attached to one of the silicon atoms. Organosilicone surfactants cause a tremendous reduction in the surface tension of water-based spray solutions and cause substantially greater spreading of the spray droplet than would be predicted by the reduction in surface tension. This increased spreading is thought to be due to the compact size of the lipophilic portion of the trisiloxane moiety, allowing it to transfer readily from the liquid/air interface to the leaf surface as the drop moves across the leaf (Ananthapadmanabhan et al., 1990). These surfactants provide improved rainfastness of the spray droplet and have humectant properties. Even though the increased spreading would in most cases be thought to increase the rate of droplet evaporation, these surfactants tend to slow the drying of the droplet. One problem with organosilicones is that they are unstable when the pH of the spray solution is not within the range of 6 to 8.

Salts of fertilizers are used as adjuvants in water-based spray solutions to increase the activity of foliar-applied herbicides. Common additives are ammonium sulfate, ammonium nitrate, and urea plus ammonium nitrate (e.g., 28% UAN) added at a concentration of 2 to 5%. The exact mechanism of action is not known, although increased herbicide absorption into the plant cells has been reported.

Spray Modifiers

Spray modifiers, such as stickers, increase the adhesion of spray solutions to treated plant surfaces and are often used in conjunction with wetting agents (referred to as spreader-stickers). Film-forming vegetable gels, emulsifiable resins, emulsifiable mineral oils, waxes, and water-soluble polymers have been used as stickers.

Drift control agents are materials that thicken the spray solution and thereby increase droplet size and reduce the number of very small satellite droplets. These materials include swellable polymers and hydroxyethyl cellulose or polysaccharide gums and are used at concentrations of 0.1 to 1.0 % of the volume. Invert emulsions are also used to reduce spray drift.

Drift control agents are of great value when herbicide applications are made near sensitive nontarget plants, even though they increase application costs. The

appropriate spray equipment and operating conditions must be used with these thickened solutions.

Utility Modifiers

Utility modifiers are adjuvants that are used to reduce or avoid application problems and/or increase the usefulness of a formulation. Emulsifiers and other surfactants of herbicide formulations can cause foaming with agitation of the spray mixture. Thus, antifoam agents are used to prevent or reduce excessive foaming in the spray tank. Antifoam agents are typically silicones and are used at 0.1% by volume.

Kerosene or diesel fuel added to the spray tank at the same rate can often inhibit foaming. Compatibility agents are used to help with mixing and/or application problems that may occur when a combination of pesticides is used. They can also be used when herbicides are applied in combination with a suspension, slurry, or true solution of fertilizers. Compatibility agents can counter separation problems that occur with hard or cold water.

Reference

Weed Science: Principles and practices, Thomas J. Monaco, Stephen C. Weller and Floyd M. Ashton, 4th Ed., John Wiley and Sons, Inc. New York.

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ALL THE BEST
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Stay Home Be Safe