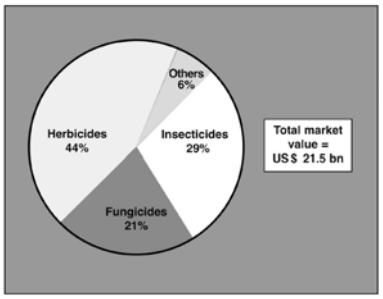
Section 6: Insecticides and their formulation

- Insecticidal properties of certain plants and minerals long known.
- Insecticides (pesticides directed at insects and related arthropods) became popular in the first half of the 1900's, and very popular in the second half.
- Now represent the principal technique used for pest management once they reach a damaging level, and in some cases, to keep them from attaining damaging level.

This graph should give you some perspective on the magnitude of pesticide use, and the relative importance of insecticides (adapted from Matthews 1992).



Insecticides

- Insecticides not universally appreciated, primarily because the health and environmental problems they can cause are becoming better known.
- Number of products being introduced in decreasing.
- Cost of products increasing markedly.
- Mammalian toxicity is decreasing.

Issues affecting introduction of new products

- Available market (cotton and mosquitoes critical).
- Lack of phytotoxicity.
- Human toxicity.
- Environmental hazards (non-target affects).
- Only a small number of products meet the market and safety standards of national agencies.
- Development time 6-7 years; cost $12 million.

Types of insecticides

- Two principal means of classification, based on:
  - How they get to the insect.
  - Chemical nature of the toxicant.
- Note that many products reach the insect in more than one way.

Neem-based insecticides have multiple effects: toxicity, growth regulator, and repellency.

Classification based on routes of contact

- Contact - often by walking on treated surface, problem with short-lived products.
- Residual - longer-lived products, duration of days to months (years).
- Stomach poisons - must be ingested, provides some specificity.
- Translaminar - passes through leaf, upper to lower surface.

More routes of contact

- Systemic - vascular translocation, upwards and outwards. Treat roots to maximize. coverage. Phloem feeding and animal parasites also affected.
- Quasi-systemic - localized movement, increasing coverage.
- Fumigant - toxic vapors inhaled, useful for concealed and immobile stages.

Classification based on chemical structure

Early insecticides (natural, based on plant derivatives, oils, heavy metals).

- Plant derivatives.

  Pyrethrum from *Chrysanthemum.*

  Rotenone from roots of derris plant.

  Nicotine from tobacco plant.

  Neem from neem tree, *Azadirachta indica*.

Short-lived, variable mammalian toxicity.

Chemical structure, continued

- Oils.

  Work by suffocation.

  Some aquatic and plant hazards. Dormant and summer oils.

  Monomolecular films for water surface, interferes with surface tension.

Affects mostly small and sessile insects, eggs, and mosquitoes.

Chemical structure, continued

- Heavy metals.

  Toxicants based on copper, arsenic, fluorosilicate, lead, sodium.

Persistent, highly toxic, rarely used now.

Chemical structure, continued

- So-called “modern” synthetic insecticides

  Developed during or after World War II.

  Most act by interfering with nervous transmission, hence called “nerve poisons.”

Classes of products include chlorinated hydrocarbons, organophosphates, carbamates, avermectins, formamidines, etc.

Chemical structure, continued

Chlorinated hydrocarbons (organochlorines), began to be developed in 1940s.

First of the truly residual products, often safe for humans (e.g., DDT).

Persistence led to accumulation.

Products include BHC (HCH), aldrin, dieldrin, endosulfan, lindane, toxaphene.

Chemical structure, continued

- Organophosphates, began to be developed in 1940s.
  - More toxic but less persistent.
  - Still widely used but disappearing.

Products include malathion, parathion, diazinon, dimethoate, disulfoton, dichlorvos, fenthion.

Chemical structure, continued

- Carbamates, developed in the 1950s
  - Intermediate between chlorinated hydrocarbons and organophosphates in toxicity and persistence.
  - Some still important.

Products include carbaryl, methomyl, aldicarb, carbofuran, propoxur.

Chemical structure, continued

- Synthetic pyrethroids, developed in 1970s

  Low toxicity to mammals, high toxicity to insects, considerable stability, some repellency

Products include permethrin, cypermethrin, cyfluthrin, allethrin.

Chemical structure, continued

- Formamidines, developed in 1970s
  - Different mode of action than most classes, so useful where resistance develops
  - Also active against eggs
  - Products include chlordimeform, amitraz

Chemical structure, continued

- Avermectins, developed in 1980s
  - Derived from fermentation of soil-inhabiting bacterium, Streptomyces avermitilis
  - Important for treatment of animals for insect and helminth parasites, but also crop pests
  - Only moderately toxic to mammals, short-lived
  - Products include abamectin, emamectin, ivermectin, milbemectin

Chemical structure, continued

- Nicotinoids, introduced in 1990s
  - Similar to nicotine in mode of action, but more persistent
  - Systemic
  - Useful for resistance management but overused so resistance may become problem
  - Products include imidacloprid, acetamiprid

Chemical structure, continued

- Naturalytes, developed in 1990s
  - Derived from fermentation of an actinomycete, Sacharopolyspora spinosa
  - Broadly active against pests, but very safe for beneficial insects
  - Moderately residual
  - First product is spinosad

Chemical structure, continued

- Insect Growth Regulators, began introduction in 1970s
  - By resembling natural hormones, interfere with growth and development
  - Fairly specific to insects, so fairly safe
  - Does not provide immediate kill
  - Various types of insect growth regulators: ecdysone, JH analogues, anti JH, chitin synthesis inhibitors
  - Products include diflubenzuron, fenoxycarb, cyromazine, methoprene

New chemistries

- In recent years, many novel products have been introduced. Each seems to have its own mode of action, including unique means of disrupting respiration, development, and nervous function.
- Only time will tell whether these new products develop into new classes of products.
- At the very least, they afford opportunity to rotate among classes of insecticides, a common resistance management approach.

“Kitchen” chemistry

- Homeowners unfamiliar with pesticides often assume that household products are safer than commercial pesticides.
- Insecticidal products include:
  - Vegetable oil
  - Dish detergent
  - Detergent plus oil
  - Garlic or tobacco extract
  - Ammonia (for slugs)
  - Citrus oil (d-limonene)
  - “Fantastik” and “409” household cleaners

Formulation of insecticides

- Formulation makes the active ingredient (toxicant) easier to use, and more effective through the addition of emulsifiers, wetting agents, stickers, spreaders, etc.
- In some cases it also determines the hazards to the applicator and non-target organisms.
- The choice of formulation can be as important as the choice of toxicant.

Formulations

- Formulations applied as liquids
  - Water soluble powders - powder added to water when needed; powder dissolves.
  - Suspension (flowable) - a solid premixed with a small amount of liquid; a syrupy material that is diluted.
  - Water-miscible liquid - similar to a suspension, but with liquid active ingredient.
  - Solution - toxicant is dissolved; may be applied with or without dilution, depending on product.

More liquid formulations

-Wettable powders - powder that will be suspended in water (doesn't dissolve), so requires constant agitation; very common but abrades application equipment.

-Emulsifiable concentrate - toxicants dissolved in organic solvent; mixes with water and forms milky white fluid that does not precipitate; common, not abrasive, sometimes phytotoxic.

-Oil - toxicant in oil.

More liquid formulations

-Microcapsule - toxicant is in polymer until ingested by insect, then release; not common, but minimizes toxicity to nontarget organisms

-Paint - toxicant mixed into paint for residual effects

-ULV - ultra-low volume; liquid applied in very small droplets with little or no dilution

- Aerosol - liquid under high pressure in small cans, small droplets are produced

-Fumigants - liquid that turns to vapor when released, penetrates dense substrates

Dry formulations

- Formulations applied without liquid
  - Dust - very finely divided, and diluted with inert dry product such as talc
  - Granule - larger amount of toxicant in larger particles; when very large called pellets
  - Briquettes -still larger particles; applied to water where toxicant is released slowly over time

More dry formulations

-Impregnated plastic - insecticide in plastic strip, released as liquid or gas over a prolonged period (dog collars, ear tags, etc.)

-Baits - toxicant combined with a dry or liquid food-based attractant; animal ingests toxicant with bait

Why so many chemicals?

- Chemicals are inherently diverse, in many cases stable, and amenable to modification.
- For these reasons, they can be formulated in many ways to improve their pest-killing power, stability, and utility.
- Although they are not without problems, this flexibility is the key to their success and widespread use.

There are numerous ways to formulate insecticides and to deliver them. Shown here are treated seed, sprayed onto livestock, injected under plastic mulch, and foliar application by aircraft.

Questions on insecticides and formulations

- Can you name three of the older “modern” classes of insecticides? Three of the newer “modern” classes?
- There is a lot of interest now in plant-derived products and in oils. Are they new classes of insecticides?
- Can you name and distinguish between 10 liquid formulations? 4 dry formulations?

Pesticide labels

- The pesticide label contains all the information needed on use, storage, safety, disposal, and treatment of poisoning.
- The formulation is also indicated, though often cryptically:
  - WP for wettable powder
  - SP for soluble powder
  - EC for emulsifiable concentrate
  - D for dust
  - G for granule
  - S for solution
  - F for flowable

This is part of a typical pesticide label. An awful lot of information, and most of it too small to read! Nevertheless, it is an important document.

Components of the pesticide label

- Product or trade name - reflects company making sale, formulation and toxicant; same active ingredient may bear different names when sold by different companies or in different formulations
- Ingredients - toxicant or AI (chemical name plus common name) and inert ingredients (not specified)

Components of the pesticide label, continued

- Type of pesticide - insecticide, nematicide, etc.
- Use - destination such as soil, flower crop, mosquito control, etc.
- Net contents
- Name and address of manufacturer
- EPA registration number
- Establishment number - point of manufacture

Components of the pesticide label, continued

- Signal words and symbols - indication of hazard level: danger-warning-caution
- Precautionary statements - more statements on personal or environmental hazards
- Route of entry - statements about toxicity if swallowed, inhaled, eye and skin contact
- Action statement - what to do if contact/poisoning occurs
- Protective clothing and equipment

Toxicity categories and signal words on pesticide labels.

- I. DANGER-POISON plus skull and crossbones. These are highly toxic and usually require a special license to purchase.
- II. WARNING. Moderately toxic.
- III. CAUTION. Slightly toxic.
- IV. CAUTION. Even less toxic. Even so, the statement “keep out of reach of children” is required.

Components of the pesticide label, continued

- Environmental hazards
- Physical or chemical hazards - flammability, corrosiveness
- Classification statement - general or restricted use pesticide
- Re-entry statement - how long to remain away from treatment
- Storage and disposal instructions
- Directions for use - how much, how to apply

Some label terminology that might confuse you

- Preplant - used before the crop is planted
- Preemergence - used before the crop or pests emerge
- Band - application of a strip over or along a crop row
- Broadcast- uniform application over a specific area
- Crack and crevice - treatment of crack where insects are sheltered
- Foliar - application to the leaves

More label terminology

- Dip - submergence of a plant or animal in a bath of the pesticide
- Drench - saturating the soil with the pesticide
- In-furrow - application to the furrow in which the crop is planted
- Pour-on - pouring the pesticide along the back of livestock
- Side-dress - application along the side of a crop row
- Lay-by - application along with, or shortly after, last cultivation of a crop

Questions about label application directions

- Can you list 10 important items that are found on insecticide labels?
- Can you distinguish between pre-plant and pre-emergence treatments? Dip and pour-on? Side-dress and lay-by? Band and in-furrow? Drench and broadcast?

Adjuvants

- Adjuvants are non-toxic materials added to a formulation or tank mixture to enhance the product. Though not usually explained (they are part of the "inert" ingredients) they serve several purposes, such as:
  - Buffers - allowing mixing of materials with different acidities
  - Safeners - reduce phytotoxicity
  - Foaming agents - reduce drift

More adjuvant properties

- Wetting agents - allow wettable powders to mix with water and stick where needed
- Emulsifiers - allow petroleum-based materials to mix with water
- Spreaders - allow a pesticide to form a uniform layer on the treated surface
- Stickers - allow a pesticide to stay on the treated surface

How toxic is an insecticide?

- Insecticides vary greatly in their toxicity.
- Toxicity normally is expressed as LD_{50} values. This is the amount necessary to be lethal to 50% of the subjects tested.
- Following is a chart that indicates how much active ingredient, by toxicity category, will be lethal or otherwise harmful - and the signal words associated with each category.

EPA labeling toxicity categories by hazard indicator.

Hazard indicators	Toxicity categories			
	I (Danger-Poison)	II (Warning)	III (Caution)	IV (Caution)
Oral LD_{50}	Up to and including 50 mg/kg	From 50 t0 500 mg/kg	From 500 to 5,000 mg/kg	Greater than 5,000 mg/kg
Inhalation LD_{50}	Up to and including 0.2 mg/liter	From 02. to 2 mg/liter	From 2 to 20 mg/liter	Greater than 20 mg/liter
Dermal LD_{50}	Up to and including 200 mg/kg	From 200 to 2,000 mg/kg	From 2,000 to 20,000 mg/kg	Greater than 20,000 mg/kg
Eye effects	Corrosive; corneal opacity not reversible within 7 days	Corneal opacity reversible within 7 days; irritation persisting for 7 days	No corneal opacity; irritation reversible within 7 days	No irritation
Skin effects	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irritation at 72 hours

Questions about insecticide toxicity

- Do you know the differences between acute and chronic toxicity.
- Are warning labels a good indication of chronic toxicity?
- Is consumption of insecticide residue on food more likely to result in acute toxicity? Chronic toxicity?

Pesticide safety

- Exposure to pesticides normally occurs by one of the following means:
  - Oral exposure - not washing hands before eating, drinking or smoking; splashing pesticide into mouth; mistaking pesticide for drink
  - Inhalation - breathing vapors while mixing; breathing fumes indoors; using a poorly fitted respirator; breathing pesticide drift
  - Dermal/eye exposure - splashing mixture; spraying under windy conditions; wearing contaminated clothing; rubbing eyes or forehead; failure to wear protective clothing; re-entry of sprayed fields too early; failure to bath properly

Avoiding exposure

- Avoiding exposure is not difficult, but it happens anyway, because:
  - It is too hot or humid to wear proper protective gear
  - Applicators get complacent because they experience no adverse effects
  - Proper equipment is not available
  - A new or more toxic material is used without following the precautions on the label
  - Workers re-enter sprayed field or building too early, or don't wash after handing produce that has been treated

Personal protective equipment

- When handling toxic materials, use appropriate equipment such as:
  - Long-sleeved shirt, long pants, waterproof boots, hat, gloves
  - Chemical resistant gloves, clothing, hood, apron, boots
  - Respirator (perhaps air-supplying respirator) and eye protection
- The toxicity and risk of exposure determine the level of protection needed. Read the label!

Using personal safety equipment is common sense

The type of protective equipment must be adjusted according the the hazards involved.

Hazards

- Remember, accidents WILL occur.
- You must plan for mistakes and equipment failures.
- Use the least toxic material, know the risks associated with use of the product, and use personal protective gear.
- Mark or label treated areas, and obey re-entry requirements

Questions about personal safety

- Can you list the types of exposure and the ways in which exposure to pesticide occurs?
- What protective steps can be taken to prevent exposure to applicators?

Questions from supplementary reading

- Reading 18, destruction of gypsy moth eggs
  - What is the postulated pesticidal mode of action of vegetable oil?
  - Is timing of oil application a critical factor in obtaining control of gypsy moth?
  - How practical do you expect this approach to be on large trees?