ENT-605 Insecticides and their Application 3(2-1)

THEORY

Introduction; nomenclature, classification on the basis of mode of entry, chemical nature, mode of action, toxicity and insecticides formulations; compatibility, physicochemical properties, mode of action, residues of insecticides; hazards and safety measures; functioning of various types of hand and power operated equipments for insecticide application.

PRACTICALS

Computation, preparation and field application of different formulations of insecticides; identification, classification, handling and maintenance of application equipments.

BOOKS RECOMMENDED

1. Dovener, R.A. Mueninghoff, J.C. and Volgar, G.C. 2002. Pesticides formulation and delivery systems: meeting the challenges of the current crop protection industry. ASTM, USA

2. Dodia, D.A. Petel, I.S. and Petal, G.M. 2008. Botanical Pesticides for Pest Management. Scientific Publisher (India) Jodhpur.

3. Ishaaya, I. and Degheele, D. 1998. Insecticides with Novel Modes of Action:

Mechanism and Application. Norosa Publishing House, New Delhi.

4. Mathews G.A. 2002. Pesticide Application Methods. 4th Ed. Intercept. UK.

5. Otto, D. and Weber, B. 1991. Insecticides: Mechanism of Action and Resistance.

Intercept Ltd., U.K.

6. Roy, N.K. 2006. Chemistry of Pesticides. Asia Printograph Shahdara Delhi.

7. Saleem, M.A. 2004. Principles of Insect Toxicology. Vol.-I. Izhar sons Printers.

looper etc., have been controlled by this method.

ii) **Sterilization by chemicals**

The chemicals used for the sterilization are organo metals, DMF, Tepa, Metapa hempa, Colchicine etc. these chemicals can be applied to the insects orally, by injection, by spraying etc.

iii) **Hybrid sterility**

When two closely related species are crossed, the hybrids are all sterile just like a mule. This is called hybrid sterility. Mid term

VII. CHEMICAL CONTROL

Chemical control is the control of insect pests with the help of pesticides.

PESTICIDE

Any substance or mixture of substance intended for preventing, killing, repelling or controlling any organism which is declared pest.

Classification of Pesticides

Pesticides can be claassified as: Pisicides ⇒ Fishes

A. Insecticides.

B. Rodenticides.

C. Acaricides. → To control the Mites.

D. Weedicides.

E. Fungicideds. Avicides ⇒ To control bird

A. INSECTICIDES

Any material that disrupts he vital processes of insects by chemical action is called an insecticide.

Classification of Insecticides

Classification can be done according to following:

1. Mode of Entry.
2. Mode of Action.
3. Mode of chemical Nature.

I. MODE OF ENTRY

1. **Stomach Insecticides**

Juvinile Hormone mimik → Insect Regulators.
Ecdysis/Ecdysin Agonist

These insecticides are applied on the plants when the chewing insects eat the plants. The insecticides along with food enter into stomach and kill the insect by chemical action.

2. **Contact Insecticides**

These insecticides are applied directly on the insects when they are damaging the crops. Such insecticides when come in contract with the body wall of the insects, enter the body through the body wall. These insecticides are used against sucking insects.

Repellant
Microbial insecticides
bacteria, fungi.

3. **Systemic Insecticides**

These insecticides are applied through the soil and by spraying. They are absorbed by the roots and other parts of plants, and translocated to all parts of plant. When the insects feed on such plants, they are killed. These are actually the stomach poisons. These are best against sucking insect pests.

4. **Fumigants**

Clogging

These insecticides are mostly in the form of vapors & in the form of solids which give fumes into the air with the ordinary temperature. These enter the body of the insect by inhaling through spiracles. Examples: Aluminum phosphide (Celphos, detia, delicia, postoxin), methyl-bromide, EDCT (Ethylene dichloride carbon tetrachloride).

II. MODE OF ACTION

1. **Physical Insecticides**

Those insecticides which insect pests through their physical action.

2. **Protoplasmic Insecticides**

Those insecticides which kill the insect through their action on the protoplasm of cells.

3. **Respiratory insecticides**

Thse are those insecticides which kill the insects by checking the respiration of insects.

methoxyfherozides Synaptic Poison
Axonic Poison

4. **Nerve Poisons**

These are those insecticides which kill the insects by their action on nervous system of insects.

5. **Miscellaneous Insecticides**

a) Insect Attractants:e.g., Methyl eugenol, gyplure, hexaplure etc.

b) Insect Repellents: e.g., creosote, mercurous chloride, tricholorobenzene etc.

III. MODE OF CHEMICAL NATURE

According to the chemical nature, insecticides are divided into two main groups:

1. **Inorganic Insecticides**

Some of the first insecticide ever used are in this category such as arsenics, sulphur, Paris green, sodium floride etc.

2. **Organic Insecticides**

i) **Natural organics**

A) **Animal Origin:**

Oils: fish oil. Oils used as insecticides are of two types:

Summer spray Oils: These are sprayed in spring when buds of plant are sprouted.

Dormant Spray Oils: These are sprayed in winter when buds are dormant. Also called winter oils.

Mode of Action of Oils: Oils action is of physical nature. Spiracles of insects are filled by oils and blockage of air inhalation cause suffocation which results in the death of insects.

B) **Plant Origin:** e.g., Rotenone, Nicotine, Ryania, Derris, Pyrethrum etc.

(b) **Synthesized Organics**

(c) **Organochlorine Insecticides** (Chlorinated hydracarbons):

Salient Characteristics: This is group of synthetic chemicals. These take a long time to disappear from environment and accumualte slowly in the bodies of insect.

Spinosad
Emamectin benzoate
imidacloprid
Diafenthiuron

Mode of Action: It unstabilize the peripheral nervous system. Ultimatley there is hypertoxicity, paralysis and finally death of the insects.

Antidotes: If sudden poisoning occurs in human being, then following antidotes of these chemicals such as atropine sulfate, raw egg and milk etc. can be used.

Range of Target Pest Insects: These insecticides are effective against a variety of insects especially beetles, weevils, mosquitoes. house flies, lice, fleas etc.

Examples:

DDT, Toxaphene, BHC, Aldrin, Dieldrin, Chlordane, Heptachlor, and Endrin.

b) Organophosphorus Insecticides

Salient characteristicsL They are not as persistent as chlorinated hydrocarbons. It may be contact, stomach or fumigants in action. These insectides dor not accumulate in fat bodies of animals.

Mode of Action:

These insecticides inhibit the production of cholinestrase enzyme which removes acetylcholine (liquid) from the synapse, due to an impulse will go on passing and disturb the insect continuously. Finally death of insect occurs.

Toxicity: It varies in toxicity from extremely hazardous to slightly hazardous chemicals.

Antidotes: Same as in case of chlorinated hydrocarbons.

Range of Target Pest insects: These are applicable for may insects e.g, sucking insect pests of cotton. Bollworms, squash bug, aphids etc.

Examples:

Acephate (Orthene), Azinphos methly (Gusathion.M), Cartap (Padan), Diazinon (Basudin), Dicrotophos (Bidrin, Carbicron), Dichlorvos (Nogos, DDVP, Vapona), Fenthion (Lebaycid), fenitrothion (Sumithion), Formothion (Anthio), Malathionn, Mevinphos (Phosdrin), MICP (Mipcin), parathion Methyl (Folidol M), Phosphamidon (dimecron), Phorate

Methomedophos
Profenofos

neo-Neonicotinoides
Biopesticides
Microbial insecticides   Chloropyrifos

(Thimet), Primiphos methyl (Actellic), Triazophos (hostathion, Trichlorfon (Dipterex), Dimethoate (Cygon, perfekthion, Rogor), Disulfoton (Disyston) Monocroptophos (Azodrin, Nuvacron), Oxydemeton Methyl (Metasystox,). Phosmet (Imidan

c) Carbamates

Salient Characteristics: It is the new group of synthetic insecticides.

Mode of Action: These are similar to the organophosphates in properties and action.

Antidotes: Same as in chlorinated hydrocarbons.

Range of Target Pest Insects: These are more effective than previous, for insect pests of different crops.

Examples: Carbofuran, Carbosulfan

Aldicarb (Temik), Carbaryl (Sevin), Carbaryl plus Gamma BHC (Sevidol), Carbofuran (Furadan) Methomyl (Lannate) etc.

d) Synthetic Pyrethroids

Salient Characteristics: These have low toxicity to man and other vertebrate animals.

Mode of Action: Same as in organophosphates.

Antidotes: Same as in Organochlorines.

Range of Target Pest Insects: These have a wide range of its effectiveness including insect pests of cotton, wheat and other field crops.

Examples:

Cypermethrin (Ripcord, Cymbush, Sherpa, Arrivo), Cyermethrin plus profenofos (Polytrin-C), Permethrin (Ambush) Decamethrin (Decis), Fenvalevate (Sumicidin), Nurelle. Danitol and Mavrik.

B. RODENTICIDES

These chemicals disturb the vital processes of rodents (rats, shrews, squirrels etc,) by chemical action.

Examples:

Brodifacoum (Klerat), Coumatralyl (Racumin), Sodium

INSECTICIDE APPLICATION EQUIPMENTS

The insecticide application equipments are divided into two categories:

A. Ground Application Equipments

These are the equipments with the help of which we apply the insecticide on gound by standing on ground.

B. Aerial Application Equipments

It consists of sprayers, dusters, dusters, granule applicators and soil applicators.

1. **Sprayers**: These are the machines by which the liquid insecticides are applied in the form of thin coating on the surface of objects. These are of following types:
   - i) Hand atomizers (e.g, lady hand sprayer)
   - ii) Knapsack sprayers
   - iii) Wheelbarrow sprayers
   - iv) Power sprayers
   - v) Air sprayers
   - vi) Hydraulic sprayers
2. **Dusters**: These are the machines which apply the powder insecticides in the form of thin coating on the surface of objects. These are of following types:
   - i) Hand operated dusters
     - a) Shaker type dusters
     - b) Crank or rortary dusters.
   - ii) Power operated dusters e.g., Viller's power duster.
3. **Granule Applicators:** These are the machines which scatter the granular insecticides in the field. These are of two types:
   - i) Hand operated granule applicators
   - ii) Power operated granule applicators
4. Soil Applicators: These are the machines which apply the insecticides into the soil e.g., soil injector.

PRACTICAL

QUANTITATIVE MEASUREMENTS OF PESTICIDES

SOME IMPORTANT TERMS

1. Formulation

The particular form of a pesticide in which it is manufactured and marketed is called its formulation. It is mixture of an active ingredient with one or more materials. Such as carrier or diluent. To make it save for storage, dilution and application.

Thiodan 35EC means formulation of Thiodan is 35 EC which shows 35% of active ingredient. Rest 65% is carrier or inert material which makes emulsifier with the poison.

Dusts, baits fumigants, aerosols and granules are usually applied at each strength purchased, while the emulsifiable concentrates, wettable powder and suspension concentration are diluted with water before use.

ABC 40 EC means an insecticide ABC with the formulation of 40% Em, Emulsifiable Concentrates,

ABC 40 WP means an insecticide ABC with the formulation of 40% Wettable Powder.

ABC 40 SC means kan insecticide ABC with the formulation of 40% Soluble Concentrates.

2. Concentration

Amount of active ingredient or active material in a given volume or weight after formulation of mixture. It is also measured in percentage.

3. Dose

It is the amount of actural poison in volume. Unit area present in the given amount of insecticides. It is measured in the unit of a.i. (active ingredient) or a.m.

(active material).

4. **Total Quantity of Poison (T.Q.P).**

It is the second dose which consists of the amount of insecticide including poison as well as carrier. It is measured in the units of volume (like ml, lbs, gallons etc.).

5. **Total Quantity of Spray Material**

It is the amount of total material to be applied in field including posion, carrier and water added to insecticide for spraying purposes. It is also measured in the units of vlume.

EXAMPLES

1. Calculate the quantity of given formulation of Aldrin 20% active material and total quantity of spray material to be used in an acre field when the recommended dose is 0.5 lbs active material/acres to be applied at a concentration of 0.01% Calculate the quantity of poison.

Data

Formulation of Aldrin	=	20%
T.Q.S.M.	=	?
Dose	=	0.5 lbs a.m
Concentration	=	0.1%
T.Q.P	=	?

Solution

According to formula

T.Q.P. = (Dose / Formulation) × 100

T.Q.P. = (0.5 / 20) x 100

= 2.5 lbs.

2. Calculate the does of the ABC 2.5 WP poison against the insect pests of vegetables. The recommended dose is 200 ml active material at a concentration of 0.07%.

Data

Formulation	=	2.5%
Dose	=	200 ml a.m.

Concentration = 0.07%
T.Q.P. =?
T.Q.S.M. =?

Solution
According to formula;
T.Q.P. = (Dose / Formulation) x 100
T.Q.P = (200 / 2.5) x 100 = 8000 ml = liter.
T.Q.S.M. = (Dose / Concentration) x 100

= (200 / 0.07) x 100 = 285727 ml
= 285.717 liter.

E.P.M. Is the educational project of Mustafavi students movement

Modes of Action and Target Pests for Insecticides

- Insecticides are chemicals that kill insects … they may also kill other organisms at commonly used rates.
- Their "safe" but effective use depends on
  - (1) target insects' greater exposure than nontarget organisms;
  - (2) their breakdown over time;
  - (3) differences in toxicity of the active ingredient to different species;
  - (4) differences in rates of detoxification among target and nontarget organisms.
- Many insecticides are registered for use in the U.S., and they differ widely in effectiveness to different insects, nontarget toxicity, and persistence

Overview

- Insecticides … by chemical structure and modes of action
- Why structures and modes of action matter
- What’s effective against what?
- Alternative insecticides
- Available references

Chemical names, common names, and trade names …

- Chemical name: 2-Methyl-3-phenylphenyl)methyl (1S,3S)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate
- Common name: bifenthrin
- Trade name (original) Capture
- Generic products (and "re-names"): Talstar, Brigade, Bifenthrin, Discipline, Sniper, Ortho Home Defense Max, Scotts LawnPro Step 3, and others.

Insecticides

- Organochlorines
  - DDT and others long-since banned) plus endosulfan (Thiodan, Endosulfan, Thionex) (Group 2A)
- Organophosphates (Group 1B)
  - clorethoxyfos (Fortress)
  - chlorpyrifos (Lorsban, Dursban, many more)
  - diazinon (Diazinon)
  - dimethoate (Cygon, Dimate, Dimethoate)
  - malathion
  - methyl parathion (Penncap-M)
  - terbufos (Counter)
- Carbamates (Group 1A)
  - acephate (Orthene)
  - carbaryl (Sevin)
  - carbofuran (Furadan)
  - methomyl (Lannate)
  - thiodicarb (Larvin)

Organochlorines were the first synthetic organic insecticides. Many were very persistent in the environmnent. Almost none are currently labeled for use in the US. Organophosphates and carbamates were developed in the 1950s through 1980s … they are less persistent, but several were more acutely toxic to mammals, posing greater risks to applicators.

Insecticides

Pyrethroids came to market primarily in the 1980s and 1990s. Their mode of action is similar to that of DDT, but they are much less persistent and effective at greatly lower doses.

- Pyrethroids (Group 3)
  - bifenthrin (Capture, Brigade, Bifenthrin, Bifenture, Discipline, Fanfare, Sniper, Tundra, more)
  - cyfluthrin (Baythroid, Renounce, Tombstone, more)
  - cypermethrin (Ammo)
  - esfenvalerate (Asana, Adjourn)
  - fenpropathrin (Danitol)
  - lambda-cyhalothrin (Warrior, Silencer, more) (related, gamma cyhalothrin = Pro-axis)
  - permethrin (Ambush, Pounce, Arctic, Permethrin, Perm-UP, and more)
  - tefluthrin (Force)
  - zeta-cypermethrin (Mustang Max)

Neonics were first marketed in the late 1980s, and many new products came to market during the last 20 years.

Insecticides

- Neonicotinoids (Group 4A)
  - acetamiprid (Assail)
  - clothianidin (Poncho, Belay)
  - imidacloprid (Admire, Provado, Couraze, Imida, Macho, Malice, Montana, Nuprid, Torrent, Widow, more)
  - dinotefuran (Venom)
  - thiamethoxam (Actara, Platinum, Cruiser)
- Spinosyns (Group 5)
  - spinosad (Tracer, Success, Entrust)
  - spinetoram (Radiant)

Additional insecticide structures

- Avermectins and similar compounds (Group 6)
  - abamectin (Agri-Mek, Abba, Epi-Mek, Zoro)
  - emamectin benzoate (Proclaim)
- Juvenile hormone analogs (Group 7)
  - pyriproxyfen (Esteem)
- Benzoylureas (Group 15)
  - Diflubenzuron (Dimilin)
  - Novaluron (Rimon)
- Indoxacarb (Group 22)
  - Indoxacarb (Avaunt)
- Tetronic acid derivatives (Group 23)
  - Spirotetramat (Movento)
- Anthranilic diamides (Group 28)
  - chlorantraniliprole (Altacor, Coragen)
  - flubendiamide (Belt/Synapse)
- Diacyl hydrazines (Group 18)
  - methoxyfenozide (Intrepid)
  - tebufenozide (Confirm)
  - azadirachtin (neem)
- Phenylpyrazoles (Group 2)
  - fipronil (Regent)

Many other chemical structures have been identified as insecticidal and “satisfactorily” low in nontarget toxicity, persistence, etc.

Miticides

Other types of chemical structures are used as miticides … a pesticide that is widely effective against a range of insects usually is NOT effective against mites.

- Organochlorines
  - dicofol (Kelthane, Dicofol) (Group un)
- Avermectins (Group 6)
  - abamectin (Agri-Mek, Abba, Epi-Mek, Zoro)
- Tetronic acid derivatives (Group 23)
  - spiromesifen (Oberon)
- Neuronal inhibitors
  - bifenazate (Acramite) (Group 25)

Understanding insecticides

- ***An Introduction to Insecticides***, by George Ware, at
  - http://ipmworld.umn.edu/ware-intro-insecticides
- ***Insecticides: Chemistries and Characteristics***, by Jeffrey Bloomquist, at
  - http://ipmworld.umn.edu/bloomquist-insecticides

Insecticide Modes of Action

- IRAC Mode of Action Classification
  - Insecticide Resistance Action Committee
  - 28+ modes of action and insecticide groups

http://www.irac-online.org/documents/moa-classification/?ext=pdf

http://pested.okstate.edu/pdf/insecticide%20moa.pdf

http://www.irac-online.org/content/uploads/IRAC-general-MoA-Poster-v2-2_Mar2012.pdf

Insecticide Modes of Action

- Group 1: **Acetylcholinesterase inhibitors**
  - 1A: carbamates: Sevin, Furadan, Orthene, Lannate, Vydate
  - 1B: organophosphates: Counter, Fortress, Lorsban, Diazinon, Dimethoate, Malathion, Penncap-M
- Group 2: GABA-gated chloride channel antagonists
  - 2A: Endosulfan (an organochlorine); 2B: Regent
- Group 3: **Sodium channel modulators**
  - (DDT, methoxychlor) all pyrethroids, and natural pyrethrins
- Group 4: **Nicotinic acetylcholine receptor promoters and antagonists (acetylcholine mimics)**
  - 4A: neonicotinoids: Assail, Admire/Provado, Actara/Platinum, Poncho, Cruiser, Venom

Insecticide Modes of Action

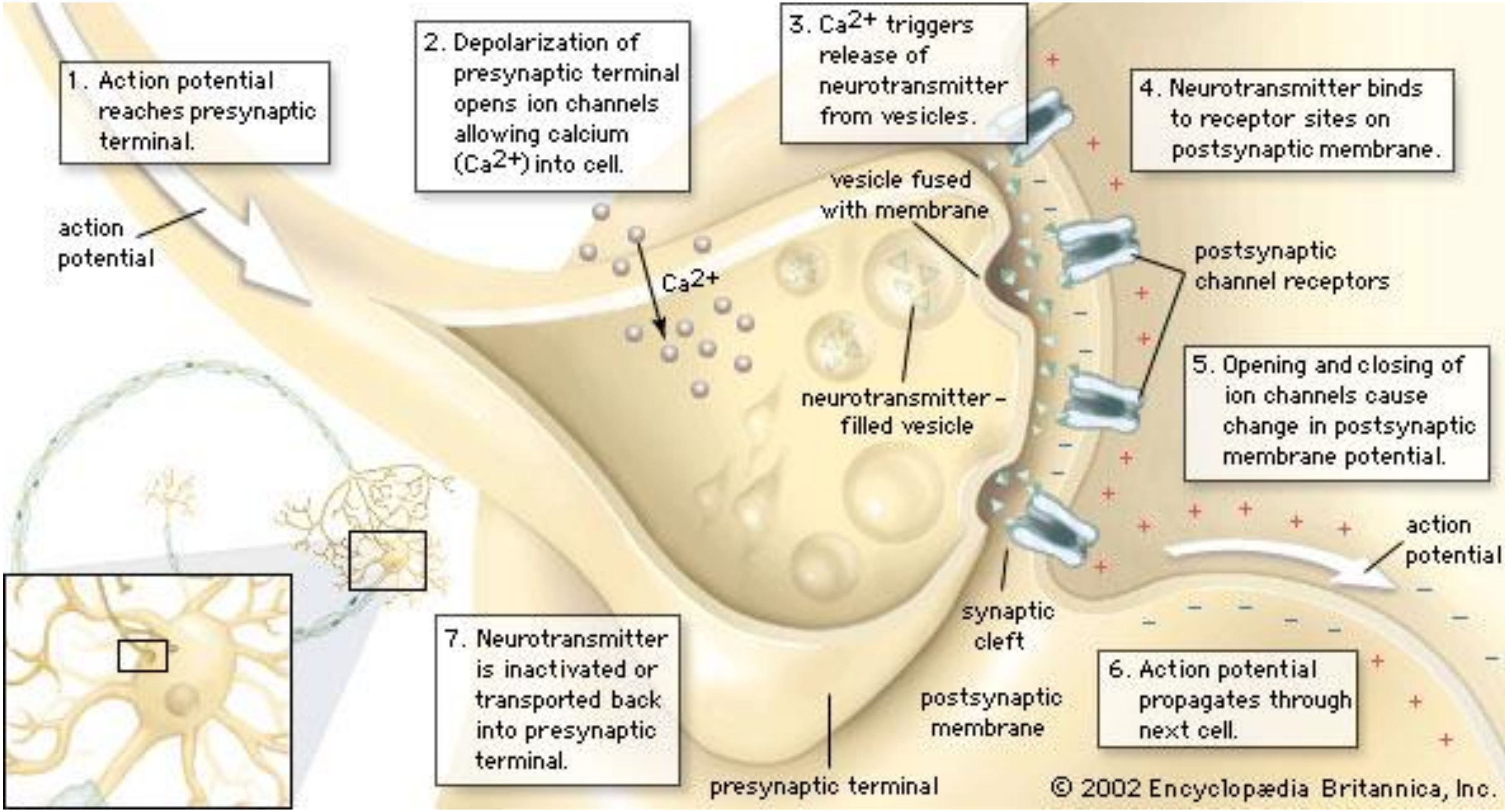
- Group 5: Nicotinic acetylcholine receptor promoters (different from Group 4)
  - spinosad (SpinTor, Entrust)
  - spinetoram (Delegate, Radiant)
- Group 6: Chloride channel activators
  - abamectin (Agri-Mek)
  - emamectin benzoate (Proclaim)
- Group 7: Juvenile hormone mimics
  - pyriproxyfen (Esteem); others include hydroprene, kinoprene, methoprene, and fenoxycarb)
- Group 11: Microbial disruptors of insect midgut membranes:
  - *Bacillus thuringiensis* (with multiple subspecies) (and multiple trade names)
  - These include the toxins that make up GMO Bt corn and cotton
- Group 15: Chitin inhibitors
  - Diflubenzuron (Dimilin)
  - novaluron (Rimon)
- Group 18: Ecdysone (molting hormone) promoters / mimics & molting disruptors
  - tebufenozide (Confirm), methoxyfenozide (Intrepid)

Insecticide Modes of Action

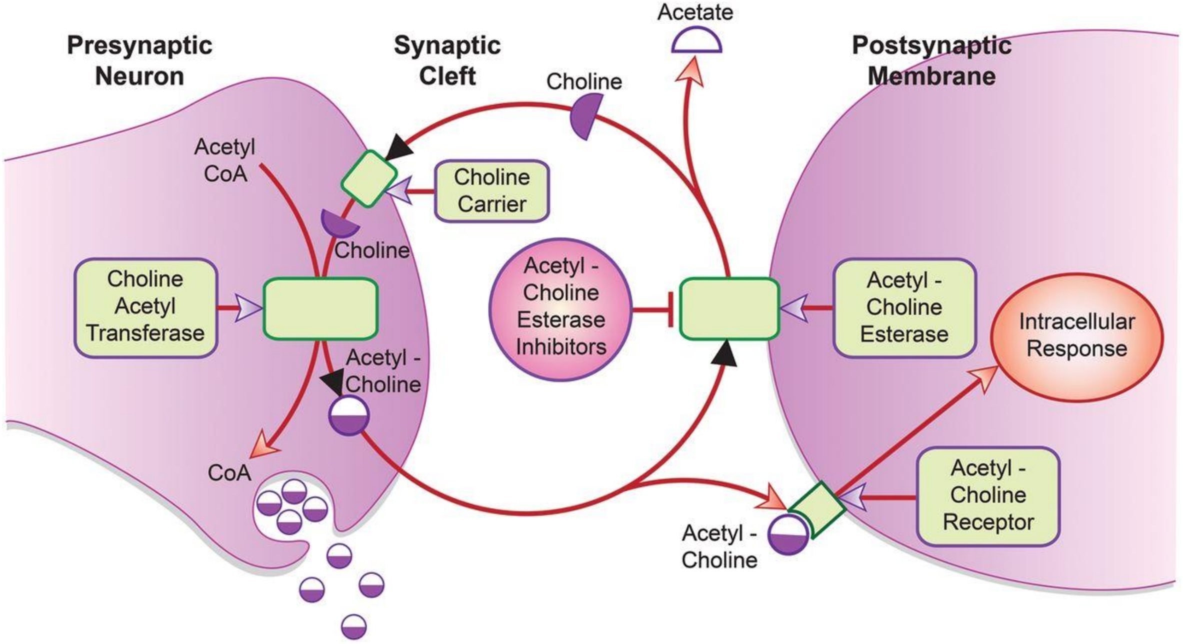
- Group 21: Mitochondrial electron transport inhibitors
  - rotenone
- Group 22: Voltage-dependent sodium channel blockers
  - indoxacarb (Avaunt)
- Group 23: Lipid synthesis inhibitors
  - spiromesifen (Oberon)
  - Spirotetramat (Movento)
- Group 28: Ryanodine receptor modulators
  - chlorantraniliprole (Altacor, Coragen)
  - flubendiamide (Belt/Synapse)
- Group un: Unknown mode of action
  - dicofol (Kelthane), [azadirachtin (neem)]

It is not necessary to know/remember any of these … do know that there are modes of action and registered insecticides that work differently than the primary groups described above.

Nerve impulse transmission … axonic and synaptic. (Most insecticides are nerve poisons.)

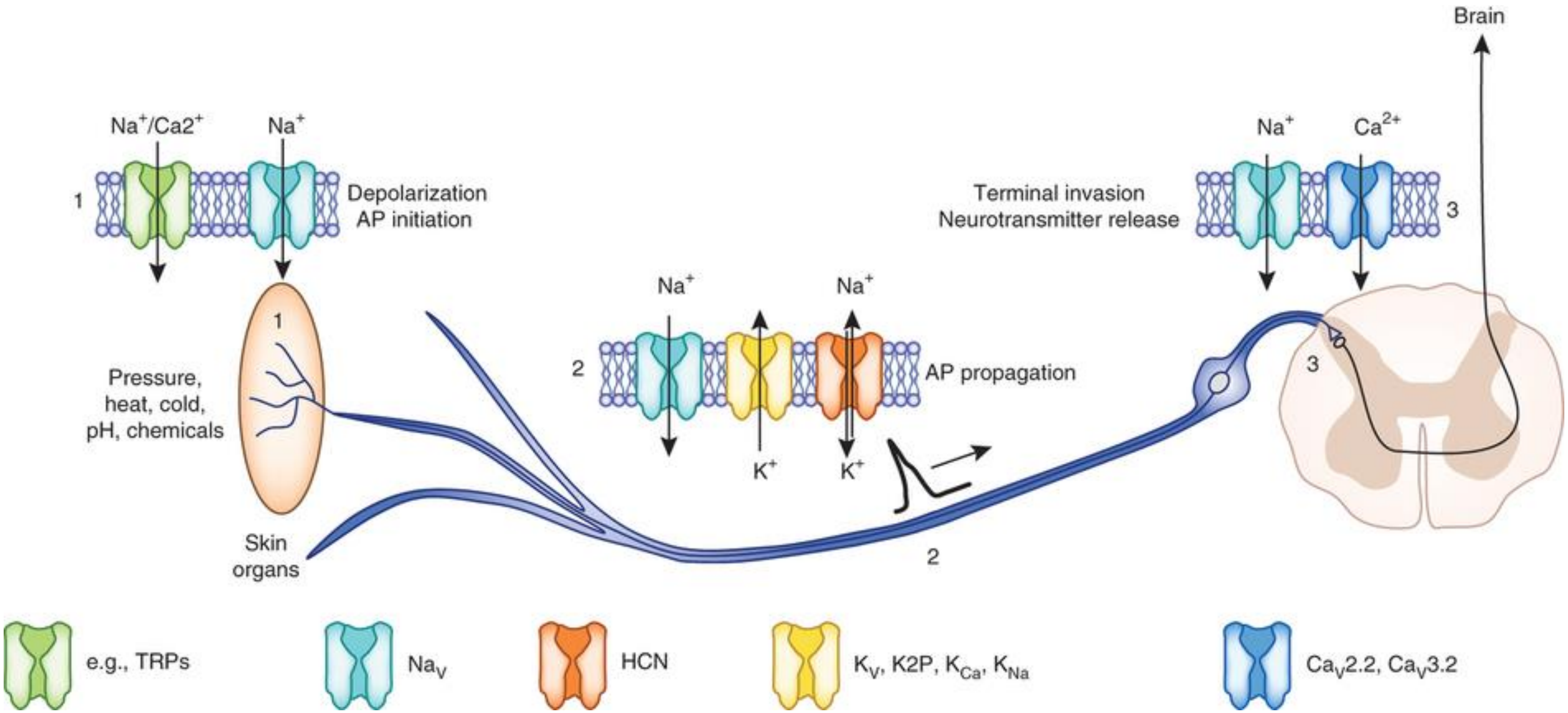


Group 1, acetylcholinesterase inhibitors



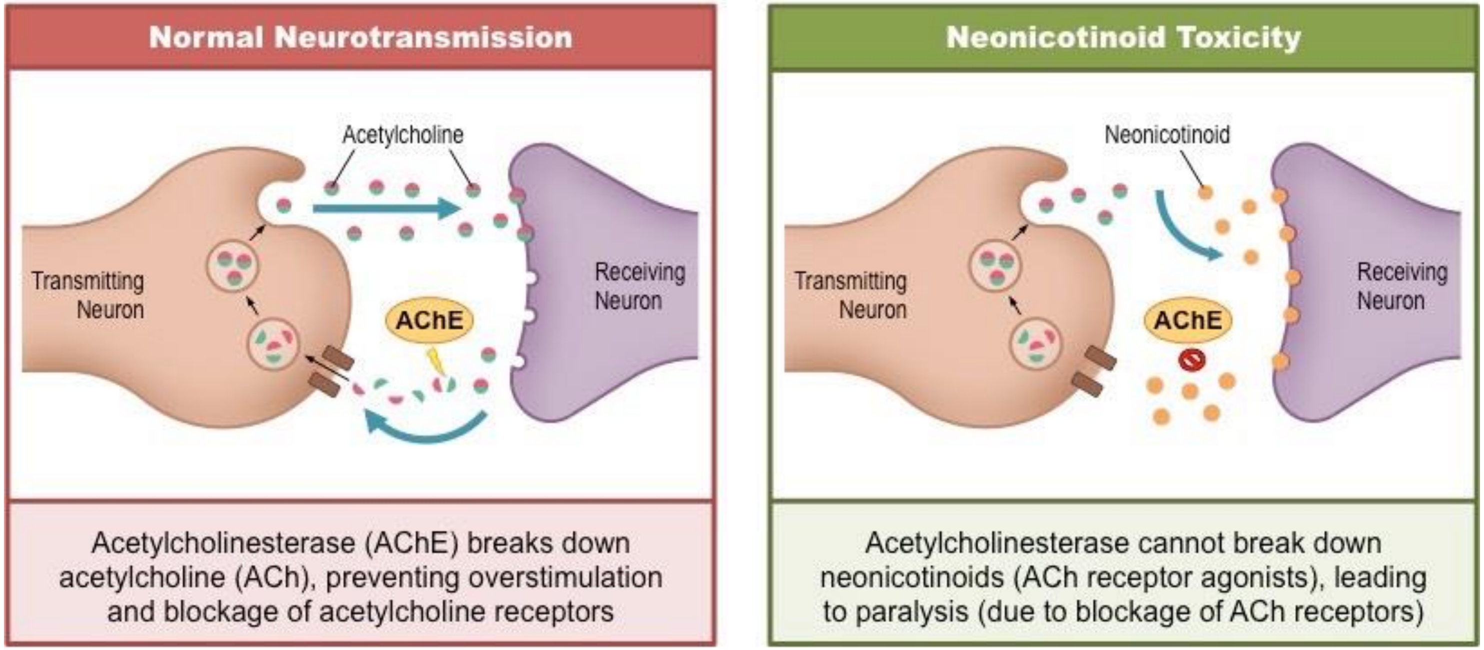
- When a nerve impulse reaches the end of an axon, it must be transmitted across a synapse to a receptor. Acetylcholine is one of the common neurotransmitters that does this. It is then broken down by acetylcholinesterase.
- Organophosphates and carbamates “tie up” acetylcholinesterase and prevent it from breaking down acetylcholine, causing repeated “firing” of the nerve receptor … poisoned insects often exhibit tremors because of this.

Group 3, sodium channel modulators (axonic poisons) DDT, pyrethroids, and natural pyrethrins



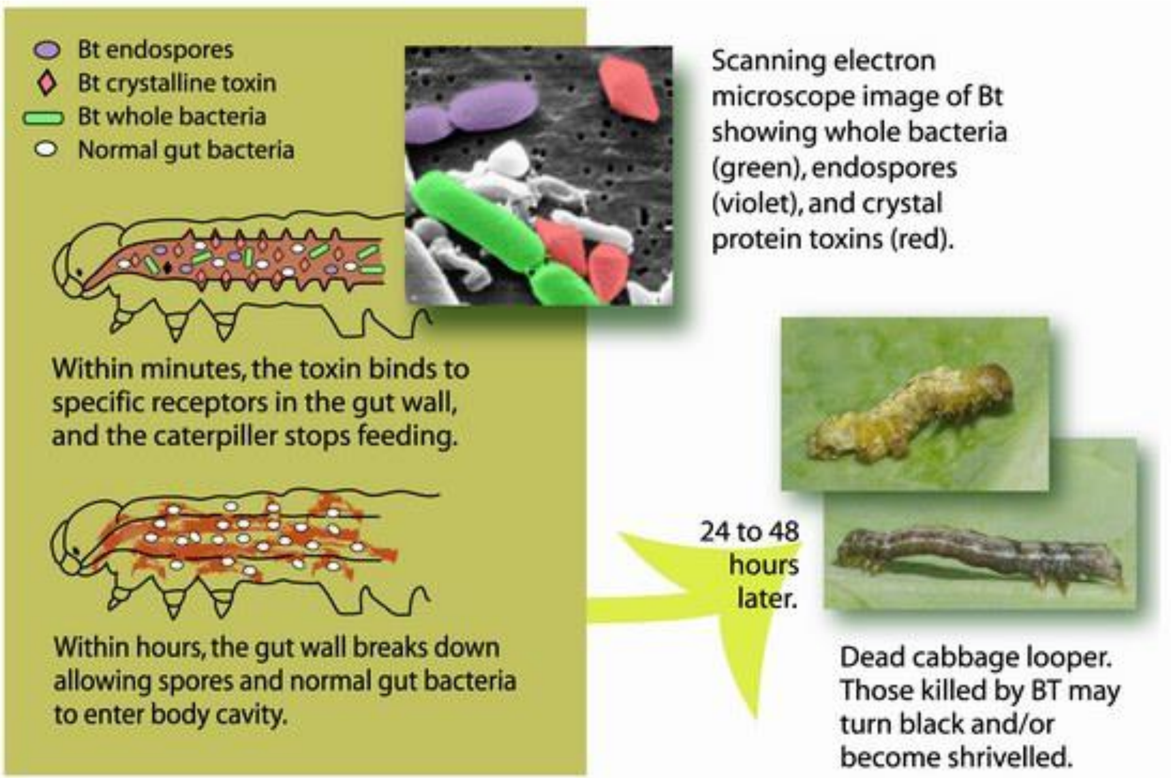
- Nerve impulse transmission along an axon depends on movement of sodium and potassium ions into and out of the axon.
- Sodium channel modulators (Group 3 mode of action) interfere with this by blocking sodium channels.

Group 4, acetylcholine mimics (neonicotinoids)



- When a nerve impulse reaches the end of an axon, it must be transmitted across a synapse to a receptor. Acetylcholine is the neurotransmitter that does this. It is then broken down by acetylcholinesterase.
- Neonicotinoids mimic acetylcholine but are not broken down by acetylcholinesterase. They attach to acetylcholine receptors in the receiving neuron or muscle cell, causing repeated “firing” of the receptor or blockage of the receptor.

Group 11: Microbial disruptors of insect midgut membranes



- *Bacillus thuringiensis* is a bacterium, and it is used in sprayable insecticides and as a source of genes for transgenic crops. Its toxins do not act as nerve poisons. Instead it causes the gut wall to break down, and gut bacteria enter the insect's body cavity. In Bt crops, only the crystalline toxin is produced, not whole bacteria or spores. Different strains and different crystalline toxins are specific to certain insect groups. None have been shown to be toxic to vertebrate animals.

So why are chemical structures and modes of action important?

- Insecticides work if (1) they remain intact within an insect to reach a target site and (2) the target site is susceptible to their attachment and interference.
- Differences among species in natural susceptibility to an insecticide and evolution of resistance in populations of a given species result primarily from (1) increased metabolism or breakdown of insecticide molecules – related to their structure – and from (2) receptor sites that are not susceptible to insecticide attachment and interference.
- Repeated use of insecticides within the same structural family or mode of action group result in more rapid development of resistance
- Rotating among structural families and modes of action – assuming there are alternatives that are effective – is recommended to maximize long-term effectiveness of insecticides and miticides.

So what is the range of target pests for the different groups / modes of action?

- Group 1A, carbamates, acetylcholinesterase inhibitors
  - Furadan: few remaining labeled uses.
  - Orthene: effective against aphids and certain Leps.
  - Sevin: effective against many beetles; not great against most Leps; kills natural enemies of aphids and mites and triggers their outbreaks in susceptible crops.
  - Larvin and Lannate … some Lep activity (generally not as effective as pyrethroids), some aphid activity. Lannate's residual activity is very short.

Of these, only Sevin (carbaryl) is used widely. It remains a common garden and small farm insecticide.

- Group 1B, organophosphates, acetylcholinesterase inhibitors
  - Counter and Fortress: soil-applied for corn rootworm control
  - Lorsban: Soil and seed treatment uses against root and seed maggots, corn rootworm larvae, wireworms, and white grubs; foliar uses against miscellaneous, Leps, beetles, aphids
  - Diazinon: Seed treatment uses against seed maggots, wireworms, white grubs … homeowner formulations have been “un-registered”
  - Dimethoate: Moderately effective against aphids and leafhoppers, some miticidal action.
  - Malathion: Most often used against aphids

- Group 3, DDT, pyrethroids and natural pyrethrins; sodium channel modulators
  - Pyrethroid products include permethrin, Asana, Capture/Brigade/Talstar, Baythroid, Danitol, Force, Warrior/Proaxis, Mustang Max. OMRI-approved Natural pyrethrins include Pyganic, Pyrenone, etc.
  - In general, pyrethroids are good against a range Leps and beetles, as well as grasshoppers, stink bugs, plant bugs, and some thrips.
  - Most compounds in this group are ineffective against most aphids and mites and trigger more severe infestations of these pests by killing their natural enemies.
  - Force is labeled for soil use against corn rootworm larvae.
  - Natural pyrethrins are effective against several beetles but break down **very** rapidly. Using synergists (not OMRI-approved) and spraying at night increases effectiveness.

- Group 4A, neonicotinoids; nicotinic acetylcholine receptor promoters and antagonists
  - Products that are active primarily against aphids, leafhoppers, etc. (plus systemically against corn flea beetle and cucumber beetles) include Gaucho, Cruiser, and Poncho, Admire, Provado, Venom, etc. Assail is used against a broader range of orchard pests.
- Group 5, spinosyns, nicotinic acetylcholine receptor promoters that differ from group 4A
  - Tracer/Success/SpinTor, Entrust, Delegate and Radiant … effective primarily against Lep larvae

Effective primarily against Lepidopteran larvae…

- Group 6: Chloride channel activators
  - emamectin benzoate (Proclaim)
- Group 11: Microbial disruptors of insect midgut membranes:
  - *Bacillus thuringiensis* (with multiple subspecies) (and multiple trade names) (Transgenic corn used for corn rootworm control contains toxins from unique Bt isolates that effective against rootworms)
- Group 15: Chitin inhibitors
  - Novaluron (Rimon) (also effective against Colorado potato beetle)
- Group 18: Ecdysone (molting hormone) promoters / mimics & molting disruptors
  - 18A: tebufenozide (Confirm), methoxyfenozide (Intrepid)
- Group 22: Voltage-dependent sodium channel blockers
  - indoxacarb (Avaunt)
- Group 28: Ryanodine receptor modulators
  - chlorantraniliprole (Altacor/Coragen)
  - flubendiamide (Belt/Synapse)

Specific miticides …

- Group 6: Chloride channel activators
  - abamectin (Agri-Mek)
- Group 23: Lipid synthesis inhibitors
  - spiromesifen (Oberon) (also effective against whiteflies)
- Group 25: Neuronal inhibitors (unknown mode of action)
  - bifenazate (Acramite)
- Group un: Unknown mode of action
  - dicofol (Kelthane)

Pyrethroids that have some miticidal action include Capture and Danitol, but these are not usually the best choices for mite control.

Resistance Management

- Simple rules:
  - Do not use insecticides in the same MOA group repeatedly in the same crop/field/season
  - Rotate among MOAs at least across generations
  - Where an insect pest is not controlled by application(s) of an insecticide in a given MOA group, do NOT switch to another insecticide within the same MOA group
  - If the target pest migrates into the region from an area with known resistance to a particular MOA, do not rely on an insecticide from that MOA group for control at your site

Alternative insecticides

- Benefits:
  - Less persistent in the environment
  - Most are less toxic to nontarget organisms
    - More specific modes of action
- Examples include
  - Botanical insecticides
    - Synergists may be beneficial
  - Soaps and oils
  - Microbial insecticides
  - Growth regulators
  - Pheromones

Botanicals

- Prepared from plants
  - Crude dusts or powders (pyrethrum)
  - Extracts or resins (pyrethrins, neem seed oils)
  - Isolated, refined components (d-limonene, linalool)

  Always -- minimal alteration of naturally occurring compounds
- Strengths and weaknesses
  - Rapid action
  - Rapid degradation
  - Low toxicity to mammals (in general, not always)
  - Minimal technology required for preparation

Older botanicals and their origins

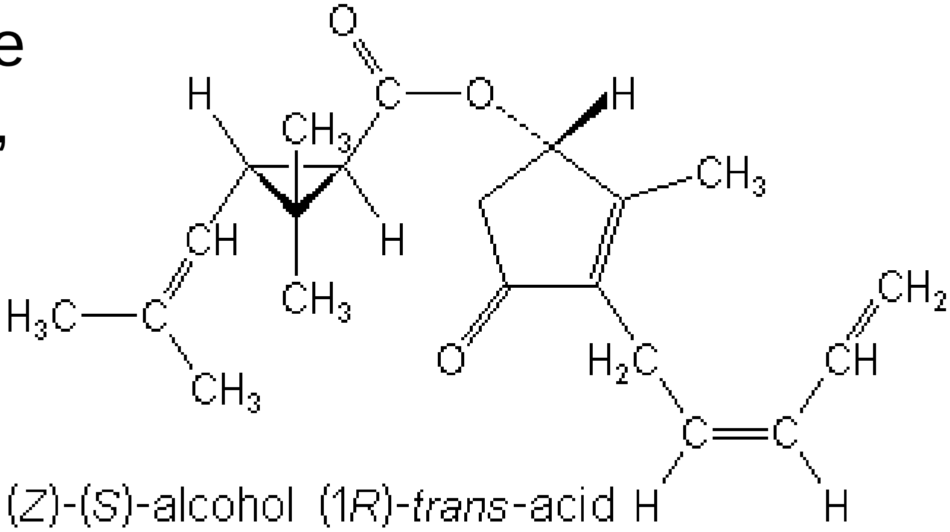
- Nicotine – *Nicotiana* spp.
- Pyrethrins – *Chrysanthemum cinerariaefolium*
- Rotenone – *Derris, Lonchocarpus* and other legumes
- ~~Sabadilla – *Schoenocaulon officinale* (a tropical lily)~~
  - ~~Similar veratrine alkaloids in white hellebore, *Veratrum album*~~
- ~~Ryania – *Ryania speciosa*~~
- Others
  - Soaps, horticultural oils, essential oils, diatomaceous earth

Modes of action, toxicity, and uses of "old" organic insecticides derived from plants

Nicotine	Acetylcholine mimic	Toxicity: Mod-High (dermal and oral)	Greenhouse / Homoptera
Pyrethrins	Na+ / K- ion trans in axons	Toxicity: Low	Animals, humans, organic crops
Rotenone	Electron transfer in cellular respiration	Toxicity: Moderate (implicated in Parkinson's disease)	Beetles in organic crops
~~**Sabadilla**~~	~~Nerve membrane function~~	~~Toxicity: Low (but mucous membrane irritant)~~	~~Squash bug~~
~~**Ryania**~~	~~Calcium channel disruptors (axonic)~~	~~Toxicity: Low~~	~~Beetles, caterpillars in organic crops~~

Regulatory and marketing status in the United States

- Only pyrethrins are widely available with labels covering a range of crop, animal, indoor, and human uses



More recent botanicals (and similar ingredients) and their origins

- Linalool and d-limonene – citrus oil derivatives
- Neem – *Azadirachta* spp. and *Melia* spp.
- Garlic oils
- Hot pepper oils
- Microbials
  - Toxins from *Bacillus thuringiensis* and other soil micro-organisms (avermectins, spinosyns)

Azadirachta windbreak.
(E. Fernandez, http://www.css.cornell.edu/ecf3/Web/new/AF/arid.html)

Modes of action, toxicity, and uses

Citrus derivatives	Nerve cell stimulants	Toxicity: Low	On pets, indoor plants
Neem	Multiple actions, ecdysone agonist	Toxicity: Very Low (medicinal uses)	Many crop pests
Garlic oil	?	Toxicity: Low	Many labeled uses, limited positive data on effectiveness
Hot pepper extracts	?	Toxicity: Low	
Microbials	Multiple	Toxicity:Low	Many for *Bt* and other products

Effectiveness of currently available botanicals

- Older botanicals
  - Generally well understood based on field trials and small plot trials from 1920s through 1950s
- More recent products
  - More unsupported label claims

Insecticidal soaps

- Salts of fatty acids
- Kill insects by disrupting membranes (including tracheal linings)
- Work only against those insects that are wetted by the spray ... no residual action
- Effective against aphids, whiteflies, mites, and other soft-bodied, not-too-mobile pests
- Best-known brand names are Safer's and M-Pede

Oils … may be vegetable oils or highly refined petroleum oils

- Dormant oils for fruit and landscape trees
  - Against overwintering aphid eggs, mite eggs, scales
- Stylet oils
  - reduce virus transmission, may suppress powdery mildew
- Summer oils
  - Against mites, aphids, other soft-bodied pests
- Coverage is essential (upper and lower leaf surfaces); oils kill by suffocating pests that are sprayed directly

Absorbents & abrasives

- Clays, diatomaceous earth, silica aerogels
  - disrupt the insect's cuticle and kill by dehydration
- Kaolin clay ... "Surround"

Microbials … will cover these under biological control

- Bacteria
- Viruses
- Fungi
- Microsporidia (Protozoans)
- Nematodes

Insect growth regulators

- Because they are enclosed in an exoskeleton, insects must "shed their skins", or molt, to grow larger. The molting process in immatures and the transformation from larva to pupa to adult is regulated by hormones.
- One is **ecdysone (molting hormone)** secreted by the prothoracic gland; it stimulates shedding of the cuticle.
- Another is **juvenile hormone (JH)**. JH is secreted from the corpora allata; it suppresses adult characteristics. As growth during each stage triggers secretion of ecdysone, if juvenile hormone is present, the cuticle is shed and replaced, and the insect reaches its next juvenile stage.
- As the immature insect grows and eventually discontinues production of juvenile hormone, secretion of ecdysone in the absence of JH triggers pupation and subsequent development of adult form.
- Synthetic hormones that mimic JH and ecdysone have been developed for use as insecticides that disrupt insect development and cause death.

- Juvenile hormone mimics
  - methoprene
  - hydroprene
  - kinoprene
  - pyriproxyfen
  - diflubenzuron (Dimilin)
  - buprofezin
  - hexaflumuron (Sentricon termite control)
  - novaluron (Rimon)
- Ecdysone agonists (= promoters) Existing compounds target Lepidoptera
  - tebufenozide (Confirm)
  - methoxyfenozide (Intrepid)
  - halofenozide (Mach 2, against cutworms in turf)

Useful References

- Pest Management in Wisconsin Field Crops
  - https://learningstore.uwex.edu/Pest-Management-in-Wisconsin-Field-Crops2016-P155.aspx
- Pest Management in Indiana Field Crops
  - https://mdc.itap.purdue.edu/item.asp?Item_Number=ID-179
- Midwest Vegetable Production Guide
  - http://btny.purdue.edu/Pubs/ID/ID-56/
- Midwest Fruit Pest Management Guide
  - https://ag.purdue.edu/hla/Hort/Documents/ID-465.pdf

What you should really know … what does all this nerve impulse transmission and mechanism of poisoning really mean?

- Explain axonic inhibition.
- Explain ACH inhibition.
- Explain AC mimicry.
- How does Bt kill insects?
- For the organophosphates, carbamates, pyrethroids, neonicotinoids, and Bt toxins … how do they kill insects (MOA) and what insects – in general – do they work effectively against?

HOW INSECTICIDES ARE USED

Pesticide Sale and Use

- Pesticides … include insecticides, herbicides, fungicides, bactericides, rodenticides … all are regulated by the US EPA
- General-use pesticides are sold to homeowners, residents, farmers, and others … with no requirement to produce evidence of training
- Restricted-use pesticides are sold only to licensed applicators and may be used only by or under the supervision of a licensed applicator (commercial or private)

Legal status of pesticide labels

- Crops, rates, restrictions, pre-harvest intervals, re-entry intervals, other safety precautions, etc. stated on a pesticide label are legally binding
- Rarely "policed" for homeowners, gardeners, etc., but …
- Violations by farmers and custom applicators may result in fines, imprisonment, and business-destroying lawsuits
- "The label is the law."

Pesticide Applicator Licensing (in IL)

- Commercial Applications … people who apply pesticides for hire, by ground or by air
  - Commercial Applicator (boss and maybe also the actual worker)
    - Needs to pass an exam in one or more of various categories, including field crops, rights-of-way, turf, aquatic, grain facilities, fruits and vegetables, etc.
  - Commercial Operator .. the person who applies the pesticides
    - Needs to pass a “General Standards” test and work for a licensed applicator
- Private applicator … pretty much means farmer applicator

Illinois Pesticide Safety Education Program

- See Illinois PSEP … http://web.extension.illinois.edu/psep/
- Training provided by University of Illinois Extension
- Testing administered by the Illinois Department of Agriculture

Drift

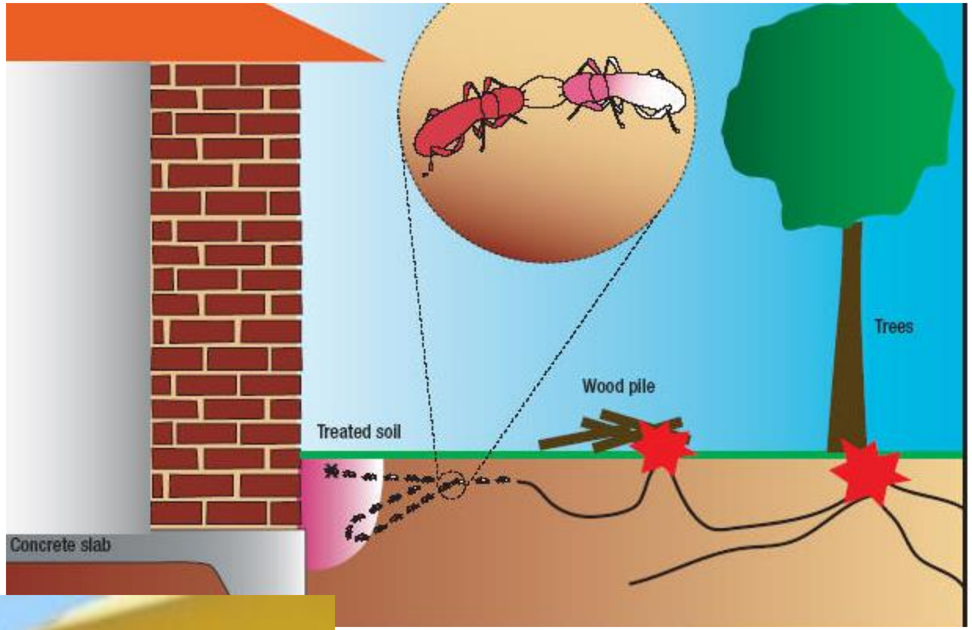
- Off-target movement of pesticide applications via drift – spray particles or vapors – is one of the most important problems associated with pesticide misuse
- DriftWatch – FieldWatch … http://www.fieldwatch.com/
- Penalties (fines) for violations do not reimburse victims for losses associated with misuse … usually drift. Suits and court decisions (or settlements) do this.
  - Many custom applicators routinely defy label restrictions on field crop herbicide applications in spring herbicide applications made when winds exceed label-specified limits
  - Many applicators / growers defy label restrictions by spraying insecticides on fruits, vegetables, field corn, and soybeans when crops (or weeds in orchards) are in bloom … in conflict with label restrictions.

I. Soil-applied & seed-treatment insecticides

- Soil-applied for residual control:
  - Applied to kill insects in treated soil at time of application and for a period up to several weeks later; incorporated (at least lightly) or injected to mix with soil
    - Applied at planting for control of rootworms, cutworms, wireworms, grubs, seed and root maggots, etc. in field crops, vegetables, small fruits, gardens
    - Applied as soil treatments for termite control around houses, other buildings
    - Examples:
      - Organophosphates: Lorsban/Dursban, Counter, Diazinon
      - Pyrethroids: Force, Fortress
    - Band applications instead of broadcast applications are most common in crops

I. Soil-applied & seed-treatment insecticides

- Soil-applied residual insecticides
  - Typically have (or should have) half-lives of (very roughly) 30 to 90 days
  - Typically are low to very low in water solubility (so that they do not leach out of the treatment zone in spring rainfall)
  - Are not bound too tightly to soil particles as to be unavailable in contact with insects
  - Historic problems have included too-great persistence (aldrin, dieldrin, heptachlor, chlordane, and other organochlorines) and too-great solubility and too little persistence (enhanced degradation of carbofuran / Furadan)


Treated soil
Wood pile
Trees
Concrete slab


SMARTCHOICE

I. Soil-applied & seed-treatment insecticides

- Seed-applied residual insecticides
  - Insecticides applied to seed at seed company facility or as a planter-box mixture
  - Kill insects that feed directly on seeds and below-ground portions of seedlings
  - Common seed protectants have included diazinon, Lorsban, lindane, and permethrin
  - Targets: seedcorn maggot, other seed and root maggots, wireworms, white grubs, seedcorn beetles, and symphylans
  - IF effective, seed treatments are appealing because they use a lot less insecticide than band or broadcast applications


LP800

I. Soil-applied & seed-treatment insecticides

- Soil-applied for systemic uptake
  - Applied at planting or transplanting or as a side-dress
  - Historically in IL: Furadan and Thimet in corn, cucurbits, and/or potatoes for control of flea beetles, cucumber beetles, Colorado potato beetle, or aphids feeding on foliage
  - Elsewhere: Temik and Di-Syston in potatoes, (citrus), and wheat … problems with leaching into groundwater
  - Currently: Neonicotinoids such as Admire (imidacloprid) and Platinum (thiamethoxam) in similar crops against similar pests and in urban use for tree and shrub insect control
  - Control usually begins a few days after application and persists 2 to 4 weeks; somewhat dependent on precipitation; neonicotinoids used around trees and shrubs may remain active for a year or more

I. Soil-applied & seed-treatment insecticides

- Seed-applied for systemic uptake
  - Old O-Ps and carbamates that are systemic were not used as seed treatments because they were phytotoxic (poisonous to the seeds)
  - Current systemic seed treatments are sold under the trade names Cruiser, Gaucho, Poncho, and FarMore – all are neoniconitoids
    - On field crops, vegetables, and some ornamental plants
    - Targets include bean leaf beetle, corn flea beetle, cucumber beetles, leafhoppers, and aphids for 1 – 3 weeks after seedling emergence
    - Greater persistence and off-target movement may pose risks to pollinators

II. Soil fumigants

- Primary fumigant against insects, pathogens, and weeds in the soil is methyl bromide
  - Applications usually made to raised beds tarped with plastic (for specialty crops)
  - Fumigant gas kills organisms present at the time of fumigation; dissipates in a few days
  - Cost = several hundred dollars to $2,000 per acre
  - In IL, crops are “plasticulture” strawberries; some peppers and tomatoes
  - Soil fumigation is rare in IL, but in FL, TX, and CA (and a few other areas), fumigating before planting high-value fruits and vegetables is common.
  - Phase-out of methyl bromide because of its ozone-depleting effects presents a major challenge



III. Foliar-applied insecticides

- Foliar "knock-down" insecticides (with little or no residual control intended)
  - Very few insecticides are applied with the intent that they NOT last at least a few days, but insecticides that kill only the insects that are present at the time of application or persist for only a short time include: dormant oils, soaps, pyrethrins, and malathion.
  - Most insecticides that break down rapidly have short **preharvest intervals** (as do some others that are very low in toxicity to consumers who eat treated produce); this can be especially important in fruits and vegetables where control may be necessary right up to the time the crop is picked.

III. Foliar-applied insecticides

- Foliar residual insecticides … Most applications of insecticides to plant foliage, by aerial or ground sprayers, are intended to last for a few to several days as residues on plant foliage
  - Most last from 3 to 10 days as effective residues
  - Treatments remain effective if sprays dry before rainfall of up to 1 inch
  - In general, most foliar residual sprays are effective as contact poisons … insects that crawl across treated surfaces are killed when insecticides are absorbed through the insect’s cuticle




IV. Animal insecticides

- Insecticides are applied directly to animals for control of lice, flies, grubs, ticks, mites, mosquitoes, etc.
  - Application methods for residual insecticides include:
    - Self-treatment devices such as back rubbers and dust bags
    - Controlled-release devices such as ear tags and flea collars
    - High-pressure sprays and mists
    - Pour-on on spot-on treatments that distribute in the coat
  - Application methods for systemic insecticides include:
    - Pour-ons and spot-ons
    - Feed additives
    - Injections


FRONTLINE®
3 Applicators
Kills fleas, flea eggs & ticks
Plus for dogs
• Fast-acting
• Kills ticks including those that may transmit Lyme disease
• Waterproof
For Dogs 89-132 lbs.
Lift Here To Open
ACTIVE INGREDIENTS
fipronil 9.8%
(S)- methoprene 8.8%
INERT INGREDIENTS 81.4%
TOTAL 100.0%
KEEP OUT OF REACH OF CHILDREN
CAUTION
Contains 3-0.136 fl oz (4.02 ml) applicators
MERIAL

V. Surface residual sprays

- Surfaces may be barn walls, bin walls, baseboards, wall voids, carpets, and more
  - Sprays applied to barn walls, wooden fences, etc. for fly control
  - Empty-bin sprays applied to grain bin walls for control of weevils, “bran bugs,” Indianmeal moth, etc.
  - Baseboard sprays and wall void treatments for cockroach control
  - Foundation and crawl-space sprays to control crickets, other “invaders”

VI. Aerosol space sprays

- Examples include "bombs" for flea control, mists for fly control in livestock buildings, aerosols in food processing plants – often pyrethrins or pyrethroids with short residual and low toxicity
- These are not fumigants … the active ingredient is dispersed in very small droplets of liquid that float through the air and deposit on exposed surfaces (including insects' cuticles). They do not move as a gas into closed spaces such as cabinets, drawers, etc.

VII. Space and Commodity Fumigants

- Examples: methyl bromide, phosphine, chloropicrin, sulfuryl fluoride, and even carbon dioxide.
- In agriculture, used to disinfest stored grains, flour, flour mills and other food processing plants, and ripe fruits and vegetables (Mediterranean fruit fly and similar pests).
- In general, fumigants are EXTREMELY toxic and require special training and equipment for safe handling

Fumigation chamber

Insecticides: Environmental Fate and Toxicity

An initial recommendation: Be fair and cautious in what analogies you use to represent low concentrations ...

Mackay, D. 1988. On low, very low, and negligible concentrations. ***Environmental Toxicology and Chemistry*** 7: 1-3.

- Mackay notes that many people like to portray low concentrations of chemicals as negligible by using analogies that minimize ...
  - 1 ppm = 1 inch in 16 miles
  - 1 ppb = 2 seconds in a lifetime

- ...but if a cubic meter of a solid or liquid contains 10^{28} molecules...
  - 1 part per quadrillion = 10 billion molecules
  - Mackay referred to this as "the enormity of tinyness."

Concentrations to small to matter?

- A volume of soil 1 acre in area by 1-inch deep contains 3,120 cubic yards of topsoil.
- At 1 ton per cubic yard, this volume weighs 6,240,000 lbs.
- At an application rate of 0.14 lb a.i. per acre, a pyrethroid applied in a band along the row in corn at planting for soil insect control is present at 0.022 ppm in the top inch of the field as a whole and ~0.10 ppm in the top inch of the treated band … and it <u>kills</u> insects for a few weeks.

- Mackay also offered some more understandable analogies ... analogies that can be visualized:

- In a cubic meter of space:
- 1 ppm = a sugar cube
- 1 ppb = a broken pencil lead
- 1 ppt = a grain of salt

- Mackay argued that the significance of low concentrations depends on how the chemicals in question act in an organism.

- "Disruptives"... low concentrations may be negligible
- "Distributives"... partitioning among media make magnify concentrations
- "Directives" ... if the chemical damages DNA for example, a single or a few molecules at the "right" place might be enough to cause injury

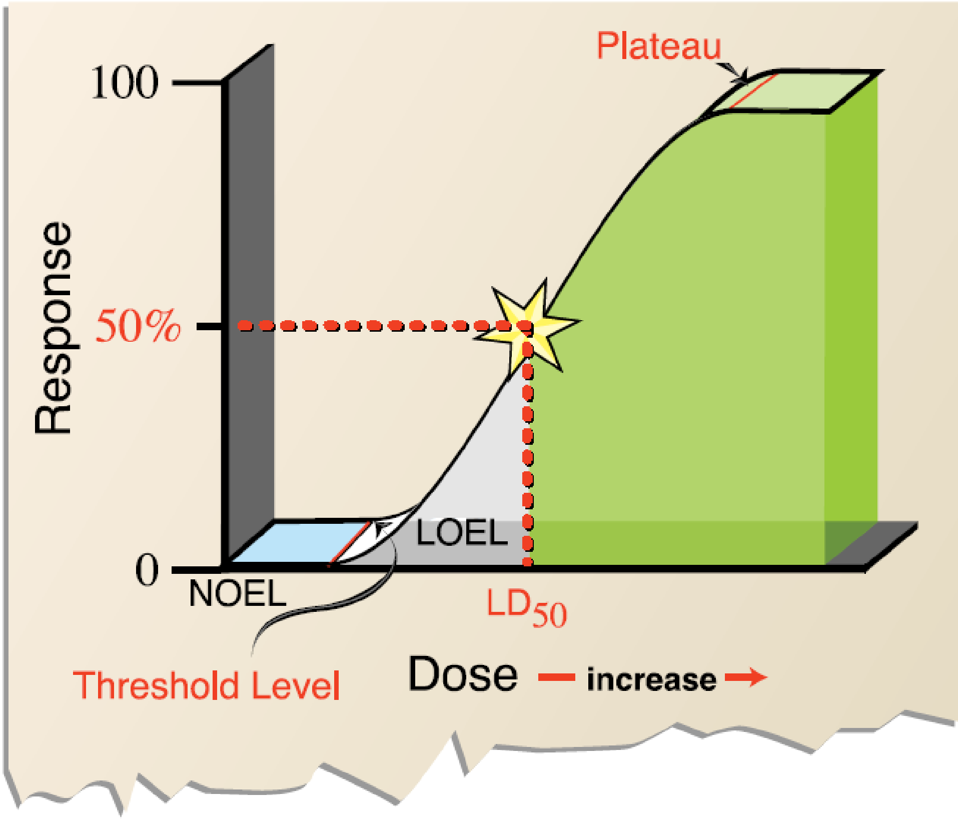
Why toxicology?

Read this.

- Pesticides are poisons, intentionally
  - They poison nontarget as well as target species because their modes of action are not specific to pest insects and not all insects are pests.
  - Humans, other mammals, fish, birds, and nontarget invertebrates (including natural enemies of pests) may be posioned.
- Lorenz, E.S. 2009. Potential Health Effects of Pesticides. http://pubs.cas.psu.edu/freepubs/pdfs/uo198.pdf. Covers …
  - Hazard = toxicity X exposure. Hazards are reduced by formulating low-concentration products and low-dust products; applying them to specific locations; requiring personal protective equipment (gloves, masks, etc.); imposing re-entry regulations and pre-harvest intervals (PHIs)
  - Toxicity may be viewed in different ways: acute vs. chronic; route of exposure (ingestion, inhalation, or dermal exposure); endpoint (skin or mucous membrane irritation, death, mutagenicity, carcinogenicity)

- Lorenz, continued
  - Signal words based on acute LD_{50}s…
    - Danger/Poison
    - Danger
    - Caution
  - Pesticide applicators are warned of symptoms of acute poisoning for insecticides, fungicides, and herbicides

Carbaryl (N-methyl carbamate)	Sevin	Malaise, muscle weakness, dizziness, sweating Headache, salivation, nausea, vomiting, abdominal pain, diarrhea Nervous system depression, pulmonary edema in serious cases
Chlorpyrifos (organophosphate)	Dursban	Headache, excessive salivation and tearing, muscle twitching, nausea, diarrhea Respiratory depression, seizures, loss of consciousness Pinpoint pupils
Endosulfan (organochlorine)	Thiodan	Itching, burning, tingling of skin Headache, dizziness, nausea, vomiting, lack of coordination, tremor, mental confusion Seizures, respiratory depression, coma
Malathion (organophosphate)	Cythion	Headache, excessive salivation and tearing, muscle twitching, nausea, diarrhea Respiratory depression, seizures, loss of consciousness Pinpoint pupils
Methyl Parathion (organophosphate)	Penncap-M	Headache, excessive salivation and tearing, muscle twitching, nausea, diarrhea Respiratory depression, seizures, loss of consciousness Pinpoint pupils
Phosmet (organophosphate)	Imidan	Headache, excessive salivation and tearing, muscle twitching, nausea, diarrhea Respiratory depression, seizures, loss of consciousness Pinpoint pupils
Pyrethrins (natural origin)		Irritating to skin and upper respiratory tract Contact dermatitis and allergic reactions—asthma
Pyrethroids (synthetic pyrethrin)	Cypermethrin, permethrin	Abnormal facial sensation, dizziness, salivation, headache, fatigue, vomiting, diarrhea Irritability to sounds or touch Seizures, numbness



A "rule" of toxicology often applied to the acute toxicity of substances is that "the dose makes the poison." Studies that use laboratory animals are used to estimate the dose-response relationship for a pesticide, and one common outcome of such studies is the estimation of an LD_{50} – the dose (milligrams of toxicant per kilogram of body weight for the test animal) that killed 50 percent of the animals in the test and is likely to kill 50 percent of animals in a similar population.

Toxicity: the ability of a compound to cause injury or death

Mammalian Oral LD_{50} values for:

Pesticide	mg/kg
DDT	113-118
chlordane	457-590
methyl parathion	14
chlorpyrifos	135-163
terbufos	2-5
malathion	885-2800
aldicarb	1
carbaryl	850
carbofuran	8-14
permethrin	430-4,000
rotenone	60-1500
nicotine	50-60
sabadilla	4,000
pyrethrins	1200-1500
microbials	NA

LD_{50} = dose that causes death to 50 percent of the animals to which it is administered in laboratory bioassays.

In general, the insecticides that have been developed after the organophosphates and carbamates have been less toxic to mammals.

But what about long-term impacts of chronic exposures?

- Do pesticides cause other effects that may or may not be related to their primary mode of action as acute poisons?
  - Cancer?
  - Birth defects?
  - Endocrine effects?
- And how should testing for these effects be done?

References

Read this.

- Avery, Dennis. 1995. Saving the Planet Through Pesticides and Plastics. Hudson Institute, Indianapolis. (A biased and unscientific piece meant to arm the ill-informed with quotes instead of insights … "the gods' honest truth is it's not that simple." You can forego reading this … just understand that it's "out there.")
- Baier, C. 2000. Saving the Planet Through Pesticides and Plastics: A Critical Review. http://www.webpages.uidaho.edu/etox/resources/book_reviews/Planet.pdf
- Whitford, F., et al. 2003. Pesticide Toxicology: Evaluating Safety and Risk. http://www.extension.purdue.edu/extmedia/PPP/PPP-40.pdf (A description of how required toxicological testing of pesticides is done.)

- **Reasons for concerns about pesticides in environmental quality and human health result from a pesticide's:**

- persistence
- transport
- toxicity

If a pesticide is at all toxic to nontarget organisms, it's persistence (buildup over time) and its likelihood of movement to groundwater and surface water are important characteristics.

- **Persistence** is one determiner of the magnitude of residues in soil or on foods. Persistence can be represented by determining a pesticide's half-life. Half-lives in soil for a few organochlorine and organophosphate insecticides:

• DDT	3-10 yrs
• Heptachlor	7-12 yrs
• Chlordane	2-4 years
• Ethyl parathion	14 days
• Chlorpyrifos	30 – 90 days
• Diazinon	40 days

Ranking persistence (in a very general way):

- Longest
  - Inorganics such as lead arsenate
  - Chlorinated hydrocarbons
  - Neonicotinoids (some)
- Medium
  - Organophosphates
  - Carbamates
  - Pyrethroids
  - Neonicotinoids (some)
- Shortest
  - Botanicals
  - Soaps
  - Microbials

- **Rates of breakdown are dependent on:**
- concentration (extremely high concentrations degrade more slowly)
- temperature and moisture (increasing levels of either tend to speed breakdown)
- pH (organophosphates especially ... alkaline conditions speed hydrolysis, even in the spray tank)
- UV light speeds breakdown (especially for microbials)

- **Breakdown products (metabolites) can themselves be persistent & toxic:**
  - aldrin to dieldrin; heptachlor to heptachlor epoxide ... Metabolites are more persistent and more toxic
  - Alar (daminozide) to UDMH ... a carcinogen by current standards (apple story of 1980s)
  - aldicarb to aldicarb sulfoxide in watermelons & other cucurbits treated illegally (metabolite is more toxic than the original active ingredient) (watermelon story of 1990s)

Transport

- Residues may be carried away from application sites, often to unwanted destinations.
- Transport in/by water is influenced by persistence, water solubility, and soil sorption (K_{OC})

We will discuss how neonicotinoids compare with these in a later lecture.

Compound	Soil Half-life	K_{OC}	Water Sol. (ppm)
DDT	3-10 yrs	--	0.006
chlordane	2-4 yrs	--	0.1
parathion (methyl)	5 days	9800	57
chlorpyrifos (Lorsban)	30-90 days	4600	1
terbufos (Counter)	21-35 days	578	5
aldicarb (Temik)	70 days	28	6,000
carbofuran (Furadan)	30-90 days	45	320
carbaryl (Sevin)	10 days	230	40
permethrin (Pounce, Ambush)	30 days	10,600	0.04
esfenvalerate (Asana)	35 days	5,300	0.002
atrazine	60 days	100	33
alachlor	15 days	170	242

- In general, the values that trigger some concern about a pesticide's potential for environmental transport are a **half-life greater than 21 days**, a **soil sorption index of 300 to 500 (or less)**, and a **water solubility of greater than 30 ppm**. Triggering one or more of these concerns does NOT mean that a pesticide should not be used at all; it simply means that uses should be appropriate.

- So ... certain pesticides end up in ground water and surface water for specific reasons.
- Compounds most common in groundwater detections have been
  - old chlorinated compounds
  - Aldicarb (a carbamate sold under the trade name Temik)
  - nitrates
  - the herbicides atrazine, metolachlor, alachlor, and a few others.
  - Neonicotinoids – now and in the future??

- Reasons: persistence, <u>volume of use</u>, solubility, soil sorption.

- Low solubility / high soil sorption do not prevent surface water contamination
  - Pesticides attached to soil particles can be carried by erosive runoff (or by wind) and end up in water and aquatic organisms. Such problems are especially likely for preplant treatments applied to bare soil in the spring (rainy season).

- Risks of unwanted transport at mixing and loading sites (and toxic waste sites) are high for all compounds regardless of sorption, solubility, or normal persistence. High concentrations outweigh other characteristics. Some related issues to consider ...
  - Locations of ag chem facilities (and other point sources of various contaminants) in relation to community water wells
  - Location and construction of farm wells and mixing/loading practices
  - "Land-farming" to dispose of contaminated soils

Back to acute toxicity and LD_{50}s

- LOW numbers indicate GREATER toxicity!!
- LD_{50} values are not complete indicators even for acute toxicity.
- Toxicity is influenced by route of exposure, dilution, and combinations with other chemicals.
- Other types of injury (besides death) occur.
- Many individuals are more susceptible than average.
- Test animals may not accurately represent humans.

- OBVIOUSLY … Environmental toxicity is also an issue ... toxicity to fish (pyrethroids, rotenone, many others), bees (carbaryl, some neonicotinoids, many others), birds (DDT, Furadan), and plants (lead arsenate, others) are all concerns.

Chronic toxicity: Pesticides as carcinogens ... many have been identified

- Cancer tests use maximum tolerated doses (MTD's) as first screen. Does constant high dose cause different effects than what we should expect from occasional low doses? Are there threshold doses below which injury would not occur?
- Ames' bacterial mutagenicity test: Lots of positives among natural and synthetic compounds. Did this mean all those natural compounds really are carcinogens? (http://potency.berkeley.edu/pdfs/handbook.pesticide.toxicology.pdf)
- Data (relatively few) that exist from animal trials on the carcinogenicity of natural compounds show about the same percent positives as animal trials on synthetics. Do the samples (trials) represent the populations of compounds?

- **Possible conclusions:**
- Ames and others in this camp are wacko, wrong, paid off, or misdirected.
- Lots of compounds really are carcinogens. (And there's no need to add more synthetic ones.) OR (And the synthetic ones are negligible additions with useful roles.)
- The way we identify carcinogens is greatly flawed. (So what's a better way and what do we do until we improve the protocol?)

Erroneous logic:

- Humans evolved in the presence of natural compounds; they are therefore safer. (Consider that tests of carcinogenicity are done on rodents and that they too evolved in the presence of natural compounds). Also consider that cancer remains for the most part a disease associated primarily with aging ... how much impact on the evolution of a species?)
- All known human carcinogens also cause cancer in high-dose rodent studies, so all compounds that cause cancer in high-dose rodent trials must be human carcinogens.
- A ppb just isn't going to cause any effect.

- **Wiser Conclusions:**
  - Persistent pesticides have caused and continue to cause problems. We should not continue current uses or approve new compounds and use patterns to pose the excessive risks because of their presistence.
  - Transport in water, on soil, etc. moves compounds to unwanted sites; at these sites the pesticides pose health risks or may be more persistent. Challenge: to identify environmental transport risks of specific compounds and select chemicals and use patterns that minimize risks.
  - Most insecticides are broad-spectrum poisons that affect humans, other vertebrates, beneficial insects, etc. Challenge: to develop pesticides with selective toxicity.
  - We do not know the answers to all the questions about the risks posed by pesticides.

Neonicotinoid Insecticides

- Who are they? (Common compounds)
- How are they used?
- What are their characteristics?
- Current issues
  - Persistence
  - Solubility / transport
  - Toxicity (to bees)
  - Need for use, impact, return on investment

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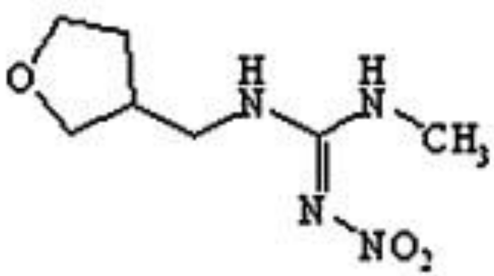
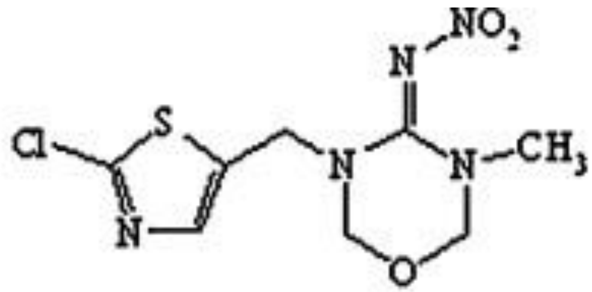
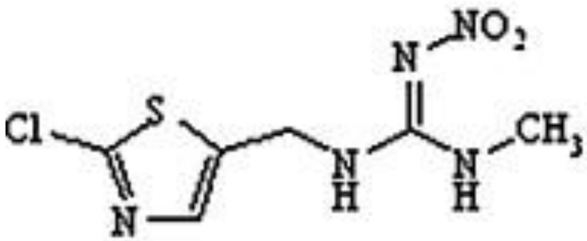
- The Effectiveness of Neonicotinoid Seed Treatments in Soybean. https://www.extension.umn.edu/agriculture/soybean/pest/docs/effectiveness-of-neonicotinoid-seed-treatments-in-soybean.pdf



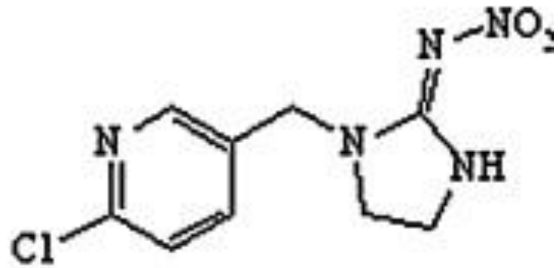
Dinotefuran



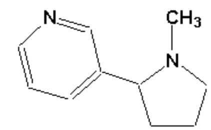
Thiamethoxam



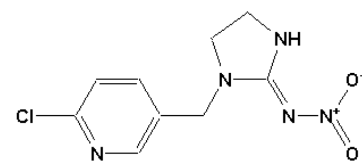
Clothianidin



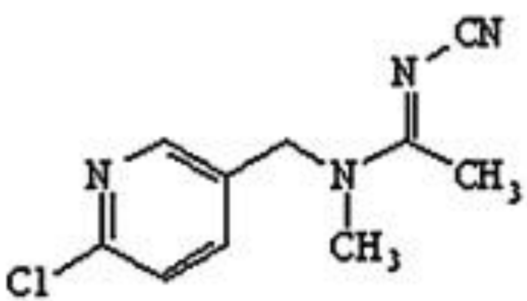
Imidacloprid



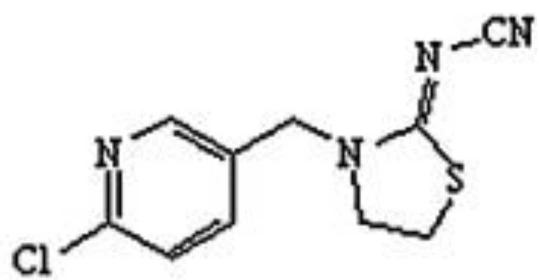
Nicotine (55 mg/kg)



Imidacloprid (424-475 mg/kg)



Acetamiprid



Thiacloprid

Major Uses of Neonicotinoids

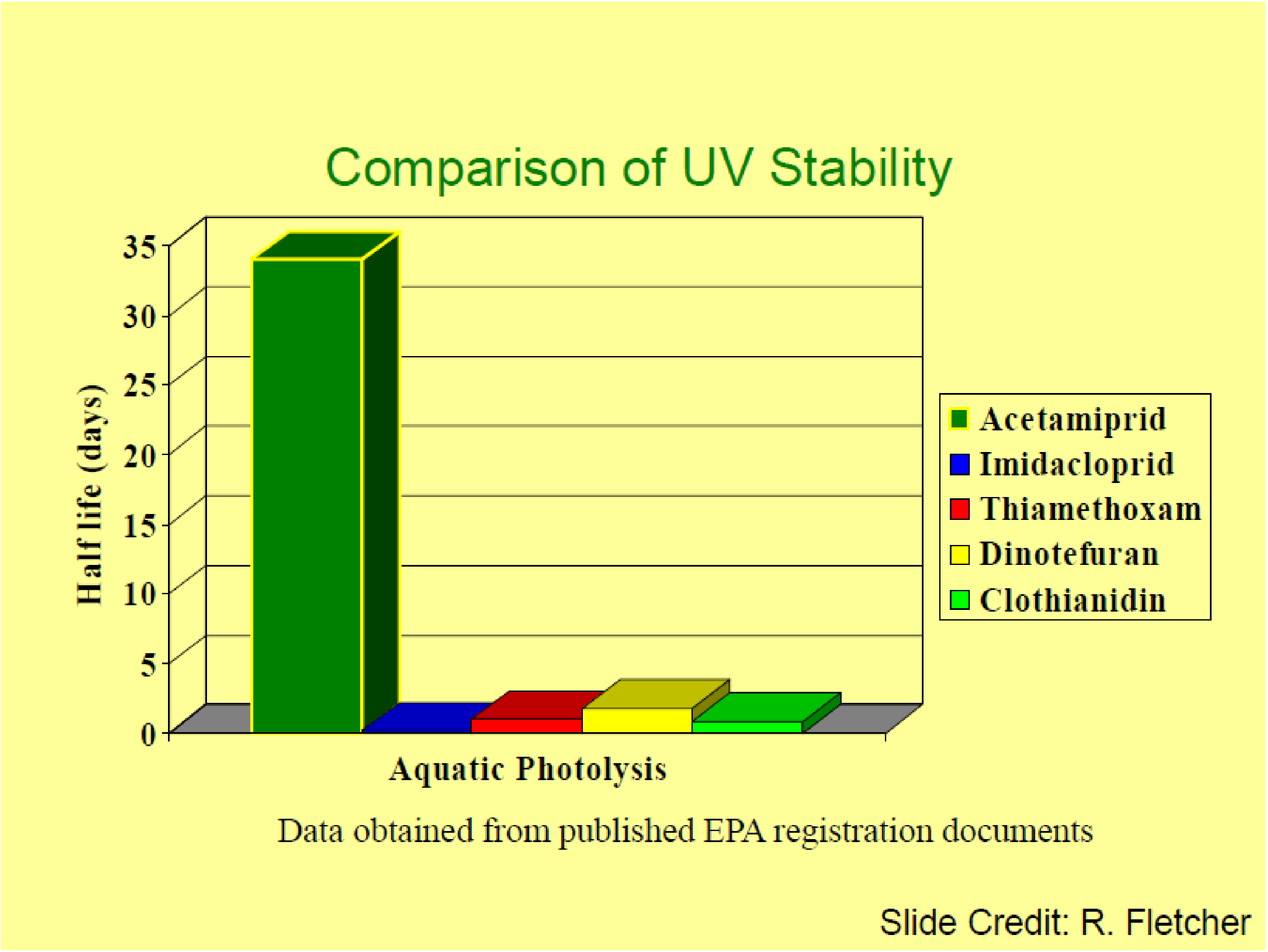
- Seed treatments for corn and soybeans (clothianidin/Poncho and thiamethoxam/Cruiser) for flea beetle, cutworm, and bean leaf beetle control; some rootworm control
- Soil applications for grub control in lawns and systemic control of Japanese beetle adults (and other insects) on ornamental plants (imidacloprid/Bayer Advanced Insect Control and several others)
- Seed treatments for cucurbits (pumpkins, squash, cucumbers, melons) for cucumber beetle control (thiamethoxam/ Farmore)
- Soil/systemic applications for Colorado potato beetle control (imidacloprid/Admire)
- Foliar applications to orchard crops for plum curculio, aphid, and Lepidopteran (codling moth / oriental fruit moth) control (acetamiprid/Assail ~~and thiacloprid/Calypso~~)

Table 3.1 Half-life in Soil of Neonicotinoids

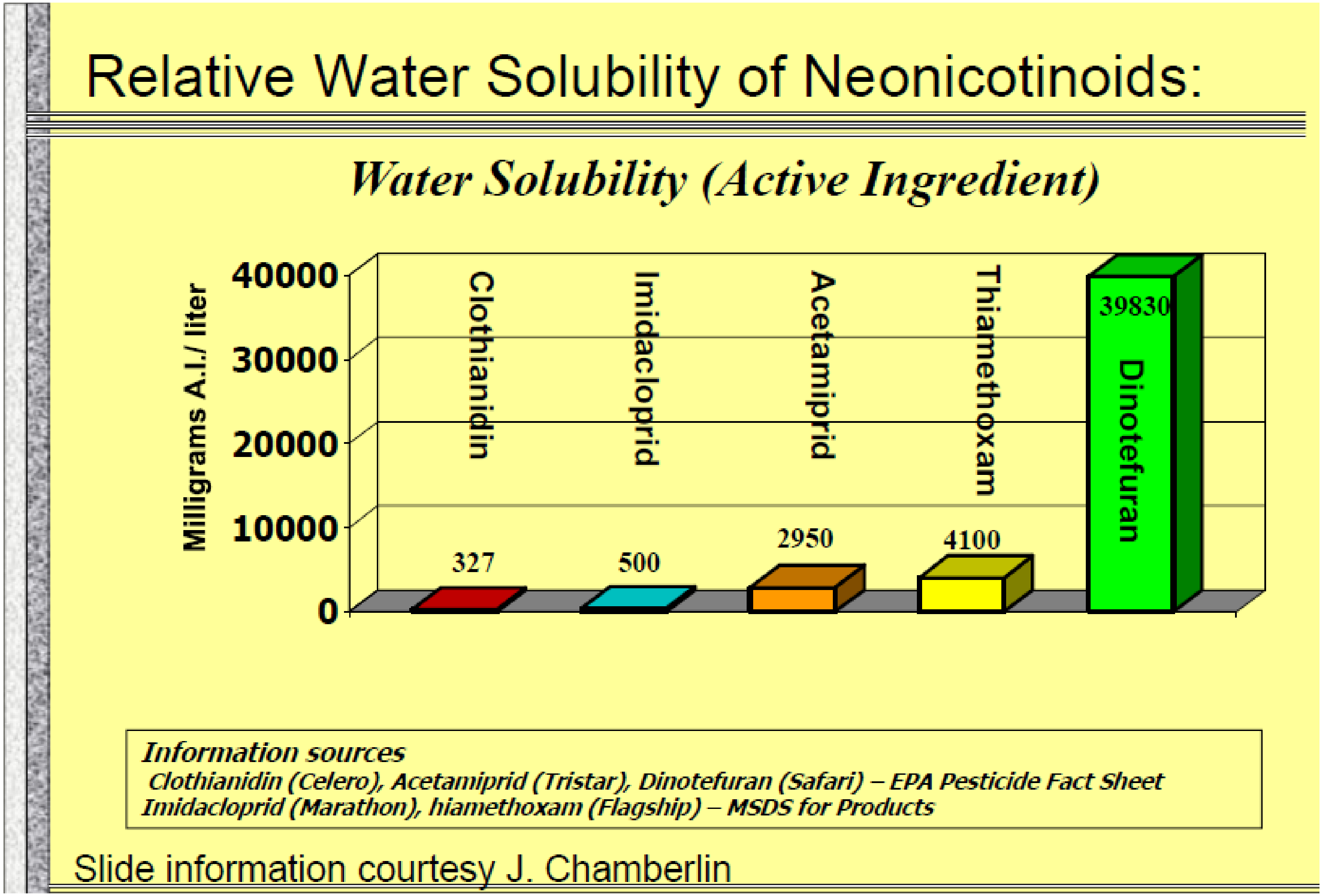
Neonicotinoid	Half-life in Soil (aerobic soil metabolism)
Acetamiprid	1–8 days[1]
Clothianidin	148–1,155 days[2]
Dinotefuran	138 days[3]
Imidacloprid	40–997 days[4]
Thiacloprid	1–27 days[5]
Thiamethoxam (See note below)	25–100 days[6]

Note: Clothianidin is a primary metabolite of thiamethoxam.

Sources: 1. EPA 2002; 2. EPA 2003a; 3. EPA 2004; 4. NPIC 2010; 5. EPA 2003b; 6. Syngenta Group 2005

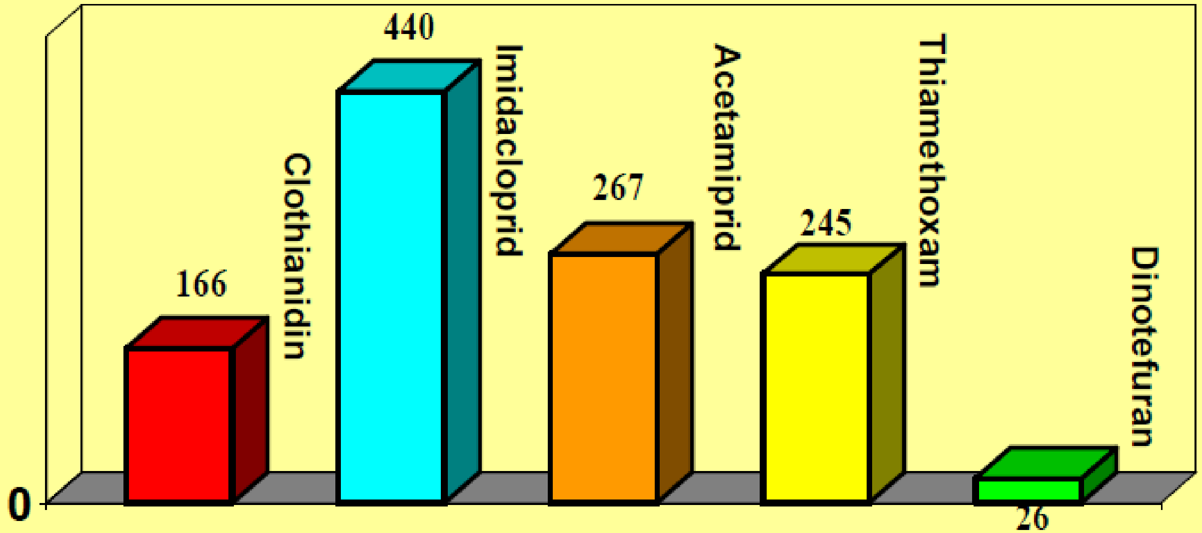


Comparison of UV Stability
Half life (days)
0
5
10
15
20
25
30
35
Aquatic Photolysis
Acetamiprid
Imidacloprid
Thiamethoxam
Dinotefuran
Clothianidin
Data obtained from published EPA registration documents
Slide Credit: R. Fletcher



Solubility of permethrin (Pounce)is 0.4 ppm; solubility of chlorpyrifos (Lorsban) is 1 ppm … in comparison with most other insecticides, the neonicotinoids are more soluble in water than most.

K_{oc} Values of Neonicotinoids:



Source Data: EPA Pesticide Fact Sheets

These soil sorption indices are low to moderate.

Table 1. Neonicotinoid pesticide mammalian toxicities (mg/kg of body weight).

Common name	Rat oral LD_{50}	Rabbit dermal LD_{50}
Acetamiprid	450	>2,000 (Tristar®)
Clothianidin	>5,000	>2,000 (Acceleron®)
Imidacloprid	4,870 (Gaucho®)	>2,000 (Admire®)
Thiamethoxam	>5,000	>2,000

Table 2. Neonicotinoid pesticide wildlife toxicity ranges.

Common name	Bird acute oral LD_{50} (mg/kg)*	Fish LC_{50} (ppm)**	Bee LD_{50} †
Acetamiprid	PNT	PNT	MT
Clothianidin	PNT	PNT	HT
Imidacloprid	MT	MT	HT
Thiamethoxam	ST	PNT	HT

Table 5.1 Toxicity of Neonicotinoids

Neonicotinoid	Known Toxicity to Honey Bees[1]		
		Contact LD_{50}	Oral LD_{50}
Acetamiprid	M	7.1 µg/bee[2]–8.09 µg/bee[3]	8.85–14.52 µg/bee[3]
Clothianidin	H	0.022 µg/bee[2]–0.044 µg/bee[4]	0.00379 µg/bee[5]
Dinotefuran	H	0.024 µg/bee[2]–0.061 µg/bee[6]	0.0076–0.023 µg/bee[6]
Imidacloprid	H	0.0179 µg/bee[4]–0.243 µg /bee[7]	0.0037 µg/bee[7]–0.081 µg/bee[8]
Thiacloprid	M	14.6 µg/bee[2]–38.83 µg/bee[9]	8.51–17.3 µg/bee[9]
Thiamethoxam	H	0.024 µg/bee[10]–0.029 µg/bee[2]	0.005 µg/bee[10]

H = highly toxic; M = moderately toxic
Toxicity: Highly toxic: LD_{50} < 2 µg/bee; Moderately toxic: LD_{50} 2–10.99 µg/bee; Slightly toxic: LD_{50} 11–100 µg/bee; Practically non-toxic: LD_{50} >100 µg/bee.

Sources: 1. WSDA 2010; 2. Iwasa et al. 2004; 3. EC 2004b; 4. EPA 2003a; 5: EC 2005; 6. EPA 2004; 7. Schmuck et al. 2001; 8. Nauen et al. 2001 ; 9. EC 2004a; 10. Syngenta Group 2005.

Neonicotinoids and Bees

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Multiple Routes of Pesticide Exposure for Honey Bees Living Near Agricultural Fields

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Abstract Top

Populations of honey bees and other pollinators have declined worldwide in recent years. A variety of stressors have been implicated as potential causes, including agricultural pesticides. Neonicotinoid insecticides, which are widely used and highly toxic to honey bees, have been found in previous analyses of honey bee pollen and comb material. However, the routes of exposure have remained largely undefined. We used LC/MS-MS to analyze samples of honey bees, pollen stored in the hive and several potential exposure routes associated with plantings of neonicotinoid treated maize. Our results

Abstract

… Neonicotinoid insecticides, which are widely used and highly toxic to honey bees, have been found in previous analyses of honey bee pollen and comb material. However, the routes of exposure have remained largely undefined. We used LC/MS-MS to analyze samples of honey bees, pollen stored in the hive and several potential exposure routes associated with plantings of neonicotinoid treated maize. Our results demonstrate that bees are exposed to these compounds and several other agricultural pesticides in several ways throughout the foraging period. During spring, extremely high levels of clothianidin and thiamethoxam were found in planter exhaust material produced during the planting of treated maize seed. We also found neonicotinoids in the soil of each field we sampled, including unplanted fields. Plants visited by foraging bees (dandelions) growing near these fields were found to contain neonicotinoids as well. This indicates deposition of neonicotinoids on the flowers, uptake by the root system, or both. Dead bees collected near hive entrances during the spring sampling period were found to contain clothianidin as well, although whether exposure was oral (consuming pollen) or by contact (soil/planter dust) is unclear. We also detected the insecticide clothianidin in pollen collected by bees and stored in the hive. When maize plants in our field reached anthesis, maize pollen from treated seed was found to contain clothianidin and other pesticides; and honey bees in our study readily collected maize pollen. These findings clarify some of the mechanisms by which honey bees may be exposed to agricultural pesticides throughout the growing season. These results have implications for a wide range of large-scale annual cropping systems that utilize neonicotinoid seed treatments.

Article

Prev

Insecticide Residues in Pollen and Nectar of a Cucurbit Crop and Their Potential Exposure to Pollinators

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Section: Toxicology

Neonicotinoids are systemic insecticides widely used on many pollinated agricultural crops, and increasing evidence indicates that they move to some extent into pollen and nectar. This study measured levels of neonicotinoid residues in pollen and nectar from a pumpkin crop treated with formulated products containing imidacloprid, dinotefuran, and thiamethoxam using different timings and application methods. Environmental conditions have a significant effect on overall residue levels; nectar residues were 73.5-88.8% less than pollen residues, and metabolites accounted for 15.5-27.2% of the total residue amounts. Foliar-applied treatments and chemigated insecticides applied through drip irrigation during flowering resulted in the highest residues of parent insecticide and metabolites, which may reach average levels up to 122 ng/g in pollen and 17.6 ng/g in nectar. The lowest levels of residues were detected in treatment regimens involving applications of insecticides at planting, as either seed dressing, bedding tray drench, or transplant water treatment.

Keywords: **neonicotinoid residues**; **pollen**; **nectar**; **pollinators**; **Cucurbitaceae**

- The parent neonicotinoids and several metabolites were identified and quantified in 92.1, 88.2, and >98% of the pollen, nectar, and leaf samples from the treated plots, respectively.
- The bedding tray drench resulted in the lowest residue levels of imidacloprid, ranging from 0.1 to 6.7 ng/g in pollen and from ND to 0.5 ng/g in nectar.
- Applications of the low label rate of imidacloprid in transplant water resulted in significantly higher ($p < 0.05$) residue amounts in pollen, ranging from 13.2 to 40.1 ng/g, than in nectar, ranging from 3.8 to 7.3 ng/g.
- The highest residues of imidacloprid were found in samples from plots receiving the high label rate but as split applications in transplant water followed 3 weeks later by drip chemigation.

- We presented here evidence to support our hypothesis that higher residues are present in pollen and nectar if systemic neonicotinoids are applied closer to flowering. Foliar treatments and chemigation through drip irrigation applied during flowering resulted in the highest residues of parent insecticide and metabolites. The three neonicotinoids in the study showed similar residue profiles in pollen and nectar with regard to the split transplant-drip treatment regimen. The lowest levels of residues were detected in treatment regimens involving applications of insecticides at planting, as either seed dressing, bedding tray drench, or transplant water treatment. The uptake and translocation of residues from these at-planting applications clearly decreased as the growing season progressed and the crop approached flowering. If neonicotinoids are needed for insect control on cucurbits, they should be applied at planting or shortly after to mitigate the exposure to pollinators.

ARE NEONICOTINOIDS KILLING BEES?

A Review of Research into the Effects of Neonicotinoid Insecticides on Bees, with Recommendations for Action

Jennifer Hopwood, Mace Vaughan, Matthew Shepherd, David Biddinger, Eric Mader, Scott Hoffman Black, and Celeste Mazzacano

THE XERCES SOCIETY FOR INVERTEBRATE CONSERVATION

Exposure of bees to neonicotinoids

- Neonicotinoid residues found in pollen and nectar are consumed by flower-visiting insects such as bees. Concentrations of residues can reach lethal levels in some situations.
- Neonicotinoids can persist in soil for months or years after a single application. Measurable amounts of residues were found in woody plants up to six years after application.
- Untreated plants may absorb chemical residues in the soil from the previous year.
- Products approved for home and garden use may be applied to ornamental and landscape plants, as well as turf, at significantly higher rates (potentially 120 times higher) than those approved for agricultural crops.
- Direct contact with foliar neonicotinoid sprays is hazardous to pollinators, and foliar residues on plant surfaces remain toxic to bees for several days.
- Neonicotinoids applied to crops can contaminate adjacent weeds and wildflowers.

Effects on honey bees

- Imidacloprid, clothianidin, dinotefuran, and thiamethoxam are highly toxic to honey bees.
- Thiacloprid and acetamiprid are mildly toxic.
- After plants absorb neonicotinoids, they slowly metabolize the compounds. Some of the resulting breakdown products are equally toxic or even more toxic to honey bees than the original compound.
- Honey bees exposed to sublethal levels of neonicotinoids can experience problems with flying and navigation, reduced taste sensitivity, and slower learning of new tasks, which all impact foraging ability.

Exposure of bees to neonicotinoids

- Application methods other than seed coatings (foliar sprays, soil drenches, and trunk injections) apply a higher dosage per plant and may result in much higher—even toxic—levels of neonicotinoid residues in pollen and nectar.
- Application of neonicotinoids shortly before and during bloom may lead to higher residue levels in pollen and nectar.
- Application by soil drench or trunk injection may result in high residue levels in blossoms of woody ornamental species more than a year after treatment.

Imidacloprid	Application as seed dressing, soil drench, granules, injection, or spray to a wide range of field and tree crops, as well as ornamental plants, trees, and turf. (Also, topical use on pets for flea control and application to buildings for termite control.)	Admire Gaucho Imicide Provado Macho Malice Sepresto Widow Wrangler	Bayer Advanced 3-in-1 Insect, Disease, & Mite Control Bayer Advanced 12 Month Tree & Shrub Insect Control Bayer Advanced 12 Month Tree & Shrub Protect & Feed Bayer Advanced Fruit, Citrus & Vegetable Insect Control Bayer Advanced All-in-One Rose & Flower Care concentrate DIY Tree Care Products Multi-Insect Killer Ferti-lome 2-N-1 Systemic Hi-Yield Systemic Insect Spray Hunter Knockout Ready-To-Use Grub Killer Lesco Bandit Marathon Merit Monterey Once a Year Insect Control II Ortho Bug B Gon Year-Long Tree & Shrub Insect Control Orhto MAX Tree & Shrub Insect Control Surrender Brand GrubZ Out
Thiacloprid	Application as foliar spray to cotton and pome fruit crops.	Calypso	
Thiamethoxam	Application as seed dressing, soil drench, injection, granules, or foliar spray to a wide range of field crops, as well as ornamental plants and turf.	Actara Adage Crusier Centric Platinum	Flagship Maxide Dual Action Insect Killer Meridian

So …

- Expect increasing regulatory action (maybe).
- Until then … we should not use neonicotinoids that are especially toxic to bees if applications (even seed treatments) will result in bee kill. Particularly toxic neonics include …
    - Imidacloprid (Admire Pro, many homeowner products)
    - Thiamethoxam (Actara, Platinum)
    - Clothianidin (Poncho seed treatments)
    - Dinotefuran (Scorpion, Venom)
- Use of these products (imidacloprid and thiamethoxam) as seed treatments on cucurbits presents little or no systemic risk, but later uses do result in more significant contamination of pollen and nectar.
- Seed treatments on corn and soybean seeds … these large scale of uses presents real risks, and at least in soybeans, with no evidence of return on investment.

Effectiveness and Return on Investment …

- The Effectiveness of Neonicotinoid Seed Treatments in Soybean
  - https://www.extension.umn.edu/agriculture/soybean/pest/docs/effectiveness-of-neonicotinoid-seed-treatments-in-soybean.pdf

In 2011, more than 80 percent of corn, more than 50 percent of cotton, and about 40 percent of soybean acres were planted with neonicotinoid-treated seed, a total area described as "roughly the size of California." (Douglas and Tooker 2015).

To summarize: For typical field situations, independent research demonstrates that neonicotinoid seed treatments do not provide a consistent return on investment (Hodgson and VanNostrand 2012, 2013, 2014; Seagraves and Lundgren 2012; McCarville et al. 2014). The current use of neonicotinoid seed treatments in soybean and other crops far exceeds pest pressures.