AGROCHEMICALS

Population: 1B in 1830 to 5B in 1986 to >45B (2017)

From: Pesticides and Health: Myths and Reality, Prof. Allan Felsot, ACSH

Table 1. Percentage Use of Pesticide Classes on Major Crops During Crop Years 2003 or 2004

Crop	Herbicide	Insecticide	Fungicide
Corn	95	29	<1
Soybean	97	4	1
Wheat	45	7	2
Cotton	98	64	7
Potato	91	84	91
Apple	42	94	90

USDA NASS 2004, 2005

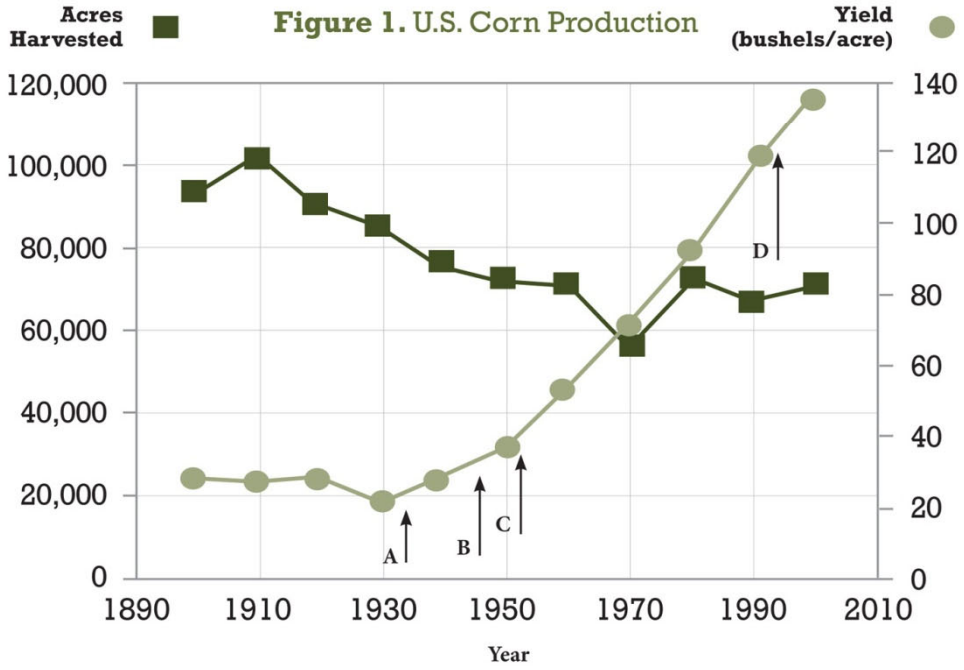


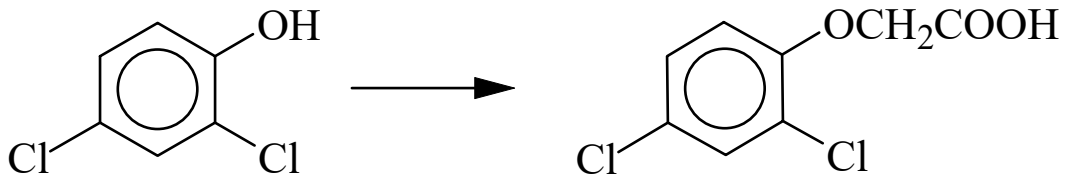
Figure 1. U.S. Corn Production

Historical trend in U.S. corn production and approximate timeline for introduction of crop production technologies. A: hybrid seeds; B: mineralized fertilizers; C: soil insecticides; D. transgenic crops (Carpenter et al. 2002).

HERBICIDES: kill other plants

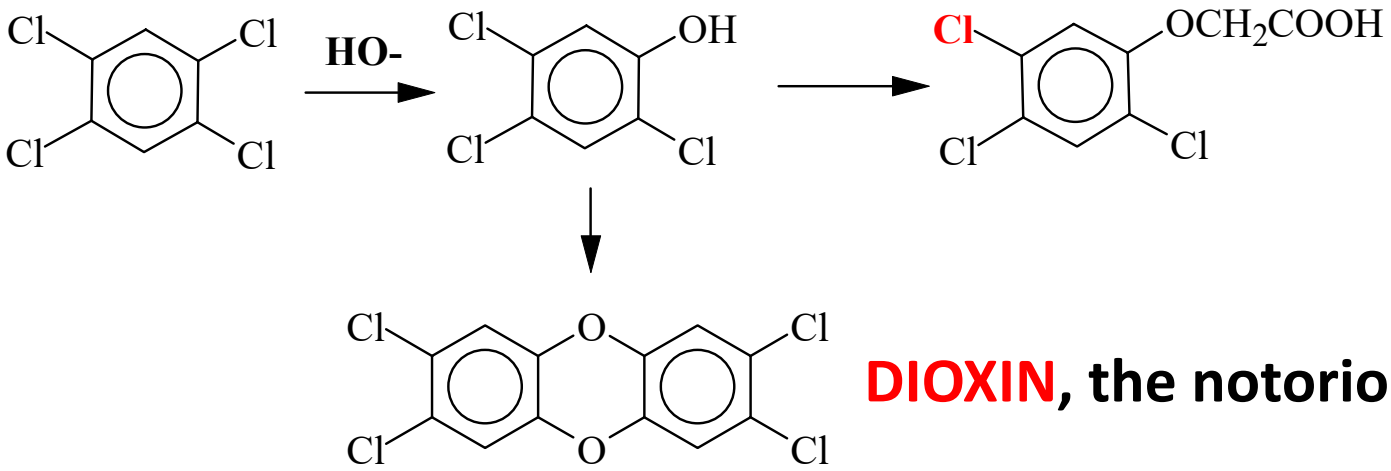
Weeds compete for fertilizer, water: most farm crops are treated

1946 saw introduction of 2,4-D (2,4-dichlorophenoxyacetic acid)



2,4-D

2,4,5-T **2,4,5-trichlorophenoxyacetic acid**



2,4,5-T

DIOXIN, the notorious poison

2,4-D

- kills broadleaf plants at 100g-1kg per acre
- cheap (use >100M kg/yr)
- low mammalian toxicity ~500mg/kg orally, 1.5g/kg dermally
- degrades quickly in soil, does not concentrate
- can use on wheat, barley, corn, sugar, rice, GRASS (home use)

contains NO dioxin: one of safest home weed herbicides

- imitates AUXIN, (3-indoleacetic acid), natural growth regulator
- causes plants to grow too rapidly, young cells do not mature properly, clog food transport system

2,4,5-T always contains some dioxin

- more effective on brush, blackberries, around power lines,
- AND THE VIETNAM JUNGLES

US used 70M Liters of 50:50 2,4-D/2,4,5-T in Vietnam:
AGENT ORANGE (DRUMS): sprayed neat, not diluted

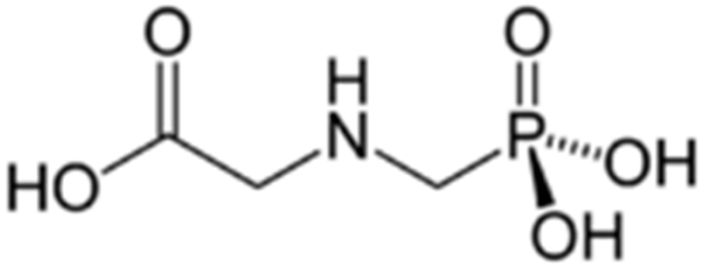
Puss, oozing acne and birth defects found on people sprayed - stopped use in 1970. EPA permitted use on rice, rights of way, home use till 1985 (later in Canada)

Yushchenko claims his opponents poisoned him in September, scarring his face.

Former Ukranian President poisoned by dioxin in 2004

Grant Bruce
(BSc UVic 1983)
Hatfield Consultants

ROUNDUP (Monsanto)
Glyphosate



- general purpose herbicide that kills all vegetation
- low human toxicity: LD_{50} ~ 4g/kg
- Rel. environmentally benign – deactivates in soil quickly
- stops biosynthesis of the aromatic amino acids (phenylalanine, tyrosine, tryptophan) so *inhibits protein synthesis*

GM: corn, soybeans, canola, sugar beets (Monsanto);
Kentucky Blue Grass (Scott)

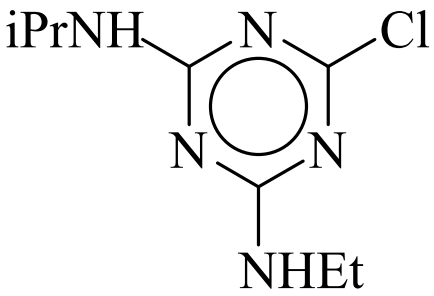
Glyphosate bans are spreading but…

A report by the UN and World Health Organization (WHO) in 2016 concluded that: …*'the controversial pesticide glyphosate is unlikely to pose a carcinogenic risk to humans from exposure through the diet'.* [from Chemistry World, Royal Society of Chemistry, May 22, 2016]

Monsanto vs. Schmeiser (1997): Monsanto sued farmer for using GM canola but he contended the seed blew onto his fields from adjacent farms. Monsanto won but was awarded no damages.

ATRAZINE

(Ciba-Geigy, Shell, Syngenta)



Used at 1-2 kg/acre

LD_{50} ~5g/kg

Corn is able to remove -Cl and deactivate (US: 30 Mkg/y)
Disrupts photosynthesis: can be applied to pre-tilled land

Controversy: Banned by EU in 2004
detected in ground waters: associated the *feminization of frogs*

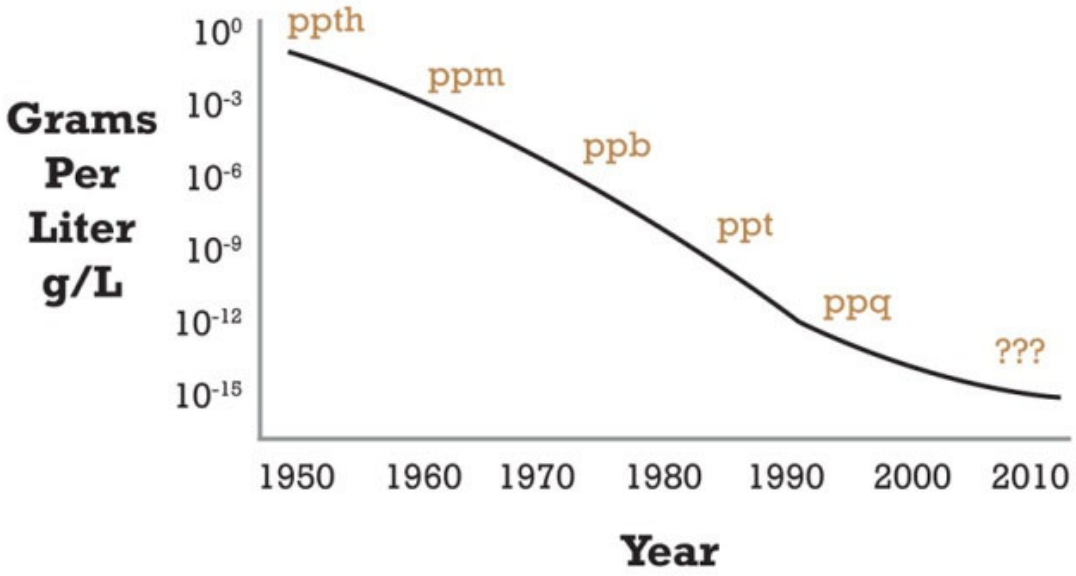
However, extensive studies conclude that it poses little risk to humans through drinking water (main exposure route). ***The link below gives an idea of how the WHO reviews data and sets limits based on published studies:***
https://www.who.int/water_sanitation_health/dwq/chemicals/antrazine.pdf

Pesticide residues on fruit / vegetables are very small

Natural carcinogens, *e.g. aflatoxin* in the mold on peanuts and corn is *much more dangerous*

Risk from carcinogens:
1/3000 motor cycle
1/300 smoking
1/25 car driving
25 x strike by lightning!!

Figure 10. Analytical Technology Has Advanced Faster than Biological Understanding



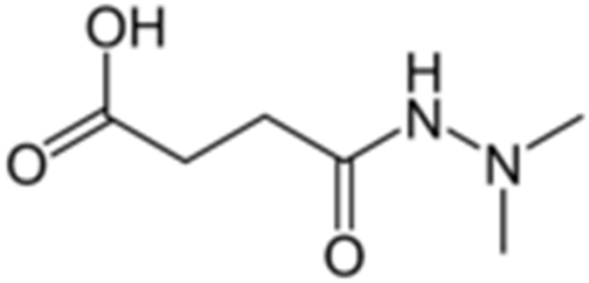
Depiction of change in detection limits (1 ppm = 10^{-3} g/L) over the last 60 years of contaminant monitoring. For year 2010, uncertainty is expressed owing to the unreliability of detections reported at parts per quadrillion (ppq) and lack of articles reporting detections lower than 1 part per trillion (ppt).

From: Pesticides and Health: Myths and Reality, Prof. Allan Felsot, ACSH

Daminozide (ALAR)

Uniroyal

The great apple juice scare of '89!



- **1963-89 ALAR sprayed on apples: prevents bruising**
- **Feb '89: '60 Minutes' piece alleges ALAR is a carcinogen**
- **Summer 1989: Supermarkets refuse to accept ALAR-sprayed apples**
- **Winter '89: FDA bans ALAR**
- **1990: Washington apple growers file suit (dismissed '94)**

60 Minutes story:

https://www.youtube.com/watch?v=7mwrWgqF4Ac

ACSH recap in 2009

https://www.youtube.com/watch?v=ZRO-4umbDys

Later shown that:

- **ALAR IS a carcinogen *but…***
- **effects observed at equiv. 20,000L juice/day *and…***
- **toxins growing on bruised apples far more potent carcinogens!**

What is the moral of this story?

INSECTICIDES

<500 BC	Burning Sulfur;
1500	Arsenic
1800	Nicotine (Sulfate)
1900's	Lead Arsenate

1900	Extract of dried chrysanthemum = PYRETHRUM
1920-1940	Japan main supplier – then war
>1940	Africa main supplier

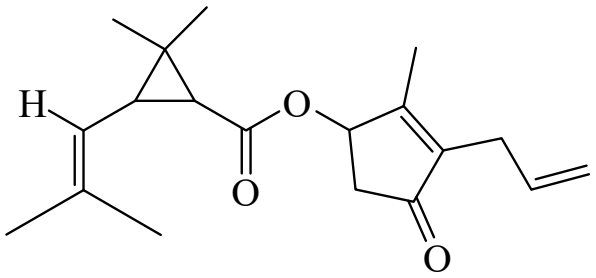
Have to hit insect

Decomposes in sunlight

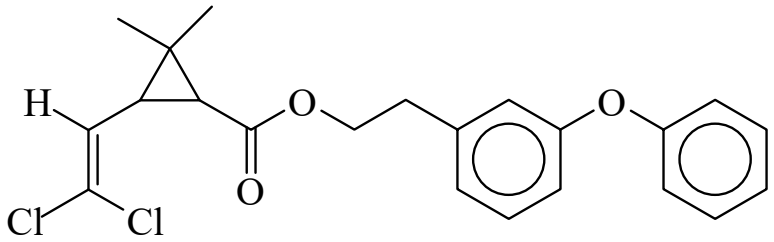
(no good for crops)

Low mammalian toxicity

By 1949 had developed more stable synthetic ones (Pyrethroids):



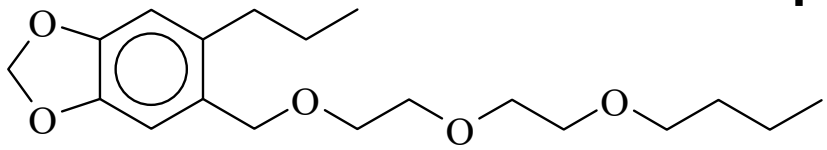
Allethrin



Permethrin

LD_{50} = 2g/kg

Keep Na^+ channels open: paralysis



Piperonyl butoxide

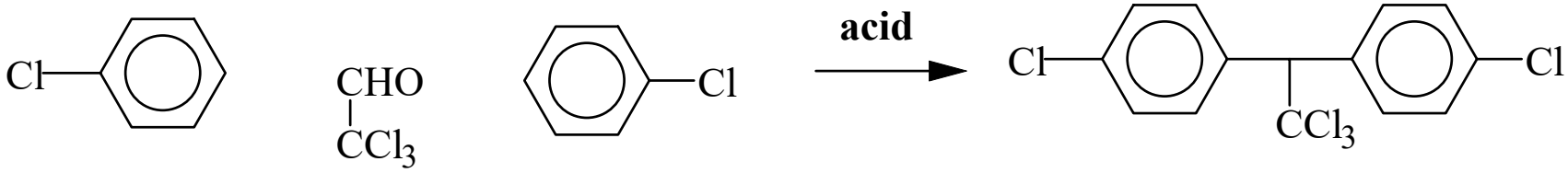
Enzyme inhibitor

Allethrin could be used in sunlight, but needs a synergist, piperonyl butoxide, to prevent insect recovery: RAID

Permethrin: cheaper, need less, more stable *ca.* 50 g/acre: AMBUSH, POUNCE

THE CHLORINATED PESTICIDES

DDT (1873, Germany); insecticidal properties, 1939



CHEAP ***ca.*** **20 g per penny in 1940**

dichlorodiphenyltrichloroethane

Wartime - pyrethrum supply cut off by Japan
Troops were lice and tick infected
Copper, Lead needed for military use

Tried DDT as 10% powder mixed with talc directly on millions of troops
3M people treated in Naples in 1943 alone!

Mechanism: Na^+ channels don't close, continuous nerve impulses

DDT THE GOOD

- Cheap
- Effective against all insects
- Extremely persistent
- Low toxicity to non-insects (2-3 g/kg on skin)

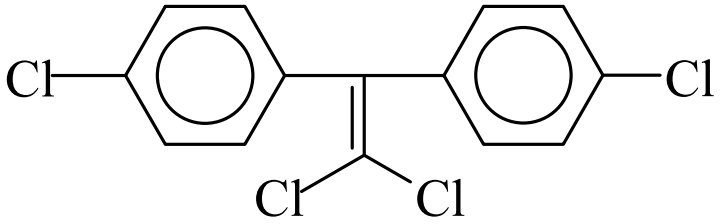
DDT THE BAD

- Cheap – indiscriminate use
- Effective against all insects – kills 'good' insects too
- Extremely persistent – around for > 20 y
- Effects on birds

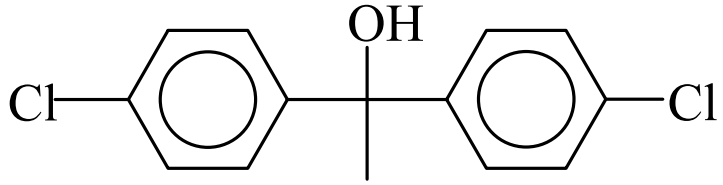
DDT – some effects:

- Crop yields went up
- Stopped Gypsy Moth in East, Spruce Budworm in West
- Reduced malaria, killed louse (Typhoid), Flea (Plague) and Tetse Fly (Sleeping sickness)

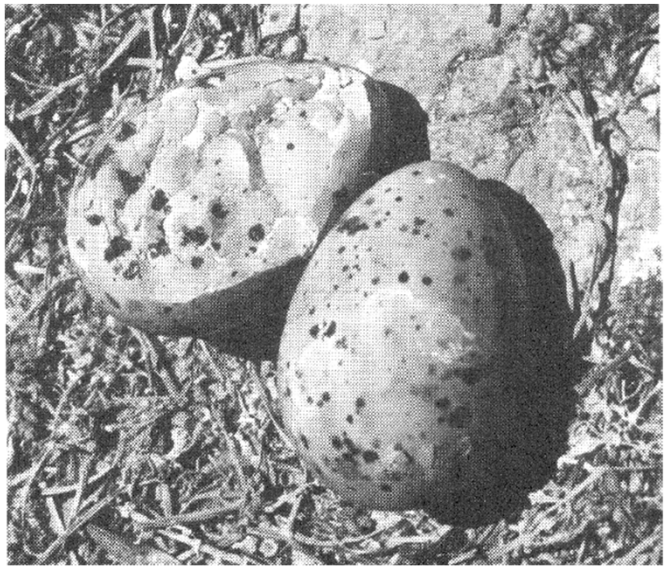
Insect Resistance - overrated!! Some insects have developed DDT-ase which dehydrochlorinates DDT to DDE; however that is easy to overcome by blocking the enzyme, e.g. with chlorofenthol



DDE



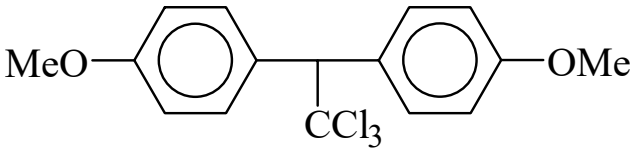
Chlorofenthol



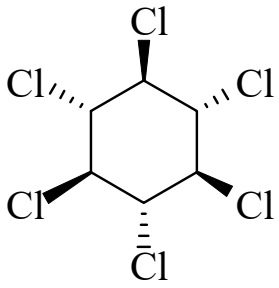
Crushed and normal eggs in a Caspian tern nest. DDT residues and consequent thinning have been related to such breakage.

Rachel Carson's Silent Spring (1962) and decline of Bald Eagle populations led to reduced NA usage, and eventual ban in 1972

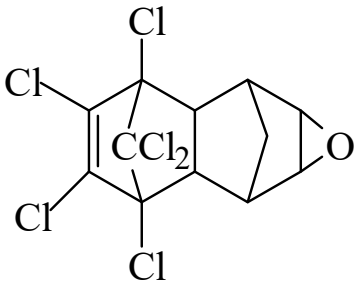
In Canada, Methoxychlor is widely used – degrades more quickly



Methoxychlor



Lindane



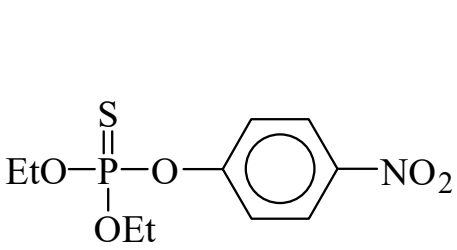
Dieldrin

But many much more toxic ones were also made:

Lindane **LD_{50} 100mg/kg**
Dieldrin **LD_{50} 50 mg/kg**

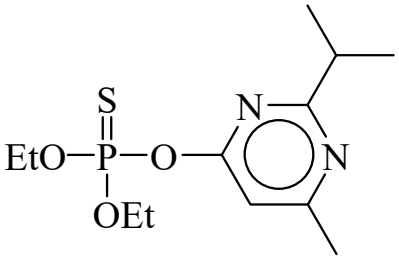
toxic to fish, mammals, humans... most phased out now but residues remain buried in soils, ocean muds, lake bottoms....

THE ORGANOPHOSPHATES - THE NERVE GASES (LIQUIDS)



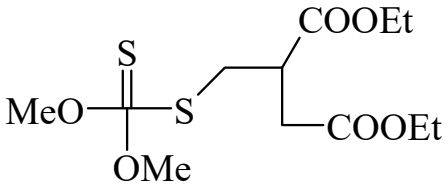
Parathion

LD50 8mg/kg



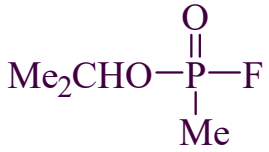
Diazinon

80mg/kg



Malathion

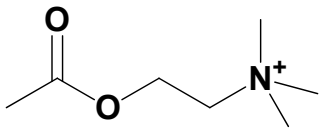
1g/kg



Sarin

0.01mg/kg (man)

Very effective – more toxic to ALL LIVING SPECIES except malathion – safest garden insecticide with methoxychlor

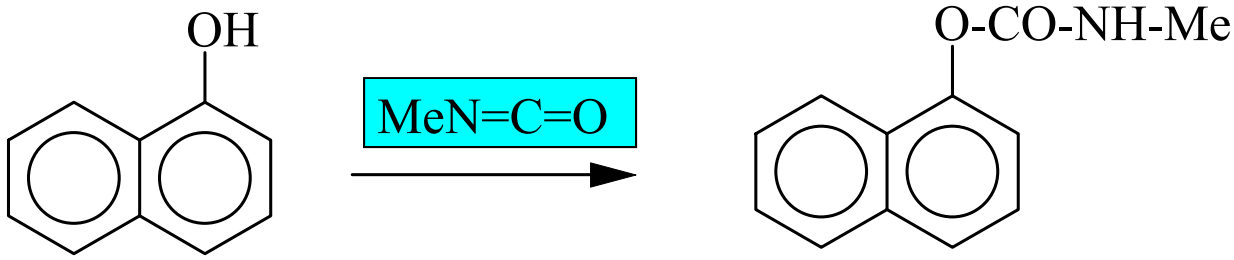


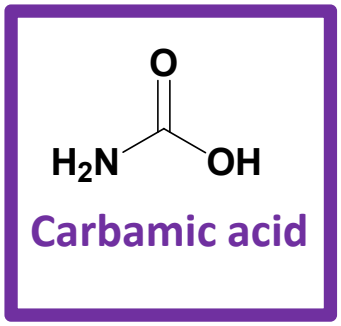
OP are Acetylcholine esterase (ACE) inhibitors:

- **Acetylcholine required for transmission of nerve impulses**
- **ACE limits nerve impulses**
- **Block ACE = continuous nerve impulses, convulsions, death**

Note: *Botulinus toxin* works the opposite way - prevents synthesis of acetylcholine - no impulses so paralysis

THE CARBAMATES: CARBARYL (SEVIN)





ACE inhibitors: *not permanent*, less toxic

Methyl isocyanate killed > 15000 people in Bhopal, India (1984) when 25-40 tons leaked from a ruptured valve in 40 mins

More than 40,000 people strongly affected (eyes, lungs) and estimates that as many as 800,000 show some effects

Union Carbide paid out >500 M$ but never cleaned up the site

Now wholly owned by Dow Chemicals (since 1999)

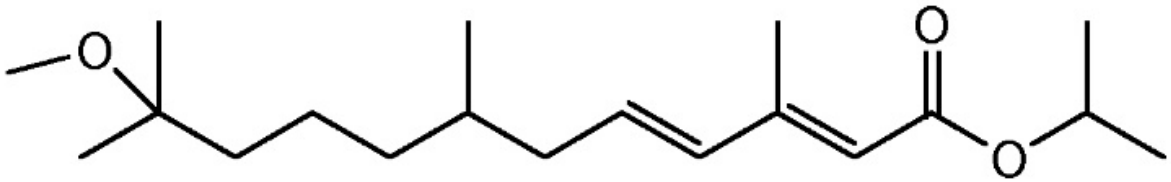
Figure 16.33 A male gypsy moth uses its large antennae to detect pheromones from a female.

Where are we going?

Insects attract each other via PHEROMONES: can we stop them reproducing? Insect Birth Control?

Or we can stop them maturing with hormones

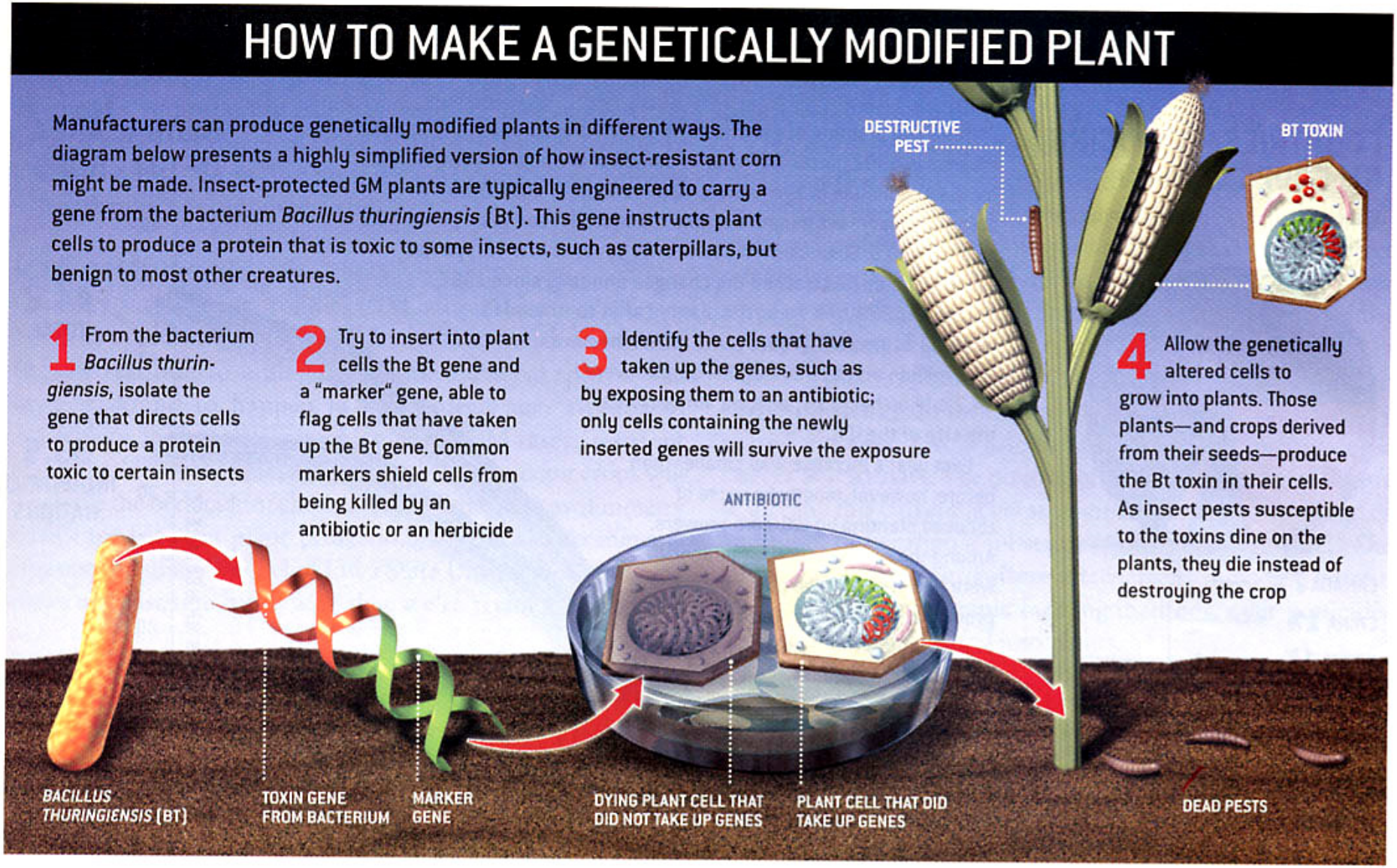
Methoprene is approved by WHO for use in drinking water cisterns to control mosquito larvae:

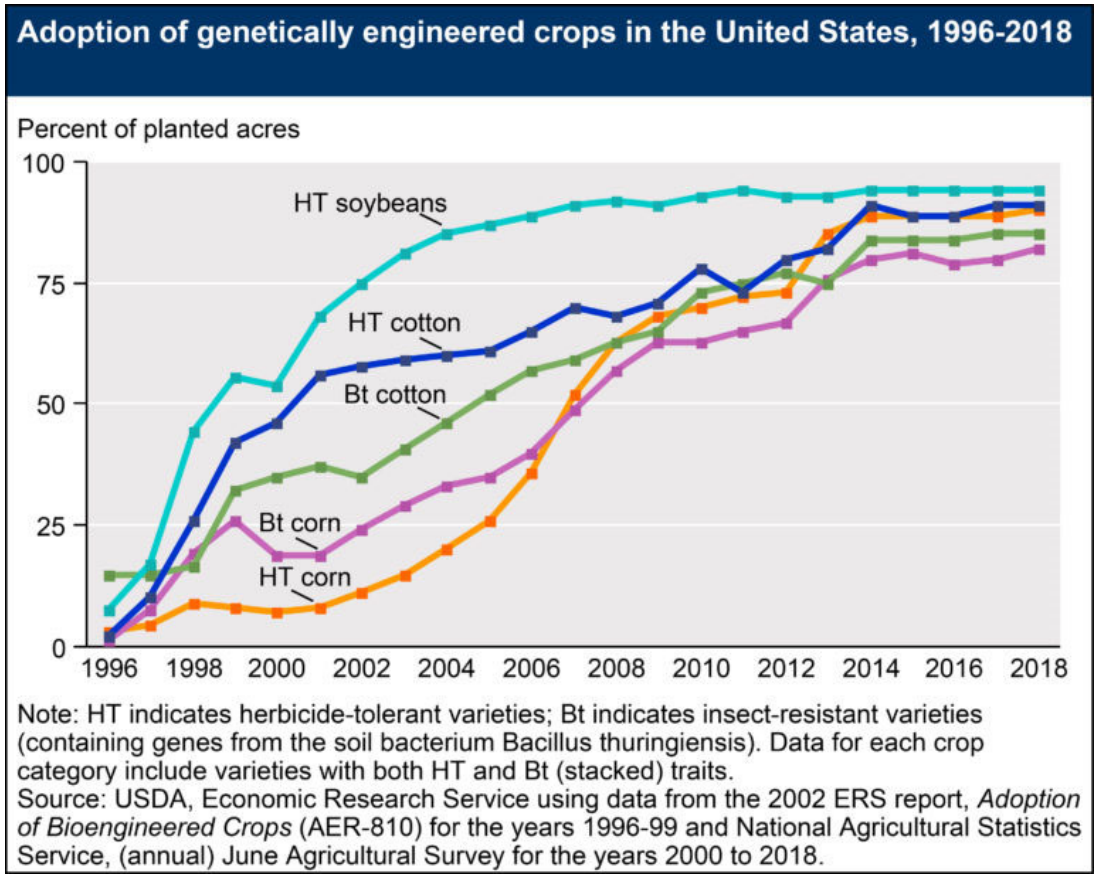


keeps insect in juvenile stage, or with immature organs

Sandoz sells this for use in flea collars (Precor)

Genetic modification of plants





Currently:

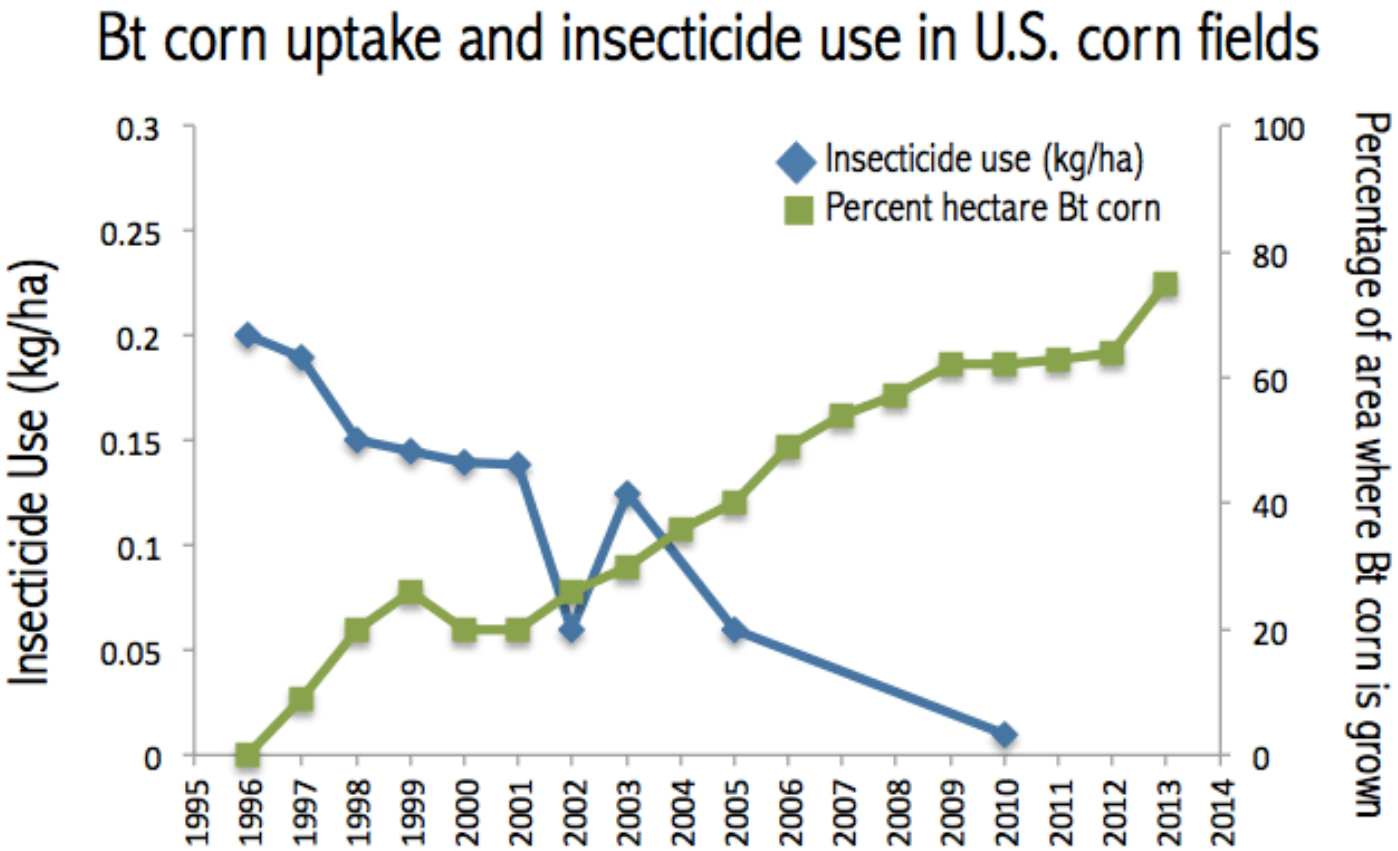
Sugar Beets
Soybeans
Corn
Cotton

Canola

New:
Rice
Tomatoes

with additional vitamin A

Using GMO plants can dramatically lower the need for insecticides:



Adapted from Malakof D. and Stokstad E. Pesticide Planet. Science Magazine. 16 August 2013.

Roundup Ready **GMO's have DNA inserted from organisms that possess a version of the enzyme that is *NOT* inhibited by glyphosate.**

Main issue:

Heavy reliance on Roundup is creating *'super weeds'* showing resistance to glyphosate. See: http://www.weedscience.com/