Pesticide Introduction

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ECS 3119 – Pesticides and Fish and Wildlife Resources
Skamania Lodge – Stevenson, WA
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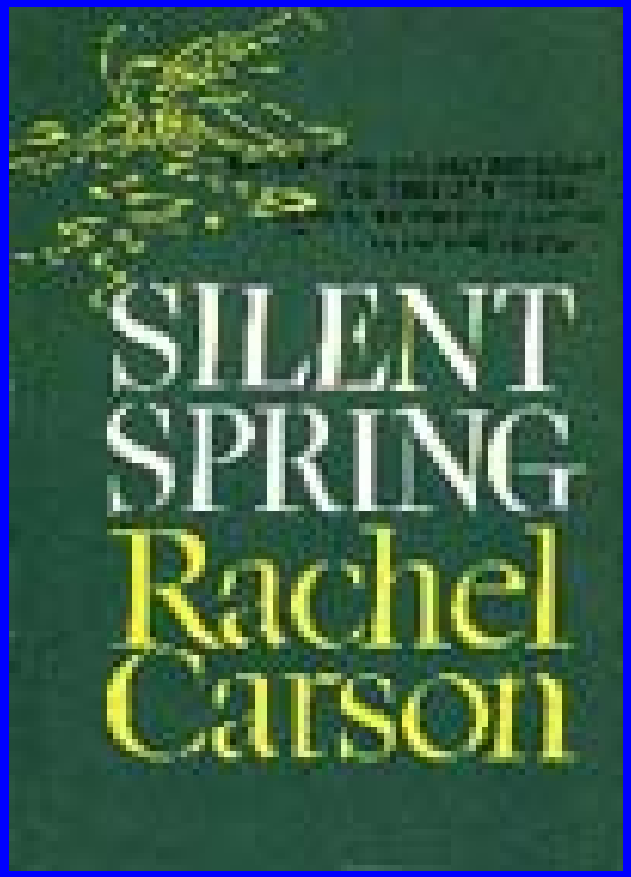
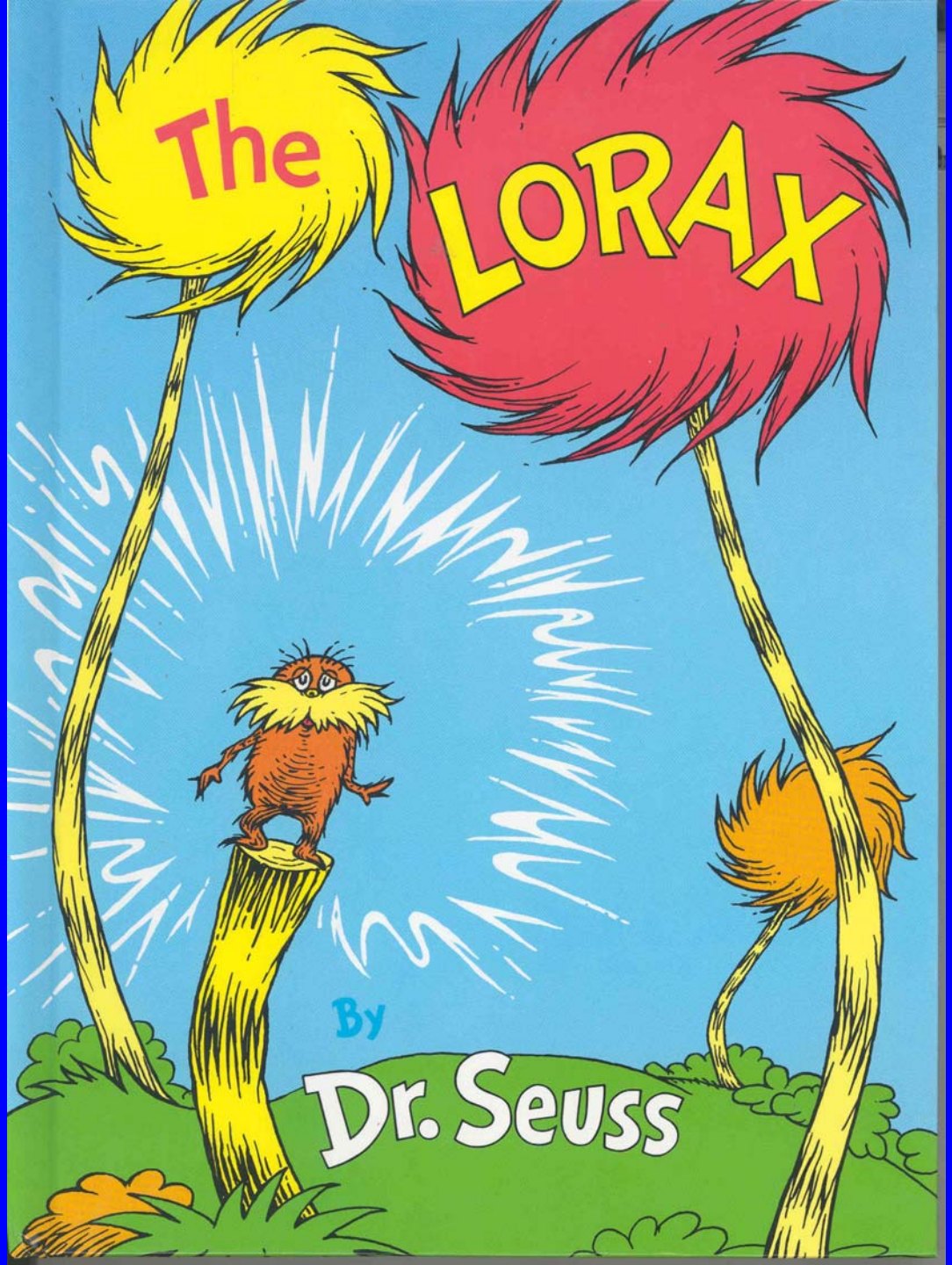


- Published in 1962, Rachel Carson warned society of the harm associated with synthetic chemicals, especially chlorinated pesticides like DDT.

- Not only does Silent Spring get credit for sparking the environmental movement, but it led to the creation of new agencies in the Federal government to oversee the use of agricultural pesticides and to much needed legislation to ensure that these regulations were enforced.

Federal Environmental Actions

- National Environmental Policy Act (NEPA) 1969
- Environmental Protection Agency (EPA) 1970
- Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) 1947, 1972 (Federal Environmental Pesticide Control Act), Amended 1975, 1978, 1988 and 1996
- Federal Water Pollution Control Act Amendments of 1972 (1977 & 1987). Currently known collectively as the Clean Water Act (CWA)
- Toxic Substances Control Act (TSCA) 1976
- Resource Conservation and Recovery Act (RCRA) 1976 (Amended 1984)
- Comprehensive Environmental Response, Conservation, and Liability Act (CERCLA) 1980



Required Reading

Pesticide:

any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest.

Pesticide Statistics

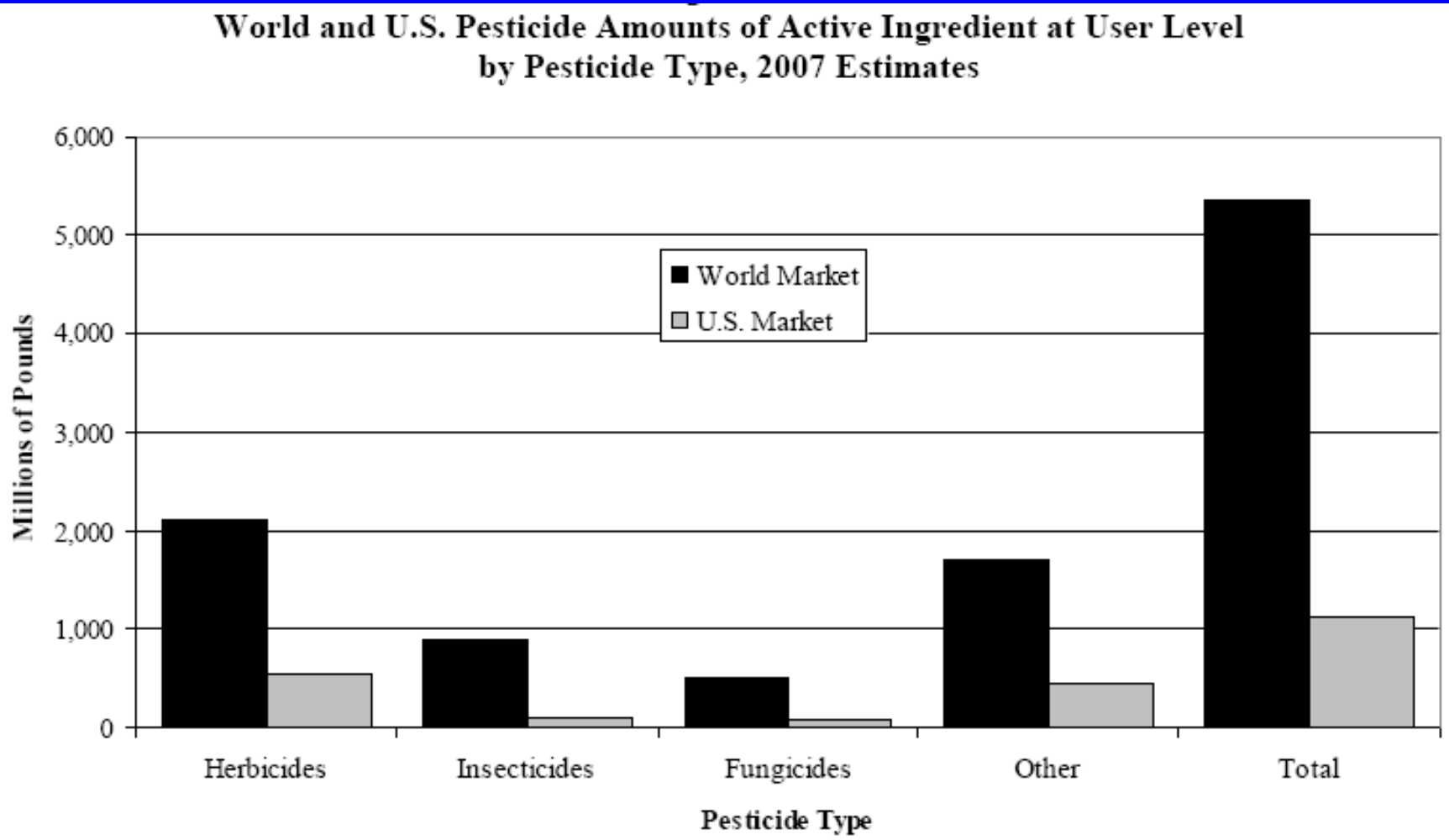
~ 5.2 billion pounds of active ingredient (a.i.) used annually worldwide

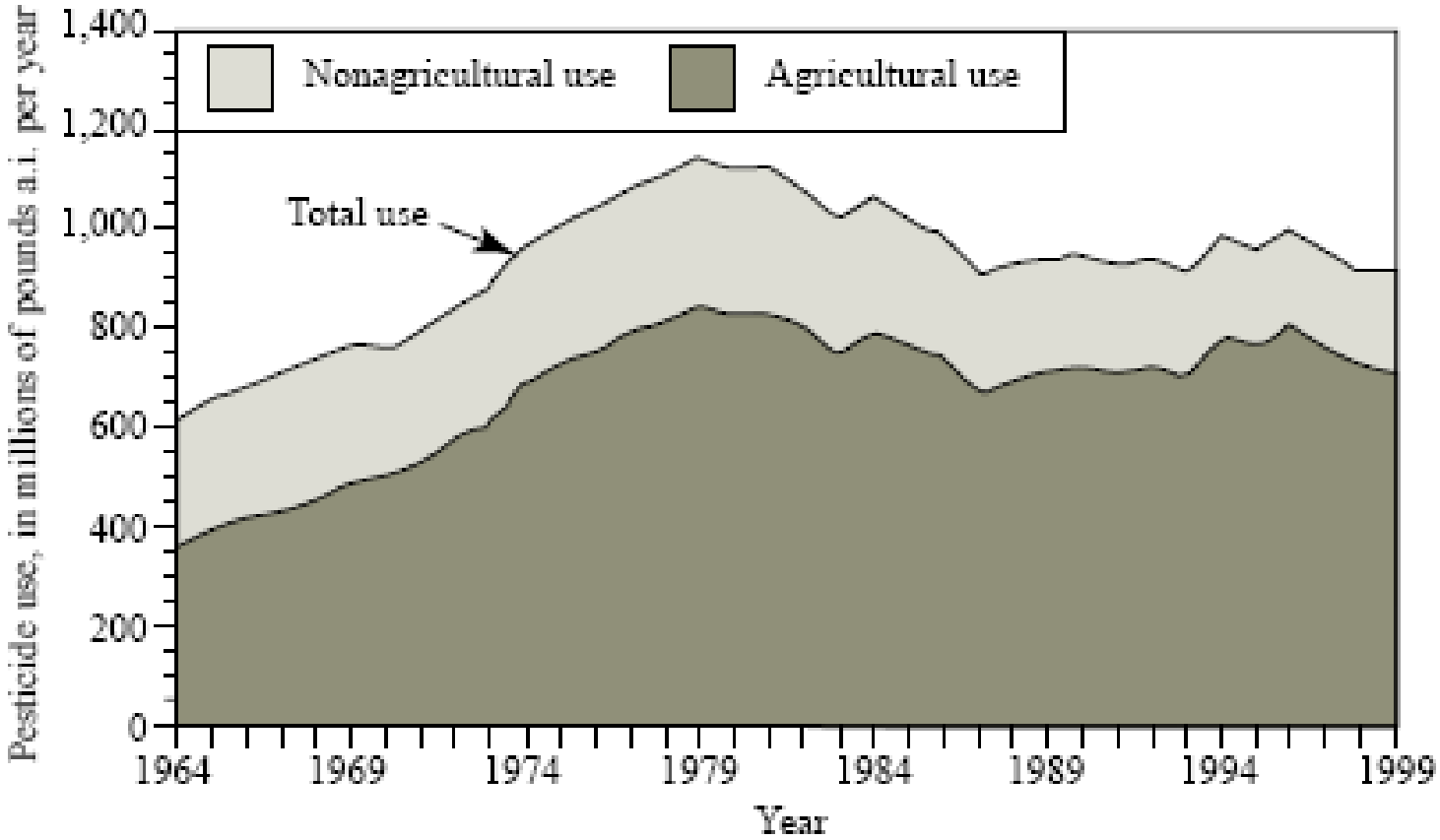
~ 1.1 billion pounds a.i. used per year in the U.S. (conventional and other pesticides) +

- ~ 389 million lbs. of specialty biocides +
- ~ 2.61 billion lbs. of chlorine/hypochlorites +
- ~ 954 million lbs. of wood preservatives

- $12.5 billion in U.S. sales/year (2007)
- $39.4 billion worldwide sales in 2007

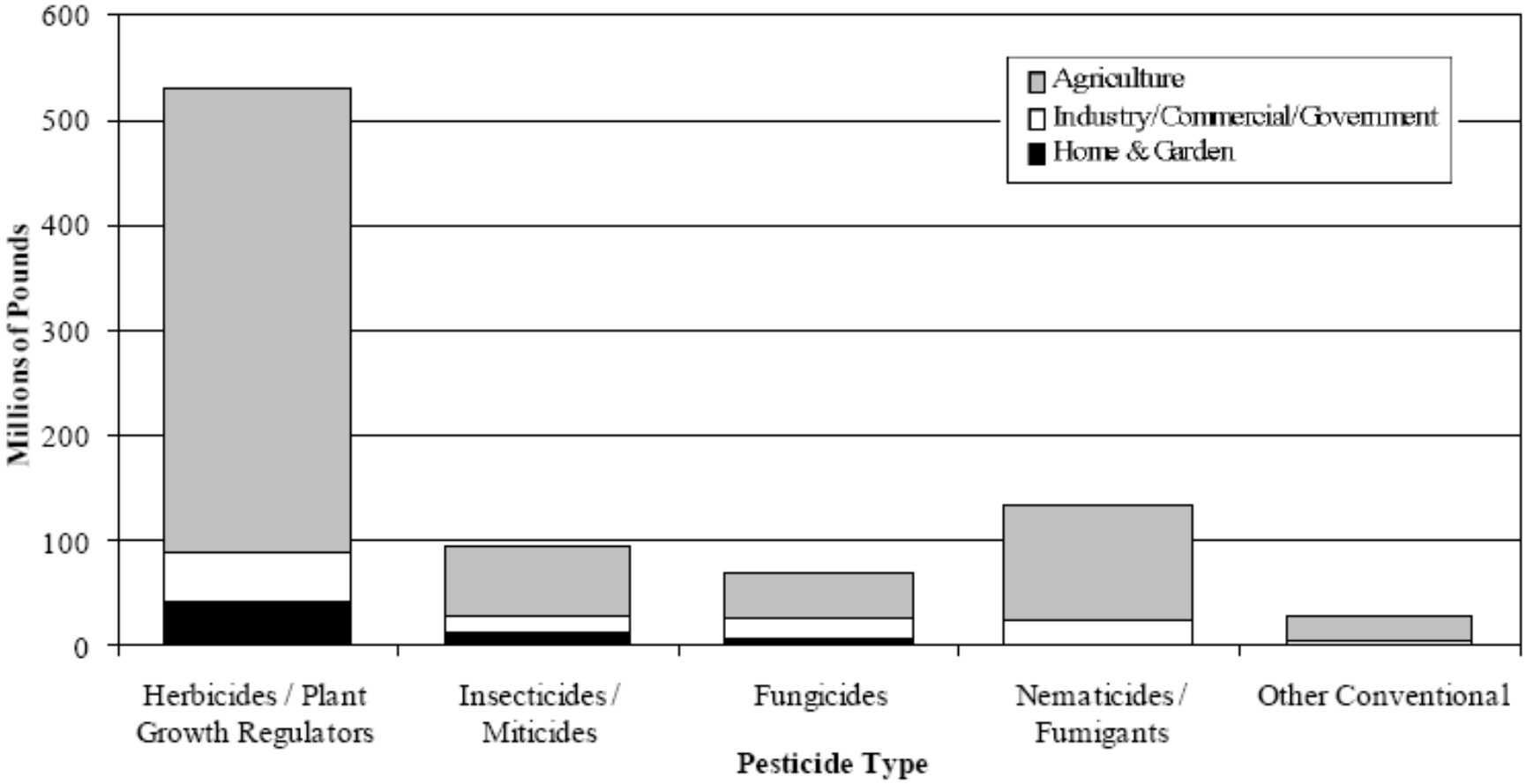
http://www.epa.gov/opp00001/pestsales/07pestsales/market_estimates06-07.pdf


World and U.S. Pesticide Amounts of Active Ingredient at User Level
by Pesticide Type, 2007 Estimates
6,000
5,000
4,000
3,000
2,000
1,000
0
Millions of Pounds
World Market
U.S. Market
Herbicides
Insecticides
Fungicides
Other
Total
Pesticide Type



Estimated amounts of pesticides use in the United States for agricultural and nonagricultural purposes from 1964 to 1999 (source Donaldson *et al.*, 2002).

Amount of Conventional Pesticide Active Ingredient Used in the United States by Pesticide Type and Market Sector, 2007 Estimates



Most Commonly Used Conventional Pesticide Active Ingredients - 2007

Agriculture	Home & Garden	Industry/Comm/Gov
Glyphosate (H)	2,4-D (H)	2,4-D (H)
Atrazine (H)	Glyphosate (H)	Glyphosate (H)
Metam sodium (Fum)	Carbaryl (I)	Chlorothalonil (F)
Metolachlor-S (H)	MCPP (H)	MSMA (H)
Acetochlor (H)	Pendimethalin (H)	Diuron (H)
Dichloropropene (Fum)	Pyrethroids (I)	Pendimethalin (H)

Components of a Pesticide Product

- active ingredient(s) + inert ingredient(s) = formulated or “end-use” products

- a.i. = the component (s) that kills or otherwise affects the pest (listed on the label).

- Inerts = an ingredient which is not "pesticidally" active (not required on the label).

  - This does not necessarily imply that these ingredients are non-toxic, non-flammable, or otherwise non-reactive; thus, the term “other ingredient” is more commonly being used.

Pesticide Statistics

~1100 a.i. and ~20,000 formulations registered in the U.S.

(~11,200 products registered in WA State alone)

WSDA data

In FY2010 (conventional pesticides)

- 41 new a.i. were registered representing many new uses & products (~513)
- 210 new uses (food and nonfood) for previously registered a.i.

http://www.epa.gov/pesticides/fees/2010annual_report/pria_annual_report_2010.pdf

PLATEAU®

herbicide

FOR WEED CONTROL, NATIVE GRASS ESTABLISHMENT AND TURF GROWTH SUPPRESSION ON PASTURES, RANGELAND AND NONCROP AREAS

ACTIVE INGREDIENT:

Ammonium salt of imazapic (±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid*	23.6%
INERT INGREDIENTS	76.4%
TOTAL	100.0%

*Equivalent to 22.2% (±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid
(1 gallon contains 2.0 pounds of active ingredient as the free acid)

U.S. Patent No. 4,798,619
EPA Reg. No. 241-365

KEEP OUT OF REACH OF CHILDREN

CAUTION!/PRECAUCION!

Si usted no entiende la etiqueta, busque a alguien para que se la explique a usted en detalle. (If you do not understand the label, find someone to explain it to you in detail.)

In case of an emergency endangering life or property involving this product, call day or night, 800-832-HELP.

See inside for Additional First Aid, Precautionary Statements, Directions for Use and Conditions of Sale and Warranty

BASF Corporation
26 Davis Drive
Research Triangle Park, NC 27709

BASF

"Inert/Other" Ingredients

EXAMPLES

- Synergist
- Diluent
- Carrier
- Sticker
- Spreader
- Surfactant
- The same chemical can be active in some and inert in other pesticides.

CATAGORIES OF INERTS

- List 1 - Toxic concern
- List 2 - Potential toxic concern
- List 3 - Unknown toxicity
- List 4 - Minimal concern
- Inerts can be toxic in and of themselves or enhance the toxicity of an active ingredient.

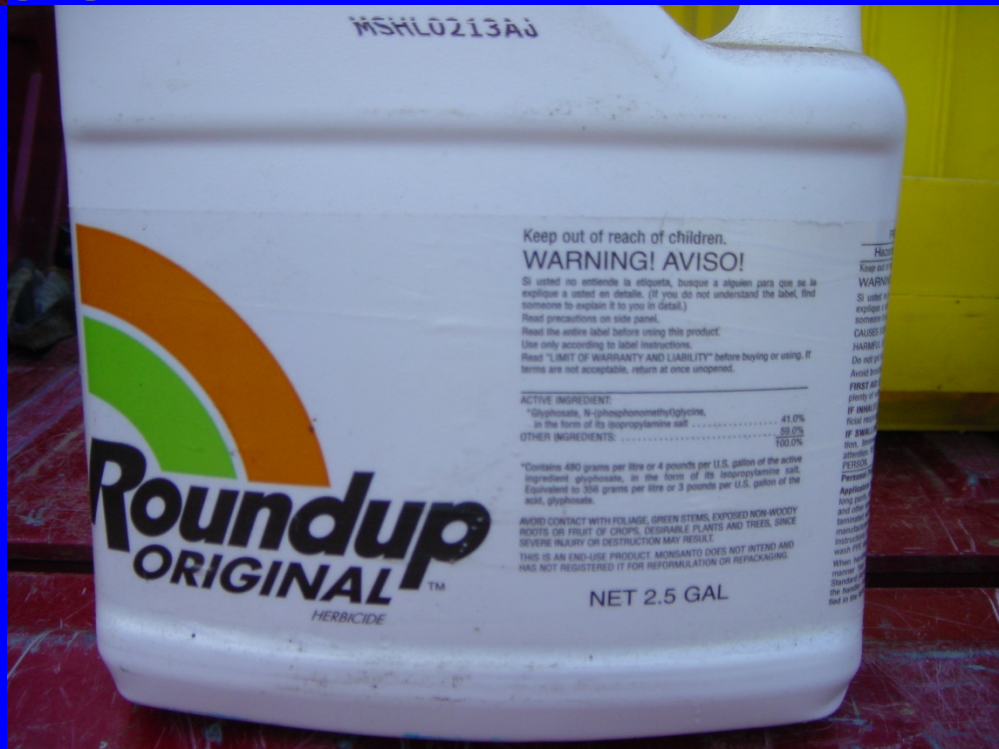
Rodeo (w/o surfactant)

RBT 96-hr. LC_{50} = 106 mg/L

GLYPHOSATE

Roundup Original

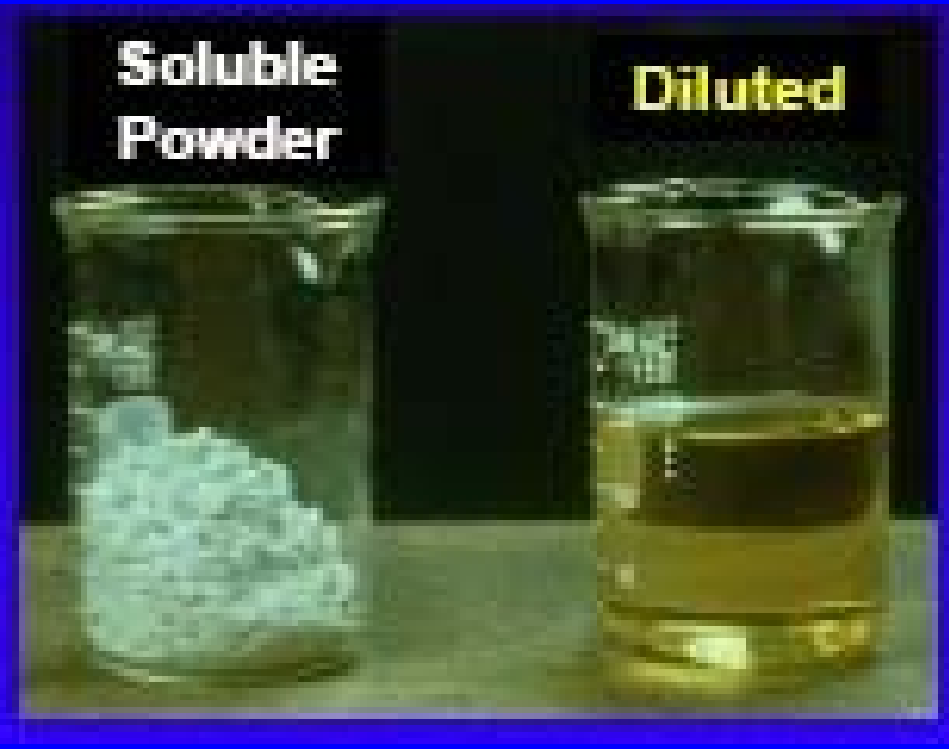
RBT 96-hr. LC_{50} = 8.2 mg/L



Formulation Types

- D = dust (*and d is for drift*)
- DF or F = dry flowable or flowable
- EC or E = emulsifiable concentrate (*w/solvent so easily absorbed*)
- G = granular
- S = solution
- SP = soluble powder
- ULV = ultra-low volume concentrate
- WSB or WSP = water-soluble bag or powder
- WP or W = wettable powder

See Formulation Guide in "Crop Protection Handbook"


Soluble
Powder
Diluted

Wettable
Powder
Diluted

Adjuvant -

Aids the operation or improves the effectiveness of a pesticide.

Examples:

- Wetting agents
- Spreaders
- Emulsifiers
- Dispersing agents
- Solvents
- Solubilizers
- Stickers
- Surfactants

Surfactant: a substance that reduces the interfacial or surface tension of a system or a surface-active substance (e.g. a group of non-ionic surfactants are the alkylphenol ethoxylates (APEs).

TANK-MIX is:

- A combination of two or more pesticides in the same spray tank to reduce the number of spray operations (convenience tank-mix) or to obtain better pest control than if the products were applied alone (positive tank-mix).
- The compatibility section of the label may also advise on tank-mixes which are known to be incompatible or on specific mixing instructions to be used with compatible mixes.
- A positive tank-mix occurs when a product label recommends a mixture to give an enhanced effect when the tank-mix is used.

Roundup
ORIGINAL
HERBICIDE
NET 2.5 GAL
WARNING! AVISO!
LI 700
NON-IONIC
PENETRANT
ACIDIFIER
DEPOSITION AID
DRIFT CONTROL AGENT
LOVELAND INDUSTRIES INC.
DANGER: Keep Out of Reach of Children
NET CONTENTS: 2.5 U.S. Gallons (9.462 litres)
MSR00113BJ
QUAMASTER
CAUTION!
NET 2.5 GAL

Toxicity Categories

Study	Category I	Category II	Category III	Category IV
Acute Oral	≥ 50 mg/kg	>50-500 mg/kg	>500-5000 mg/kg	>5000 mg/kg
Acute Dermal	≥ 200 mg/kg	>200-2000 mg/kg	>2000-5000 mg/kg	>5000 mg/kg
Acute Inhalation	≥ 0.05 mg/liter	>200-2000 mg/liter	>2000-5000 mg/liter	>5000 mg/liter
Eye Irritation	Corrosive or corneal involvement or irritation persisting >20 days	Corneal involvement or irritation clearing in 8-20 days	Corneal involvement or irritation clearing in < 7 days	Minimal effects clearing < 24 hrs
Skin Irritation	Corrosive	Severe irritation > 72 hrs	Moderate irritation > 72 hrs	Mild or slight irritation
Signal Word	**DANGER**	**WARNING**	**CAUTION**	**CAUTION**

http://www.epa.gov/pesticides/health/tox_categories.htm

Categories of Pesticides Based on Target Pests

- Insecticides
- Acaricides
- Molluscicides
- Algaecides
- Avicides
- Herbicides
- Fungicides
- Nematicides
- Microbiocides
- Rodenticides
- Piscicides

<u>Special Use</u> –
Wood Preservatives
Fumigants
Sterilants

- Selective or non-selective

Examples of Pesticides Grouped by Target Organism

Insecticides

Aldrin
Carbaryl
Carbofuran
Chlordane
Diazinon

Methyl Parathion
Ethyl Parathion
Toxaphene
Disulfoton
Malathion

Bt (Bti, Btk)
Permethrin
Spinosad
Dieldrin
Heptachlor

Examples of Pesticides Grouped by Target Organism

Herbicides/Algaecides

Alachlor	Dichlobenil	Triclopyr
Atrazine	Diuron	Imazapyr
Bromacil	Trifluralin	Diquat
2,4-D	Acrolein	Endothal
Glyphosate	Metsulfuron	

Examples of Pesticides Grouped by Function

Fumigants

Tetraethyl dithiopyrophosphate
Metam-sodium
1,3-Dichloropropene
Methylbromide
Cadmium Calcium Copper Zinc Chromate Complex
Chloropicrin

Examples of Pesticides Grouped by Function

<u>Wood Preservatives</u>

Creosote

Chromated Copper Arsenicals (CCA)

Pentachlorophenol

Pesticides by Chemistry

- Inorganics
- Biologicals
- Organics

PESTICIDES BY CHEMISTRY

Inorganic Pesticides

- metals
- metalloids
  (arsenic, boron)
- chlorates, borates

Inorganic Pesticides

Sulfur (S)

- Oldest pesticide (1000 BC); sulfur candles for bedbug fumigation & smallpox quarantine
- Today, an insecticide/acaricide & fungicide
- Accumulates in sediments and soil when used repeatedly
- Forms H_2S, toxic to almost all life, under anaerobic conditions in water.

Inorganic Pesticides

Arsenic (As)

- Contact stomach poison w/ insecticidal, herbicidal, bactericidal and protozoeal action
- A very early insecticide; Paris Green (copper acetoarsenite) used for Colorado potato beetle in 1800s
- Causes diarrhea and flaccid paralysis, especially pentavalent arsenic
- Disrupts carbohydrate oxidation & ATP production needed for muscle activity
- Accumulates in sediments and soil when used repeatedly

Inorganic Pesticides – Boron (B)

- Insect larvicidal & herbicidal action
- A required nutrient, but toxic at high levels to animals
- In plants, interferes with osmoregulation causing chlorosis & necrosis
- A respiratory irritant
- Affects stomach, intestines, liver, kidney, and brain; in insects acts as a stomach poison & cuticle wax absorber
- Accumulates in sediments and soil when used repeatedly
- At high levels, causes embryotoxicity in bird eggs

Inorganic Pesticides – Copper (Cu)

- In 1800s used as a fungicide; now algaecide use
- Bordeaux Mix in France against mildew on grapes
- Accumulates in soil/sediments when used repeatedly
- Few mammalian/avian effects – only at extremely high doses
- Pronounced toxicity to aquatic species at ppb concentrations & low hardness; salmonids & invertebrates especially sensitive

Chlorates, Borates and Metaborates

(ClO_3, BO_3, and $NaBO_2$s)

- Nonselective herbicides, toxic to all plants – kills phloem, increase respiration, decrease catalase activity, depleting reserves
- Used along roads & as defoliant/desiccant, 30-50x more toxic than NaCl and long soil half-life
- Acts as sterilant alone or in combos
- Highly soluble, absorbed through roots
- Membrane irritation, blood cell & kidney damage; weight loss in mammals and birds plus reduced egg production

Biological Pesticides – Bacillus thuringiensis (Bt)

- Bacterial pesticide acts primarily as stomach poison
- Non-toxic to vertebrates and selective to insects and other invertebrates
- Target organisms: moths and other Lepidoptera
- Bti (israeliensis) is a mosquito larvacide
- Incorporated into crops such as corn – GMO
- Trade names include: Foray, Dipel and Thuricide

ORGANIC PESTICIDES BY CHEMICAL FAMILY

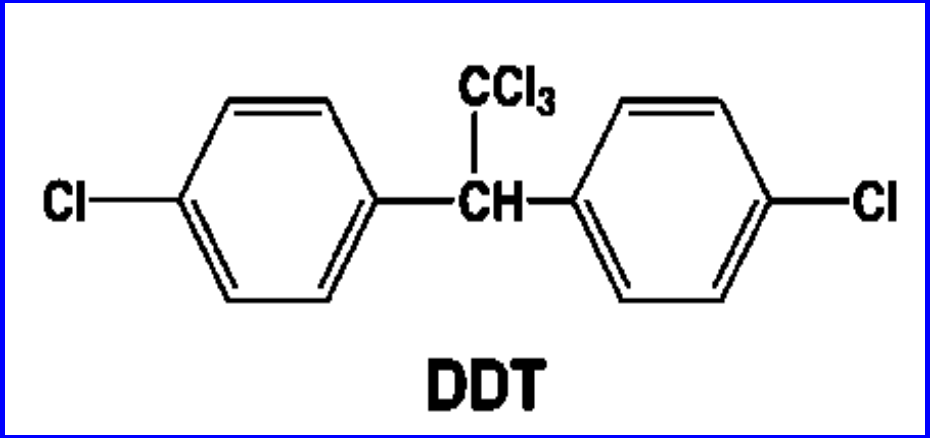
- <u>Substituted Organics</u>
  - Organochlorine
  - Chlorophenoxys
  - Triazines
  - Carbamates
  - Pyrethroids
  - Sulfonylureas
  - Organophosphates
  - Imidazolinones

+ many, many more. See:

http://www.hclrss.demon.co.uk/summ_groups.html

Organochlorine Pesticides- OCs

DDT	HCH
Endrin	Endosulfan
Toxaphene	HCB
Dieldrin	Dicofol
Mirex	Methoxychlor



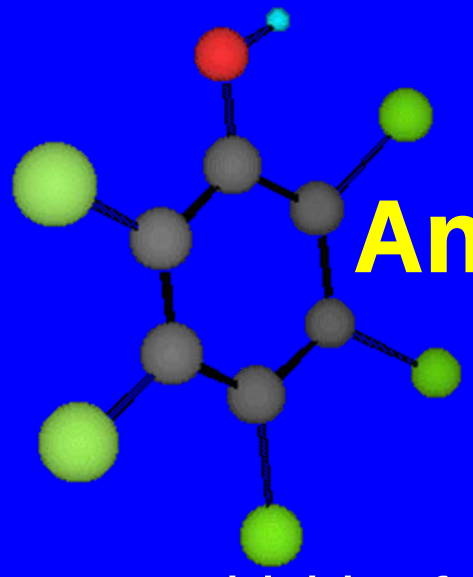
- Long half-lives (years, decades)
- Affect plasma membranes including nerve membranes
- Low acute toxicity to mammals & birds, but acutely toxic to invertebrates & fish [endrin, toxaphene, endosulfan]
- Most are lipophilic; some bioaccumulate and biomagnify
- DDT causes egg shell thinning, especially in fish-eating birds and other raptors.
- Many are known or suspected endocrine disruptors.

Organochlorine Pesticides - DDT

- Chemically stable $T_{1/2}$ = 17+ yrs in soil
- Lipophilic ($T_{1/2}$ = 8 yr) and poorly metabolized
- Affect nervous system axons, causing "leakage" of Na^+ ions; neurons fire impulses spontaneously, causing muscle twitch-- "DDT jitters"-- followed by convulsions and death
- Toxicity to insects enhanced at low temperatures
- Highly toxic to fish, especially eggs
- Biomagnifies in food web
- Generally low acute toxicity to birds, but affects egg shell thickness, egg weight

DDT/DDE Acute Toxicity

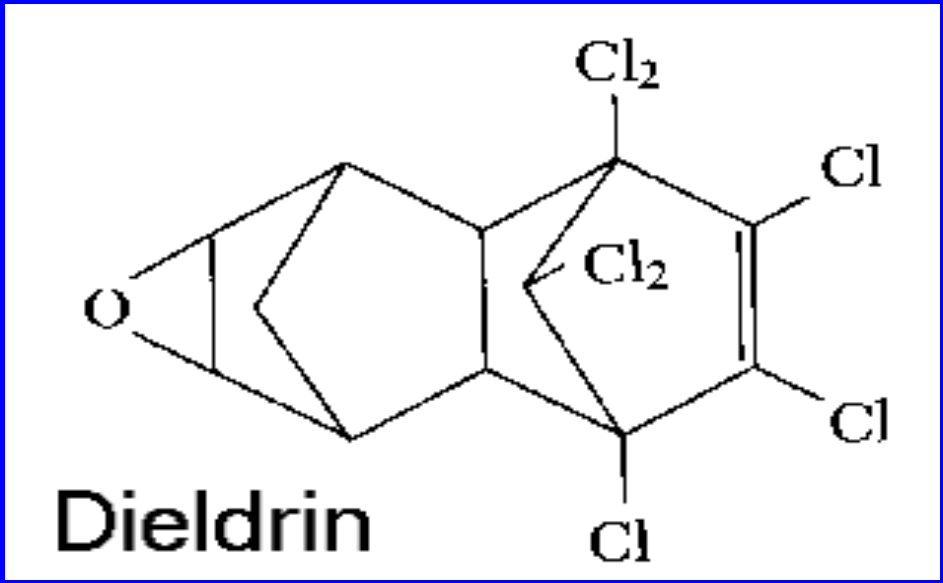
- *Daphnia- LC_{50} = 0.36 µg/L*
- *Mayfly- LC_{50} = 0.3 µg/L*
- *Carp- LC_{50} = 3,000 µg/L*
- *Rat- LD_{50} = 113 mg/kg*
- *Mallard- LD_{50} >2,240 mg/kg*



An Important Substituted OC: (Pentachlorophenol) PCP

- Herbicide, fungicide, insecticide, & preservative
- Absorbed by inhalation, dermal, & oral routes, affects respiratory, cardiovascular, CNS, & immune systems
- Linked to blood & lymph cancers
- Found in blood & urine, slowly metabolized
  - ($T_{1/2}$ in urine 20 days)
- Metabolized to pentachloroanisole (residue in fish)
- Dioxins often present as contaminants at PCP sites

Cyclodienes

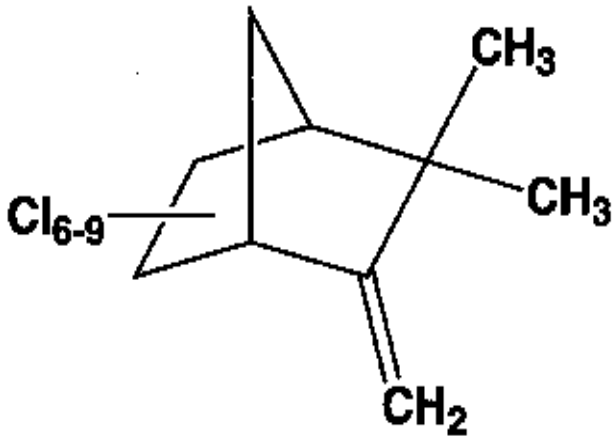


- Endrin
- Dieldrin
- Endosulfan
- Aldrin
- Chlordane
- Heptachlor
- Mirex

- Extremely persistent & lipophilic
- Also biomagnify
- Resistance now common
- Potent neurotoxins, disrupt transmission at ganglia
- Toxicity increases w/ temperature

Polychloroterpenes: Toxaphene

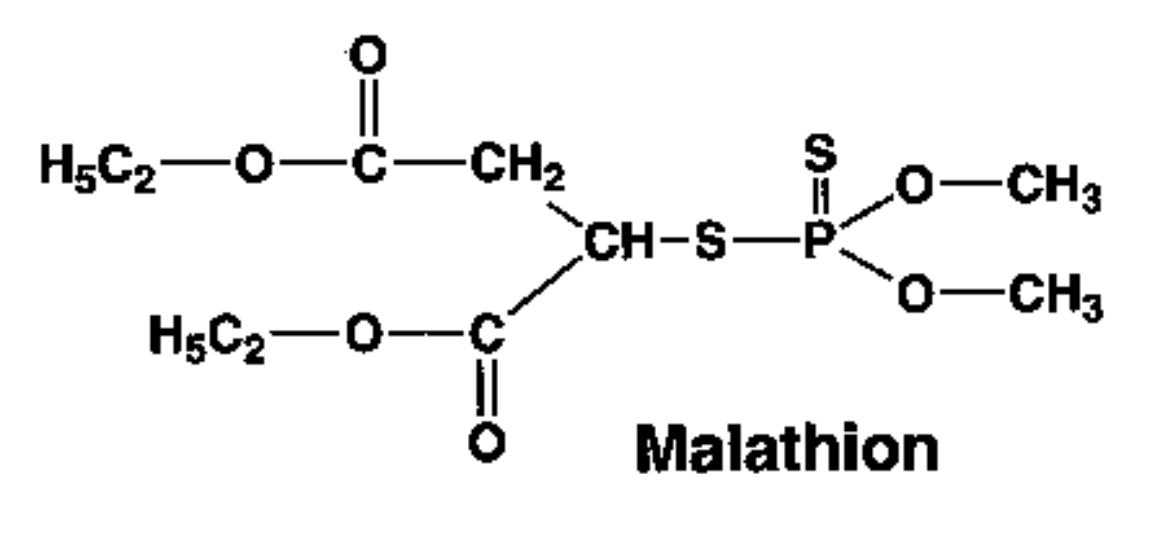
- Mixture of > 170 10-Carbon polychlorinated derivatives
- Persist in soil
- Highly toxic to birds & mammals, less toxic to fish, more readily metabolized
- Not as lipophilic as other OCs
- Act on neurons, causing Na/K imbalance, similar to cyclodienes
- More volatile than other OCs
- Analyzed with difficulty
- Used on cotton, alfalfa, rodents, domestic animals



Toxaphene: A Mixture of Chlorinated Camphene

Organophosphates (OPs)

Malathion
Methamidophos
Monocrotophos
Famphur
Disulfoton
Naled
Diazinon
Azinphos-methyl
Parathion



Example - Malathion

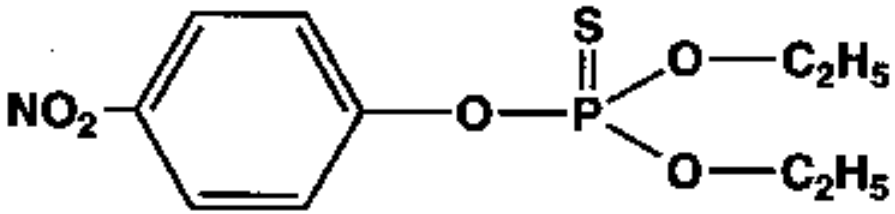
- Half-Life in Soil 24 hrs to 6 days
- Half-Life in Water 1.5 days to 21 weeks
- Half-Life in Air 1.5 days
- Log K_{OH} 2.36 (moderately lipophilic)
- Boiling Point 156-157 C
- Solubility in Water 143 ppm at 20 C

Malathion Toxicity

Rat Oral LD50	*1375 - 2800 mg/kg*	*moderately toxic*
Invertebrate EC50	*0.001 ppm - 1 ppm*	*super to highly toxic*
Mallard LD 50	*1485 mg/kg*	*moderately toxic*
Chicken LD50	*948 mg/kg*	*moderately toxic*
Oral LC50 Bobwhite Quail	*3497 ppm*	*slightly toxic*
Oral LC50 Pheasants	*2639 ppm*	*slightly toxic*
Walleye LC50	*0.064 ppm*	*extremely toxic*
Brown Trout LC50	*0.101 ppm*	*highly toxic*
Cutthroat Trout LC50	*0.280 ppm*	*highly toxic*
Fathead Minnows LC50	*8.6 ppm*	*moderately toxic*

Phenyl OPs – more stable

- Parathion
- Diazinon
- Fenthion
- Fenitrothion
- Temephos

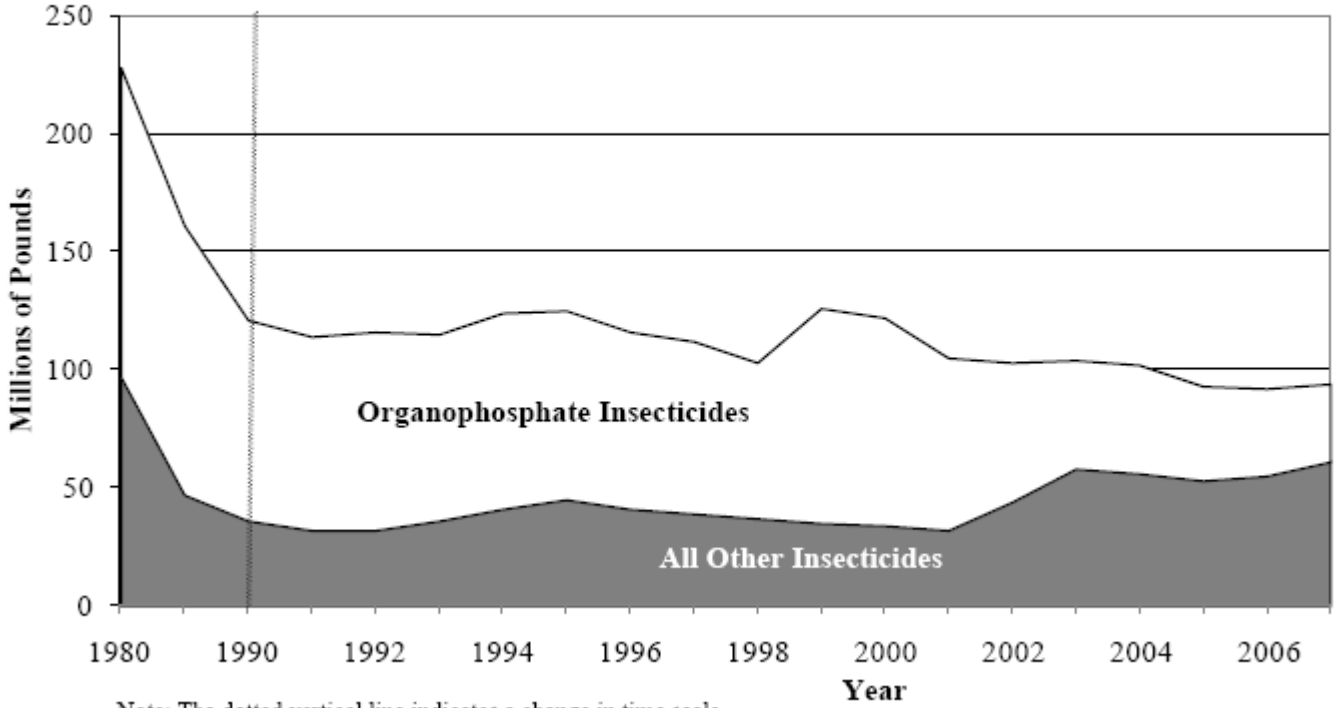


Ethyl-Parathion

OP History & Characteristics

- Originally WW II nerve agents
- Most acutely toxic to mammals & birds
- Cause acetylcholinesterase inhibition (AChE Testing)
- Not lipophilic, Metabolized easily
- Often somewhat soluble but typically hydrolyze within a few hours or days

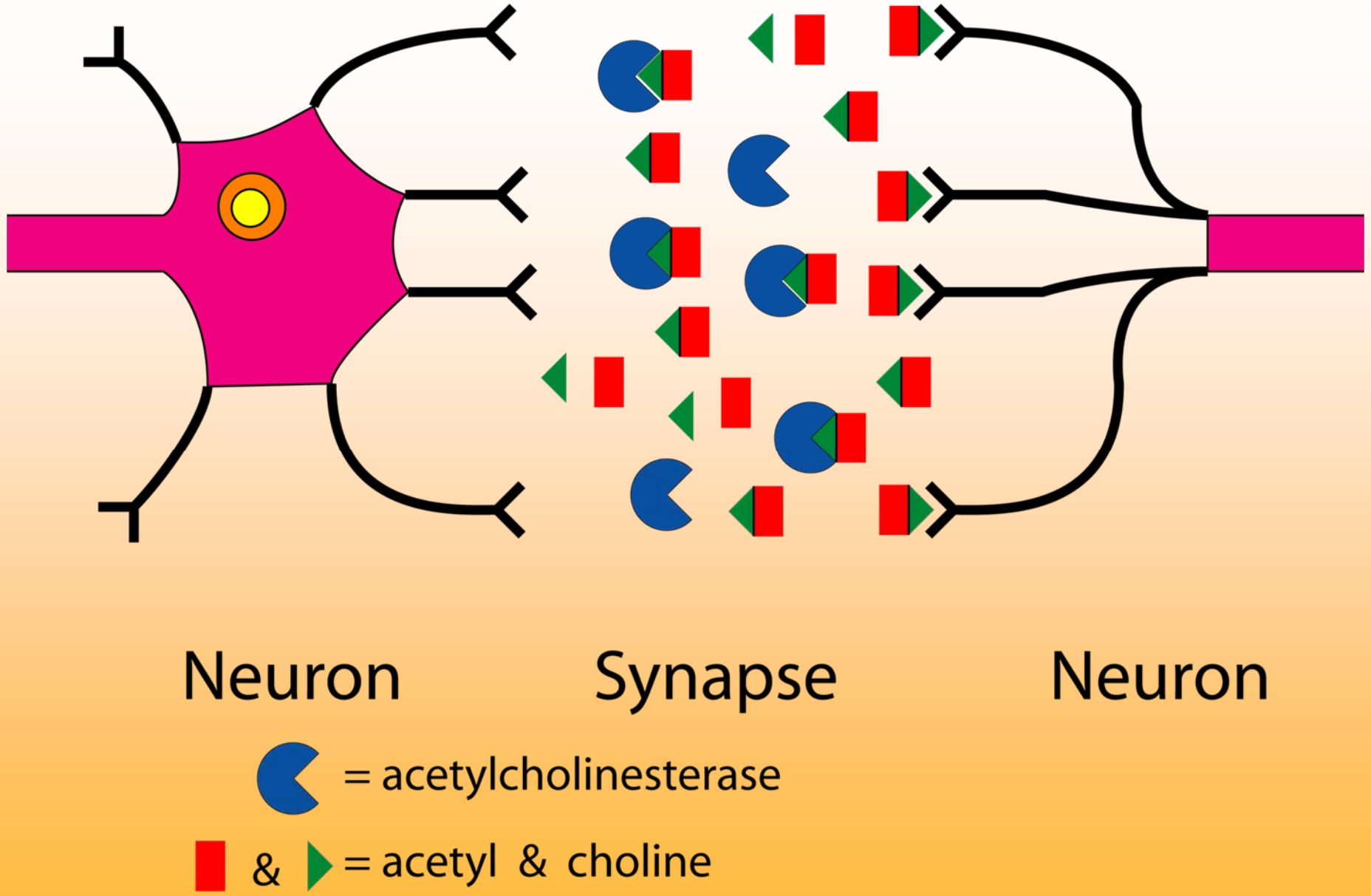
Total Amount of Organophosphate and All Other Insecticide Active Ingredients Used in the United States in All Market Sectors, 1990–2007



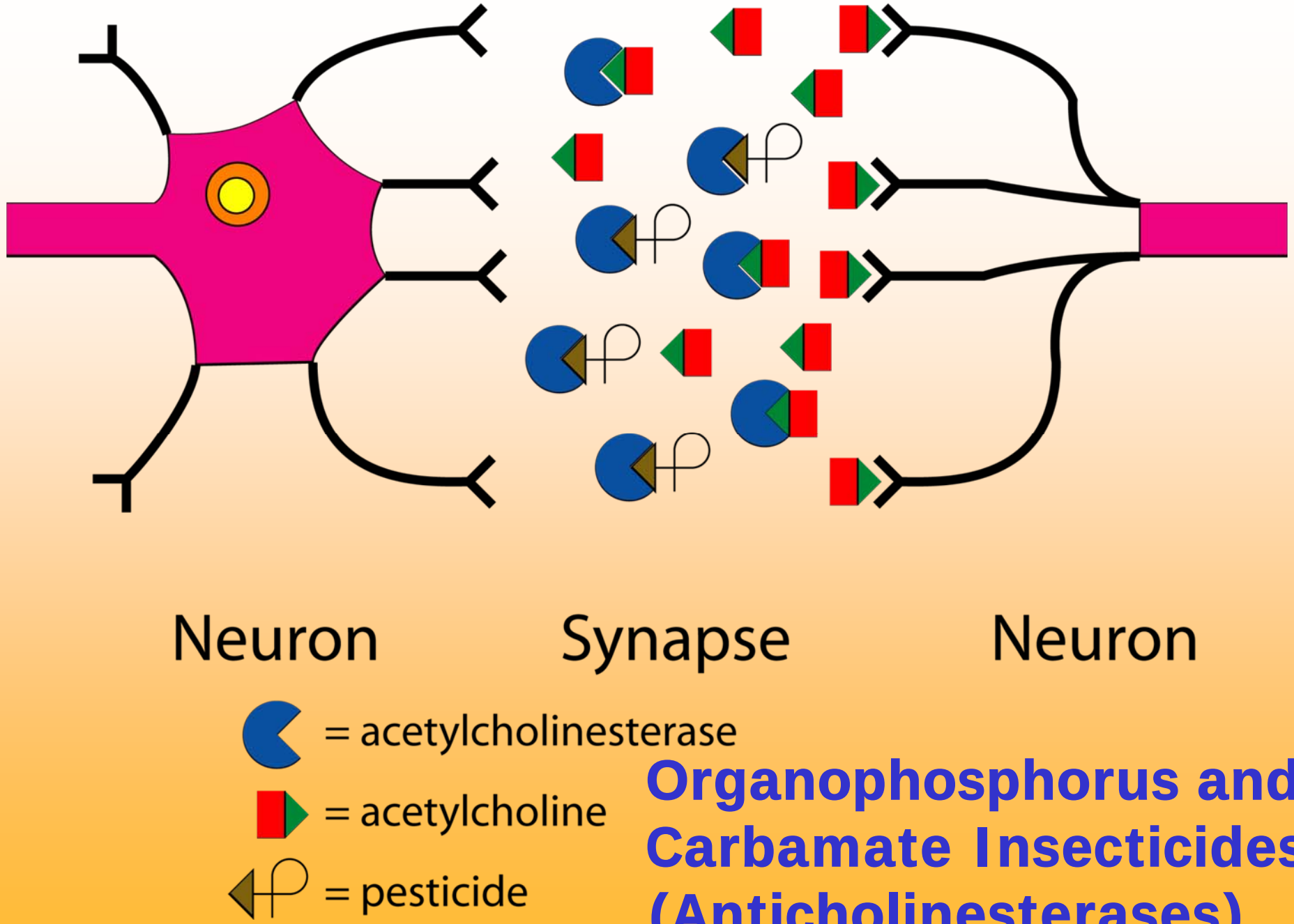
Note: The dotted vertical line indicates a change in time scale.

Active Ingredient	2007
	Rank
Chlorpyrifos	1
Malathion	2
Acephate	3
Naled	4
Dicrotophos	5
Phosmet	6
Phorate	7
Diazinon	8
Dimethoate	9
Azinphos-Methyl	10

http://www.epa.gov/opp00001/pestsales/07pestsales/market_estimates06-07.pdf

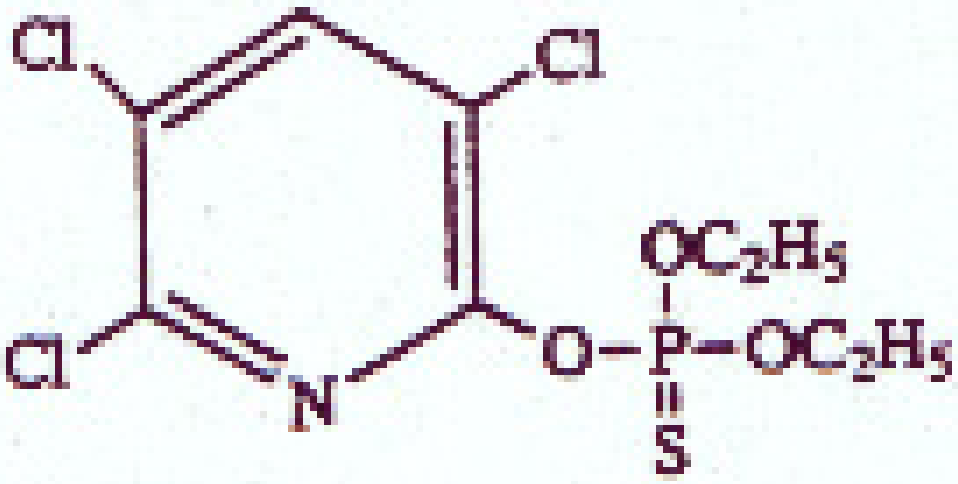


Overview of the nervous system



Organophosphorus and Carbamate Insecticides (Anticholinesterases)

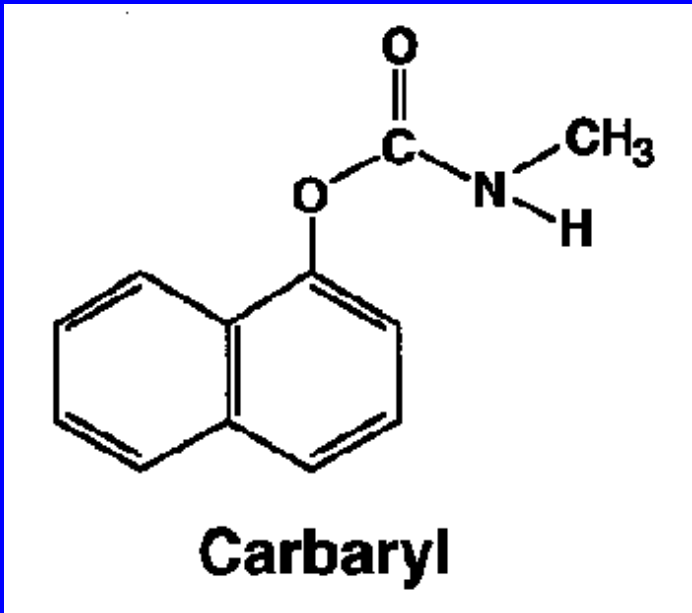
Chlorpyrifos – A Hybrid OP/OC (a chlorinated organophosphorus)



Chlorpyrifos

Carbamates

- Derivatives of carbamic acid
- Also Inhibit AChE
- Reversible inhibition, unlike OPs

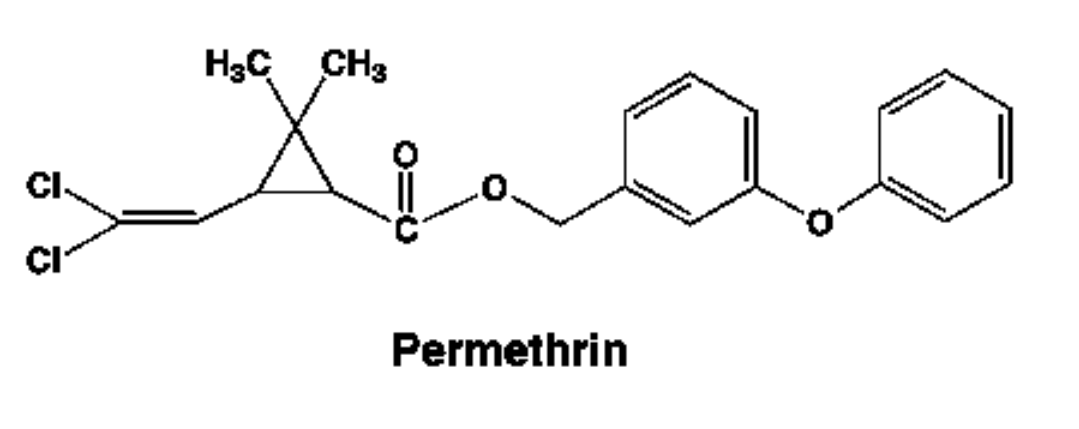


Examples

- **Carbaryl**
- **Bendiocarb**
- **Carbofuran**
- **Propamocarb**
- **Propoxur**
- **Aldicarb**

Pyrethrins & Pyrethroids

- Pyrethrin
- Resmethrin
- Sumithrin
- Permethrin
- Cypermethrin



- Pyrethrum is contained in Chrysanthemum plants, costly & unstable in light, prototype for pyrethrin
- Effective insecticides at very low rates
- Low toxicity to birds & mammals; readily metabolized
- Super toxic to aquatic species
- Low leachability but sorbs to soil w/ long half-life
- Axonic poisons; keep Na^+ channels open in neuronal membranes
- Several generations – progressively less susceptible to UV and more toxic

Phenoxyacetic Acid Herbicides (= chlorophenoxy acids)

Examples

2,4-D (numerous formulations)

MCPA

Mecroprop

Triclopyr

- Auxins (dicot growth inhibitors/regulators)
- Soluble systemics, Absorbed by roots
- Often detected in ground & surface waters
- Moderate acute toxicity to birds & mammals
- Possible endocrine disruptors
- Linked to non-Hodgkin's Lymphoma (2,4-D, MCPA) in some studies
- 2,4-D linked to ovarian tumors in canines
- Amine formulations less toxic to aquatic species and less volatile

Triazine Herbicides

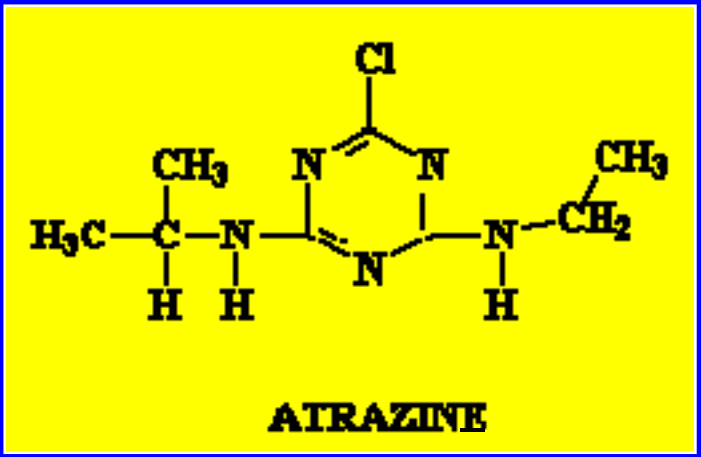
Examples

Atrazine

Simazine

Cyanazine

Prometon

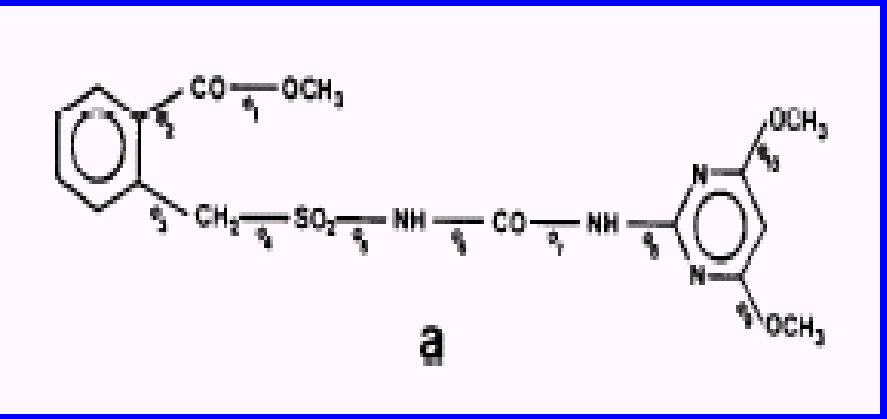


- Systemics, inhibit photosynthesis & plant enzymes in broadleaves, leading to chlorosis and death
- Fairly water-soluble & fairly volatile
- Hydrolyzed at pH 5.8-6.5; otherwise stable ($T_{1/2}$ = 5-37 wks in soil; up to 83 wks in anaerobic waters)
- Slightly to moderately toxic to mammals, highly toxic to some fish, extremely toxic to some invertebrates, cause frog deformities & mortalities at labeled rates

Sulfonylurea Herbicides

Examples

- Chlorsulfuron
- Metsulfuron
- Halosulfuron
- Bensulfuron
- Nicosulfuron
- Sulfmeturon



- Systemics, inhibit amino acid synthesis & cell division in dicot roots & shoots (& some grasses)
- Practically nontoxic on acute basis
- Hydrolyzed under acidic, high temperature conditions
- Very stable in high pH soils & waters
- Extremely phytotoxic but few known effects on vertebrates or inverts directly (limited data)
- Can volatilize and move off-site harming non-target plants

Quiz or Questions?