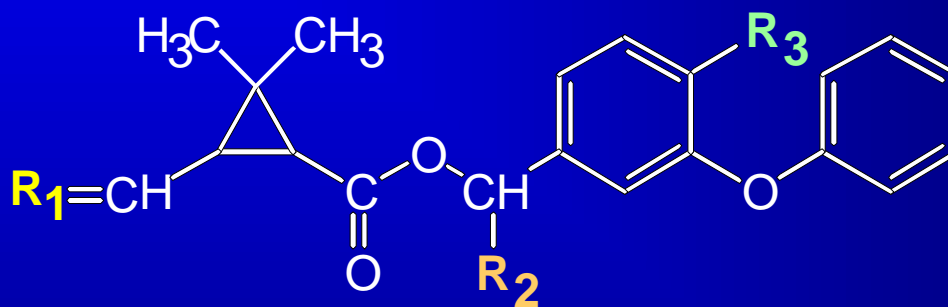


Synthetic Pyrethroids and California Surface Water

Use patterns, properties, unique aspects



Frank Spurlock

Environmental Monitoring
California Department of Pesticide Regulation

I. Introduction: California Surface Water & Pesticides

II. California Ag and Urban Insecticides

use trends

pyrethroid active ingredients

pyrethroid use patterns

III. Pyrethroid Environmental Fate Overview

IV. Pyrethroid Aquatic Risk Assessment Issues

Pesticides and water quality



1980s

rice herbicides
molinate and thiobencarb

1980s

endosulfan

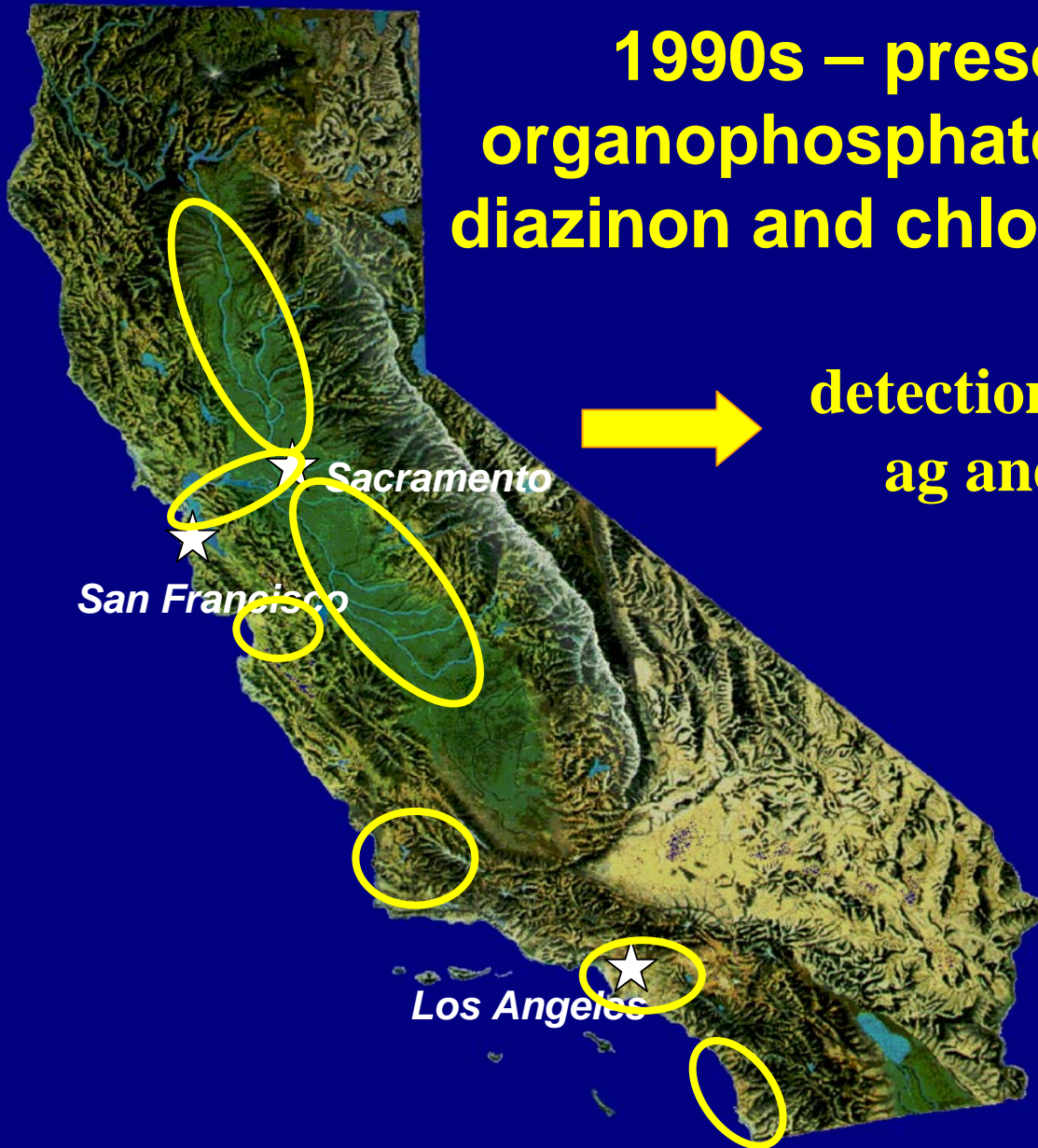
★ **Sacramento**

★ **San Francisco**

★ **Los Angeles**

Pesticides and water quality

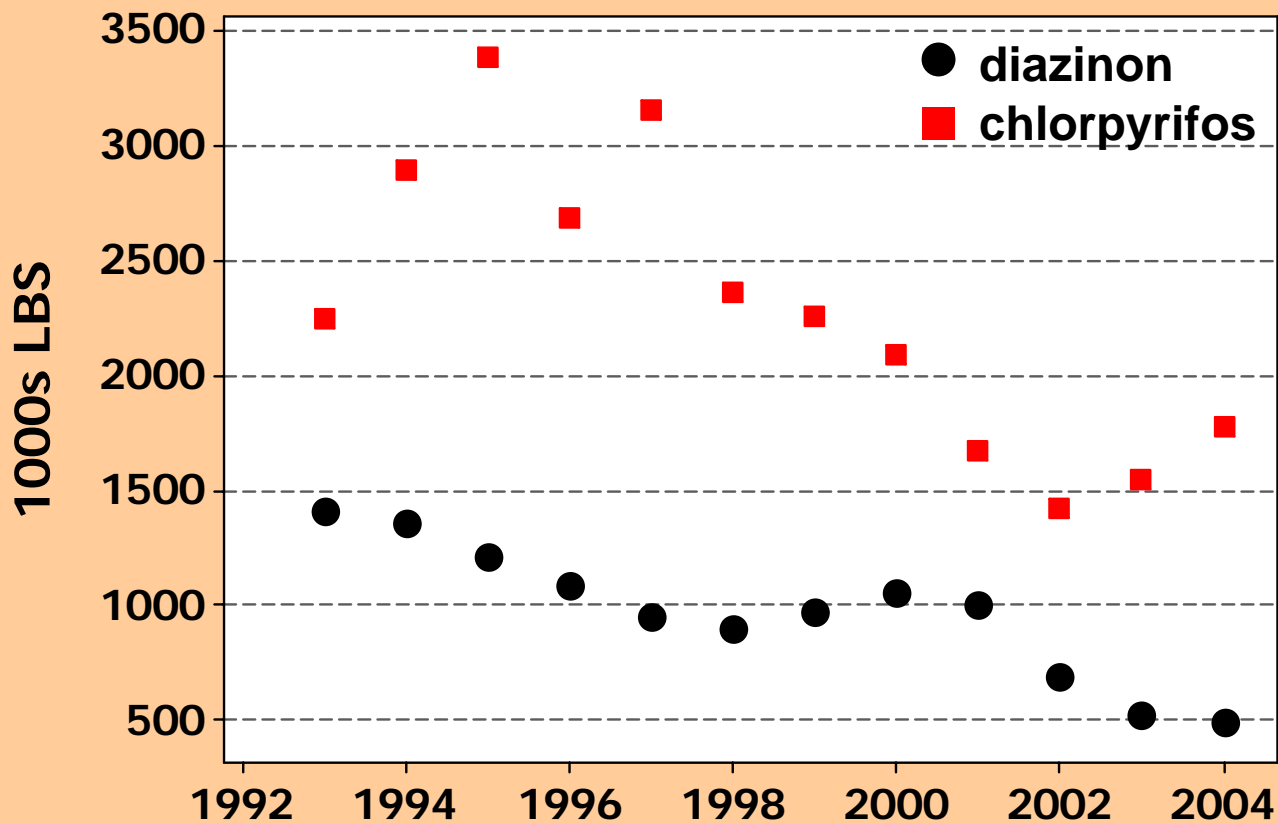
**1990s – present
organophosphates, e.g.
diazinon and chlorpyrifos**



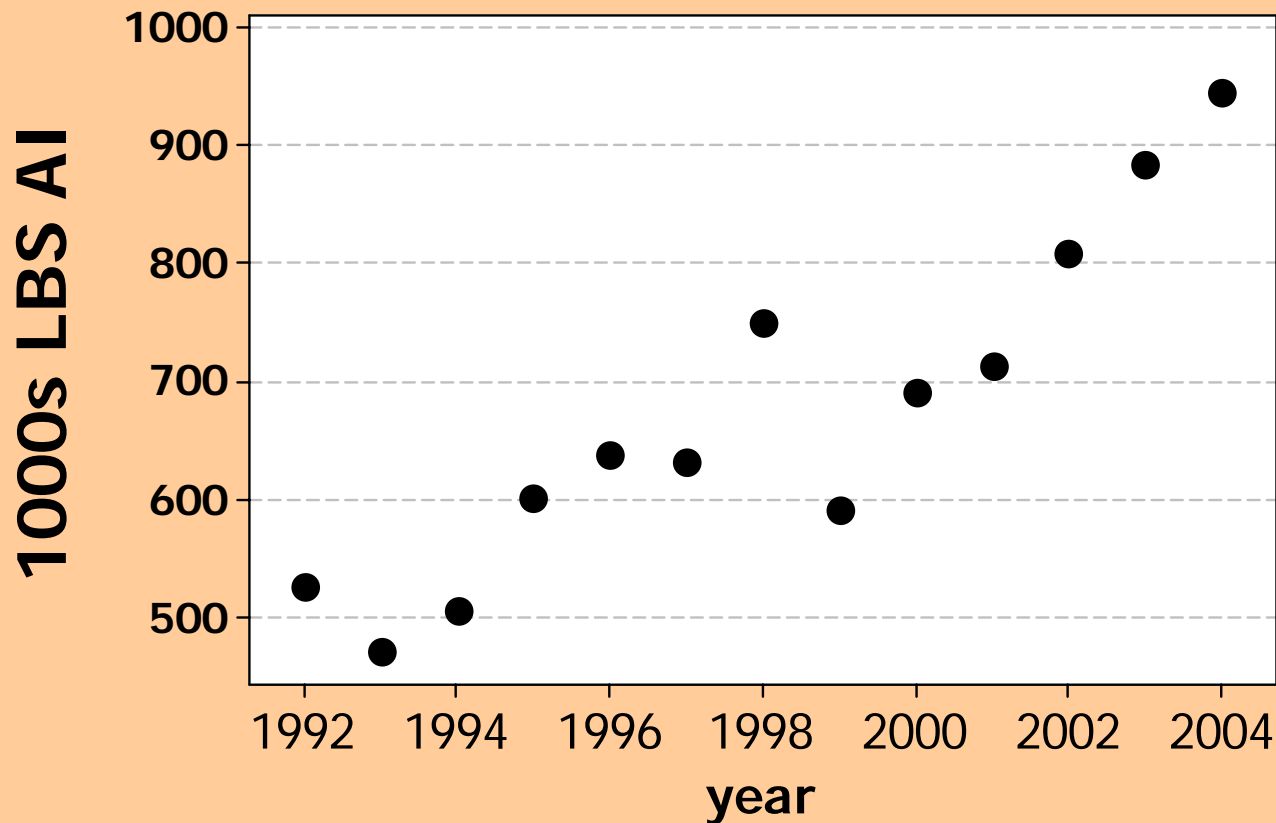
**detections and toxicity in both
ag and urban waterways**

Diazinon and chlorpyrifos use trends

production ag and commercial structural



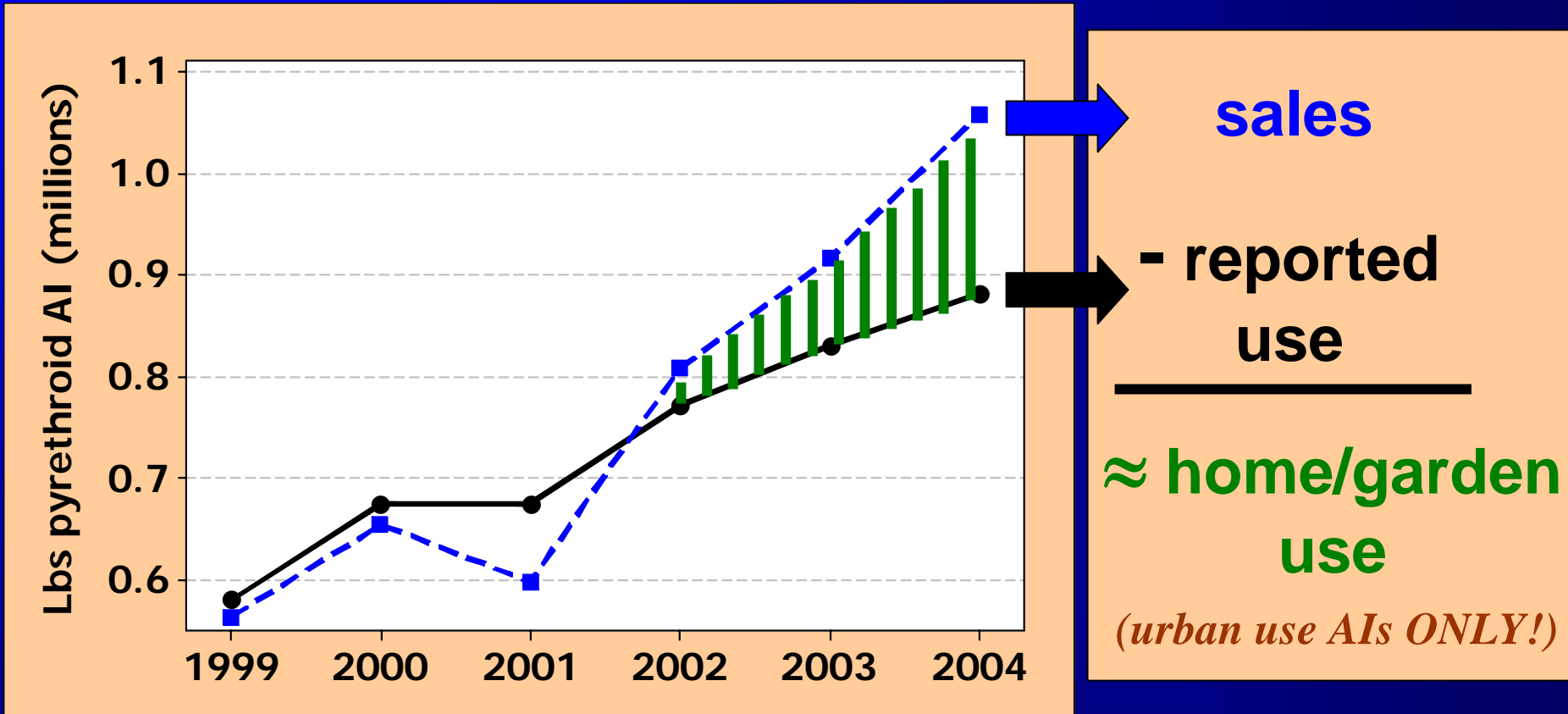
Synthetic pyrethroid use trend - Σ 25 AIs *production ag and commercial structural*



2004 TOP 7
permethrin
cypermethrin
bifenthrin
cyfluthrin
fenpropathrin
 λ -cyhalothrin
esfenvalerate

**>30000 lbs
use in 2004**

Inferring home & garden use trend from sales and reported (ag + structural) use



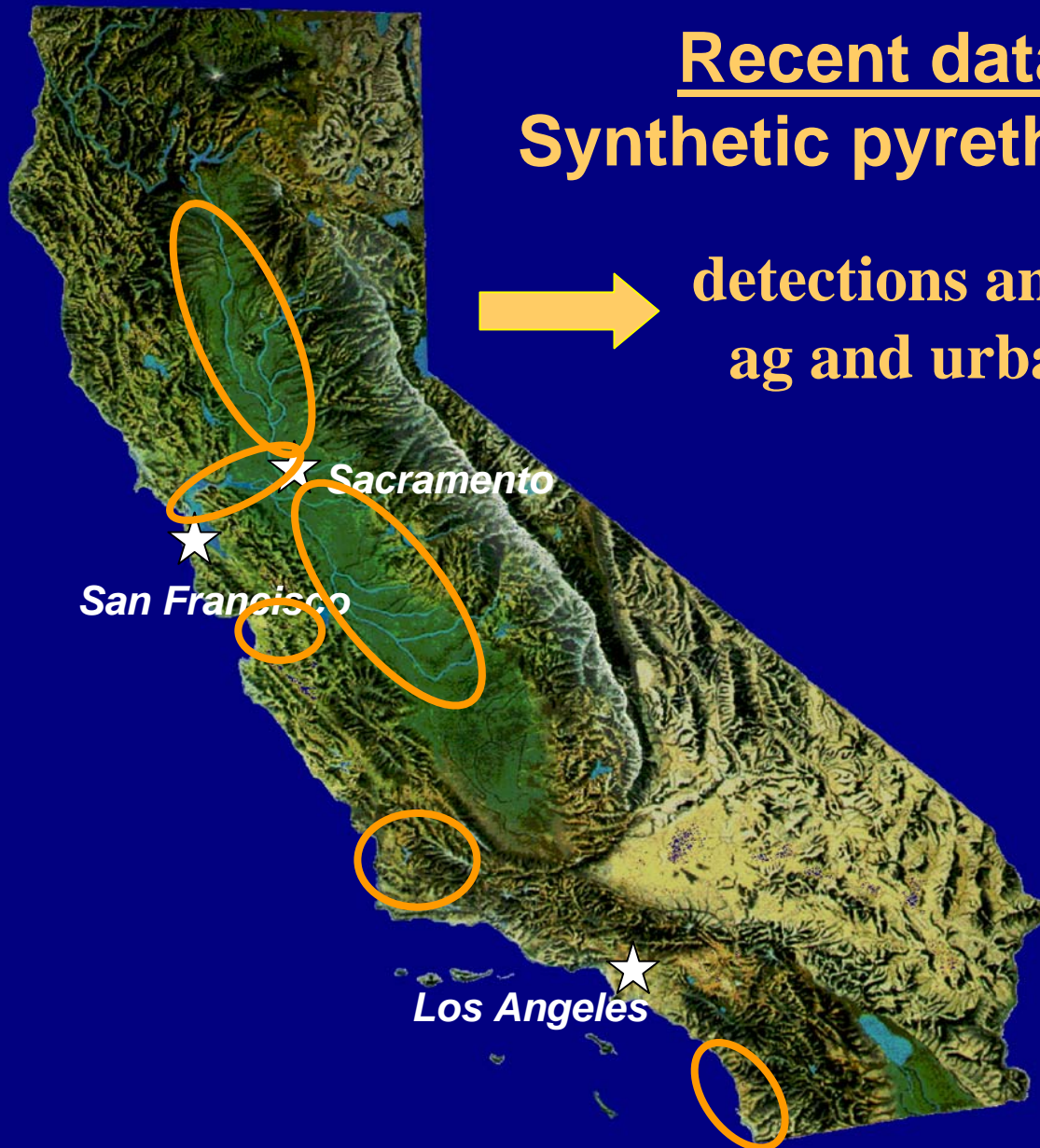
OP urban use phaseout

Pesticides and water quality

Recent data

Synthetic pyrethroids

detections and bioassay toxicity in
ag and urban aquatic sediments



bifenthrin
cypermethrin
cyfluthrin
 λ - cyhalothrin
permethrin
esfenvalerate
fenpropathrin
deltamethrin

Current California registrations

- 25 synthetic pyrethroids (including isomerically-enriched mixtures)

ALLETHRIN		DELTAMETHRIN
S-BIOALLETHRIN		ESFENVALERATE
D-TRANS ALLETHRIN		ETOFENPROX
D-ALLETHRIN		FENPROPETHRIN
ESBIOTHRIN		IMIPROTHRIN
BIFENTHRIN		PERMETHRIN
CYFLUTHRIN		PHENOTHRIN
BETA-CYFLUTHRIN		PRALLETHRIN
CYPERMETHRIN		RESMETHRIN
(S)-CYPERMETHRIN		TAU-FLUVALINATE
CYPHENOTHRIN		TETRAMETHRIN
LAMBDA CYHALOTHRIN		TRALOMETHRIN
GAMMA CYHALOTHRIN		

Current California registrations

- 25 active ingredients registered (including isomerically-enriched mixtures)
- 1255 synthetic pyrethroid products registered, 197 registrants (1/2006)

Current California registrations

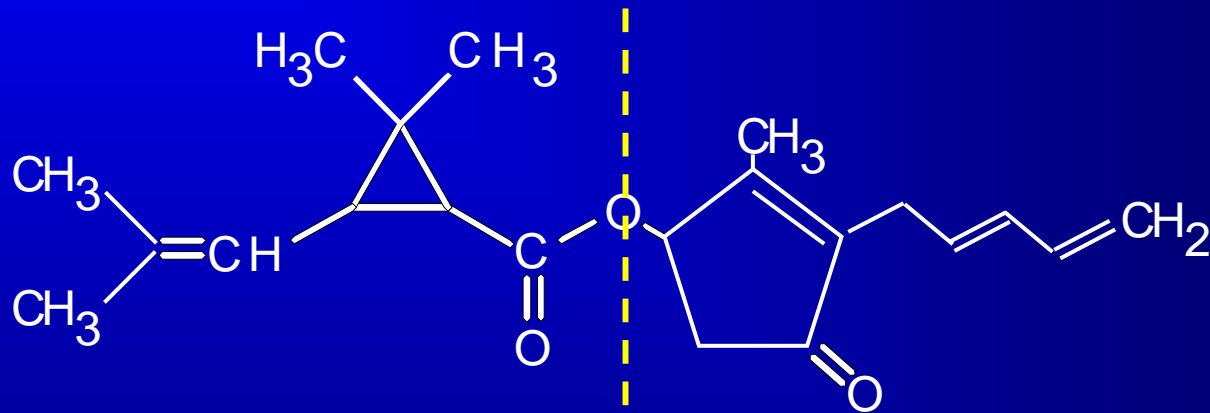
- 25 active ingredients registered (including isomerically-enriched mixtures)
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- **> 40% of ALL insecticide products**

Current California registrations

- 25 active ingredients registered (including isomerically-enriched mixtures)
- 1255 synthetic pyrethroid products registered, 197 registrants (1/2006)
- > 40 % of ***ALL insecticide products***
- Total 2004 sales: ~ 1.3M lbs AI, > \$160M

Use patterns and characteristics

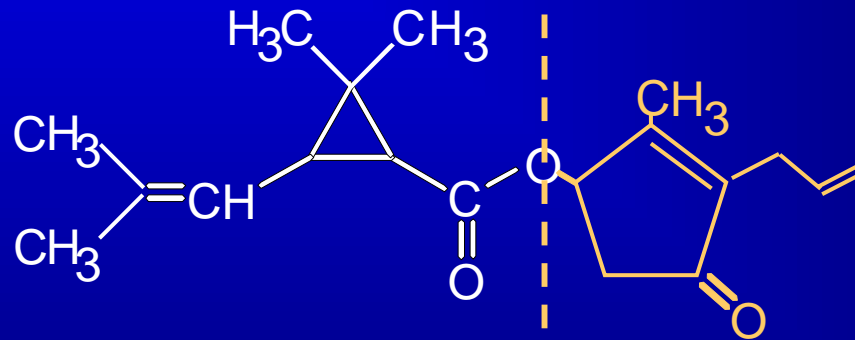
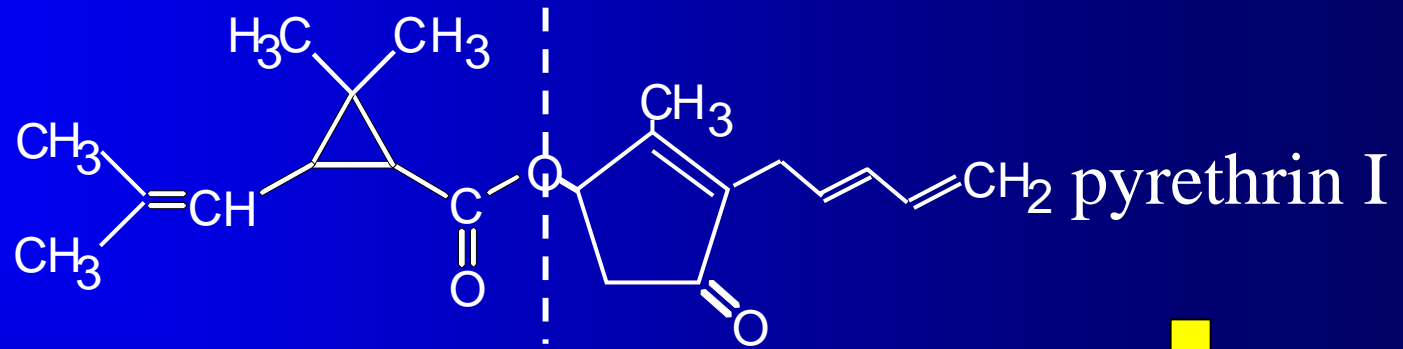
pyrethrin I



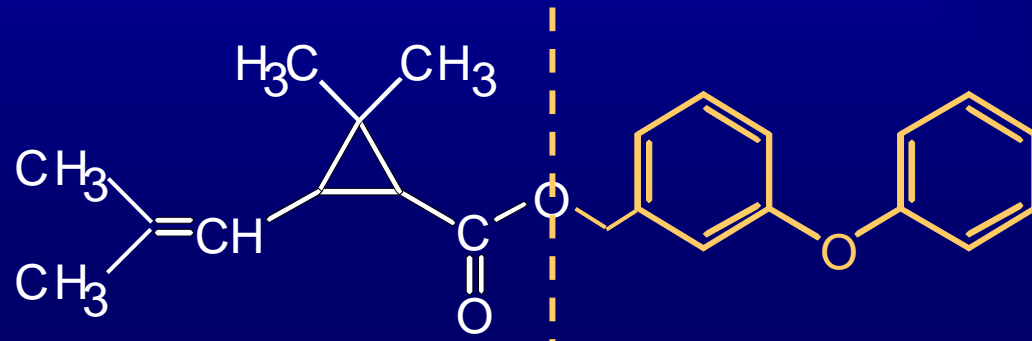
chrysanthemic
acid

pyrethrolone
(alcohol)

Early syntheses: alcohol substitutions

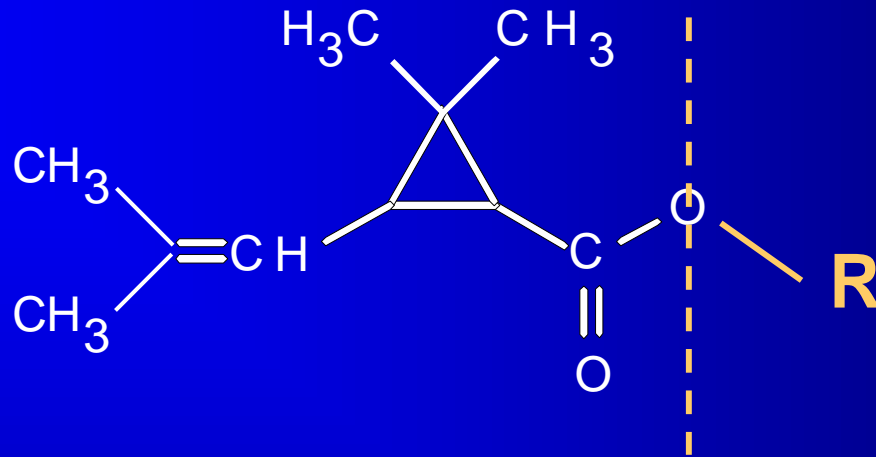


allethrin



phenothrin

Early syntheses: alcohol substitutions



CA registered AIs

allethrins

cyphenothrin

imiprothrin

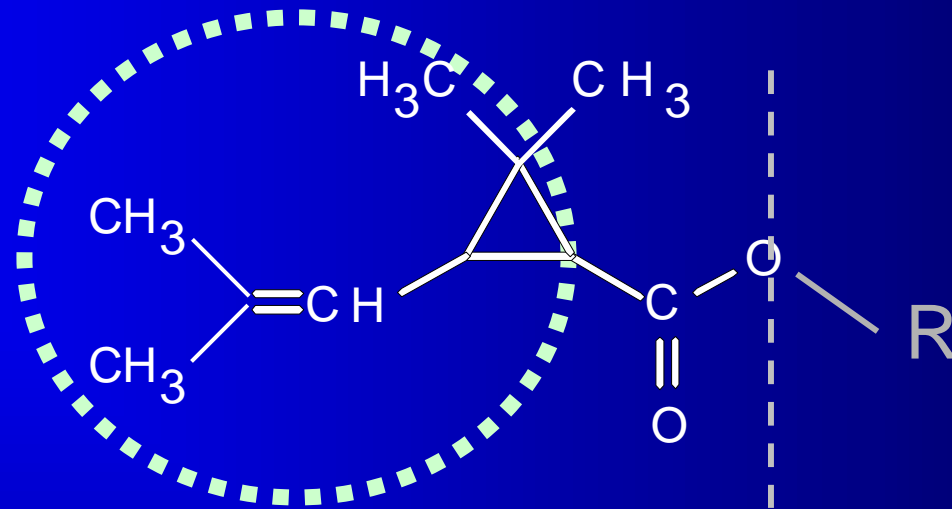
prallethrin

phenothrin

resmethrin

tetramethrin

Early syntheses: alcohol substitutions



*** PHOTOLABILE ***

$t_{1/2} \sim$ hours

Nonag uses:

aerosol ant/roach sprays
fly/wasp sprays
indoor foggers
carpet/upholstery sprays
pet products
commercial/institutional
crack/crevice

CA registered AIs

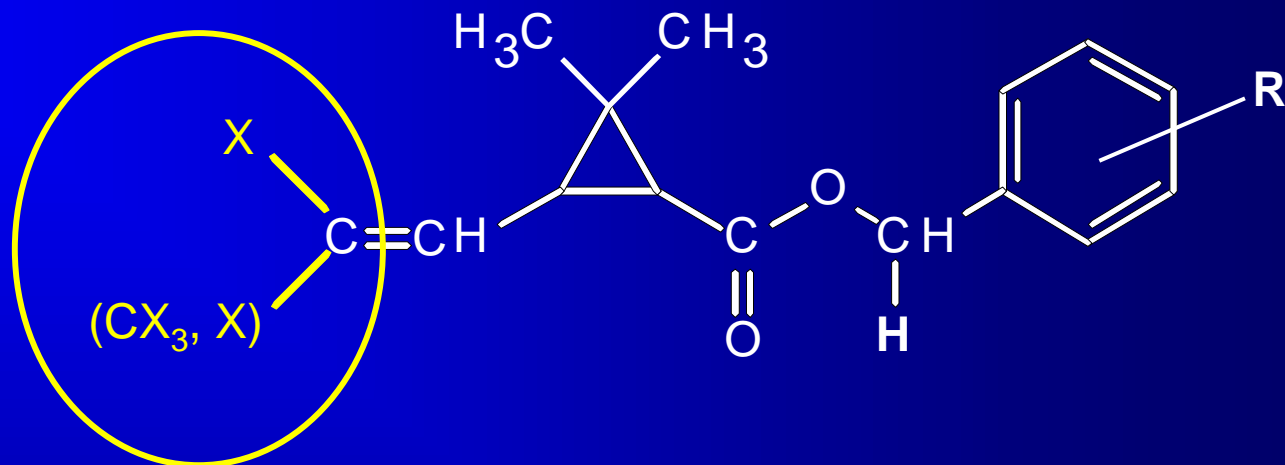
allethrins
cyphenothrin
imiprothrin
prallethrin
phenothrin
resmethrin
tetramethrin

~ 8%

CA
sales

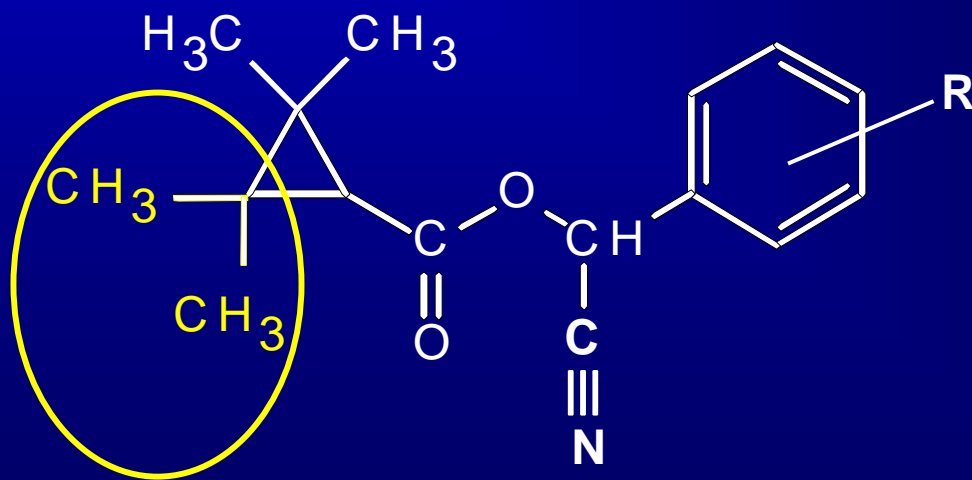
Later syntheses

vinyllic halogens

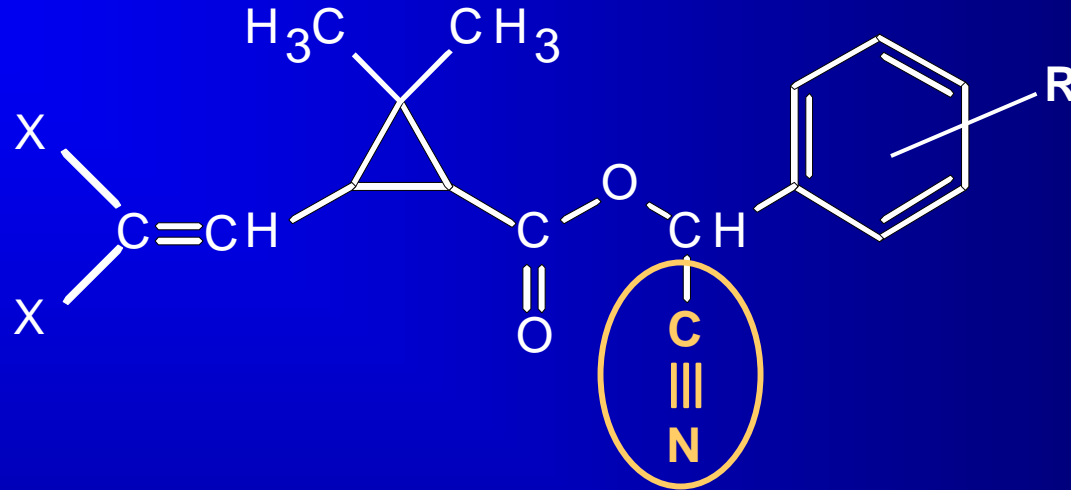


**improved
photostability**

tetra-alkylcyclopropane
ester

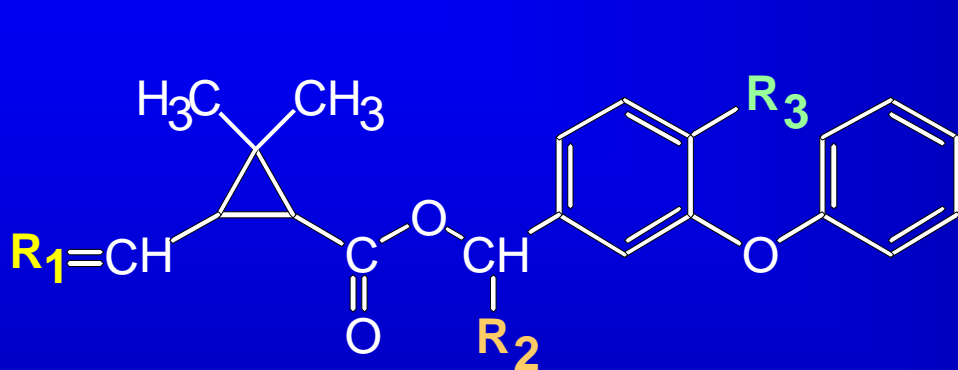


Later syntheses

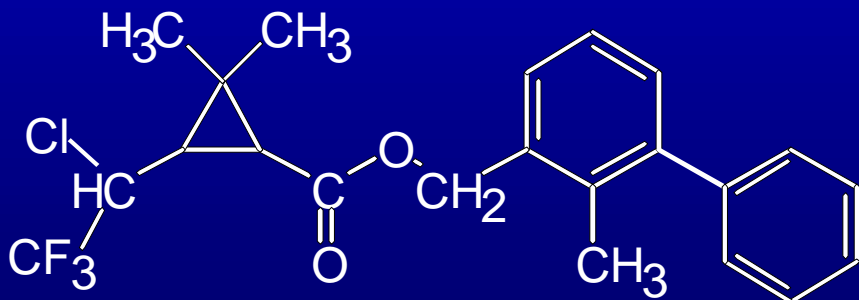


α -cyano substitution
marked increase in
insecticidal activity
("type II" pyrethroids)

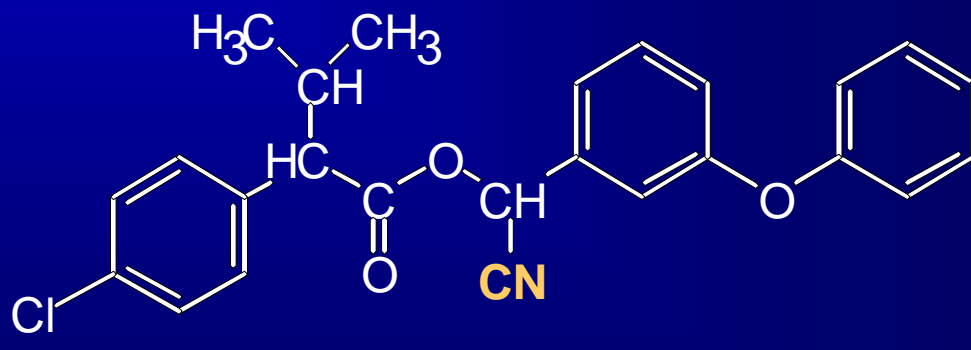
Examples of photo-stable type I and II pyrethroids



R_1	R_2	R_3	
CCl_2	CN	F	cyfluthrin
CCl_2	CN	H	cypermethrin
$CClCF_3$	CN	H	cyhalothrin
CCl_2	H	H	permethrin



bifenthrin



fenvalerate

Photo-stable pyrethroids

- **Primary focus of pyrethroid water quality concerns**

Photo-stable pyrethroids

- **Primary focus of pyrethroid water quality concerns**
- **> 90% CA pyrethroid use**
 - Agricultural , numerous crops
 - Nursery, turf and sod
 - Institutional/commercial
 - Pet products and shampoos
 - Animal husbandry premises
 - horses, livestock, barns
 - Landscape maintenance -
 - golf courses, parks, buildings
 - Structural
 - building exteriors, crack & crevice
 - termite applications
 - Home and garden
 - lawns, ornamental flowers, indoor uses

Photo-stable pyrethroids

- Primary focus of pyrethroid water quality concerns
- Broad range of uses
- **General Use Categories & 2004 amount:**

Agricultural **(~ 300k lbs)**

permethrin (140k)

fenpropathrin (40k)

esfenvalerate (30k)

Comm'l structural & landscape maint. **(~ 640k lbs)**

permethrin (320k)

cypermethrin (200k)

Est.remaining urban uses **(~ 100k lbs)**

bifenthrin (50k)

esfenvalerate (30k)

permethrin (20k)

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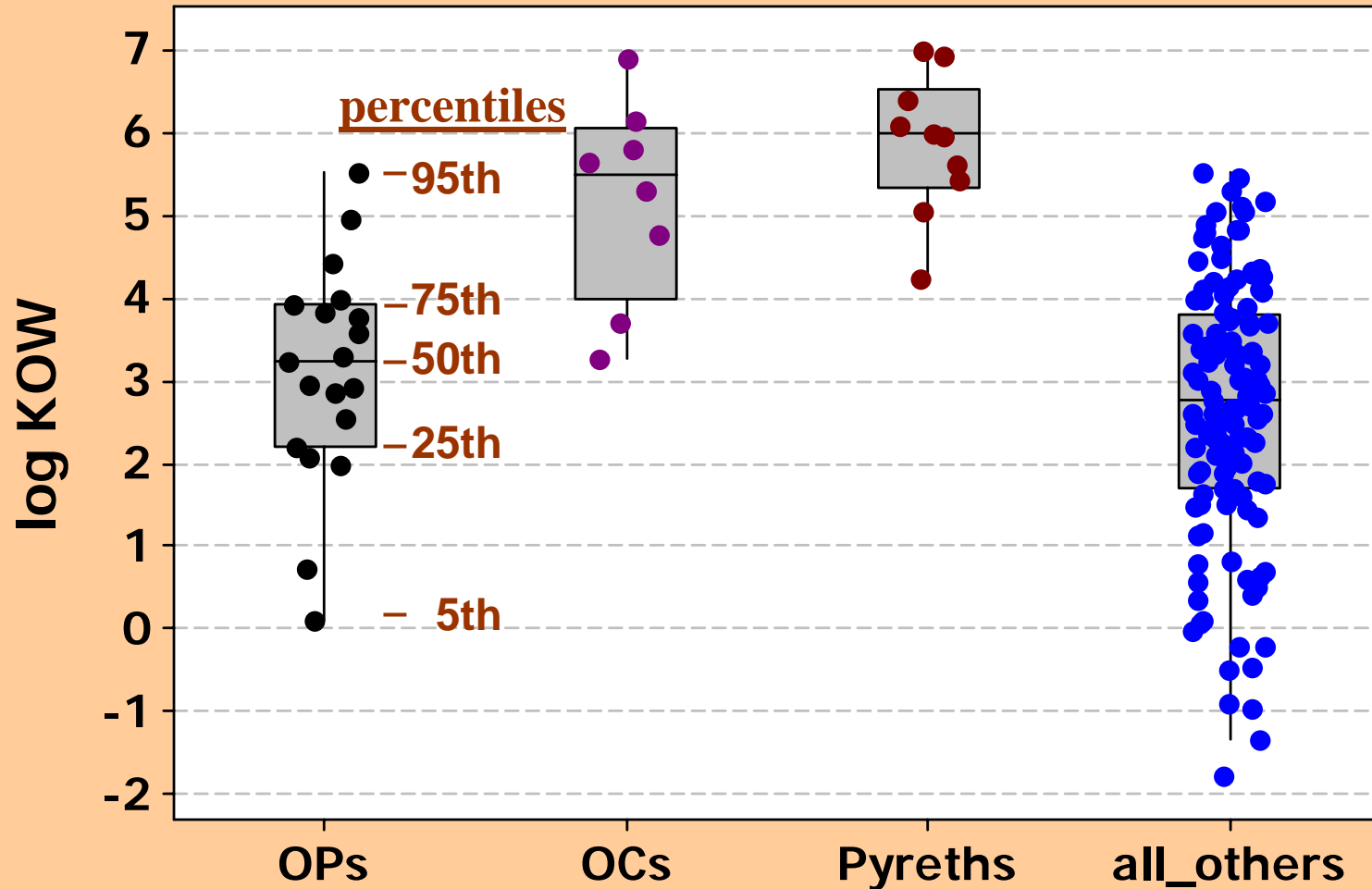
permethrin (20k)



permethrin: 40 - 50% of all pyrethroid sales

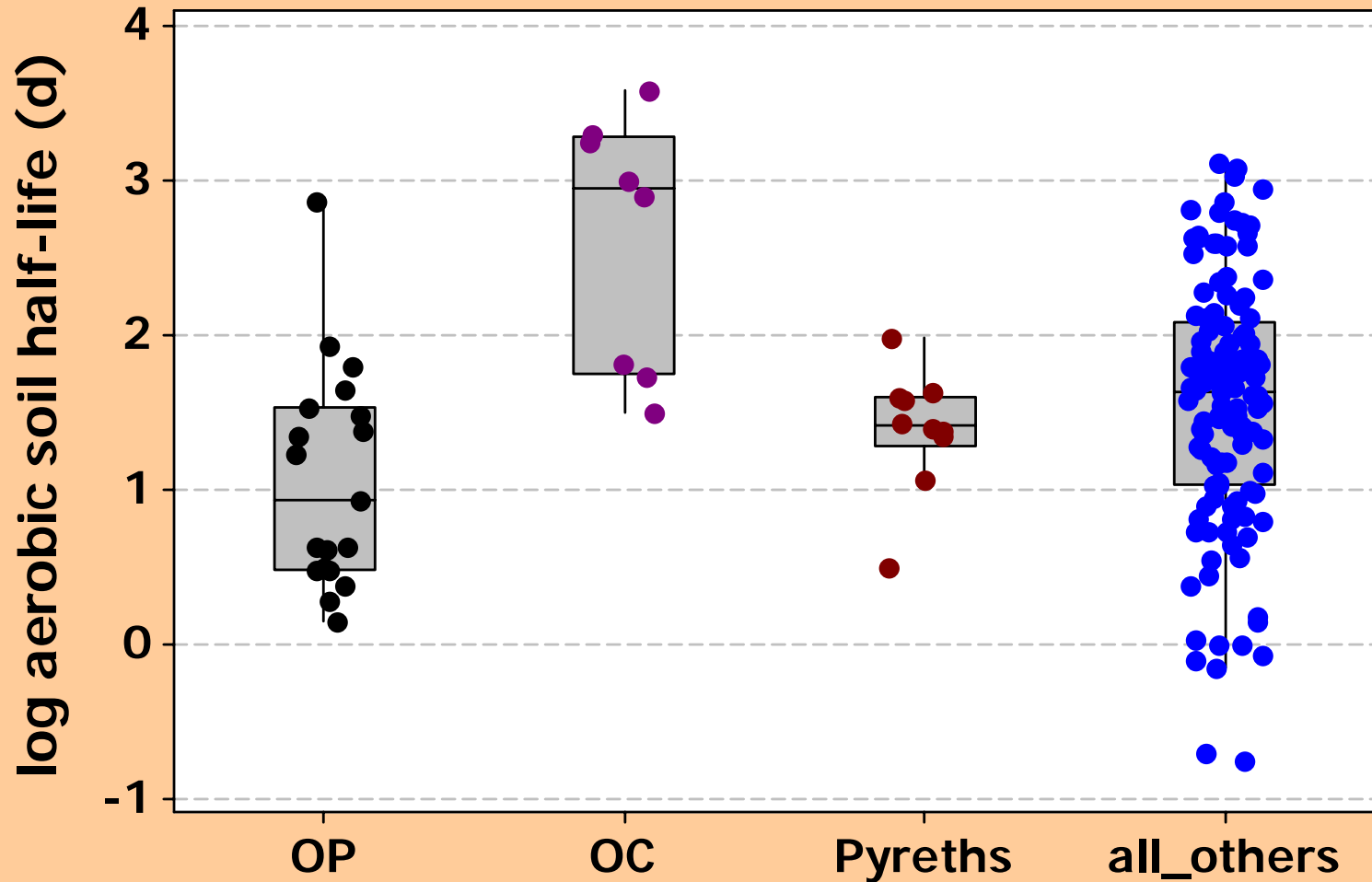
Pyrethroid properties

hydrophobicity



Pyrethroid properties

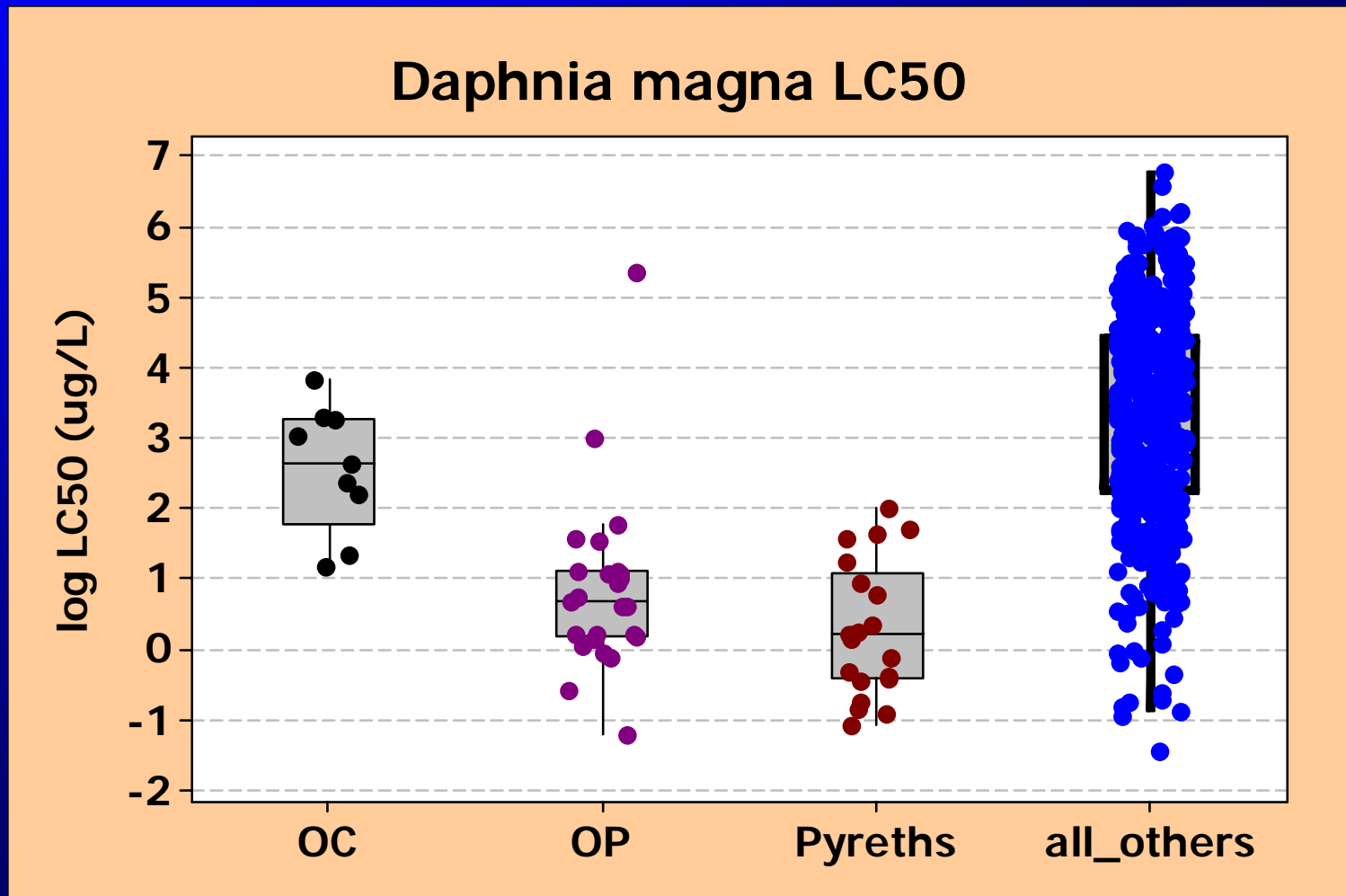
soil persistence



Pyrethroid properties

relative potential acute aquatic toxicity

("water-only" data)



Pyrethroid aquatic risk assessment issues

Pyrethroid aquatic risk assessment issues

- bioavailability -
 - dissolved organic matter?
 - sediment characteristics?
 - organic carbon characteristics?
 - measurement – selective methods,
e.g. SPME

Pyrethroid aquatic risk assessment issues

- bioavailability
- co-occurrence common-additive toxicity - universal?
Type I + Type II?

Pyrethroid aquatic risk assessment issues

- bioavailability
- co-occurrence and additive toxicity
- chirality - stereoisomeric selectivity in toxicity
=> biological degradation?

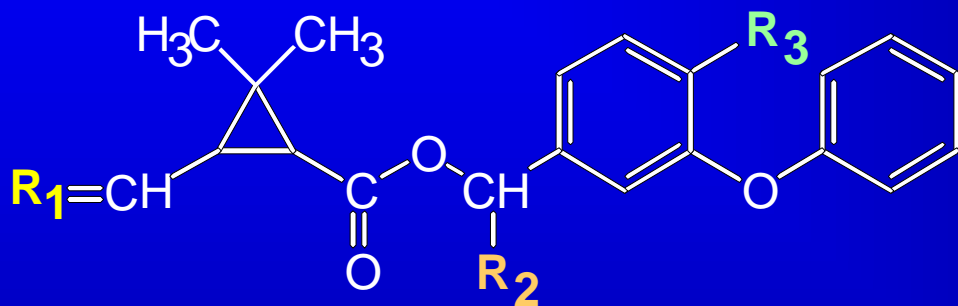
Pyrethroid aquatic risk assessment issues

- bioavailability
- additive toxicity - universal? Type I + Type II?
- chirality - selectivity: toxicity, degradation
- mechanisms of off-site movement in urban environment?
principal contributing uses?

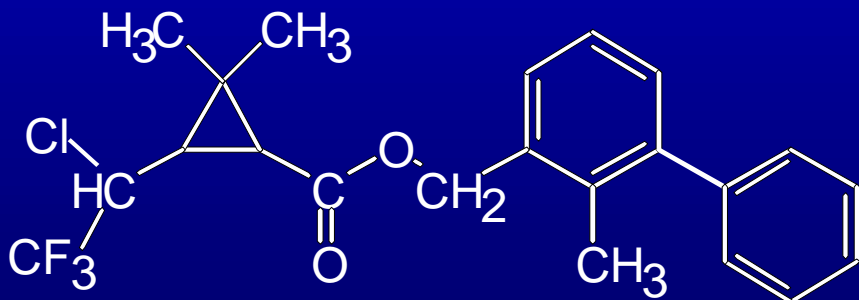
Pyrethroid aquatic risk assessment issues

- bioavailability
- additive toxicity - universal? Type I + Type II?
- chirality - selectivity in toxicity, degradation
- urban off-site movement mechanisms?
- synergist co-occurrence?
PBO, MGK-264 (*N*-octyl bicycloheptene dicarboximide)

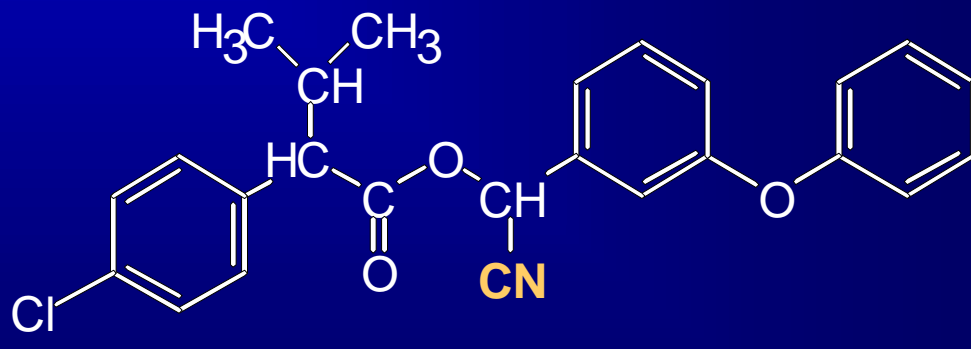
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bifenthrin



fenvalerate