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Pyrethroids in urban runoff

Donald Weston

University of California, Berkeley

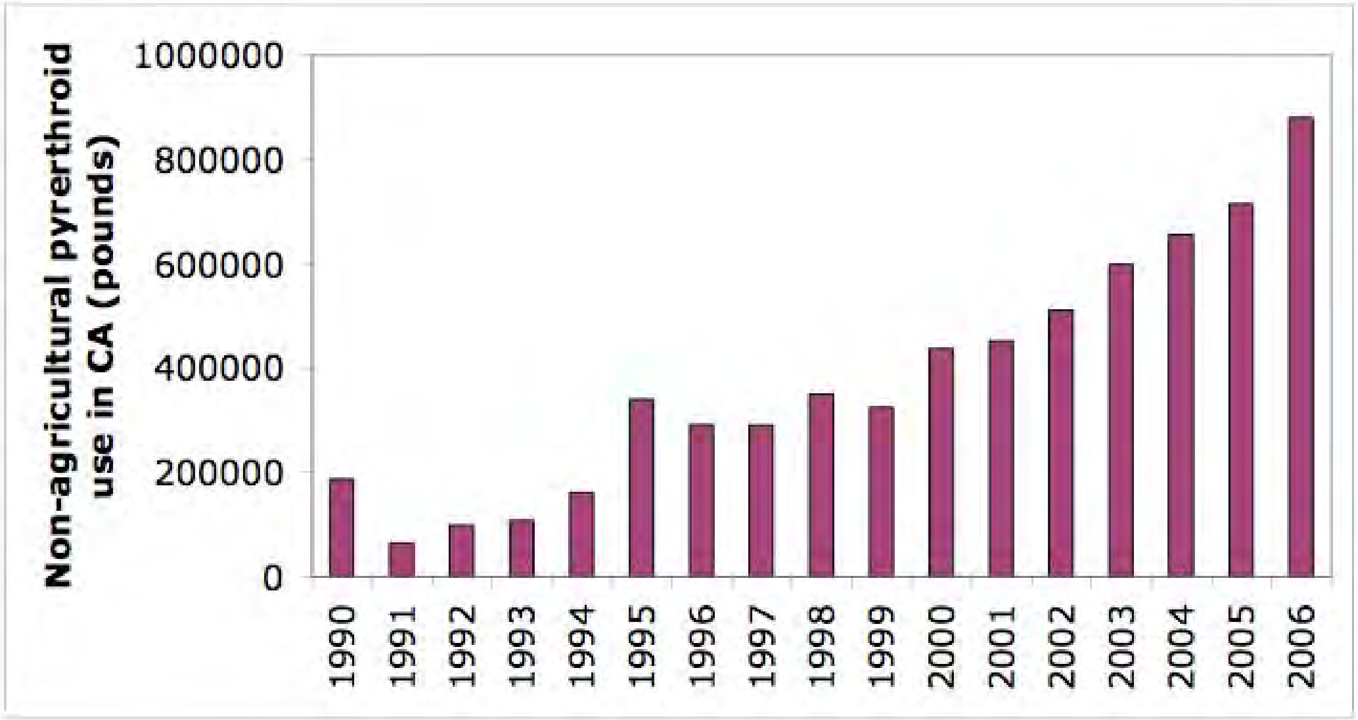
Some basic pyrethroid facts

- They are insecticides produced synthetically, but modelled after pyrethrin, a natural chrysanthemum-derived insecticide

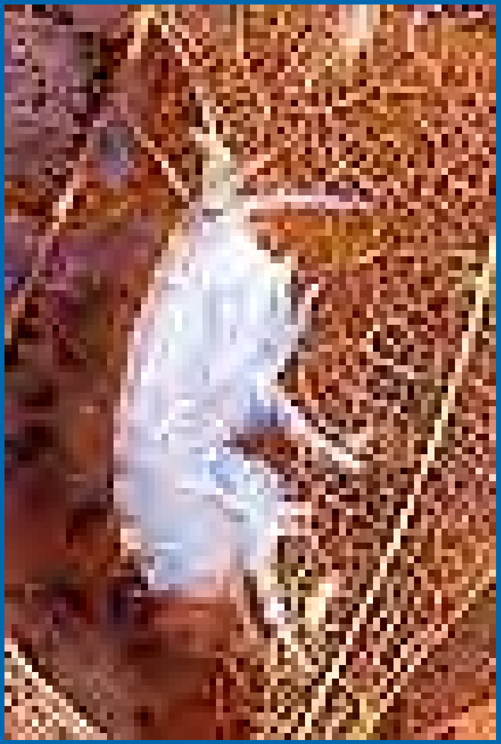
- Recognizable by "…thrin" suffix for most members of the class (e.g., bifenthrin, permethrin, cypermethrin)

- Dominant insecticide used by homeowners and by professional pest control firms. Substantial use in CA agriculture, though organophosphates still dominate.

Annual trends in pyrethroid use in California



The tools:
Hyalella toxicity test



- One of two species with nationally standardized protocols for freshwater sediment testing.
- Sediment testing - Bring sediment in to the lab, add Hyalella, count survivors after 10 days.
- Water testing - Bring water sample in to the lab, add Hyalella, count survivors after 4 days.

Our initial urban creek sediment studies

Location	Number of samples	% toxic to Hyalella	% with pyrethroids at concentrations expected to be toxic
Roseville	26	81%	88%
Pittsburg	21	86%	95%

Subsequent studies have confirmed similar findings in many other urban creeks statewide.

Pyrethroid sensitivity of Hyalella azteca

Pyrethroid	H. azteca survival 96-h LC50 (ng/L)	H. azteca impaired movement 96-h EC50 (ng/L)
Bifenthrin	7.7	3.3
Cyfluthrin	2.3	1.9
Cypermethrin	2.3	1.7

C. dubia survival 48 to 96-h LC50 (ng/L)
50-70
140
194

C. dubia data from Mokry and Hoagland, 1990; Yang et al., 2006.

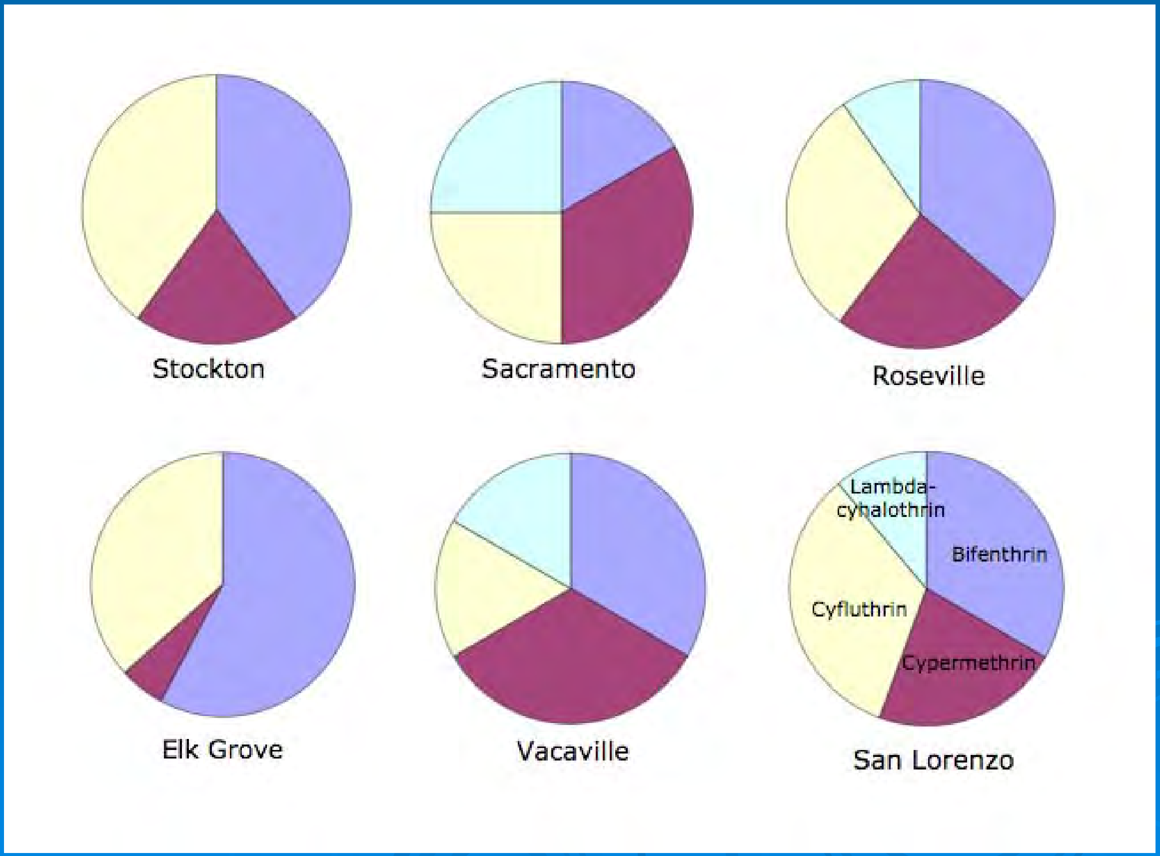
Roseville storm drain

Urban drain pump station

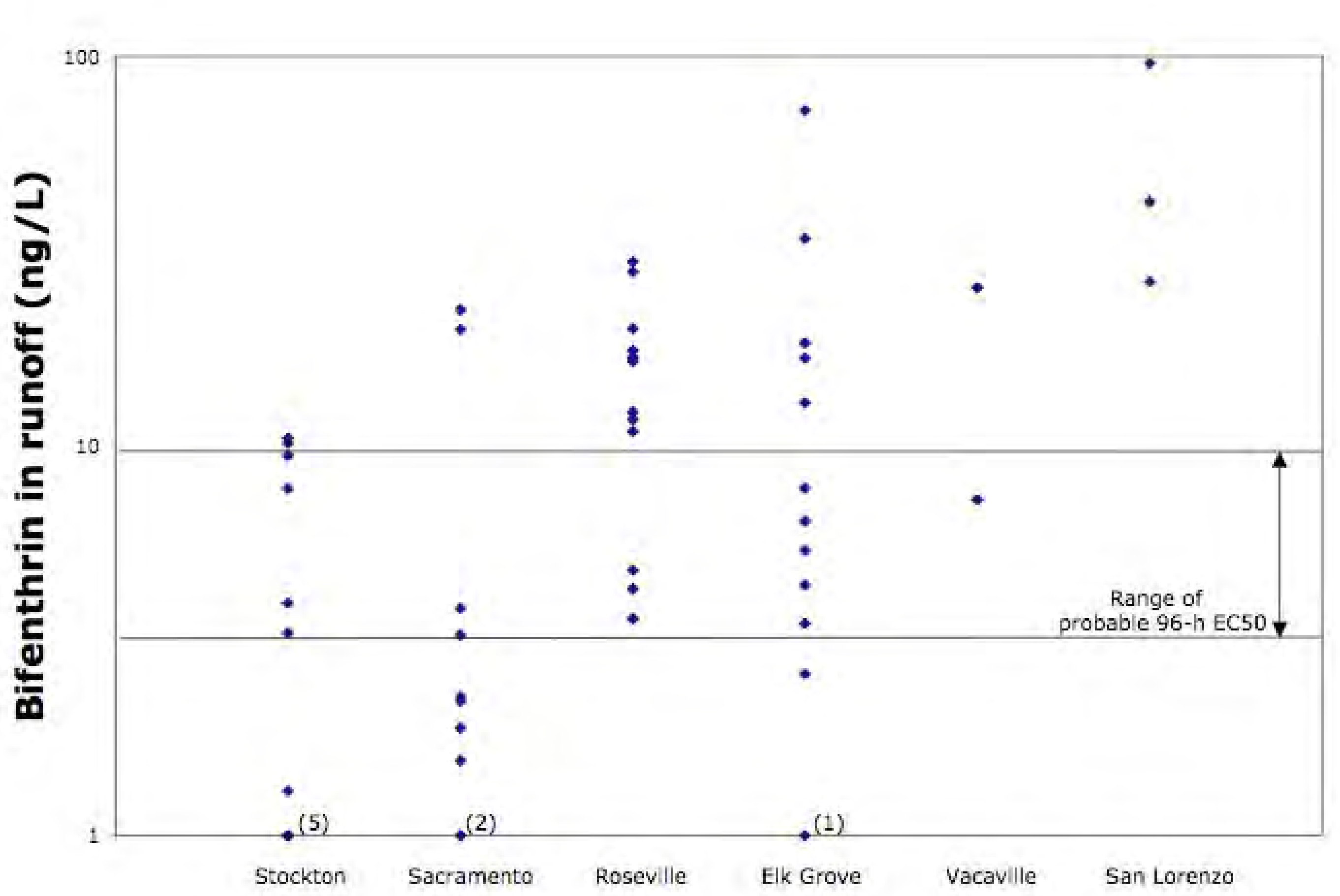
Summary of our urban runoff studies

Location	Number of samples	% toxic to Hyalella	% with pyrethroids at concentrations expected to be toxic
Stockton	12	83%	67%
Sacramento	10	80%	70%
Roseville	12	no data	100%
Elk Grove	12	no data	92%
Vacaville	2	100%	100%
San Lorenzo	3	100%	100%

Occasions that each pyrethroid exceeded its Hyalella EC50, as percent of total exceedances



Bifenthrin in urban runoff



Further evidence implicating pyrethroids as the principal cause for observed toxicity

Toxicity Identification Evaluations (TIE) using:

1. Reduced temperature
2. Piperonyl butoxide (PBO)
3. Engineered enzymes

TIE approach #1: Reduced temperature

Pyrethroids are atypical in that they become more toxic at lower temperatures

Effect of temperature on Hyalella EC50s

	EC50 (ng/L) at 23 C	EC50 (ng/L) at 17 C
Bifenthrin	3.3	1.6
Cyfluthrin	1.9	0.5
Cypermethrin	1.7	0.9

TIE approach #2: PBO (piperonyl butoxide)

PBO inhibits activity of one of the enzymes that would ordinarily detoxify pyrethroids, making them more toxic.

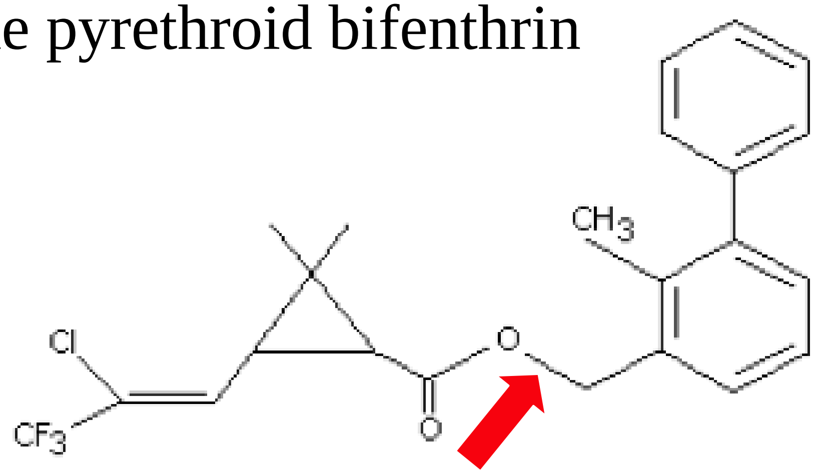
Effect of PBO on <u>Hyalella</u> EC50s

	EC50 (ng/L) without PBO	EC50 (ng/L) with PBO
Bifenthrin	3.3	1.0
Cyfluthrin	1.9	0.6
Cypermethrin	1.7	0.5

TIE approach #3: Engineered esterases

Add enzymes engineered to breakdown specific pyrethroids and organophosphate pesticides, and determine which enzyme reduces the toxicity.

The pyrethroid bifenthrin



Enzymes tested

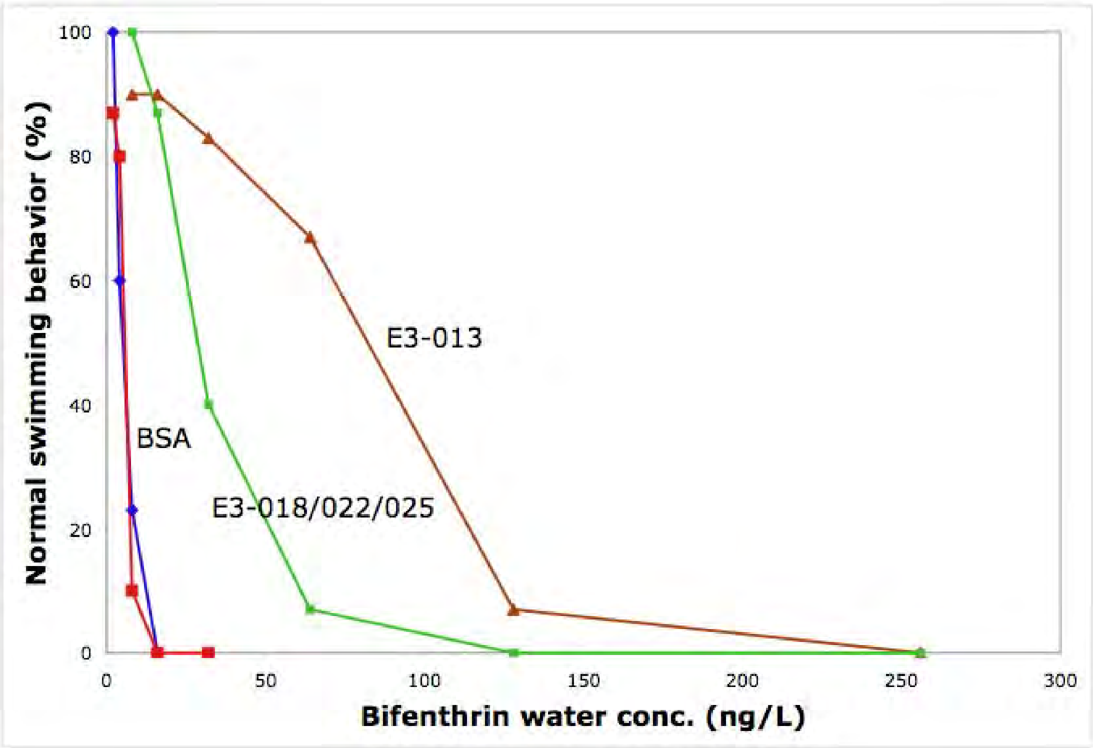
OPDA: Organophosphate degrading enzyme, effective against chlorpyrifos, diazinon, and some other OPs.

E3-013: Esterase designed for degradation of the pyrethroid bifenthrin.

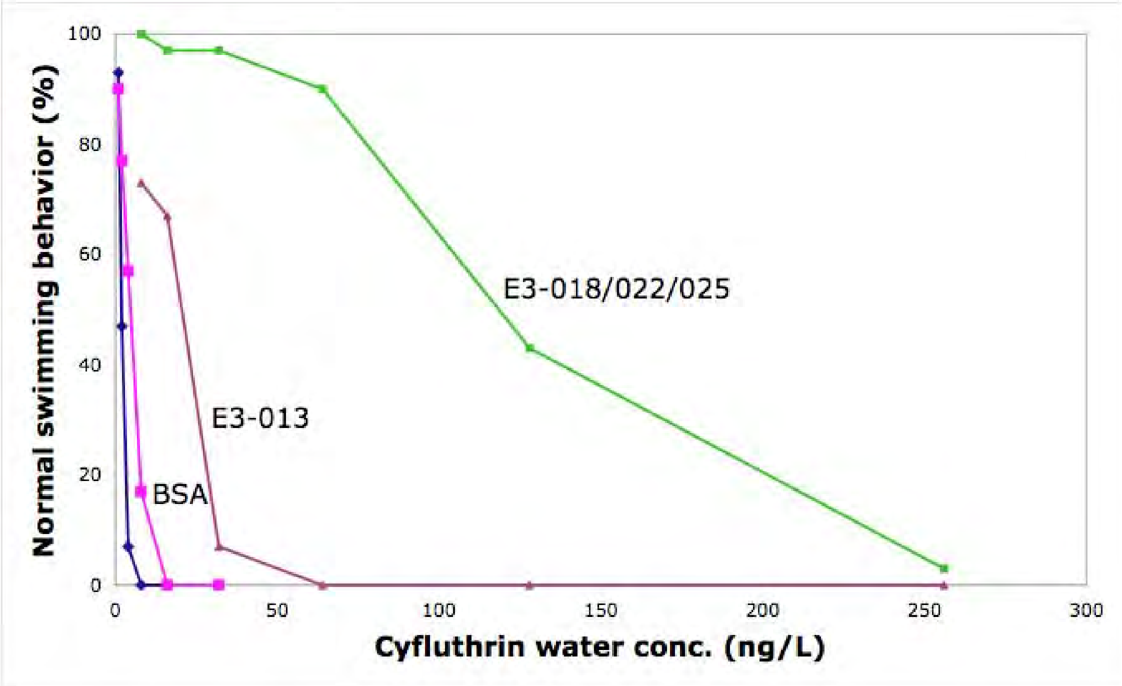
E3-018/022/025: A mix of esterases, each designed to be effective against different isomers of the pyrethroid cypermethrin.

BSA Control: No enzymatic activity. Control for DOM.

E3-013 enzyme with bifenthrin



E3-018/022/025 enzymes with cyfluthrin



Urban runoff TIEs

(values are EC50s and 95% conf. interval, as % effluent)
Green highlight indicates results consistent with pyrethroid

	Regular test	Low Temp.	PBO	BSA	E3 Enzymes
LP (Stockton) (Feb.)	70.8 (58.1-83.7)	36.5 (26.6-46.7)	15.8 (12.5-19.3)		
ML (Stockton) (Feb.)	26.0 (20.0-31.7)	12.4 (8.4-17.1)	3.2 (2.0-4.3)		
Vacaville (Feb.)	21.1 (17.2-25.2)	14.6 (12.5-17.0)	11.8 (9.3-14.3)		62.2 (45.2-91.9)
#104 (Sacramento) (Feb.)	57.9 (51.7-65.0)	28.0 (21.1-37.4)	25.8 (20.0-31.7)		>100
#28 (Sacramento) (May)	23.0 (18.0-28.2)	13.3 (10.6-16.2)	5.7 (4.7-6.7)	29.4 (24.2-35.8)	36.5 (30.1-43.5)
WR (Stockton) (Sept.)	21.9 (16.4-27.1)		8.5 (6.1-10.4)	33.1 (27.0-38.9)	80.2 (67.4-92.7)

So where are the pyrethroids coming from?

Soil in freshly treated Roseville yard
(7500 ng/g cyfluthrin)

Sediment suspended in runoff from Roseville drain
(240-470 ng/g cyfluthrin)

Sediment in Roseville urban creeks
(3-180 ng/g cyfluthrin)

Hyalella LC50
(11 ng/g cyfluthrin)