Pyrethroid Insecticide Concentrations, Toxicity, and Loads in Surface Waters of the San Joaquin Valley, California

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Project Goals:

- Assess the occurrence of pyrethroid insecticides in bed sediments of San Joaquin Valley streams and rivers
- Assess toxicity of bed sediments to benthic organism, *Hyalella azteca* , and contribution to toxicity from pyrethroids
- Assess the transport of pyrethroid insecticides in suspended sediments of west-side streams during irrigation season
- Assess basin-wide transport of pyrethroid insecticides during winter storms

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Chemical Analysis and Toxicity Testing

- Pyrethroid Analysis by U.S. Geological Survey, (Smalling and Kuivila, 2008)
- Toxicity Testing: (Don Weston, UC Berkeley—10 day exposures), (Amweg et al., 2005; Maund et al., 2002; Weston et al., 2009)

USGS Pyrethroid Method

Pyrethroid Insecticide	Method Detection Limit (ng/g dry sediment)	Mean Recovery (%)	Relative Standard Deviation (%)
Allethrin	1.5	82.2	7.4
Bifenthrin	2.2	97.4	7.6
Cyfluthrin	2.0	82.3	6.3
λ-Cyhalothrin	2.4	89.9	9.1
Cypermethrin	2.6	86.6	7.8
Deltamethrin	2.5	82.3	9.0
Esfenvalerate	2.1	82.5	7.6
Fenpropathrin	2.1	90.3	6.2
τ-Fluvalinate	2.6	99.3	9.4
Permethrin (cis and trans)	1.0	92.9	2.8
Resmethrin	1.9	88.5	5.7
Sumithrin	1.3	101	3.3
Tetramethrin	1.4	82.8	4.3

Why Study Pyrethroids

- Increased Use in California (Partially replacing organophosphate insecticides)
- Low water solubility, but high adsorption on suspended and bed sediments
- Potential toxicity to benthic organisms
- Analytical methodology is very different from organophosphate insecticides

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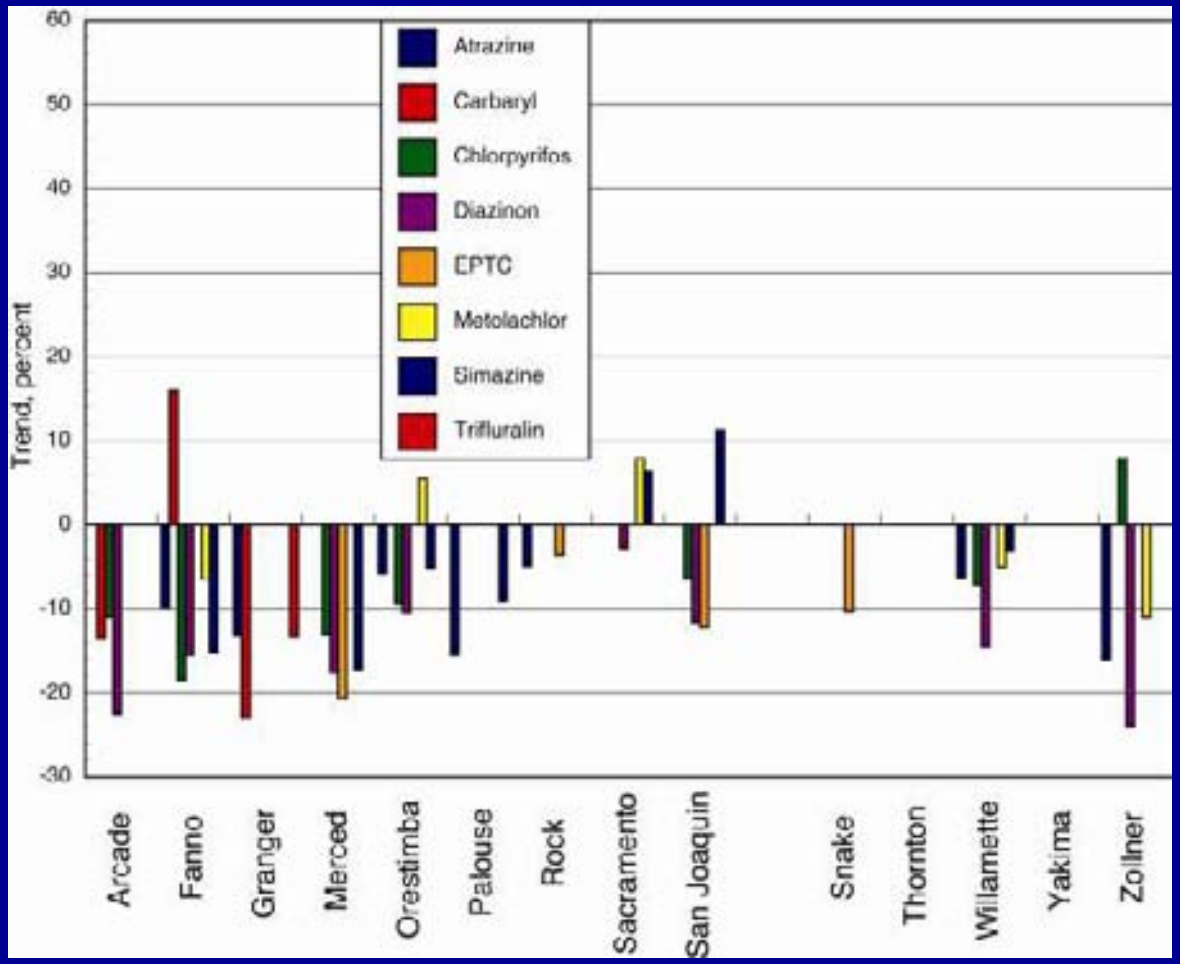
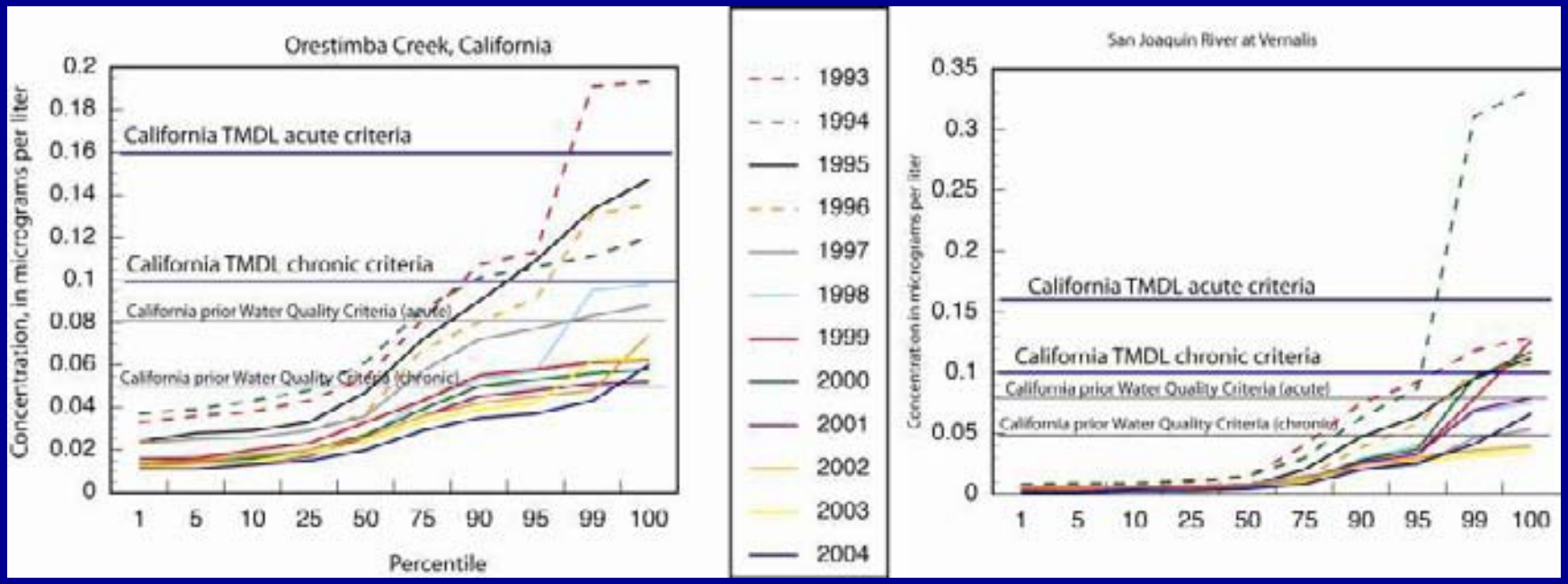
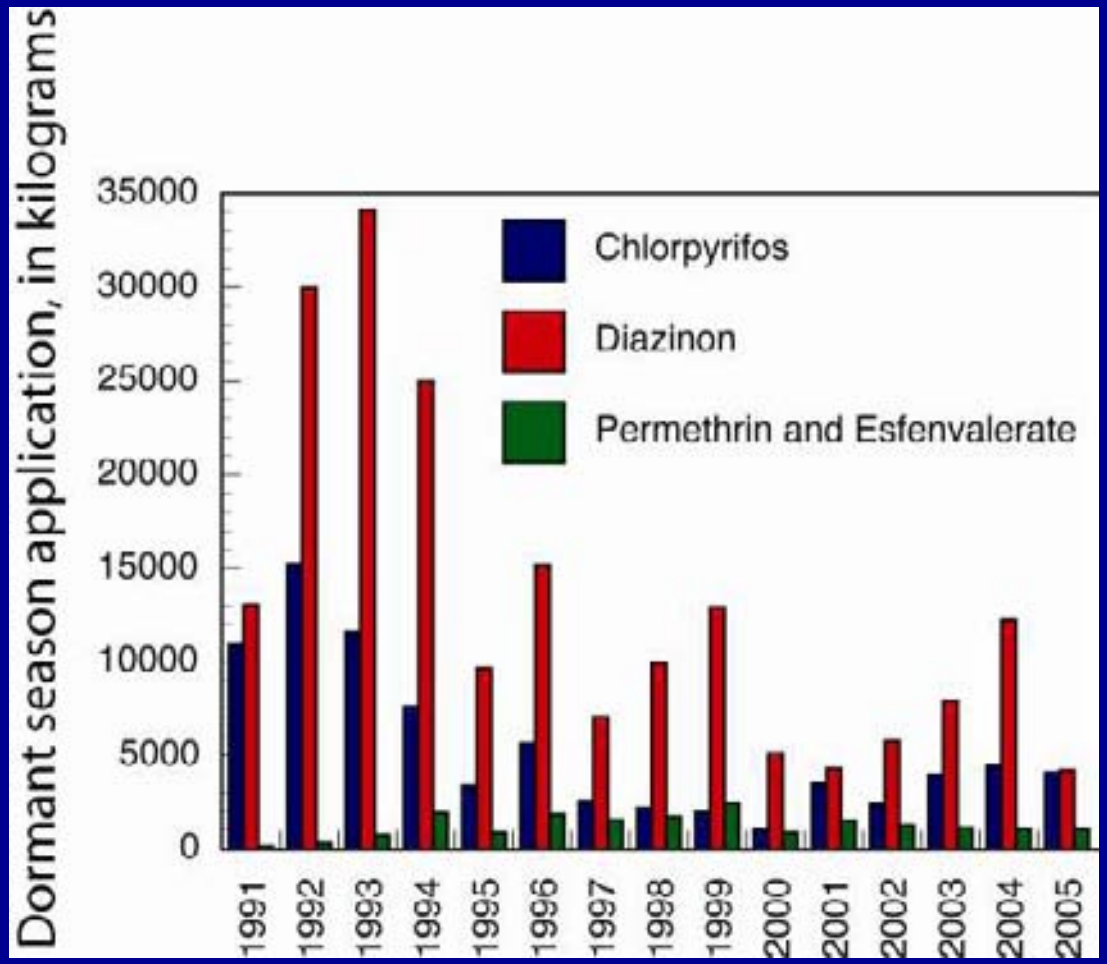
Trends in Pesticide Concentrations



Modeled Diazinon Concentrations



Dormant Spray Insecticides



Commonly Used Pyrethroids

- Permethrin
- Cypermethrin
- Cyfluthrin
- Esfenvalerate
- Bifenthrin
- Lambda cyhalothrin

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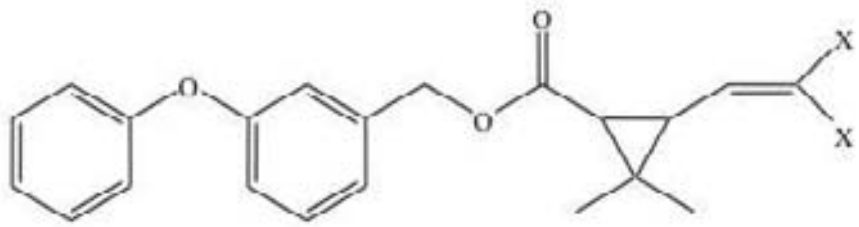
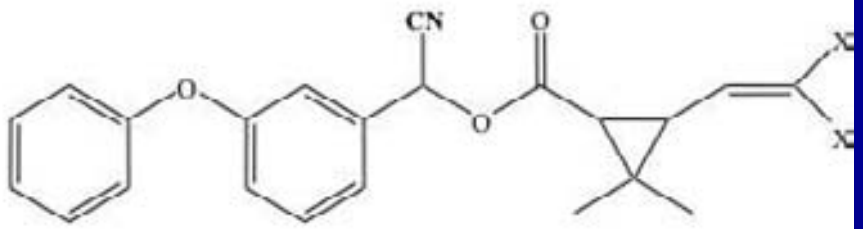
Pyrethroid Chemical Structures

Type I



Permethrin (Ambush)
Bifenthrin (Talstar, Biflex, Capture)

Type II



Cypermethrin (Cymbush)
Cyfluthrin (Baythroid
Esfenvalerate (Asana)
lambdacyhalothrin (Karate, Warrior)

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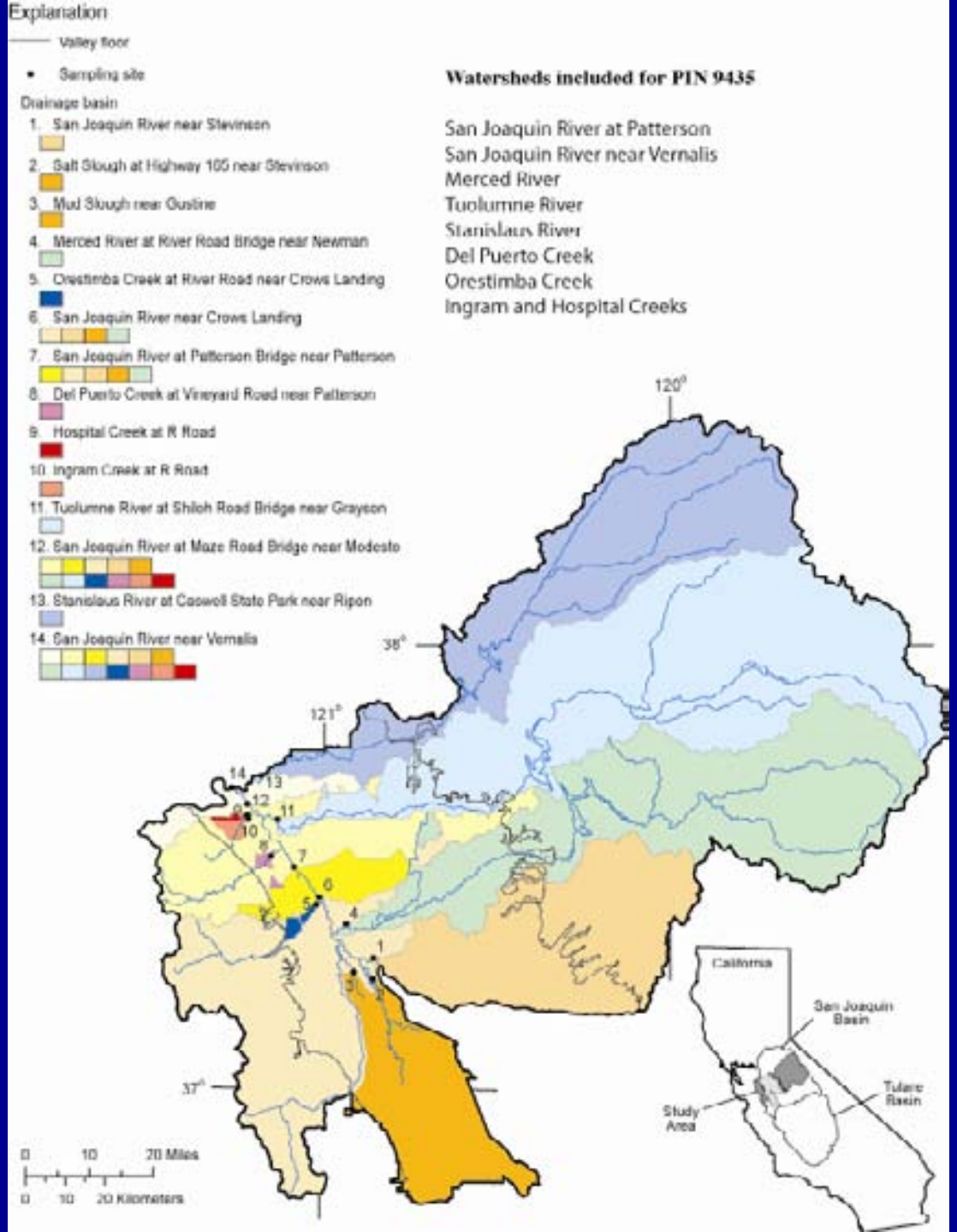
Study Area

- Streams of western and eastern San Joaquin Valley


Explanation
Valley floor
Sampling site
Drainage basin
1. San Joaquin River near Stevinson
2. Salt Slough at Highway 165 near Stevinson
3. Mud Slough near Gustine
4. Merced River at River Road Bridge near Newman
5. Orestimba Creek at River Road near Crows Landing
6. San Joaquin River near Crows Landing
7. San Joaquin River at Patterson Bridge near Patterson
8. Del Puerto Creek at Vineyard Road near Patterson
9. Hospital Creek at R Road
10. Ingram Creek at R Road
11. Tuolumne River at Shiloh Road Bridge near Grayson
12. San Joaquin River at Maze Road Bridge near Modesto
13. Stanislaus River at Caswell State Park near Ripon
14. San Joaquin River near Vernalis
Watersheds included for PIN 9435
San Joaquin River at Patterson
San Joaquin River near Vernalis
Merced River
Tuolumne River
Stanislaus River
Del Puerto Creek
Orestimba Creek
Ingram and Hospital Creeks
120°
38°
121°
37°
California
San Joaquin Basin
Tulare Basin
Study Area
0 10 20 Miles
0 10 20 Kilometers

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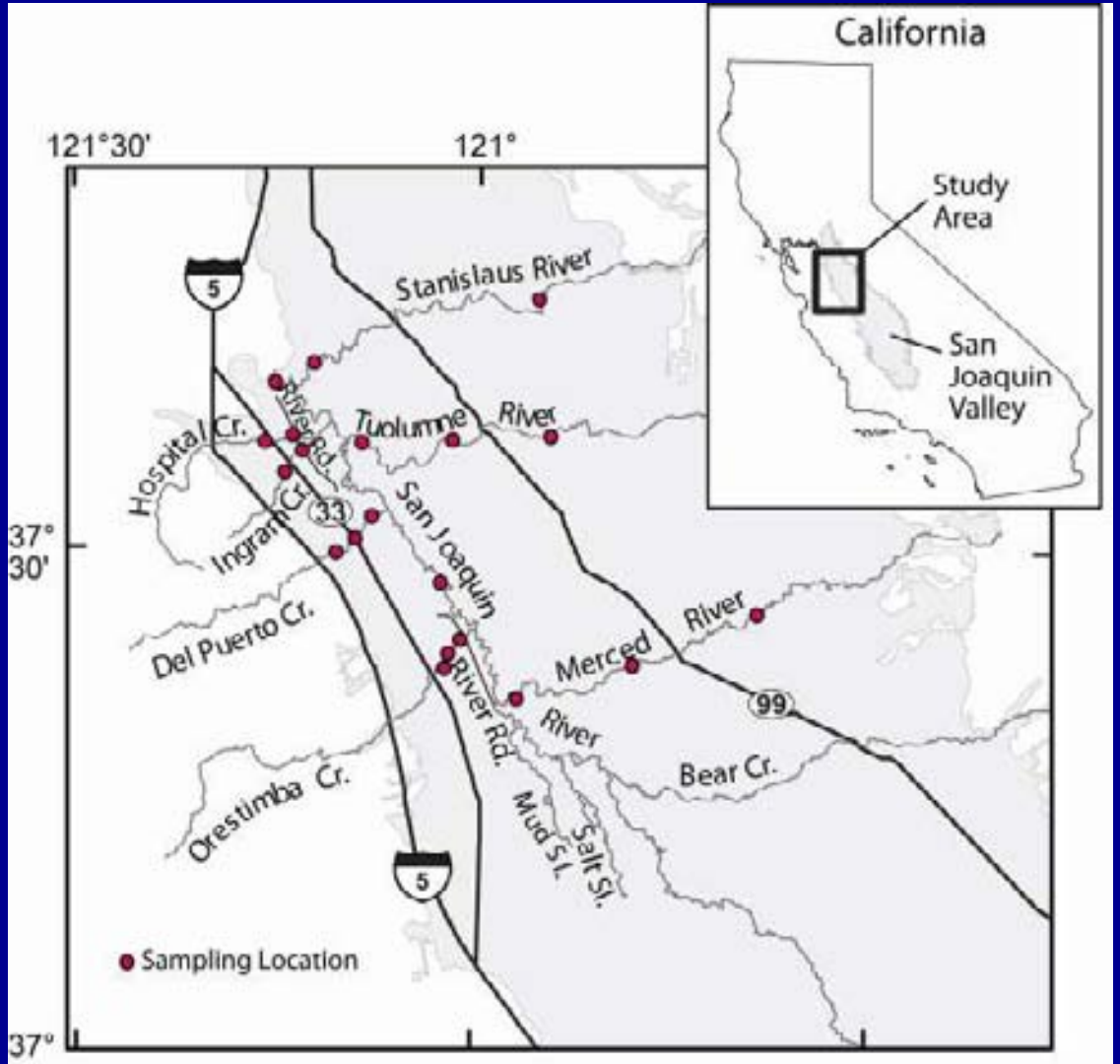
California
Study Area
San Joaquin Valley
121°30'
121°
37° 30'
37°
Stanislaus River
Tuolumne River
Merced River
San Joaquin River
River Rd.
Hospital Cr.
Ingram Cr.
Del Puerto Cr.
Orestimba Cr.
Bear Cr.
Mud Sl.
Salt Sl.
5
33
99
Sampling Location

Results, Bed Sediments, Irrigation Season

- Nine of the 13 pyrethroids detected
- Pyrethroids detected in 97% of samples from west-side streams (1-20 ng/g)
- Most commonly detected bifenthrin, cyhalothrin, permethrin
- Pyrethroids detected in 48% of eastside tributaries (All less than 1 ng/g)
- San Joaquin River (only trace amounts of bifenthrin

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Results, Toxic Units

- TU = Actual sediment concentration of the analyte on organic carbon basis /
- Reported 10-d LC_{50} concentration of the analyte on an organic carbon basis

- 50% survival at 1 TU if pyrethroids are sole source of toxicity; Complete mortality above 1 TU

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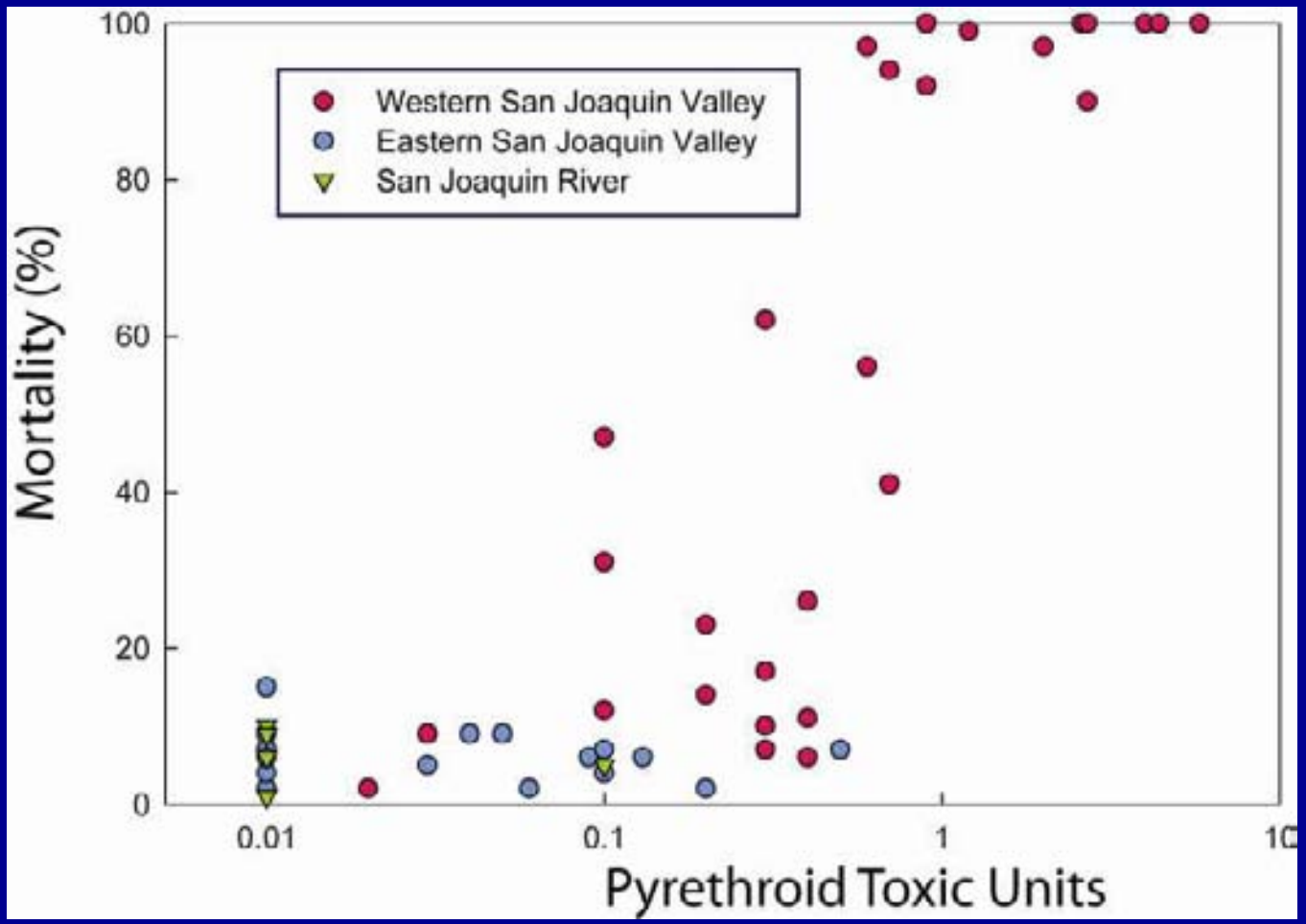
Irrigation Season Results



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Irrigation Season Results, Summary

- Locations have TU's greater than one: Ingram and Hospital Creeks
- Del Puerto and Orestimba Creeks: Mortality observed, but less than Ingram and Hospital
- East-side tributaries: Very little mortality
- San Joaquin River: Very little mortality
- Bifenthrin, Cyhalothrin, Cypermethrin, Cyfluthrin: Greatest contributors to toxicity

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Suspended Sediments, Irrigation Season

- Co[redacted]es

Site	% organic carbon	Bifenthrin	Cyfluthrin	Cyhalothrin	Cypermethrin	Esfenvalerate	Fenpropathrin	t-Fluvalinate	Permethrin	Resmethrin
Del Puerto	2.5	(0.7)	ND	(0.7)	ND	ND	ND	ND	ND	ND
Hospital Creek (2)	1.2	9.6	ND	ND	ND	ND	ND	ND	(0.4)	ND
Ingram Creek (2)	1.1	ND	ND	11.1	ND	5.1	ND	ND	ND	ND
Orestimba Creek (3)	1.6	(0.3)	ND	ND	ND	ND	ND	ND	1.1	ND

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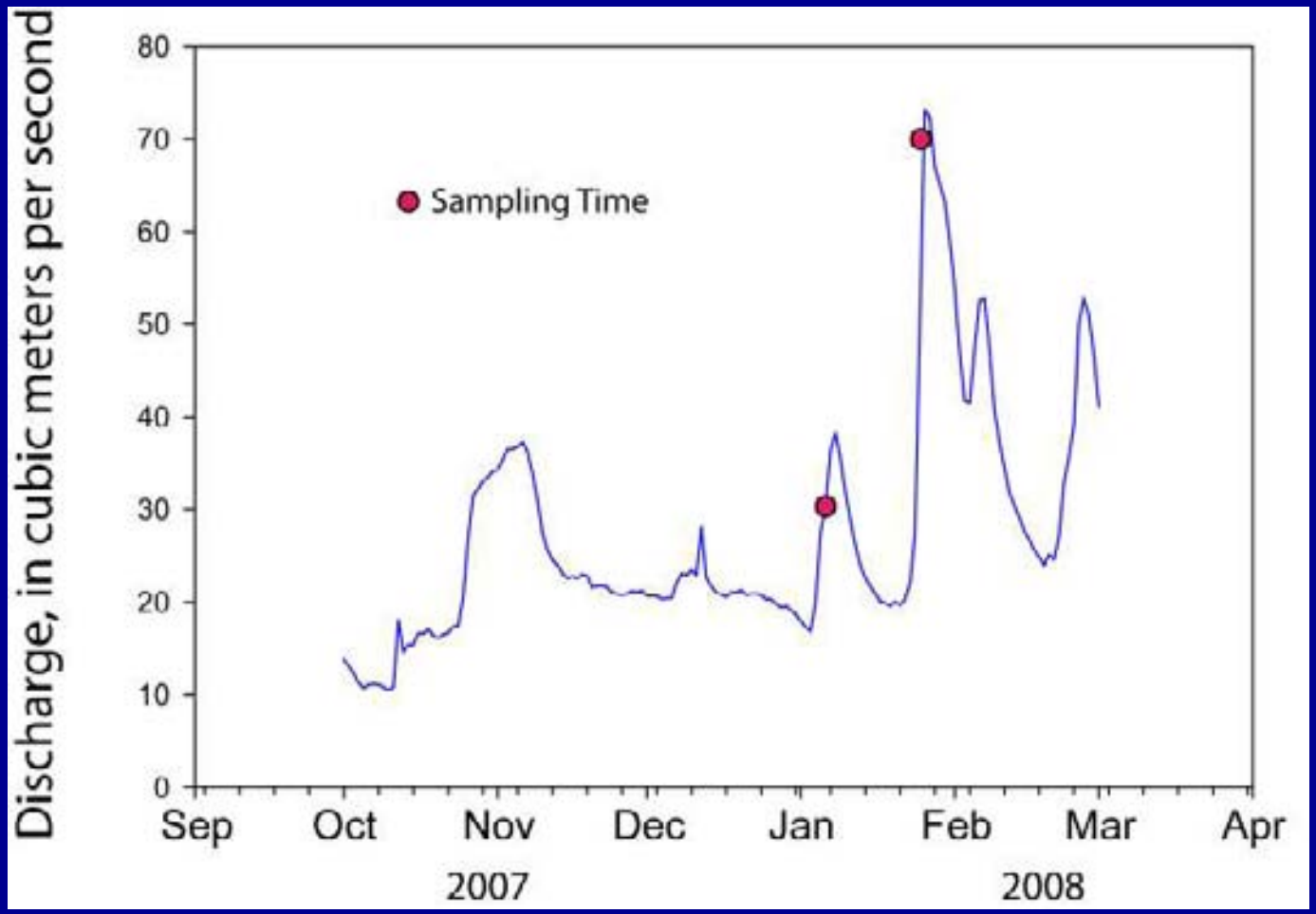
Suspended Sediment Storm Samples



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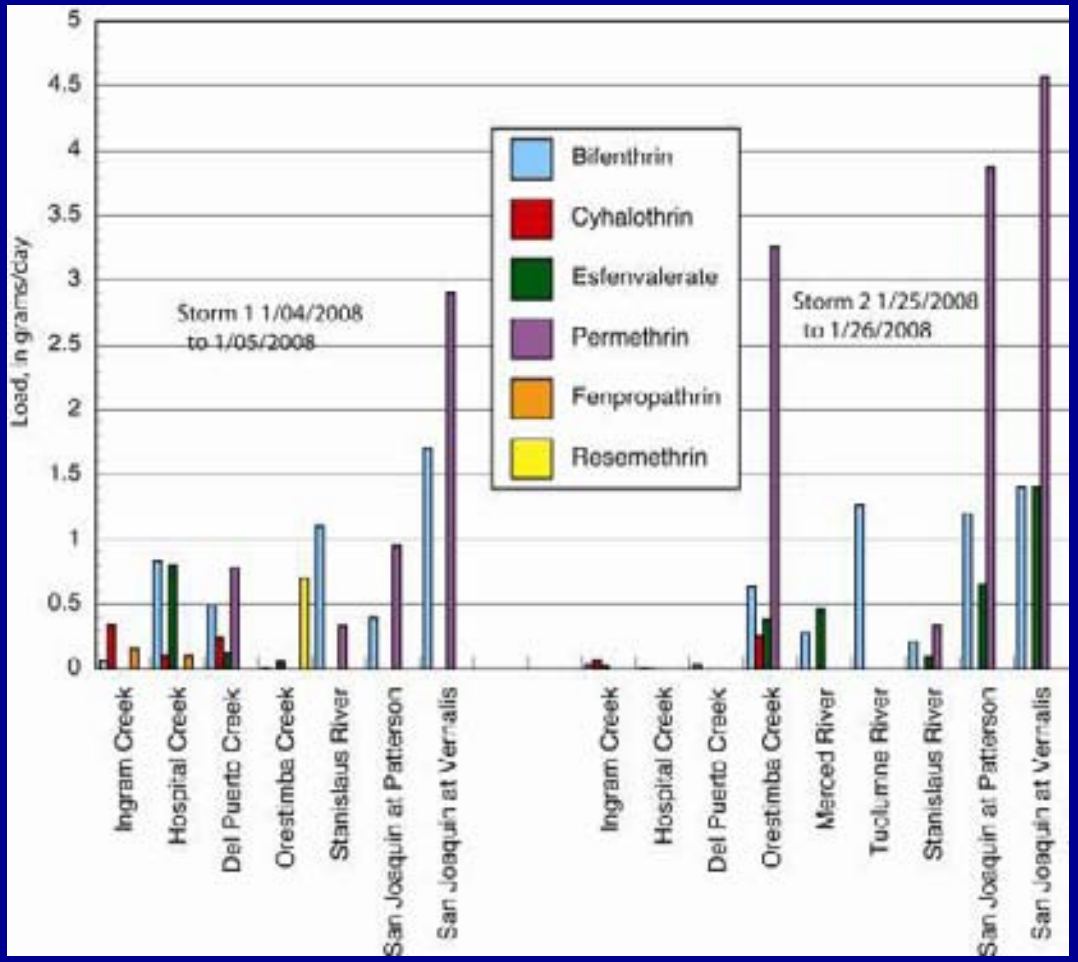
Pyrethroid Loads, Storm Samples



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Storm Samples: Summary

- Highest individual concentration: Bifenthrin at Stanislaus River, 51 ng/g
- Highest permethrin concentration: 15.9 ng/g at Stanislaus River
- All west and east side tributaries had detectable concentrations of pyrethroids

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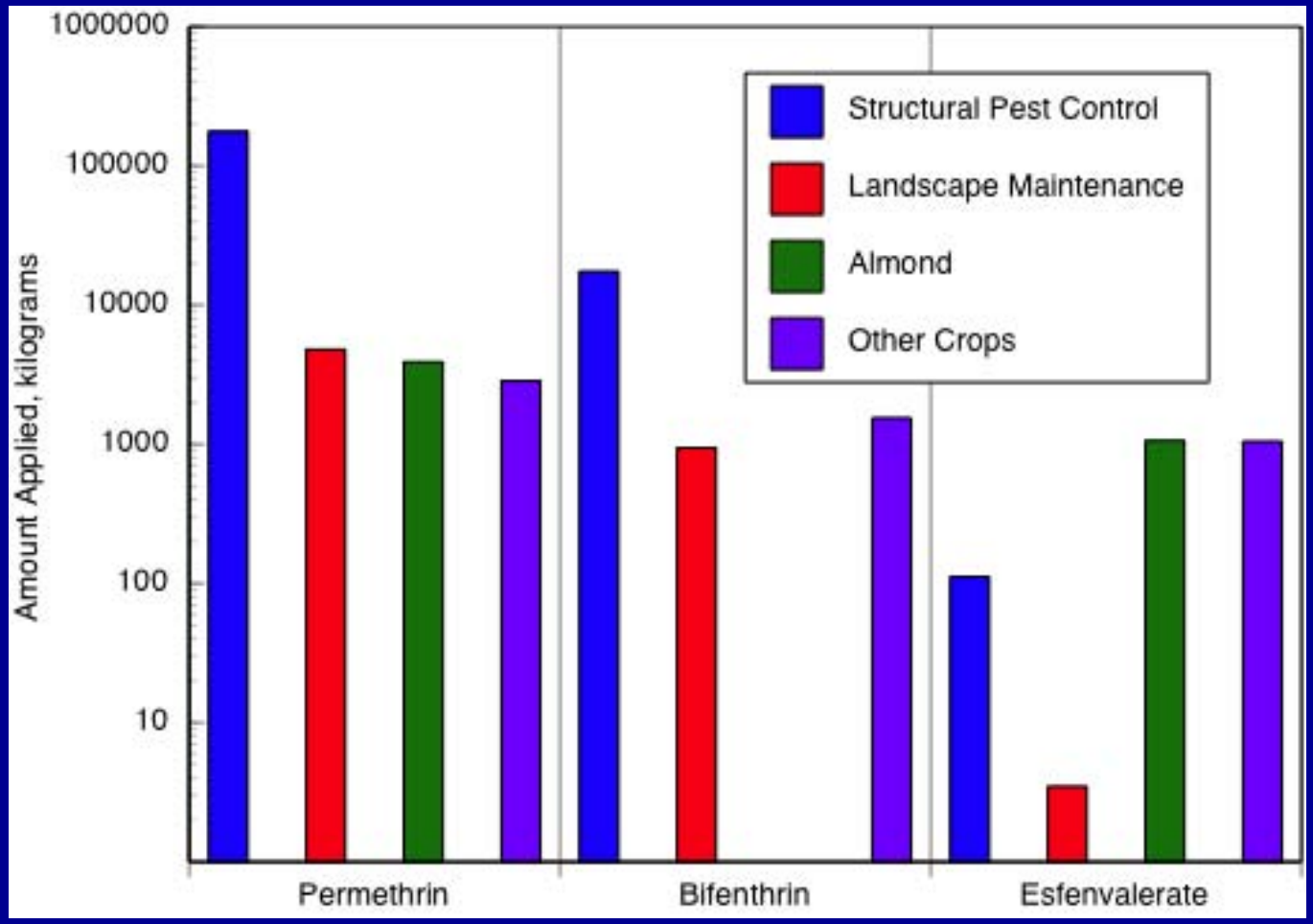
Are Stormwater Concentrations From Recent Applications: (Dormant Sprays?)



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Summary

- Bifenthrin, Cyhalothrin, and Permethrin: Most commonly detected in bed sediments
- Small west side creeks have most frequent occurrence and highest toxicity of bed sediments
- Ingram/Hospital Creeks: Occurrence linked to agricultural use?
- East tributaries and SJR had low toxicity of sediments and low pyrethroid concentrations
- In contrast, eastern tributaries contribute to load of pyrethroids in San Joaquin River