

Methods Development for the Analysis of Pyrethroid Pesticides in Environmental Samples

Public Meeting for
CALFED Funded Project ERP-02-P42
April 25, 2007

Joint Project Between:
U.S. Geological Survey
California Department of Fish and Game
California Department of Pesticide Regulation
California Department of Food and Agriculture

Project Personnel

- Principle Investigators
 - USGS: Kathy Kuivila, Michelle Hladik
 - CDFG: Dave Crane
 - CDPR: Kean Goh
- Scientists
 - CDFG: Abdou Mekebri
 - CDFA: Jane White, Steven Siegel
 - CDPR: Carissa Ganapathy

Agenda

- 9:00 – Introduction, Overview of Pyrethroids (use, fate, toxicity)
- 9:30 – Water and Sediment Methods: **CDFA**
- 9:50 – Water, Sediment and Biota Methods: **CDFG**
- 10:10 – Break
- 10:20 – Water, Sediment and Colloid Methods: **USGS**
- 10:40 – Results of Round-Robin Water and Sediment Samples
- 11:00 – Summary
- 11:20 – **PWG Methods**
- 11:30 – Question and Answer

Proposal and Funding

- Original proposal included both **analytical method development** and **2 field studies** (use on rice and orchards)
- CALFED **funded the method development** part and suggested that the field component should wait until methods had been developed and validated
- Project was set to start in 2004 but due to contracting delays did not start until 2005
- Project has had technical advisory committee meetings once a year
- Website for dissemination of data
<http://www.cdpr.ca.gov/docs/sw/swpyreth.htm>

Project Objectives

- Develop, test and validate methods for analysis of 6 or more pyrethroids insecticides in **water, colloids, sediments, and biota**
- Pyrethroids in original work plan
 - bifenthrin
 - λ -cyhalothrin
 - cyfluthrin
 - cypermethrin
 - esfenvalerate
 - permethrin

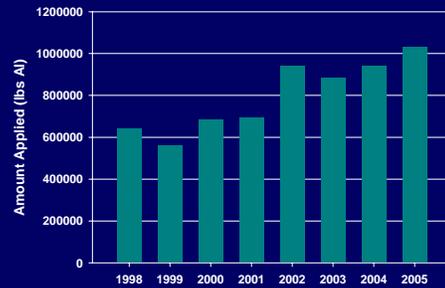
Approach

- **LABORATORIES:**
 - US Geological Survey
 - California Dept. of Fish and Game
 - California Dept. of Food and Agriculture
- **MATRICES:**
 - Water and Bed Sediment – All 3 Labs
 - Suspended sediments – USGS
 - Colloids: USGS
 - Biota: CDFG

Technical Advisory Committee

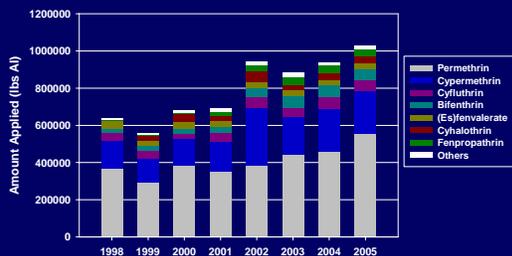
- Input on priorities from regulatory and toxicological viewpoints
- Members
 - Bill Croyle- CV RWQCB
 - Ag waiver program
 - Robert Holmes- CV RWQCB
 - Lower Sacramento River Watershed Program, SWAMP
 - Karen Larsen- CV RWQCB
 - Sacramento River Watershed Program
 - Jeff Miller- AquaScience (toxicology)

Pyrethroid Use in California PUR Database



<http://www.cdpr.ca.gov/docs/pur/purmain.htm>

CA Use by Pyrethroid



<http://www.cdpr.ca.gov/docs/pur/purmain.htm>

Additional Pyrethroids Added

- Throughout the project additional compounds
 - Not added to all matrices
 - Not added by all labs
- Mainly agricultural
 - Deltamethrin
 - Fenpropathrin
 - α -Fluvalinate
- Urban/public health
 - Resmethrin
 - Sumithrin
 - Allethrin
 - Tetramethrin
 - Tralomethrin

Pyrethroid Fate

- Water Solubility
 - 0.01-10 ppb
- Sorption:
 - Log K_{ow} 4-7
 - Log K_{oc} 4.5-6
 - Usually associated with sediments
 - Soil half lives of months
- Photolysis and Hydrolysis
 - Fairly stable
 - Hydrolysis half lives of weeks to months
- Low vapor pressure
 - Not readily volatilized
- Environmental fate reviews (bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, permethrin)
 - <http://www.cdpr.ca.gov/docs/empmpubs/envfate.htm>

Pyrethroid Toxicity- Water

Pesticide	Fresh Water		Salt Water	
	48 h- LC ₅₀ (ng/L)	Organism	96 h- LC ₅₀ (ng/L)	Organism
Bifenthrin	70	<i>Ceriodaphnia dubia</i>	4	<i>Americamysis bahia</i>
Cyfluthrin	140	<i>Ceriodaphnia dubia</i>	2	<i>Americamysis bahia</i>
Cypermethrin	130	<i>Ceriodaphnia dubia</i>	5	<i>Americamysis bahia</i>
Deltamethrin	37	<i>Daphnia magna</i>	17	<i>Americamysis bahia</i>
Esfenvalerate	240	<i>Daphnia magna</i>	38	<i>Americamysis bahia</i>
Permethrin	75	<i>Daphnia magna</i>	20	<i>Americamysis bahia</i>

Data from: Data from U.S. EPA Ecotox and DPR Ecotox

Pyrethroid Toxicity- Water and Sediment

Pesticide	Water		Sediment	
	48 h- LC ₅₀ (ng/L)	Organism	10 d- LC ₅₀ (µg/kg)	Organism
Bifenthrin	70	<i>Ceriodaphnia dubia</i>	5	<i>Hyalella azteca</i> ²
Cyfluthrin	140	<i>Ceriodaphnia dubia</i>	10	<i>Hyalella azteca</i> ²
Cypermethrin	130	<i>Ceriodaphnia dubia</i>	3-6	<i>Hyalella azteca</i> ³
Esfenvalerate	240	<i>Daphnia magna</i>	15	<i>Hyalella azteca</i> ²
Permethrin	75	<i>Daphnia magna</i>	110	<i>Hyalella azteca</i> ²

Water data from: Data from U.S. EPA Ecotox and DPR Ecotox
 Sediment data from: Amwag et al., 2005, *Environ. Toxicol. Chem.*, 24, 966-972
 Maund et al., 2002, *Environ. Toxicol. Chem.*, 21, 9-15

Outline of Project Scope

- Method detection limits
 - How low do they need to be?
 - Current MDLs in water and sediment
- Sample holding times
- Extract holding times
- Sorption studies
 - Sorption to sample containers that affect analysis

MDLs Needed

- Optimal MDL use LC₅₀/10
 - Water
 - ~0.2 ng/L
 - Sediment
 - ~0.3 µg/kg
- Acceptable MDL equal to LC₅₀
 - Water 2 ng/L
 - Sediment 3 µg/kg