Pyrethroid Insecticides: Analysis, Occurrence and Fate in the Sacramento and San Joaquin Rivers and Delta

Kathryn Kuivila, US Geological Survey
David Crane, California Department of Fish and Game
Kean Goh, California Department of Pesticide Regulation

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TAC Meeting March 22, 2006

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Proposal and Funding

- Analytical method development

- Contract with USGS completed in early 2004 with subsequent subcontracts to CDFG and CDPR

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Project Objectives

Develop, test and validate methods for analysis of 6 or more pyrethroids insecticides in water, colloids, sediments, and biota.

Pyrethroids:

bifenthrin
cyfluthrin
cypermethrin
esfenvalerate
lambda-cyhalothrin
permethrin

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Approach

LABORATORIES:

US Geological Survey
California Dept of Fish and Game
California Dept of Food and Agriculture

MATRICES:

Water: all 3 labs
Sediments:
- Bed sediments – CDFG, USGS, CDFA
- Suspended sediments - USGS

Colloids: USGS
Biota: CDFG

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Scope of Work

Task 1: Project Management and Administration

Task 2: Project Design and Oversight

formation of TAC and annual meetings
public meeting near completion of method development
study design (literature review and method validation process)

Task 3: Analytical Method Development and Validation

development of analytical methods
sample collection and preservation methods
validation of analytical methods

Task 4: Methods for Toxicity Testing (USGS funded)

Task 5: Draft and Final Report

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Current Timeline for Deliverables

Contract signed with USGS on January 5, 2004 but subcontracts with CDFG and CDPR delayed until late 2004
CALFED has approved one-year no cost extension as of February 16, 2006

Annual TAC meeting	April 2005, March 2006, February 2007?
Public meeting	April 1, 2007
Analytical methods validated	July 1, 2007
Draft final report	Oct 1, 2007
Final report	Dec 31, 2007
Project ends	Jan 4, 2008

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Responsibilities of the TAC

- Participate in annual meetings
- Input on priorities from regulatory and toxicological viewpoints
- Review draft final report
- Suggestions for field studies with validated method

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Agenda for Meeting

10:00	Overview of Project
	Update on method development
	Questions raised at last TAC meeting
	Laboratory Inter-calibrations
12:00	Lunch
	Monitoring and sampling results
	Discussion- other priorities, changes, suggestions
	Wrap-up, next meeting
15:00	Meeting ends

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Update of Method Development

Pyrethroid	CDFA	CDFG	USGS
Bifenthrin	x	x	x
Cyfluthrin (beta)	x (4)	x	x
Cyhalothrin (lambda and gamma)	x	x	x
Cypermethrin (alpha, beta, theta, zeta)	x	x	x
Esfenvalerate/fenvalerate	x	x	x
Permethrin (cis and trans)	x	x	x
Deltamethrin	x	x	x
Fenpropathrin	x		x
tau-Fluvalinate			x
Resmethrin	x	x	x
Sumithrin			x
Allethrin		x	x
Tetramethrin		x	x

Update of Method Development

Lab	Medium	Extraction Method	Volume	Analysis Method	MDLs
USGS	Water	Filtered sample; HLB cartridge with bottle rinse	1 L	GC/MS	2-5 ng/L
	Sediment (bed and suspended)	MASE/GPC/ Florisil	5 g (dry weight)	GC/MS	1-8 ng/g using carbon/alumina clean-up, now using florisil
CDFG	Water	Whole water; liq/liq extraction	1 L	GC-ECD & GC/MS	1-5 ng/L
	Sediment (bed)	ASE/GPC/ Florisil	5 g (dry weight)	GC-ECD & GC/MS	1-4 ng/g
	Tissue	ASE/GPC/ Florisil	10 g (fresh weight)	GC-ECD & GC/MS	1-5 ng/g estimated
CDFA	Water	Whole water; liq/liq extraction, florisil clean-up	1L	GC/MS & GC-ECD	1- 4 ng/L
	Sediment (bed)	Solvent shake, florisil clean-up	20 g (wet weight)	GC/MS & GC-ECD	0.1 – 0.2 ug/kg

Question from last TAC meeting

Sorption of pyrethroids onto container issue
- Addressed for most laboratory analytical purposes
- USGS received additional money from EPA for field sampling SOP

Pyrethroid isomers, more pyrethroids (fenpropathrin)
- Added as many isomers as we could find
- Added more pyrethroids, including West Nile and home use

Stability in solvents
- Each lab has tested stability, providing write-ups for the final report

Include costs per sample
- CDFG and CDFA will

Website for dissemination of data
- http://www.cdpr.ca.gov/docs/sw/swpyreth.htm

Environmental fate reviews (bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, permethrin)
- http://www.cdpr.ca.gov/docs/empm/pubs/envfate.htm

Inter-laboratory Calibrations

- Water Samples
  - American River water spiked with suspended sediments and pyrethroids
  - More “normal” environmental sample
  - Both samples spiked with pyrethroids at two concentrations
    - 2-5 times reporting limit
    - near highest environmental concentration
  - All labs will analyze spiked and unspiked solutions
  - USGS will analyze SSC, % organic C on SSC and DOC
  - Other possibilities
    - “nasty” sample, Willow Slough, Winter ’07?
    - known sediments with pyrethroids spiked into American River water

Inter-laboratory Calibrations

- **Sediment Samples**
  - **Sediments will be spiked at two concentrations**
  - **Try to find real environmental samples with pyrethroids**
    - **Central coast samples?**
  - **Check into SRM for pyrethroids and performance evaluation sample**

Issues to discuss

- New TAC member?
- Running a public meeting
- Format of final report