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

US Geological Survey
California Department of Fish and Game
California Department of Pesticide Regulation

project funded by CALFED Ecosystem Restoration Program

TAC Meeting February 14, 2007
Proposal and Funding

• Analytical method development

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

• Contract with USGS completed in early 2004 with subsequent subcontracts to CDFG and CDPR
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
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: Draft and Final Report
## Current Timeline for Deliverables

Contract signed with USGS on January 5, 2004 but subcontracts with CDFG and CDPR delayed until late 2004. CALFED approved a one-year no cost extension.

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Public meeting</td>
<td>April, 2007</td>
</tr>
<tr>
<td>Analytical methods validated</td>
<td>July 1, 2007</td>
</tr>
<tr>
<td>Draft final report</td>
<td>Oct 1, 2007</td>
</tr>
<tr>
<td>Final report</td>
<td>Dec 31, 2007</td>
</tr>
<tr>
<td>Project ends</td>
<td>Jan 1, 2008</td>
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</table>
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
Agenda for Meeting

• Project Update
• Method Summary
• Inter-lab calibrations
• Public Meeting
• Final Report
## Update of Method Development

<table>
<thead>
<tr>
<th>Pyrethroid</th>
<th>CDFA</th>
<th>CDFG</th>
<th>USGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Cyfluthrin (beta)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Cyhalothrin (lambda and gamma)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Cypermethrin (alpha, beta, theta, zeta)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Esfenvalerate/fenvalerate</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Permethrin (cis and trans)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Fenpropathrin</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>tau-Fluvalinate</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Resmethrin</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Sumithrin</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Allethrin</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Tetramethrin</td>
<td></td>
<td></td>
<td>X</td>
</tr>
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</table>
## Update on Method Development

<table>
<thead>
<tr>
<th>Lab</th>
<th>Medium</th>
<th>Extraction Method</th>
<th>Volume</th>
<th>Analysis Method</th>
<th>MDLs</th>
</tr>
</thead>
<tbody>
<tr>
<td>USGS</td>
<td>Water</td>
<td>Filtered sample; HLB cartridge with bottle rinse</td>
<td>1 L</td>
<td>GC/MS</td>
<td>2-5 ng/L</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>MASE/Carbon Alumina/GPC</td>
<td>5 g (dry weight)</td>
<td>GC/MS</td>
<td>1-5 ng/g</td>
</tr>
<tr>
<td></td>
<td>Colloids</td>
<td>SPME</td>
<td>In progress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDFG</td>
<td>Water</td>
<td>Whole water; liq/liq extraction</td>
<td>1 L</td>
<td>GC-ECD &amp; GC/MS</td>
<td>1-5 ng/L</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>ASE/GPC/Florisil</td>
<td>5 g (dry weight)</td>
<td>GC-ECD &amp; GC/MS</td>
<td>1-4 ng/g</td>
</tr>
<tr>
<td></td>
<td>Tissue</td>
<td>ASE/GPC/Florisil</td>
<td>10 g (fresh weight)</td>
<td>GC-ECD &amp; GC/MS</td>
<td>1-5 ng/g estimated</td>
</tr>
<tr>
<td>CDFA</td>
<td>Water</td>
<td>Whole water; liq/liq extraction, florisil clean-up</td>
<td>1 L</td>
<td>GC/MS &amp; GC-ECD</td>
<td>1- 8 ng/L (MRL 5-15 ng/L)</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>Solvent shake, florisil clean-up</td>
<td>20 g (wet weight)</td>
<td>GC/MS &amp; GC-ECD</td>
<td>0.1 – 0.9 ng/g (MRL 1-1.5 ng/g)</td>
</tr>
</tbody>
</table>
Water and Sediment Methods

- Optimized for equipment and instrumentation available

- Lower detection limits can only be achieved with more sensitive instruments or larger samples
  - DFG will present data from triple-quad MS
  - Larger samples not feasible for some samples (suspended sediments), also increases matrix
Method Development Questions

Sorption of pyrethroids onto containers
Addressed for most laboratory analytical purposes (bottle rinse)
USGS received additional money from EPA for field sampling SOP

Stability in solvents for calibration standards
Tested with multiple sets over several months
<10% change over six months

Water and sediment sample stability (following slides)

Include costs per sample
CDFG and CDFA

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
Pyrethroid Stability in Water

• CDFA- spikes in sediment water
  – Liquid:liquid extraction with Florisil clean-up
  – Spike
    • 87-100% recovery at 0 days
    • 50-100% recovery at 4 days
    • 50-90% recovery at 7 days
  – Keeper solvent (10 mL hexane)
    • 95-100% recovery at 0 days
    • 65-100% recovery at 4 days (most compounds better than before keeper)

• USGS SPE Cartridges
  – Pyrethroids are stable for 28 days on HLB cartridge (frozen)

• Need to analyze water samples quickly, within 24 hours is optimal
Pyrethroid Stability in Sediment

• CDFA- pyrethroid spikes onto sediment
  – Stable for one month

• USGS Analysis of sediment
  – Extracted after collection and after one year
  – Lamda-cyhalothrin concentrations were the same
Pyrethroid Inter-Lab Comparisons Water

- Spiked American River water (with 500 mg/L CBD sediment) and CBD water (6 mg/L DOC; 14 mg/L suspended sediment)
- Samples spiked in 20 L soda kegs
- With continuous stirring, water was pumped into 1 L glass bottles
- 2 concentrations: 10 ng/L and 100 ng/L
- Each lab received samples and spiking solution (2 ng/mL)
- Samples extracted within 48 hours (2 used liquid:liquid and one used SPE + filter extract)
- GC-ECD and MS detection
- No detects in blanks for any of the labs
Spiking Solution

• Sent out spiking solution (used by USGS) to labs
• Agreed on concentration of spike (± 10%)

Low Level Water Samples (10 ng/L)

• 10 ng/L
• One lab: below MRL
• Lab # 1 ~3-9 ng/L
• Lab # 2 ~ 3-8 ng/L
American River Sediment Water (500 mg/L) spiked at 100 ng/L

Lab 1
Lab 2
Lab 3
Colusa Basin Drain Water spiked at 100 ng/L

- Bifenthrin
- Fenpropathrin
- Cyhalothrin
- Permethrin
- Cyfluthrin
- Cypermethrin
- Etovalerate
- Deltamethrin

The graph shows the concentration of various insecticides in the drain water from three different laboratories (Lab 1, Lab 2, and Lab 3). The x-axis represents different insecticides, and the y-axis represents the concentration in ng/L.
Pyrethroid Water Summary

- 10 ng/L did not work well, too low with 500 mg/L sediment
- Sediment water (500 mg/L),
  - Highest suspended sediment concentration
  - Fairly good agreement but concentrations measured were lower than expected (50-70%)
- Colusa Basin Drain
  - Better recovery (>70%) and all concentrations with one standard deviation
  - Composition more similar to most waters sampled
Pyrethroid Inter-Lab Comparisons Sediment

• Sediment collected from Salinas area by DPR
• All labs received 2 1-L jars of sediment
• Extractions were completed within one month
• One lab used shaking, one microwave and one pressurized solvent extraction
Sediment Extracted for Pyrethroids

- Bifenthrin
- Cyfluthrin
- Cyhalothrin
- Cypermethrin
- Fenpropathrin
- Fenvalerate/Esfenvalerate
- Permethrin

Lab 1
Lab 2
Lab 3
Pyrethroid Inter-Lab Comparisons

Sediment

• Slight differences in concentrations due to extraction methods
• Sonication has been shown to quantify 30% less than heated or pressurized extractions for OC and OP pesticides on aged sediments
• Also retain less matrix
Public Meeting

• Must be held in April
• Room reserved at Cal EPA for April 25\textsuperscript{th} 9 am – 1pm
  • Change location?
• Topics to cover
  • Methods
    • Water and Sediment
    • Advantages and Disadvantages
    • Validation (inter-lab calibrations)
• Groups to Invite
Final Report

• Validated methods must be given to CALFED by July 1
  • Include full methods
  • Recoveries
  • MDLs
  • Include inter-lab calibrations

• Final Report
  • No desired format
  • Stability, sorption