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 pyrethroid insecticides in water, colloids, sediments, and biota

• Pyrethroids in original work plan
  – bifenthrin
  – 3,4-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

Additional Pyrethroids Added

- Throughout the project additional compounds
  - Not added to all matrices
  - Not added by all labs

- Mainly agricultural
  - Deltamethrin
  - Fenpropathrin
  - τ-Fluvalinate

- Urban/public health
  - Resmethrin
  - Sumithrin
  - Allethrin
  - Tetramethrin
  - Tralomethrin

Pyrethroid Fate

- Water Solubility
  - 0.01-10 ppb

- Sorption:
  - Log Kow 4-7
  - 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/empm/pub/envfate.htm

Pyrethroid Toxicity - Water

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Fresh Water</th>
<th>Salt Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>48 h. LC50 (ng/L)</td>
<td>96 h. LC50 (ng/L)</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>70</td>
<td>4</td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>140</td>
<td>2</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>130</td>
<td>5</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>37</td>
<td>17</td>
</tr>
<tr>
<td>Esfenvalerate</td>
<td>240</td>
<td>38</td>
</tr>
<tr>
<td>Permethrin</td>
<td>75</td>
<td>20</td>
</tr>
</tbody>
</table>

Data from: Data from U.S. EPA Ecotox and DPR Ecotox
### Pyrethroid Toxicity - Water and Sediment

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Water</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>48 h- LC₅₀ (μg/L)</td>
<td>16 d- LC₅₀ (μg/kg)</td>
</tr>
<tr>
<td></td>
<td>Organism</td>
<td>Organism</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>70</td>
<td>Ceriodaphnia dubia</td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>140</td>
<td>Ceriodaphnia dubia</td>
</tr>
<tr>
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</tr>
</tbody>
</table>

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

### 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