Environmental Fate and Aquatic Toxicology of the Synthetic Pyrethroids

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On behalf of the PWG member companies: Bayer, DuPont, FMC, Pytech, Syngenta, Valent
Outline

- Environmental Fate
  - Lab data
  - Adsorption
  - Fate-o-cosm
- Aquatic Toxicology
  - Lab data
  - Equilibrium Partitioning Theory
  - Species Sensitivity Distributions
  - Microcosm and Mesocosm Studies
- Sediment Analytical Method
Physical and Chemical Properties of Pyrethroids

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### Pyrethroid Abiotic - Fate Properties

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Hydrolysis Half Life, days</th>
<th>Photolysis Half life, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 7</td>
<td>pH 9</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>183</td>
<td>1.8</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>274</td>
<td>1.9</td>
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<tr>
<td>Deltamethrin</td>
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<td>2.2</td>
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<tr>
<td>Esfenvalerate</td>
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<td>Stable</td>
</tr>
<tr>
<td>Fenpropathrin</td>
<td>555</td>
<td>14</td>
</tr>
<tr>
<td>Lambda-cyhalothrin</td>
<td>Stable</td>
<td>8.7</td>
</tr>
<tr>
<td>Permethrin</td>
<td>Stable</td>
<td>242</td>
</tr>
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</table>
## Pyrethroid Biotic - Degradation (lab studies)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Aerobic Soil Half Life, days</th>
<th>Anaerobic Soil Half Life, days</th>
<th>Aerobic Aquatic Half Life, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>96</td>
<td>Stable</td>
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<tr>
<td>Cyfluthrin</td>
<td>12</td>
<td>34</td>
<td>3.0</td>
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<tr>
<td>Cypermethrin</td>
<td>28</td>
<td>55</td>
<td>7.4</td>
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<tr>
<td>Deltamethrin</td>
<td>24</td>
<td>29</td>
<td>80</td>
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<tr>
<td>Es/fenvalerate</td>
<td>39</td>
<td>90</td>
<td>72</td>
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<tr>
<td>Fenpropathrin</td>
<td>22</td>
<td>276</td>
<td></td>
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<tr>
<td>Lambda-cyhalothrin</td>
<td>43</td>
<td></td>
<td>22</td>
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<tr>
<td>Permethrin</td>
<td>40</td>
<td>197</td>
<td></td>
</tr>
</tbody>
</table>
Adsorption to Soils etc.

- $K_{oc}$ values in the range of 100,000 - 1,000,000 ml/g
  - Primary driver for E-fate behavior
- Fast & strong adsorption results in
  - Zero leachability and low runoff potential
    - Pyrethroids will move with soil particles - erosion
  - Rapid removal of chemical from the water column
  - Only short periods of bioavailability in water column
- Interpretation of water residue samples
  - Chemical “detected” in water samples may well be bound to suspended sediment or DOC
    - Must know the context of “detects”
      - “Total” or “dissolved”
Pyrethroid adsorption to organic carbon is extensive
- Sediment Kocs typically 100,000+
- 99%+ adsorbed
- Equilibrium between pore water & sediment reached in a few days
Factors Impacting Pyrethroid Interactions in Aquatic Systems - a complex system

Runoff Entry - pyrethroid almost exclusively adsorbed to Sediment

Drift Entry - pyrethroid in spray droplets

Uptake & metabolism in plants

Total Suspended Solids content - rapidly adsorbs “free” chemical

Microbial degradation of chemical in water phase

Microbial degradation of chemical in sediment

LIGHT
Fate-o-cosms: Pyrethroid fate in the environment?

Distribution of \textit{lambda}-cyhalothrin between water, aquatic plants and sediment in static ditch microcosms systems 0.43 m$^3$

L-cyhalothrin applied into the water column

Rapid decline in water column concentrations

Sediment & plant concentrations peak in 1-3 days, then decline – sorption & degradation

Relatively low proportion of dose reaching the sediment

Key Aquatic Dissipation Processes

- In aquatic ecosystems
  - Rapid binding to plants, sediments and organic matter
  - Greatly reduces exposure of water-column and sediment organisms to the bioavailable fraction
- Metabolism in/on plants causes much faster degradation in addition to microbial processes in soil and aquatic phase.
  - Only chemical which desorbs into aqueous phase can exert biological effect
- Majority of pyrethroid in sediment phase
Pyrethroid Aquatic Toxicity Studies

- PWG review of aquatic tox laboratory data
  - Covering 9 synthetic pyrethroids from introduction in mid 70’s
  - >600 reports from registrants & open literature
  - >3000 endpoints covering >220 different aquatic species

- Evaluation criteria applied & most reliable species endpoints for each pyrethroid listed
  - 650 acute values
  - 60 chronic values

- What is the best way to utilize this data set?
Equilibrium Partitioning Theory (EqP)

Nonionic Organic Chemicals

- Tool to normalize toxicity results across sediments due to the high variability in bioavailability sediments
  - Developed based on field and lab observations (e.g., PAHs)
- Normalizes toxicity based on the organic content of the sediment using Koc
- Water column toxicity data can be used to predict sediment toxicity
- Not a perfect model - expect to be within 2 or 3x of actual value - has limits
## Sediment Toxicity Data for Pyrethroids

L(E)C50 values for sediment organisms in ug/g sediment organic carbon

<table>
<thead>
<tr>
<th>Organism</th>
<th>Bif</th>
<th>Cyf</th>
<th>L-cy</th>
<th>Cyp</th>
<th>Del</th>
<th>Esf</th>
<th>Per</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyalella azteca*</td>
<td>0.52</td>
<td>1.1</td>
<td>0.45</td>
<td>0.36</td>
<td>0.79</td>
<td>1.5</td>
<td>10</td>
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<tr>
<td>Leptocheirus plumulosus</td>
<td>5.9</td>
<td>0.85</td>
<td></td>
<td>1.6</td>
<td></td>
<td>4.4</td>
<td></td>
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<tr>
<td>Asellus aquaticus</td>
<td></td>
<td></td>
<td></td>
<td>1.4</td>
<td></td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>Chironomus tentans</td>
<td>45</td>
<td>5.1</td>
<td>5.3</td>
<td></td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chironomus riparius</td>
<td></td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
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<td>22</td>
</tr>
</tbody>
</table>

EqP Applied to Pyrethroid Sediment Toxicity Data

<table>
<thead>
<tr>
<th>Exposure type</th>
<th>1% OC sediment</th>
<th>3% OC sediment</th>
<th>13% OC sediment</th>
<th>Geometric mean</th>
<th>Water alone (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sediment effect conc. (ug/kg)</td>
<td>Sediment effect conc. (ug/g OC)</td>
<td>Water effect conc. (ng/L)(^a)</td>
<td>Sediment effect conc. (ug/kg)</td>
<td>Sediment effect conc. (ug/g OC)</td>
</tr>
<tr>
<td>Hyalella 10 day LC(_{50})</td>
<td>3.6</td>
<td>0.36</td>
<td>1.2</td>
<td>13</td>
<td>1.3</td>
</tr>
<tr>
<td>Chironomus 10 day LC(_{50})</td>
<td>18</td>
<td>0.60</td>
<td>1.9</td>
<td>67</td>
<td>2.2</td>
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<tr>
<td></td>
<td>23</td>
<td>0.13</td>
<td>0.6</td>
<td>62</td>
<td>0.48</td>
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<tr>
<td></td>
<td>na</td>
<td>na</td>
<td>1.1</td>
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<td>na</td>
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<tr>
<td></td>
<td>na</td>
<td>na</td>
<td>3.6</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

\(^a\) Based on Koc of 310,000 for cypermethrin (Laskowski, 2002)

\(^b\) Study endpoint 96 hour EC\(_{50}\)
Pyrethroids and EqP Theory

- Pyrethroid \textit{H.azteca} and \textit{C. tentans} sediment toxicity data are in agreement with EqP Theory
- Organic carbon is a reasonable basis for normalizing sediment effect concentrations across sediments
- Calculated aqueous concentrations adequately represents exposure in sediment
- Can normalize sediment results for comparison water only toxicity studies
Species Sensitivity Distributions – a tool for interpretation

- Y-axis is a probability scale showing cumulative frequency.
- Can estimate % species affected at concn X or concn at which X% of species affected.
- The flatter the slope, the wider the sensitivity distribution.

Cumulative probability

96 h LC$_{50}$ (ug l$^{-1}$)

Less Sensitive

Probability $Y = 0.6982 + 1.8635 \log X$

$r^2 = 0.99 \ P < 0.0001$
Relative Sensitivities of Arthropod Species (Cypermethrin)

- Cumulative percent rank
- LC/EC50 (ug/L)

Species:
- Hyalella azteca
- Americanus bahia
- Hyalella azteca
- 'Water-column' arthropods
- 'Epibenthic/benthic' arthropods
- Cumulative percent rank
- LC/EC50 (ug/L)
Pyrethroid Species Sensitivity Distributions

Fish – water exposure data

Cumulative Percent of Species Affected

LC50 (µg/L)

Cypermethrin
Esfenvalerate
Lambda-Cyhalothrin
Permethrin
Deltamethrin
Fenpropathrin
Pyrethroid Species Sensitivity Distributions

Arthropods – water exposure data

- Cypermethrin
- Esfenvalerate
- Lambda-Cyhalothrin
- Permethrin
- Bifenthrin
- Deltamethrin
- Fenpropathrin
- Cyfluthrin

Cumulative percent of species affected vs. LC50 (µg/L)
Implications from Species Sensitivity Distributions (SSDs)

- All the synthetic pyrethroids have a similar spectrum of toxicity across aquatic species.
- Fish consistently less sensitive than arthropods.
- No inherent difference in sensitivity of water-column vs. epibenthic/benthic arthropods.
## Pyrethroid Chronic Toxicity – Lowest NOECs (water-only, µg/L)

<table>
<thead>
<tr>
<th>Pyrethroid</th>
<th>Fish</th>
<th>Crustacean</th>
<th>Insect</th>
<th>Mollusk</th>
<th>Algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>0.012 (2)</td>
<td>0.0011 (2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>0.025 (3)</td>
<td>0.0002 (2)</td>
<td></td>
<td>991 (1)</td>
<td></td>
</tr>
<tr>
<td>λ-Cyhalothrin</td>
<td>0.031 (2)</td>
<td>0.0002 (2)</td>
<td>1000 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>0.077 (1)</td>
<td>0.0004 (2)</td>
<td>1300 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>0.017 (4)</td>
<td>0.0010 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esfenvalerate</td>
<td>0.018 (5)</td>
<td>0.0004 (3)</td>
<td>0.79 (1)</td>
<td>1000 (4)</td>
<td></td>
</tr>
<tr>
<td>Fenpropathrin</td>
<td>0.091 (1)</td>
<td>0.0120 (2)</td>
<td>0.33 (1)</td>
<td>0.87 (6)</td>
<td></td>
</tr>
<tr>
<td>Permethrin</td>
<td>0.140 (3)</td>
<td>0.0078 (2)</td>
<td>0.030 (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Parentheses () = number studies available
Microcosms, Mesocosms and Field Studies

- **Experimental Ecosystems**
  - One of the most sophisticated tools available to aquatic toxicologists
  - Study impacts on multiple species together
    - Along with interactions between species
  - Environmentally realistic conditions

- Available for all pyrethroids
Summary of Cypermethrin Effects in Mesocosms

<table>
<thead>
<tr>
<th>Concentration (ng/L)</th>
<th>Cladocera</th>
<th>Copepoda</th>
<th>Rotifera</th>
<th>Chironomidae</th>
<th>Ephemeroptera</th>
<th>Trichoptera</th>
<th>Odonata</th>
<th>Amphipoda</th>
<th>Hydracarina</th>
<th>Oligochaeta</th>
<th>Gastropoda</th>
<th>Fish</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Red: Decline, no recovery
- Orange: Decline, recovery
- Blue: No effect
- Gray: Increase

Giddings, et al, 2001 ETC 20:660
Comparison of Mesocosm NOEC and LOEC with LC50 Distributions (Cypermethrin)

Giddings, et al, 2001 ETC 20:660
Aquatic Field Studies

- Useful tools for studying the effect and fate of pyrethroids under environmental realistic conditions
- Aquatic toxicity
  - Trends are relatively consistent across pyrethroids
  - See effects on sensitive species, typically followed by recovery
  - Trend in sensitivity is from amphipods, isopods, midges, mayflies, copepods, and cladocerans to fish, snails, oligochaetes, and rotifers
  - High inherent toxicity of pyrethroids in standard laboratory toxicity tests are mitigated under field conditions
  - Single species laboratory data is protective of field conditions
Pyrethroid Sediment Analytical Method

- Freshwater and estuarine sediment trace residue method for 8 of the most widely-used pyrethroid insecticides
  - Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and permethrin
- Extraction and clean-up techniques are simple and straightforward
- The limit of quantitation (LOQ) is:
  - 1 µg/kg for permethrin and 0.1 µg/kg for others
- Validated in an independent lab
  - Morse Labs
Sediment Extraction and Clean-up

- Extracted 50 g of sediment by shaking with a mixture of methanol/water and hexane for 1 hour
  - Pyrethroids extracted from sediment by the aqueous methanol
  - Extracted pyrethroids are then partitioned into hexane layer.
  - Centrifuged the samples to separate aqueous and organic layers

- For clean-up load hexane extract on to silica Bond Elut™ solid phase extraction cartridge
  - Pyrethroids will be retained on cartridge.
  - Washed with hexane
  - Eluted the pyrethroids with a solution of hexane/diethyl ether
  - Concentrate eluatrate and re-dissolved in 1 mL of an acetone + 0.1% peanut oil solution

- Residue quantitation by GC-MS/NICI
Method Validation Data for Freshwater Sediment

LOQ spike at 0.1 ug/kg - LOQx10 1 ug/kg for 7 cpds,

(1 and 10 ug/kg for permethrin)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bifenthrin</th>
<th>Fenpropathrin</th>
<th>Lambda-cyhalothrin</th>
<th>Permethrin</th>
<th>Cyfluthrin</th>
<th>Cypermethrin</th>
<th>Esfvenalervate</th>
<th>Deltamethrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>ND</td>
<td>ND</td>
<td>&lt;0.1 ug/kg</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>&lt;0.1 ug/kg</td>
<td>ND</td>
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<tr>
<td>Control</td>
<td>ND</td>
<td>ND</td>
<td>&lt;0.1 ug/kg</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>&lt;0.1 ug/kg</td>
<td>ND</td>
</tr>
<tr>
<td>LOQ spike 1</td>
<td>103%</td>
<td>102%</td>
<td>84%</td>
<td>97%</td>
<td>107%</td>
<td>107%</td>
<td>75%</td>
<td>88%</td>
</tr>
<tr>
<td>LOQ spike 2</td>
<td>106%</td>
<td>94%</td>
<td>99%</td>
<td>105%</td>
<td>102%</td>
<td>102%</td>
<td>82%</td>
<td>78%</td>
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<tr>
<td>LOQ spike 3</td>
<td>107%</td>
<td>107%</td>
<td>94%</td>
<td>94%</td>
<td>107%</td>
<td>105%</td>
<td>82%</td>
<td>84%</td>
</tr>
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<td>LOQ spike 4</td>
<td>107%</td>
<td>108%</td>
<td>93%</td>
<td>101%</td>
<td>104%</td>
<td>73%</td>
<td>86%</td>
<td>86%</td>
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<td>LOQ spike 5</td>
<td>109%</td>
<td>107%</td>
<td>108%</td>
<td>108%</td>
<td>110%</td>
<td>104%</td>
<td>84%</td>
<td>102%</td>
</tr>
<tr>
<td>Mean Recovery</td>
<td>106%</td>
<td>104%</td>
<td>93%</td>
<td>100%</td>
<td>106%</td>
<td>106%</td>
<td>78%</td>
<td>88%</td>
</tr>
<tr>
<td>RSD</td>
<td>2.1</td>
<td>5.7</td>
<td>11.0</td>
<td>5.2</td>
<td>2.6</td>
<td>2.9</td>
<td>6.0</td>
<td>10.1</td>
</tr>
<tr>
<td>10x LOQ spike 1</td>
<td>100%</td>
<td>110%</td>
<td>106%</td>
<td>97%</td>
<td>111%</td>
<td>111%</td>
<td>105%</td>
<td>104%</td>
</tr>
<tr>
<td>10x LOQ spike 2</td>
<td>111%</td>
<td>115%</td>
<td>121%</td>
<td>124%</td>
<td>127%</td>
<td>130%</td>
<td>122%</td>
<td>116%</td>
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<tr>
<td>10x LOQ spike 3</td>
<td>109%</td>
<td>116%</td>
<td>113%</td>
<td>107%</td>
<td>119%</td>
<td>120%</td>
<td>117%</td>
<td>111%</td>
</tr>
<tr>
<td>10x LOQ spike 4</td>
<td>102%</td>
<td>108%</td>
<td>104%</td>
<td>93%</td>
<td>108%</td>
<td>105%</td>
<td>99%</td>
<td>99%</td>
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<tr>
<td>10x LOQ spike 5</td>
<td>115%</td>
<td>116%</td>
<td>118%</td>
<td>117%</td>
<td>120%</td>
<td>122%</td>
<td>115%</td>
<td>109%</td>
</tr>
<tr>
<td>Mean Recovery</td>
<td>107%</td>
<td>113%</td>
<td>112%</td>
<td>108%</td>
<td>117%</td>
<td>118%</td>
<td>112%</td>
<td>108%</td>
</tr>
<tr>
<td>RSD</td>
<td>5.8</td>
<td>3.3</td>
<td>6.6</td>
<td>12.1</td>
<td>6.5</td>
<td>8.3</td>
<td>8.4</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Analytical Method Conclusions

- The limit of quantitation (LOQ) is 1 µg/kg for permethrin and 0.1 µg/kg for all others
  - LOD - 0.01 - 0.06 µg/kg (permethrin 0.2 ug/kg)
- Mean validation recoveries for all pyrethroids were between 78-118% with RSD values of ≤13%
- The methodology is suitable for analysis of ultra-trace residues of widely used pyrethroid insecticides in CA freshwater and marine sediments
- The method is simple and cost-effective to carry out and has been successfully used for routine analyses in commercial laboratories
  - Batch of 10 to 12 samples can be prepared, extracted and analyzed in 7 man hours
  - Cost < $300 per sample
  - Run routinely for > 150 sediment samples from wide range of central valley locations
  - Low to Moderate equipment cost for NCI detector
Analytical next steps

- Widely available sediment methods
  - Move to performance based standards of acceptability
  - Ensure standards are available, meaningful (e.g. positional isomer ratios) & well characterized
  - Round Robin study needed – more EPA approved labs who can easily perform sediment analyses.
    - Will require an (aged) “standard sediment” sample
    - Also for SPME negligible depletion methodology

- Recommended Analytical Approaches
  - Measure TSS in all pyrethroid water phase analyses
  - Measure %OM & % dry weight for sediment studies
  - Report residues on a dry weight basis
  - Perform SPME analysis for sediment samples to complement the “total” method
E-fate and Ecotox Summary

- The bioavailability of pyrethroids in the environment must be considered when evaluating pyrethroid toxicity and exposure data.
- Equilibrium partitioning theory works for the pyrethroids.
- There is abundant information on pyrethroid fate and toxicity in aquatic systems.
  - Including environmentally realistic large scale field studies.
- No inherent difference in sensitivity between water-column and sediment organisms.
  - Data from water column organisms can be used to predict effects to sediment dwellers.
Path Forward

- A large body of E-fate and Ecotox data is available
  - The challenge is using it all!
- Target additional studies to area’s that will help resolve the risk and regulatory questions
  - Have a clearly defined Management Goal
PWG Contacts

- **Member Companies**
  - Bayer, DuPont, FMC, Pytech, Syngenta, Valent

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