RAPID ANALYSIS OF SYNTHETIC PYRETHROIDS IN STORMWATER

Rapid Trace Analysis of Synthetic Pyrethroids in Stormwater Using online pre-concentration followed by Liquid Chromatography-Tandem Mass Spectrometry

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Riverside, CA 92507
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Outline

- What are synthetic pyrethroids?
- Why develop a new method?
- Pyrethroid use, toxicity, and occurrences
- Analytical considerations; reference material stability and instrument robustness
- Why choose LC-MS-MS? Current methods.
- Equipment and analytical method
- Method Performance; successes and challenges
What are synthetic pyrethroids?

Bifenthrin
Fenpropathrin
Deltamethrin

λ-Cyhalothrin
Esfenvalerate

Cyfluthrin
Cypermethrin
Permethrin
Why develop a new method?

Client Needs

Regulation & Permits
Basin Plan Obj, NPDES, MS4

Usage

Toxicity Research
Where are these contaminants coming from?
Pyrethroid Use in CA for Structural Pest Control

Data from CALPIP (2013)
## Toxicity Data

<table>
<thead>
<tr>
<th>Pyrethroid</th>
<th>LC$_{50}$ Hyalella Azteca, ng/L</th>
<th>5-10$^{th}$ % LC$_{50}$</th>
<th>PAL Benchmark (Invert.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permethrin</td>
<td>$39.1^{(1,4)}$</td>
<td>$35 - 76^{(5)}$</td>
<td>$1.4^{(6)}$</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>$2.2^{(1,4)}$</td>
<td>$&lt;3.8 - 15^{(5)}$</td>
<td>$1.3^{(6)}$</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>$2.0^{(3)}$</td>
<td>$3 - 6.4^{(5)}$</td>
<td>$69^{(6)}$</td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>$8.7^{(1,4)}$</td>
<td>$&lt;4 - 12^{(5)}$</td>
<td>$7.4^{(6)}$</td>
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<tr>
<td>Cyhalothrin-$\lambda$</td>
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<td>$&lt;4 - 10^{(5)}$</td>
<td>$2.0^{(6)}$</td>
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<tr>
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<td>$1.1^{(1,4)}$</td>
<td>$3 - 9^{(5)}$</td>
<td>$4.1^{(6)}$</td>
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<tr>
<td>Esfenvalerate</td>
<td>$3.5-8.0^{(2,4)}$</td>
<td>$3 - 8^{(5)}$</td>
<td>$17^{(6)}$</td>
</tr>
</tbody>
</table>

6) http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm
Historical Data

Occurrences in water samples

- **Bifenthrin**
  - 61% <MDL
  - 14% J Flag
  - 10% 1-5
  - 9% 5-10
  - 6% 10-50
  - 4% >50

- **Permethrin**
  - 77% <MDL
  - 11% J Flag
  - 7% 1-5
  - 3% 5-10
  - 2% 10-50
  - 1% >50

Data from Babcock Laboratories since 2012
How low can we go?

- At or below acute toxicity values
- Be able to differentiate sample from blank (ultra low levels)
- Be able to recover analytes at low levels with accuracy and precision in matrix
How low can we go?

- At or below acute toxicity values
- Be able to differentiate sample from blank (ultra low levels)
- Be able to recover analytes at low levels with accuracy and precision in matrix

1.0 ng/L
Other considerations

- Aquatic toxicity studies vary
- Pyrethroids extremely lipophilic
- Certain SP’s degrade through hydrolysis or photolysis (Laskowski, 4)
- Absorption in sediment, suspended solids
- Pyrethroids can be a mixture of 2-8 stereoisomers
# Current Methods

<table>
<thead>
<tr>
<th>Analyte</th>
<th>USGS (GCMSMS)</th>
<th>CDFG (GCMSMS-ECNI)</th>
<th>CDFG (GC-ECD)</th>
<th>CA Dept. Food &amp; Agri. (GC-ECD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permethrins</td>
<td>2.0, 0.6</td>
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<td>15, 3.5</td>
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<tr>
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<td>5.0, 1.8</td>
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<tr>
<td>Cypermethrins</td>
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<td>15, 1.8</td>
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## Babcock Methods

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<td>MDL (ng/L)</td>
<td>RL (ng/L)</td>
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<td></td>
<td></td>
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</table>
Why choose LC-MS-MS?

- Availability; other work with drinking water UCMR₃, PPCPs
- Sensitivity/robustness challenges of GC-MS-MS or GC-MS-ECNI
- Few compounds that can’t be analyzed; adaptable to new targets
- Adaptable to chiral analysis
- Future in environmental analysis? Detecting known unknowns.
Equipment

- Thermo Scientific TSQ Quantum Ultra
- (2) HPLC Pumps Accela 600 and 1250
- CTC PAL Autosampler equipped with two valves
- Phenomenex Kinetex 2.6um Phenyl-Hexyl
- Thermoscientific HESI-II Probe
LC Parameters

- Variable flow rate (0.2-0.5-0.2mL/min)
- High flow loading - 5.0mL of 100% aqueous sample
- Online SPE using Hypersil 12µm aQ Gold columns (Thermo)
- SPE elution with mobile phase; methanol, water, and 0.002% ammonium hydroxide, elution focusing with ACN
MS Parameters

- Analytes all detected as [M+NH$_4$]$^+$
- Desolvation Temp: 250C
- Sheath gas: 40arb, Aux Gas: 40arb
- Capillary Temp: 225C
- CID pressure: 1.0mTorr Argon
- All collision energies optimized by direct infusion with eluent
Online SPE (Load)

- HPLC pump
- analytical column
- Aux pump
- 5mL syringe
- waste
- 5mL Loop

Diagram showing the connection between the HPLC pump, analytical column, Aux pump, 5mL syringe, and waste.
Online SPE (Transfer)

- **matrix** to waste
- HPLC pump
- **analytical column**
- **valve1 switch**
- **5mL syringe**
- waste
- Aux pump
- **online SPE**
- **5mL Loop**

- 91x508
Online SPE (Transfer)

- 5mL syringe
- waste
- valve1 switch
- Aux pump
- 5mL Loop
- HPLC pump
- matrix to waste
- analytical column
- online SPE
Online SPE (Elute)

- HPLC pump
- Analytical column
- Valve 2 switch
- Aux pump
- 5mL syringe
- Waste
- Matrix to waste
QED Scan - Bifenthrin

- **Test06 #8793**
  - RT: 9.64
  - AV: 1
  - NL: 7.77E3

- **F+: c ESI d Full ms2 440.200 [50.000-550.000]**
  - M+18
  - M+H

- **m/z** values:
  - 181.13
  - 218.26
  - 232.77
  - 267.28
  - 306.94
  - 354.74
  - 409.17
  - 423.03
  - 440.30
  - 480.16
  - 523.63
  - 545.39
  - 57.53
  - 93.14
  - 141.45
  - 218.26
  - 267.28
  - 306.94
  - 354.74
  - 409.17
  - 423.03
  - 440.30
  - 480.16
  - 523.63
  - 545.39

- **Relative Abundance**:
  - 0
  - 5
  - 10
  - 15
  - 20
  - 25
  - 30
  - 35
  - 40
  - 45
  - 50
  - 55
  - 60
Permethrin – 1.0ng/L

RT: 10.59
AA: 162091
SN: 1360

1.88E4
TIC F: + c ESI
SRM ms2
408.100
[183.099-
183.101] MS
ICIS Test08
Fipronil + Degs – 1.0 ng/L

RT: 4.00 - 8.00

Fipronil
RT: 5.90
AA: 32772

Fipronil Sulfide
RT: 6.17
AA: 44865

Fipronil Sulfone
RT: 6.37
AA: 28473

Fipronil Desulfanyl
RT: 5.82
AA: 56376

NL: 9.87E3
TIC F: - c ESI
SRM ms2 434.800
[329.999 - 330.001] MS
ICIS Test08

NL: 1.25E4
TIC F: - c ESI
SRM ms2 418.800
[261.999 - 262.001] MS
ICIS Test08

NL: 8.30E3
TIC F: - c ESI
SRM ms2 450.800
[281.999 - 282.001] MS
ICIS Test08

NL: 1.55E4
TIC F: - c ESI
SRM ms2 386.800
[350.999 - 351.001] MS
ICIS Test08
## Blank Spike Data

<table>
<thead>
<tr>
<th>CA Rank</th>
<th>Analyte</th>
<th>Spike Conc (ng/L)</th>
<th>Rep1 (ng/L)</th>
<th>Rep2 (ng/L)</th>
<th>Rep3 (ng/L)</th>
<th>Rep4 (ng/L)</th>
<th>Avg % Rec</th>
<th>% RSD</th>
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<td>1</td>
<td>Permethrins</td>
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<td>10.6</td>
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<td>9.8</td>
<td>9.6</td>
<td>95%</td>
<td>7.2%</td>
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<td>8.6</td>
<td>88%</td>
<td>11%</td>
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<tr>
<td>6</td>
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<td>8.4</td>
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<tr>
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<tr>
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<td>20%</td>
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<td>8.8%</td>
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<td>10.6</td>
<td>10.7</td>
<td>104%</td>
<td>3.6%</td>
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</table>
## Matrix Spike Data

Simulated Matrix with 25mg/L TSS, 10.0 NTU

<table>
<thead>
<tr>
<th>CA Rank</th>
<th>Analyte</th>
<th>Spike Conc (ng/L)</th>
<th>Rep1 (ng/L)</th>
<th>Rep2 (ng/L)</th>
<th>Rep3 (ng/L)</th>
<th>Rep4 (ng/L)</th>
<th>Avg % Rec</th>
<th>% RSD</th>
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<td>8.6</td>
<td>9.1</td>
<td>9.0</td>
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<td>88%</td>
<td>3.1%</td>
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<tr>
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<td>Bifenthrin</td>
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<tr>
<td>5</td>
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<td>11%</td>
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<td>4.7%</td>
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<tr>
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<td>Sumithrin</td>
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<td>9.3</td>
<td>9.8</td>
<td>9.9</td>
<td>9.6</td>
<td>96%</td>
<td>2.5%</td>
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<tr>
<td>10</td>
<td>tau-Fluvalinate</td>
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<td>8.2</td>
<td>9.6</td>
<td>7.4</td>
<td>8.8</td>
<td>85%</td>
<td>11%</td>
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<tr>
<td>11</td>
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<td>5.6</td>
<td>6.1</td>
<td>6.4</td>
<td>59%</td>
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<td>9.2</td>
<td>8.5</td>
<td>85%</td>
<td>6.7%</td>
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<tr>
<td>13</td>
<td>Allethrin</td>
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<td>7.1</td>
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<td>7.8</td>
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<td>14</td>
<td>Tralomethrin</td>
<td>10</td>
<td>9.7</td>
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<td>10.6</td>
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<td>3.8%</td>
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<tr>
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<td>10</td>
<td>6.3</td>
<td>6.7</td>
<td>7.6</td>
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<td>7.9%</td>
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<tr>
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<td>Acrinathrin</td>
<td>10</td>
<td>10</td>
<td>12</td>
<td>12</td>
<td>11</td>
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<td>6.2%</td>
</tr>
<tr>
<td>NA</td>
<td>Cyphenothrin</td>
<td>10</td>
<td>8.4</td>
<td>9.0</td>
<td>9.0</td>
<td>8.6</td>
<td>87%</td>
<td>3.2%</td>
</tr>
<tr>
<td>NA</td>
<td>Etofenprox</td>
<td>10</td>
<td>7.7</td>
<td>7.8</td>
<td>8.3</td>
<td>8.1</td>
<td>80%</td>
<td>3.5%</td>
</tr>
<tr>
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<td>Flucythrinate</td>
<td>10</td>
<td>8.4</td>
<td>8.5</td>
<td>9.0</td>
<td>9.4</td>
<td>88%</td>
<td>5.2%</td>
</tr>
<tr>
<td>NA</td>
<td>Kadethrin</td>
<td>10</td>
<td>7.5</td>
<td>8.2</td>
<td>10.7</td>
<td>10.1</td>
<td>91%</td>
<td>17%</td>
</tr>
<tr>
<td>NA</td>
<td>- Permethrin-13C6 (Surr)</td>
<td>10</td>
<td>9.6</td>
<td>9.4</td>
<td>9.2</td>
<td>9.0</td>
<td>93%</td>
<td>2.8%</td>
</tr>
</tbody>
</table>
## Analyte Stability

Simulated Matrix with 25mg/L TSS, 10.0 NTU

<table>
<thead>
<tr>
<th>CA Rank</th>
<th>Analyte</th>
<th>Spike Conc (ng/L)</th>
<th>Day 0 (%Rec)</th>
<th>Day 1 (%Rec)</th>
<th>Day 4 (%Rec)</th>
<th>Day 6 (%Rec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Permethrins</td>
<td>20</td>
<td>93%</td>
<td>85%</td>
<td>71%</td>
<td>70%</td>
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<tr>
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<td>Bifenthrin</td>
<td>20</td>
<td>92%</td>
<td>82%</td>
<td>70%</td>
<td>91%</td>
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<tr>
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<td>20</td>
<td>93%</td>
<td>89%</td>
<td>82%</td>
<td>73%</td>
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<tr>
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<td>20</td>
<td>93%</td>
<td>80%</td>
<td>98%</td>
<td>94%</td>
</tr>
<tr>
<td>5</td>
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<td>20</td>
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<td>80%</td>
<td>53%</td>
<td>58%</td>
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<td>6</td>
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<td>92%</td>
<td>103%</td>
<td>78%</td>
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<tr>
<td>7</td>
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<td>20</td>
<td>93%</td>
<td>96%</td>
<td>103%</td>
<td>90%</td>
</tr>
<tr>
<td>8</td>
<td>Deltamethrin</td>
<td>20</td>
<td>103%</td>
<td>105%</td>
<td>89%</td>
<td>96%</td>
</tr>
<tr>
<td>-</td>
<td>Permethrin-13C6 (Surr)</td>
<td>10</td>
<td>109%</td>
<td>103%</td>
<td>96%</td>
<td>107%</td>
</tr>
</tbody>
</table>

Stored in 40mL unpreserved VOA vials in refrigerator
Analytical Challenges

- CRM Availability
- Low response from Cyfluthrin/Esfenvalerate
- CRM Degradation; $\alpha$-cyano pyrethroids form a carboximidate(?) in methanol
- Stereoisomer confusion/labeling
- Unable to do tefluthrin or transfluthrin by ESI
- Preservation (tetramethrin issues)
- Solubility very low and Log(P) high
Developments

- Holding time study and preservation study of simulated matrix with ACN keeper
- Split samples from UC Davis last fall for bioswales.
- Try different online SPE media or analytical column
- Apply method to Fipronil and degradates
- Analyte confirmation
- Chiral separation
Developments

- Holding time study and preservation study of simulated matrix with ACN keeper
- Split samples from UC Davis last fall for bioswales. Mixed results from split lab
- Try different online SPE media or analytical column – Done
- Apply method to Fipronil and degradates - Done
- Analyte confirmation – Done
- Chiral separation – Limited success
References


6) EPA Aquatic Life Benchmark List http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm