1. Study highlights

- Study Number: 270
- Title: Urban monitoring in Southern California watersheds FY 2017-2018
- Author: Robert Budd

County: Los Angeles, Orange, San Diego

Study area: Ballona Creek, Bolsa Chica Channel, Bouquet Creek, Coyote Creek, Donninguez Channel, Garden Grove Creek, Los Angeles River, Salt Creek, San Diego River, San Gabriel River, Wood Canyon Creek

Land Use Type: ☒ Urban

Water body type: ☒ Storm drain outfall, ☒ Creek, ☒ River

Objectives: 1. Determine pesticide presence and concentrations in runoff from urban neighborhoods in southern California watersheds; 2. Compare pesticide concentrations to aquatic benchmarks; 3. Determine the toxicity of a subset of samples to Hyalella azteca in 96-hr water column testing; 4. Determine potential pyrethroid toxicity of sediments.

Sampling period: July 1, 2017 – June 30, 2018

Pesticides monitored:

2,4-D, azoxystrobin, bifenthrin, bromacil, carbaryl, chlorantraniliprole, chlorfenapyr, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, desulfinyl fipronil, desulfinyl fipronil amide, dicamba, diflubenzuron, diuron, etofenprox, esfenvalerate, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, imidacloprid, indoxacarb, isoxaben, lambda cyhalothrin, malathion, MCPA, oryzalin, oxadiazon, oxyfluorfen, pendimethalin, permethrin, prodiamine, propiconazole, pyraclostrobin, pyriproxyfen, simazine, triclopyr, trifluralin.

Major findings:
Bifenthrin was the most frequently detected (72%) pyrethroid insecticide in water samples collected at southern California monitoring locations between July 1, 2017 and June 30, 2018. Bifenthrin concentrations exceeded the lowest aquatic benchmark (BM) set by the US EPA in 70% of samples. Six other pyrethroids were detected at lower frequencies. All detections of permethrin (28%) and deltamethrin (21%) exceeded their respective aquatic benchmarks. Almost all lambda cyhalothrin detections (32%) were benchmark exceedances (30%). Detected cyfluthrin (49%) concentrations exceeded BM in 30% of samples, while cypermethrin was detected in 17% of samples with an associated 2% exceedance. Esfenvalerate and etofenprox were both detected in 1 sample (2%); only etofenprox concentrations exceeded BM.

Fipronil was also detected frequently (76%) at concentrations above its aquatic BM (73%). Several of fipronils degrade by-products were also detected in surface waters, including fipronil sulfone (67%), desulfinyl fipronil (63%), fipronil amide (35%), desulfinyl fipronil amide (20%), and fipronil sulfide (12%). Only fipronil sulfone exceeded BM values in 47% of samples. Fipronil amide and desulfinyl fipronil amide do not have established aquatic BM values.

The neonicotinoid imidacloprid was the most frequently detected pesticide (92%). All of the imidacloprid detection concentrations were above the US EPA aquatic benchmark of 0.01 µg /L. The only other insecticides detected above reporting limits were the organophosphate malathion (20%) and the carbamate carbaryl (18%), with 6% of malathion concentrations above BM.

Several herbicides and fungicides were present in surface water samples, including triclopyr (78%), 2,4-D (78%), diuron (69%), dicamba (22%), chlorfenapyr (15%), propiconazole (14%), isoxaben (14%), oryzalin (10%), oxadiazon (10%), simazine (8%), MCPA (6%), and chlorantraniliprole (4%). Pendimethalin (7%), pyraclostrobin (2%), and pyriproxyfen (2%) were each detected in one sample. None of the herbicides or fungicide concentrations were above their respective aquatic BM.

No other pesticide was detected in water samples within the sampling period.

96-hr water column toxicity tests were conducted using the test organisms *Hyalella azteca* and *Chironomus dilutus*. For toxicity testing using *H. azteca*, three samples were collected at storm drain outlets; one during a storm event and two during the dry season. Fifteen samples were collected within receiving waters; thirteen during the dry season and two during storm events. Significant toxicity was observed in all samples collected at storm drains, with 96–100 percent mortality during all events. Samples collected within receiving waters experienced a wide range of toxicity, with 100% mortality observed during storm events and 0–100% mortality during the dry season. For *Chironomus* testing, two samples were collected at storm drains; one during the dry season and one during a storm event. Two samples were collected at receiving waters during the dry season. Both storm drain samples were significantly toxic (98–100% mortality), but both receiving water samples were not significantly toxic (0–6%).

Six sediment samples were analyzed for the pyrethroids bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda cyhalothrin, and permethrin. Bifenthrin was detected in every sample. Cyfluthrin,
Deltamethrin, esfenvalerate, and permethrin were detected in five samples (83%). Lambda cyhalothrin was detected in 67% of samples, while cypermethrin was detected in 33% of samples. Neither resmethrin or fenpropathrin were detected in any of the three samples they were analyzed for. Bifenthrin accounted for the largest average percentage (56%) of toxicity units (TUs; an indicator of potential toxicity) per sampling event, followed by deltamethrin (25%), cyfluthrin (8%), lambda cyhalothrin (6%), cypermethrin (2%), esfenvalerate (2%), and permethrin (<1%).

- Recommendations for pesticides that need a CDFA analytical method (from SWMP):
  Sulfometuron-methyl, prallethrin, DDVP

### 2. Pesticide detection frequency

Table 1. Pesticides detected in water. Complete data set in Appendix.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Number of samples</th>
<th>Number of detections</th>
<th>Detection frequency (%)</th>
<th>Reporting limit (ug/L)</th>
<th>Lowest USEPA benchmark (BM)(ug/L)*</th>
<th>Number of BM exceedances</th>
<th>BM exceedance frequency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>18</td>
<td>14</td>
<td>78</td>
<td>0.05</td>
<td>299.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Azoxyystrobin</td>
<td>49</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>44</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>53</td>
<td>38</td>
<td>72</td>
<td>0.001</td>
<td>0.0013</td>
<td>37</td>
<td>70</td>
</tr>
<tr>
<td>Bromacil</td>
<td>49</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>6.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>49</td>
<td>9</td>
<td>18</td>
<td>0.02</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Chlorantraniliprole</td>
<td>49</td>
<td>2</td>
<td>4</td>
<td>0.02</td>
<td>4.47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Chlorfenapyr</td>
<td>13</td>
<td>2</td>
<td>15</td>
<td>0.1</td>
<td>2.915</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>49</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>53</td>
<td>26</td>
<td>49</td>
<td>0.002</td>
<td>0.0074</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>53</td>
<td>9</td>
<td>17</td>
<td>0.005</td>
<td>0.069</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>53</td>
<td>11</td>
<td>21</td>
<td>0.005</td>
<td>0.0041</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>Desulfynifl fipronil</td>
<td>49</td>
<td>31</td>
<td>63</td>
<td>0.01</td>
<td>0.59</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Desulfynifl fipronil amide</td>
<td>49</td>
<td>10</td>
<td>20</td>
<td>0.01</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dicamba</td>
<td>18</td>
<td>4</td>
<td>22</td>
<td>0.05</td>
<td>61</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Diflubenzuron</td>
<td>49</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.00025</td>
<td>IC</td>
<td>0</td>
</tr>
<tr>
<td>Diuron</td>
<td>49</td>
<td>34</td>
<td>69</td>
<td>0.02</td>
<td>2.4</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Esfenvalerate</td>
<td>53</td>
<td>1</td>
<td>2</td>
<td>0.005</td>
<td>0.017</td>
<td>IC</td>
<td>0</td>
</tr>
<tr>
<td>Etofenprox</td>
<td>49</td>
<td>1</td>
<td>2</td>
<td>0.02</td>
<td>0.17</td>
<td>IC</td>
<td>1</td>
</tr>
<tr>
<td>Fipronil</td>
<td>49</td>
<td>37</td>
<td>76</td>
<td>0.01</td>
<td>0.011</td>
<td>IC</td>
<td>36</td>
</tr>
<tr>
<td>Fipronil amide</td>
<td>49</td>
<td>17</td>
<td>35</td>
<td>0.01</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fipronil sulfide</td>
<td>49</td>
<td>6</td>
<td>12</td>
<td>0.01</td>
<td>0.11</td>
<td>IC</td>
<td>0</td>
</tr>
<tr>
<td>Fipronil sulfone</td>
<td>49</td>
<td>33</td>
<td>67</td>
<td>0.01</td>
<td>0.037</td>
<td>IC</td>
<td>23</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>49</td>
<td>45</td>
<td>92</td>
<td>0.01</td>
<td>0.01</td>
<td>IC</td>
<td>45</td>
</tr>
<tr>
<td>Indoxacarb</td>
<td>49</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>75</td>
<td>IC</td>
<td>0</td>
</tr>
<tr>
<td>Isoxaben</td>
<td>49</td>
<td>7</td>
<td>14</td>
<td>0.02</td>
<td>10</td>
<td>VA</td>
<td>0</td>
</tr>
<tr>
<td>Lambda Cyhalothrin</td>
<td>53</td>
<td>17</td>
<td>32</td>
<td>0.002</td>
<td>0.002</td>
<td>IC</td>
<td>16</td>
</tr>
<tr>
<td>Malathion</td>
<td>49</td>
<td>10</td>
<td>20</td>
<td>0.02</td>
<td>0.049</td>
<td>IA</td>
<td>3</td>
</tr>
<tr>
<td>MCPA</td>
<td>18</td>
<td>1</td>
<td>6</td>
<td>0.05</td>
<td>170</td>
<td>VA</td>
<td>0</td>
</tr>
<tr>
<td>Oryzalin</td>
<td>49</td>
<td>5</td>
<td>10</td>
<td>0.02</td>
<td>13</td>
<td>VA</td>
<td>0</td>
</tr>
<tr>
<td>Oxadiazon</td>
<td>49</td>
<td>5</td>
<td>10</td>
<td>0.02</td>
<td>5.2</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Oxyfluorfen</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>0.29</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>14</td>
<td>1</td>
<td>7</td>
<td>0.05</td>
<td>5.2</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Permethrin</td>
<td>53</td>
<td>15</td>
<td>28</td>
<td>0.002</td>
<td>0.0014</td>
<td>IC</td>
<td>15</td>
</tr>
<tr>
<td>Prodimine</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>1.5</td>
<td>IC</td>
<td>0</td>
</tr>
<tr>
<td>Propiconazole</td>
<td>49</td>
<td>7</td>
<td>14</td>
<td>0.02</td>
<td>21</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Pyraclostrobin</td>
<td>49</td>
<td>1</td>
<td>2</td>
<td>0.02</td>
<td>1.5</td>
<td>NVA</td>
<td>0</td>
</tr>
<tr>
<td>Pyriproxyfen</td>
<td>49</td>
<td>1</td>
<td>2</td>
<td>0.015</td>
<td>0.015</td>
<td>IC</td>
<td>1</td>
</tr>
<tr>
<td>Simazine</td>
<td>49</td>
<td>4</td>
<td>8</td>
<td>0.02</td>
<td>2.24</td>
<td>NVA</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2. Pesticides detected in sediment. Complete data set in Appendix IV.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Number of samples</th>
<th>Number of detections</th>
<th>Detection frequency (%)</th>
<th>Reporting limit (µg/L)</th>
<th>Lowest USEPA benchmark (BM)(µg/L)*</th>
<th>Number of BM exceedances</th>
<th>BM exceedance frequency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclopyr</td>
<td>18</td>
<td>14</td>
<td>78</td>
<td>0.05</td>
<td>5900 NVA</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>1.9 FC</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Only current RL listed, FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NVA, non-vascular acute; VA, vascular acute; na, value not available; dash, not applicable

*Sediment Toxicity Units (TUs) are calculated using the formula, use TU = C/LC50 * % TOC * 10, where C = concentration (µg/kg dry weight), LC50 is derived from accepted published values (from Amweg et al. 2005, Toxicol. Chem. 24:966-972; Amweg and D.P. Weston 2007, Environ. Toxicol. Chem. 26:2389-2396; Maund et al. 2002, Environ. Toxicol. Chem., 21:9-15), % TOC is stated in the sediment results Appendix III, and 10 is a conversion factor. One TU is equal to the LC50. If using other LC50 values, list value and reference.

3. Tracking Benchmark Exceedances (BME) or Sediment Toxicity (TU)

Table 3. For further data analysis: pesticides that have ≥ 10% aquatic benchmark exceedances [BME] [Table 1] or ≥ 1 sediment toxicity units [TU] [Table 2]) for 3 consecutive years are recommended for further detailed data analysis (Ambient Urban Monitoring Methodology SOP METH014)
<table>
<thead>
<tr>
<th>Area</th>
<th>Pesticide</th>
<th>Water</th>
<th>Sediment</th>
<th>Current year (i)</th>
<th>i - 1</th>
<th>i - 2</th>
<th>Last written evaluation (reference)</th>
<th>Further data analysis (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permethrin</td>
<td>X</td>
<td></td>
<td>28</td>
<td>43</td>
<td>41</td>
<td>2013</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>Bifenthin</td>
<td>X</td>
<td></td>
<td>1.27</td>
<td>1.86</td>
<td>2.28</td>
<td>2013</td>
<td>Y</td>
</tr>
</tbody>
</table>
### 4. QC

Table 4. Laboratory Quality Control (QC) Summary

<table>
<thead>
<tr>
<th>QC Type</th>
<th>Water Samples</th>
<th>Sediment Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Number</td>
<td>Number of QC out of control</td>
</tr>
<tr>
<td>Lab Blanks</td>
<td>208</td>
<td>0</td>
</tr>
<tr>
<td>Matrix Spikes/Duplicates</td>
<td>208</td>
<td>0</td>
</tr>
<tr>
<td>Laboratory Control Spikes/Duplicates</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Blind Spikes</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>Surrogate Spikes</td>
<td>78</td>
<td>6</td>
</tr>
<tr>
<td>Other QC:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Describe** Enter No. Enter No. Enter No. Enter No.

**Explain out of control QC and interpretation of data:**

Two labeled surrogates are used in the multi-analyte LC screen; atrazine-d5 and imidacloprid-d4. All atrazine-d5 surrogates were within QC controls. Six imidacloprid-d4 samples were below acceptable recovery levels. All surrogates below acceptable levels were samples collected during a rain event which had a high level of matrix effects.

### 5. Supporting Information

Submit the following Supporting Information combined into one PDF file with your report:

Index of Supporting Information
Appendix I. Study protocol
Appendix II. Sampling site information and pictures
Appendix III. Water quality data
Appendix IV. Water or sediment monitoring data
Appendix V. Aquatic toxicity data
Appendix VI. Analytical methods
Appendix VII. Aquatic toxicity methods