Constituents of Emerging Concern

*Current Regulatory Framework and Results on Russian River Watershed Pilot Study*

Jeremiah Puget – Regional Water Board
Dr. Alvina Mehinto – Southern CA Coastal Water Research Project
Dr. Rebecca Sutton – San Francisco Estuary Institute
Jennifer Sun – San Francisco Estuary Institute

Item No. 7
North Coast Regional Water Quality Control Board
February 8, 2018
Presentation Outline

- Background on Statewide Efforts *(15 min.)*
- Russian River Pilot Study Results
  - Water & Sediment - Analytical & BioAnalytical Screens
    - Dr. Alvina Mehinto – SCCWRP *(15 min.)*
  - Fish Tissue
    - Dr. Rebecca Sutton- SFEI *(15 min.)*
  - Pesticides
    - Jennifer Sun – SFEI *(15 min.)*
- Next Steps
- Questions and Comments
Constituents of Emerging Concern
Challenges to Current Monitoring

• Too many chemicals to monitor
  - Over 100,000 known chemicals
  - More discovered every year

• No standardized analytical methods for unexpected and/or unknown chemicals incl. metabolites, byproducts

• Relevant toxicity data often unavailable
  - Chronic sub-lethal toxicity is of concern
  - Toxicity potential of chemical mixtures understudied
Pathways to the Environment

**Treated Wastewater**
- Permitted Discharges
- Recycled Water
- Biosolids

**Septic Tanks**

**Landfills**

**Agricultural Runoff**

**Industrial Discharges**

**Storm Water Runoff**

Tracey Saxby, Kate Moore, Jason C. Fisher, Jane Thomas, Jane Hawkey, Integration and Application Network, University of Maryland Center for Environmental Science (ian.umces.edu/imagelibrary).
Regulatory Framework for CECs

• Recycled Water Policy (2009)
  – Monitoring Strategies for Chemicals of Emerging Concern in Recycled Water (2010)
  – Monitoring Strategies for Chemicals of Emerging Concern in California's Aquatic Ecosystems (2012)

• Policy Amendment (2013)
  – Included monitoring and reporting of recycled water used for groundwater recharge projects

  – Updated CEC Panel Recommendations for Recycled Water (Draft report is currently available for public review)
Regulatory Framework for CECs

Constituents of Emerging Concern

- SWAMP: Surface Water Assessment
- Non-point Source
- Recycled Water
- Storm Water
- Oil Field Produced Water
- Irrigated Lands Regulatory Program
- Mussel Watch
- GAMA: Groundwater Assessment
State Water Board Role

- Identify and improve the knowledge base
- Work with DWQ, DDW, Regions, and Expert Panel to develop and implement monitoring strategies for recycled water and other types of discharges
- Track and help evaluate effectiveness of regulatory interventions
- Direct pilot monitoring in ambient recommended by expert panel
Origin of the Ecosystem Panel

• State of knowledge regarding CECs is incomplete

• Regulatory requirements need to be based on best available peer-reviewed science

• Experts needed to guide future monitoring activities

• All members of Recycled Water Panel retained, with the addition of experts in marine resources & antibiotic resistance
Is there a better way to monitor CECs?

- Adaptive management
  - Collect and *interpret* data
  - *Adjust* target parameters, monitoring effort
  - Test promising *new* technologies
Is there a better way to monitor CECs?

- **New monitoring tools**
  - *bioanalytical tools* to screen for toxicants by mode of action
  - *non-targeted analysis* to identify toxicants that elude targeted methods

- **Develop monitoring thresholds**
  - *Monitoring Trigger Levels* (MTLs)
  - Measured environmental concentrations (MEC)
  - Predicted environmental concentrations (PEC)

- **Research initiatives**
  1. Developing *bioanalytical screening tools*;
  2. Filling *data gaps* on CEC sources, fate, occurrence and toxicity; and
  3. Assessing the *relative risk* of CECs and other monitored chemicals.
CEC Monitoring Methods

**Biological**
- Bioassessment

**Chemical**
- Targeted
  - Non-targeted

**Bioanalytical**
- Bioanalytical
Russian River CEC Pilot Study
Russian River CEC Pilot Study

• Are CECs in WWTP effluent and storm water runoff present?
• What is the relative contribution of treated wastewater effluent and storm water runoff to CEC loading into the watershed?
• Do bioanalytical tools effectively screen for the occurrence of CECs?
• What is the extent and magnitude of CECs are in the water column, sediments and fish tissue?
• Which pesticides applied in the Russian River watershed are of highest priority for monitoring
Tools for Russian River CEC Study

- Targeted Chemistry
- Bioanalytical
- BioAssessment
Screening for CECs in Water and Sediment from the Russian River Watershed

Dr. Alvina Mehinto, Dr. Keith Maruya
Southern California Coastal Water Research Project
Effect-Based Monitoring

- Framework currently considered by the State Water Board

- New tools proposed to:
  - Streamline existing monitoring approaches
  - Enhance capabilities to identify new and/or unknown contaminants
  - Identify ecologically relevant impacts
What Are Cell Assays?

• Cells engineered to respond to specific classes of CECs

• Light intensity is proportional to the concentration of bioactive chemicals

• Results expressed relative to a known/reference chemical
  
  ➢ *Bioanalytical equivalent concentration (BEQ, ng/L)*
What Are Cell Assays?

1. Cell culture
2. Add cells + samples
   Incubate plate
3. Add substrate
   Then incubate
4. Measure fluorescence

Sample extraction
Advantages of Cell Assays

• Rapid method to screen for hundreds of contaminants simultaneously in one assay

• Integrated measure of known and unknown chemicals acting via a common mode of action
  
  ➢ *Potential for linkage to toxicity*

• Technology adopted by pharmaceutical, cosmetic and industrial companies to develop their products
Objectives and Study Design

What is the extent and magnitude of endocrine active CECs in water and sediment in the Russian River Watershed?

- Water, sediment and effluent samples collected
- Sample analyses:
  - Cell assay bioscreening (estrogen and glucocorticoid receptor)
  - Targeted analyses of known CECs
### Estrogenic Screen of Water Samples

<table>
<thead>
<tr>
<th></th>
<th>Effluent #1</th>
<th>Effluent #2</th>
<th>Mirabel</th>
<th>Piner Creek</th>
<th>Santa Rosa Crk</th>
<th>El Roble</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER Bioscreen (ng E2 equiv/L)</td>
<td>&lt;0.5</td>
<td><strong>1.9</strong></td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td><strong>Targeted chemical analyses (ng/L)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17b-estradiol (E2)</td>
<td>&lt;0.5</td>
<td><strong>0.6</strong></td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>estrone</td>
<td>&lt;0.5</td>
<td><strong>11.0</strong></td>
<td>0.5</td>
<td>0.6</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>bisphenol A</td>
<td>&lt;10</td>
<td>12.0</td>
<td>&lt;10</td>
<td>55.0</td>
<td>16</td>
<td>&lt;10</td>
</tr>
<tr>
<td>4-nonylphenol</td>
<td>60.8</td>
<td>247</td>
<td>25.4</td>
<td>53.3</td>
<td>62</td>
<td>63</td>
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<tr>
<td>Chem. equiv. (ng/L)</td>
<td>&lt;0.5</td>
<td><strong>1.6</strong></td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
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</table>
# Estrogenic Screen of Sediment Samples

<table>
<thead>
<tr>
<th></th>
<th>Lytton Spring</th>
<th>Mirabel</th>
<th>Piner Creek</th>
<th>Santa Rosa Crk</th>
<th>El Roble</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ER Bioscreen</strong></td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td><strong>0.09</strong></td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>(ng E2 equiv./g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Targeted chemical analyses (ng/g)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17b-estradiol (E2)</td>
<td>&lt;0.12</td>
<td>&lt;0.12</td>
<td><strong>0.23</strong></td>
<td>&lt;0.12</td>
<td>&lt;0.12</td>
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<tr>
<td>estrone</td>
<td>&lt;0.12</td>
<td>0.14</td>
<td><strong>1.3</strong></td>
<td>0.4</td>
<td>0.28</td>
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<tr>
<td>bisphenol A</td>
<td>1.4</td>
<td>1.9</td>
<td>15</td>
<td>4.6</td>
<td>&lt;1.0</td>
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<tr>
<td>4-nonylphenol</td>
<td>20</td>
<td>34</td>
<td>29</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>bifenthrin</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td><strong>130</strong></td>
<td>1.96</td>
<td>&lt;0.2</td>
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<tr>
<td>Chem. equiv. (ng/L)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td><strong>0.36</strong></td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
Understanding cell assay effect thresholds is key.

Fish studies have shown that exposure to 2 – 4 ng E2/L had no effect on growth and survival.

- Effluent BEQ of 1.9 ng E2/L (without dilution) = low concern
- River water BEQ < 0.5 ng E2/L = no concern
Conclusions

• CECs present low to moderate concern in the Russian river

  ➢ Water concentrations of pharmaceuticals below MTLs

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Max. measured conc. (ng/L)</th>
<th>Monitoring trigger level (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diclofenac</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
<tr>
<td>Estrone</td>
<td>0.56</td>
<td>6</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
</tbody>
</table>

  ➢ Some pesticide concentrations in sediment were > MTLs

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Max. measured conc. (ng/g)</th>
<th>Monitoring trigger level (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>130</td>
<td>0.052</td>
</tr>
<tr>
<td>Fipronil</td>
<td>3.4</td>
<td>0.09</td>
</tr>
<tr>
<td>Permethrin</td>
<td>4.9</td>
<td>0.073</td>
</tr>
</tbody>
</table>
Conclusions

• CECs present low to moderate concern in the Russian river

• Cell assays provided a reliable and integrated measure of estrogenic chemicals

• Routine application of cell assays could provide a cost-effective strategy to prioritize sites requiring more chemical and toxicity testing
CECs in Sport Fish
R1 CEC Pilot Monitoring

Rebecca Sutton, Thomas Jabusch, Jay Davis
San Francisco Estuary Institute
Study Objectives

MQ3. What is the extent and magnitude of PBDE and PFOS contamination in fish tissue in the Russian River Watershed?

Polybrominated diphenyl ethers (PBDEs)
Study Objectives

MQ3. What is the extent and magnitude of PBDE and PFOS contamination in fish tissue in the Russian River Watershed?

Perfluorooctane Sulfonate (PFOS)
Study Design

6 popular fishing sites
Sacramento Pikeminnow (5)
Sacramento Sucker (5)
Redear Sunfish (1)
Smallmouth Bass (1)
Largemouth Bass (1)

PBDEs (13 analytes)
PBDE 15, 28, 33, 47, 49, 66, 75, 99, 100, 153, 154, 155, 183

PFASs (13 analytes)
PFBA, PFBS, PFPA, PFHx, PFHxS, PFHpA, PFOA, PFOS, PFOSA, PFNA, PFDA, PFUA, PFDoA
### Safe to Eat Thresholds

<table>
<thead>
<tr>
<th></th>
<th>California: Advisory Tissue Levels</th>
<th>Minnesota: Meal Advice Categories</th>
<th>Michigan: Fish Consumption Screening Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 servings/week</td>
<td>2 servings/week</td>
<td>1 serving/week</td>
<td>16 meals/month</td>
</tr>
<tr>
<td>&lt; 100 ppb</td>
<td>100-210 ppb</td>
<td>210-630 ppb</td>
<td>12 meals/month</td>
</tr>
<tr>
<td>PBDEs</td>
<td></td>
<td></td>
<td>8 meals/month</td>
</tr>
<tr>
<td>&gt; 630 ppb</td>
<td></td>
<td></td>
<td>4 meals/month</td>
</tr>
<tr>
<td>&lt; 40 ppb</td>
<td>&gt; 40-200 ppb</td>
<td>&gt; 200-800 ppb</td>
<td>≤ 9 ppb</td>
</tr>
<tr>
<td>PFOS</td>
<td></td>
<td></td>
<td>&gt; 9-13 ppb</td>
</tr>
<tr>
<td>≤ 19-38 ppb</td>
<td></td>
<td></td>
<td>&gt; 13-19 ppb</td>
</tr>
</tbody>
</table>
PBDE Results

Number of detections:
- PBDE 183
- PBDE 155
- PBDE 154
- PBDE 153
- PBDE 100
- PBDE 99
- PBDE 75
- PBDE 66
- PBDE 49
- PBDE 47
- PBDE 33
- PBDE 28
- PBDE 15

% of Sum PBDEs:
- PBDE 183
- PBDE 155
- PBDE 154
- PBDE 153
- PBDE 100
- PBDE 99
- PBDE 75
- PBDE 66
- PBDE 49
- PBDE 47
- PBDE 33
- PBDE 28
- PBDE 15
PBDEs by Species

Sacramento Pikeminnow
Sacramento Sucker
Smallmouth Bass
Largemouth Bass
Redear Sunfish
Russian River
SF Bay

Lowest Advisory Tissue Level
3 - 54 ppb
0.1 - 30 ppb
30 ppb

Sum of PBDEs (ppb)
PBDEs by Site

To Ocean

- Black dots represent Sacramento Pikeminnow.
- White circles represent Sacramento Sucker.

Sites include:
- Russian R @ Ukiah WWTP
- Russian R @ Cloverdale WWTP
- Russian R @ Riverfront Park
- Russian R @ Johnson's Beach
- Russian R @ Monte Rio
PFOS & Other PFASs Results

Number of detections

- PFUA
- PFPA
- PFOA
- PFOS
- PFOSA
- PFNA
- PFHx
- PFHxS
- PFHpA
- PFDaDA
- PFDA
- PFBA
- PFBS
PFOS by Species

PFOS Concentration (ppb)

Birds “Wildlife Diet” Guidelines

Mammals

Sacramento Pikeminnow
Sacramento Sucker
Smallmouth Bass
Largemouth Bass
Redear Sunfish
Russian River
SF Bay
SoCal

10 - 26 ppb
2-17 ppb
1 - 11 ppb

Lowest Minnesota Meal Advice Threshold
Conclusions

• Fish tissue findings suggest minimal concern
  – Levels of PBDEs and PFOS generally below available consumption thresholds
  – For PFOS, potential for impacts further up the food chain
• Periodic monitoring (e.g., every 5-10 years) is recommended
Current Use Pesticides
R1 CEC Pilot Monitoring

Jennifer Sun, Rebecca Sutton, Diana Lin
San Francisco Estuary Institute
Study Objectives

MQ4. Which pesticides applied in the Russian River watershed are of highest priority for monitoring?

MQ5. What is the extent and magnitude of pesticide contamination in Russian River water and sediment?
Pesticide Prioritization

DPR Surface Water Monitoring Program modeling tool

Use + Toxicity + Pesticide Properties

Prioritization
Pesticide Prioritization

DPR Pesticide Use Database (2012-2014 data, monthly) + USEPA Aquatic Life Benchmarks or DPR equivalents (acute or chronic) + Physical-chemical properties

Prioritized Pesticide list
### 1. Prioritization List
(Analytical Lab Selection)

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Water Toxicity Benchmark (ug/L)</th>
<th>DPR Use Score</th>
<th>DPR Toxicity Score</th>
<th>DPR Final Score</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene thiourea (MANCOZEB degradate)</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>Spring</td>
</tr>
<tr>
<td>PENDIMETHALIN</td>
<td>5.2</td>
<td>4</td>
<td>4</td>
<td>16</td>
<td>Spring</td>
</tr>
<tr>
<td>CYPRODINIL</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>16</td>
<td>Fall</td>
</tr>
<tr>
<td>OXYFLUORFEN</td>
<td>0.29</td>
<td>3</td>
<td>5</td>
<td>15</td>
<td>Spring</td>
</tr>
<tr>
<td>THPA; 482-HA; APF (FLUMIOXAZIN degradates)</td>
<td>0.49</td>
<td>3</td>
<td>5</td>
<td>15</td>
<td>Spring</td>
</tr>
<tr>
<td>CHLORPYRIFOS</td>
<td>0.04</td>
<td>2</td>
<td>6</td>
<td>12</td>
<td>Summer</td>
</tr>
<tr>
<td>IMIDACLOPRID</td>
<td>1.05</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>Fall</td>
</tr>
<tr>
<td>PYRACLOSTROBIN</td>
<td>1.5</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>Fall</td>
</tr>
<tr>
<td>SIMAZINE</td>
<td>2.24</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>Spring</td>
</tr>
<tr>
<td>TRIFLOXYSTROBIN</td>
<td>2.76</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>Fall</td>
</tr>
<tr>
<td>DIFENOCONAZOLE</td>
<td>5.6</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>Fall</td>
</tr>
<tr>
<td>QUINOXYPHEN</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>Fall</td>
</tr>
</tbody>
</table>
Study Design

5 co-located sites

USGS - CWSC

Sediment
September 2016
118 pesticides

Water
Oct 2016 (“first fall flush”)
162 pesticides (dissolved)
131 pesticides (particulate)
Pesticides in sediment were low

- No exceedances of USGS benchmarks
- Largest number of detections at the mixed use ag- and urban site
- Six pesticides detected
  - Fungicides: boscalid, iprodione
  - Legacy insecticides: DDT, DDD, DDE
  - Pyrethroid insecticide: bifenthrin
Pesticides in water were low, but highest in urban-influenced areas

- No pesticides detected in particulate phase
- 16 pesticides detected in dissolved phase

*May have received limited stormwater runoff*
Stormwater runoff may not have been captured at northern sites.
Pesticides in water were low, but highest in urban-influenced areas

- No pesticides detected in particulate phase
- 16 pesticides detected in dissolved phase
- **Fungicides** are most abundant, but not highly toxic
- Several urban pesticides detected were not prioritized, esp. toxic insecticides

*May have received limited stormwater runoff*
Two urban insecticides exceeded chronic invertebrate thresholds

Weston & Lydy et al. 2014

USEPA 2017 revised benchmark

Pesticide Concentration (ng/L)
Imidacloprid

polystyrene insulation, vinyl siding, adhesives, sealants, textiles for outdoor use, pressure-treated wood decking

USEPA 2017 revised benchmark
Conclusions

• Pesticides from **agricultural runoff** are not likely a **major concern** during the fall, based on this study
  – Pesticide use varies seasonally – this study did not characterize risks from **spring runoff**
  – Pesticide concentrations may be higher nearer to sources

• Some **urban insecticides** currently exceed or are approaching levels of concern
  – **Imidacloprid** exceeded a USEPA chronic invertebrate benchmark
  – **Fipronil degradates** are approaching or exceed chronic invertebrate threshold
  – **Bifenthrin** is approaching a USGS sediment benchmark

Recommended for monitoring in receiving waters by California Statewide CEC Expert Panel
Pesticide Monitoring Partners

• **USGS** National Water Quality Assessment: Stream Quality Assessment Project
  – 2017 spring monitoring
  – Trenton Road and Riverfront/Pull-Out sites

• **DPR, SWRCB, CASQA**: statewide framework for urban pesticide monitoring
Lessons Learned

✓ BioAnalytical tools show promise

✓ Initial screening results for water and fish tissue suggest minimal concern for impacts; however, keep an eye on PFOS

✓ Urban use insecticides warrant a closer look

✓ Continue implementing improved monitoring strategies
Next Steps

What can be done?

✓ Prudent usage of products or use alternative products
✓ Proper disposal (*Medicines collected regionally*)
✓ Improve treatment technologies
✓ Implement expert panel recommended monitoring strategies
✓ Efficient and proper use of recycled water
✓ Implement the Recycled Water Policy
I WANT YOU To Properly Dispose Unwanted Medication
Partnerships

• Other agencies
• Municipalities
• Advocates
• Academia
• Public

✅ Together we can assess conditions and minimize harmful effects
"Hmphh. Happy as clams, indeed. They're just all on Prozac."

To be continued....
Questions?