A multi-agency pilot project on contaminants of emerging concern (CECs) in California coastal bivalves

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Southern California Coastal Water Research Project

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QUICK FACTS

- Only program of its kind that is national in scope; 300 Sites nationwide
- Longest running coastal contaminant monitoring program (25 years)
- 120 chemicals measured in oysters, mussels and sediment
- Broad federal, state & local partnerships

![Graph showing average ∑PBDE* (ng/g dry) by region and state](graph.png)
REFOCUSING MUSSEL WATCH

• **Stakeholders wanted more focus on CECs**
  - NOAA agreed and held a 2009 workshop in CA to redesign the program

• **Annual 2009 MW budget re-directed for CA pilot study**
  - $475K from NOAA; $360K for analytical costs
  - Leveraging from multiple partners doubled funds committed to study
  - Key capabilities and expertise also brought to table

• **Multiagency committee formed to establish study elements**
  - CEC analyte list
  - Expansion/relocation of sampling stations
  - Sampling schedule & logistics
  - Analytical performance goals
  - Data management & interpretation
PARTICIPANTS

• Planning
  – K. Maruya, S. Bay, S. Weisberg (SCCWRP)
  – D. Gregorio, (SWRCB)
  – S. Klosterhaus, M. Sedlak, J. Davis (SFEI)
  – J. Christensen, G. Lauenstein, K. Kimbrough, T. Collier (NOAA)
  – D. Alvarez, E. Furlong (USGS)
  – T. Smith, L. Huff (EPA)
  – J. Kucklick (NIST)

• Field Collection
  – C. Beegan, E. Siegel, E. Duncan (SWRCB)
  – D. Tsukada, D. Diehl (SCCWRP)
  – P. Salop (Applied Marine Sciences)
  – J. Engle (Marine Science Institute, MARINe)
STUDY OBJECTIVES

• What is the occurrence (freq of detection, concentration) of CECs in the coastal California environment?

• How does CEC occurrence vary with land use?

• How does CEC occurrence vary with proximity to discharge of WWTP effluent and stormwater runoff?

• What CECs are detectable in the water column using passive sampling devices (PSDs)?

• What is the relationship between CEC accumulation by PSDs and bivalve tissue?
STUDY ELEMENTS

• Double the number of existing stations – add locations impacted by POTW and stormwater discharge – add locations in reference or reserve areas (e.g. ASBS, NERR) – keep stations established for time trends analysis (e.g. RMP)

• Stratify stations (N=68) using GIS tools according to
  – surrounding land use
    o urban, low/mixed development, agricultural
  – discharge scenario
    o POTW, stormwater or none

• Deploy passive sampling devices (PSDs) at 11 stations – target both POPs and water soluble CECs (e.g. pharmas) – can PSDs act as bivalve mimics?
TARGET CECs

• **Mussel (Mytilus spp.) tissue**
  - Pharmaceuticals & personal care products (PPCPs) (88 analytes)
    - e.g. carbamazapine, triclosan
  - Industrial & commercial chemicals (52 analytes)
    - flame retardants (PBDEs, HBCD)
    - surfactants (4-nonylphenol)
  - Current use pesticides (27 analytes)
    - pyrethroids, chlorpyrifos, dachthal
  - Nanomaterials (single walled C nanotubes)
  - Persistent organic pollutants (120 analytes)
  - Trace metals (14)

• **PSDs**
  - Polyethylene & solid phase microextraction (SPME) devices
    - POPs (PCBs, DDTs, chlordanes) (>80 analytes)
  - Polar chemical integrated sampler (POCIS) (156 analytes)
    - water soluble CECs (e.g. synthetic musks)
MORE PARTICIPANTS

• **Analytical**
  - J. Ramirez, A. Brewster (TDI Brooks)
  - R. Grace, C. Navaroli (Axys Analytical)
  - M. LaGuardia (VIMS)
  - L. Ferguson (Duke)
  - W. Lao (SCCWRP)
  - K. Smalling (USGS)

• **Data interpretation and synthesis**
  - N. Dodder, R. Schaffner (SCCWRP)
  - M. Edwards, A. Jacob, S. Bricker, G. Piniak (NOAA)
### OCCURRENCE OF CECs

<table>
<thead>
<tr>
<th>Tissue Analyte (ng/g dry wt.)</th>
<th>POCIS Analyte</th>
<th>No. stations</th>
<th>Detection Frequency</th>
<th>Min</th>
<th>Max</th>
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<tbody>
<tr>
<td>4-Nonylphenol Monooethoxylate</td>
<td>Nonylphenol</td>
<td>32-</td>
<td>100</td>
<td>91</td>
<td>6</td>
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<tr>
<td>4-Nonylphenol Diethoxylate</td>
<td>Nonylphenol</td>
<td>14</td>
<td>100</td>
<td>470</td>
<td>96</td>
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<tr>
<td>4-Nonylphenol Diethoxylate</td>
<td>Nonylphenol</td>
<td>25</td>
<td>88</td>
<td>25</td>
<td>ND</td>
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<tr>
<td>BDE-47</td>
<td>BDE-47</td>
<td>66</td>
<td>66</td>
<td>83</td>
<td>6.6</td>
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<tr>
<td>DDMU</td>
<td>BDE-99</td>
<td>62</td>
<td>4.8</td>
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<tr>
<td>Sertraline</td>
<td>Sertraline</td>
<td>22</td>
<td>64</td>
<td>1.4</td>
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<tr>
<td>Lomefloxacin</td>
<td>Lomefloxacin</td>
<td>56</td>
<td>62</td>
<td>29</td>
<td>ND</td>
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<tr>
<td>HBCD, gamma</td>
<td>HBCD, gamma</td>
<td>19</td>
<td>58</td>
<td>0.69</td>
<td>ND</td>
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</table>

<table>
<thead>
<tr>
<th>Water Concentration (ng/L)</th>
<th>Freq Det</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
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<tbody>
<tr>
<td>Bromoform</td>
<td>100</td>
<td>32</td>
<td>5.3</td>
<td>77</td>
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<tr>
<td>Tris(1-chloro-2-propyl)phosphate (TCPP)</td>
<td>90</td>
<td>410</td>
<td>ND</td>
<td>3100</td>
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<tr>
<td>Diethyl phthalate</td>
<td>90</td>
<td>150</td>
<td>ND</td>
<td>600</td>
</tr>
<tr>
<td>Diethylhexylphthalate (DEHP)</td>
<td>80</td>
<td>400</td>
<td>ND</td>
<td>1105</td>
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<tr>
<td>Galaxolide (HHCB)</td>
<td>80</td>
<td>150</td>
<td>ND</td>
<td>1300</td>
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<tr>
<td>Acetophenone</td>
<td>80</td>
<td>11</td>
<td>ND</td>
<td>47</td>
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<td>Cotinine</td>
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<td>2.7</td>
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<td>d-Limonene</td>
<td>70</td>
<td>15</td>
<td>ND</td>
<td>46</td>
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<tr>
<td>Caffeine</td>
<td>70</td>
<td>10</td>
<td>ND</td>
<td>32</td>
</tr>
<tr>
<td>Tributyl phosphate</td>
<td>70</td>
<td>6.6</td>
<td>ND</td>
<td>25</td>
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<tr>
<td>Carbamazepine</td>
<td>70</td>
<td>2.6</td>
<td>ND</td>
<td>21</td>
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<td>Trimethoprim</td>
<td>70</td>
<td>0.3</td>
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<td>2</td>
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<td>N,N-diethyltoluamide (DEET)</td>
<td>60</td>
<td>10</td>
<td>ND</td>
<td>69</td>
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<tr>
<td>Tris(2-chloroethyl)phosphate (TCEP)</td>
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<td>7.6</td>
<td>ND</td>
<td>56</td>
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<td>Camphor</td>
<td>50</td>
<td>30</td>
<td>ND</td>
<td>92</td>
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<tr>
<td>Benzophenone</td>
<td>50</td>
<td>0.89</td>
<td>ND</td>
<td>5.1</td>
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EFFECT OF LAND USE

Alkylphenols

Current Use Pesticides

Pharmaceuticals/Personal Care Products

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Low De</th>
<th>Mixed Dev</th>
<th>Urban</th>
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<tbody>
<tr>
<td>n</td>
<td>8</td>
<td>30</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>total concentration (ng/g dw)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
PSD VS. TISSUE ACCUMULATION

SPME

PED

![Graph showing tissue concentration vs. water concentration for PCB-118, chrysene, and γ-chlordane in SPME and PED methods.](image)
SUMMARY AND CONCLUSIONS

• Most targeted CECs were very low or not detected

• PBDEs and alkylphenols were frequently detected in mussels at concentrations similar to POPs

• CEC concentrations were higher on average at stations
  – in urban areas
  – impacted by stormwater

• Coastal water quality monitoring programs should focus on urbanized waterways impacted by stormwater runoff
SUMMARY AND CONCLUSIONS (cont.)

- A different suite of CECs were frequently detected in water at ng/L concentrations
  - chlorophosphate flame retardants (e.g. TCEP)
  - phthalates
  - galaxolide

- *Mytilus* tissue concentrations of POPs and PAH were correlated with water concentrations determined from PSDs

- *PSDs can be employed in coastal monitoring of CECs that*
  - *are not taken up by bivalves (e.g. water soluble PPCPs)*
  - *bioaccumulate in bivalves such as Mytilus*
SUMMARY AND CONCLUSIONS (cont.)

• A multiagency partnership was created that resulted in
  – the design and performance of a pilot study on CECs to inform coastal monitoring across CA
  – increased spatial coverage and relevance of coastal monitoring sites to State, regional and local stakeholders
  – leveraging of core federal program funds, key expertise and facilities, and in kind services from various partners that doubled the scope of the study
  – a more comprehensive coastal water quality monitoring strategy ("Beyond Mussel Watch")

• Results will inform future regional and national CEC studies
  – Background water quality (ASBS)
  – Great Lakes Initiative
  – Chesapeake/mid-Atlantic region
  – Puget Sound