Non-targeted analysis update

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RMP Emerging Contaminant and Exposure and Effects Combined Workgroup meeting: May 15 and 16, 2012
Motivation for Project

• Predictions that some chemicals in use have significant bioaccumulation potential but are not monitored

• Recognition that there may be unmeasured contaminants in samples missed by targeted analysis

- 22263 organic chemicals in use in Canada and US were screened
- 610 compounds were possibly P&B
- 62% were halogenated
  - 181 fluorinated
  - 116 chlorinated
  - 10 iodidated
- 148 measured or detected
Motivation for Project

• Predictions that some chemicals in use have significant bioaccumulation potential but are not monitored

• Recognition that there may be unmeasured contaminants in samples missed by targeted analysis
Tools Facilitating Untargeted Analysis

- Lists of chemicals with bioaccumulation potential
- Comprehensive mass spectral libraries (e.g. NIST Mass Spectral Library)
- GC x GC Time of Flight Mass Spectrometry
Instrumental Method: GC×GC-TOF (Simplified Description)

co-eluting peaks 1st GC column

- retention time (s)
- intensity

separated peaks 2nd GC column

- transfer to 2nd column
- retention time (s)
- 1 modulation

Experimental DDE Spectrum

- indistinguishable, overlapping mass spectra
- X=5Br, 2H

Library DDE Spectrum

- Br
- -Br
- 301
- 380
- 461
- 540, 5Br

m/z

intensity (％)

Intensity

Intensity

Retention time (s)
Pros and Cons

• Pros
  – GC x GC and spectral deconvolution produces high-quality spectra
  – Very high ability to resolve complex mixtures
  – Library searching using NIST MS library

• Cons
  – Misses polar compounds and those not amenable to electron impact ionization
  – Data handling is labor intensive
  – Library incomplete for many contaminants
  – Bias toward halogenated compounds
Objectives

• Provide information to San Francisco Bay water managers so that contaminants can be further studied
• Identify not routinely monitored contaminants in a higher trophic organism
# Harbor Seal Blubber Samples

<table>
<thead>
<tr>
<th>Age</th>
<th>Sex</th>
<th>Location</th>
<th>Inside or Outside Bay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pup and Adult</td>
<td>M</td>
<td>Fitzgerald Marine Reserve</td>
<td>Outside</td>
</tr>
<tr>
<td>Adult</td>
<td>F</td>
<td>Limantour Beach (Point Reyes National Seashore)</td>
<td>Outside</td>
</tr>
<tr>
<td>Adult</td>
<td>F</td>
<td>Baker Beach</td>
<td>Inside</td>
</tr>
<tr>
<td>Adult</td>
<td>M</td>
<td>Angel Island</td>
<td>Inside</td>
</tr>
<tr>
<td>Adult</td>
<td>F</td>
<td>Richmond Marina</td>
<td>Inside</td>
</tr>
<tr>
<td>Adult</td>
<td>M</td>
<td>Alaska</td>
<td>Outside</td>
</tr>
</tbody>
</table>
Sample (1 g of seal blubber)

Pressurized Fluid Extraction (Dionex ASE)

Dichloromethane (DCM) extract

Size Exclusion Chromatography (600 mm x 25 mm PLGel)

Lipid reduced extract

Size Exclusion Chromatography (300 mm x 7.5 mm PLGel)

Lipid reduced extract

Fractionation by Si/Al column

Non polar extract  Mid polarity extract  More polar extract

GC x GC TOFMS (LECO Pegasus)
Total compounds found per location

- Angel Island
- Baker Beach
- Richmond Marina
- Fitzgerald Marine Reserve
- Point Reyes National Sea Shore
- Alaska

Legend:
- Orange: unidentified
- Gray: identified
Compounds type versus collection location

- Angel Island
- Baker Beach
- Richmond Marina
- Fitzgerald Marine Reserve
- Point Reyes National Sea Shore
- Alaska

- Mixed
- F
- Br
- Cl
## Chlorinated Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS#</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dechlorane 602</td>
<td>31107-44-5</td>
<td>flame retardant</td>
</tr>
<tr>
<td>p,p'-Dichlorodiphenyl sulfone</td>
<td>80-07-9</td>
<td>polymer starting material for &quot;Udel&quot;</td>
</tr>
<tr>
<td>Hexachlorofulvene</td>
<td>6317-25-5</td>
<td>polymer use?</td>
</tr>
<tr>
<td>Dichlorobenzil</td>
<td>21854-95-5</td>
<td>dyes, resins, disinfectant?</td>
</tr>
<tr>
<td>Dichlorobenzophenone</td>
<td>5293-97-0</td>
<td>?</td>
</tr>
<tr>
<td>Dichloroanthracene</td>
<td>605-48-1</td>
<td>combustion product?</td>
</tr>
</tbody>
</table>

**Dichlorodiphenylsulfone**  
**On Howard and Muir List**  

**Hexachlorofulvene**

**Dichlorobenzil**

**Dichlorobenzophenone**
# Fluorinated Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS#</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>octafluorodecane</td>
<td>--</td>
<td>degradation product?</td>
</tr>
<tr>
<td>1,1,2,2-Tetrafluoro-1,2-diphenylethane</td>
<td>425-32-1</td>
<td></td>
</tr>
<tr>
<td>4,4'-Difluorodiphenylmethane</td>
<td>457-68-1</td>
<td>polymer subunit</td>
</tr>
<tr>
<td>Difluorobenzophenone</td>
<td>345-92-6</td>
<td>polymer use?</td>
</tr>
<tr>
<td>Monofluorobenzophenone</td>
<td>345-83-5</td>
<td>polymer use?</td>
</tr>
</tbody>
</table>

![Structural formulas](image_url)

1,1,2,2-Tetrafluoro-1,2-diphenylethane

4,4'-Difluorodiphenylmethane

fluorobenzophenones
# Miscellaneous Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS#</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haloacetate esters</td>
<td>68144-72-9 (e.g.)</td>
<td>possibly wastewater origin?</td>
</tr>
<tr>
<td>Chlorinated Hydrocarbons</td>
<td>--</td>
<td>Below chloroparaffin MW range</td>
</tr>
<tr>
<td>Bayer 28,589</td>
<td>728-40-5</td>
<td>musk-like</td>
</tr>
<tr>
<td>tetrabromobiphenyl</td>
<td>16400-50-3</td>
<td></td>
</tr>
</tbody>
</table>

![Molecular structures](image)

- Bayer 28,589
- Chlorinated Hydrocarbons
- Haloacetate esters
# Pesticides

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS#</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>82657-04-3</td>
<td>Pesticide, stable</td>
</tr>
<tr>
<td>Chloropropylate</td>
<td>5836-10-2</td>
<td>pesticide, miticide</td>
</tr>
<tr>
<td>Dicofol</td>
<td>115-32-2</td>
<td>Pesticide, cotton, citrus</td>
</tr>
</tbody>
</table>

![Bifenthrin](image1.png)  
Bifenthrin

![Chloropropylate](image2.png)  
chloropropylate

![Dicofol](image3.png)  
Dicofol
Next Steps

• Verify identified compounds
• Identify unknowns with help of Ed White from NIST
• Run halogen filters developed by Hilton
• Written summary report
<table>
<thead>
<tr>
<th>ID</th>
<th>Age</th>
<th>Sex</th>
<th>Location</th>
<th>Tissues</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-2118</td>
<td>Weaner</td>
<td>M</td>
<td>Fitzgerald Marine Reserve</td>
<td>Liver, Serum, Whole Blood</td>
</tr>
<tr>
<td>HS-2120</td>
<td>Adult</td>
<td>M</td>
<td>Angel Island</td>
<td>Liver, Serum, Whole Blood</td>
</tr>
<tr>
<td>HS-2028</td>
<td>Adult</td>
<td>F</td>
<td>Pt. Reyes Nat. Seashore</td>
<td>Liver</td>
</tr>
<tr>
<td>HS-2122</td>
<td>Adult</td>
<td>M</td>
<td>Fitzgerald Marine Reserve</td>
<td>Liver, Serum, Whole Blood</td>
</tr>
<tr>
<td>HS-2125</td>
<td>Adult</td>
<td>F</td>
<td>Richmond Marina</td>
<td>Liver, Serum, Whole Blood</td>
</tr>
<tr>
<td>HS-10</td>
<td>Adult</td>
<td>M</td>
<td>Alaska</td>
<td>Liver</td>
</tr>
</tbody>
</table>
General Approach

Extraction
- Blood—Focused Microwave Extraction
- Liver—Pressurized fluid extraction

Cleanup
- Size exclusion only

Derivatization
- Derivatize with MSTFA to create TMS derivatives
• Verify Compound and Compound ID (in progress)
  – Spring/Summer 2012
• Liver and blood analysis (in progress)
  – Spring/Summer 2012 chemical analysis
  – Summer/Fall 2012 data analysis
• Mussel tissue samples
  – Fall 2012/Winter 2013
• First manuscript
  – Winter 2103