Comparison of Multiple Bioassays to High-Resolution Gas Chromatography for Quantification of Polychlorinated Biphenyls and Dioxins/Furans in Sediment

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Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 14-17 June 2010 in Denver, CO.
Dioxin in Sediment is Important, Costly Issue in the Pacific Northwest

- Dioxins are primary risk drivers in Puget Sound and are key to the Puget Sound Cleanup Initiative
- The Dredge Material Management Program has proposed revised background-based guidelines for suitability determination for in-water dredge material disposal, which likely means more sediment dioxin testing will be required
- High-Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS, EPA 1613b) is “gold standard” for sediment dioxin testing but costly with long turn around times
- Bioassays have potential to provide much cheaper, quicker quantitative dioxin results for sediments but have not been evaluated for sediment in low, dredge material-relevant concentration range of 4 and 10 ppt TEQ
qPCR-Based Assay: Procept (EPA 4430)

Dioxin Activates Receptor

Activated Receptor Captures Probe

Receptor-Probe Complex Trapped

 Probe is PCR Amplified And Measured

AhRC PCR™

6/16/2010
http://www.eichrom.com/dioxin
Cell-Based Assays: CALUX (EPA 4435) and 101-L

Environmental Ligands: PCDHs, PCBs, Dioxins, and Furans

Induction of light is directly proportional to concentration of dioxin TEQ in the sample.

**DRE** = Dioxin Responsive Element

**Dioxin-like compounds:** PCDHs, PCBs, Dioxins, and Furans

**ARN** = AhR Nuclear Translocator protein

**AhR Complex** = Aryl hydrocarbon Receptor Complex

OSV Bold Research Cruise

Collective effort of multiple State and Federal Agencies to characterize non-urban influenced sediment samples throughout the sound for determination of natural background contaminant concentrations to support DMMP revised sediment management guidelines

An additional 21 urban influenced samples were retrieved from project archives and included in the data set
Sediment Sampling Methods
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Sediment Analysis Methods

• High-Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS)
  – SGS Laboratories, Wilmington, NC

• XDS-CALUX®
  – Xenobiotic Detection Systems Laboratory, Durham, North Carolina

• 101-L & Procept
  – Engineering Research & Development Center Laboratory, US Corps of Engineers, Vicksburg, MS
Bioassay vs. HRGC/MS Evaluation Methods

- Bioassay performance was evaluated against HRGC/MS by
  - Bivariate Least-Squares Regression
    - Does not assume error-free independent variable
    - Considers variances of both independent and dependant variables simultaneously
    - Sample-specific variances were estimated for HRGC/MS and bioassay results by extrapolating calibration standard variances based on sample concentrations
  - Relative percent differences
  - False positive/false negative rates
## Results

<table>
<thead>
<tr>
<th></th>
<th>HRGCMS</th>
<th>CALUX</th>
<th>101L</th>
<th>Procept</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>0.0440</td>
<td>0.340</td>
<td>0.893</td>
<td>-0.136</td>
</tr>
<tr>
<td>max</td>
<td>11.6</td>
<td>17.0</td>
<td>22.6</td>
<td>184</td>
</tr>
</tbody>
</table>

Correlation coefficients

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.708</td>
<td>0.166</td>
<td>-0.162</td>
<td></td>
</tr>
</tbody>
</table>
**Results**

CALUX
BLS Regression Results
\[ Y = 3.67x + 1.08, \quad R = 0.59 \]

101-L
BLS Regression Results
\[ Y = 0.265x + 4.09, \quad R = 0.02 \]

1% False (+) 27% False (+) 1% False (-)
Results

**CALUX**
BLS Regression Results
\[ Y = 3.67x + 1.08, R = 0.59 \]

**101-L**
BLS Regression Results
\[ Y = 0.265x + 4.09, R = 0.02 \]
# Laboratory Duplicate Results

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% fines</th>
<th>% organic carbon</th>
<th>CALUX Results</th>
<th>RPD</th>
<th>101L Results</th>
<th>RPD</th>
<th>HRGCMS Results</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPS_3</td>
<td>55%</td>
<td>1.55</td>
<td>4.18</td>
<td>3%</td>
<td>5.23</td>
<td>13%</td>
<td>1.33</td>
<td>15%</td>
</tr>
<tr>
<td>QC_1 (CPS_3 split)</td>
<td></td>
<td></td>
<td>4.07</td>
<td></td>
<td>4.59</td>
<td></td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>HC_2</td>
<td>98%</td>
<td>3.65</td>
<td>8.54</td>
<td>19%</td>
<td>7.59</td>
<td>10%</td>
<td>0.774</td>
<td>125%</td>
</tr>
<tr>
<td>QC_2 (HC_2 split)</td>
<td></td>
<td>4.33</td>
<td>7.05</td>
<td></td>
<td>8.40</td>
<td></td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td>NCPS_2</td>
<td>54%</td>
<td>0.640</td>
<td>5.35</td>
<td>90%</td>
<td>2.96</td>
<td>13%</td>
<td>1.07</td>
<td>15%</td>
</tr>
<tr>
<td>QC_3 (NCPS_2 split)</td>
<td></td>
<td>0.949</td>
<td>2.03</td>
<td></td>
<td>3.38</td>
<td></td>
<td>0.923</td>
<td></td>
</tr>
<tr>
<td>PPS_1</td>
<td>98%</td>
<td>2.31</td>
<td>7.16</td>
<td>5%</td>
<td>4.31</td>
<td>30%</td>
<td>2.04</td>
<td>73%</td>
</tr>
<tr>
<td>QC_4 (PPS_1 split)</td>
<td></td>
<td>2.03</td>
<td>6.82</td>
<td></td>
<td>5.86</td>
<td></td>
<td>0.947</td>
<td></td>
</tr>
<tr>
<td>SPSB_0</td>
<td>80%</td>
<td>2.24</td>
<td>9.68</td>
<td>57%</td>
<td>5.41</td>
<td>7%</td>
<td>1.46</td>
<td>8%</td>
</tr>
<tr>
<td>QC_5 (SPSB_0 split)</td>
<td></td>
<td>2.07</td>
<td>5.36</td>
<td></td>
<td>5.79</td>
<td></td>
<td>1.57</td>
<td></td>
</tr>
</tbody>
</table>

average: 35% 15% 47%
Laboratory Duplicate Results for Other Parameters

RPD for Field Split Samples vs. Percent Fines

RPD for Field Split Samples vs. TOC
## Results

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>HRGCMS</th>
<th>CALUX</th>
<th>101L</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>FBA3-32-2</em></td>
<td>41.0</td>
<td>18.6 ✓</td>
<td>11.1 x</td>
</tr>
<tr>
<td><em>T115-S1-CS-0803</em></td>
<td>19.2</td>
<td>88.7 ✓</td>
<td>6.06 x</td>
</tr>
<tr>
<td><em>T115-S2-01-ZA-0803</em></td>
<td>31.5</td>
<td>71.0 ✓</td>
<td>18.2 ✓</td>
</tr>
<tr>
<td><em>T115-S2-02-ZA-0803</em></td>
<td>24.1</td>
<td>104 ✓</td>
<td>12.5 x</td>
</tr>
<tr>
<td><em>T115-S2-CS-0803</em></td>
<td>23.3</td>
<td>75.7 ✓</td>
<td>20.6 ✓</td>
</tr>
<tr>
<td><em>T18-S1-C5</em></td>
<td>22.3</td>
<td>60.2 ✓</td>
<td>20.5 ✓</td>
</tr>
<tr>
<td><em>PO-BA-25-SS-A</em></td>
<td>23.6</td>
<td>14.1 x</td>
<td>7.65 x</td>
</tr>
<tr>
<td><em>PO-BA-25-SC-Z</em></td>
<td>67.2</td>
<td>16.3 ✓</td>
<td>13.4 x</td>
</tr>
<tr>
<td><em>PO-UP-22-SC-A</em></td>
<td>40</td>
<td>11.4 x</td>
<td>9.61 x</td>
</tr>
<tr>
<td><em>PO-UP-22-SC-B</em></td>
<td>28.2</td>
<td>3.90 x</td>
<td>18.7 ✓</td>
</tr>
<tr>
<td><em>PO-UP-20-SC-A</em></td>
<td>39.2</td>
<td>15.4 ✓</td>
<td>12.6 x</td>
</tr>
<tr>
<td><em>PO-UP-20-SC-B</em></td>
<td>54.1</td>
<td>8.64 x</td>
<td>11.9 x</td>
</tr>
</tbody>
</table>

67% 33%

### Notes
- Urban samples are shown in italics
- * Urban samples used for screening evaluation purposes only not included in regression or correlation analysis. Check marks indicate assay >15 ppt TEQ and x's indicate assay <15 ppt TEQ.
- a. value was truncated to zero for correlation analysis
- b. estimated value below lowest calibration standard concentration
- c. estimated variance value for this datapoint was negative for 101L so it was not included in the analysis.
Discussion

- Assays performed well in the concentration range of interest
  - False positive errors for CALUX and 101-L < 27 percent
  - False negative errors for CALUX and 101-L < 10 percent
- RPDs indicate that sampling error may have contributed significantly to total error in this study
- Assays performed poorly for urban samples containing concentrations > 15 ppt TEQ; however, samples originated from separate studies
- Factors contributing to poor performance may include
  - Presence of co-contaminants
  - Proximity to known sources
  - Variations in sample percent moisture
  - Sample heterogeneity and differences in sample preparation
- Recommend assay performance be evaluated on site-specific basis considering uniformity of sediment, presence of co-contaminants and known sources
Acknowledgements

• Special thanks to Choo Yaw Ang, USACE ERDC, for assistance with laboratory analysis, development of variance information and general project support