Defining Biota-Sediment Accumulation Factors for the San Jacinto River Waste Pits, Texas

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Why the San Jacinto River Waste Pits?
- Placed on US EPA NPL of Superfund sites in 2008

Why biota-sediment accumulation factors (BSAF)?
BSAFs are an important parameter in the calculation of sediment protective concentration levels (PCLs) under the Texas Risk Reduction Program (TRRP)

\[
\text{PCL}_{\text{BSAF}} = \frac{\text{RBEL}_{\text{Fish}}}{\text{BSAF}}
\]

where the RBEL_{Fish} represents the risk-based exposure limit for human ingestion of fish or shellfish tissue.

http://www.epa.gov/med/Prods_Pubs/bsaf.htm

This research project was not....
1. A Superfund project
2. A risk assessment
3. A study to support of remedial actions
4. A study of the Houston Ship Channel
5. A consulting project for the State of Texas, EPA or NGOs

Study objectives included...
1. Measurement of concentrations of dioxin, furan, and PCB in fish, invertebrate, and sediment samples at the SJRWP
2. Estimation of site-specific biota sediment accumulation factors (BSAF) values for targeted invertebrates and fish
3. Delineation of trophic position of sampled organisms at the the SJRWP site
4. Modeling of bioaccumulation of dioxins, furans, and PCBs using QSAR and the Gobas/Arnot framework
5. Establishment of a combined approach to determine site-specific BSAFs for other contaminated sites

Initial site visit performed by TDSHS, TCEQ and Baylor in October 2009
Sampling events performed in March, August and December 2010

March 2010
- Low salinity ~2ppt
- Low water temperature ~12°C
- Strong currents and waves
- Few organisms collected
August 2010 - selected for further study
- More typical salinity ~15ppt
- High water temperature ~30°C
- Limited currents and waves
- Many organisms collected

December 2010
- More typical salinity ~15ppt
- Low water temperature ~10°C
- Limited currents and moderate waves
- Moderate organisms collected

Locations of sediment sampling during August 2010, San Jacinto River Waste Pits

Locations and methods employed for fish and shellfish sampling during August 2010, San Jacinto River Pits

Sampling during August 2010, San Jacinto River Pits

Species Collected – Sample Dates 2,3

Organisms collected, identified and enumerated during August 2010 from the San Jacinto River Pits, Texas
C and N Isotopic Analysis of Biota

Dry sample at 60 °C

Homogenize

Place ~1 mg into tin cups

Analyzer δ¹³C and δ¹⁵N

Thermo- Electron DELTA V Advantage isotope ratio mass spectrometer
(ThermoQuest, Waltham, MA)

The San Jacinto River Food Web

Trophic positions of organisms collected during August 2010 from the San Jacinto River Pits, Texas

<table>
<thead>
<tr>
<th>Species or Taxon</th>
<th>N</th>
<th>Mean Δ¹³C</th>
<th>Trophic Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herring gulls</td>
<td>6</td>
<td>16.86</td>
<td>2.28</td>
</tr>
<tr>
<td>Herring gulls - small</td>
<td>6</td>
<td>16.27</td>
<td>2.28</td>
</tr>
<tr>
<td>Herring herring</td>
<td>6</td>
<td>17.31</td>
<td>2.28</td>
</tr>
<tr>
<td>Dermatobranchus</td>
<td>6</td>
<td>17.00</td>
<td>2.38</td>
</tr>
<tr>
<td>Mycteria cypus</td>
<td>10</td>
<td>16.39</td>
<td>2.16</td>
</tr>
<tr>
<td>Anhinga capensis</td>
<td>6</td>
<td>16.22</td>
<td>2.16</td>
</tr>
<tr>
<td>Anhinga capensis - large</td>
<td>6</td>
<td>16.22</td>
<td>2.16</td>
</tr>
<tr>
<td>Anhinga capensis - smaller</td>
<td>6</td>
<td>16.22</td>
<td>2.16</td>
</tr>
<tr>
<td>Mycteria rectirostris</td>
<td>10</td>
<td>18.90</td>
<td>2.51</td>
</tr>
<tr>
<td>Mycteria rectirostris - large</td>
<td>6</td>
<td>16.39</td>
<td>2.51</td>
</tr>
<tr>
<td>Mycteria rectirostris - small</td>
<td>6</td>
<td>16.39</td>
<td>2.51</td>
</tr>
<tr>
<td>Pycnonotus sinensis</td>
<td>12</td>
<td>19.31</td>
<td>2.79</td>
</tr>
<tr>
<td>Pycnonotus sinensis - larger</td>
<td>6</td>
<td>19.71</td>
<td>2.79</td>
</tr>
<tr>
<td>Pycnonotus sinensis - smaller</td>
<td>6</td>
<td>19.96</td>
<td>2.79</td>
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<tr>
<td>Pycnonotus sinensis - juvenile</td>
<td>5</td>
<td>20.29</td>
<td>2.97</td>
</tr>
<tr>
<td>Pycnonotus sinensis - young</td>
<td>5</td>
<td>20.14</td>
<td>2.34</td>
</tr>
</tbody>
</table>

R² = 0.45
p = 0.018

Significant relationship between trophic positions at the San Jacinto River Pits and Mad Island Marsh Preserve

Significant relationship between trophic positions at the San Jacinto River Pits and Mad Island Marsh Preserve

The San Jacinto River Food Web

Phytoplankton – Zooplankton

Detritus – Periphyton

Striped Mullet

Gulf Menhaden

Gizzard Shad

Gulf Killifish

Pinfish

Silverside

Mussels

Hard Clam

Ladyfish

Flounder

Speckled Seatrout

Hardhead Catfish

Red Drum

Black Drum

Blue Crab

Fiddler Crab

Shrimp

Sediment Benthic invertebrates

Piscivores

Direct Sediment Contact

Target Analytes

Dioxins

Furans

dl-PCBs
Organics Analysis in Biological Tissues

General Method Overview

- Homogenization
- Extractions
  - Solid-liquid extractions
- Cleanup
  - Gel Permeation Chromatography
  - Column Chromatography
- Concentration and Analysis

Limitations of Historical Methods

- Analysis of Organics – EPA Method 1316B
  - High inherent cost
    - Time
    - Labor-intensive
    - Solvents
    - Expertise
    - Variability
    - Accuracy, etc

USEPA Method 1613

- Develop a high-throughput low cost analytical method for measuring Dioxins, Furans, and PCBs in biological tissues.
  - Combine the extraction and 4 cleanup techniques into a single automated step
  - Expand EPA Method 1613 to include PCBs
**Pressurized Liquid Extraction**

- High pressure (1500 psi)
- Adjustable extraction temperatures (30 to 200 °C)
- Wide range of organic solvents and weak acids
- Multiple extraction cycles

**Dionex – Accelerated Solvent Extractor (ASE) 350**

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**Adsorbents Optimization**

- Different adsorbents and ratios can be experimentally examined
GPC-UV chromatograms of 10 g fish composite
• A) fish, silica, and celite (1:1:1)
• B) fish, silica, and florasil (1:1:1)
• C) fish, silica, celite, and florasil (1:1:1:1)

Overall Conclusion
• Elimination of Gel Permeation Chromatography

Homogenized mass of ~40 g anhydrous Na2SO4 and ~10 g fish composites
~10 g Al2O3 (basic)
~5 g Celite and ~0.5 g Carbopack
~10 g Florasil
~5 g Silica

For Fish
dl-PCBs: 93 ± 2.4%
PCDD/Fs: 86 ± 3.0%

For Crabs
dl-PCBs: 76 ± 5.4%
PCDD/Fs: 93 ± 2.8%

For Clams
dl-PCBs: 92 ± 2.5%
PCDD/Fs: 87 ± 2.2%
### Matric Spike Experiments

<table>
<thead>
<tr>
<th></th>
<th>dl-PCBs</th>
<th>Dioxins</th>
<th>Furans</th>
<th>All surrogates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>6.1</td>
<td>12.2</td>
<td>5.7</td>
<td>8.0</td>
</tr>
<tr>
<td>Clams</td>
<td>2.6</td>
<td>11.3</td>
<td>6.4</td>
<td>7.3</td>
</tr>
<tr>
<td>Crabs</td>
<td>11.7</td>
<td>6.2</td>
<td>6.4</td>
<td>7.3</td>
</tr>
<tr>
<td>Fish</td>
<td>7.5</td>
<td>7.2</td>
<td>7.7</td>
<td>7.5</td>
</tr>
<tr>
<td>All matrices</td>
<td>7.0</td>
<td>9.2</td>
<td>6.6</td>
<td>7.5</td>
</tr>
</tbody>
</table>

### Surrogate Recovery

<table>
<thead>
<tr>
<th></th>
<th>dl-PCBs</th>
<th>Dioxins</th>
<th>Furans</th>
<th>All surrogates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>83</td>
<td>74</td>
<td>67</td>
<td>72</td>
</tr>
<tr>
<td>Clams</td>
<td>97</td>
<td>97</td>
<td>81</td>
<td>89</td>
</tr>
<tr>
<td>Crabs</td>
<td>70</td>
<td>81</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>Fish</td>
<td>82</td>
<td>75</td>
<td>71</td>
<td>74</td>
</tr>
<tr>
<td>All matrices</td>
<td>83</td>
<td>82</td>
<td>74</td>
<td>78</td>
</tr>
</tbody>
</table>

### Methods Comparison

**New Method**
- Surrogate Recoveries: 72 - 103%
- Time: 2 hours/sample
- Solvent: 33%
- Cost: $150 to $250/sample

**USEPA Method 1613B**
- Surrogate Recoveries: 17 - 197%
- Time: 8 to 12 hours/sample
- Solvent: 100%
- Cost: $700 to $1000/sample

### % Lipid Determination

**Gravimetric Determination**
- Same ASE parameters used during the extraction of contaminants

### Sample Analysis and Results Summary

#### HRGC–MS/ECNI

<table>
<thead>
<tr>
<th>Congeners</th>
<th>Concentration ng g⁻¹ lw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clam</td>
<td>5.16-7.11</td>
</tr>
<tr>
<td>Crab</td>
<td>0.82-7.15</td>
</tr>
<tr>
<td>Fish</td>
<td>1.86-9.48</td>
</tr>
</tbody>
</table>

#### HRGC–HRMS

<table>
<thead>
<tr>
<th>Congeners</th>
<th>Concentration ng g⁻¹ lw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non ortho PCBs</td>
<td>6.34-300</td>
</tr>
<tr>
<td>Mono ortho PCBs</td>
<td>1.09-180</td>
</tr>
<tr>
<td>PCDD/Fs</td>
<td>3.31-9.82</td>
</tr>
<tr>
<td></td>
<td>0.76-4.18</td>
</tr>
<tr>
<td></td>
<td>0.015-0.035</td>
</tr>
</tbody>
</table>
Concentration Profiles

**Log (Concentration pg g⁻¹ lw)**

- Clams
- Crabs
- Fish

Contribution (%)

- Fish
- Crabs
- Clams
- Sediments

Non-ortho PCBs
Mono-ortho PCBs
PCDD/Fs

Conventional EPA Method
- Sample homogenization
- Addition of surrogate standards and extraction
- Silica/Alumina column
- Activated carbon column
- Florisil column
- Silver nitrate or copper column
- Addition of internal standard and GC/NI/MS

Pressurized Liquid Extraction

- Sample homogenization
- Pressurized Liquid Extraction Cleanup
- Addition of internal standard and GC/NI/MS

Sediment Analysis

Conventional and modified techniques for analysis of PCDD/Fs and d-PCBs

Sample spiked with isotopically labeled surrogate standards.
- Samples spiked with surrogates were allowed to come to equilibrium for ~20 min prior to extraction.
- Copper powder was activated with 20% (v/v) nitric acid, and subsequently rinsed with deionized water, acetone, and n-hexane.
- Sulfur was removed from the sediment extracts using activated copper powder (~3 g in 5 mL toluene). The sample extract was allowed to interact with the copper powder for 30 min after extraction to remove sulfur.
ePLE Key Findings

- The extracts cleanliness was evaluated with GPC-UV technique and full scan GC-MS in EI mode.
- Full scan GC-MS chromatograms and spectra were used to evaluate the ePLE efficiency at removing bulk interferences.
- Silica, alumina, and Florisil® significantly retained extractable potential interferences.
- The ePLE eliminated the need for further extract cleanup.

Method Validation

Analytical method was validated with triplicate spiked and recovery experiments (sediment fortified with target analytes) and triplicate analysis of NIST Standard Reference Material (SRM) 1944 samples.

- Sediment samples (10g) were fortified with target analytes prior to extraction.
- Surrogates and internal standards (%)* were added prior to analysis.
- Average recoveries for dioxins, furans, and PCBs were 80%, 81%, and 70%, respectively.
- SRM 1944 aliquots were spiked with surrogate prior to extraction.
- SRM 1944 recoveries for PCB-105 and 118 were within ±20% of certified values.
- SRM 1944 recoveries for 3 dioxins and 8 furans were >100% of reference values.

Analytical Improvements

Efficiency of the enhanced PLE was compared to EPA method 1613 in terms of analyte recoveries, analysis time, and volume of solvent used.

<table>
<thead>
<tr>
<th>Compared</th>
<th>EPA Method 1613</th>
<th>Enhanced PLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>~12 hours</td>
<td>~3 hours</td>
</tr>
<tr>
<td>Solvent volume</td>
<td>~1,200 ml</td>
<td>~300 ml</td>
</tr>
<tr>
<td>Average Recovery (%)</td>
<td>21–115%</td>
<td>21–100%</td>
</tr>
</tbody>
</table>

*Sedins and furans. **Dioxins, furans, and di-PCBs

Comparison of recoveries and sample preparation of EPA method 1613 and enhanced PLE.

Sediment Concentrations

Average contribution to total contaminant load by contaminant class

- Total dioxins: 3,501 pg/g (20)
- Total furans: 17,080 pg/g (20)
- Total PCBs: 514 pg/g (20)

Concentration (pg/g dw) - Lowest Site: Highest Site

- Dioxins: 36 pg/g - 514 pg/g
- Furans: 5,514 pg/g - 57,770 pg/g
- di-PCBs: 515 pg/g - 4,124 pg/g

Average dioxins, furans, and di-PCBs distribution profile for the entire site. Lowest and highest concentrations in the waste pit.
### Sediment Summary (pg/g TOC)

<table>
<thead>
<tr>
<th>Sediment Summary (pg/g TOC)</th>
<th>Mean</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment 1</td>
<td>59</td>
<td>57</td>
</tr>
<tr>
<td>Sediment 2</td>
<td>55</td>
<td>52</td>
</tr>
<tr>
<td>Sediment 3</td>
<td>52</td>
<td>49</td>
</tr>
<tr>
<td>Sediment 4</td>
<td>51</td>
<td>48</td>
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<tr>
<td>Sediment 5</td>
<td>48</td>
<td>45</td>
</tr>
<tr>
<td>Sediment 6</td>
<td>45</td>
<td>41</td>
</tr>
<tr>
<td>Sediment 7</td>
<td>42</td>
<td>38</td>
</tr>
<tr>
<td>Sediment 8</td>
<td>39</td>
<td>36</td>
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<td>Sediment 9</td>
<td>36</td>
<td>32</td>
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<tr>
<td>Sediment 10</td>
<td>33</td>
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</tr>
<tr>
<td>Sediment 11</td>
<td>30</td>
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<td>Sediment 12</td>
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<td>Sediment 13</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>Sediment 14</td>
<td>21</td>
<td>17</td>
</tr>
<tr>
<td>Sediment 15</td>
<td>18</td>
<td>14</td>
</tr>
</tbody>
</table>

### Physical Characterization

- Moisture content was determined by drying an aliquot of sediment sample (~5 g in triplicate) at 110 °C until constant weight.
- TC, TOC, and BC analysis was performed using a Flash EA 1112 Series (ThermoQuest, Waltham, MA).

### Sediment Physical Characterization

<table>
<thead>
<tr>
<th>Sediment Physical Characterization</th>
<th>% moisture</th>
<th>% TOC</th>
<th>% BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment 1</td>
<td>20</td>
<td>0.36</td>
<td>0.02</td>
</tr>
<tr>
<td>Sediment 2</td>
<td>51</td>
<td>1.46</td>
<td>0.15</td>
</tr>
<tr>
<td>Sediment 3</td>
<td>57</td>
<td>1.58</td>
<td>0.17</td>
</tr>
<tr>
<td>Sediment 4</td>
<td>44</td>
<td>1.37</td>
<td>0.21</td>
</tr>
<tr>
<td>Sediment 5</td>
<td>23</td>
<td>0.44</td>
<td>0.04</td>
</tr>
<tr>
<td>Sediment 6</td>
<td>37</td>
<td>1.19</td>
<td>0.13</td>
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<tr>
<td>Sediment 7</td>
<td>47</td>
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</tr>
<tr>
<td>Sediment 8</td>
<td>18</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>Sediment 9</td>
<td>14</td>
<td>0.13</td>
<td>0.04</td>
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<tr>
<td>Sediment 10</td>
<td>51</td>
<td>12.70</td>
<td>0.40</td>
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<tr>
<td>Sediment 11</td>
<td>48</td>
<td>7.76</td>
<td>0.33</td>
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<tr>
<td>Sediment 12</td>
<td>63</td>
<td>2.43</td>
<td>0.28</td>
</tr>
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<td>Sediment 13</td>
<td>57</td>
<td>1.53</td>
<td>0.15</td>
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<tr>
<td>Sediment 14</td>
<td>46</td>
<td>2.05</td>
<td>0.23</td>
</tr>
<tr>
<td>Sediment 15</td>
<td>36</td>
<td>1.38</td>
<td>0.12</td>
</tr>
</tbody>
</table>

### Bioaccumulation

- Bioaccumulation: accumulation of chemicals in living tissue.
- The capacity of chemicals to bioaccumulate is an important factor when understanding how humans are exposed.
- Environmental laws address bioaccumulation in many ways:
  - The movement of chemicals from sediment into fish tissue
  - The capacity of new industrial chemicals to accumulate in the environment and in fish tissue

### Biota-sediment accumulation factors (BSAF)

- BSAFs are commonly used to support remedial decisions
- BSAF methodologies are clearly defined by EPA (2009), generally range over larger areas
- Scope of the present study precluded ideal investigation, but focused on research questions related to site-specific bioaccumulation

### Biota-sediment accumulation factors

BSAFs are an important parameter in the calculation of sediment protective concentration levels (PCLs) under the Texas Risk Reduction Program (TRRP)

\[
\text{RBEL}_{\text{fish}} = \frac{\text{SDF}_{\text{fish}} \times \text{PCL}}{\text{RSL}}
\]

where the RBEL_{fish} represents the risk-based exposure limit for human ingestion of fish or shellfish tissue.

http://www.epa.gov/med/Prods_Pubs/bsaf.htm
Biota-sediment accumulation factors

• Ratio of the concentration in fish or crab tissue to the concentration in sediment, from paired samples.

\[
\text{BSAF} = \frac{C_{\text{tissue-lipid}}}{C_{\text{sediment-OC}}}
\]

• Clam BSAFs calculated using paired on-site sediment samples; BSAFs for crabs and black drum were calculated using the mean and geometric mean of COPC concentrations from the site.

Preliminary site-specific BSAFs for the SJRWP

<table>
<thead>
<tr>
<th>COPC</th>
<th>Clams</th>
<th>Crabs</th>
<th>Fish</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378-TCDD</td>
<td>0.076</td>
<td>0.012</td>
<td>0.023*</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.228*</td>
<td>0.175*</td>
<td>--</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>0.040</td>
<td>0.007</td>
<td>0.004*</td>
</tr>
<tr>
<td>PCB 77</td>
<td>--</td>
<td>0.052</td>
<td>0.701</td>
</tr>
<tr>
<td>PCB 105</td>
<td>0.405</td>
<td>0.107</td>
<td>0.138</td>
</tr>
<tr>
<td>PCB 114</td>
<td>0.489</td>
<td>0.234</td>
<td>0.170</td>
</tr>
<tr>
<td>PCB 118</td>
<td>0.510</td>
<td>0.223</td>
<td>0.160</td>
</tr>
<tr>
<td>PCB 125</td>
<td>0.945</td>
<td>0.276</td>
<td>0.220</td>
</tr>
<tr>
<td>PCB 126</td>
<td>5.586</td>
<td>0.407</td>
<td>0.952</td>
</tr>
<tr>
<td>PCB 156</td>
<td>0.854</td>
<td>0.144</td>
<td>0.091</td>
</tr>
<tr>
<td>PCB 157</td>
<td>1.044</td>
<td>0.134</td>
<td>0.123</td>
</tr>
<tr>
<td>PCB 167</td>
<td>1.026</td>
<td>0.227</td>
<td>0.180*</td>
</tr>
<tr>
<td>PCB 189</td>
<td>4.628</td>
<td>0.257</td>
<td>0.612</td>
</tr>
</tbody>
</table>

BSAF database: US Army Corps of Engineers

• Site-specific BSAFs calculated for the SJRWP were markedly lower than the few available in the USACE database.

• Reasons for these discrepancies:
  • PCDD/Fs: The spatial extent of sampling during the current project did not cover the migratory range of crabs or black drum. This may have led to the calculated BSAFs being lower than observed elsewhere.
  • PCBs: Higher concentrations of PCBs can be found in areas within the typical range of movement for crabs and black drum.

Biota-sediment accumulation factors

• Numerous shortcomings:
  • Inability to extrapolate easily between contaminated sites
  • Sediment sampling must be representative of geographic range of organism
  • Point estimate that does not take into account the natural variability among organisms or sediment
  • Trophic-level adjusted BSAFs
  • Trophic magnification factors (TMFs)

QSAR Modeling of BSAF
Introduction

• QSARs describe correlations between a chemical property and key characteristics of the ligand
  – Given a group of related analytes
• Comprised of independent and dependent variables
  – Independent: based on structure, physical, chemical, biological, toxicological properties and behavior
    • molecular makeup, shape, charge, logKow, solubility, surface area, etc.
  – Dependent: Property that you are trying to predict
    • BSAF, Partitioning, toxic endpoints, retention time, etc.

QSARs are only as reliable as the experimental data!

• Uniformity
  – Data must be uniform and consistent to create valid predictions
  – Requires limiting the experimental protocols (1 assay, 1 species, 1 exposure route, etc)
• Sufficient Data
  – Data must be robust enough for accuracy
  – Reduces error

Discovery Studio: Building the Model

• Create 3D molecules of our analytes
• Prepare Analytes:
  – Standardize charges
  – Retain largest fragment
  – Add hydrogens
  – 3D Geometry
  – Minimize energy
• Attach BSAF values to respective analytes (dependent property)

• Training Set: all analytes with data
  – Used to design a model that can predict activity
  – Descriptors random for training
• Model: Genetic Function Approximation
  – Prepared data is complete
Genetic Function Approximation Algorithm

- Generates high quality linear equations and regression analysis
- Evolves model equations
- Ranks regressions using Friedman’s Lack of Fit score
- Several advantages of using GFA over other techniques

**Advantages of using GFA over other techniques**

- It builds multiple models rather than a single model.
- It automatically selects which features are to be used in the models.
- It is better at discovering combinations of features that take advantage of correlations between multiple features.
- It incorporates Friedman’s L.O.F error measure, which estimates the most appropriate number of features, resists overfitting, and allows control over the smoothness of fit.
- It can use a larger variety of equation term types in construction of its models (for example, splines, step functions, high-order polynomials).
- It provides, through study of the evolving models, additional information not available from standard regression analysis (such as the preferred model length and useful partitions of the dataset).

**QSAR Model for Dioxins**

<table>
<thead>
<tr>
<th>Model</th>
<th>I</th>
<th>J</th>
<th>logP</th>
<th>CIC</th>
<th>Kappa_3</th>
<th>n</th>
<th>R²</th>
<th>R² (adj)</th>
<th>L.O.F.</th>
<th>L.O.F. (adj)</th>
</tr>
</thead>
<tbody>
<tr>
<td>logBSAF = -167.54 + 0.29 AlogP - 4.26 CIC + 73.58 Kappa_3</td>
<td>0.962</td>
<td>0.958</td>
<td>0.79</td>
<td>0.78</td>
<td>0.73</td>
<td>0.91</td>
<td>0.85</td>
<td>0.91</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>logBSAF = -232.25 + 0.39 AlogP - 19.91 CIC + 74.01 Kappa_3</td>
<td>0.962</td>
<td>0.962</td>
<td>0.79</td>
<td>0.78</td>
<td>0.73</td>
<td>0.91</td>
<td>0.85</td>
<td>0.91</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>logBSAF = -117.56 - 12.29 CIC + 74.01 Kappa_3</td>
<td>0.962</td>
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<td>0.78</td>
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<td>0.01</td>
</tr>
</tbody>
</table>

IAC = mean of atomic composition
Jx = covalent radii

**Black Drum QSAR Model for dl-PCBs August 2010**

logBSAF = 43.18 – 18.48 * IAC Mean – 6.8144 * Jx

IAC Mean = mean of atomic composition
Jx = covalent radii

**Blue Crab QSAR Model for dl-PCBs August 2010**

logBSAF = 20.84 – 7.33 * IAC Mean – 4.32 * Jx

IAC Mean = mean of atomic composition
Jx = covalent radii

**Clam QSAR Model for dl-PCBs August 2010**

logBSAF = 57.24 – 23.04 * IAC Mean – 9.55 * Jx

IAC Mean = mean of atomic composition
Jx = covalent radii
• Bioaccumulation: accumulation of chemicals in and on living tissue.
  
• Bioconcentration: partitioning of chemicals from water into living tissue
  
  - Bioconcentration factor (BCF): Concentration in fish vs. concentration in water
  
• Biomagnification: increasing concentrations of chemicals in living tissue up the food chain
  
  - Biomagnification factor (BMF): Concentration in fish vs. concentration in their prey species
  
• Theoretically, BSF provides a combined measure of the diverse forces that affect bioaccumulation of chemicals in tissue.

\[
C_p = \frac{(C_{\text{water}} \times \text{Dietary intake}) + (C_{\text{water}} \times \text{Gill elimination} + \text{Fecal elimination} + \text{Growth})}{(k_d + k_s + k_e)}
\]

The concentration in black drum can be reduced to the amount of the chemical entering the fish minus the amount that is lost through metabolism or elimination and through dilution by growth of the fish itself.

\[
C_p = \frac{C_{\text{intake}}}{(k_d + k_s + k_e + k_M / (k_d + k_s + k_e))}
\]


Arnot et al., Environ Toxicol Chem 23(10):2343-55, 2004
Bioaccumulation in black drum

\[ C_P = \left( k_{12} + k_{12} \phi + C_{OC} + k_2 + k_{OP} \right) \left( k_1 + k_2 + k_{OP} \right) \]

Elimination

Arnot et al., Environ Toxicol Chem 23(10):2343-2351, 2004

The Gobas/Arnot model of bioaccumulation

- Parameterization of the model:
  - Concentrations of COPCs in water and sediment
  - Physical characteristics of water and sediment
  - Physical-chemical characteristics of the COPC (log K ow etc.)
  - Information on fish and benthic species
  - Nature of the food web to be assessed
  - No transformation was assumed.
  - Accumulation from water will contribute minimally.

Modeled concentrations (pg/g wet weight)

<table>
<thead>
<tr>
<th>COPC</th>
<th>Clams</th>
<th>Blue Crab</th>
<th>Black drum</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378-TCDD</td>
<td>2920</td>
<td>72.57</td>
<td>3.61</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>9260</td>
<td>74.19</td>
<td>7.48</td>
</tr>
<tr>
<td>PCB 77</td>
<td>56600</td>
<td>4859.24</td>
<td>807.49</td>
</tr>
<tr>
<td>PCB 105</td>
<td>5510</td>
<td>572.47</td>
<td>134.25</td>
</tr>
<tr>
<td>PCB 114</td>
<td>36600</td>
<td>2459.24</td>
<td>807.49</td>
</tr>
<tr>
<td>PCB 118</td>
<td>74.5</td>
<td>54.96</td>
<td>3.72</td>
</tr>
<tr>
<td>PCB 123</td>
<td>1530</td>
<td>220.18</td>
<td>38.34</td>
</tr>
<tr>
<td>PCB 126</td>
<td>979</td>
<td>142.83</td>
<td>17.54</td>
</tr>
<tr>
<td>PCB 189</td>
<td>108</td>
<td>50.42</td>
<td>4.89</td>
</tr>
</tbody>
</table>

Observed concentrations (pg/g wet weight)

<table>
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<th>Black drum</th>
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Modeled:observed ratio

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<tr>
<td>2378-TCDD</td>
<td>106</td>
<td>269</td>
<td>3578</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>125</td>
<td>413</td>
<td>8300</td>
</tr>
<tr>
<td>PCB 77</td>
<td>4</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>PCB 105</td>
<td>15</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>PCB 114</td>
<td>10</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>PCB 118</td>
<td>15</td>
<td>282</td>
<td></td>
</tr>
<tr>
<td>PCB 123</td>
<td>10</td>
<td>294</td>
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</tr>
<tr>
<td>PCB 126</td>
<td>8</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>PCB 137</td>
<td>7</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>PCB 187</td>
<td>7</td>
<td>485</td>
<td></td>
</tr>
<tr>
<td>PCB 189</td>
<td>2</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>

Potential reasons for discrepancies between modeled and observed concentrations in biota (avenues for future research)

1) Residence time for fish and crabs (larger ratios) – these mobile species have the opportunity to consume “uncontaminated” prey species elsewhere.

2) Biotransformation/metabolism/elimination – though data on the metabolism and elimination of PCDD/Fs and PCBs in crabs and fish is less than complete, there are some indications that some of these substances can be efficiently removed from tissue.
The Gobas/Arnot model of bioaccumulation

- Potential reasons for discrepancies between modeled and observed concentrations in biota
  3) Sediment concentrations in the model – too few data are available to characterize the nature of the distribution; arithmetic means were used. Geometric means yield lower ratios.
  4) PCDD/Fs vs. PCBs – the relatively limited extent of PCDD/F contamination will lead to higher ratios in crabs and fish, while PCB ratios will be lower because of the broader geographic spread of PCB contamination (i.e., Patrick Bayou).

Trophic magnification factors (TMFs)

- Definition: The extent to which COPC tissue concentrations change as trophic level increases.

- TMF has been recommended as a more robust approach.
- TMF has been shown to have a relationship with trophic-level corrected BSF-TL.

Biota-sediment accumulation factors

\[
\text{BSAF}_{\text{TL}} = \frac{\log(C_{\text{biota}}/C_{\text{sed}})}{\text{TL}_{\text{biota}} - \text{TL}_{\text{sediment}}}
\]

Summary of Research Findings

- Analytical measurement
  – Development of novel extraction methods, resulting in higher throughput and lower costs
  – Improved accuracy and precision
    • e.g., matrix spikes %RSD ranged 6.6 to 9.2%.
    • Valid for multiple matrices, standard reference materials
    • SJRWP may have been a source of PCBs to the HSC

- BSF
  – Importance of including lipid normalization of tissue analysis, organic carbon (and potentially black carbon) normalization of sediment
  – Dynamic field with much uncertainty, particularly for mobile organisms
  – Values in the present study appear to be biased low, potentially due to seasonal variability, sediment sampling approaches, mobile organisms, metabolism, etc
Summary of Research Findings

• BSAF QSAR
  – QSAR represents opportunity for screening contaminated sites
  – Initial QSAR models developed for BSAFs
  – Ideally QSAR models will be organism, site and chemical class specific
  – Importance of not utilizing data lacking organic carbon, lipid normalization

Future Directions

• Food web modeling
  – Presents opportunity to more comprehensively model bioaccumulation
  – Successfully applied for first time to SJRWP
  – In this study, informed by trophic position, used to developed trophic corrected BSAFs
  – Provides baseline for future research

Future Directions

• Novel methods developed would benefit from interlaboratory variability studies prior to being incorporated for regulatory use
• Examine relative importance of organic carbon vs. black carbon normalization on BSAF
• Spatial and temporal influences of salinity gradients on solubility, bioavailability and partitioning requires additional study

Future Directions

• Trophic position based on stable isotope and stomach content can improve understanding of bioaccumulation, particularly for seasonal and ontogenetic feeding web dynamics
• Uncertainty in BSAF calculation for species of concern would be improved by better understanding seasonal patterns
  – of organismal movement
  – of lipid content

Future Directions

• Uncertainty in BSAF calculation for species of concern would be improved by better understanding bioaccumulation, including QSAR modeling
  – Consistently using organic carbon, lipid
  – Uptake kinetics
  – Depuration kinetics
Future Directions

- Uncertainty in BSAF calculation for species of concern would be improved by better understanding scales of sampling schemes to develop site-specific values
  - Geographic extent of mobile organisms relative to feeding overlap with contaminated sites
  - Use of radiotelemetry technologies can refine home range estimates of time spent on sites
  - Use of trophic magnification factors

Questions?