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

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Department of Environmental Science

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1

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## Why the San Jacinto River Waste Pits?

- Placed on US EPA NPL of Superfund sites in 2008



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## 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)

$$Sed_{Soil} PCL = \frac{RBEL_{Fish}}{BSAF}$$

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](http://www.epa.gov/med/Prods_Pubs/bsaf.htm)

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## 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

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## 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

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## 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

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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

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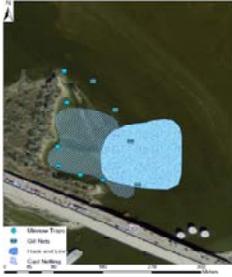
Locations of sediment sampling during August 2010, San Jacinto River Waste Pits



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



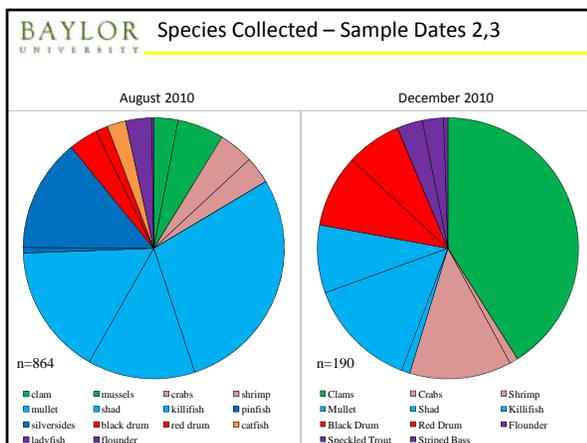
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Sampling during August 2010, San Jacinto River Pits



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**BAYLOR UNIVERSITY** The San Jacinto River Food Web

Organisms collected, identified and enumerated during August 2010 from the San Jacinto River Pits, Texas

Group	Scientific Name	Common Name	Total Number
Crustacean	<i>Callinectes sapidus</i>	Blue crab	37
Crustacean	<i>Palaemonetes pugio</i>	Grass shrimp	6
Crustacean	<i>Pneud sp</i>	Pinead shrimp	23
Mollusk	<i>Mercenaria spp</i>	Clam	26
Fish	<i>Arius felis</i>	Hardhead catfish	2
Fish	<i>Bagre marinus</i>	Gulfopssai catfish	8
Fish	<i>Brevoortia patronus</i>	Menhaden	110
Fish	<i>Caranx sp</i>	Jack	1
Fish	<i>Cyprinodon variegatus</i>	Sheepshead	2
Fish	<i>Dorosoma cepedianum</i>	Gizzard shad	5
Fish	<i>Eglos saurus</i>	Ladyfish	28
Fish	<i>Fundulus grandis</i>	Gulf killifish	132
Fish	<i>Fundulus majalis</i>	Longnose killifish	5
Fish	<i>Lagodon rhomboides</i>	Pin fish	6
Fish	<i>Morone chrysops</i>	Inland silverside	121
Fish	<i>Mugil cephalus</i>	Striped mullet	248
Fish	<i>Paralichthys albigutta</i>	Gulf flounder	2
Fish	<i>Poecilia latipinna</i>	Molly	5
Fish	<i>Pogonias cromis</i>	Black drum	31
Fish	<i>Sciaenops ocellatus</i>	Red drum	20

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### C and N Isotopic Analysis of Biota



Dry sample at 60 °C

Homogenize

Place ~1 mg into tin cups

Analyze  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$

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

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13

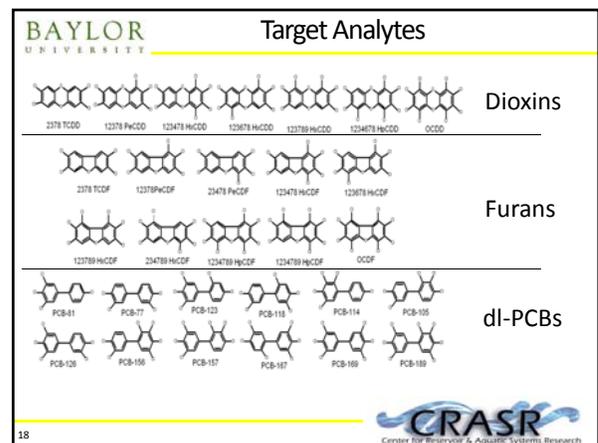
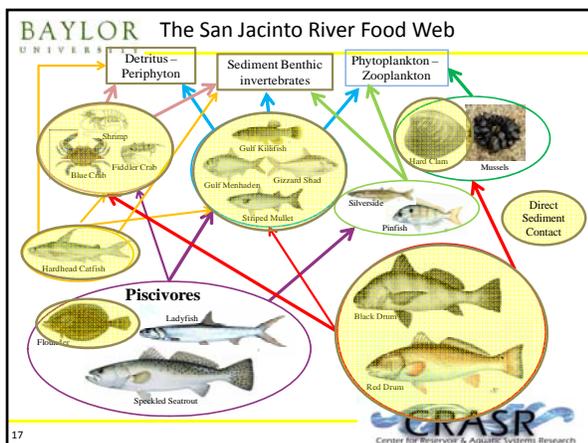
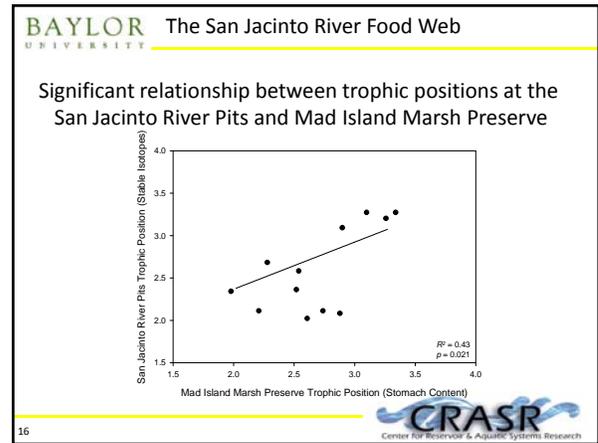
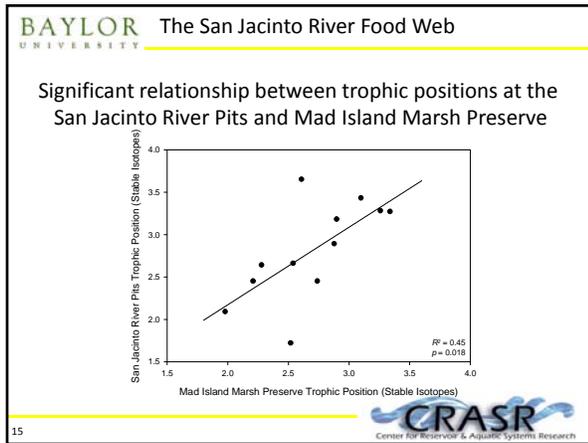
**BAYLOR UNIVERSITY** The San Jacinto River Food Web

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

Species or Taxa	N	Mean $\delta^{15}\text{N}$	Trophic Position
<i>Fundulus grandis</i>	6	15.86	1.98
<i>Mogil cephalus</i> - small	6	16.27	2.21
<i>Morone chrysops</i>	6	17.33	2.28
<i>Dorosoma cepedianum</i>	4	17.50	2.31
<i>Mercenaria</i> spp.	12	17.91	2.14
<i>Mogil cephalus</i> - large	6	18.23	2.74
<i>Cynoscion nebulosus</i>	4	18.23	3.26
<i>Brevoortia patronus</i>	10	18.60	2.61
<i>Farfantepenaeus aztecus</i>	6	18.66	2.52
<i>Callinectes sapidus</i>	6	18.89	2.54
<i>Palaemonetes pugio</i>	4	19.18	2.88
<i>Pogonias cromis</i>	12	19.42	2.90
<i>Elops saurus</i>	6	19.73	2.91
<i>Aras felis</i>	6	19.96	3.10
<i>Lagodon rhomboides</i>	5	20.29	2.97
<i>Paralichthys lethostigma</i>	6	20.74	3.34
<i>Cyprinodon variegatus</i>	1	22.74	3.92

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14



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## Organics Analysis in Biological Tissues

General Method Overview

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



Soxhlet



19

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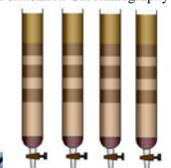
## Organics Analysis in Biological Tissues

General Method Overview

- Homogenization
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  - Column Chromatography
- Concentration and Analysis



Gel Permeation Chromatography



Column Chromatography



20

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## Limitations of Historical Methods

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



21

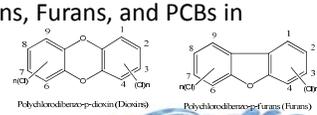
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## High-Throughput Low-Cost Method

- Ex: Measuring polycyclic aromatic hydrocarbons in seafood: Deepwater Horizon Oil Spill



- Ex: Measuring Dioxins, Furans, and PCBs in biological tissue
  - EPA Method 1613



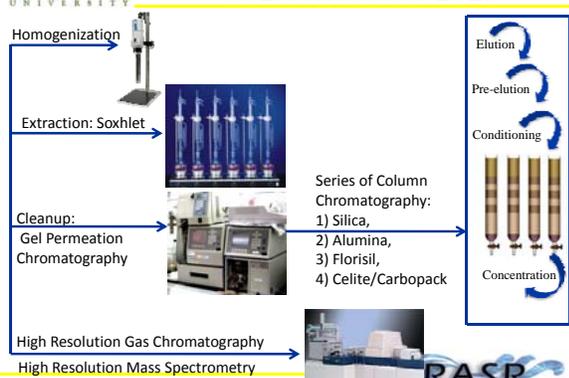
Polychlorodibenzo-p-dioxin (Dioxins)      Polychlorodibenzo-p-furans (Furans)



22

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## USEPA Method 1613



Homogenization

Extraction: Soxhlet

Cleanup: Gel Permeation Chromatography

Series of Column Chromatography:  
1) Silica,  
2) Alumina,  
3) Florisil,  
4) Celite/Carbopack

Concentration

High Resolution Gas Chromatography

High Resolution Mass Spectrometry (HRGC-HRMS)

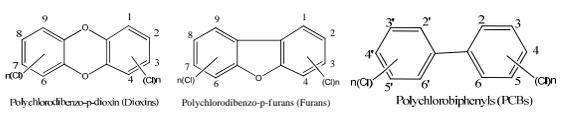


23

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## High-Throughput Low-Cost Method

- 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



Polychlorodibenzo-p-dioxin (Dioxins)      Polychlorodibenzo-p-furans (Furans)      Polychlorobiphenyls (PCBs)



24

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Enhanced pressurized liquid extraction technique capable of analyzing polychlorodibenzo-p-dioxins, polychlorodibenzofurans, and polychlorobiphenyls in fish tissue

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Polychlorodibenzofurans  
Polychlorobiphenyls  
High pressure  
Adsorbents  
Cleanup

**ABSTRACT**

A high-throughput enhanced pressurized liquid extraction technique was developed by incorporating pressurized liquid extraction and multiple cleanup techniques. UHPLC methods of polychlorodibenzo-p-dioxins, polychlorodibenzofurans (PCDFs) and dioxin-like polychlorobiphenyls (DL-PCBs) analysis in fish tissue include independent silica gel, florisil, alumina, and carbon/silica column cleanup techniques following extraction. Under the improved method, fish composite (~10 g) were extracted and cleaned simultaneously using dioxins (~100 ng), furans (~100 ng), and PCBs (~100 ng) and dioxins (~1–10 ng). Clean extracts were concentrated and then analyzed by high-resolution gas chromatography coupled with electron capture negative ionization mass spectrometry. Cleanup fraction within the extraction cell provided the analytical separation of all PCBs from PCDFs, reducing potential molecular interferences. The average recoveries for 11 of all PCBs in dichloromethane hexane (1:1, v/v) extracts were 85 ± 2.4% and PCDFs in toluene extracts were 85 ± 3.0%. The developed method was applied to measure the PCDFs and all PCBs in catfish from San Jacinto River Water Park, a high-polluted site in Texas, TX. The all PCBs were measured at 5.0–17,000 ng g<sup>-1</sup> wet sample preparation time and solvents were reduced at much as 95% and 60%, respectively, as compared to USEPA method 8163.

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### Pressurized Liquid Extraction

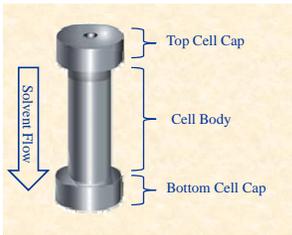
- Pressurized Liquid Extraction
  - High pressure (1500 psi)
  - Adjustable extraction temperatures (30 to 200 °C)
  - Wide range of organic solvents and weak acids
  - Multiple extraction cycles
- Dionex – Accelerated Solvent Extractor (ASE) 350



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### Pressurized Liquid Extraction



Top Cell Cap  
Cell Body  
Bottom Cell Cap

Solvent Flow

Extraction Cell

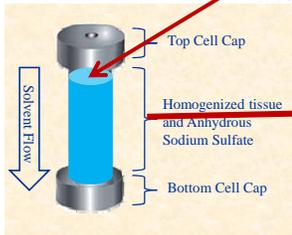


Dionex–Accelerated Solvent Extractor-350

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### Pressurized Liquid Extraction



Top Cell Cap  
Cell Body  
Bottom Cell Cap

Solvent Flow

Extraction Cell

Spike with Isotopically Labeled Surrogates

Homogenized tissue and Anhydrous Sodium Sulfate



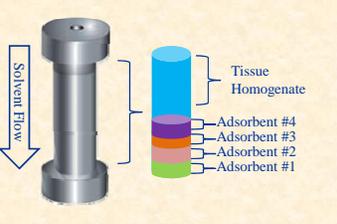
Dionex–Accelerated Solvent Extractor-350

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### Adsorbents Optimization

• Different adsorbents and ratios can be experimentally examined



Tissue Homogenate  
Adsorbent #4  
Adsorbent #3  
Adsorbent #2  
Adsorbent #1

Solvent Flow

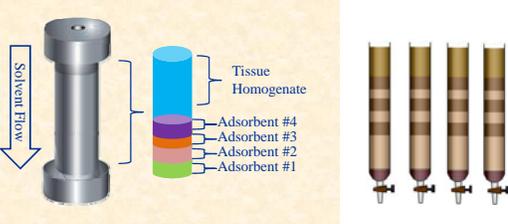
Extraction Cell

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### Adsorbents Optimization

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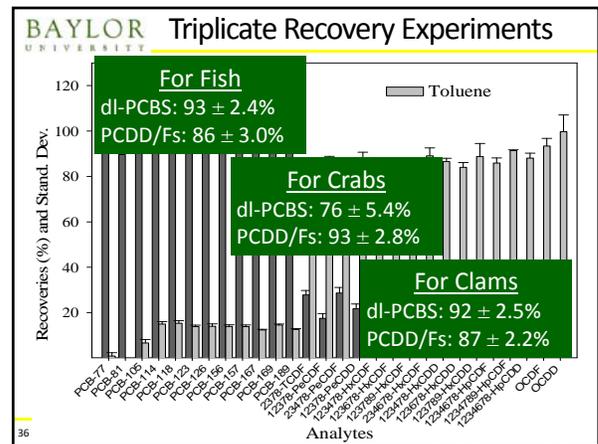
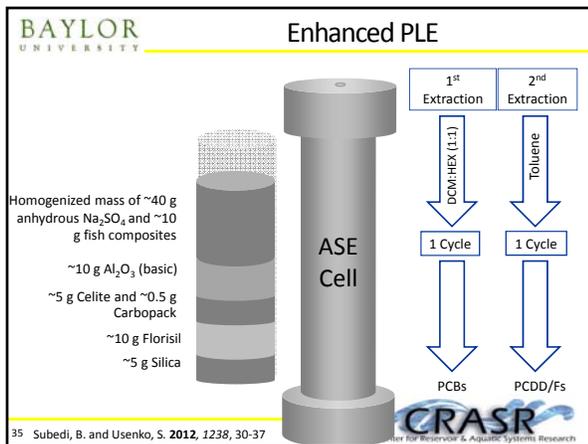
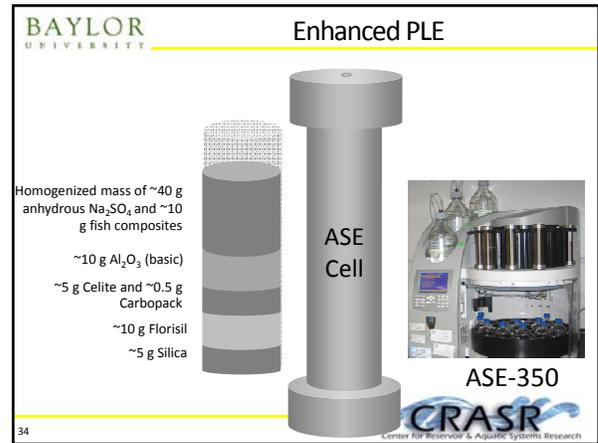
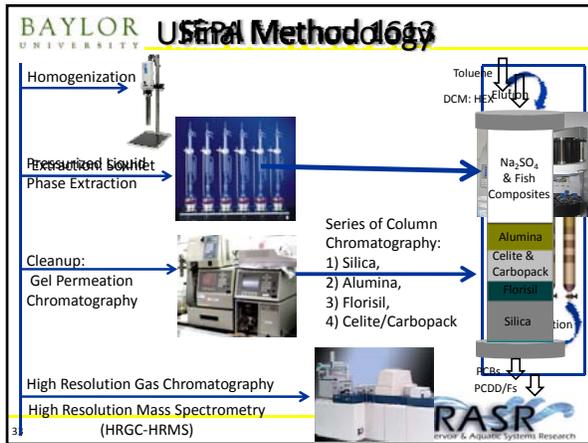
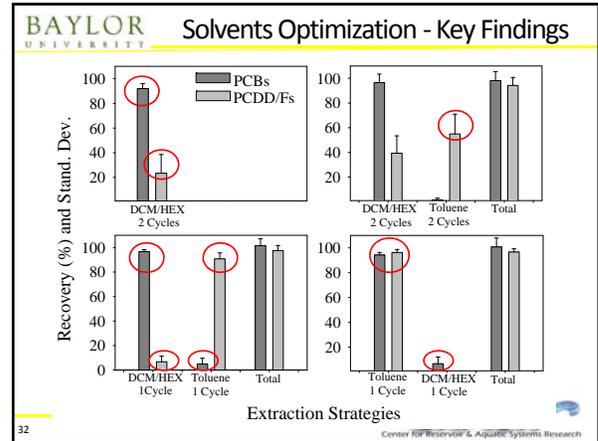
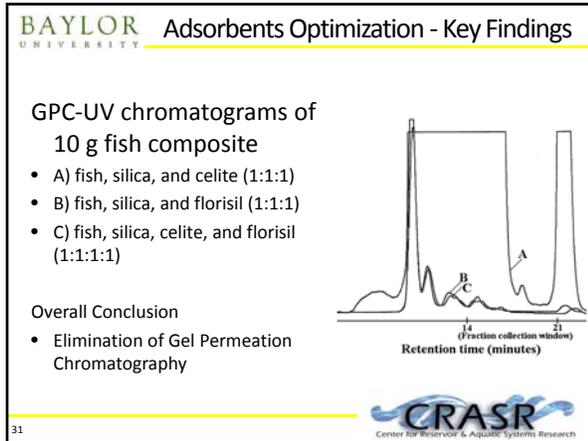


Tissue Homogenate  
Adsorbent #4  
Adsorbent #3  
Adsorbent #2  
Adsorbent #1

Solvent Flow

Extraction Cell

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35 Subedi, B. and Usenko, S. 2012. 1238, 30-37

36

### BAYLOR UNIVERSITY Matric Spike Experiments

	dl-PCBs	Dioxins	Furans	All surrogates
Sediment	6.1	12.2	5.7	8.0
Clams	2.6	11.3	6.4	7.3
Crabs	11.7	6.2	6.4	7.3
Fish	7.5	7.2	7.7	7.5
All matrices	7.0	9.2	6.6	7.5



### BAYLOR UNIVERSITY Surrogate Recovery

	dl-PCBs	Dioxins	Furans	All surrogates
Sediment	83	74	67	72
Clams	97	97	81	89
Crabs	70	81	78	78
Fish	82	75	71	74
All matrices	83	82	74	78



### BAYLOR UNIVERSITY Methods Comparison

New Method	USEPA Method 1613B
<ul style="list-style-type: none"> <li>• Surrogate Recoveries                             <ul style="list-style-type: none"> <li>• 72 - 103%</li> </ul> </li> <li>• Time                             <ul style="list-style-type: none"> <li>– 2 hours/sample</li> </ul> </li> <li>• Solvent                             <ul style="list-style-type: none"> <li>– 33%</li> </ul> </li> <li>• Cost                             <ul style="list-style-type: none"> <li>– \$150 to \$250/sample</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Surrogate Recoveries                             <ul style="list-style-type: none"> <li>– 17 - 197%</li> </ul> </li> <li>• Time                             <ul style="list-style-type: none"> <li>– 8 to 12 hours/sample</li> </ul> </li> <li>• Solvent                             <ul style="list-style-type: none"> <li>– 100%</li> </ul> </li> <li>• Cost                             <ul style="list-style-type: none"> <li>– \$700 to \$1000/sample</li> </ul> </li> </ul>



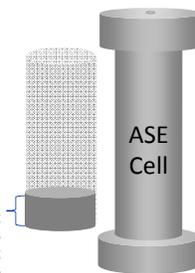
### BAYLOR UNIVERSITY % Lipid Determination

**Gravimetric Determination**

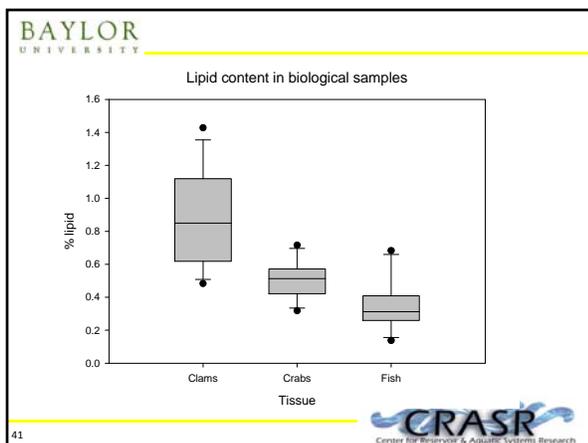
- Same ASE parameters used during the extraction of contaminants



Homogenized mass of ~20 g anhydrous Na<sub>2</sub>SO<sub>4</sub> and ~2 g fish composites







### BAYLOR UNIVERSITY Sample Analysis and Results Summary



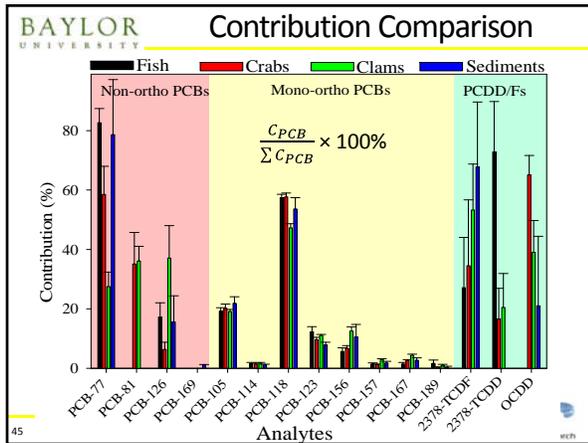
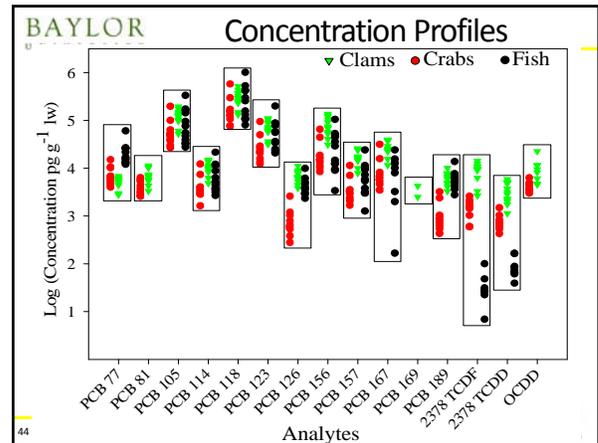
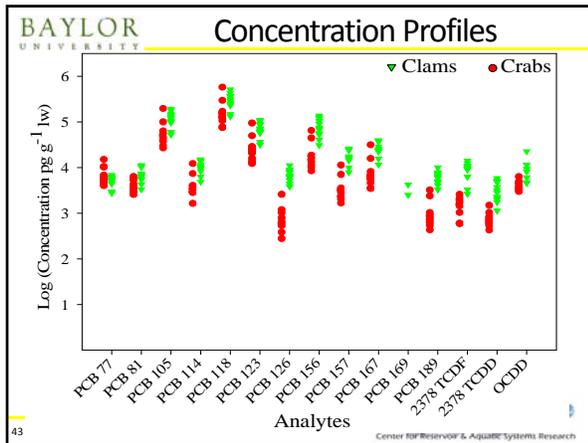
HRGC-MS/ECNI



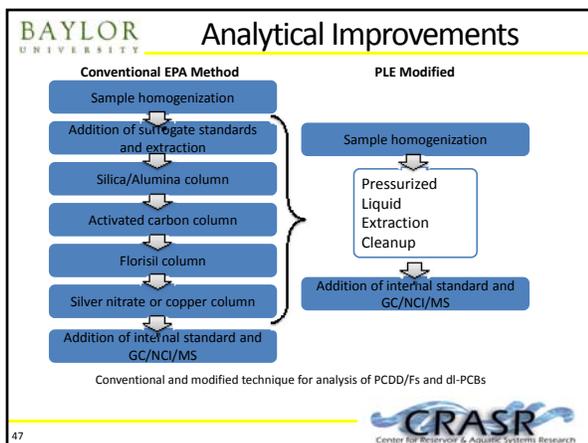
HRGC-HRMS

Congeners	Concentration ng g <sup>-1</sup> lw		
	Clam	Crab	Fish
Non ortho PCBs	5.16-7.11	0.82-7.15	1.86-9.48
Mono ortho PCBs	6.34-300	1.09-180	2.59-128
PCDD/Fs	3.31-9.82	0.76-4.18	0.015-0.038



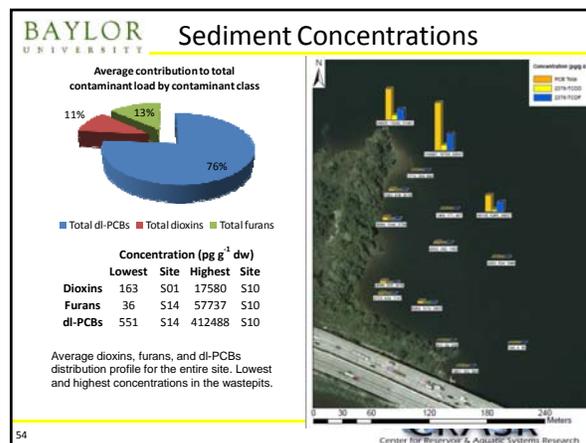
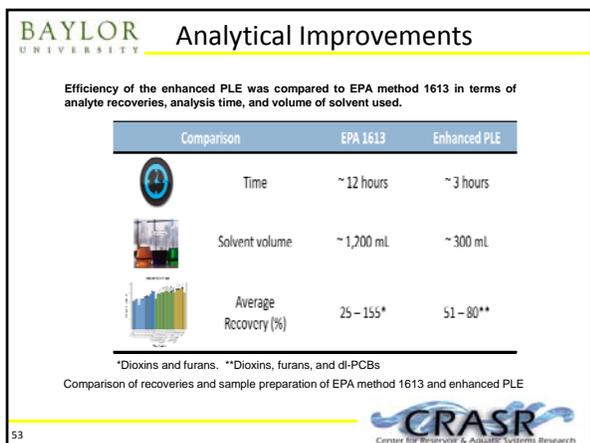
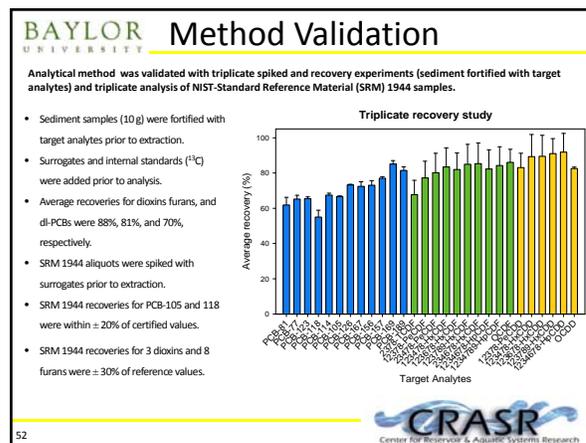
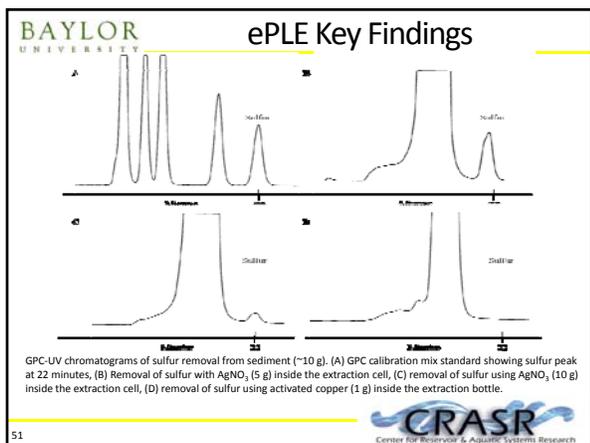
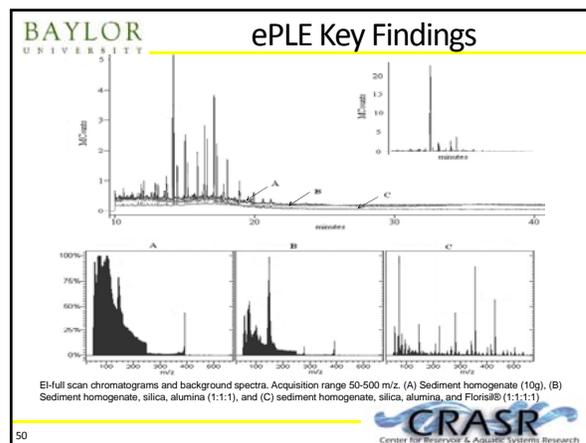
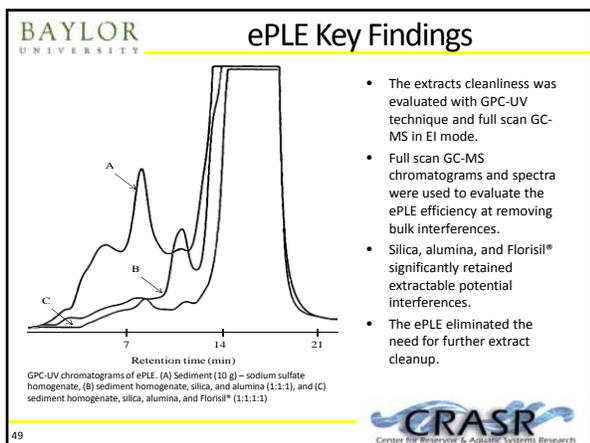


## Sediment Analysis



## Pressurized Liquid Extraction

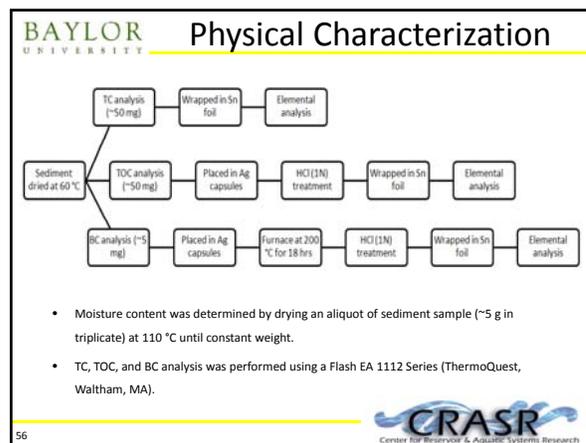
- Sediment samples (~10 g ww) were homogenized with the pre-cleaned sodium sulfate using mortar and pestle until dry.
- The homogenized sediment samples were placed on top of pre-cleaned silica, alumina, and Florisil® (1:1:1 sample to sorbent ratio) in a 100 ml ASE cell
- Samples were spiked in the ASE cell 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.



**BAYLOR UNIVERSITY** Sediment Summary (pg/g TOC)

Congener abbreviation	Date	All units: pg/g					
		Min	Max	Median	Mean	St. Dev.	Geometric
<b>Dioxins</b>							
2378-TCDD	15/15	180	240000	56000	65000	62000	34000
12378-PeCDD	0/15	--	--	--	--	--	--
123478-HxCDD	0/15	--	--	--	--	--	--
123878-HxCDD	0/15	--	--	--	--	--	--
123789-HxCDD	2/15	0	2800	--	--	--	--
1234678-HpCDD	6/15	0	4600	--	--	--	--
OCDD	15/15	1600	75000	30000	32000	22000	21000
<b>Furans</b>							
2378-TCDF	15/15	1700	500000	190000	220000	170000	130000
12378-PeCDF	14/15	0	17000	--	--	--	--
23478-PeCDF	14/15	0	13000	3800	4200	3600	--
123478-HxCDF	14/15	0	29000	9100	11000	8700	--
123878-HxCDF	14/15	0	7400	2200	2500	2100	--
123789-HxCDF	12/15	0	1400	400.0	440	390	--
234678-HpCDF	4/15	0	890	--	--	--	--
1234678-HpCDF	14/15	0	7900	2200	2700	2300	--
1234789-HxCDF	12/15	0	3300	940	1100	980	--
OCDF	11/15	0	6000	2100	2300	1700	--
<b>PCBs</b>							
PCB 77	14/15	0	42000	8300	11000	11000	--
PCB 81	3/15	0	200000	--	--	--	--
PCB 85	15/15	6000	1100000	180000	230000	210000	190000
PCB 114	15/15	400	63000	9600	18000	18000	11000
PCB 118	15/15	14000	2000000	450000	800000	730000	480000
PCB 123	15/15	2300	390000	63000	120000	110000	69000
PCB 126	14/15	0	4500	1800	2000	1500	--
PCB 156	15/15	1800	340000	150000	150000	100000	88000
PCB 157	15/15	330	64000	20000	25000	19000	15000
PCB 167	15/15	450	99000	40000	88000	28000	23000
PCB 169	4/15	0	390	--	--	--	--
PCB 189	15/15	45	13000	3200	4200	4200	2000

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**BAYLOR UNIVERSITY** Sediment Physical Characterization

Analysis ID	% moisture	% TOC	% BC
S01	20	0.26	0.02
S02	51	1.40	0.15
S03	57	1.58	0.17
S04	44	1.97	0.21
S05	23	0.44	0.04
S06	37	1.19	0.13
S07	37	1.64	0.16
S08	18	0.15	0.01
S09	34	5.67	0.28
S10	51	12.70	0.40
S11	48	7.76	0.33
S12	63	2.41	0.28
S13	57	1.53	0.15
S14	46	2.05	0.23
S15	56	1.58	0.12
Average	43	2.82	0.18
stdev	14	3.40	0.11

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**BAYLOR UNIVERSITY** 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

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**BAYLOR UNIVERSITY** 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

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**BAYLOR UNIVERSITY** 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)

$$Sed\ Soq_{Fish}^{PCL} = \frac{RBEL_{Fish}}{BSAF}$$

where the RBEL<sub>fish</sub> represents the risk-based exposure limit for human ingestion of fish or shellfish tissue.

[http://www.epa.gov/med/Prods\\_Pubs/bsaf.htm](http://www.epa.gov/med/Prods_Pubs/bsaf.htm)

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### Biota-sediment accumulation factors

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

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

- 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.

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### Preliminary site-specific BSAFs for the SJRWP

COPC	Baylor SJRWP		
	Clams	Crabs	Fish
2378-TCDD	0.070	0.012	0.023*
OCDD	0.226*	0.175*	--
2378-TCDF	0.049	0.007	0.004*
PCB 77	--	0.632	0.791
PCB 105	0.495	0.187	0.130
PCB 114	0.849	0.234	0.170
PCB 118	0.510	0.223	0.160
PCB 123	0.843	0.256	0.220
PCB 126	5.584	0.407	0.952
PCB 156	0.854	0.144	0.091
PCB 157	1.044	0.154	0.123
PCB 167	1.028	0.227	0.100*
PCB 189	4.624	0.257	0.612

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### Preliminary site-specific BSAFs for the SJRWP

COPC	Baylor SJRWP			USACE Database		
	Clams	Crabs	Fish	Clams	Crabs	Fish
2378-TCDD	0.070	0.012	0.023*	--	--	--
OCDD	0.226*	0.175*	--	--	0.001	--
2378-TCDF	0.049	0.007	0.004*	--	1.401	--
PCB 77	--	0.632	0.791	--	1.513	2.377
PCB 105	0.495	0.187	0.130	3.720	3.408	7.498
PCB 114	0.849	0.234	0.170	--	2.268	10.568
PCB 126	5.584	0.407	0.952	19,664	2,055	--
PCB 156	0.854	0.144	0.091	--	4.932	9.293
PCB 157	1.044	0.154	0.123	--	3.317	12.244
PCB 167	1.028	0.227	0.100*	--	4.262	13.176
PCB 189	4.624	0.257	0.612	--	2.781	--

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### 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.

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### 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)

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### QSAR Modeling of BSAF

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**BAYLOR UNIVERSITY** 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.

67 

**BAYLOR UNIVERSITY** Introduction

- QSARs are only as reliable as the experimental data
  - Uniformity
  - Sufficient Data
  - Appropriate descriptors
  - Focused on one scenario

68 

**BAYLOR UNIVERSITY** 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

69 

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- Appropriate Descriptors (Independent Variables)
  - Describe the biological activity (spatial, electronic, shape, etc)
  - Relate to physical, biological, chemical, toxicological properties of chemical group
- Focused on One Scenario
  - One group of chemical analytes for a specific exposure pathway, magnitude, experiment, etc.

70 

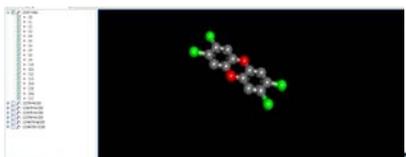
**BAYLOR UNIVERSITY** Discovery Studio: Building the Model

- 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)

71 

**BAYLOR UNIVERSITY** Discovery Studio: Building the Model

- 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



72 

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### 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

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### 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 LOF 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).

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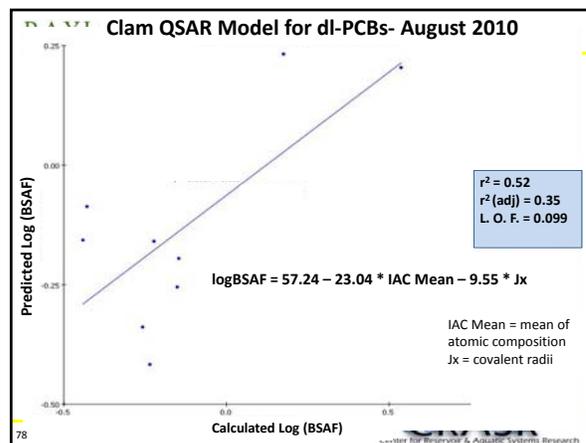
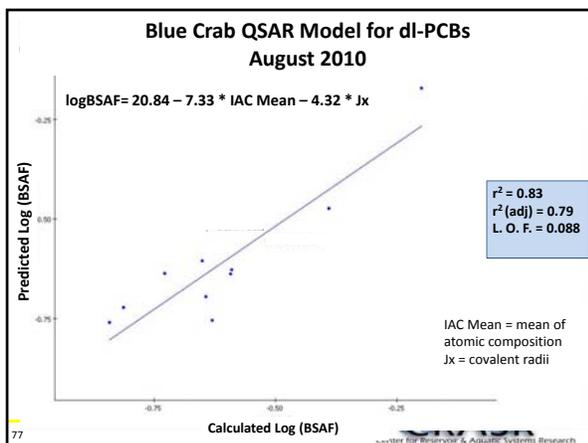
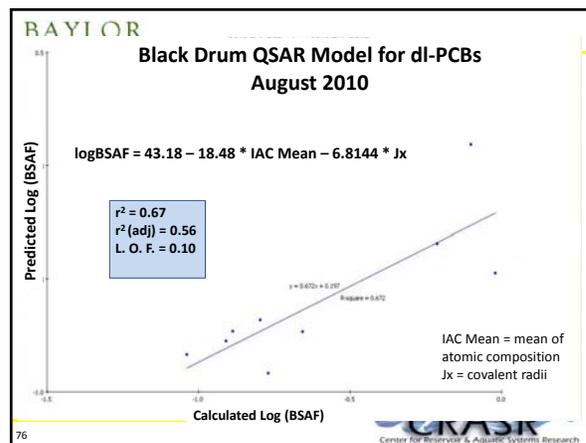
### QSAR Model for Dioxins

Model	r <sup>2</sup>	r <sup>2</sup> (adj)	r <sup>2</sup> (rank)	RMS Residual Error	Friedman L.O.F.	S.O.R. p-value
log BSAF <sub>1</sub> = -167.54 - 0.28837 * AlogP - 4.2593 * CIC + 73.582 * Kappa_3	0.9822	0.9645	0.9602	0.1578	0.06151	0.003997
log BSAF <sub>2</sub> = -167.54 - 0.28837 * AlogP - 4.2593 * CIC + 73.582 * Kappa_3	0.9822	0.9643	0.9578	0.1581	0.06175	0.00402
log BSAF <sub>3</sub> = -166.28 - 0.60451 * AlogP + 20.66 * BIC + 74.618 * Kappa_3	0.9821	0.9643	0.9572	0.1593	0.06185	0.00403
log BSAF <sub>4</sub> = -171.96 + 34.385 * Molecular_FractionalPolarSurfaceArea - 4.385 * CIC + 73.794 * Kappa_3	0.9821	0.9642	0.9562	0.1584	0.06199	0.004044
log BSAF <sub>5</sub> = -150.52 - 19.756 * BIC - 8.1272 * CIC + 72.636 * Kappa_3	0.9820	0.9640	0.9521	0.1688	0.06228	0.00407
log BSAF <sub>6</sub> = -170.01 - 3.4930 * CIC + 3.6228 * IAC_Mean + 70.765 * Kappa_3	0.9798	0.9597	0.9155	0.1682	0.06984	0.004833

**logBSAF = -167.54 - 0.29 AlogP - 4.26 CIC + 73.58 Kappa\_3**  
**r<sup>2</sup> = 0.98**  
**r<sup>2</sup> (adj) = .96**  
**L.O.F. = 0.004**

AlogP = logP, partition coefficient  
 CIC = complementary info content  
 Kappa\_3 = shape index 3<sup>rd</sup> order

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- 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, BSAF provides a combined measure of the diverse forces that affect bioaccumulation of chemicals in tissue.

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### Bioaccumulation in black drum

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### Bioaccumulation in black drum

$$C_D = (\text{water intake} + \text{dietary intake}) - (\text{gill elimination} + \text{fecal elimination} + \text{growth} + \text{elimination})$$

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.

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### Bioaccumulation in black drum

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82

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### Bioaccumulation in black drum

$$C_D = \frac{(k_1 * (m_D * \phi * C_{WT,D} + k_D * C_{WT,D})) + k_D * \sum F_i * C_{D,i}}{(k_2 + k_E + k_G + k_{1d})}$$

Intake

Gobas et al., Environ Toxicol Chem 27(13):2855-2863, 1993  
Arnot et al., Environ Toxicol Chem 23(10):2343-55, 2004

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83

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### Bioaccumulation in black drum

$$C_D = \frac{(k_1 * (m_D * \phi * C_{WT,D} + k_D * C_{WT,D})) + k_D * \sum F_i * C_{D,i}}{(k_2 + k_E + k_G + k_{1d})}$$

Intake from water      Dietary intake

Gobas et al., Environ Toxicol Chem 27(13):2855-2863, 1993  
Arnot et al., Environ Toxicol Chem 23(10):2343-55, 2004

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## Bioaccumulation in black drum

$$C_D = \frac{(k_1 * (m_2 * \phi * C_{WT,0} + k_2 * C_{WT,0})) + k_3 * \sum F_i * C_{D,i}}{(k_1 + k_2 + k_3 + k_4)}$$

Elimination

Gobas et al., Environ Toxicol Chem 27(13):2855-2863, 1993  
 Arnot et al., Environ Toxicol Chem 23(10):2343-55, 2004

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## 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<sub>OW</sub> 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.

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## TrophicTrace 4.1

Model: KABAM (K<sub>OW</sub> based) Aquatic BioAccumulation Model

Version: 1.0  
 Date: April 7, 2009  
 Developers: Environmental

When to use this model: KABAM should be used for the Log K<sub>OW</sub> of the pesticides.

Model Description: KABAM is used to calculate the bioaccumulation of pesticides in aquatic organisms. It is a model based on the Log K<sub>OW</sub> of the pesticides and the Log K<sub>OW</sub> of the organisms. It is a model based on the Log K<sub>OW</sub> of the pesticides and the Log K<sub>OW</sub> of the organisms. It is a model based on the Log K<sub>OW</sub> of the pesticides and the Log K<sub>OW</sub> of the organisms.

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COPC	Modeled concentrations (pp/g wet weight)			Observed concentrations (pp/g wet weight)		
	Clams	Blue Crab	Black drum	Clams	Blue Crab	Black drum
2378-TCDD	2920	972	7600	27.57	3.61	2.25
2378-TCDF	9260	3090	21000	74.19	7.48	2.53
PCB 77	414	138	999	--	33.20	28.17
PCB 105	15000	4990	38900	991.96	279.41	122.63
PCB 114	862	287	2380	86.02	19.43	8.57
PCB 118	36600	12200	104000	2459.24	807.49	368.28
PCB 123	5510	1840	15200	572.47	134.25	74.54
PCB 126	74.5	24.8	206	54.96	3.72	5.31
PCB 156	5370	1790	15600	655.77	94.19	38.96
PCB 157	979	326	2850	142.83	17.54	8.90
PCB 167	1530	511	4480	220.18	38.34	9.23
PCB 189	106	35.5	259	50.42	4.89	7.30

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## Bioaccumulation

COPC	Modeled:observed ratio		
	Clams	Blue Crab	Black drum
2378-TCDD	106	269	3378
2378-TCDF	125	413	8300
PCB 77	--	4	35
PCB 105	15	18	317
PCB 114	10	15	278
PCB 118	15	15	282
PCB 123	10	14	204
PCB 126	1.4	7	39
PCB 156	8	19	400
PCB 157	7	19	320
PCB 167	7	13	485
PCB 189	2	7	35

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## The Gobas/Arnot model of bioaccumulation

- Potential reasons for discrepancies between modeled and observed concentrations in biota (avenues for future research)
  - Residence time for fish and crabs (larger ratios) – these mobile species have the opportunity to consume “uncontaminated” prey species elsewhere.
  - 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.

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### The Gobas/Arnot model of bioaccumulation

- Potential reasons for discrepancies between modeled and observed concentrations in biota
  - 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.
  - 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).

91 

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### The Gobas/Arnot model of bioaccumulation

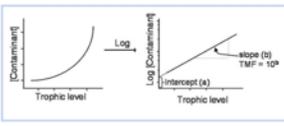
- Potential reasons for discrepancies between modeled and observed concentrations in biota
  - Variability in food web composition – trophic levels in Gulf Coast estuarine species vary from season to season, though the model assumes consistency. Seasonal variability in salinity and temperature cause changes in movement and feeding behaviors.

92 

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### Trophic magnification factors (TMFs)

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



*Borga et al., Integr Environ Assess Monit 8(1):64-84, 2012*

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

93 

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### Biota-sediment accumulation factors

$$BSAF_{TL} = \frac{\log(C_{biota}/C_{sed})}{TL_{biota} - TL_{sediment}}$$

COPC	Clams	BSAF <sub>TL</sub> Crabs	Fish
2378-TCDD	0.097	0.053	0.104
OCDD	0.271	0.318	--
2378-TCDF	0.071	0.038	0.037
PCB 77	--	0.739	0.869
PCB 105	0.540	0.332	0.294
PCB 114	0.866	0.385	0.346
PCB 118	0.554	0.373	0.333
PCB 123	0.861	0.408	0.404
PCB 126	4.521	0.554	0.971
PCB 156	0.871	0.279	0.239
PCB 157	1.038	0.292	0.285
PCB 167	1.024	0.377	0.252
PCB 189	3.832	0.409	0.745

94 

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### 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

95 

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### Summary of Research Findings

- BSAF
  - 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

96 

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## 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

97



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## Summary of Research Findings

- Food web
  - Organisms more abundant in August 2010
    - ~15 ppt, ~30°C
  - Trophic positions of organisms collected during August 2010 were not significantly different from Mad Marsh Island Preserve near Matagorda Bay
  - Black drum, blue crab and clam selected for food web modeling based understanding of feeding ecology and trophic position

98



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## Summary of Research Findings

- 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 develop trophic corrected BSAFs
  - Provides baseline for future research

99



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## 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

100



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## Future Directions

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

101



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## 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

102



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## 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

103

## Questions?



104