ASSESSING BIOAVAILABILITY OF PAHS AND PCBS WITH FIELD – DEPLOYABLE SPME

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Assessing Quality and Exposure (Risk of Contaminants)

- Traditional Indicator- Bulk sediment concentration
  - Relatively easy to measure
  - If equilibrium partitioning applies, bulk sediment measure also indicates porewater/mobile phase concentrations
  - Absent direct partitioning data:

$$K_d = \frac{W_s}{C_{pw}} = K_{oc} f_{oc}$$

  - Reality: porewater concentration is typically << predicted by this equation, due to desorption-resistant phenomena

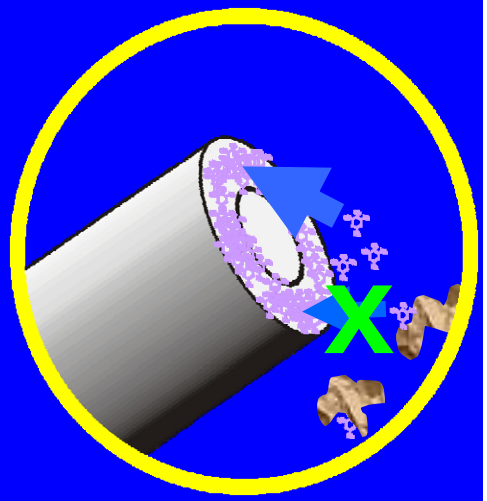
Implications: Usefulness of C_{pw}

- Bulk sediment concentration is less useful as indicator of exposure-risk
- **Porewater concentration** is better indicator (*even for active benthic uptake by ingestion)*
- Porewater is difficult to measure, but possible with solid phase micro extraction (SPME)

Field deployable SPME, capable of measuring porewater with vertical resolution

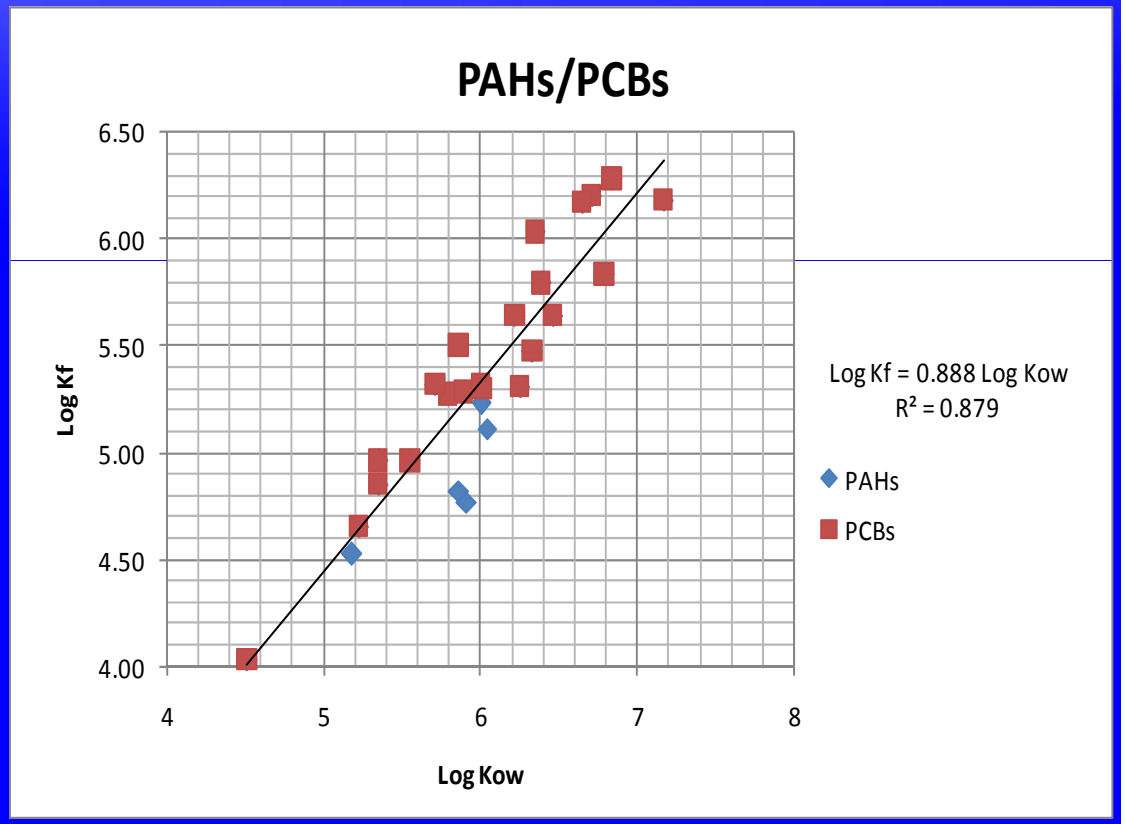
How to Measure Porewater?

- Direct in-situ measurement (PE, POM, SPME)
- Solid phase microextraction (SPME)
  - Sorbent polymer PDMS (poly-dimethylsiloxane)
  - 30 µm fiber on 110 µm core (13.6 µL PDMS/m of fiber)
  - 10 µm on 230 µm core (7 µL /m)
  - 30 µm on 1 mm core (94 µL /m)
- ng/L detection with 1 cm resolution
- Profiling field deployable system
- May require 7-30 days to equilibrate



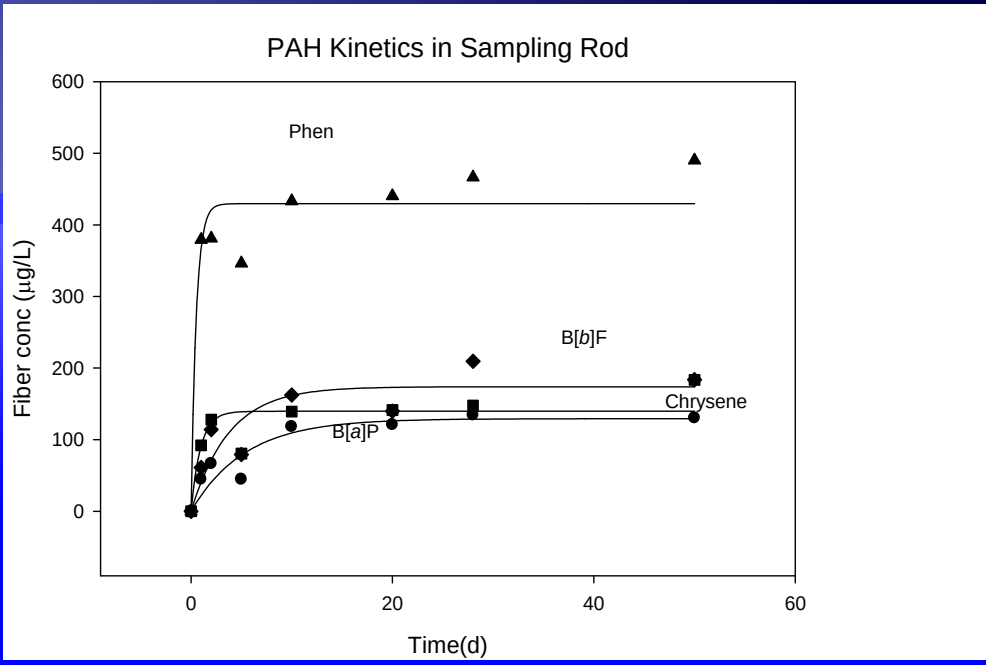
Relationship between porewater and sorbed (fiber) mass

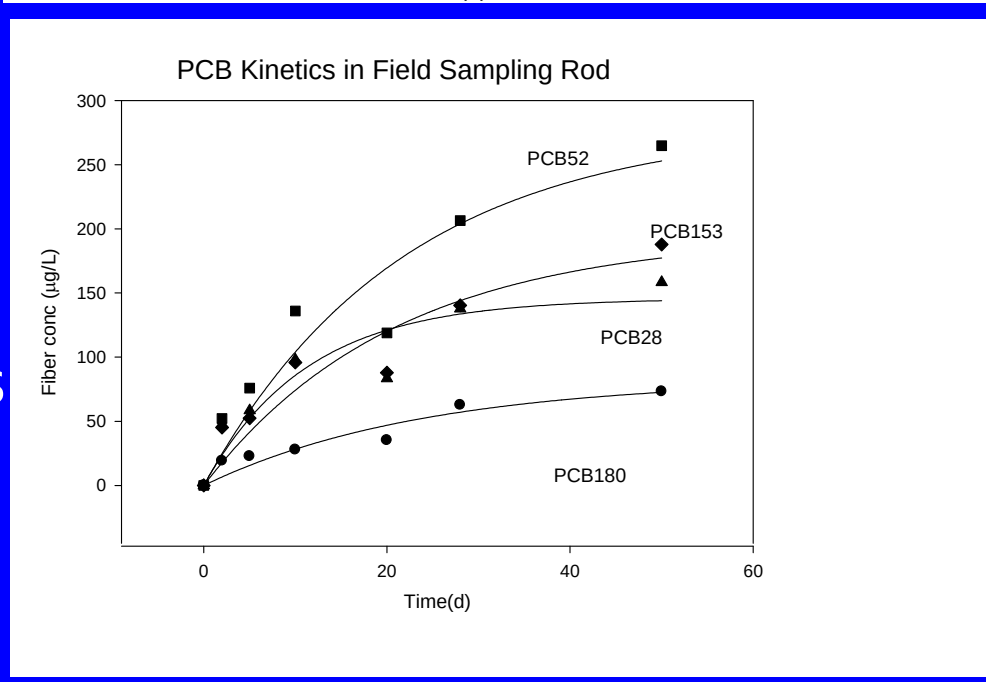
- Equilibrium K_f
  - PCB- factor of two
  - PAH +/-45%
- Fiber Volume
  - 7-94 µL/m



Kinetics

- External MT control
  - Key -Area /Volume
- PAHs relatively quick
  - 4-6 days
- High molecular weight PCBs much slower
  - 14-28 days
- Field Confirmation
  - Different exposure times
  - Different fiber thickness
  - Add tracers





TECHNICAL APPROACH

- Extraction and Analysis
  - PAHs -HPLC w/fluorescent detection
    - Extraction with 50-100 µL ACN directly in autosampling vials with inserts
  - PCBs – GC w/ECD
    - Extraction with 50-100 µL hexane directly in autosampling vials with inserts
    - Thermal desorption with splitless injection
    - Potential for co-elution of congeners
- Detection limits (1 cm 170/110 PDMS fiber)
  - 10 pg/L (High MW PCBs) to 10 ng/L (Low MW PAHs)

Laboratory Studies

- Bioaccumulation studies

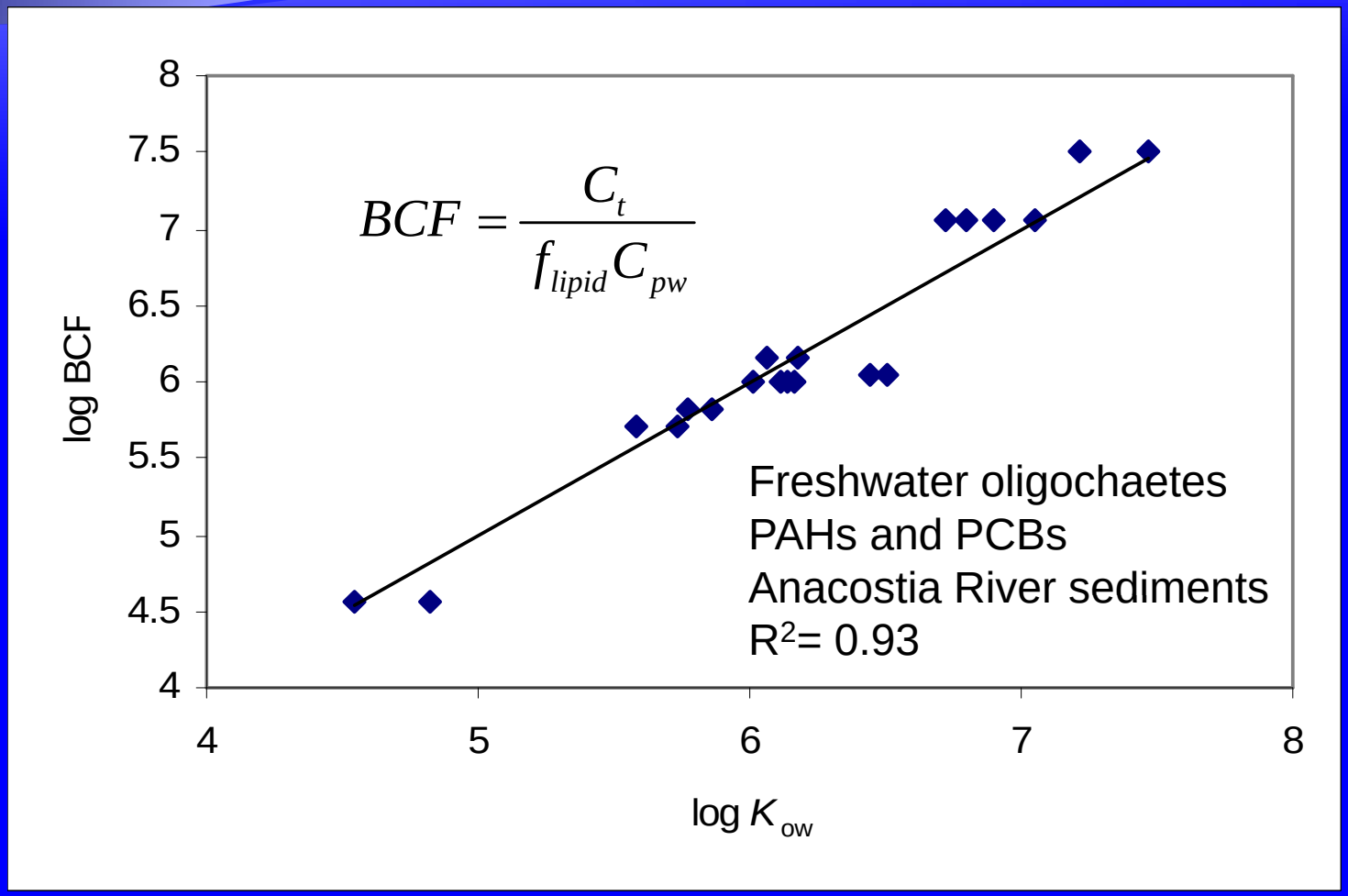
  *Ilyodilus (*freshwater oligochaete)

  - Anacostia River sediments
  - New Bedford Harbor/Brown Lake sequentially diluted sediments (3, 6, 12, 25% NBH)

  Neanthes (marine polychaete)

  - Hunter's Point sediments
- Cross-comparison of direct porewater measurements (Hunter's Point)
- Thin Layer Capping (Anacostia River)

Bioconcentration Factor Applicable to Deposit Feeders In-Situ?



In sediments and in deposit-feeding organism (porewater not route of exposure)

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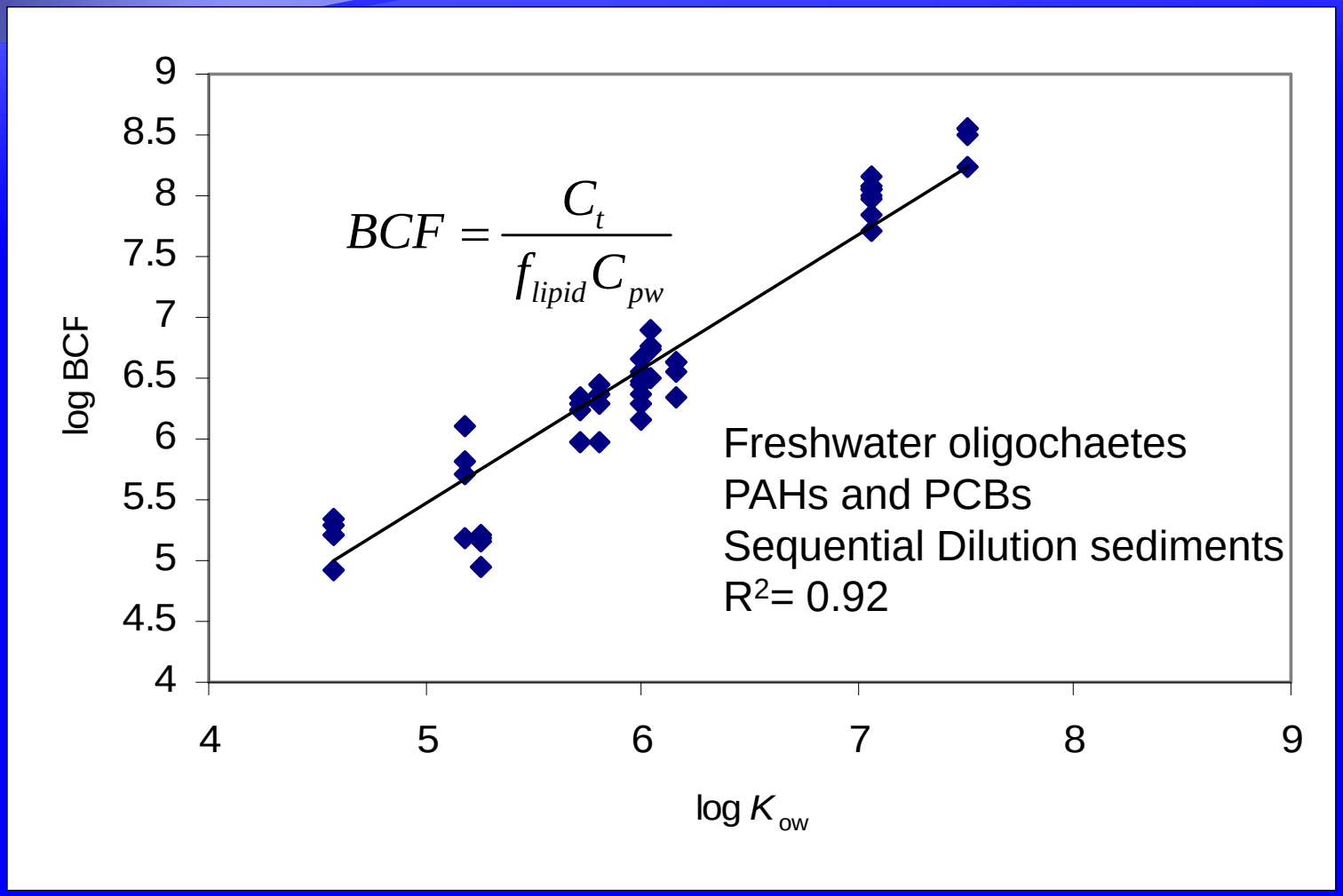

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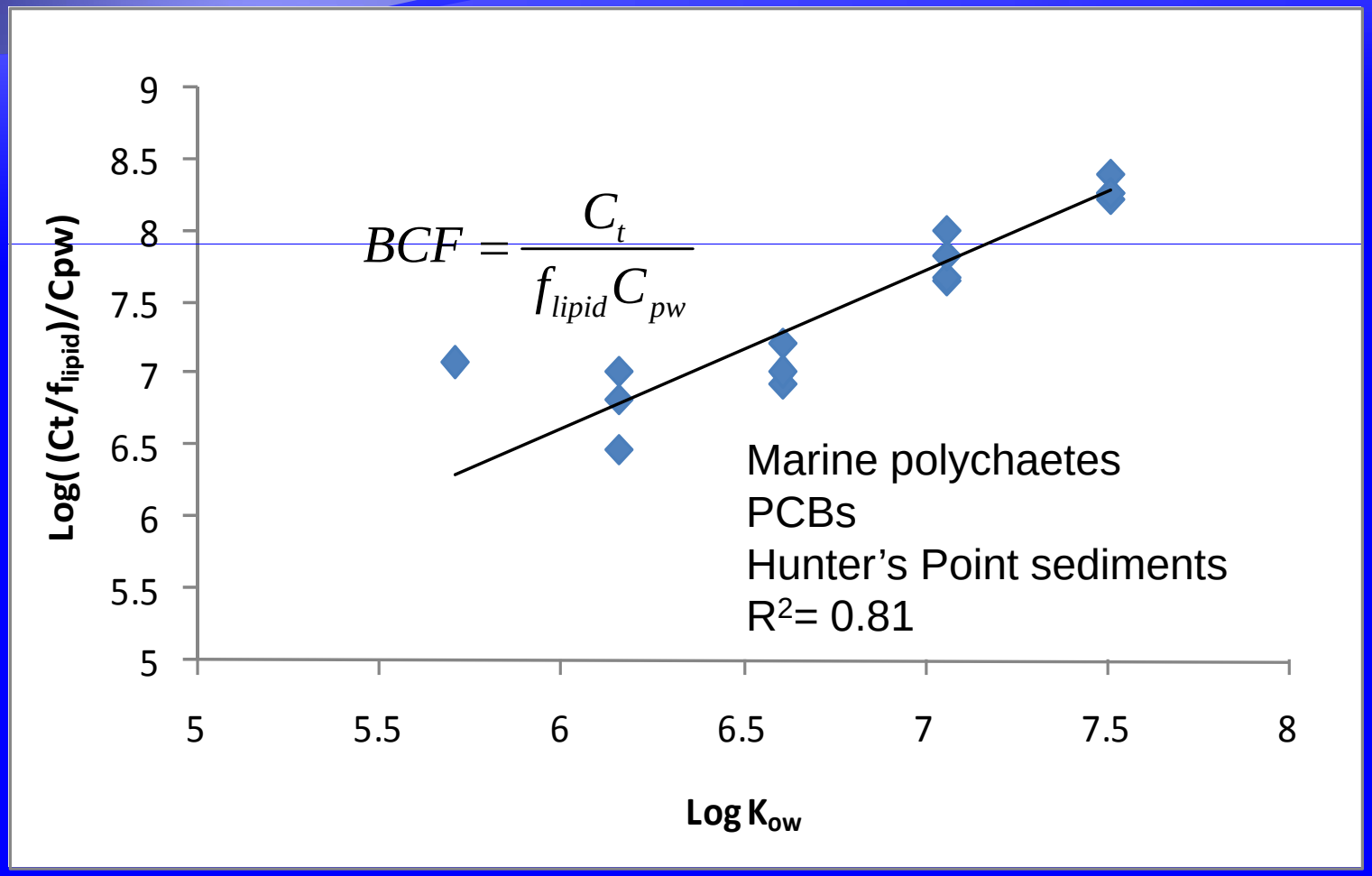

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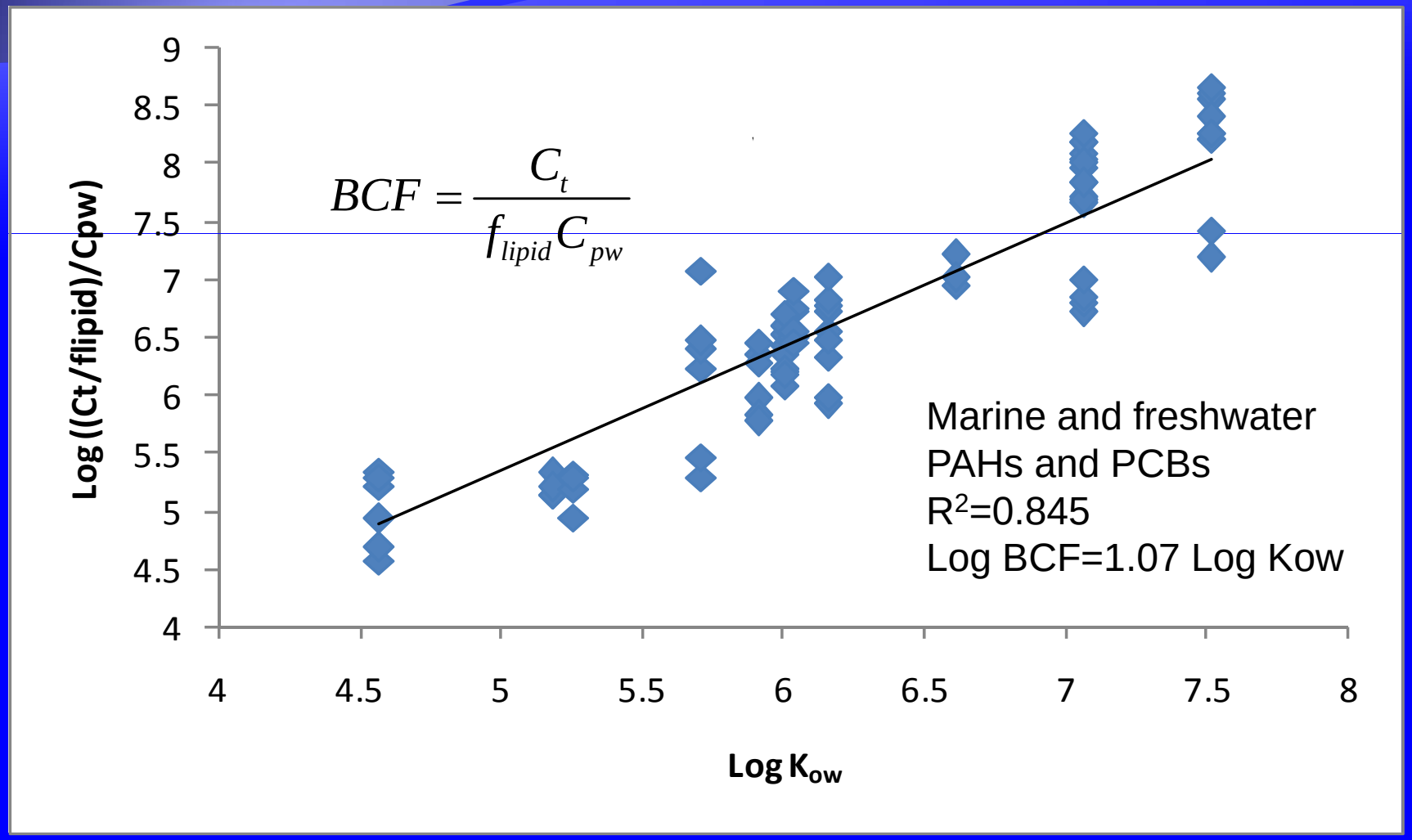
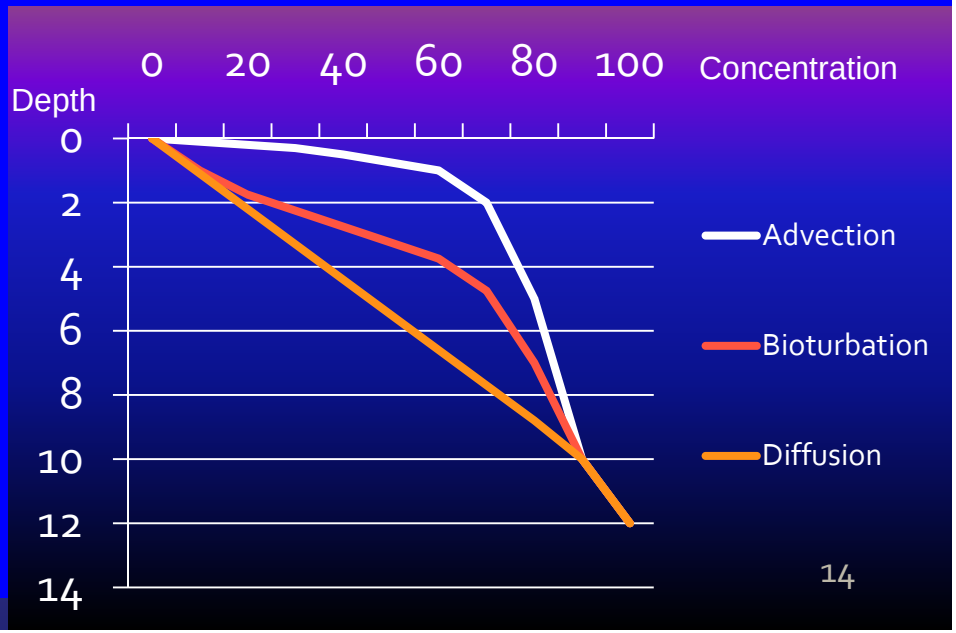


Comparison of Porewater Concentrations – Hunter's Point

PCB Congener	SPME (UT) pg/L	POM (EERC) pg/L	PE** (MIT) pg/L	Air Bridge (MIT) pg/L	Extracted Porewater Raw pg/L	Extracted Porewater TOC corr. pg/L***	Predicted Porewater Kd=Kocfoc pg/L
101	902	<915	230	602	5260	2400	6480
87	125	124	NR	NR	NR	NR	788
110	320	492	410	433	2850	1800	2340
95	880*	1460	330	667	3300	1900	8400
151	303	101	130	365	4820	670	5680
153	347	416	NR	NR	NR	NR	5440
141	134	133	NR	NR	NR	NR	1670
138	352	<2090	79	626	16300	5200	4910
149	750*	650	130	1180	15600	6200	9470
132	350*	408	720	866	20000	6100	12100

Why Field Deployable SPME?

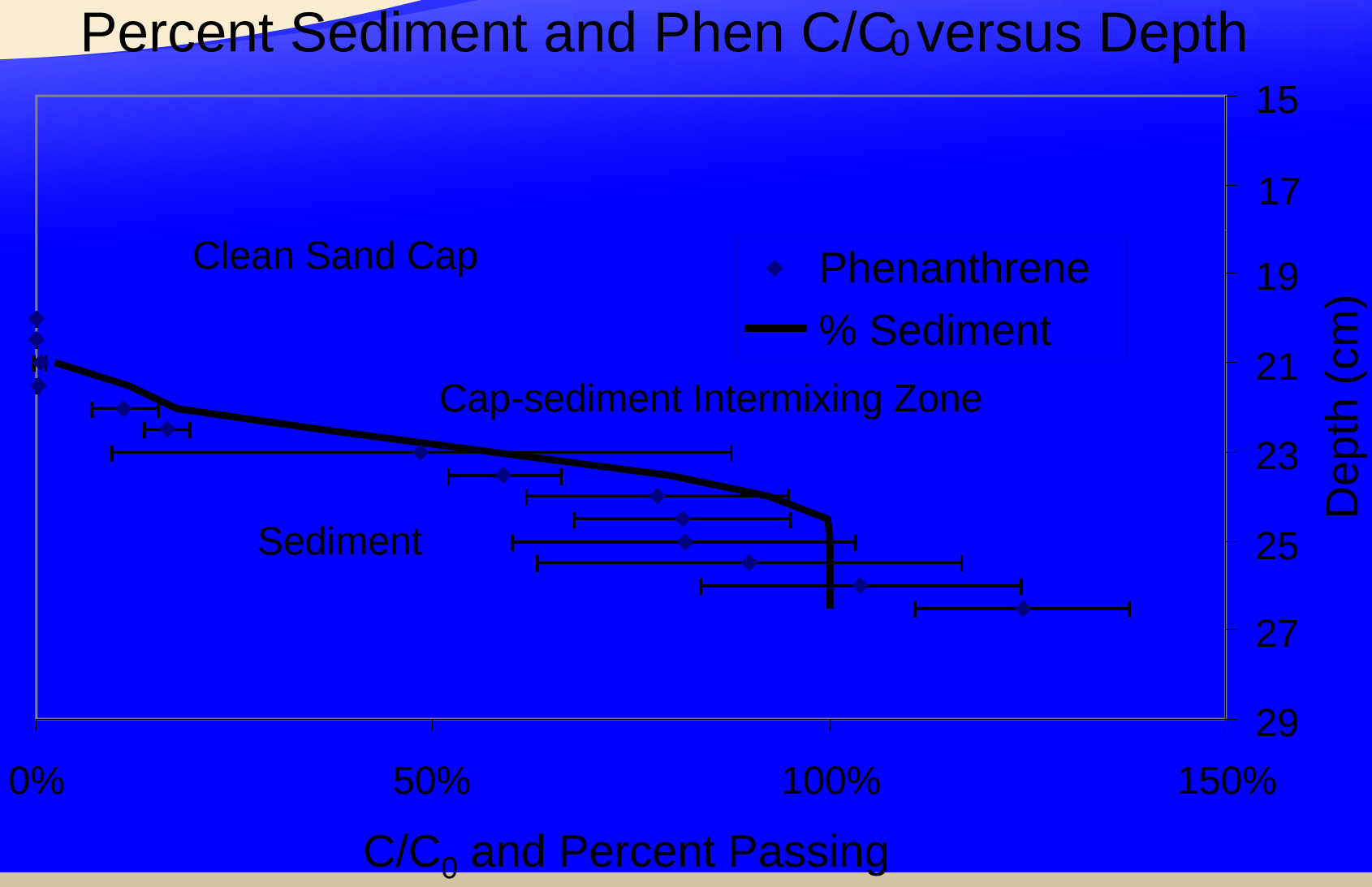
- Avoids concerns about contaminant dynamics associated with porewater extraction
- Provides in-situ profile with up to 1 cm vertical resolution depending on detection limits
  - Profiles provide rate/mechanism information
- Disadvantages
  - Deployment time
  - Analytical requirements
  - complexity



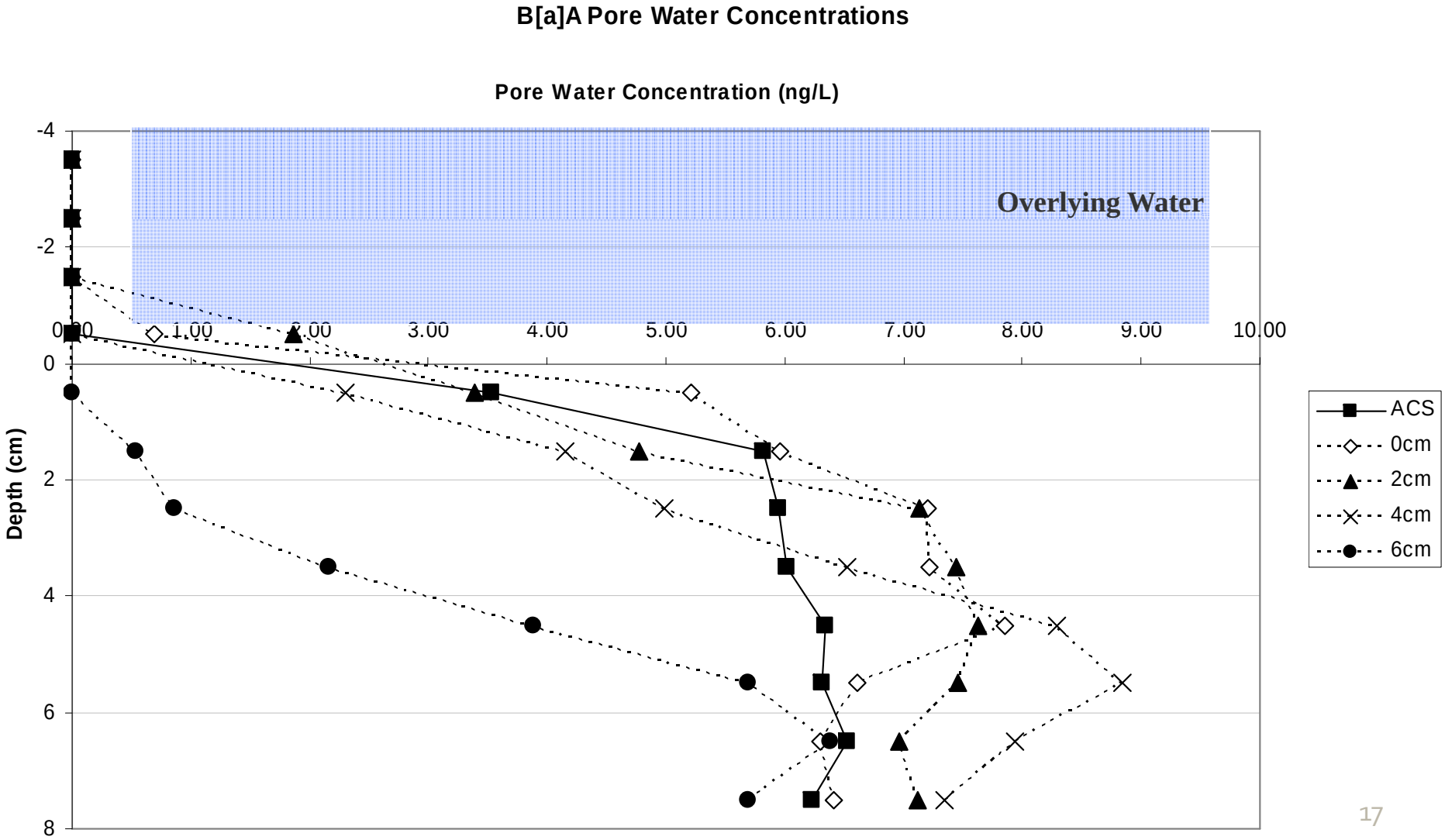
Field Applications

- Cap Performance
  - Anacostia Active Capping Demonstration
- Benthic Accumulation – Field Studies
  - Anacostia Active Capping Demonstration
    - Preliminary measurements 6/07
    - Second Round (poor organism recovery) 10/07
  - San Diego Bay/Pennsacola, FL
    - In cooperation with Sediment Ecosystem Assessment Protocol SERDP ER-1550

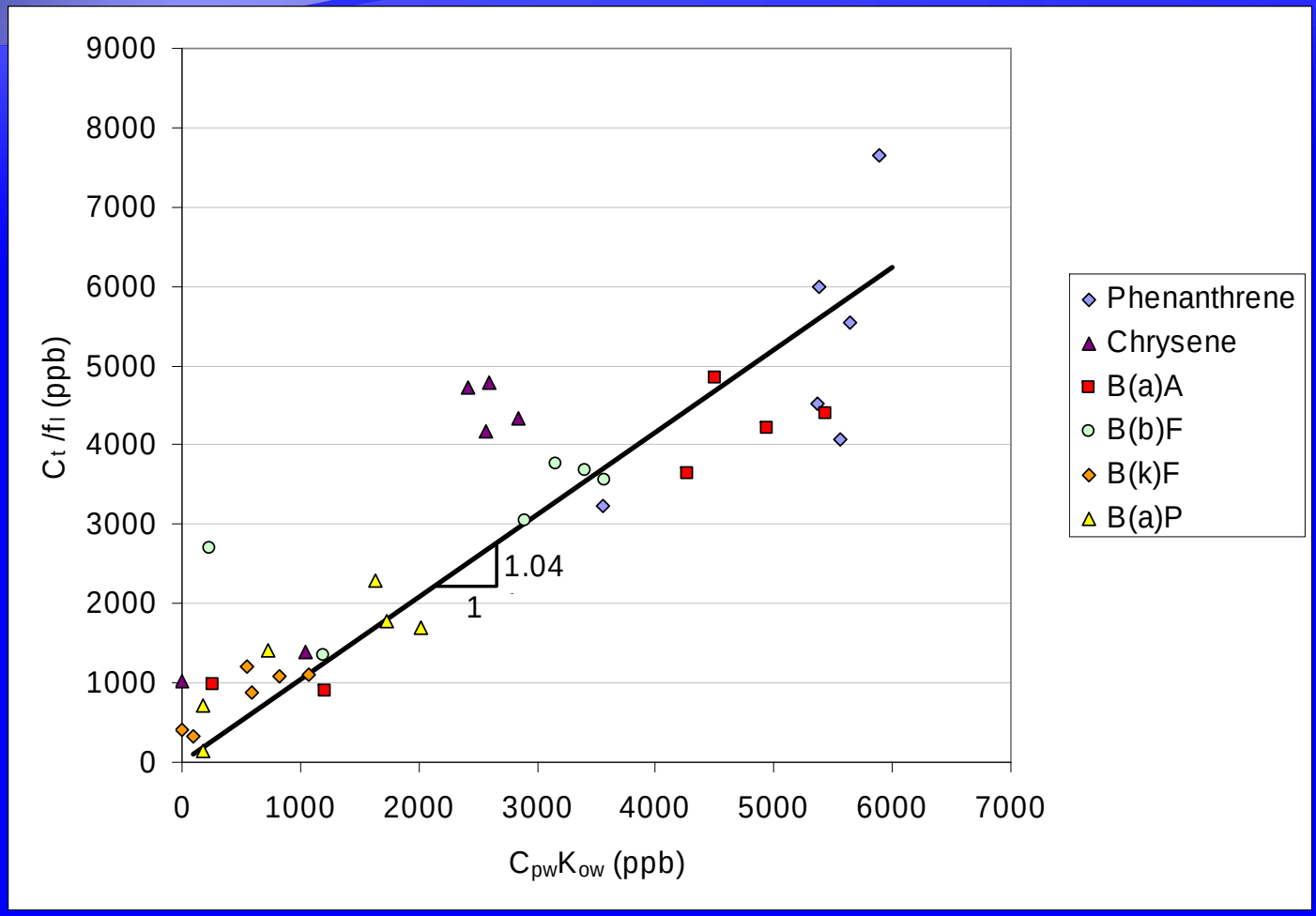
Effectiveness from Bulk Solids?



Profiling SPME to indicate cap performance

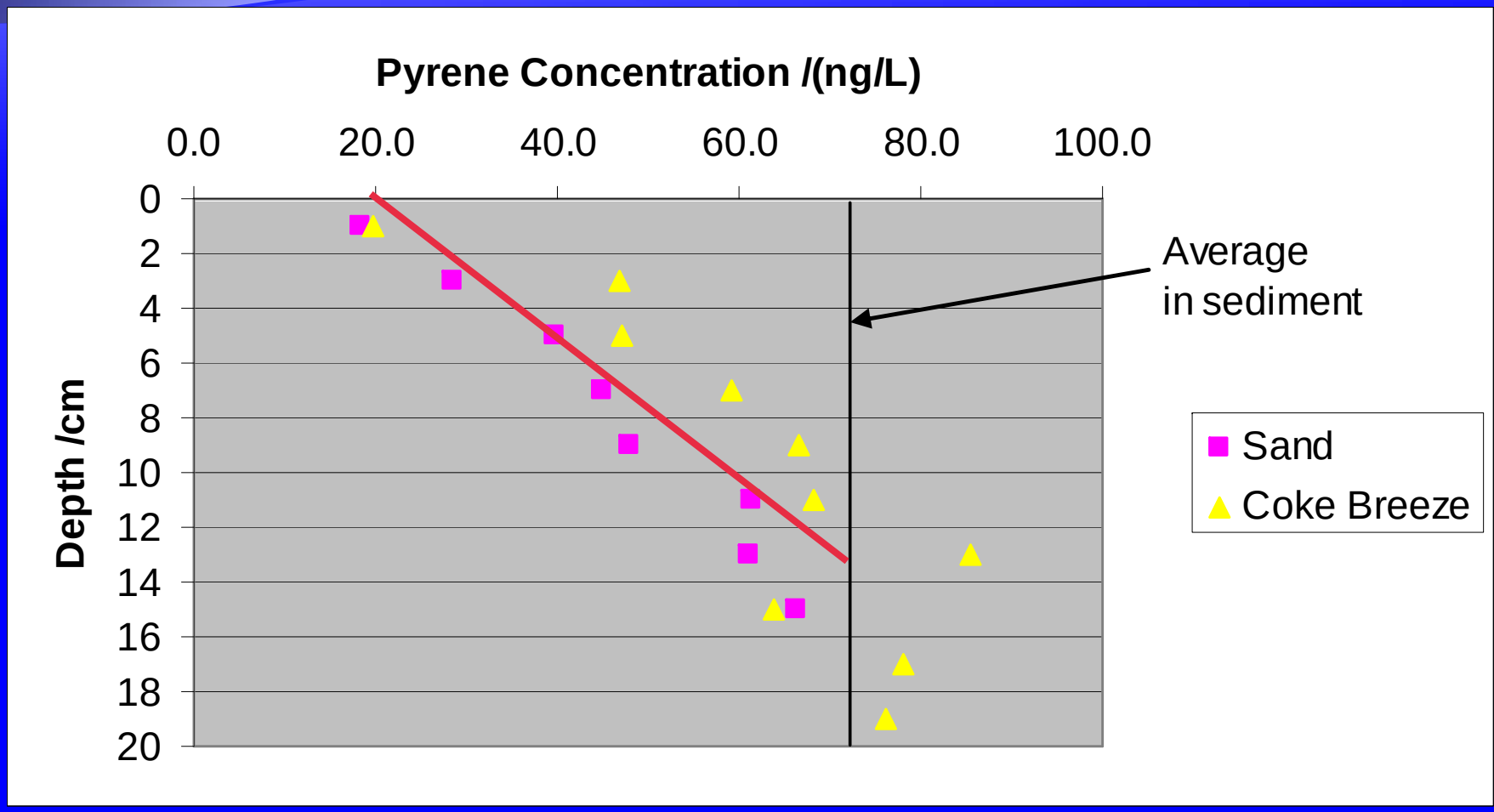


Correlation of Bioaccumulation with Profiling SPME Porewater Concentration



Unit slope is BCF estimated by K_{ow}

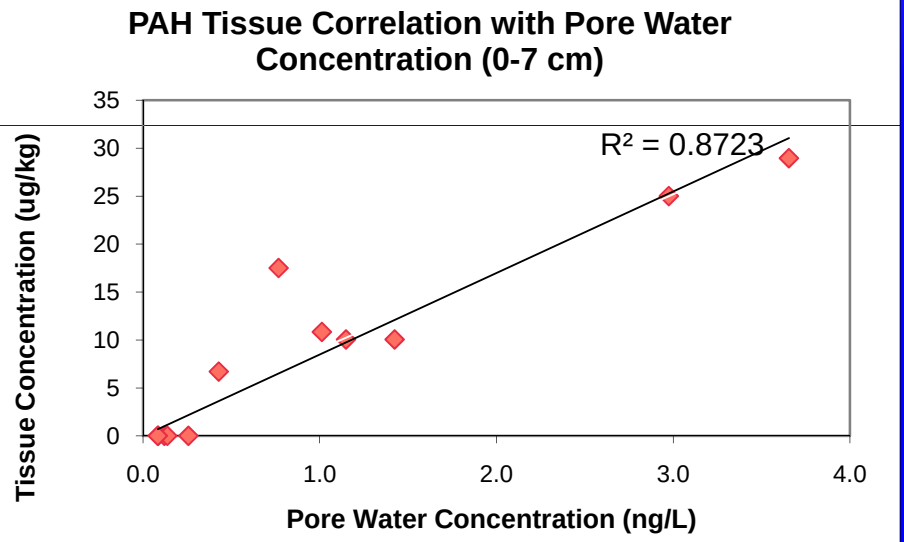
Porewater Concentration Profile Pyrene

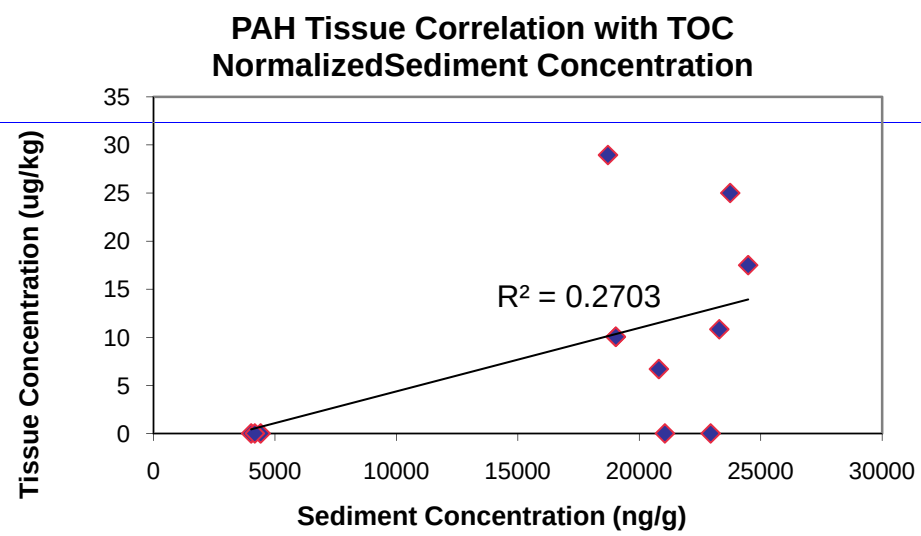


Field Deployment
Benthic Accumulation/Porewater

SPME and Body Burden San Diego Bay

PAHs – B(b)F, B(k)F, BaP in *Muscalista*

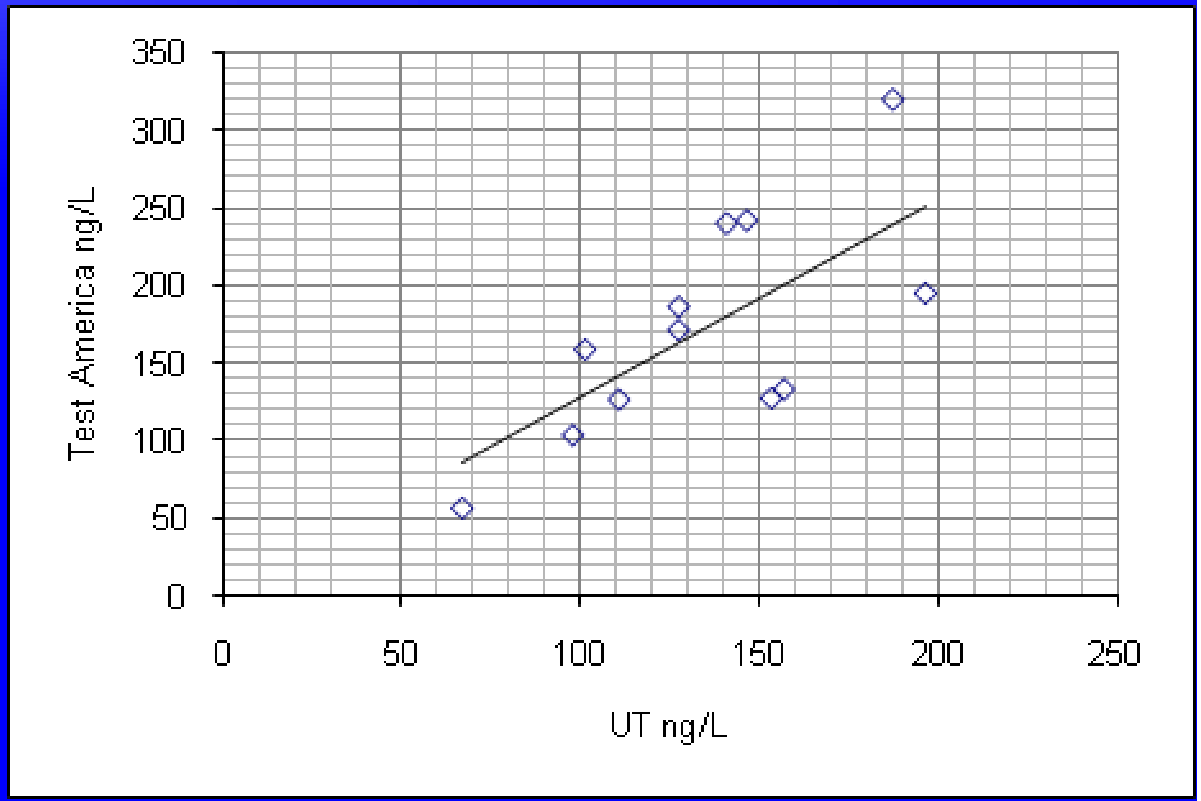




Single correlation with porewater concentrations works well for all three compounds

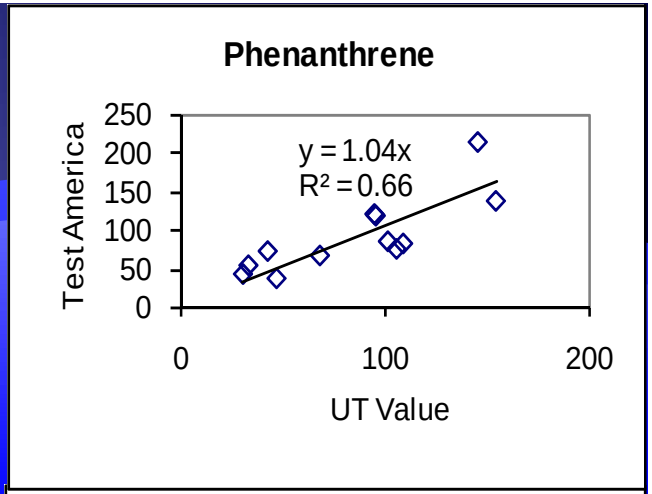
Anacostia River Sampling Field Duplicates

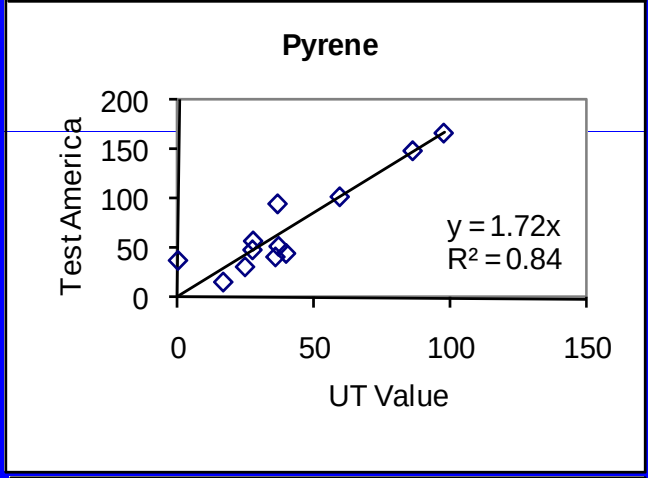
- Total PAHs 28% deviation between Utexas and TestAmerica

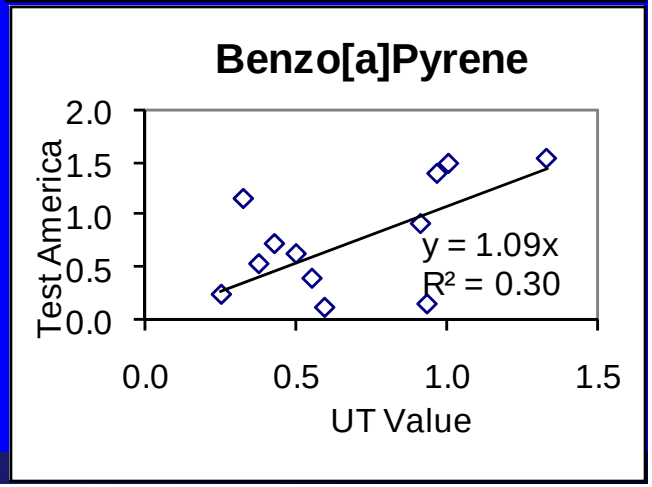


Anacostia River Field Duplicates

- Most of 28% difference associated with pyrene
- Poorest duplicate correlation with low concentration, high molecular weight compounds like BaP
- All concentrations within factor of two







Conclusions

- Direct passive measurement of porewater concentrations provides good indication of potential bioaccumulation of PAHs and PCBs in benthic deposit feeders
- Bulk solid and extracted porewater measurements are not as well correlated with bioaccumulation
- In-situ profiling with SPME provides useful information on contaminant migration rates and mechanisms and can be used, e.g., to evaluate cap performance