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

![Graph showing the relationship between Log $K_f$ and Log $K_{ow}$ for PAHs/PCBs. The line of best fit has a $R^2$ value of 0.879.](image)
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)
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?

\[ BCF = \frac{C_t}{f_{lipid} C_{pw}} \]

- Freshwater oligochaetes
- PAHs and PCBs
- Anacostia River sediments
- \( R^2 = 0.93 \)

In sediments and in deposit-feeding organism (porewater not route of exposure)
Bioconcentration Factor Applicable to Deposit Feeders In-Situ?

\[ BCF = \frac{C_t}{f_{lipid} C_{pw}} \]

Freshwater oligochaetes
PAHs and PCBs
Sequential Dilution sediments
\[ R^2 = 0.92 \]
Bioconcentration Factor Applicable to Deposit Feeders In-Situ?

\[ BCF = \frac{C_t}{f_{lipid}C_{pw}} \]

- Marine polychaetes
- PCBs
- Hunter’s Point sediments
- \( R^2 = 0.81 \)
The bioconcentration factor (BCF) can be expressed as:

$$BCF = \frac{C_t}{f_{lipid} C_{pw}}$$

where $C_t$ is the concentration of the compound in the tissue, $f_{lipid}$ is the partition coefficient for lipid, and $C_{pw}$ is the concentration in the water phase.

Marine and freshwater PAHs and PCBs
$R^2 = 0.845$
Log BCF = 1.07 Log Kow
## Comparison of Porewater Concentrations – Hunter’s Point

<table>
<thead>
<tr>
<th>PCB Congener</th>
<th>SPME (UT) pg/L</th>
<th>POM (EERC) pg/L</th>
<th>PE** (MIT) pg/L</th>
<th>Air Bridge (MIT) pg/L</th>
<th>Extracted Porewater Raw pg/L</th>
<th>Extracted Porewater TOC corr. pg/L***</th>
<th>Predicted Porewater Kd=Kocfoc pg/L</th>
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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/Pensacola, FL
    - In cooperation with Sediment Ecosystem Assessment Protocol SERDP ER-1550
Effectiveness from Bulk Solids?

Percent Sediment and Phen C/C₀ versus Depth

Clean Sand Cap

Cap-sediment Intermixing Zone

Sediment

0% 50% 100% 150% C/C₀ and Percent Passing

0% 15 17 19 21 23 25 27 29 Depth (cm)
Profiling SPME to indicate cap performance

B[a]A Pore Water Concentrations

Pore Water Concentration (ng/L)

Depth (cm)

Overlying Water

- ACS
- 0cm
- 2cm
- 4cm
- 6cm
Correlation of Bioaccumulation with Profiling SPME Porewater Concentration

Unit slope is BCF estimated by $K_{ow}$
Porewater Concentration Profile
Pyrene

Pyrene Concentration /(ng/L)

Depth /cm

- Average in sediment
- Sand
- Coke Breeze
Field Deployment
Benthic Accumulation/Porewater
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.