NEMC 2014

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Implementation of Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers for in situ Performance Evaluation of Remediation Efforts at Contaminated Sediment Sites

Courtney Thomas, David Lampert

& Danny Reible

Research Drivers

SETAC Technical Workshop
"Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments"
November 2012

"Peer-reviewed publications of more case study examples where PSMs have been used in site assessments and management decisions"
(Ghosh et al., 2014)

"Further development of the non-equilibrium PSMs in the field and further validation of PRC use in static sediment environments"
(Ghosh et al., 2014)

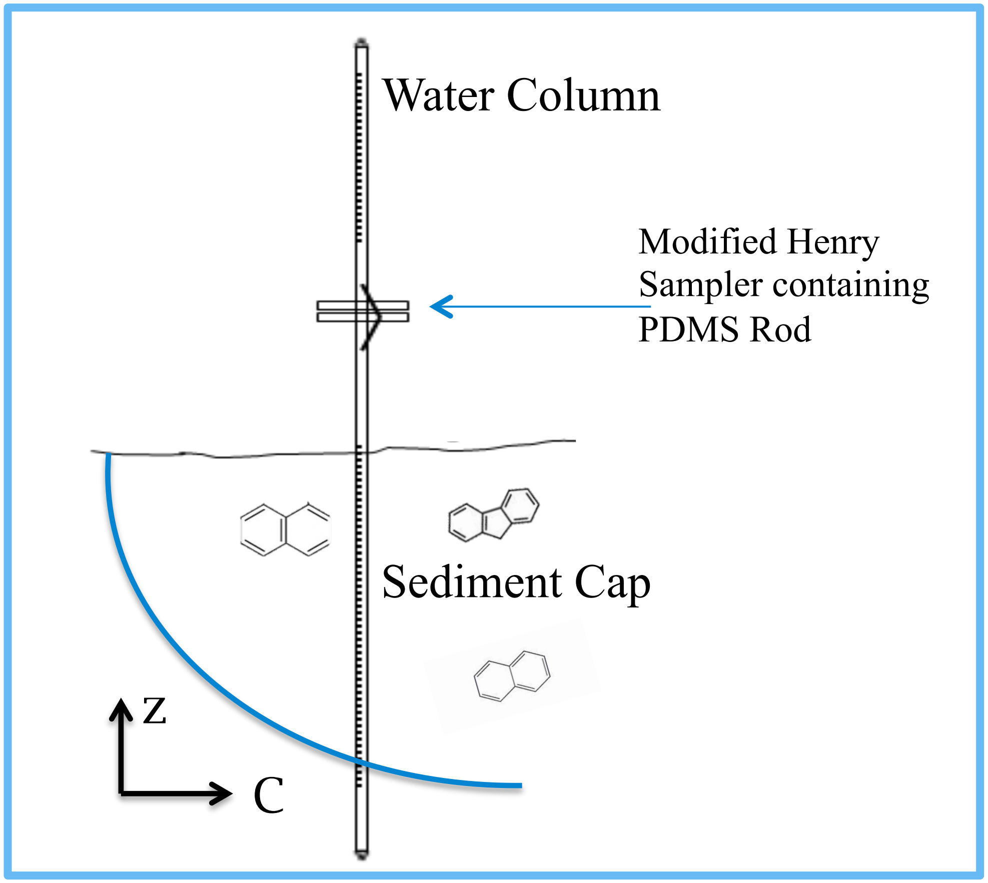
QA/QC strategies to correct for key interferences
(i.e. evaporative loss and DOM)

Routine use in the field as an in-situ technology for evaluating remedial performance

THE BIG PICTURE

Can we accurately quantify C_{free} using PSMs?

And use the information to make assessments concerning remediation goals?



The Importance of C_{free}

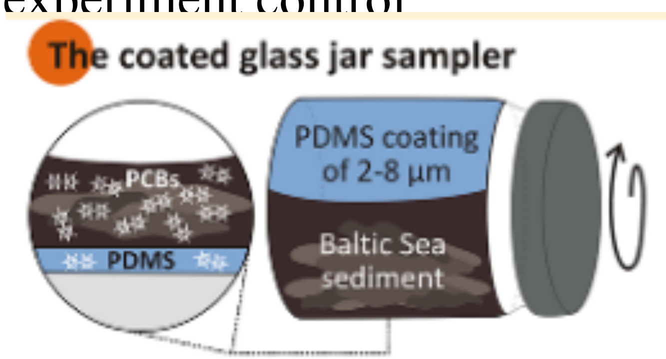
Aqueous concentration of chemicals not bound to particulate matter, colloids, or dissolved organic carbon

- Proportional to chemical activity *(Reichenberg and Mayer, 2009)*
- Better indicator of potential risk
- Direct assessor of:
  - **fate & transport** of contaminants between sediment porewater and surface water
  - **bioavailability & toxicity** of contaminants to benthic organisms *(Lu et al., 2011)*
- Sediment Quality Guidelines (SQGs) derived using Equilibrium Partitioning (EqP) Theory **estimate** C_{free} from C_{total} (bulk solids) and assumed partitioning to water (K_{d}) *(Mayer et al., 2014)*
  - Misrepresentation of risk
  - **Passive sampling methods accurately determine** $\mathbf{C_{free}}$

Passive Sampling Methods

Ex-situ

- Best to understand C↓free equilibrium condition
  - Partitioning
  - Toxicity
  - Bioaccumulation
- Reproducibility & typical experiment control

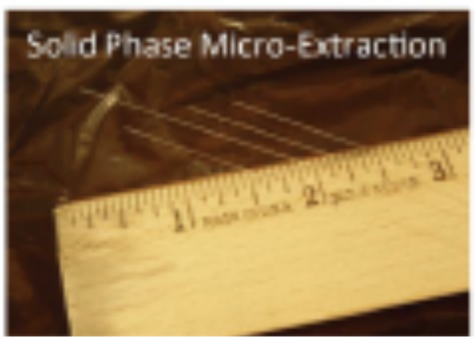


In-situ

- Best to understand C↓free field condition
  - Groundwater intrusion
  - Currents
  - Gradients & flux
  - Bioturbation

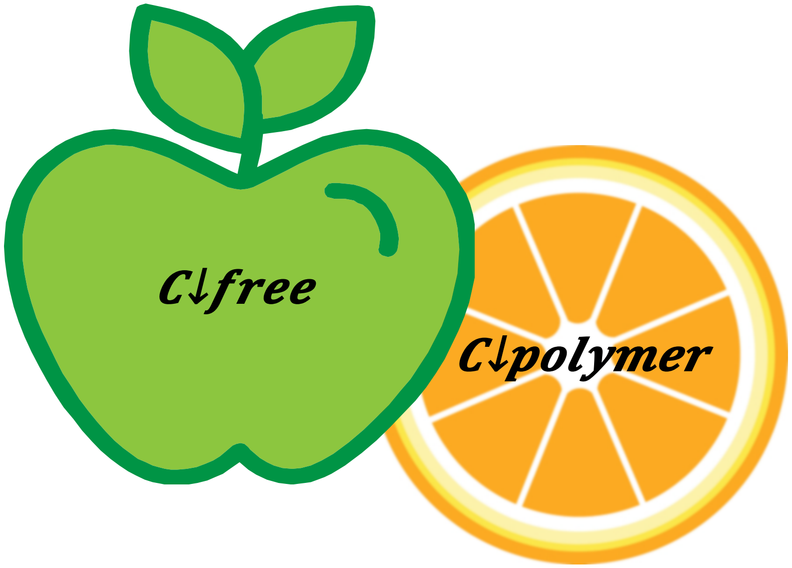
Sources:
Jahnke et al., 2012
Huckins et al., 2002
Reible and Lotufo, 2012
Gschwend et al., 2012
Oen et al., 2011

Common Passive Sampling Materials for HOCs



Images from USEPA, 2012

- Polyethylene (PE)
  - Thin rectangular sheets- High volume, good surface area to volume ratio, moderate internal diffusion rates, marginal in situ feasibility
- Polyoxymethylene (POM)
  - Molded thermoplastic- High volume, fair surface area to volume ratio, slow internal diffusion rates, marginal in situ feasibility
- Polydimethylsiloxane (PDMS)
  - Thin coating on glass fibers- Moderate volume, good surface area to volume ratio, high internal diffusion rates, good in situ feasibility
  - Hydrophobic surface after crosslinked and polymerized
  - Potential to absorb hydrophobic contaminants



At equilibrium: $C_{free} = C_{polymer} / K_{pw}$

Non−equilibrium: $C_{free} = C_{polymer} / f_{ss} K_{pw}$

Modeling Contaminant Uptake: Governing Equations

Transport within the PSM *(DRM & IRM)*

$$\partial C_{PSD}/\partial t = D_{PSD}\,\partial^2 C_{PSD}/\partial x^2$$

Transport to the PSM from the sediment *(DRM & ERM)*

$$R\,\partial C/\partial t = D\,\partial^2 C/\partial x^2$$

Internal Resistance Model *(Huckins et al., 2006)*

- transport to PSM from sediment is ignored: $\boldsymbol{C_{PSD}(x=L)=K_{PSD}\,C}$
- Exact solution from analogous heat transport problem (*Carslaw and Jaeger, 1959)*
- For t > $t_{internal} \approx 0.848L^2/D_{PSD}$, transport resistance **externally** dominated
- **PSM sorbent thicknesses have decreased causing mass transport resistances to be controlled external to the PSM**

Dual Resistance Model *(Fernandez et al., 2009)*

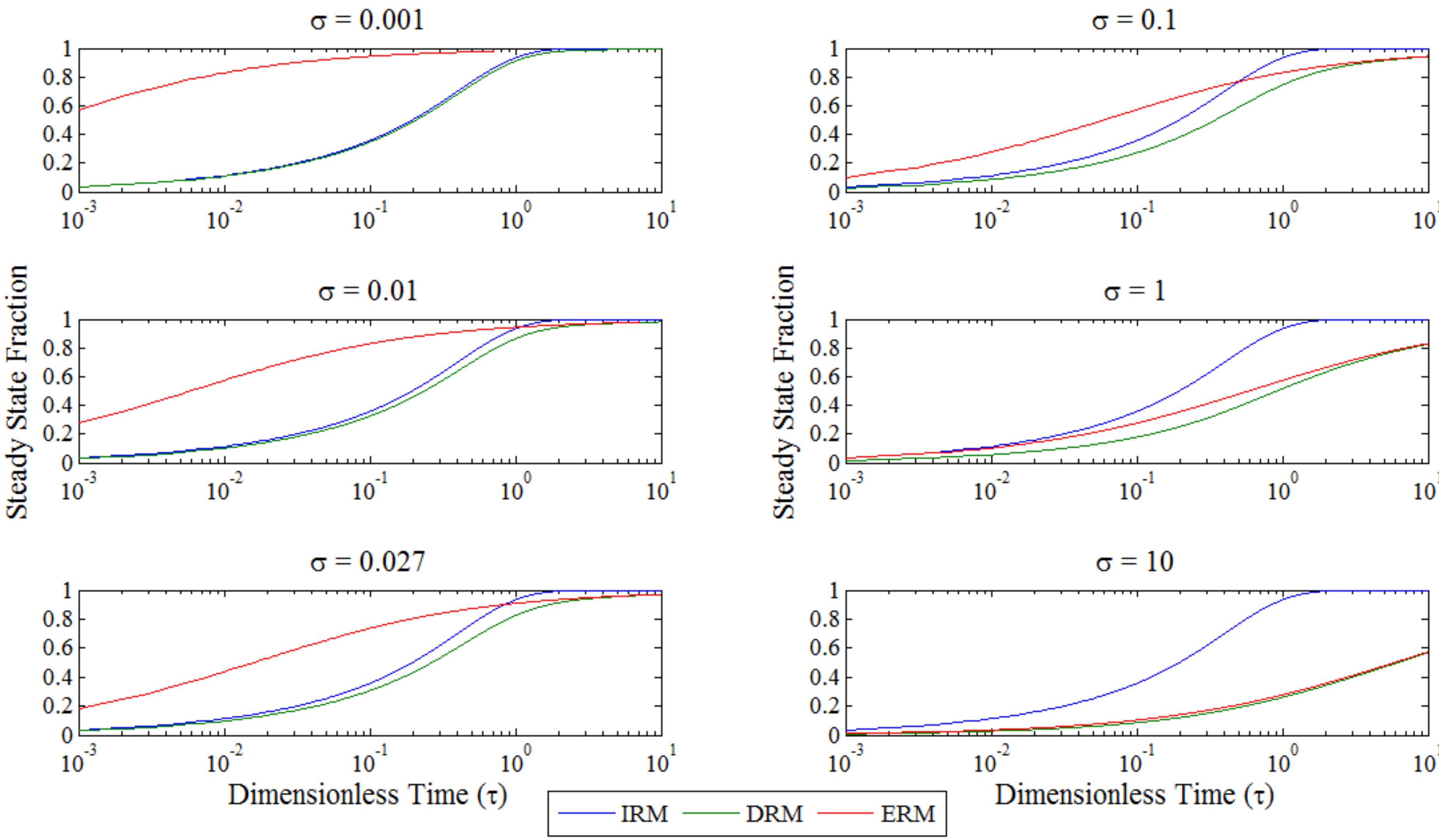
- Diffusion-based internal & external transport
- Semi-exact solution using numerical inversion of the LaPlace transform
- **Bulky & often can be simplified**

External Resistance Model *(Lampert et al., in review)*

- Exact solution from analogous heat transport problem (*Carslaw and Jaeger, 1959)*
- **Single unknown parameter RD which is a function of the transport and sorption-related retardation in the surrounding porous media**

Relative Importance of Internal & External Transport

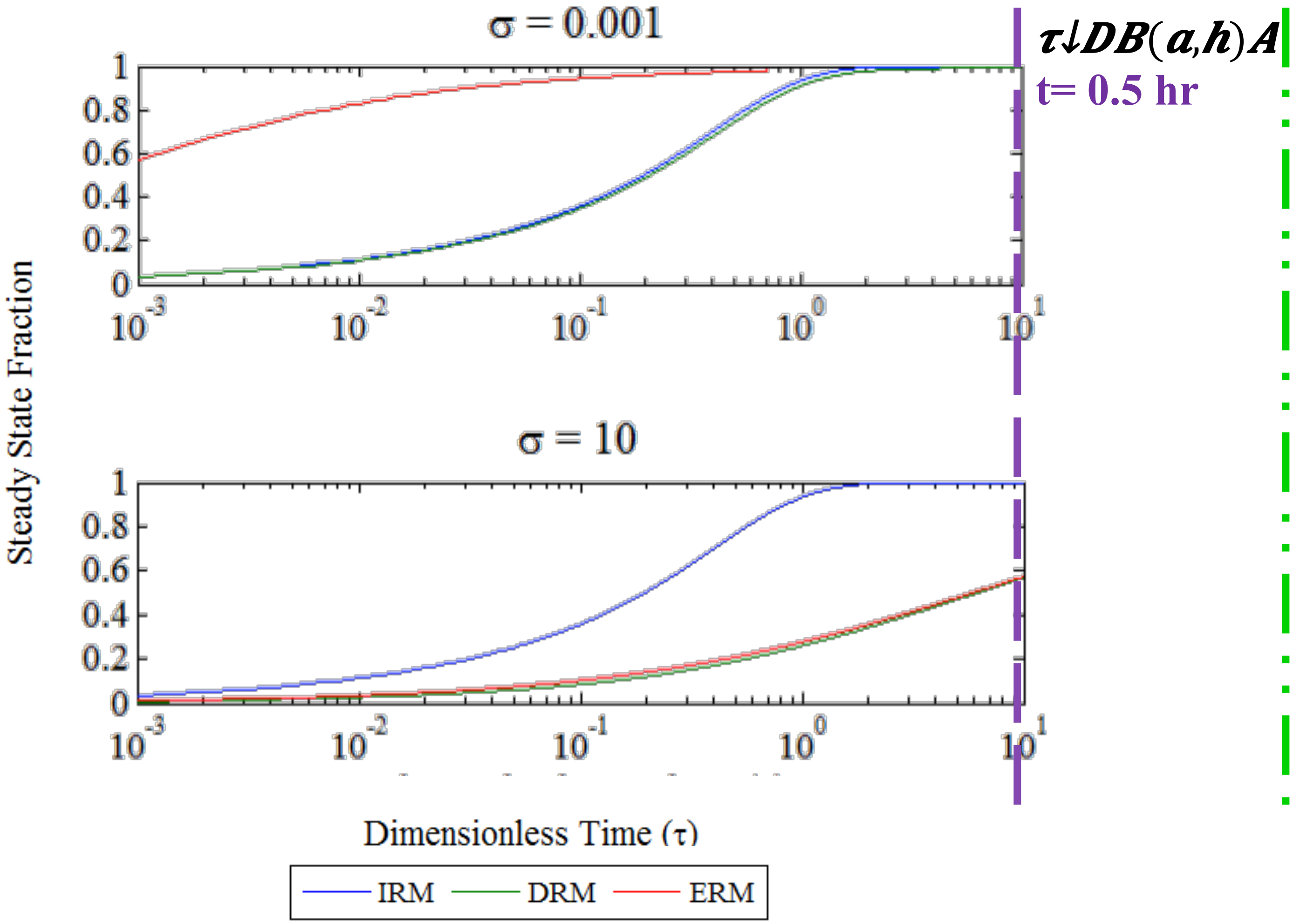
$$t_{external}/t_{internal} = 36.1 K^{2}{}_{PSD}$$



$t_{external}/t_{internal} = 36.1 K^{2}_{PSD} D_{PSD}/RD = 36.1\sigma$

for 30 µm PDMS layer

	-log	τ =		
		t = 0.5 hour	t = 1 day	t = 7 days
NAP	9.95	225	11000	75400
DB(a,h)A	11.35	9	430	3000



Off the plot!

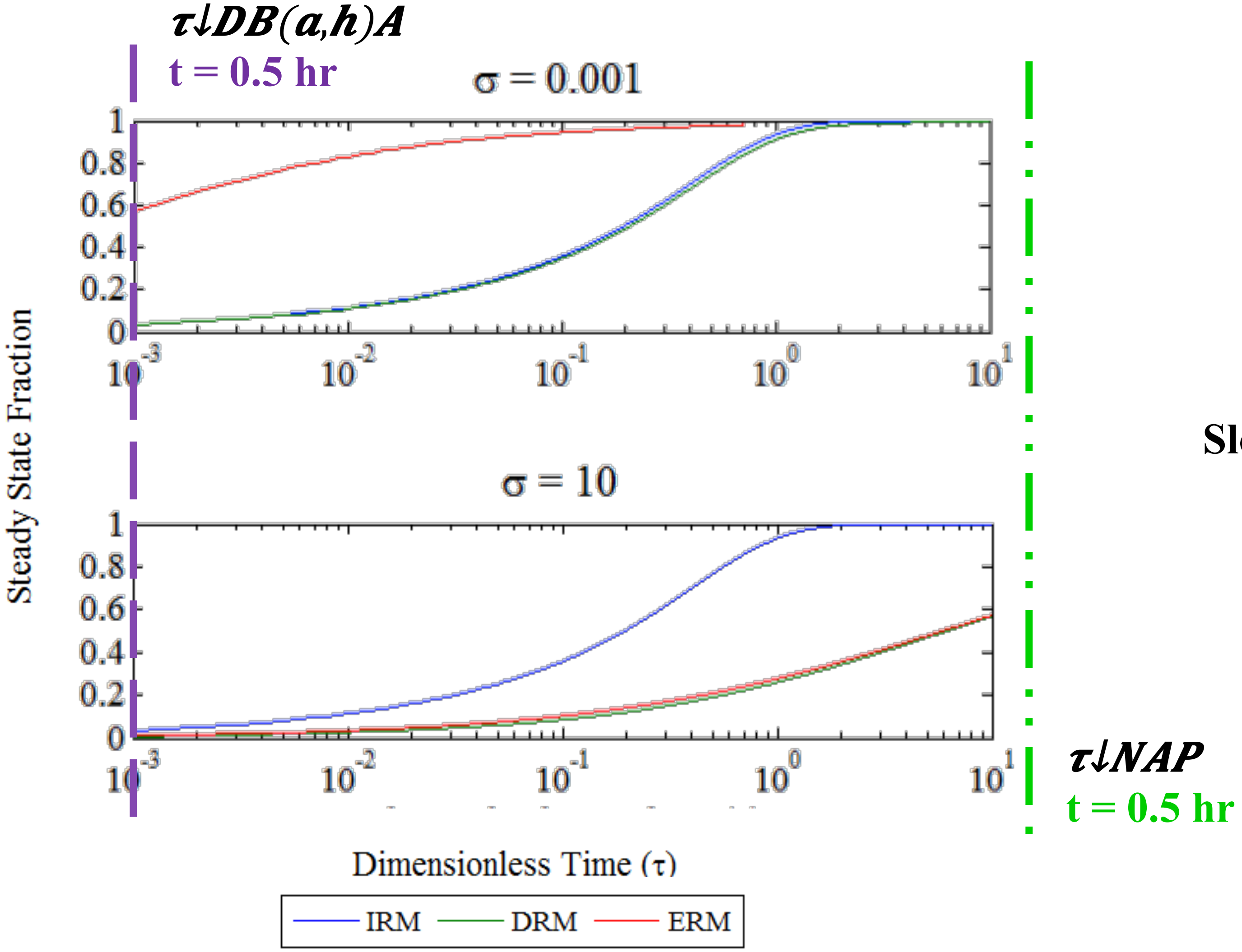
DRM & ERM are converged @ t = 0.5 hr!

τ_{NAP}

t = 0.5 hr

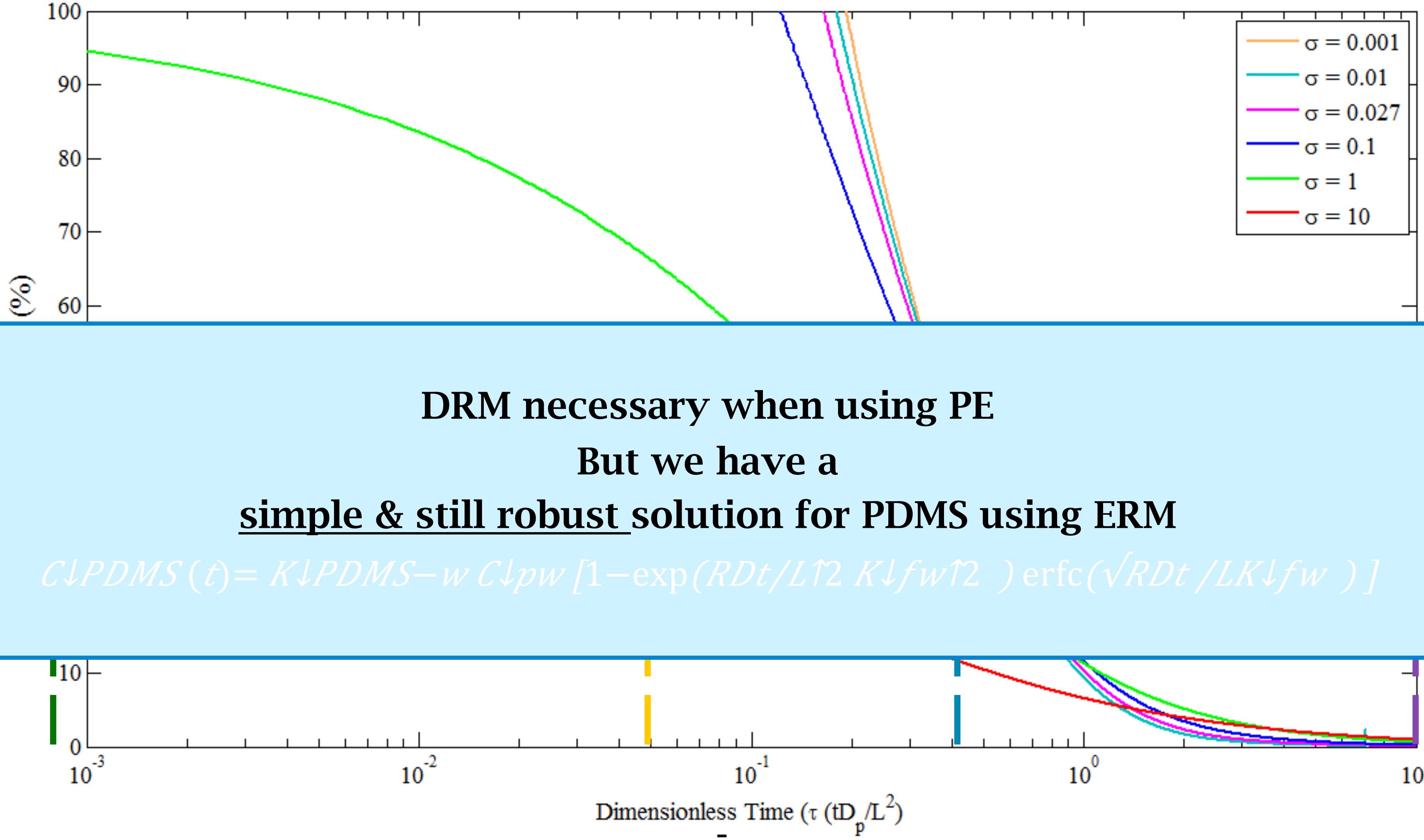
for 30 µm PE sheet

		τ =		
	-log	t = 0.5 hour	t = 1 day	t = 7 days
NAP	11.76	3.5	170	1170
DB(a,h)A	15.5	0.001	0.03	0.2



Slower kinetics

% error when neglecting internal mass resistance



DRM necessary when using PE

But we have a

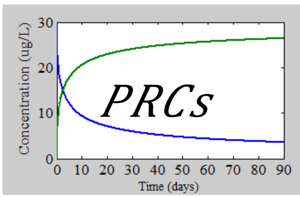
<u>simple & still robust </u>solution for PDMS using ERM

$$C_{PDMS}(t) = K_{PDMS-w}\, C_{pw}\left[1-\exp\left(\frac{RDt}{L^2 K_{fw}^2}\right)\mathrm{erfc}\left(\frac{\sqrt{RDt}}{LK_{fw}}\right)\right]$$

Modeling Contaminant Uptake

$C_{1060/1000\ \mu m}$ v $C_{230/210\ \mu m}$

$C_{t=7\ days}$ v $C_{t=30\ days}$



RD $= \beta K_{ow}^{a}$

Internal Resistance Model
Dual Resistance Model
External Resistance Model

$$f_{ss} = \left[1 - \exp\left(\frac{\mathbf{RD}t}{L^2 K_{fw}^2}\right) \operatorname{erfc}\left(\frac{\sqrt{\mathbf{RD}t}}{L K_{fw}}\right)\right]$$

Absolute Porewater Concentrations

$$C_{free} = \frac{C_{PSM}}{K_{fw} f_{ss}}$$

Comparable to Environmental Criteria

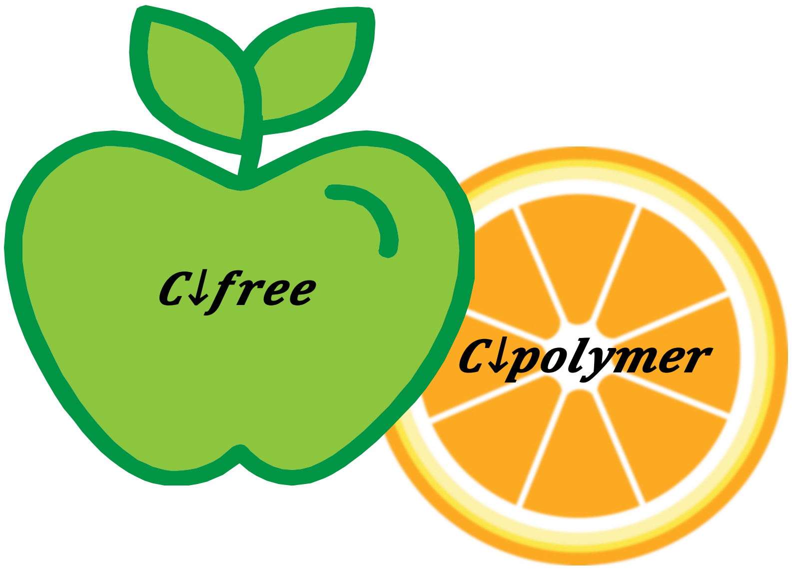
Magnitude of Diffusive Flux

$$R \frac{\partial C_{pw}}{\partial t} = D \frac{\partial^2 C_{pw}}{\partial z^2}$$

$$J = -\frac{\mathbf{RD}}{\rho_b f_{oc} K_{oc}} \frac{dC}{dz}$$

Or for highly hydrophobic contaminants,

$$J = -\mathbf{RD}/\rho_b f_{oc}$$



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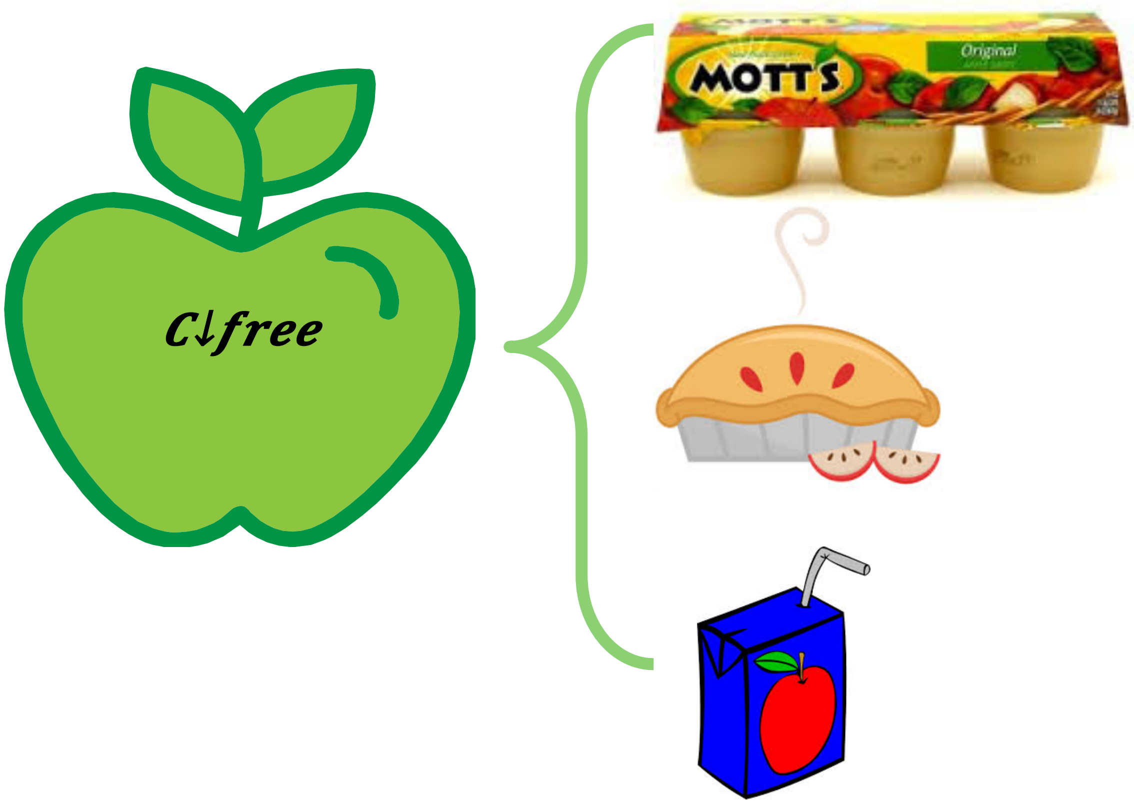


Remediation Evaluation

Vertical Profiles, Comparison with WQC, Comparison with Surface Water

Fate & Transport

Chemical Activity

Migration Potential, Flux

Toxicity & Bioaccumulation

Passive Sampling for Performance Assessment

- Provides measure of the reduction of availability and transport in in-situ treatments and sediment caps
- Potentially provides indication of migration deep within cap
- Moves away from typical performance evaluations based upon implementation metrics and physical characteristics not focused on exposure and risk
- Overcomes problems of bulk solid measurement
  - Conventional sand caps do not sorb contaminants
  - Caps (or in-situ treatments) work by sorbing contaminants and reducing availability
  - In either case, **bulk solids largely <u>irrelevant</u>**

Demonstration of *in situ* SPME PDMS methods for monitoring remediation efforts

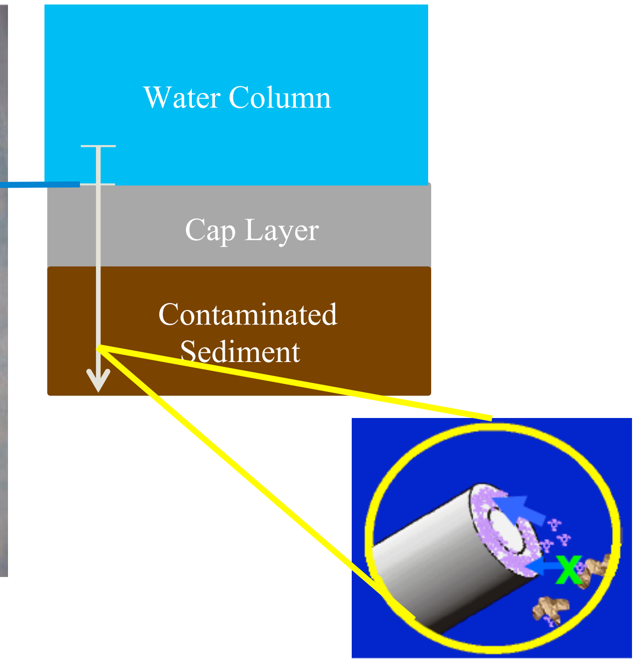
<u>Materials & Methods</u>

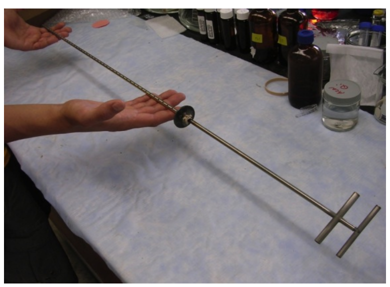
- Modified Henry Sampler

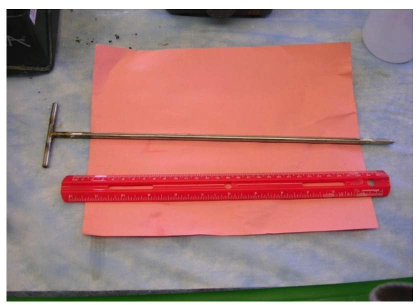
- PDMS sorbent fiber

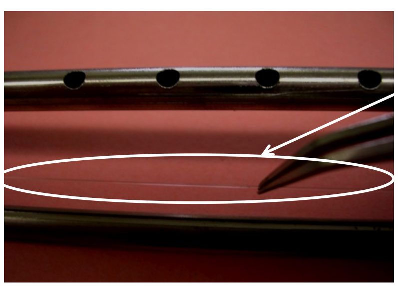
  Selective for non-polar compounds

  ≤ ng/L detection with 1 cm resolution









10 µm PDMS
210 µm core

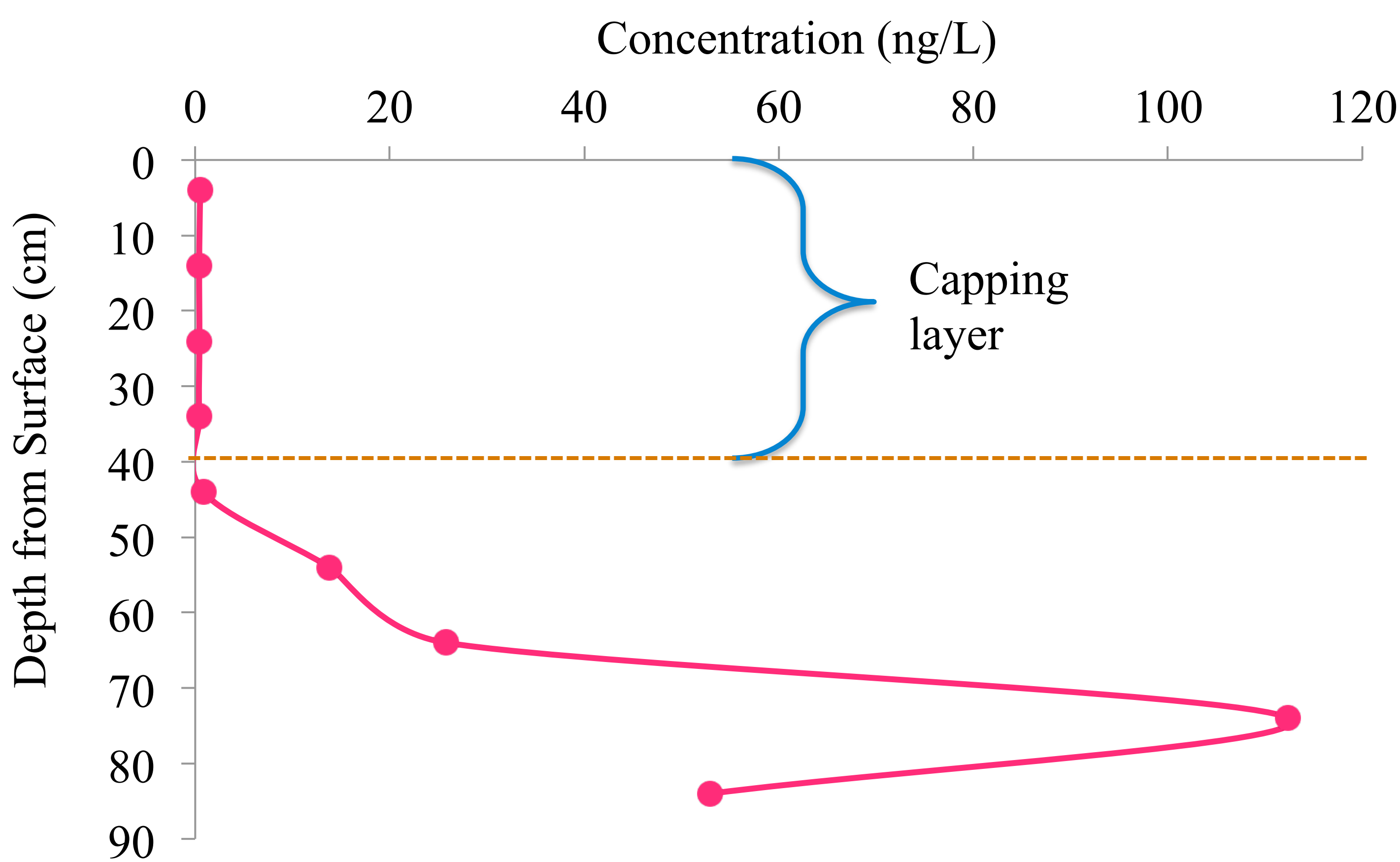
West Branch Grand Calumet River & Roxana Marsh

- COCs: PAHs, PCBs, pesticides & metals
- Remediation Activities: Sediment removal (~235,000 cu. yds in WBGCR and ~150,000 cu. yds in Roxana Marsh) & capping with sand/gravel
- Monitoring Activities: SPME porewater/surface water sampling & sediment cores (EPA)

"…appears picturesque, but the river sediment is highly contaminated." (USEPA, 2009)

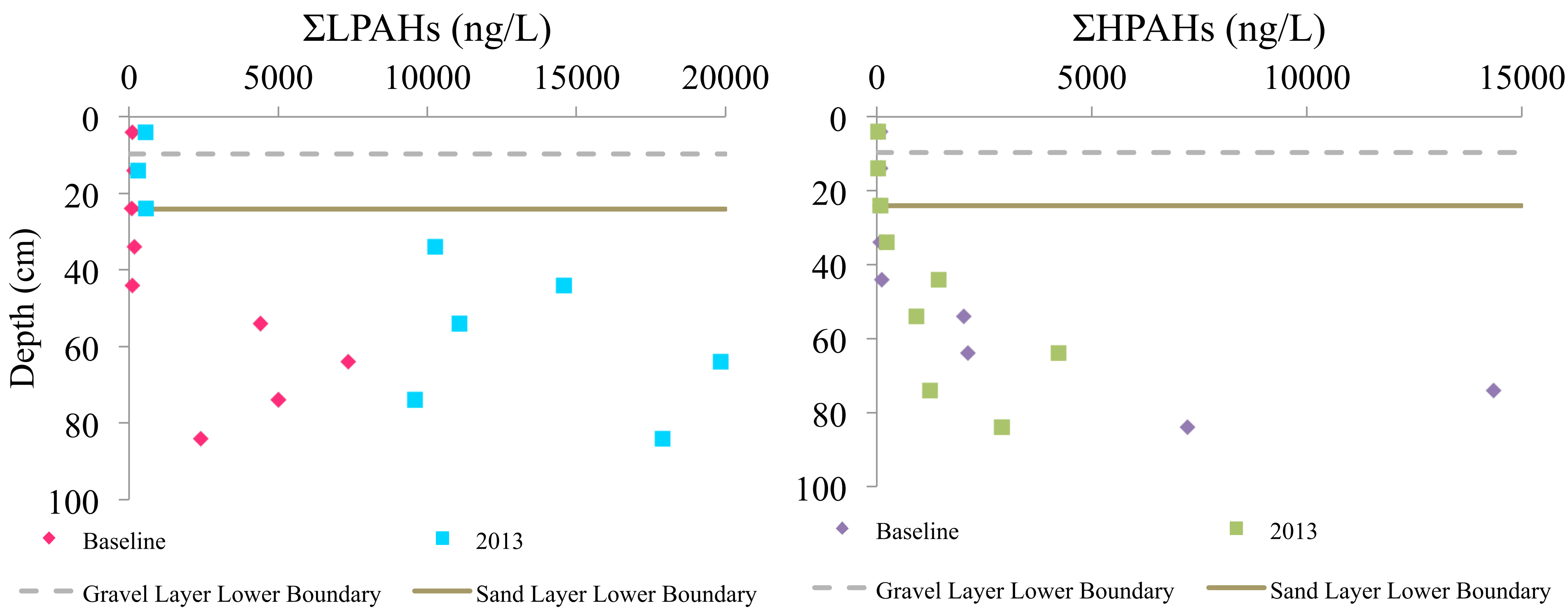
Expected Profiles

Clean cap layer (low concentrations), sharp increase in concentration below the cap layer



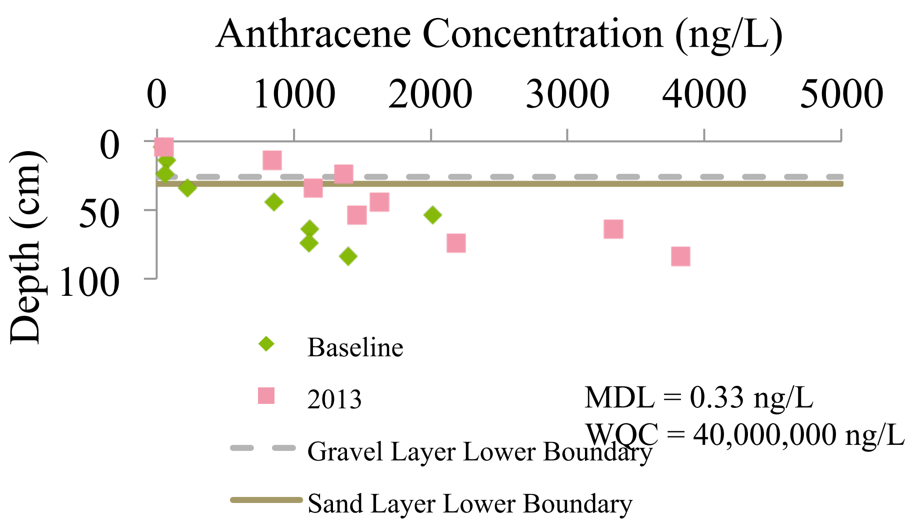
“Snapshot in time”

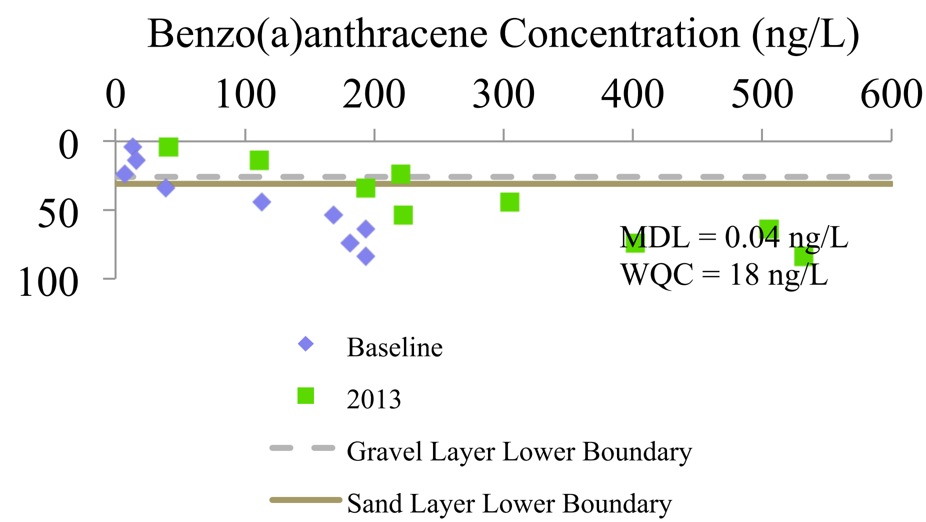
Loc 9: Defined Cap Layer

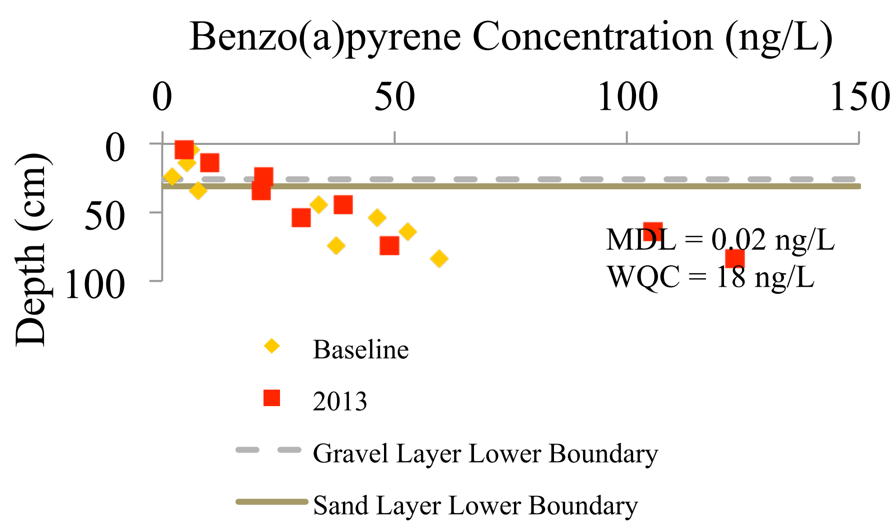


Cap Boundary Measurements provided by USEPA

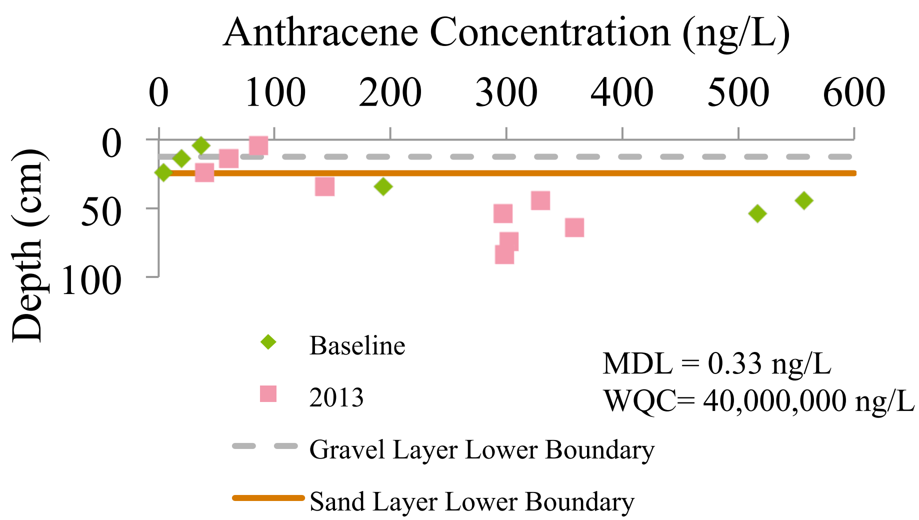
Loc 13: Highest Observed Concentration Levels (NAPL Present)

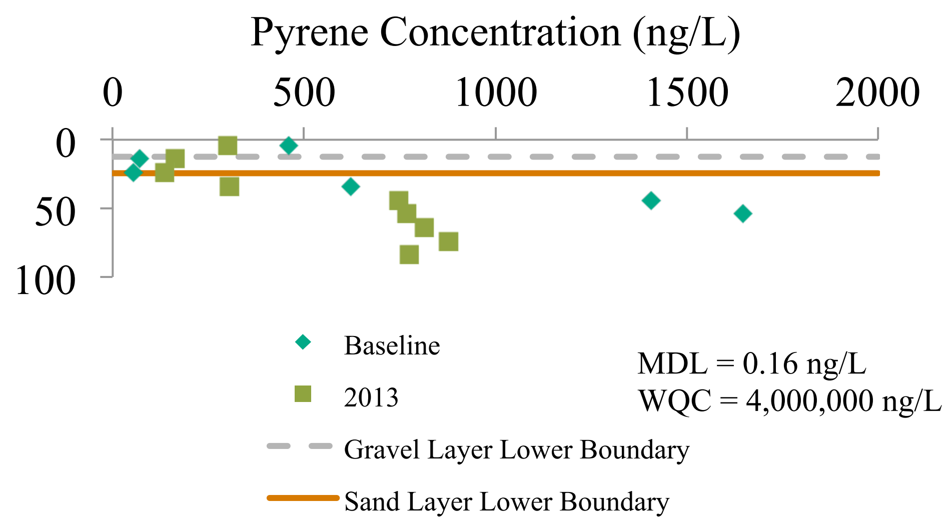


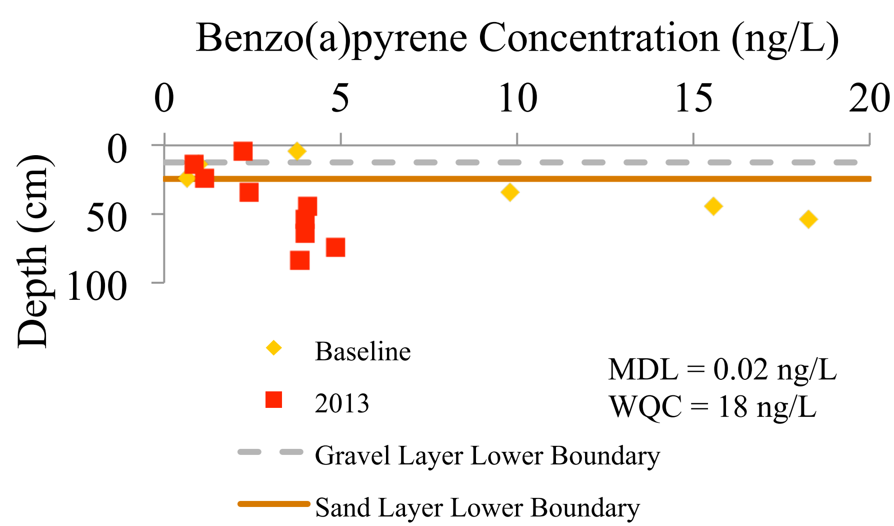




Loc 19: Surface Recontamination

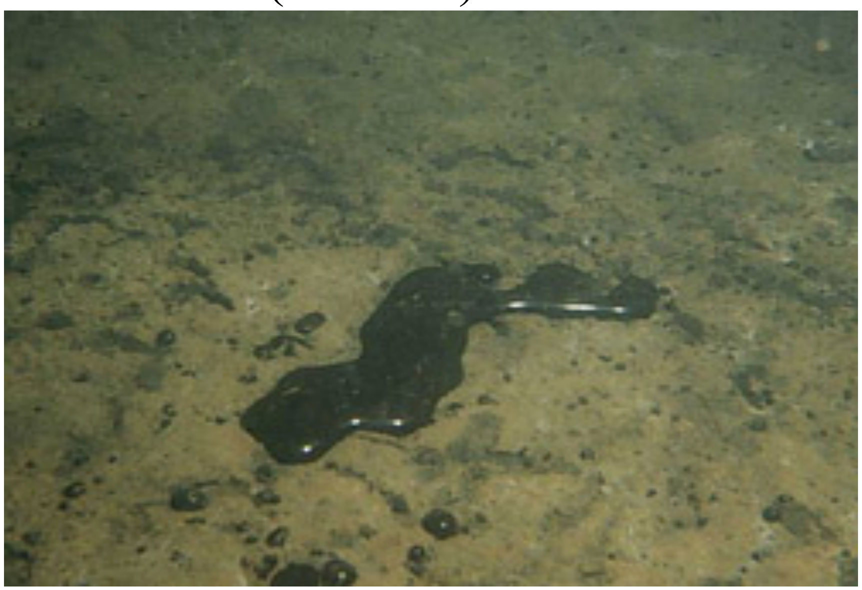






Wyckoff/Eagle Harbor

- COCs: PAHs, PCP, organics, creosote, and heavy metals
- Remediation Activities: Capping and source control
- Monitoring Activities (2011): SPME porewater sampling and grab samples/ cores (USACE)



Creosote pool

Wood treatment facility off of Bainbridge Island

The effective organic carbon partition coefficient

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

- "Measured" Koc ~ 2x estimated Koc using literature values (Baker et. al, 2007)
- Deviation between measured and bulk-solid predictions of porewater concentrations are consistent with aged contaminants and strongly solid-associated contaminants.

- Primary advantages of directly measuring porewater concentrations with SPME
  - No assumption of 100% availability
  - No dependence of theoretical estimate of Koc

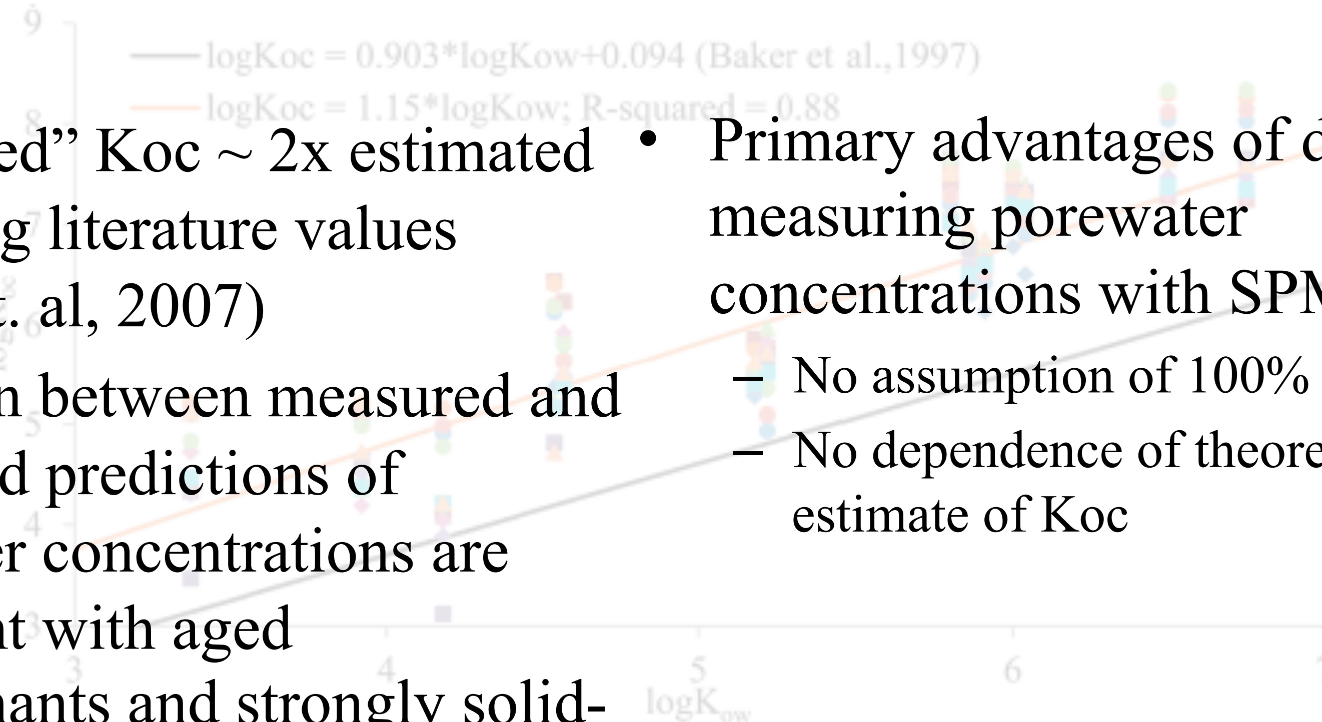


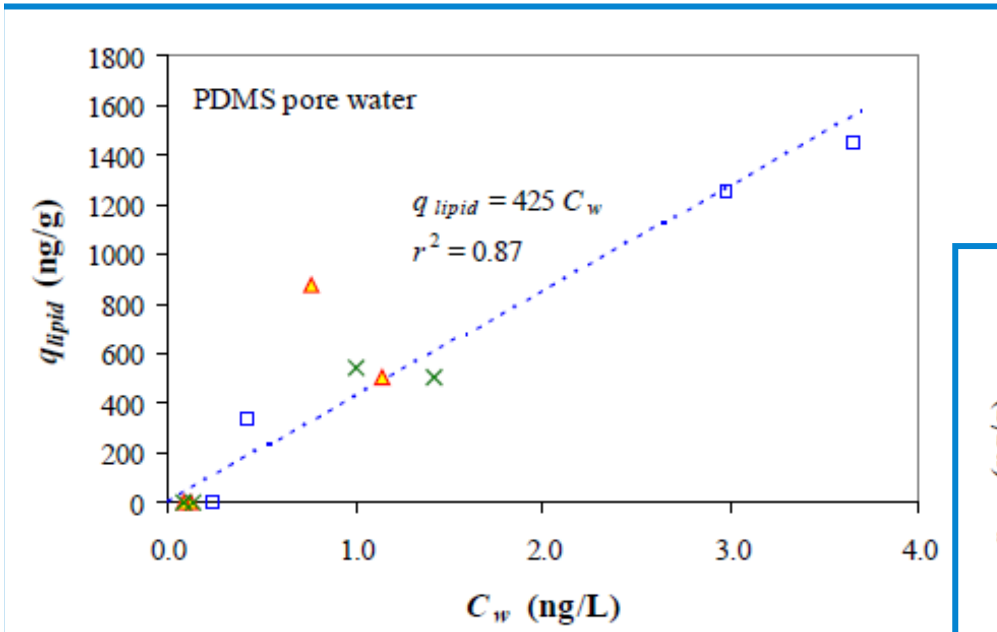
Fig. 3 log K_{oc} – log K_{ow} relationship determined from the upper 10 cm of twelve sampling locations at Eagle Harbor where grab samples and SPME samples overlapped. The orange solid line represents the best fit relationship of the field data (slope = 1.15, r^2 = 0.88). The black solid line represents the relationship determined by Baker *et al.*[28] between log K_{oc} and log K_{ow}.

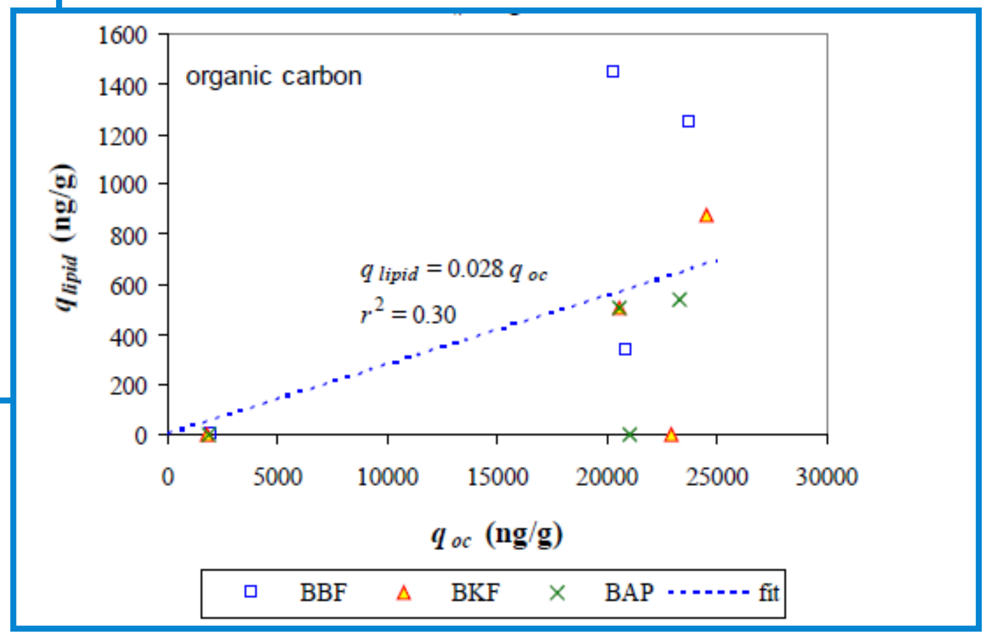
Thomas et al., 2014

Lampert, 2010

Assessing PAH Bioavailability

21-day bioaccumulation experiment using bivalve mytilida *Musculista senhousia* and 210/230 µm PDMS fiber





Bulk solids (even carbon normalized)- a weaker indicator of bioaccumulation potential than porewater concentrations

Key Points about SPME PDMS Profiling

- Porewater concentration
  - More sensitive indicator of migration in caps than bulk sediment concentration
    - Sensitive indicator of in-situ mixing processes
  - Can also indicate performance of in-situ treatment
  - Correlates with contaminant availability and bioaccumulation
- Polymer sorbents
  - Effective measures of in-situ porewater concentrations
    - No assumptions of K_{oc} or 100% availability
  - Note- detection limits and time to equilibrium strong function of hydrophobicity
    - Tracks bioaccumulation
      - dominated by more highly hydrophobic compounds
    - May not track narcosis
      - dominated by lower hydrophobicity compounds

Thank you, USACE & USEPA

Especially, Paul Schroeder, Karl Gustavson, Marc Mills, Amy Mucha, and Heather Williams

Any Questions?

US Army Corps of Engineers ®

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

THE UNIVERSITY OF TEXAS AT AUSTIN

TEXAS TECH UNIVERSITY

Thank you for your attention!

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