Combining Mass Balance Modeling with Passive Sampling at Contaminated Sediment Sites to Evaluate PCB Sources and Food Web Exposures

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Background: Some "clean ups" don't work based on food web! e.g., DDT

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Background: Sediments not always biggest source! ...

...for completed dredging projects...  
...often greater than the cleanup levels  
(Bridges et al., 2008)

Other source(s) can lead to re-contamination.  
e.g. point sources 10/20, runoff 8/20, residual sediment 8/20; other 3/20  
(Nadeau & Skaggs 2006)

Large $700 million  
likewise for Lower Duwamish Waterway, ROD (2014):  
"Total estimated net present value costs for the Selected Remedy are $342 million..."  
www.epa.gov/region10/duwamish.html

Approach: Start "Simple"

Objectives

i. Mass Balance Model (MBM)  
   => do MBM estimated conc's match measures?

ii. Passive Sampler methods to ID hypothesized sources  
   and "drive" the Mass Balance Model

iii. Integrate with Food Web Model (FWM)  
   using MBM description of exposure field,  
   is FWM biouptake consistent with measured body burdens?
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Bkgd: know mobility & tox “freely dissolved conc’s”

need water column AND porewater conc’s

Hawthorne et al. (2007)

focKoc + focKbcCn

water

(Accardi-Dey)

PE

target

PRC

concentration

sediment porous medium

DPE DSED DSED

Bkgd: use PE to get conc’s

at time = 0 with PRCs

at later time

use loss of PRCs to calculate fractional approaches to equilibration (function of site & compound)

use that result, to extrapolate target uptake to $C_{pe(\infty)}$

$\Rightarrow C_{water} = \frac{C_{pe(\infty)}}{K_{pewater}}$

Bkgd: PE Methods

Gschwend et al. 2012

Choose $(M_{pe}/V_{water})K_{pe-water} > 20$

CH₂Cl₂ CH₃OH   H₂O

Mount in frame and deploy from boat

LDPE cleaned    loaded w/ stds

GCMS extracted recovered

e.g., 10 cm wide by 50 cm long by 25 um thick

Can deploy via divers, but also from vessels

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Deployment all depths ~45 min

recovery system from boat

Bill Jaworski PE sheets 10 cm wide by 60 cm long by 25 um thick

Bkgd: Use PRCs to Find $C_{pe(\infty)}$ (lab tests)

(Apell and Gschwend 2014)

PCB #101

PCB Concentration (mg/PE)

#101 buildup in PE

time (days)

PRC decline in PE

$\frac{C_{pe}}{K_{pe-water}} = C_{pewater}$


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### Accuracy and Precision in situ in the LDW (Apell)

- \( \frac{C_{\text{sediment}}}{f_{\text{BC}}K_{\text{OC}}} \)

- \( n=522 \)

### Field Approach: Start "Simple"
- Air/Water Exchange
- CSO, Storm Drains
- Diffusion from Sediments
- Exfiltration

### LDW sampling summer-fall 2014
- 20 samplers over 4.5 miles
- left ~2 mos.

### Porewater profiles
- at Site 8

### LDW sampling (Apell et al.)

- \( \sum \) "NOAA 18" x 2 = 1.4 ng/L

### Results => bed-water gradients
- see some "hotspots" factor of 2
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**Results: Boundary Layer with ADCP (Prendergast)**

- If \( \text{Flux} = - D_{\text{water}} \frac{(C_{\text{porewater}} - C_{\text{bottom water}})}{\delta_{\text{boundary layer}}} \)
- downward-facing ADCP deployed on river bottom
- Eight locations 15 minute intervals

**Estim' Diffusive Fluxes**

Assume 100 \( \mu m \) \( \delta_{bd} \): fluxes in ng/m²/day

\[ \sum \text{fluxes out of bed } \approx 0.2 \text{ g/day} \]

**MBM modeling with EFDC (Adams and Prendergast)**

Elliott Bay September – Spring Tide – Low Tide Duwamish River

1. Average porewater-bottom water gradient was 400 pg \( \Sigma \text{PCBs/L} \) (N=19)
   - Assuming water-side controlled diffusive exchange \( (D_{\text{water}} = 4E-6 \text{ cm²/s}) \)
   - With a boundary layer thickness 0.01 cm
   - Computed flux: 1.5E-16 g \( \Sigma \text{PCBs} / \text{cm²/s} \)
2. LDW bottom area (8000 m \( \times \) 200 m) about 1.6E10 cm²
   - So total flux from the bed sediments about 0.2 g/day
3. Implies accumulate about 0.8 g \( \Sigma \text{PCBs} \) at steady state in LDW

**Putting in all together**

- Prendergast, Apell, et al.

1. The EFDC suggests a hydraulic residence time of about ~4 days in LDW estuary
2. Implies accumulate about 0.8 g \( \Sigma \text{PCBs} \) at steady state in LDW
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Putting in all together
1. total flux from the bed sediments about 0.2 g/day
2. the EFDC suggests a hydraulic residence time of about ~4 days in LDW estuary
3. fluxes => accumulate about 0.8 g \( \sum \text{PCBs} \) at steady state in LDW
4. using PE samplers in LDW water, "NOAA Status and Trend 18 PCBs" x 2
   = about 1.2 ng/L
   LDW volume is about \( 1.6 \times 10^{10} \) L, so total PCB load in water is about 20 g \( \sum \text{PCBs} \)
5. with 4-day residence time, implies have input of PCBs 5 g/day!
   Sediment diffusive fluxes ~20-30 times less!

Technical Approach: Add Upstream

Upstream Source?

Option: Bed-Water Fluxes Inc’ Due to Bio-irrigation

Option: Bioturbation Enhanced what would water-column look like?
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Option: Resuspension & Desorption?

Option: Local Resuspension Source

- High Tide
  - Bed => Water Input at only RM 3.5 adding 4 g/d Throughout Water Column

- Low Tide => not too bad

Option: Outfall Sources

- High Tide
  - Bed => Water Input at Surface near RM 3.5 adding 4 g/d

- Low Tide => need surface water data

Exposures => Food Web Model

FWM: Thiessen polygons
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**Summary**

1. PE passive samplers => water and porewater concentrations (at sub parts per trillion levels! averaged over weeks)

2. Mass balance modeling integrates water data, "points" to most important sources (guide remediation) provides "exposure field" in space and time

3. Food web modeling should translate the exposure field to quantify risks (decisions)

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