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

Philip Gschwend & Eric Adams, MIT
Mandy Michalsen, ACoE, and
Katherine von Stackelberg, NEK Assoc & HSPH
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Bkgd: some "clean ups" don't work based on food web!

e.g., DDT

=> missed sources?
Bkgd: Sediments not always biggest source!

...for completed dredging projects...
post-dredging residual levels ...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)
Bkgd: Large $$$$$$$

e.g., PCB clean up in the Hudson River

cost ~$700 million

likewise for Lower Duwamish Waterway, ROD (2014):
"Total estimated net present value costs for the
Selected Remedy are $342 million..."
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?
Approach: Start "Simple"

- **Flushing**
  - $C_{PCB}^{\text{Measured}} = C_{PCB}^{\text{Modeled}}$

- **Diffusion from Sediments**

- **Exfiltration**

- **Air/Water Exchange**

- **CSO, Storm Drains**

- **Upstream Source**
Bkgd: know **mobility** & tox’ "freely dissolved conc's"

=> need **water column AND porewater conc's**

Hawthorne et al. (2007)
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 $C_{pe}^{\infty}$

$=> C_{water} = \frac{C_{pe}^{\infty}}{K_{pew}}$
Bkgd: PE Methods

Choose \((M_{pe}/V_{water})^*K_{pe-water} > 20\)

Mount in frame and deploy from boat

LDPE cleaned loaded w/ stds mounted deployed

GCMS extracted recovered

Evaporate solvent, add injection stds, run GCMS. No extract clean up!

Add surrogate stds & extract with DCM

Clean exterior

After 1 to 3 months, recover

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

Gschwend et al. 2012
Can deploy via divers, but also from vessels

deployment all depths
~10 min
Bill Jaworski
Marine Sampling Systems Inc

recovery system from boat

camera shows PE insertion

“Comb”

bed & water samplers

PE sheets 10 cm wide by 60 cm long by 25 um thick
Bkgd: Use PRCs to Find $C_{PE}^\infty$ (lab tests)

with PCB-contaminated lake sediments

(Apell and Gschwend 2014)

$$C_{PE}^\infty / K_{PE-water} = C_{porewater}$$
Graphic User Interface allows users to process own $C_{pe}$

1. Select PRCs and enter their fractional loss after sampler deployment. Press ENTER to complete selection.

<table>
<thead>
<tr>
<th>PRC</th>
<th>Fraction PRCLoss</th>
<th>Deuterium C11</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>0.58</td>
<td>d13/C11</td>
</tr>
<tr>
<td>PCB 47</td>
<td>0.487</td>
<td>d13/C11</td>
</tr>
<tr>
<td>PCB 97</td>
<td>0.375</td>
<td>d13/C11</td>
</tr>
<tr>
<td>PCB 111</td>
<td>0.321</td>
<td>d13/C11</td>
</tr>
<tr>
<td>PCB 153</td>
<td>0.237</td>
<td>d13/C11</td>
</tr>
<tr>
<td>PCB 178</td>
<td>0.132</td>
<td>d13/C11</td>
</tr>
</tbody>
</table>

2. Enter deployment time in days
   - PE thickness in um: 60, 25.4, 0.8

3. Select target compounds:
   - all PCBs
   - all DDTs
   - all PAHs

3a. Press ENTER after final selection

PCB 188
PCB 189
PCB 190
PCB 191
PCB 192
PCB 193
PCB 194

4. Evaluate % to eq of target compounds

Results:

Fitting Kd to Kow

Kd vs Kow fit:
$y = 0.92296x + 0.95515$
$R^2 = 0.9242$


(Tcaciuc et al.)
Accuracy and Precision \textit{in situ} in the LDW (Apell) (Nov 2012-Jan 2013)

\[ \frac{C_{\text{sediment}}}{f_{oc} K_{oc}} \]

\[ C_{PE}/K_{pew} \]

\[ \pm \text{factor of 2} \]

\[ n=522 \]
Field Approach: Start "Simple" (are sediments main source now?)

- Air/Water Exchange
- CSO, Storm Drains
- Flushing
- Diffusion from Sediments
- Exfiltration

Equation: $C_{PCB}^{Measured} \approx C_{PCB}^{Modeled}$
LDW sampling summer-fall 2014

20 samplers over 4.5 miles
left ~2 mos.
Porewater profiles at Site 8

- Downriver (north)
- Through a cap that had ~10 cm deposited over it
LDW sampling

PCB bottom water concentrations (0-5 cm)

PCB pore water concentrations (0-5 cm)

∑ "NOAA 18" x 2 ≈ 1.4 ng/L

600 pg/L

see some "hotspots" factor of 2

(Apell et al.)
Results => bed-water gradients

(PW - BW) \( \sum \) PCBs gradients (ng/L)
Results: Boundary Layer with ADCP
(Prendergast)

- if \( \text{Flux} = - D_{\text{water}} \frac{(C_{\text{porewater}} - C_{\text{bottom water}})}{\delta_{\text{boundary layer}}} \) need \( \delta_{\text{boundary layer}} \)

- downward-facing ADCP deployed on river bottom

- Eight locations
  15 minute intervals
Results: Boundary Layer with ADCP

- Eight locations
  water boundary range 50-250 µm
  varying as expected with current/tide

- results lower than 2009 EFDC model-calibrated value of 400 µm.

\[
\text{fitted shear velocity } u^* = 0.7\pm0.2 \text{ cm/s}
\]
\[
\text{and layer thickness } \delta = 130 \pm 30 \text{ µm}
\]
Estim' Diffusive Fluxes

\[ 100 \, \mu m \, \delta_{bdl} \]: fluxes in ng/m\(^2\)/day

\[ \Sigma \text{fluxes out of bed} \sim 0.2 \, \text{g/day} \]

Elliott Bay

Duwamish River

esp. low molecular weight congeners
MBM modeling with EFDC (Adams and Predergast)

Elliott Bay

September – Spring Tide – Low Tide

Duwamish River

freshwater outflow near surface

high salinity at bottom near Bay

relative PCB concentration

=> FWM exposure field in space
MBM modeling with EFDC (Adams and Predergast)

Elliott Bay
September – Spring Tide – High Tide
Duwamish River

higher salinity
(and much deeper)

relative PCB concentration

Key: Res' Time ~ 4 d

now can add source
Putting in all together

1. average porewater-bottom water gradient was 400 pg $\Sigma$PCBs/L (N=19)

   assuming water-side controlled diffusive exchange ($D_{\text{water}} = 4E-6 \text{ cm}^2$/s)
   (with a boundary layer thickness 0.01 cm)

   computed flux: $1.5E-16 \text{ g}\Sigma\text{PCBs} /\text{cm}^2$/s

LDW bottom area (8000 m x 200 m) about $1.6x10^{10} \text{ cm}^2$

   so 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. implies accumulate about 0.8 g $\Sigma$PCBs at steady state in LDW
NOAA 18 averages about 600 pg/L

$\sum$PCBs ≈ 1.2 ng/L

$\times 2$

~600 pg/L
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 $\sum$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 $\sum$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

$C_{PCB}^{\text{Measured}} \overset{?}{=} C_{PCB}^{\text{Modeled}}$

- **Flushing**
- **Air/Water Exchange**
- **CSO, Storm Drains**
- **Diffusion**
- **Exfiltration**
- **Upstream Source**
Upstream Source?

(Apell, Prendergast)

**Total 20 PCBs**

- **Concentration [pg/L]**
- **River Mile**

**Duwamish River**

**EFDC modeled expectation for River source**

**need source here**

**Elliott Bay**
Option: Bed-Water Fluxes Inc' Due to Bio-irrigation

Using Sediment Profile Imaging (SPI) to Evaluate Sediment Quality at Two Cleanup Sites in Puget Sound

Part I – Lower Duwamish Waterway

July 2007

Publication No. 07-03-025
Option: Bioturbation Enhanced
what would water-column look like?

High Tide
Bed => Water
Input at 4 g/day
throughout LDW

Low Tide
=> measures too low for that source?

(time-averaged data)

(Prendergast)
Option: Resuspension & Desorption?
Option: Local Resuspension Source

(Prendergast)

High Tide
Bed $\Rightarrow$ Water
Input at only RM 3.5 adding 4 g/d
Throughout Water Column

Low Tide
$\Rightarrow$ not too bad
Option: Outfall sources into LDW surface?
Option: Outfall Sources

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

Low Tide
=> need surface water data

(Prendergast)
Exposures => Food Web Model  (after Gobas)

\[ C_{WD} = \frac{1}{\{1+(\chi_{DPC} \times D_{POC} \times \alpha_{POC} \times K_{OW} + \chi_{DPOC} \times D_{POC} \times \alpha_{DOC} \times K_{OW})\} \times 1000} \]

\[ G_D = 0.022 \times W_b^{0.65} \times e^{(0.08 \times t)} \]

\[ V_{SD} = P_{P} \times V_{POC} + P_{SED} \times OC_{SED} \]

\[ V_{WD} = \sum P \times V_{WB, i} \]

\[ G_F = \frac{([1-\epsilon_L] \times V_{LD} + [1-\epsilon_N] \times V_{OCD} + [1-\epsilon_N] \times V_{ND} + [1-\epsilon_W] \times V_{WD}) \times G_D}{W_b} \]

\[ E_D = \frac{3.0 \times 10^{-5} \times K_{OW} + 2.0}{W_b} \]

\[ K_{GB} = \frac{V_{LD} \times K_{OW} + V_{OCD} \times \beta \times K_{OW} + V_{ND} \times \beta \times K_{OW} + V_{WD} \times \beta}{\delta_L} \]

\[ C_{POW} = \frac{(1-\phi_L) \times V_{LD} + (1-\phi_N) \times V_{OCD} + (1-\phi_N) \times V_{ND} + (1-\phi_W) \times V_{WD}}{W_b} \]

\[ C_{Sediment} = \frac{C_{DPC} \times K_{OC}}{\delta_L} \]

\[ C_{PFW} = \frac{C_{DPC} \times K_{OC}}{\delta_L} \]

Legend:
- Uptake from water
- Uptake from diet
- Loss from growth
- Loss from metabolism

Note: Porewater defined by equations and parameters with defined values are presented in Tables D.1 and D.4 respectively.
PCB congeners concs in water and porewater for FWM
(von Stackelberg & Apell)

**PCB bottom water concentrations**

**PCB pore water concentrations**

www.seattleweekly.com
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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