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Use of Polyethylene Device (PED) Passive Samplers at Contaminated Sediment Sites to Support Remedial Planning and Progress Monitoring

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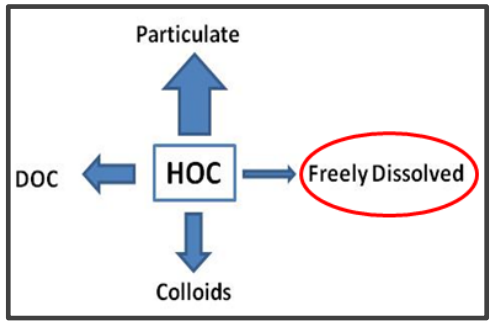
Overview

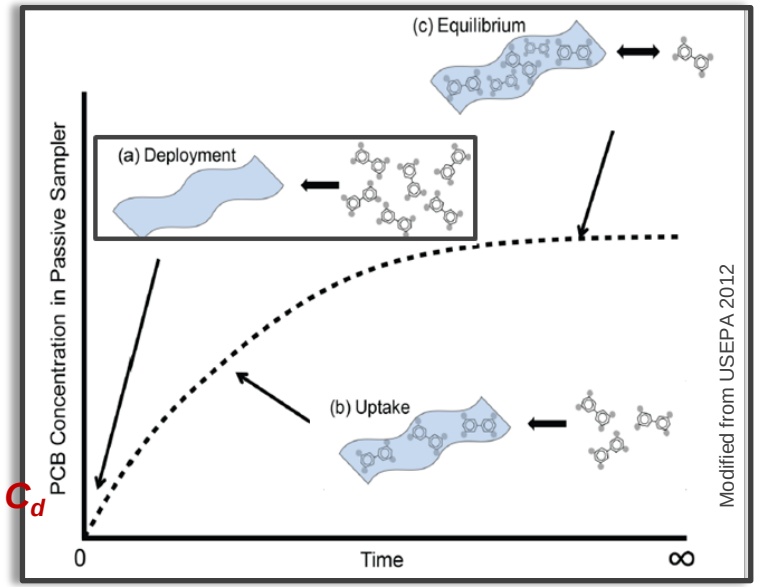
- How it works
- Deployment options
- Data analysis
- Case Study 1 – PCB-Contaminated Estuarine Harbor (Flux Measurement)
- Case Study 2 – Tidally Influenced Creek (Source Tracking)

How it works

- **At equilibrium**, dissolved water concentration (C_d):

$$C_d = \frac{C_{PED}}{K_{PED}} \quad , \quad K_{PED} \propto K_{OW}$$

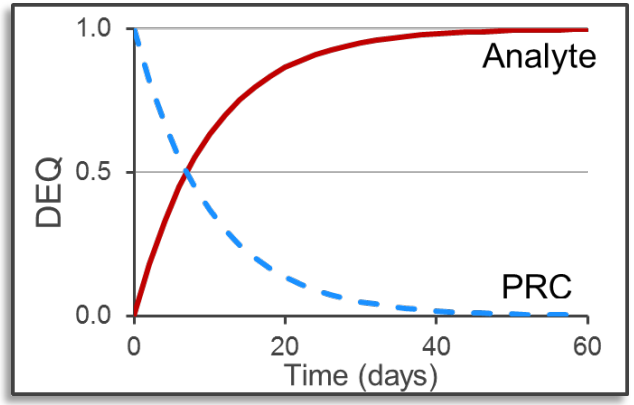




- **During uptake phase**

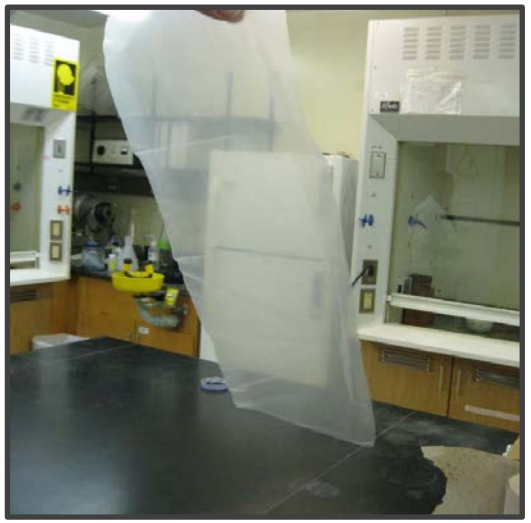
$$C_d = \frac{C_{PED}}{K_{PED} \cdot DEQ}$$

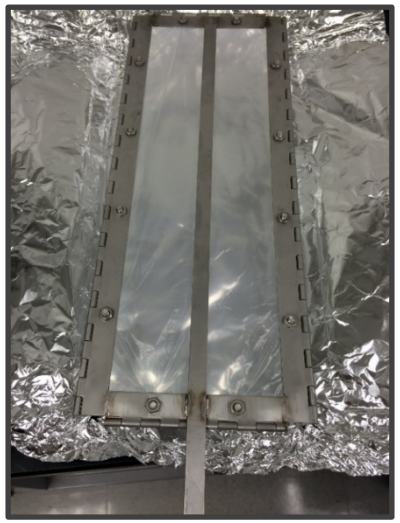
where *DEQ* = degree of equilibration, determined from the loss of PRCs



Methods - PEDs preparation

- Made from 25 µm-thick low-density polyethylene sheets
- Cut to size and cleaned
- Spiked with performance reference compounds (PRCs); at least 2 PEDs per batch retained at the lab to determine PRC concentration at $t = 0$
- Various deployment options (pictured below is frame for sediment- water interface deployment, wrapped for transport to the site)





Methods – deployment options

In situ:

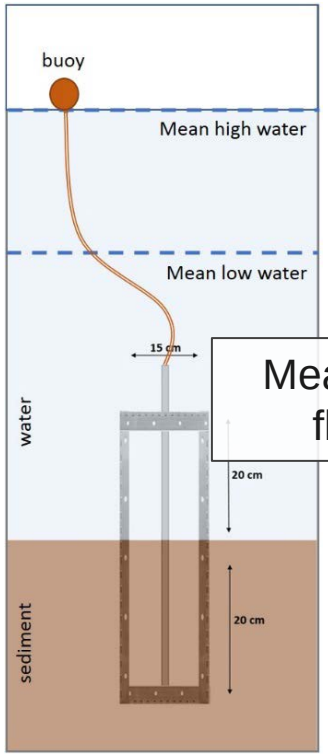
- Surface water
- Piezometer or groundwater monitoring well
- Framed PEDs inserted into the sediment (fully or partially)
- Deployment time: ~1 month

Ex situ:

- Conducted in the laboratory on field-collected sediment grab samples
- Lab exposures conducted by sediment slurry method in jars agitated on an orbital shaker

Examples of in situ deployments

In piezometers for deep porewater or groundwater measurements



Measure flux

Surface water deployment/combined with biological samplers

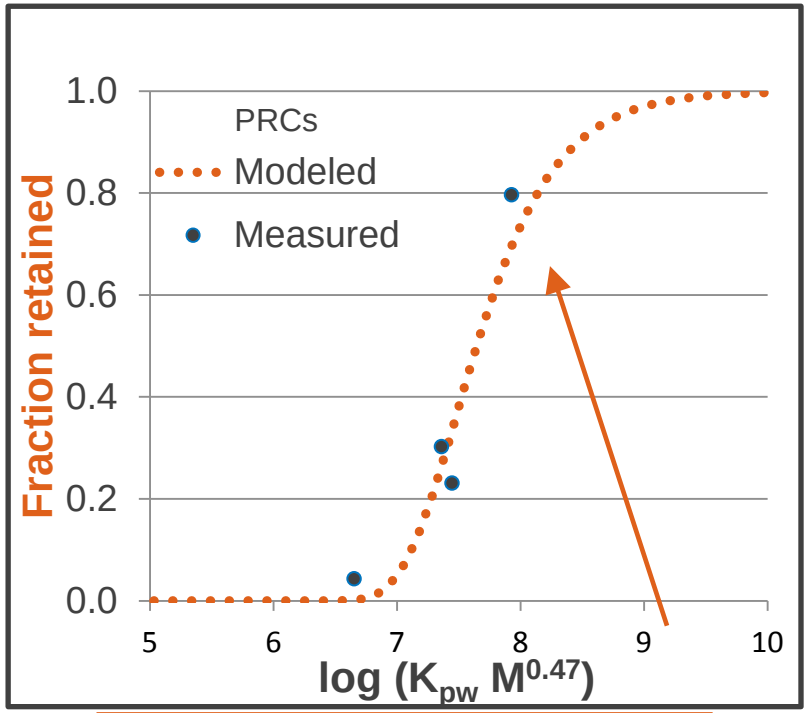
Methods – data analysis

- PED extracts analyzed using standard analytical methods
- Lab results (C_{PED}) reported in ng/g-PED
- **Sampling rate** (**Rs**) model used to determine DEQ for each congener based on the loss of PRCs:

$$DEQ = 1 - f_{MODELED}$$

- Dissolved water concentration (C_d) calculated for each congener as:

$$C_d = \frac{C_{PED}}{K_{PED}\ DEQ}$$



$$f_{MODELED} = \exp\left(-\frac{FAM^{-0.47}\ t}{m_p\ K_{pw}}\right)$$

FA – fitted parameter
M – molecular weight
t – exposure time
m_p – weight of PED
K_{pw} – PED-water partition coefficient

Case Study 1
PCB-Contaminated Estuarine Harbor

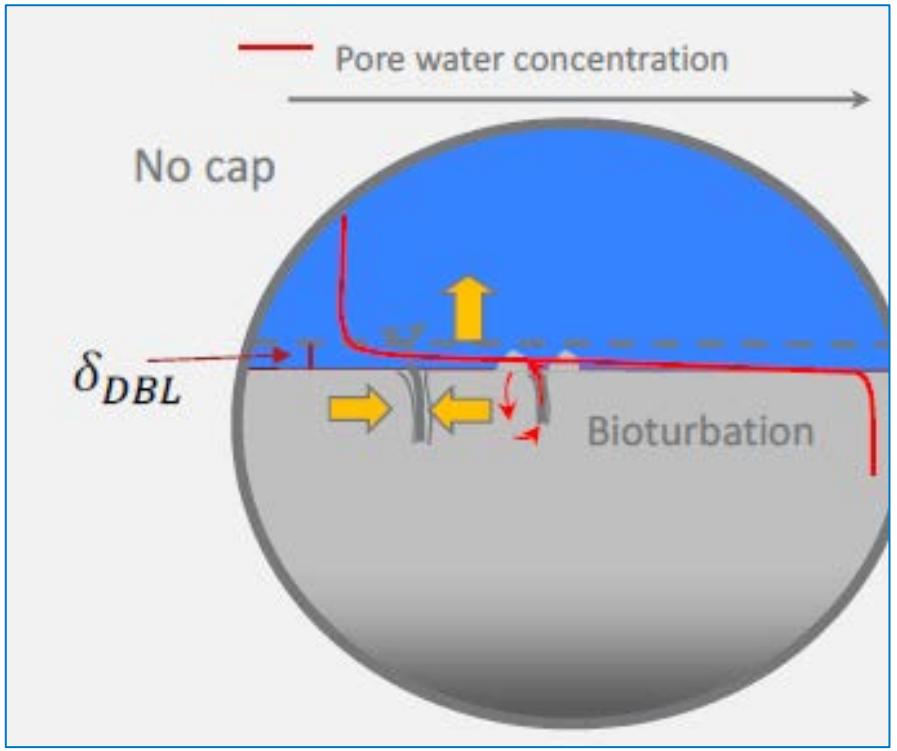
- **Site:**
  - Estuarine harbor contaminated with high levels of PCBs
  - Tidally influenced; salinity ~30 ‰; water depth 4 -10 feet
- **Project goal:**
  - Collect porewater and surface water PCB data and calculate diffusive PCB flux
  - Aid remedy design
- **Research goal:**
  - Conduct in situ vs. ex situ passive sampling comparison
  - Investigate reproducibility of the in situ and ex situ results

Case Study 1

Methods – diffusive flux

concentration gradient

$$F = -D_w \frac{(C_W - C_{PW})}{\delta_{BL}}$$



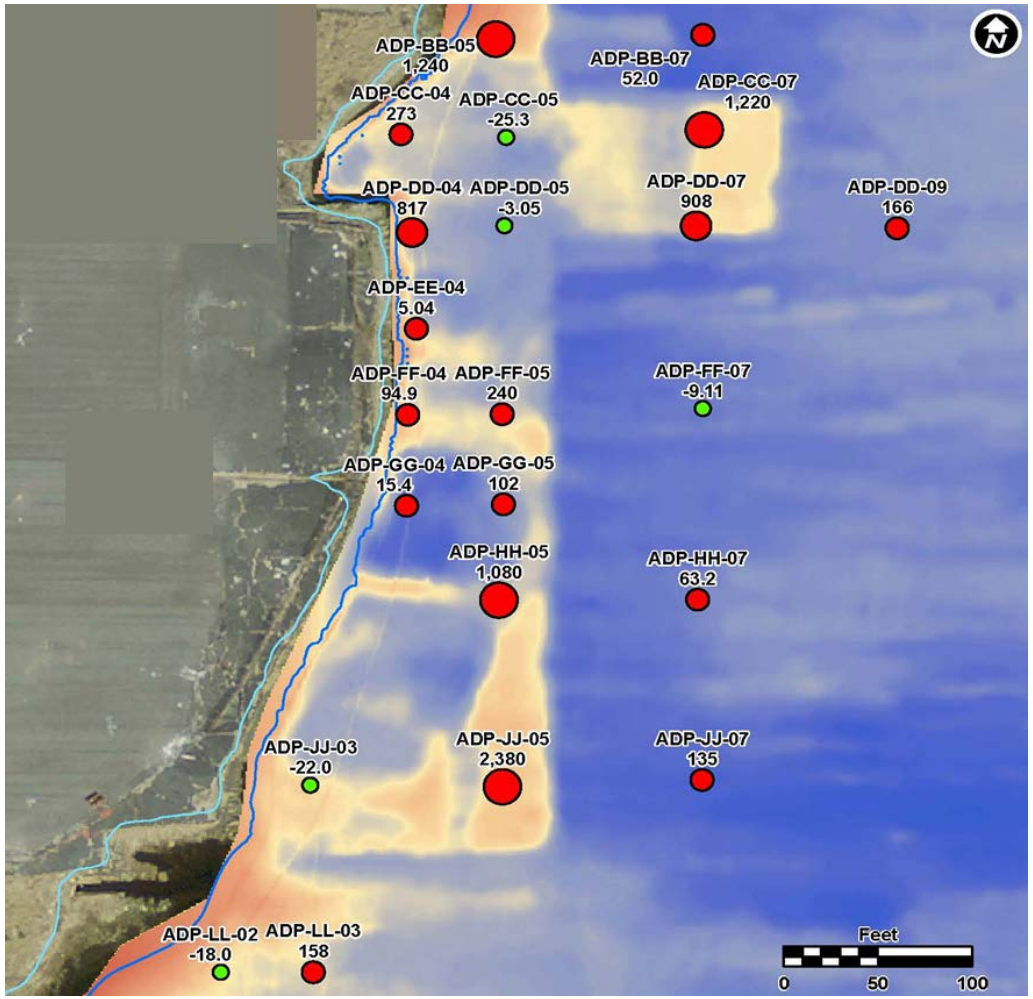
Eek and Reible, 2016

Where:

F	contaminant flux (positive when flux is from sediment to the water column)
D_W	diffusivity of total PCB in water
δ_{BL}	boundary layer thickness (0.02 cm; Fernandez et al., 2014),
C_W	PCB concentration in the water column (calculated from PED data)
C_{PW}	PCB concentration in the porewater (calculated from PED data)

Case Study 1

Results – diffusive flux



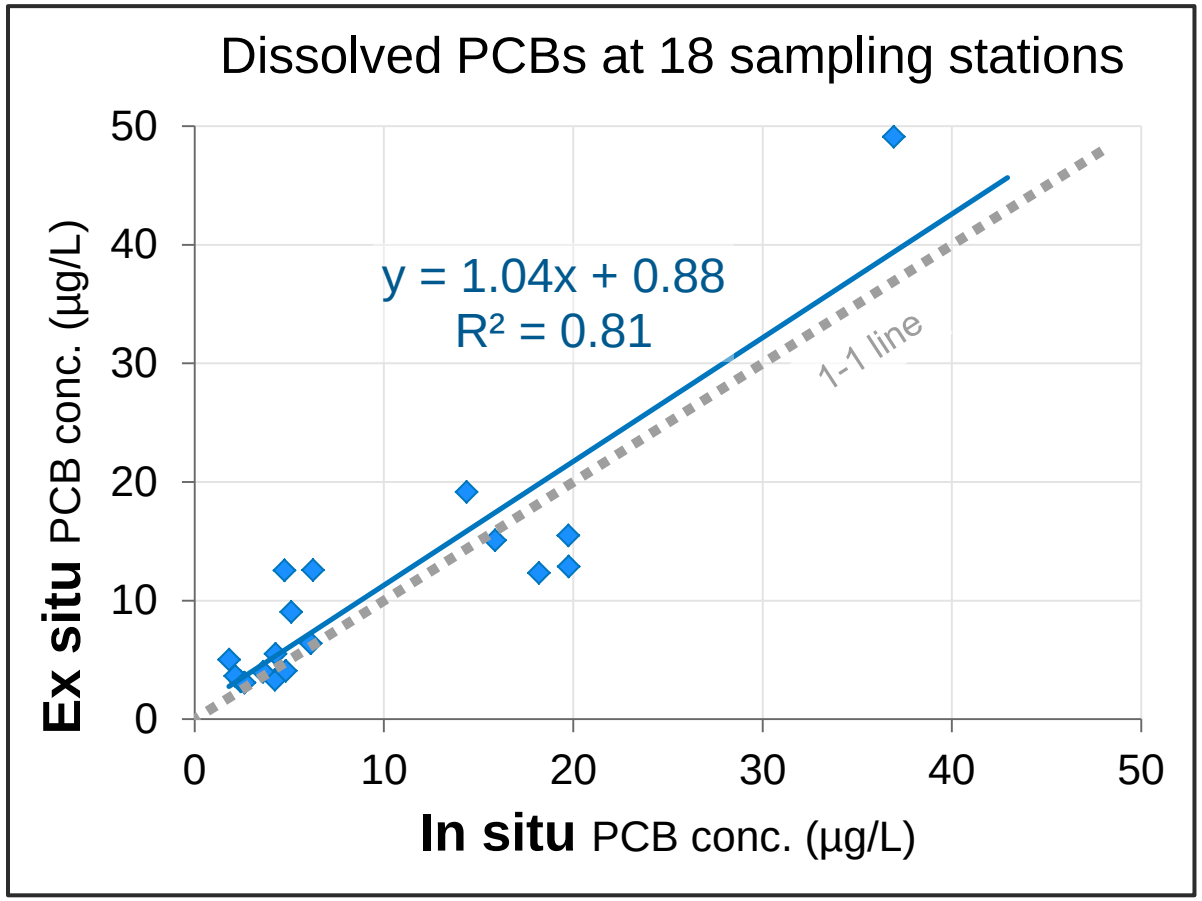
Flux of PCBs

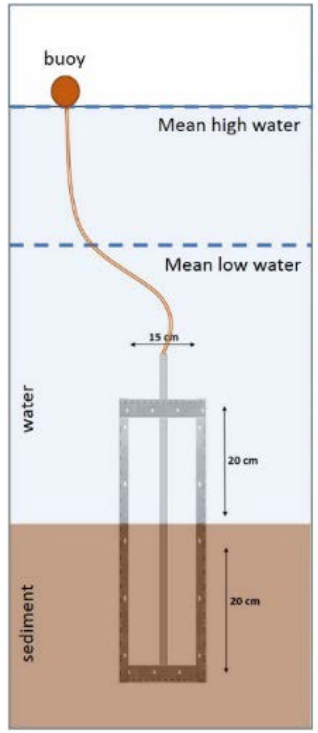
(mg/m^2/yr)

- **Positive**; from sediment to surface water
- **Negative**; from surface water to sediment

Case Study 1
Results – in situ vs ex situ

Ex situ



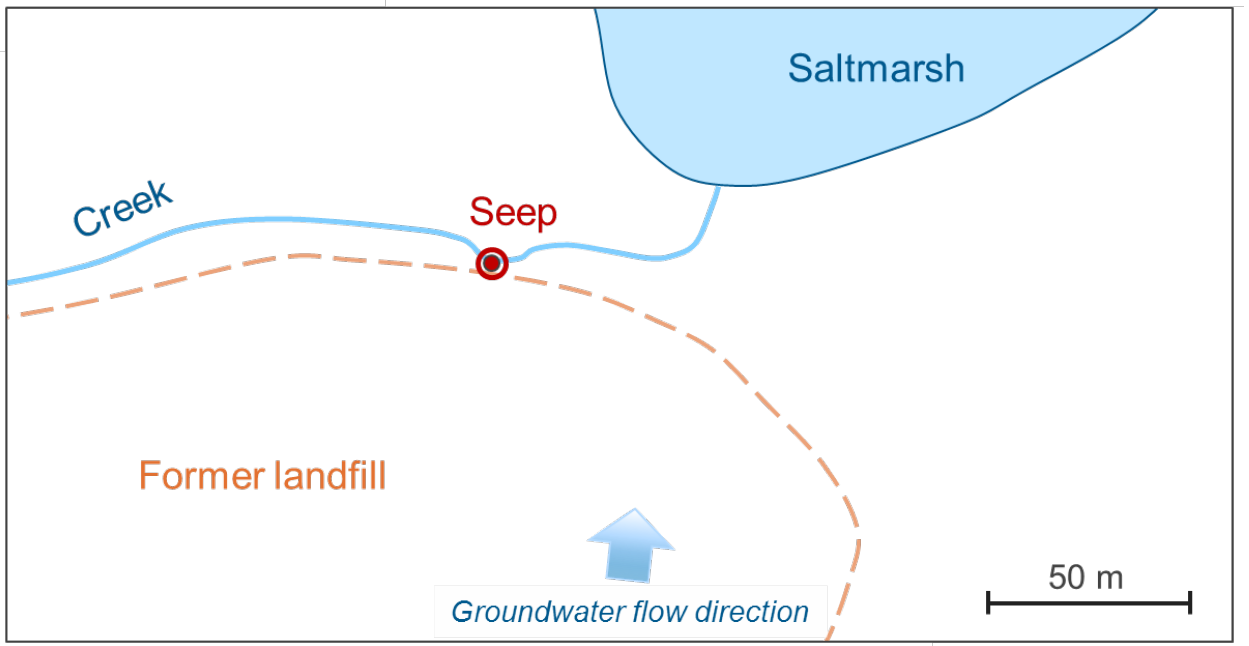


In situ

Case Study 1 – Summary

- **In situ** deployment of PEDs provide data that can be used in **remedy design** to provide information on the concentration and flux of freely dissolved hydrophobic contaminants across the sediment/water interface.
- **Ex situ** (lab) offer **comparable** results to in situ exposures and can be used when in situ deployments are difficult or risky due to significant water depths or high boat traffic.
- **Ex situ** exposures allow more cost-effective determination of site contaminant concentrations.

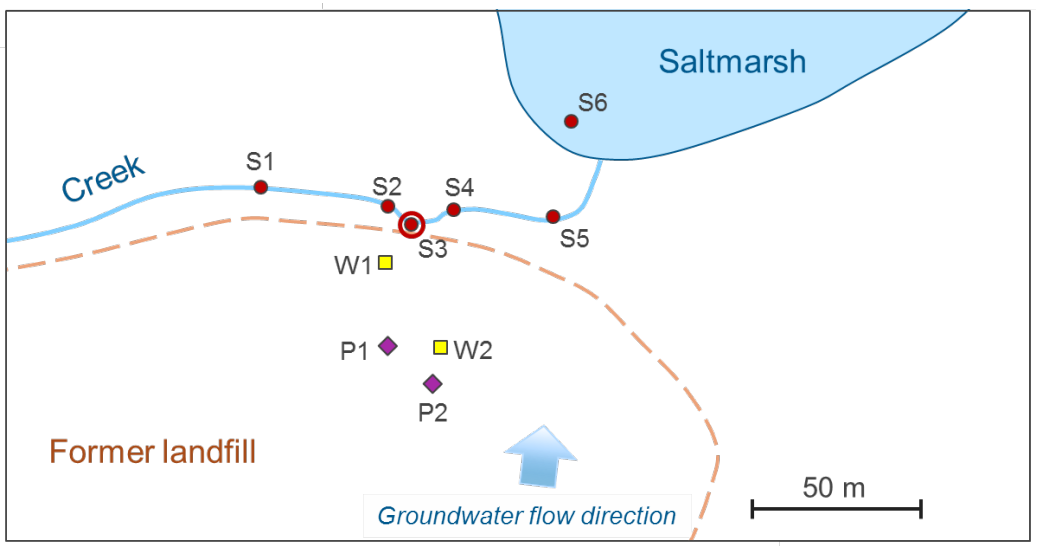
Case Study 2 - Tidally Influenced Creek



- A tidally influenced creek adjacent to a former landfill, discharging into a saltmarsh
- PCBs previously detected in sediment near the seep
- Study goal: investigate the extent of PCB contamination and identify source

Case Study 2
Methods

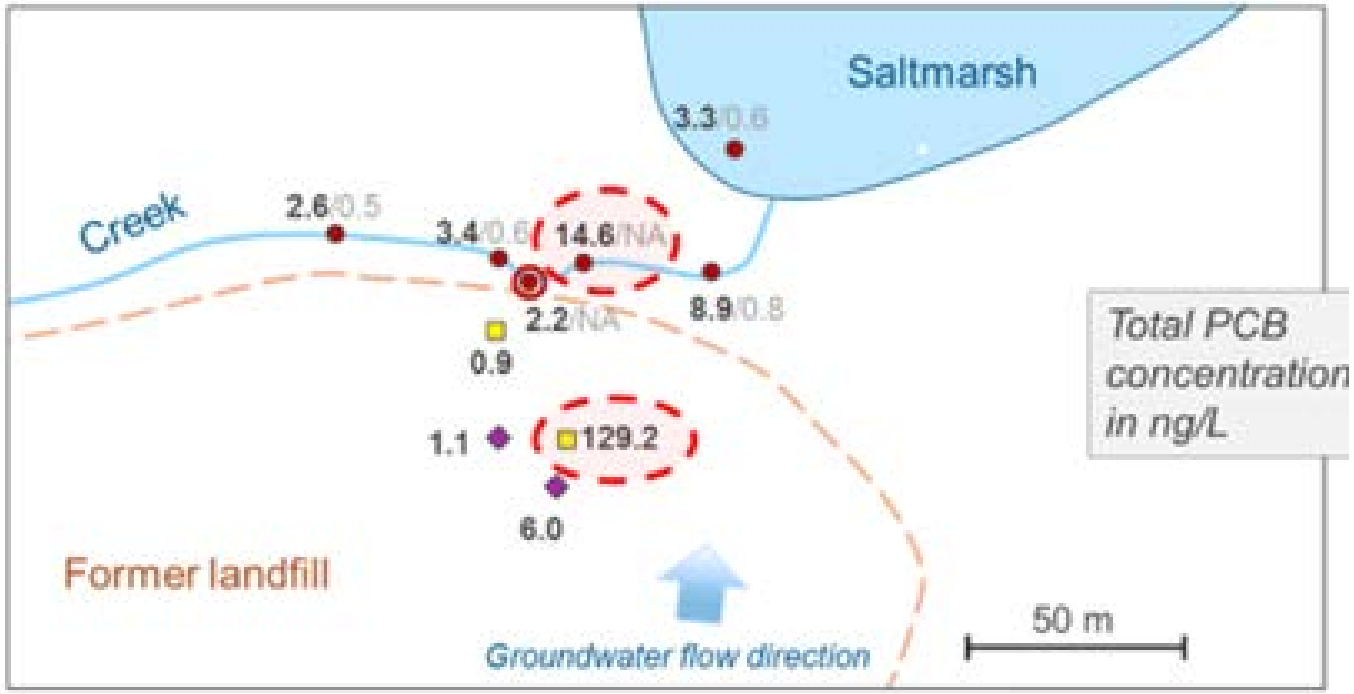
- PEDs deployed across the sediment-water interface in the creek and saltmarsh to measure porewater and surface water PCBs (●)
- PEDs also deployed in groundwater monitoring wells (▫) and piezometers (◆)
- PEDs deployed for ~30 days



Case Study 2

Results

- The highest porewater concentration (14.6 ng/L) downstream of the seep (S4)
- The highest concentration within the sampled area was in the groundwater monitoring well W2 (129.2 ng/L)



- Near freshwater chronic ambient water quality criterion (AWQC, 14 ng/L); below marine chronic AWQC (30 ng/L) and below the remedial goal for this site (40 ng/L).
- Location of the S4 station downgradient from station W2 suggests that the contaminated water in the landfill provides a source of PCBs to the creek.
- Data will be used to inform the risk assessment and aid in remedy selection.

Summary – Application of PEDs

Benefits

- Measures only freely dissolved (most bioavailable) contaminants
- Easily adjustable shape and size; robust
- Better detection limits than water sampling; inexpensive
- Time-averaged results

Assumptions

- Known partition coefficients
- PRCs present analogous properties to analytes and allow determination of fractional equilibration

Applications

- Measurement of hydrophobic contaminants in surface water, groundwater, porewater
- Diffusive flux calculation for remedy design and/or monitoring
- Source tracking and forensics

Mass transfer models

- First order – simplest, for surface water.
- Diffusion – for porewater only (surface water coming soon); 0.1>PRC DEQ>0.9
- **Sampling rate (Rs)** – used in this study; suitable for porewater and surface water

QUESTIONS?

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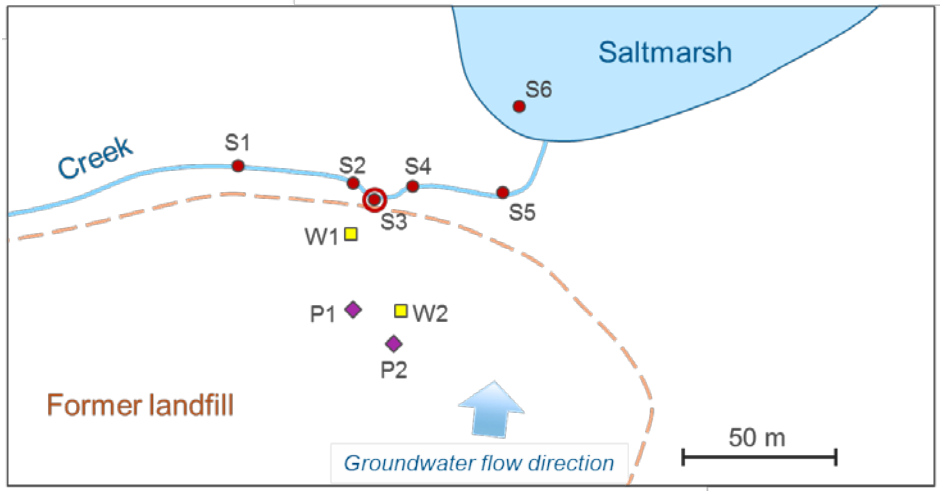
It can be done

Case Study 2
Conclusions



- PCBs were detected in all PED samples
- Surface water concentrations were low and uniform.
- The highest porewater concentration (14.6 ng/L) was found downstream of the seep (S4), but the concentration did not exceed the remedial goal for this site (40 ng/L).
- The highest concentration within the sampled area was in the groundwater monitoring well W2 (129.2 ng/L)
- Location of the S4 station downgradient from station W2 suggests that the contaminated water in the landfill provides a source of PCBs to the creek
- PCB contamination in the surface water is limited to the vicinity of S4

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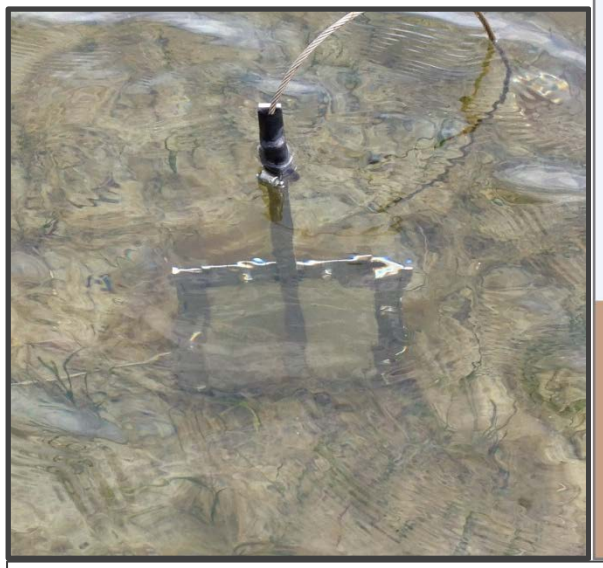
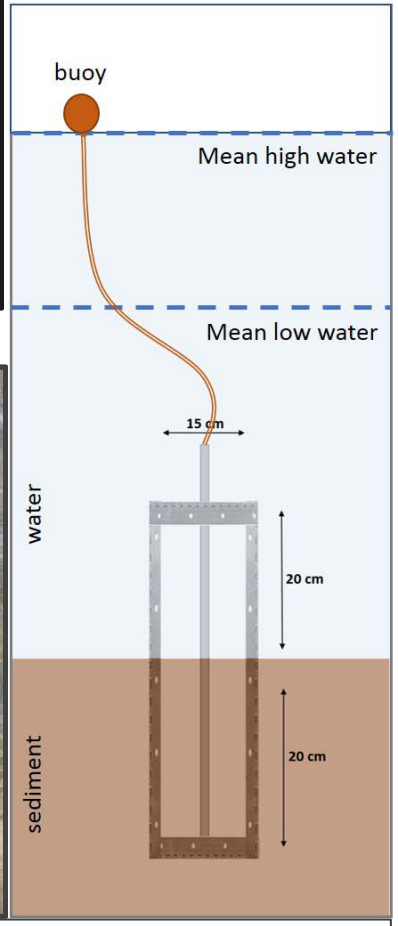
In situ deployments

In groundwater monitoring wells

In piezometers for deep porewater or groundwater measurements

Combined with biological samplers





Measure flux

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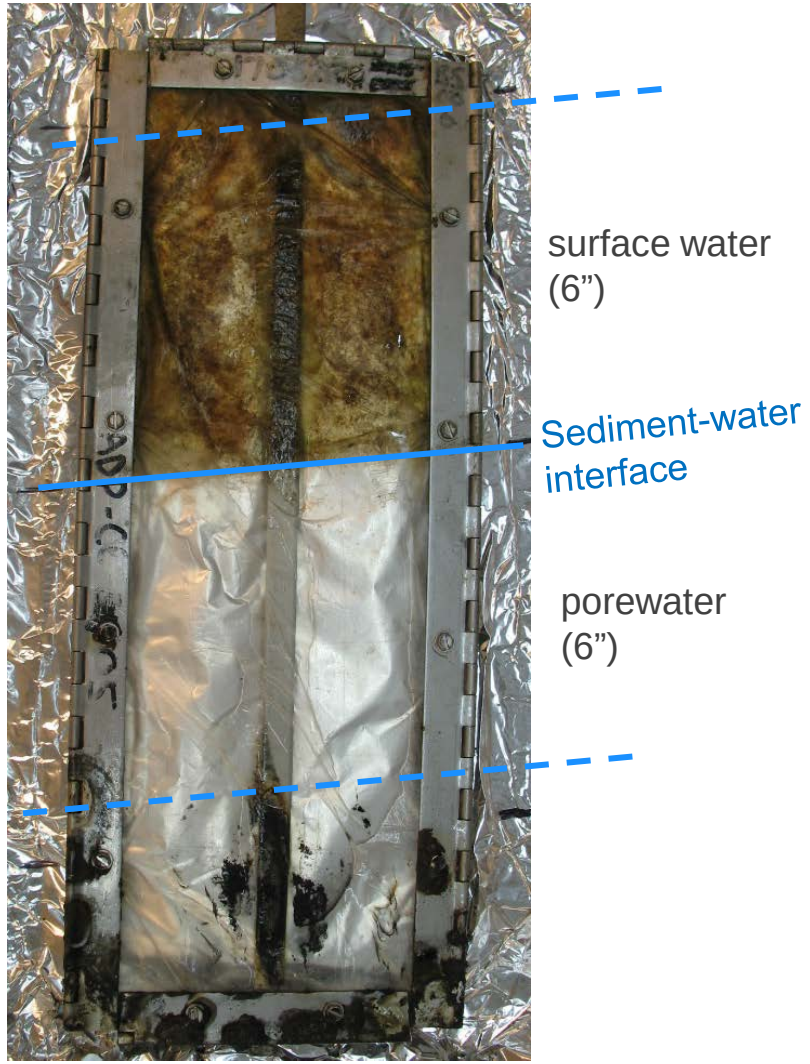
Methods – retrieval and sample prep

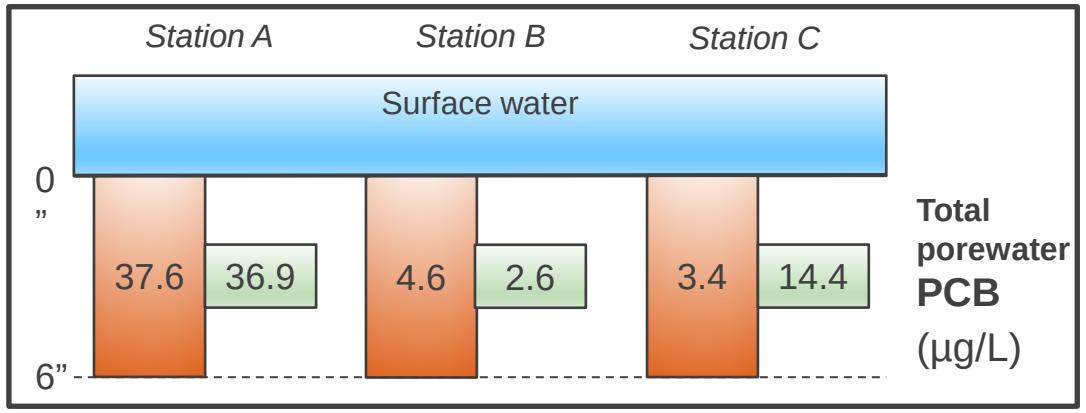
- PEDs from field deployments: retrieved, rinsed, photographed, shipped to the lab
- At the lab: photographed, cleaned, subsectioned, extracted

- PEDs from lab exposures: retrieved, cleaned, extracted

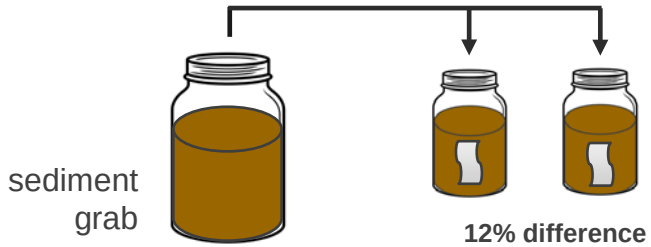


Results – measurement variability

- Equilibrium achieved for all lab exposures but not for field exposures
- Field dups (in situ):



- Lab reps (ex situ):



12% difference (average from 3 sets of duplicates)

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Case Study 2
Results