Question 1 Please indicate your experience with passive samplers at contaminated sediment sites. (Pick one)

- I use them at nearly all of my sites.
- I have used them at many sites.
- I have used them at one or two sites.
- I have never used them.
- What are passive samplers?
Passive sampling of sediment and limitations

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Passive samplers

- Passive samplers measure activity of pollutants, e.g. Porewater (Cdiss)
- uptake by diffusion

- advantage - no operational separation of particulate and dissolved phase
- need to know $K_{\text{passive-water}}$ (T, sal) and state of equilibrium (PRCs / diff. coeff.)/sampling rate

- $C_{\text{diss}} = C_{\text{passive}} / K_{\text{passive-water}}$ (at eq)
What can passive samplers be used for?

- Best for hydrophobic organic contaminants (HOCs)
  - in sediment porewater
  - also water column, air, biota
- Such as:
  - PCDD/Fs
  - PAHs
  - PCBs
  - PBDEs
  - pesticides (HCB, aldrin, dieldrin, DDT etc.)
- Maybe also MeHg, PFASs (under development)
Common types of passive samplers

- Most commonly used - single polymers:
  - Polyethylene (PE) sheets
  - Silicone (PDMS) sheets
  - PDMS-coated SPME fibers

- $K_{\text{passive-w}}$ widely available
  - Ghosh et al., 2014; Lohmann et al., 2012
  - Rusina et al., 2010

(Photo: M. Jonkers, U Utrecht)
Potential benefits of passive samplers I

- Total sediment concentration is not useful
- Complex sediment geochemistry
  - focKoc approach invalid
  - OC, BC
  - NAPL
  - Tar, coal, other particle
- Bioavailability?

(Lohmann et al., ES&T, 2005)
Potential benefits of passive samplers II

- Passive sampler as proxy for bioaccumulation (biomimetic)
- At equilibrium, similar HOC concentration in passive & benthic invertebrates
- Certainly cheaper, easier
- Same samplers across all sites

(Friedman et al., 2009)
Question 2: Where should porewater should be measured: (Pick one)

- by deploying sampler at site (in field - in situ)
- by collecting the sediment and perform porewater equilibration in the lab (in lab - ex situ)
How can we best use passive samplers?

- Life’s easy - either the passive is IN situ or EX situ

porewater Deployment or in-lab equilibration
Benefits-drawbacks:

<table>
<thead>
<tr>
<th></th>
<th>In situ</th>
<th>versus</th>
<th>ex situ</th>
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</thead>
<tbody>
<tr>
<td>Logistics:</td>
<td>two (Depl = retrieval)</td>
<td>-</td>
<td>one</td>
</tr>
<tr>
<td>Divers:</td>
<td>might be needed</td>
<td>-</td>
<td>none</td>
</tr>
<tr>
<td>Cost:</td>
<td>higher</td>
<td>-</td>
<td>cheaper</td>
</tr>
<tr>
<td>Losses:</td>
<td>chance of losses</td>
<td>-</td>
<td>only mud grab</td>
</tr>
<tr>
<td>“trueness”:</td>
<td>real conditions in field</td>
<td>-</td>
<td>chance for bias</td>
</tr>
<tr>
<td>Heterogeneity:</td>
<td>many samplers?</td>
<td>-</td>
<td>homogenize sed?</td>
</tr>
<tr>
<td>Data interpretation</td>
<td>use GUI</td>
<td>-</td>
<td>at equilibrium</td>
</tr>
</tbody>
</table>
Uptake of HOCs by passive samplers

\[ N_s = C_w K_{sw} m_s \left[ 1 - \exp \left( -\frac{R_s t}{K_{sw} m_s} \right) \right] = C_w V_e \]

\[ C_{diss} = \frac{C_{\text{passive}}}{K_{\text{passive-w}}} \]

In situ passive samplers

Ex situ passive samplers

Equilibrium

Deployment Time (days)

Concentration (ng/g Passive Sampler)
Performance Reference Compounds (PRCs)

- PRCs added before field deployment
- PRCs do not occur in nature
- Loss of PRC = f (flow, temp, biofouling)
- Indicates effective diffusion
Determination of $C_w$ using a GUI-based PRC Calculator

- SERDP/ESTCP/EPA guidance document (2017):
- use a PRC Calculation software developed by Gschwend et al. (MIT).
- based on Fernandez et al. (2009), and Appell et al. (2014).
- Works well, except for AC-addition in field
Making sense of the data

- Comparison of In situ vs Ex situ approaches:
  - Lower Duwamish River (WA)
  - Passaic River (NJ)

  (Apell et al, 2018)
  (Khairy and Lohmann, in prep)
The final slide ...

- How do passives compare from # academic laboratories?
  - Poorly.
  - Unless standardized.

(Jonkers et al, 2018)
limitations

- Deployments (in situ) and retrievals
- Time (weeks in field/lab)
- Sediment heterogeneity
- PRCs/ diffusion model/ data interpretation
- But.. Commercial laboratories offer this.
Question 3 Why do you not use passive samplers at contaminated sites? (Pick one)

Please indicate limitations of passive samplers:
- Cost (they are expensive)
- They only work in homogeneous environments
- Time and Resources to Deploy
- Data must go through extensive QA/QC
- Clean-up goals are incompatible with passives
- Not sure how to interpret the data
Thanks!

Questions?
OPTIONS for passives

1) assume equilibrium has been reached

2) 1st order kinetic model

3) Booij and Smedes - NLS approach

4) Fickian Diffusion model
   - (Fernandez; Apell; Thompson et al, 2015)

(Joyce and Burgess, 2018)