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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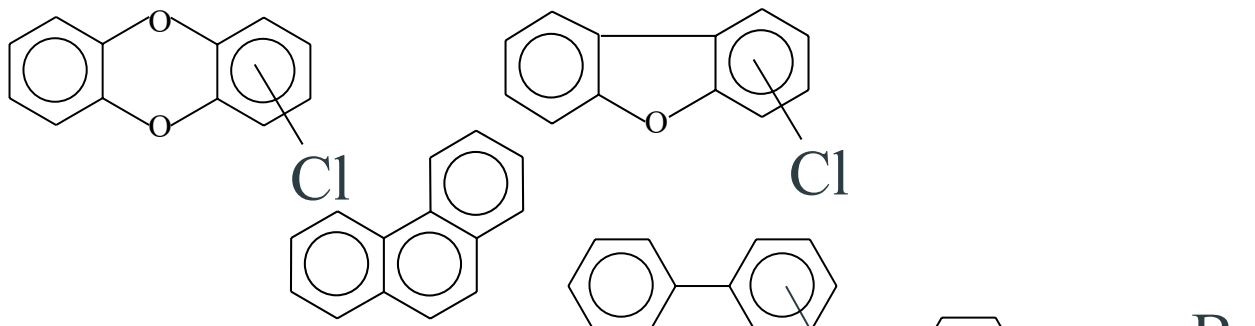
Passive samplers

- 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 $K_{passive\text{-}water}$ (T, sal) and state of equilibrium (PRCs / diff. coeff.)/sampling rate
- **$C_{diss} = C_{passive} / K_{passive\text{-}w}$ (@ 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.)

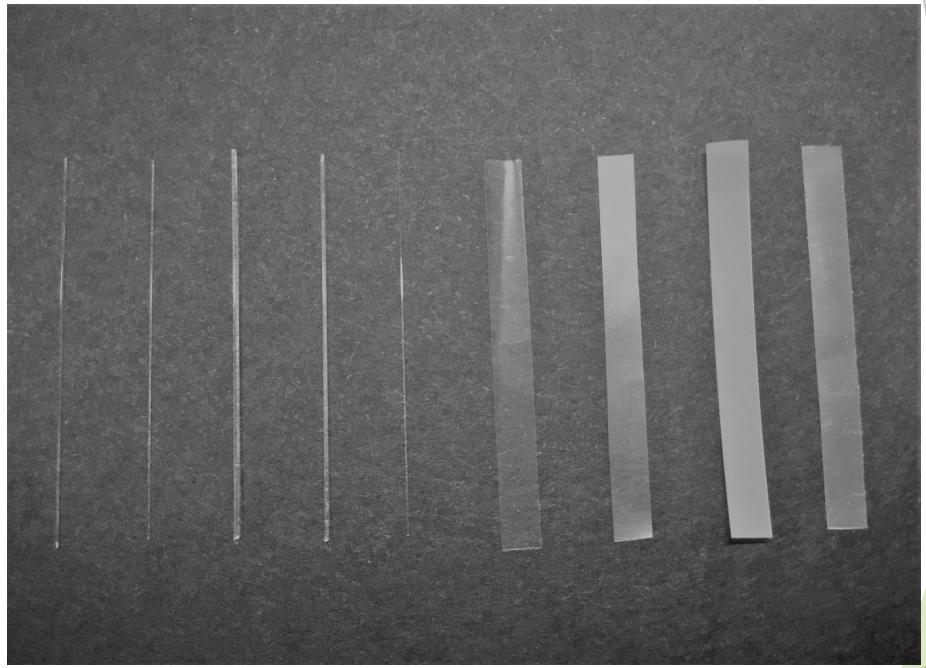


  - Maybe also MeHg, PFASs (under development)

Common types of passive samplers

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

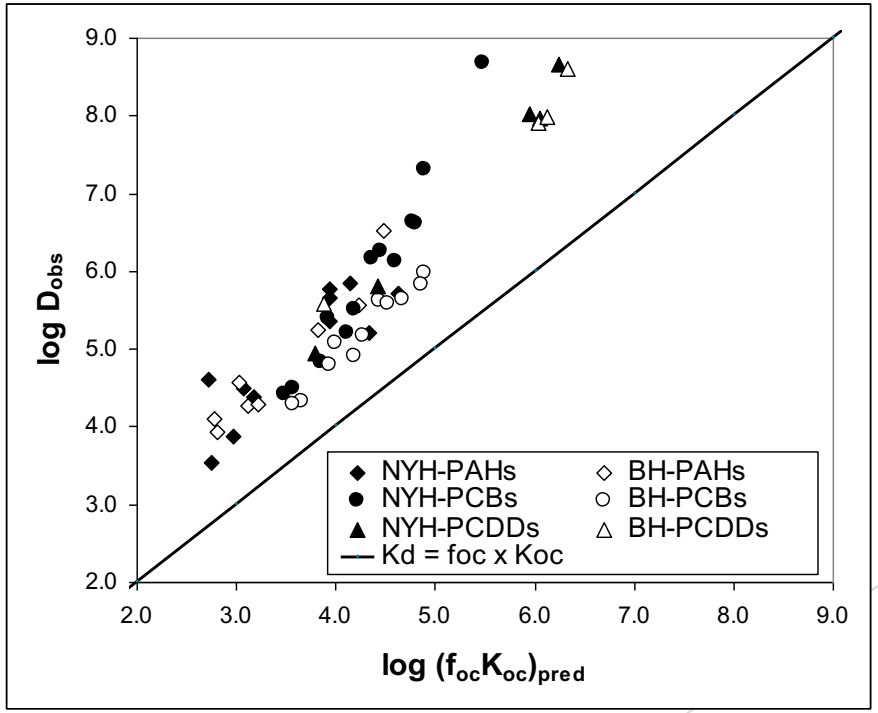
- $K_{passive\text{-}w}$ widely available
  - Ghosh et al., 2014; Lohmann et al., 2012
  - Rusina et al., 2010



(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

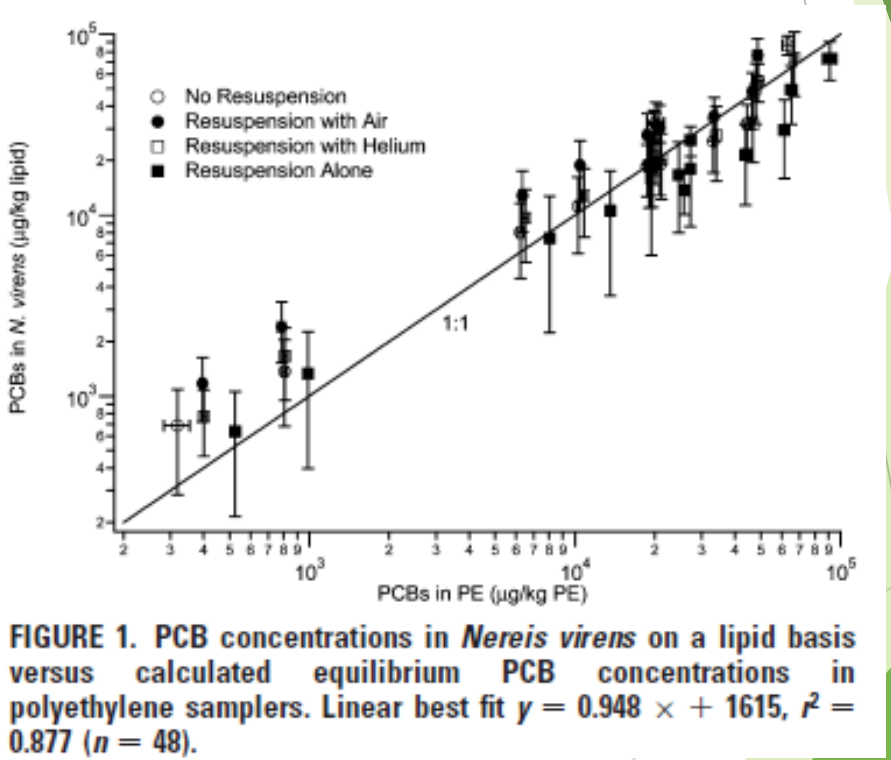


FIGURE 1. PCB concentrations in *Nereis virens* on a lipid basis versus calculated equilibrium PCB concentrations in polyethylene samplers. Linear best fit $y = 0.948 \times + 1615$, $r^2 = 0.877$ ($n = 48$).

(Friedman et al., 2009)

Question 2: Where should porewater should be measured: (Pick one)

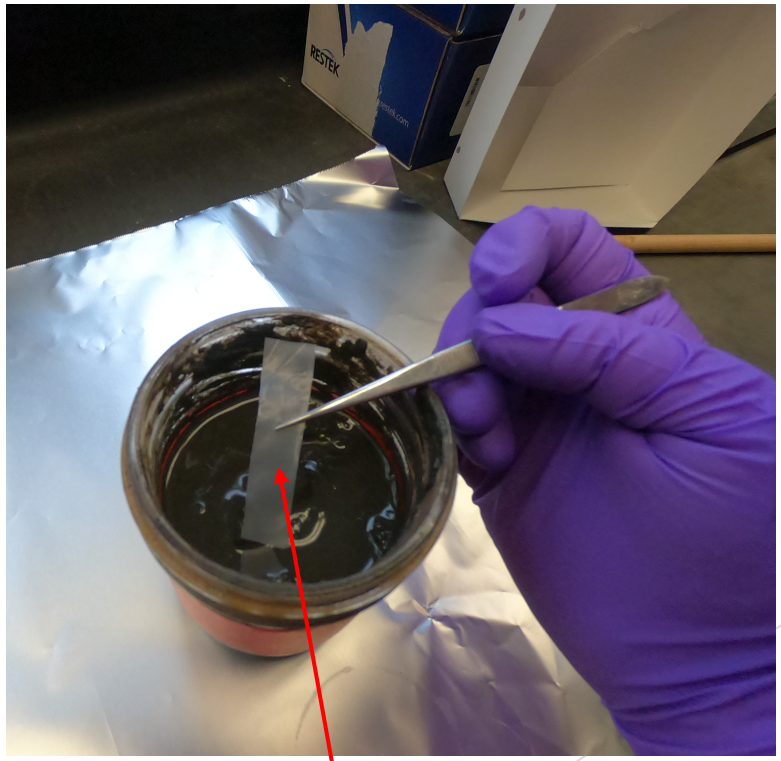
- by deploying sampler at site (in field – in situ)
- by collecting the sediment and perform porewater equilibration in the lab (in lab – ex situ)

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

PE (in aluminum frame)



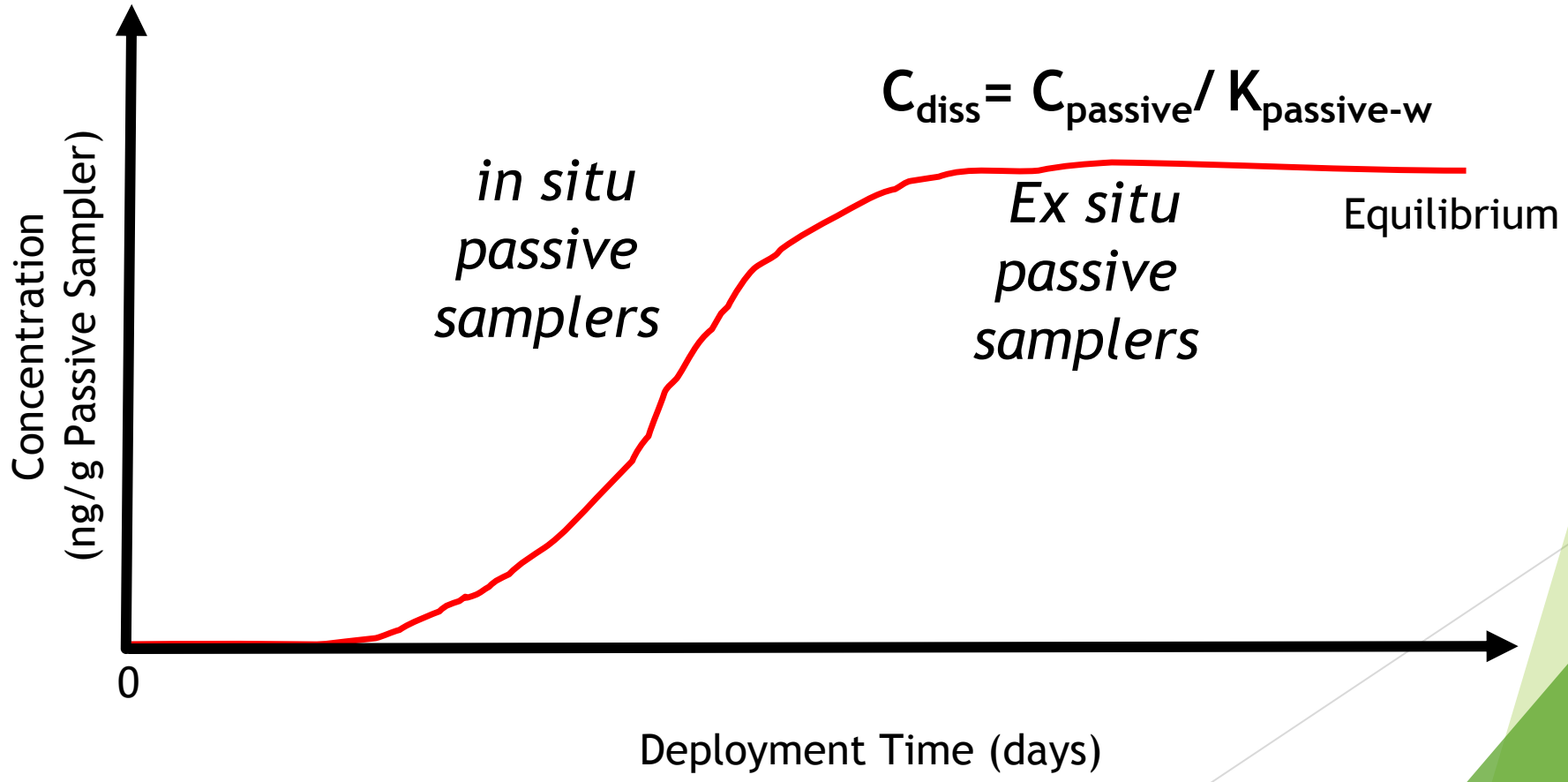
PE (not framed)

Benefits-drawbacks:
In situ versus ex situ

- Logistics: two (Depl = retrieval) - one
- Divers: might be needed - none
- Cost: higher - cheaper
- Losses: chance of losses - only mud grab
- “trueness”: real conditions in field - chance for bias
- Heterogeneity: many samplers? - homogenize sed?
- Data interpretation use GUI - at equilibrium

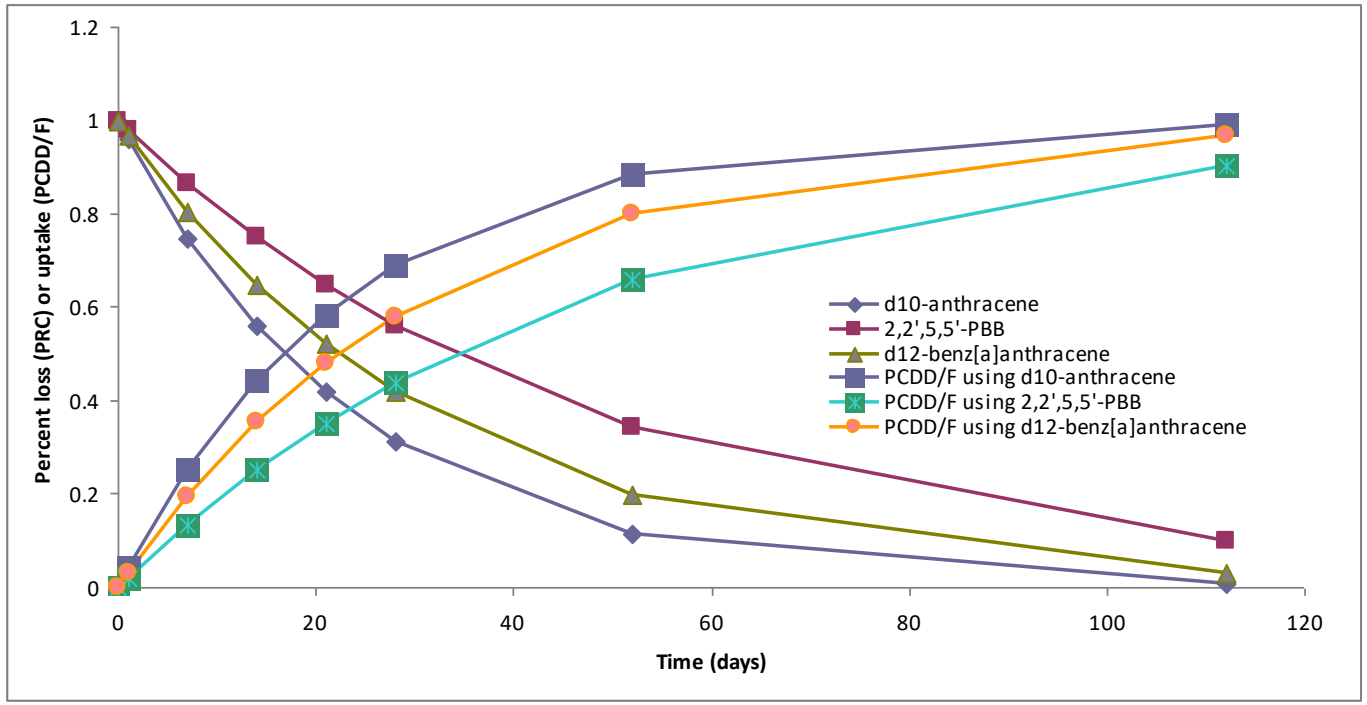
Uptake of HOCs by passive samplers

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



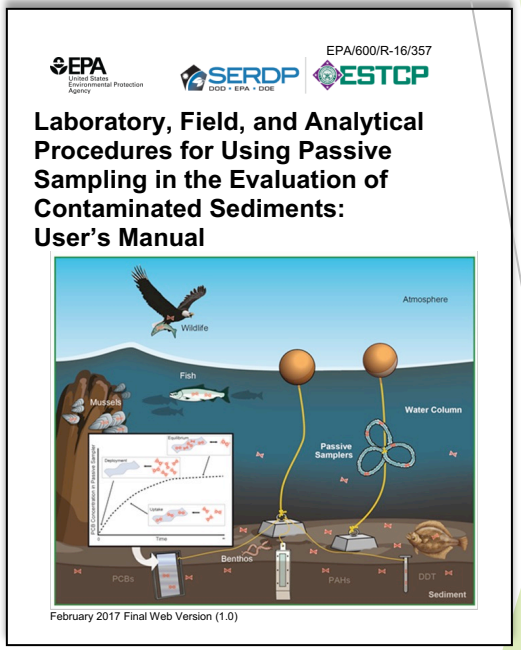
Performance Reference Compounds (PRCs)

- 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

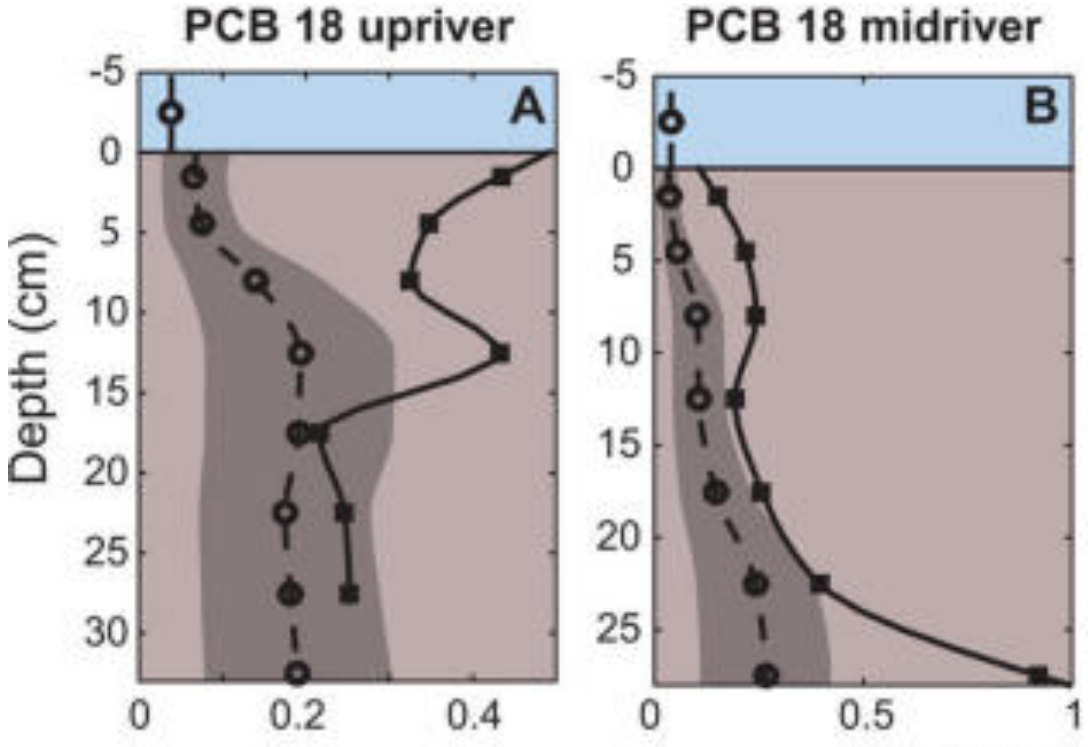
- SERDP/ESTCP/EPA guidance document (2017):
- use a PRC Calculation software developed by Gschwend et al. (MIT).
- www.epa.gov/superfund/superfund-contaminated-sediments-guidance-and-technical-support
- based on Fernandez et al. (2009), and Appell et al. (2014).
- Works well, except for AC-addition in field



Making sense of the data

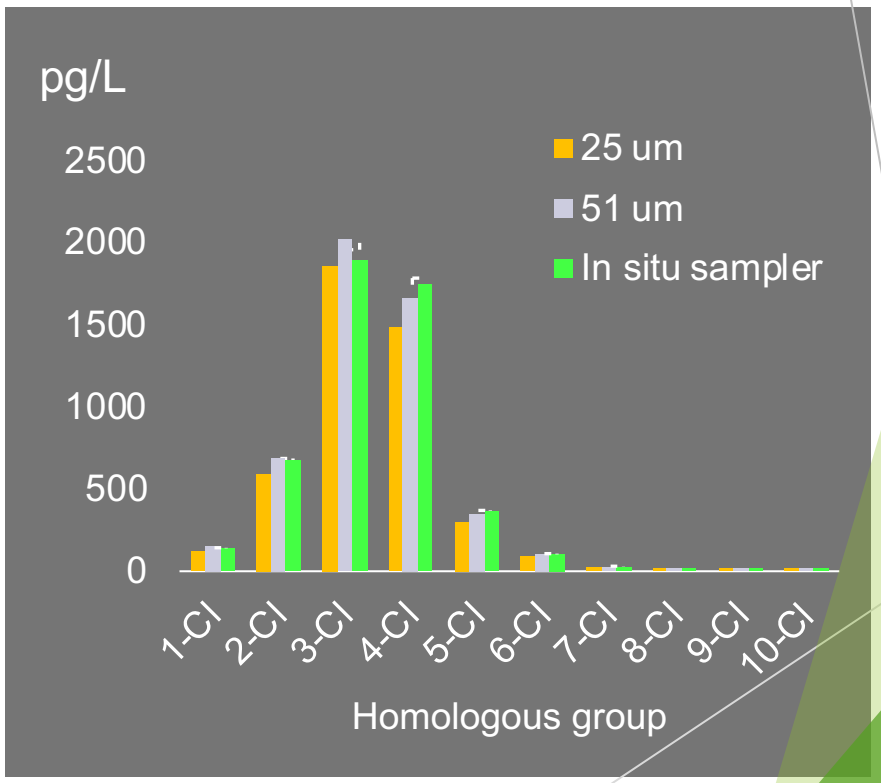
- Comparison of In situ vs Ex situ approaches:

Lower Duwamish River (WA)



(Apell et al, *2018*)

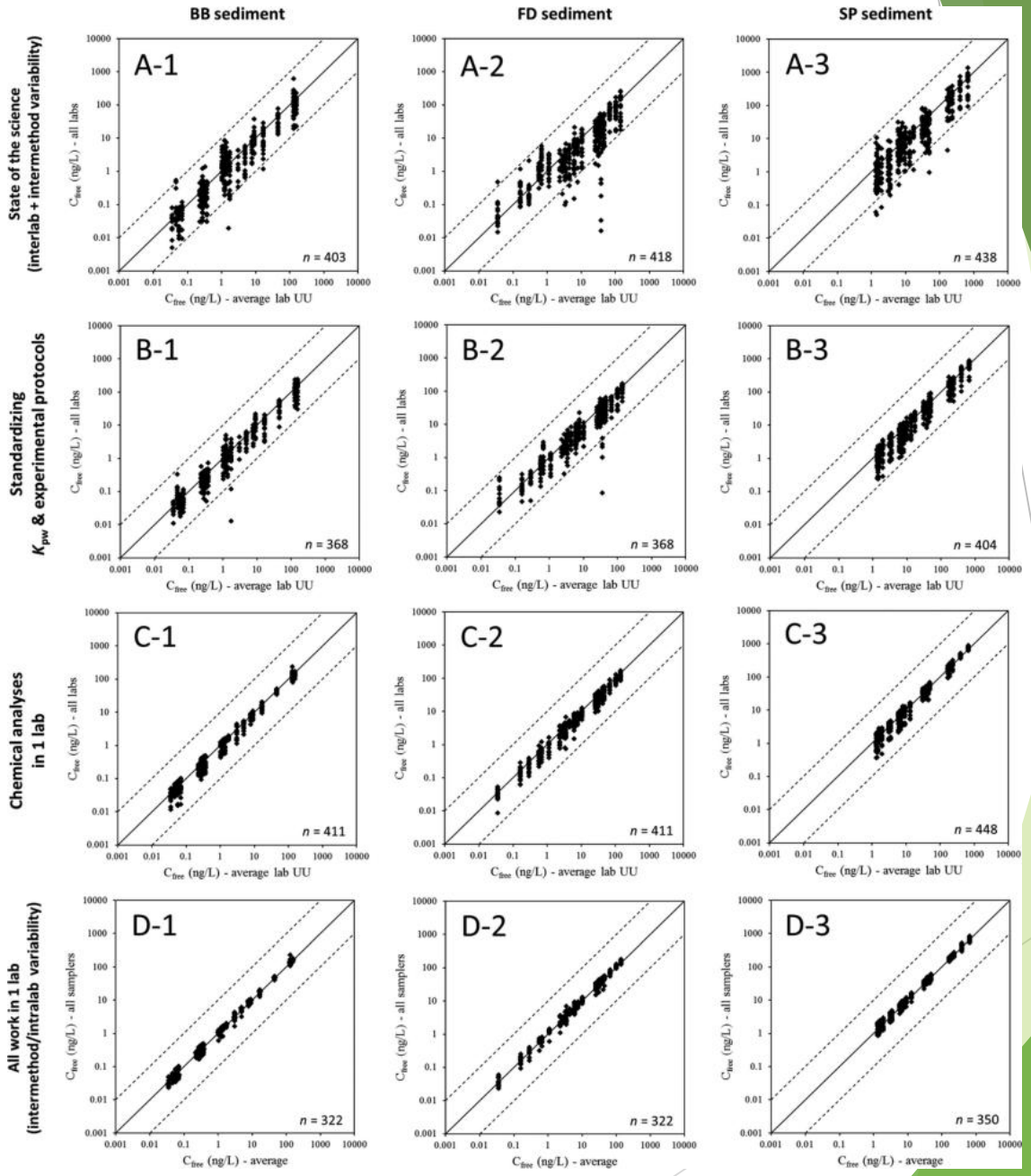
Passaic River (NJ)



(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)

$$C_{free} = \frac{C_{PS}^{\infty}}{K_{PW}} \quad (1)$$

$$C_{free} = \frac{C_{PS}^{t}}{K_{PW} \times (1 - e^{-k_e t})} \quad (2)$$

$$f_{ret} = e^{-R_s \times t/m_p \times K_{PW}} \quad (4)$$

$$C_{free} = \frac{C_{PS}^{t} \times m_p}{R_s \times t} \quad (5)$$

$$\frac{\partial C_{PS}}{\partial t} = D_{PE} \frac{\partial^2 C_{PS}}{\partial x^2} \quad \text{for } 0 < x < l \quad (6)$$

$$\frac{\partial C_{WBL}}{\partial t} = D_W \frac{\partial^2 C_{WBL}}{\partial x^2} \quad \text{for } 1 < x < l + b \quad (7)$$