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# Measuring Freely Dissolved Water Concentrations of PCBs Using Passive Samplers and Performance Reference Compounds (PRCs)

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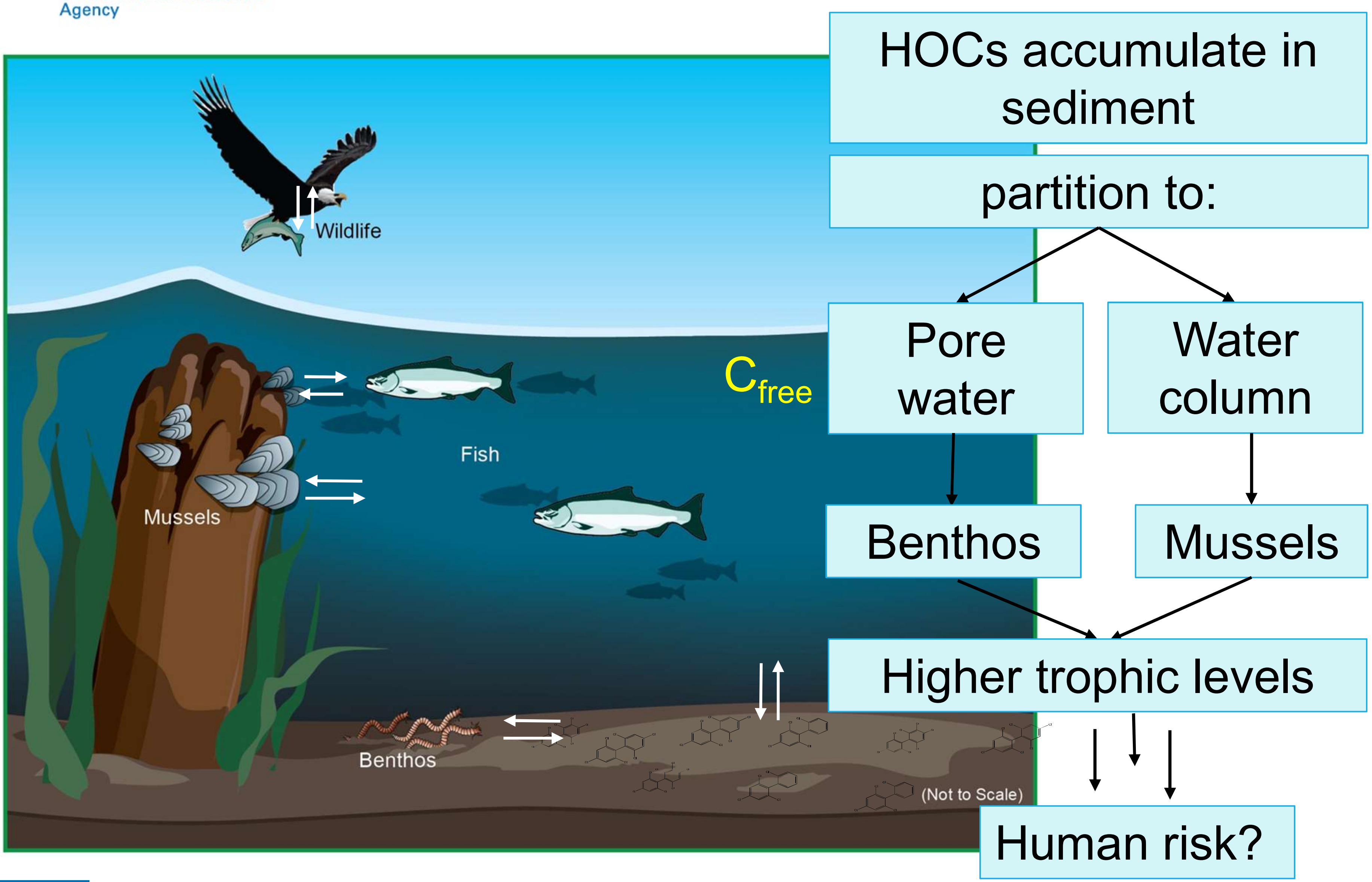
# Introduction



# $C_{free}$

What is $C_{free}$?

- dissolved and bioavailable HOC concentration in water
- often pg/L – ug/L range
- used as an exposure measure in risk management

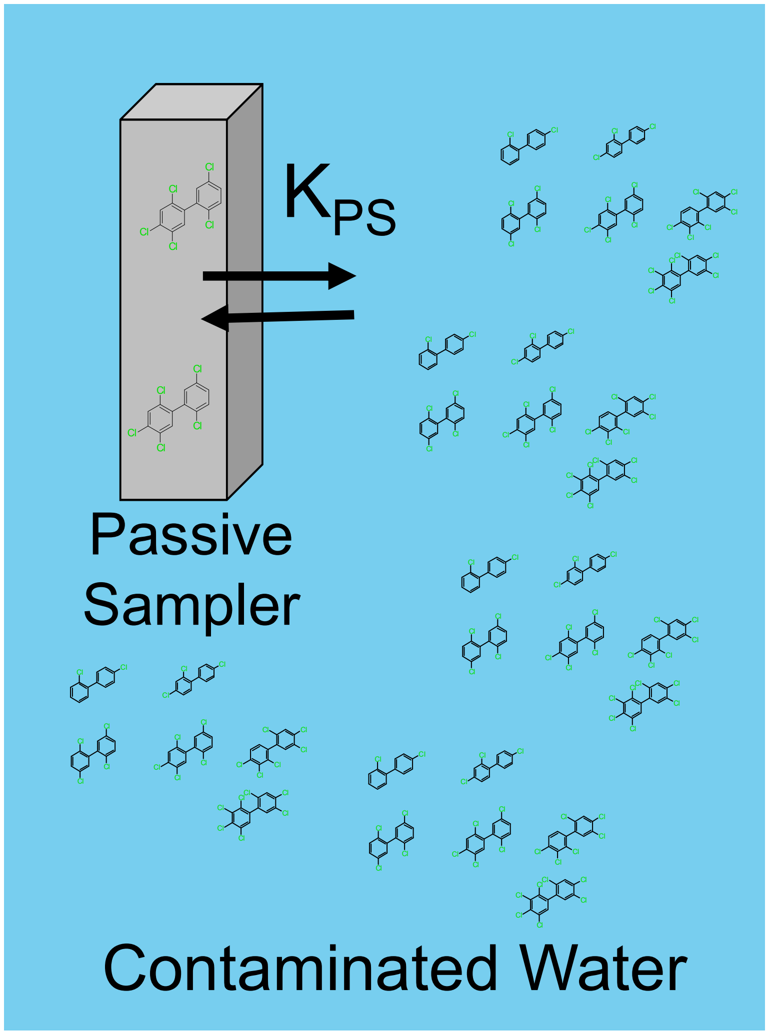
## How do you measure $C_{free}$?

### Passive Sampling

- PCBs
- PAHs
- DDTs
- Dioxins
- PBDEs

- accumulate HOCs proportionately to bioaccumulation

# Passive Sampling




- Hydrophobic organic compounds (HOCs) concentrate in hydrophobic sampler

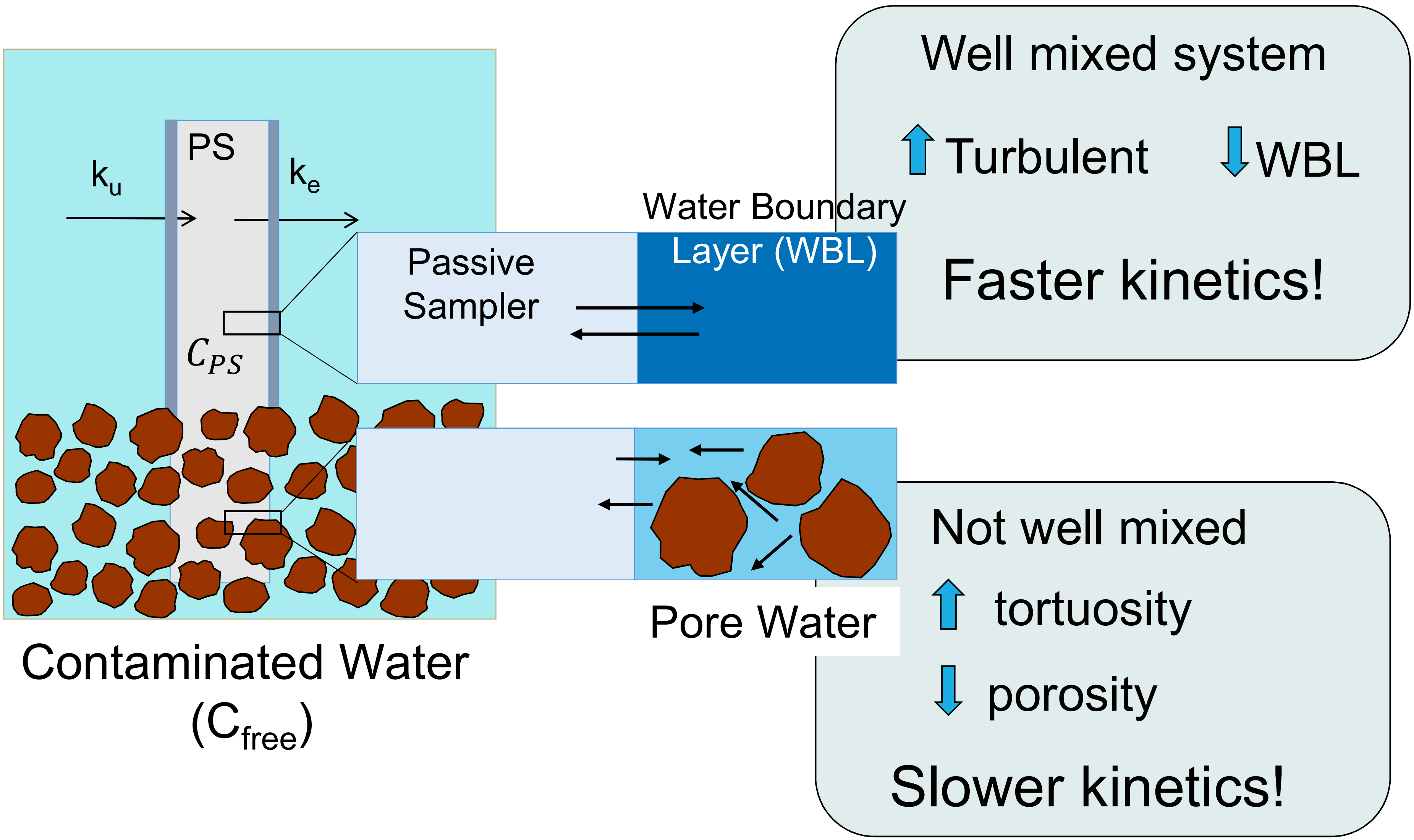
- Compounds will equilibrate ($K_{PS}$):

$$K_{PS} = \frac{C_{PS}^{\infty}}{C_{free}}$$

- Must know $K_{PS}$

- Must be at equilibrium (takes weeks-months)

# In Situ Passive Sampling



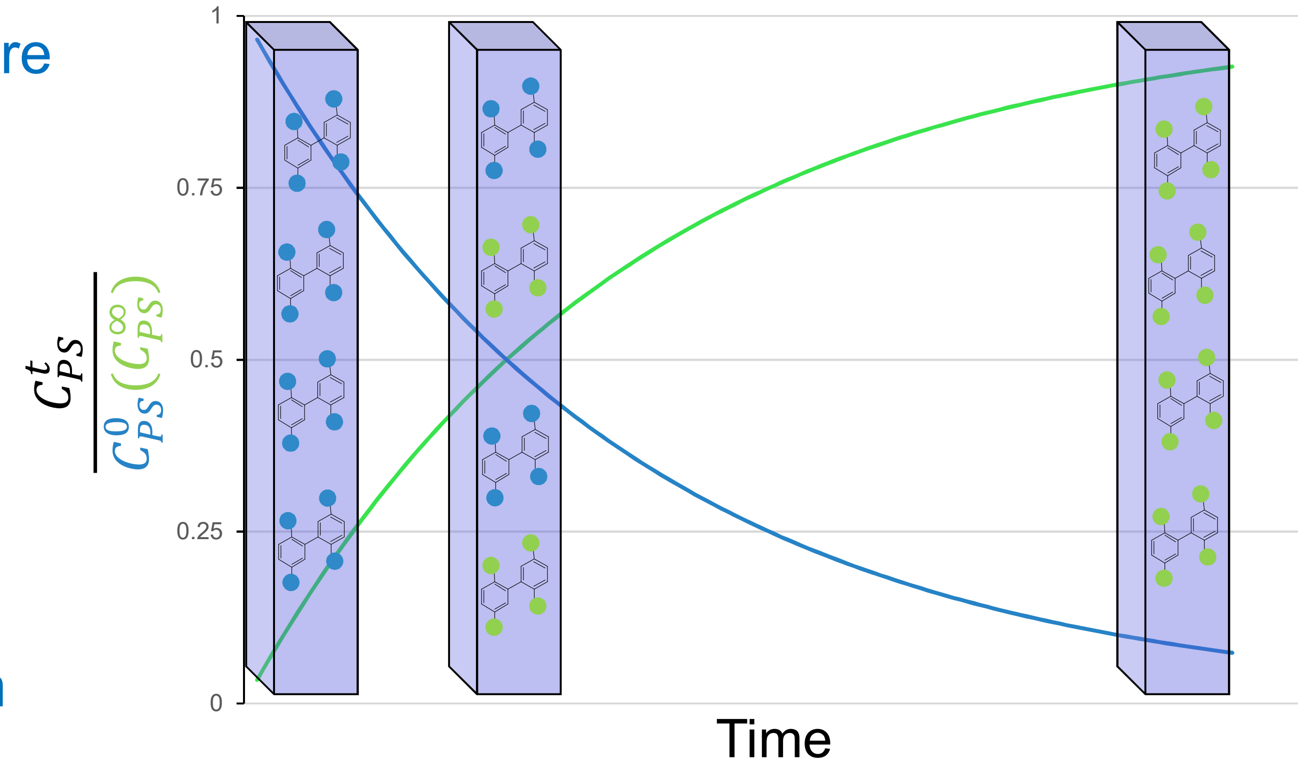
# Performance Reference Compounds (PRCs)

PRC:

- Loaded into PS before deployment
- Similar to the target HOCs
- Non-interfering

- Ensure equilibrium
- Correct for non-equilibrium using fractional equilibrium ($f_{eq}$)

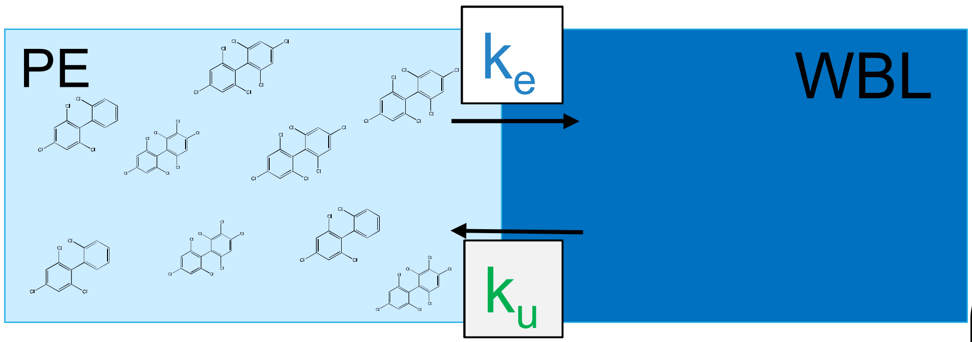
$$f_{eq} = 1 - \frac{C_{PS}^{t}}{C_{PS}^{0}}$$

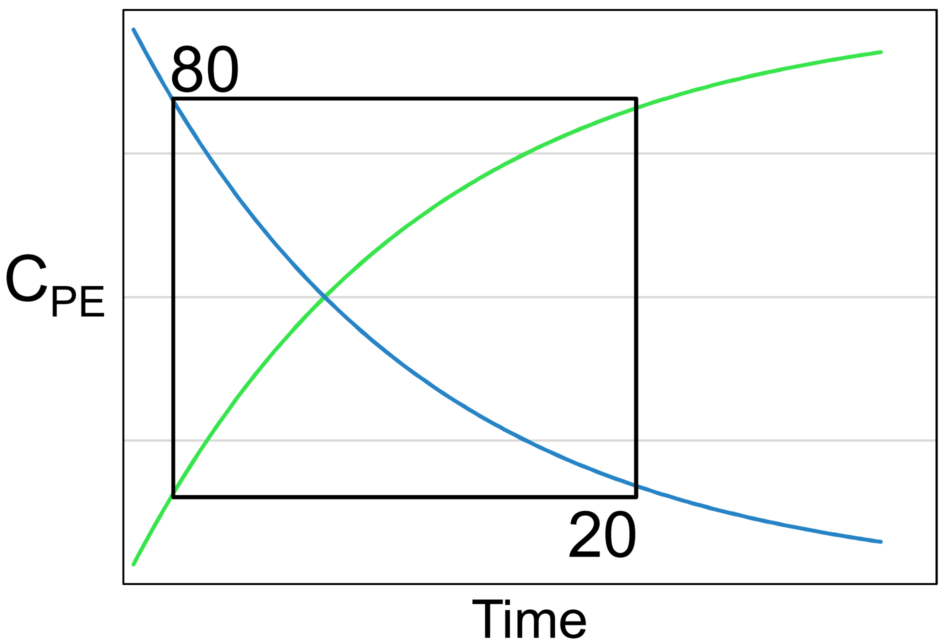



$\frac{C_{PS}^{t}}{C_{PS}^{0}} = 1$ $\frac{C_{PS}^{t}}{C_{PS}^{0}} = .5$ $\frac{C_{PS}^{t}}{C_{PS}^{0}} = 0$

$f_{eq} = 0$ $f_{eq} = .5$ $f_{eq} = 1$

# $1^{st}$ Order Model




**The model:**

$$\frac{dC_{PS}}{dt} = k_u C_{free} - k_e C_{PS}$$

**The Solution:**

$$C_{PS} = \frac{k_u}{k_e} C_{free}\left(1 - e^{-k_e t}\right)$$

$$k_e = -\frac{\ln\left(C_{PRC}^{t} / C_{PRC}^{0}\right)}{t}$$

**The drawback:**

Need a PRC for each HOC

Limited sample range “80:20”

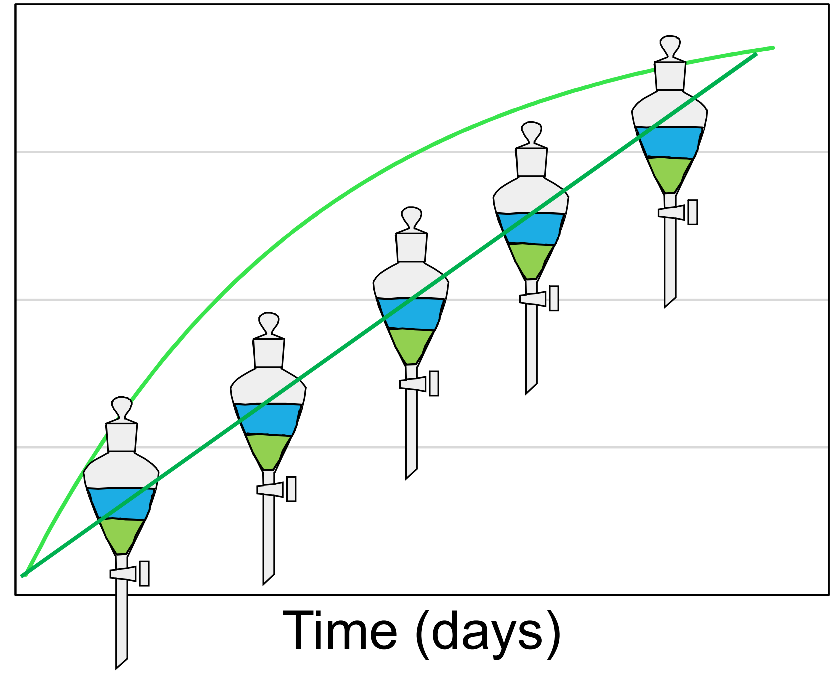
# Sampling Rate ($R_s$) Model

- $R_s$ - the volume of contaminated water "extracted" over time (L/day)

Model:

$$R_s = k_e K_{PW} m_{PS}$$

$$f = e^{\left(\frac{-R_s t}{K_{PW} m_{PS}}\right)}$$




- Interpolating $R_s$ not always easy
- Challenging depending on phase uptake control.

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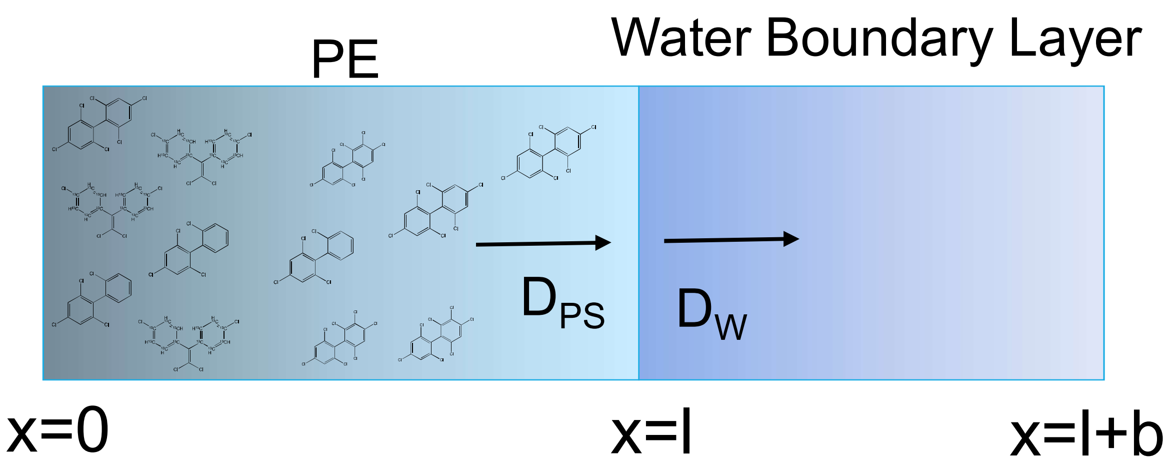
# Diffusion Model




## The model:

$$D_{PS}\frac{\delta C_{PS}}{\delta t} = D_W \frac{\delta^2 C_W}{\delta x}$$

$$\frac{\delta C_{PS}}{\delta t} = D_{PS}\frac{\delta^2 C_{PS}}{\delta x^2}$$

## The Solution:

$$\frac{\hat{C}_{PRC}^{t}}{C_{PRC}^{0}} = \frac{1}{s} - \left\{ s^{3/2}\left( \frac{K_{PS} tanh \frac{\hat{\partial}\sqrt{s}}{\sqrt{\psi}}}{\sqrt{\psi}} + coth\sqrt{s} \right) \right\}^{-1}$$

## The drawback:

Requires $D_{PS}$ and $D_W$, and solution is in LaPlace space

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# There's a GUI for that!

Graphical User Interfaces (GUI) exist to help calculate $f_{eq}$ for these models

- $R_s$ model (excel spreadsheet)

www.rs.passivesampling.net/

- LDPE in sediments

www.serdp-estcp.org ER-200915

- LDPE in water column
  - Coming Soon!
- SPME

www.depts.ttu.edu/ceweb/groups/reiblesgroup/downloads.html

To Use:

- $f_{eq}$ or $\frac{C^t_{PRC}}{C^0_{PRC}}$
- PS details
- Deployment time
- Porosity
- GUI will give $f_{eq}$ *for target HOCs!*

$$C_{free} = \frac{C^t_{PS}}{K_{PS} * f_{eq}}$$

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# Study Objectives

- Measure $C_{free}$ suite of PCBs in New Bedford Harbor water column
- Determine precision of the PCB measurements using passive sampling
- Determine the best model for estimating equilibrated passive sampler concentrations

# Study Design

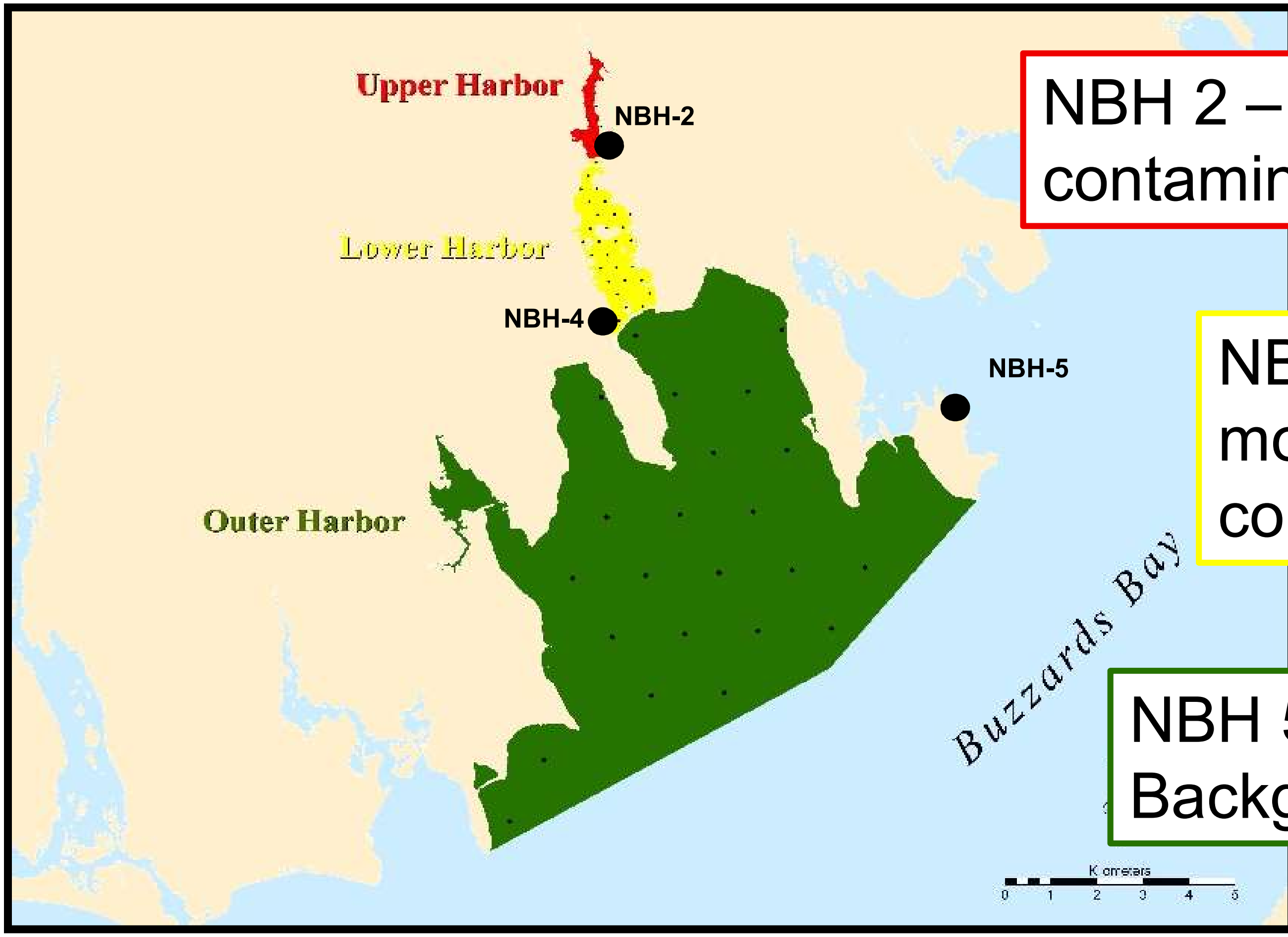
LDPE thicknesses

- 12.7 µm
- 25.4 µm
- 50.8 µm
- 76.2 µm

- LDPE were pre-loaded with six $^{13}C_{12}$-PCBs as PRCs Booij et al. (2002)
- One congener for each homolog $Cl_2$ – $Cl_7$

- Four different thicknesses = different $f_{eq}$ per sampler and congener
- Different thicknesses allowed comparisons within a model

# New Bedford Harbor, MA, USA

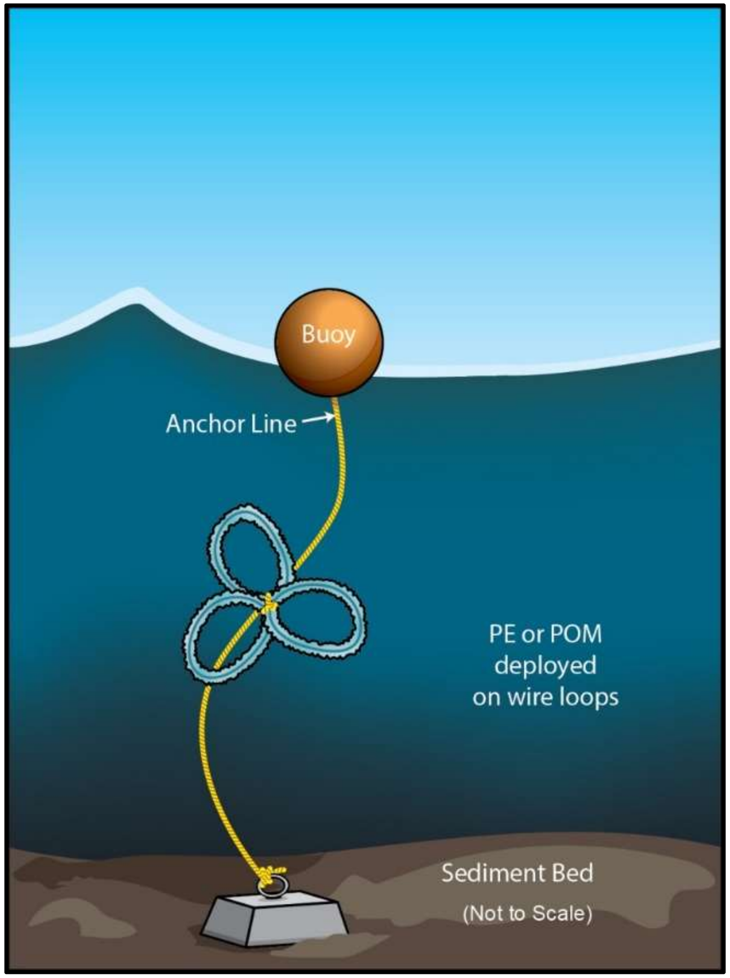



NBH 2 – Highly contaminated

NBH 4 – moderately contaminated

NBH 5 – Background

# Deployment




- LDPE deployed in triplicate
- 1 m above sediment surface
- 28 d deployment

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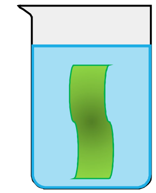
# Extraction

| | |
|---|---|
| 1 | Extract passive sampler |
| 2 | Repeat extraction 2-3x |
| 3 | Combine extracts |
| 4 | Concentrate extract |
| 5 | Transfer to storage vial |
| 6 | Analyze GC-MS |

1.


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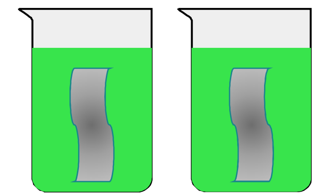

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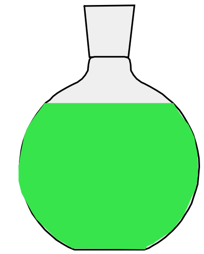
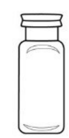


4.

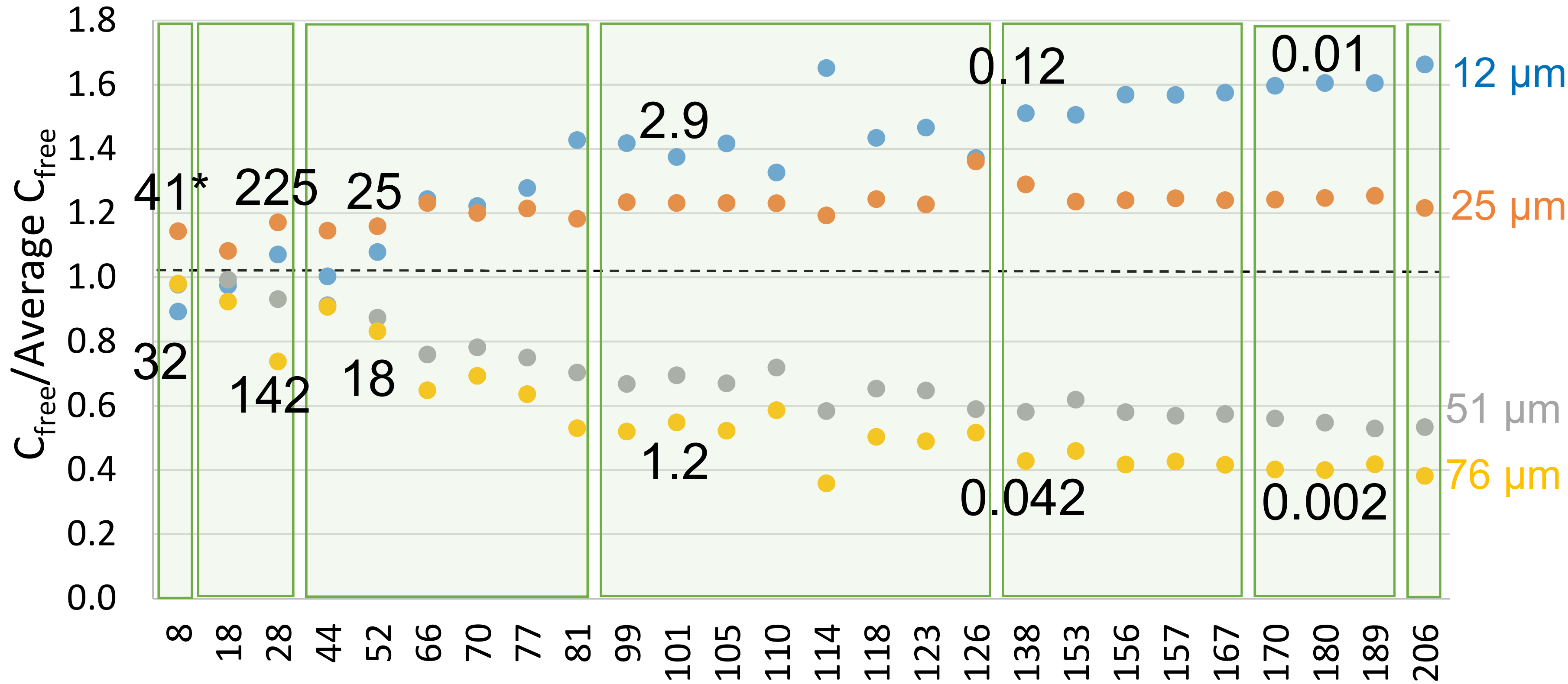


5.


6.

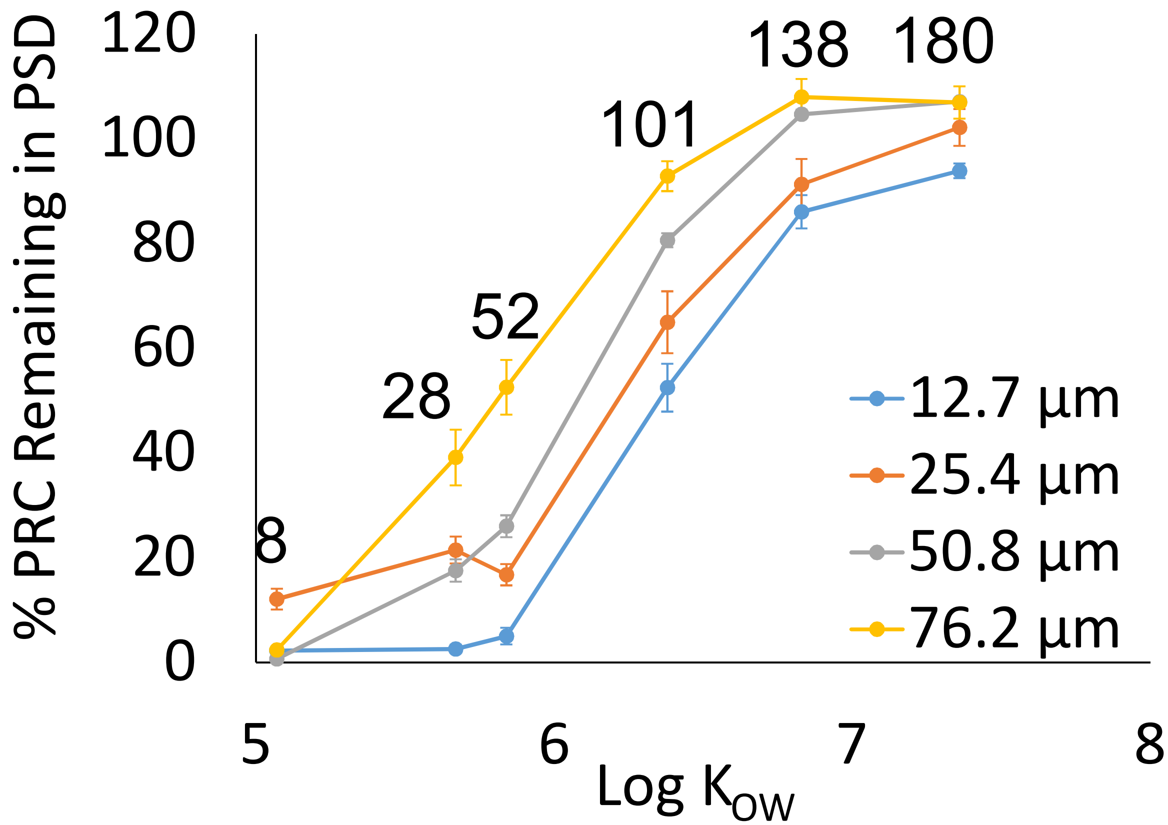

| Surrogate Standard | Average Recovery |
|---|---|
| $^{13}$C-PCB 9 | 51±9 |
| $^{13}$C-PCB 118 | 83±7 |
| $^{13}$C-PCB 188 | 76±6 |

# Are you at Equilibrium?



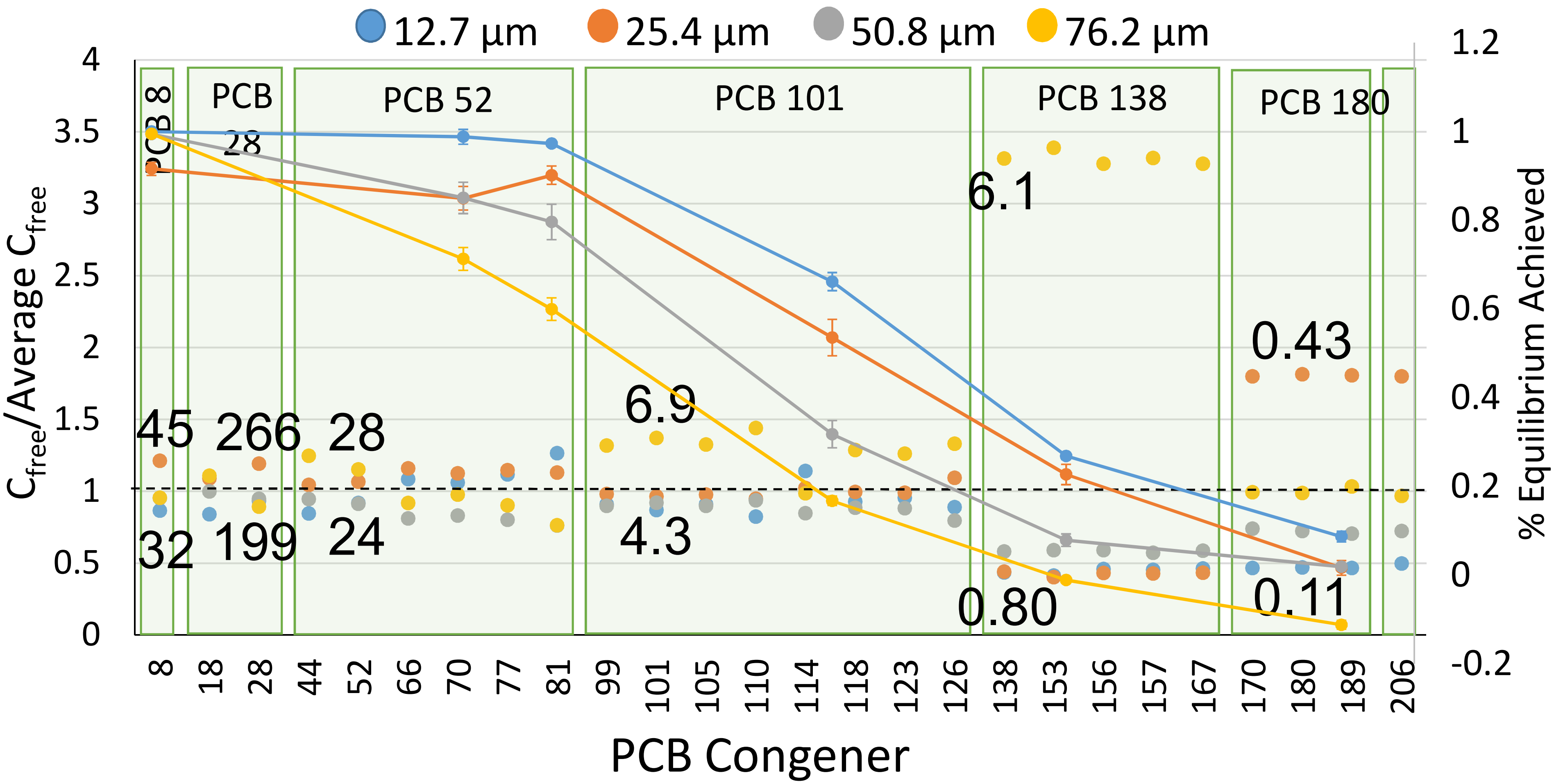

* $C_{free}$ (ng/L)

# PRC Results



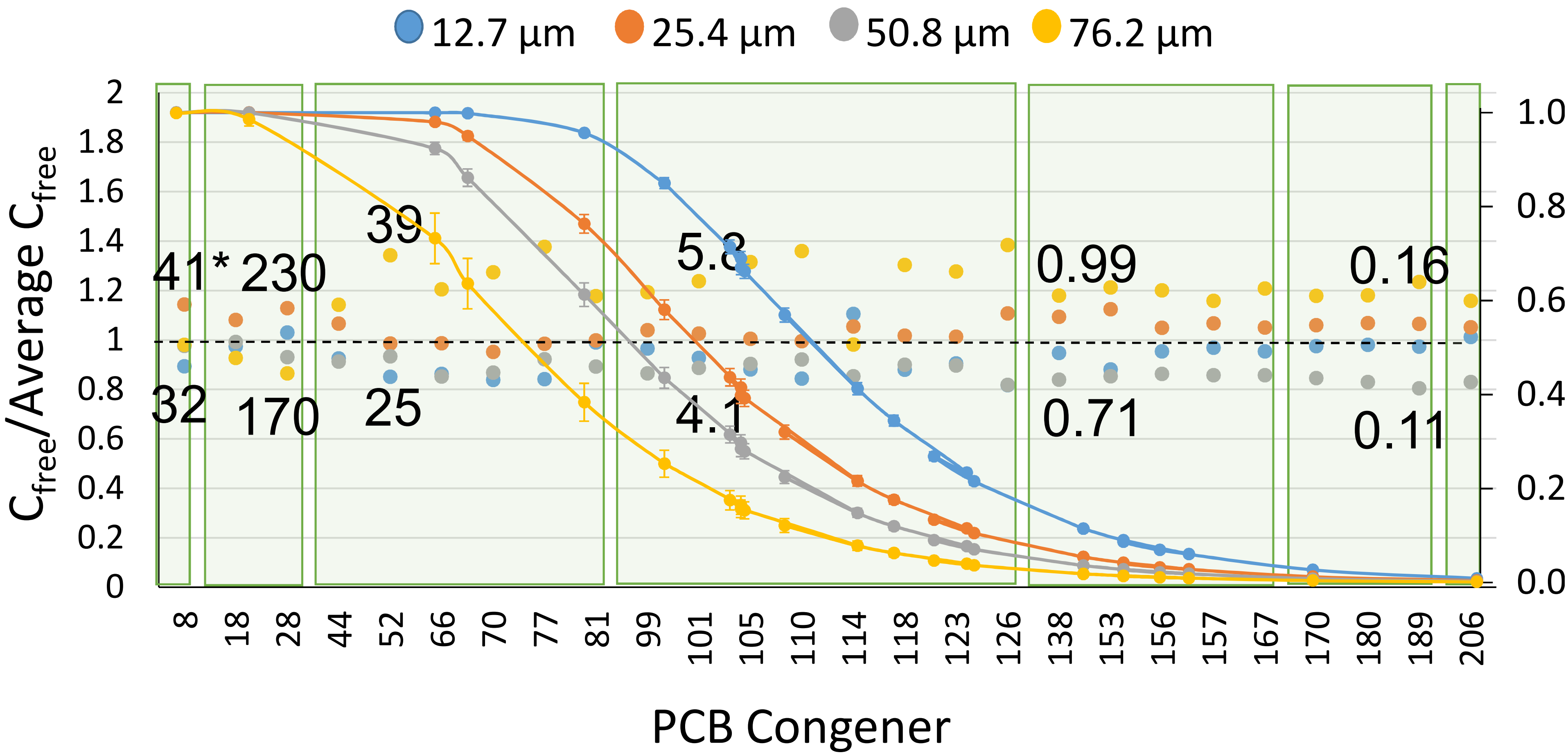

- Smaller PRCs – faster kinetics
- Thicker passive sampler – retained more PRC

# 1st Order Model



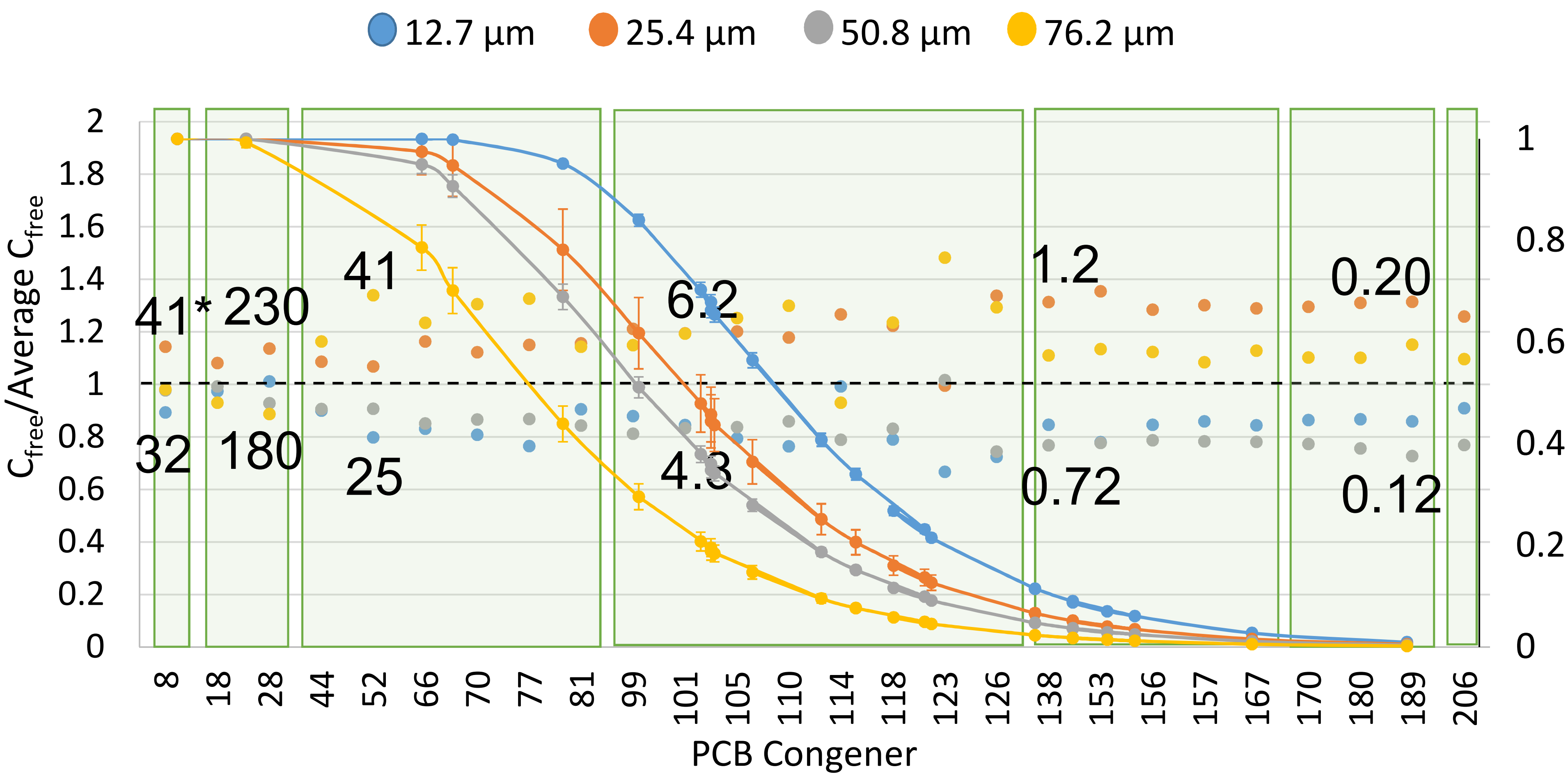

* $C_{free}$ (ng/L)

# Rs Model



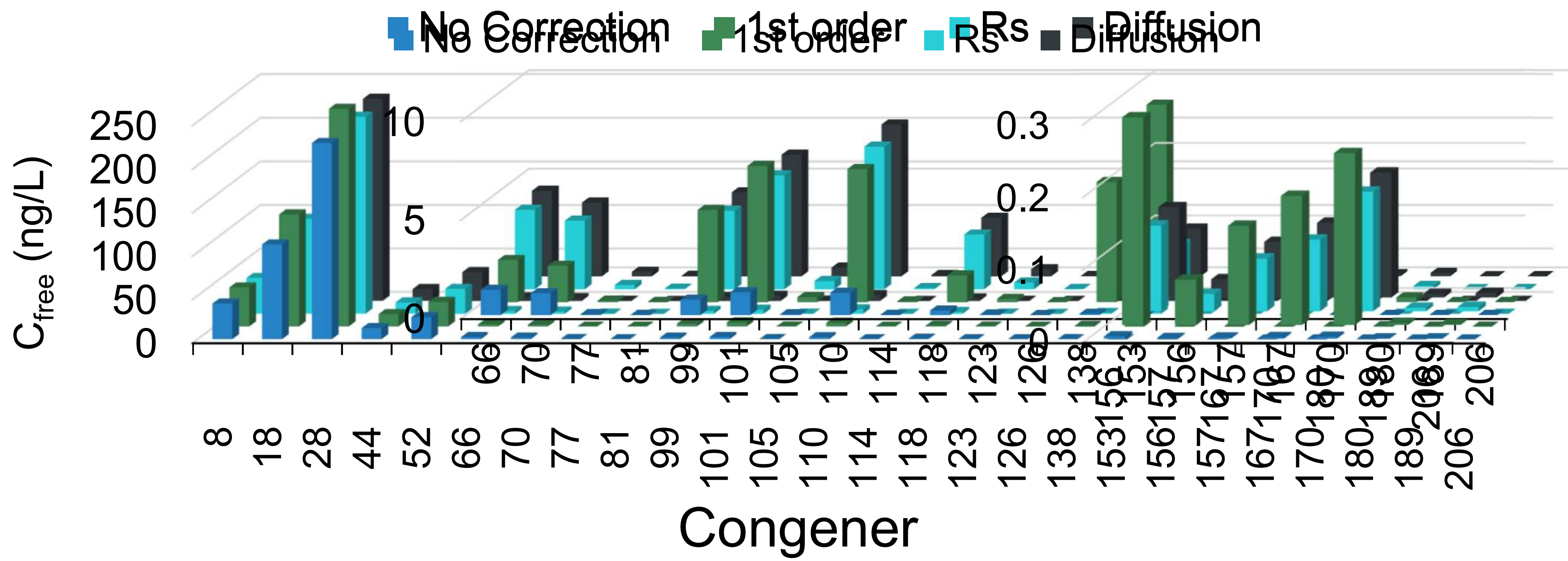

* $C_{free}$ (ng/L)

# Diffusion Model




* $C_{free}$ (ng/L)

# Water Concentrations




Using 76µm LDPE data:

- Most water soluble PCBs – highest $C_{free}$
- As compounds get bigger model correction increases
- $C_{free}$ was measured from $1.07 \times 10^{-5}$ – 200 ng/L

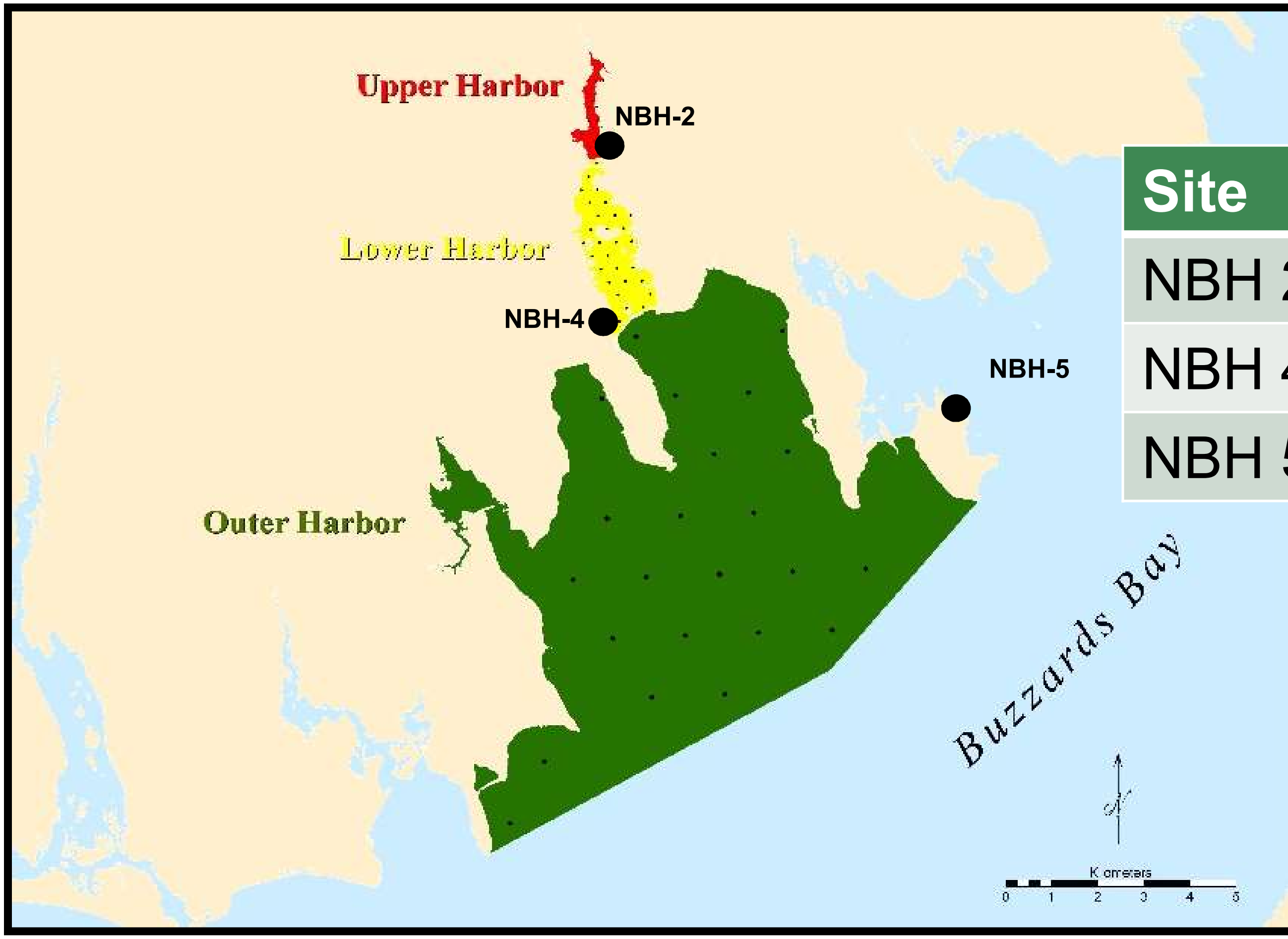
# Total PCB trends

$C_{free}$ ΣPCB (ng/L) by model and sampler

| LDPE Thickness | No Correction | 1st order | Rs | Diffusion | Average |
|---|---|---|---|---|---|
| 12.7 | 385 | 396 | 395 | 396 | 396±0.04% |
| 25 | 427 | 505 | 444 | 463 | 470±5% |
| 50 | 351 | 423 | 382 | 388 | 398±5% |
| 76 | 305 | 456 | 387 | 401 | 415±7% |
| Average | 367±12% | 445±9% | 402±6% | 412±7% | |

- RSD increased with thickness
- 1st order model had the highest RSD

# Final $C_{free}$




| Site | ΣPCB* |
|---|---|
| NBH 2 | 400 - 500 (ng/L) |
| NBH 4 | 36 – 48 |
| NBH 5 | 0.14 – 0.28 |

*Non corrected data not included

# Conclusions

- Using LDPE, the measurement of PCB $C_{free}$ is viable and precise
- Total PCB agreed better between models using the same dataset than between a single model with different datasets
  - Model may be chosen by laboratory – $R_S$ or Diffusion recommended
- Results where $f_{eq}$ is near zero should be used with discretion

# Acknowledgments

Thank you:

Barbara Bergen
Don Cobb
Michaela Cashman
Mark Cantwell
Dave Katz

# Questions?

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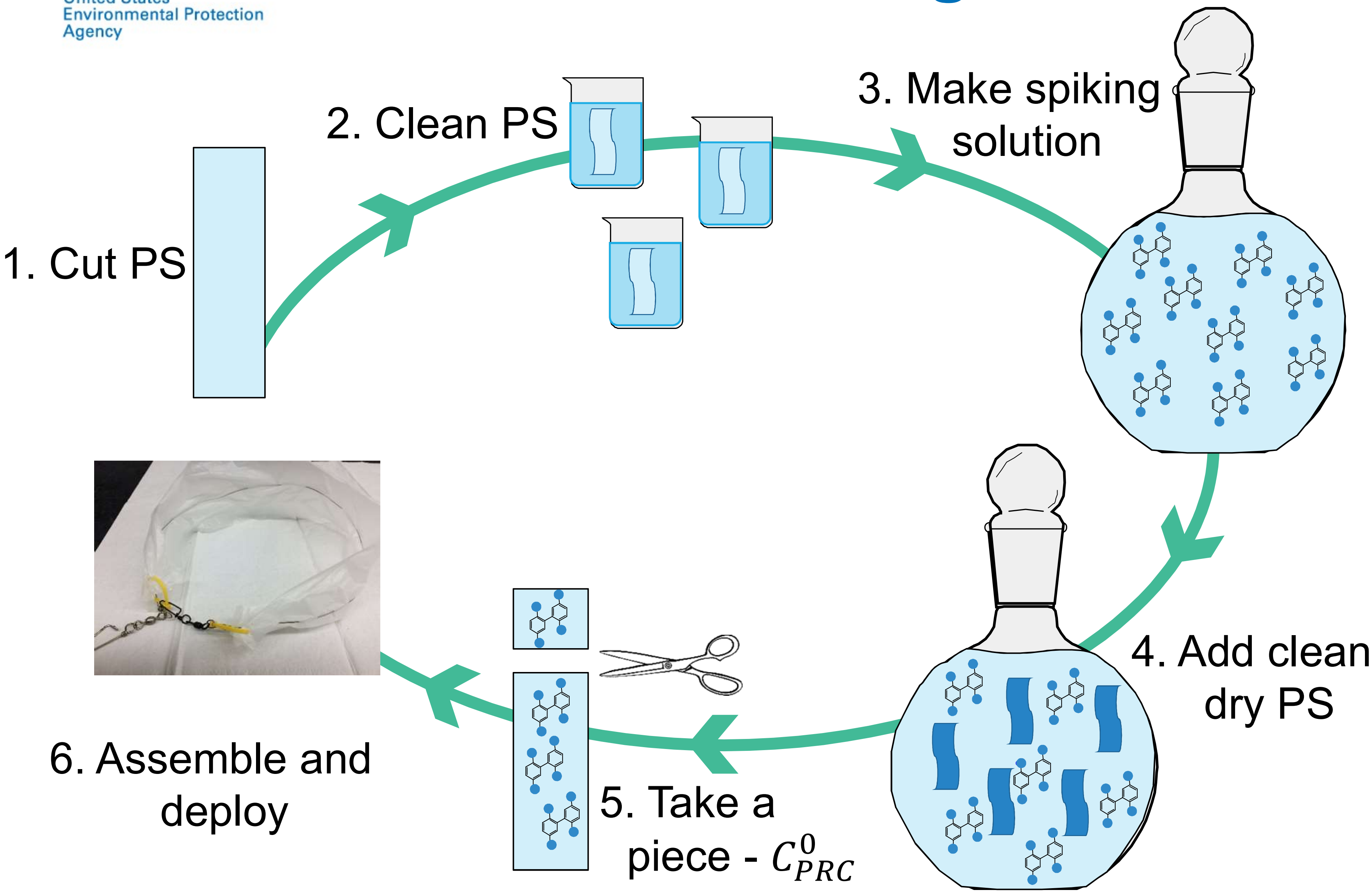
# PRC Loading



# Passive Samplers

Solid Phase Microextraction (SPME)
- Polydimethylsiloxane (PDMS)
- solventless workup
- fragile

Semi-Permeable Membrane Device (SPMD)
- lipid filled tubing
- susceptible to breakage
- complicated extraction and analysis

Thin Sheets
- Low Density Polyethylene (LDPE)
- Polyoxymethylene (POM)
- Silicone

- less sensitive to breakage
- simple geometry
- economical and commercially available