# Statistical comparison of performance reference compound (PRC)-based methods for calculating $C_{free}$

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## BACKGROUND

- Ideally, during a passive sampling deployment – all target contaminants achieve equilibrium with the passive sampler:
  - Freely dissolved concentration ($C_{free}$) can be calculated:

$$C_{free} = \frac{C_{Passive\ Sampler}}{K_{Passive\ Sampler-Water}} \qquad [1]$$

$C_{Passive\ Sampler}$ = concentration measured in passive sampler

$K_{Passive\ Sampler\text{-}Water}$ = partition coefficient relating polymer and water concentrations

- In reality, during a passive sampling deployment – many target contaminants do not achieve equilibrium with the passive sampler
  - Under *in situ* conditions & for larger, high octanol-water ($K_{OW}$) target contaminants
- If Equation 1 is used, results in under-estimating $C_{free}$
  - Under-estimating exposure and risk

## USE OF PRCS

- Performance Reference Compounds (PRCs) are an increasingly common tool for calculating adjustment factors for non-equilibrium conditions
  - For example, the fractional equilibrium ($f_{eq}$)
- Using PRCs and feq, the freely dissolved concentration ($C_{free}$) can be calculated:

$$C_{free} = \frac{C_{Passive\ Sampler} * \frac{1}{feq}}{K_{Passive\ Sampler-water}} \qquad [2]$$

under non-equilibrium conditions

- Currently, several models available for using PRC data to calculate $f_{eq}$
- This variety of models creates confusion for users as to which one(s) to apply
  - Users = risk assessors & remedial project managers at contaminated sites
  - Not necessarily passive sampling experts

## OBJECTIVES

- Generate a large passive sampler dataset and statistically compare the calculation of $C_{free}$ using four common PRC models
  - Use $C_{free}$ as the dependent variable
  - Examine effect of polymer thickness on 'rate' of achieving equilibrium
  - Hypotheses:
    - For a given contaminant:

$$H_0: C_{free}^{Model1} = C_{free}^{Model2} = C_{free}^{Model3} = C_{free}^{Model4}$$
$$H_1: C_{free}^{Model1} \neq C_{free}^{Model2} \neq C_{free}^{Model3} \neq C_{free}^{Model4}$$

- Recommend a model(s) for passive sampler users to apply

## MATERIALS AND METHODS

- Deployed (30 days) low density polyethylene (PE) samplers at three water column stations in the PCB-contaminated New Bedford Harbor Superfund site (MA, USA) (Figure 1):
  - Three thicknesses: 12, 51 and 76 μm
  - Located samplers one meter above bottom in the water column (Figure 2)
  - 9 sets of possible comparisons – here we will focus on NBH2
- Target contaminants were 27 PCB congeners
- Six $^{13}C$-labelled PCB PRCs: 8, 28, 52,101,138 and 180
- Triplicate replication per station: ANOVA with Fisher's Test used to detect differences

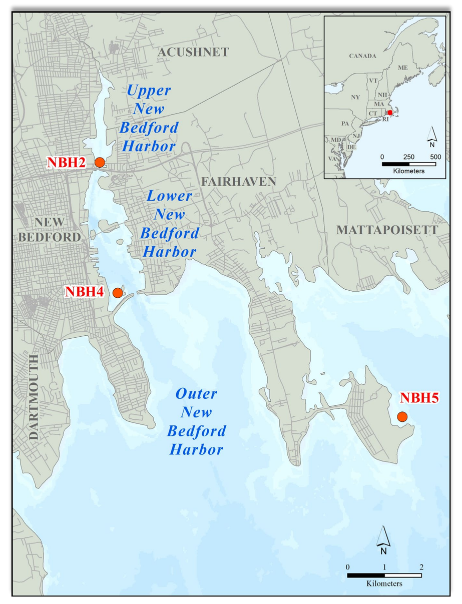


Figure 1: Sampling stations in New Bedford Harbor Superfund site (MA, USA)

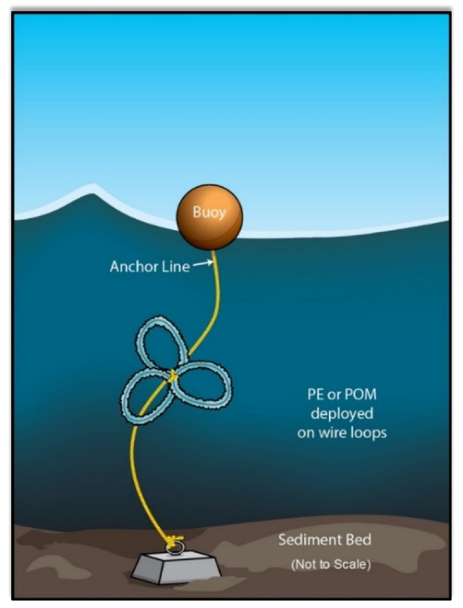


Figure 2: Passive sampler deployment configuration

- Four models compared (citation below):

(1) Equilibrium assumed: Target contaminants assumed to achieved equilibrium

$$C_{free}^{\infty} = C_{free}^{t}$$

(2) First order model: PRC data fit to simple first order kinetics model to estimate fractional equilibrium ($f_{eq}$)
(Adams et al. 2007)

$$C_{free}^{\infty} = \frac{C_{PS}}{K_{PS}} * (1 - e^{-k_e t})$$

(3) Exchange rate-based model: First order model applies PRC data to calculate corrected exchange rates ($R_s$) with a nonlinear least squares (NLS) fit
(Booij and Smedes 2010)

$$C_{free}^{\infty} = \frac{C_{PS} * m_p}{R_s * t}$$

(4) Diffusion-based model: Rate of PRC diffusion through polymer and water used to determine magnitude of $f_{eq}$
(Fernandez et al. 2009, Thompson et al. 2015)

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

Adams RG, R Lohmann, LA Fernandez, JK MacFarlane, PM Gschwend. Polyethylene Devices: Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments. *Environmental Science and Technology* **2007**, *41*: 1317–1323.

Booij K, F Smedes. An Improved Method for Estimating in Situ Sampling Rates of Nonpolar Passive Samplers. *Environmental Science & Technology* **2010,** *44:* 6789–6794.

Fernandez LA,CF Harvey, PM Gschwend. Using Performance Reference Compounds in Polyethylene Passive Samplers to Deduce Sediment Porewater Concentrations for Numerous Target Chemicals. *Environmental Science & Technology* **2009,** *43:* 8888–8894.

Thompson JM, CH Hsieh, RG Luthy. Modeling Uptake of Hydrophobic Organic Contaminants into Polyethylene Passive Samplers. *Environmental Science & Technology* **2015,** *49:* 2270–2277.

## RESULTS AND DISCUSSION

### $C_{free}$ Data

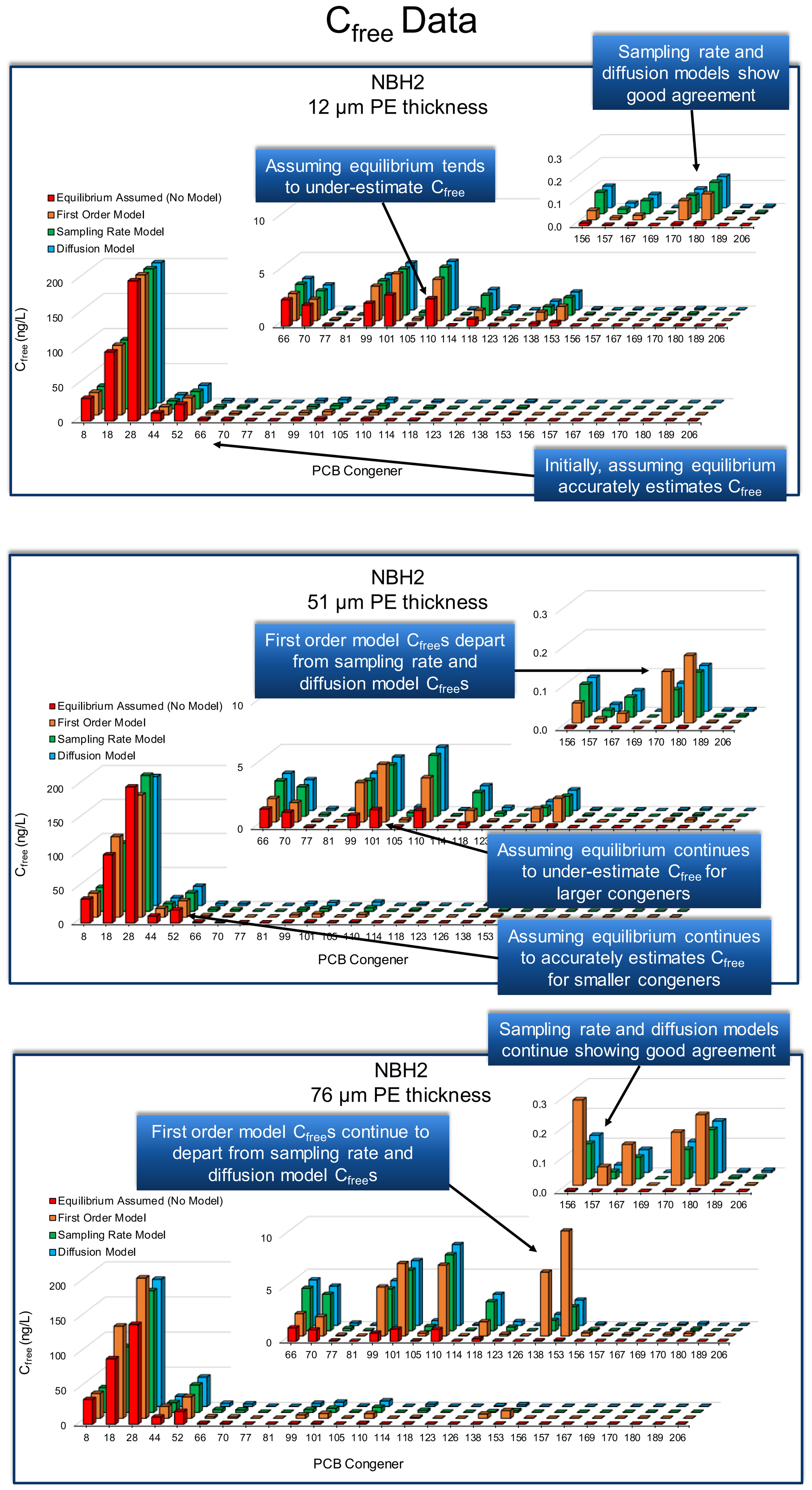


Figure 3: $C_{free}$ calculated by the four models for passive samplers deployed at New Bedford Harbor Station 2 presented by thickness of the PE (12, 51 and 76 μm)

### Statistical Analysis

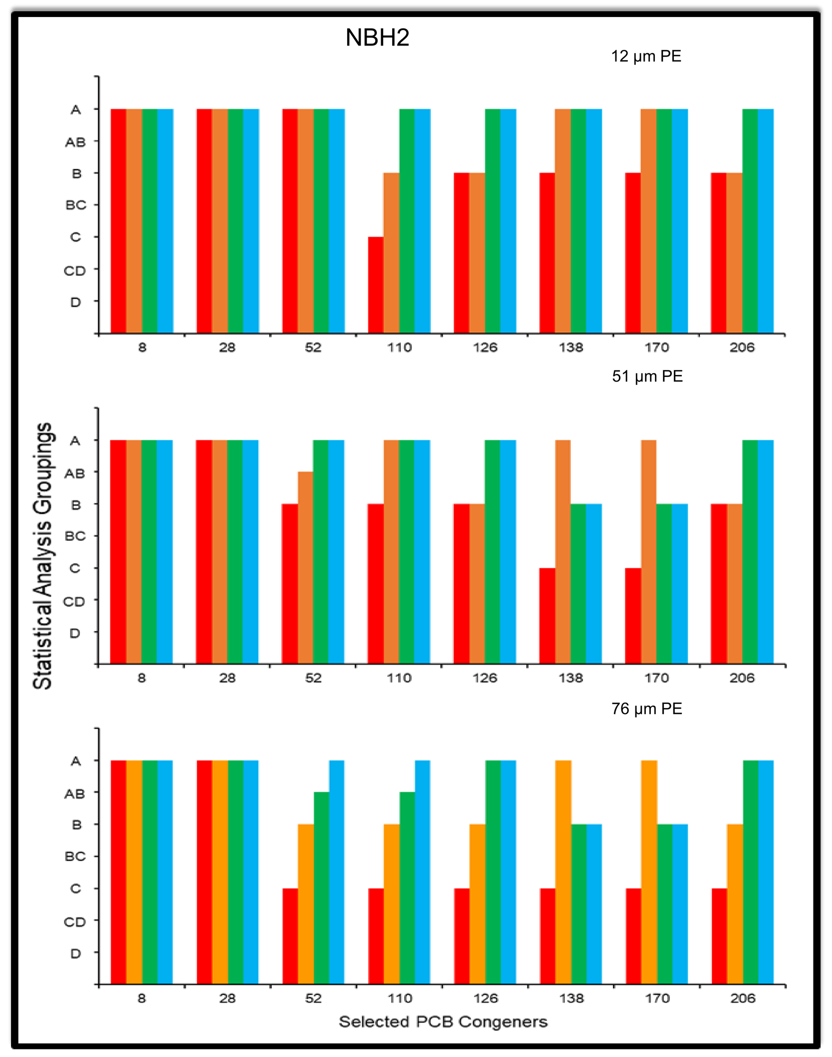


Figure 4: Subset of New Bedford Harbor Station 2 statistical analyses results for selected PCB congeners by polymer thickness

- All models generated statistically-identical $C_{free}$s (12%–23% entire data set) (Figure 4):
  - % decreases as PE thickness and congener molecule weight increase
- First order, sampling rate and diffusion models resulted in statistically-identical $C_{free}$s (12% to 42% entire data set)
- Assuming equilibrium results in significant under-estimations of $C_{free}$ (77%–88% entire data set)
- Sampling rate and diffusion models produced statistically-identical $C_{free}$s (85–100% entire data set)

## SUMMARY

- In most cases, the sampling rate and diffusion models resulted in statistically-identical $C_{free}$s
- More validation of modelled $C_{free}$ values is needed
  - Available comparable data suggests diffusion and sampling rate models provide accurate estimates of $C_{free}$
- Recommend use of diffusion and sampling rate models for analyzing PRC data to calculate $C_{free}$
  - Models available in spreadsheet and graphic user interfaces (GUI)
  - Diffusion model GUIs available on-line (e.g., U.S. EPA & SERDP websites)