Time Scale of Integration in Equilibrium Passive Sampling

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Ghosh et al., 2025

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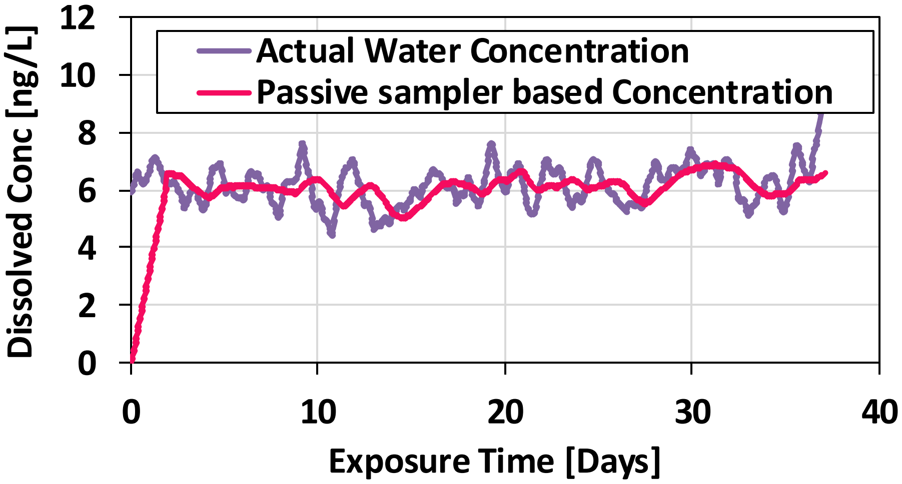
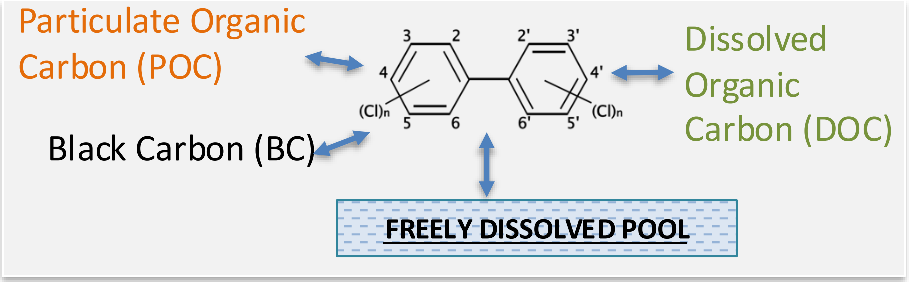
INTRODUCTION

PASSIVE SAMPLING



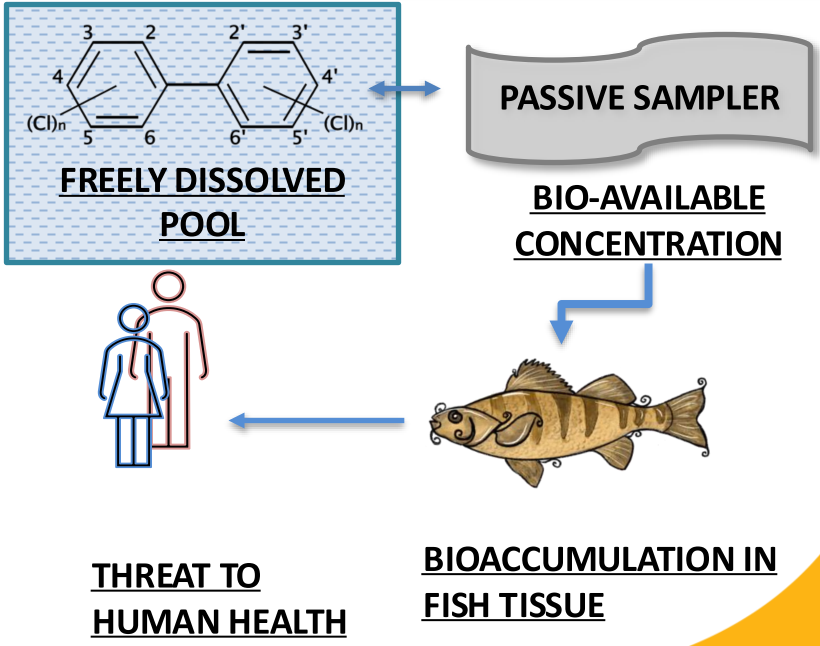


Particulate Organic Carbon (POC)

Black Carbon (BC)

Dissolved Organic Carbon (DOC)

FREELY DISSOLVED POOL



FREELY DISSOLVED POOL

PASSIVE SAMPLER

BIO-AVAILABLE CONCENTRATION

BIOACCUMULATION IN FISH TISSUE

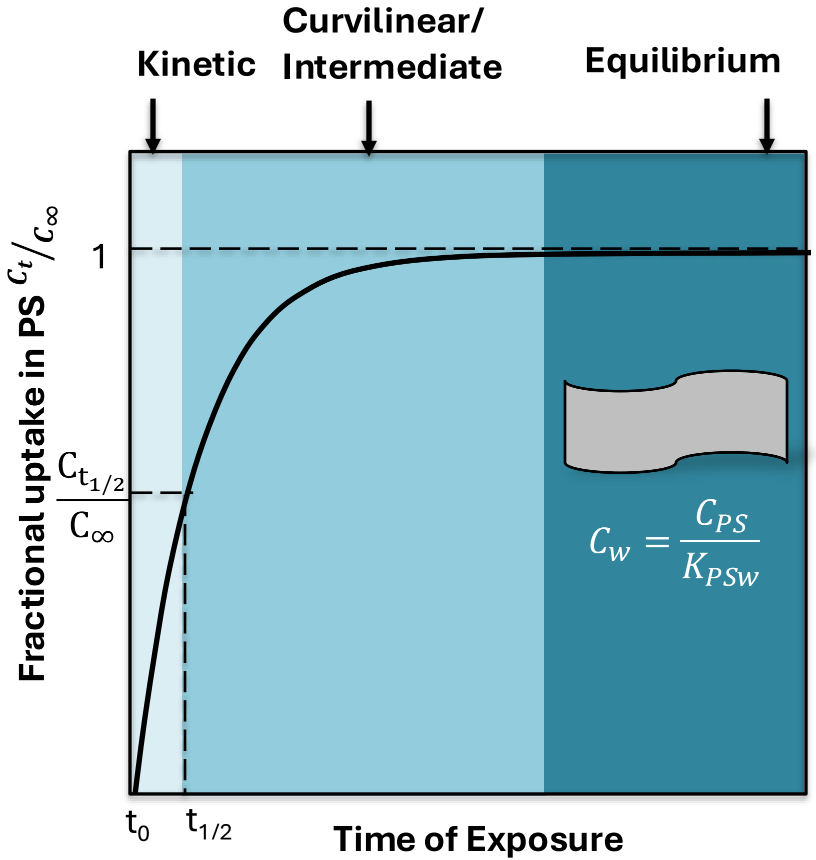
THREAT TO HUMAN HEALTH

Passive sampling:

- Allows measurement of the **freely dissolved concentrations** (thermodynamic driving force for bio uptake).
- Avoids need for **collecting large volume grab samples** to reach very **low detection limits** of analytical instruments [ng/L to pg/L]
- **Time averaged** measurement instead of a snapshot in time.

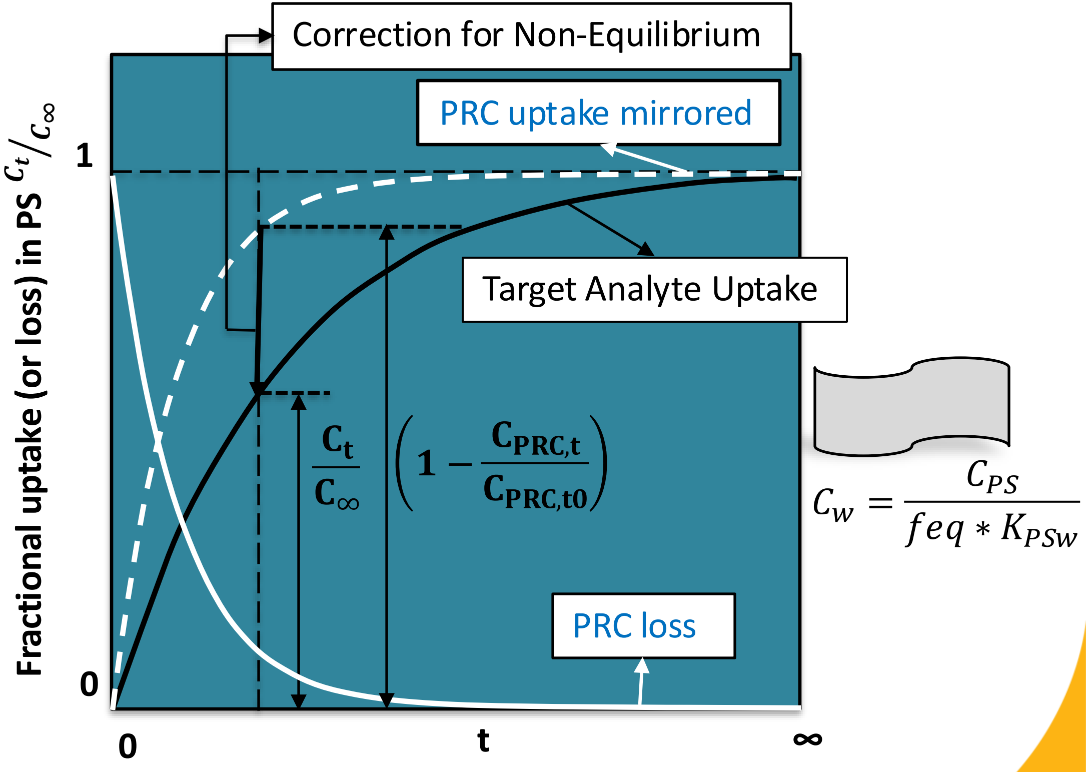
INTRODUCTION

CORRECTION FOR NON-EQUILIBRIUM



$$C_w = \frac{C_{PS}}{K_{PSw}}$$

Non-Equilibrium conditions:



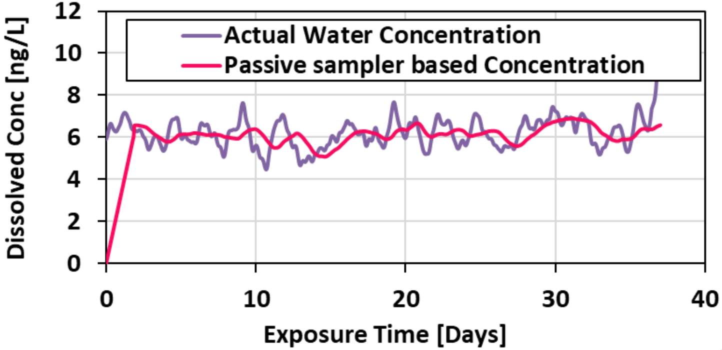
$$C_w = \frac{C_{PS}}{feq * K_{PSw}}$$

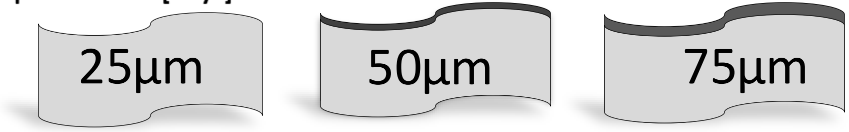
OBJECTIVE

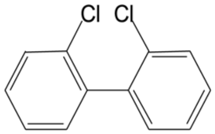
What is the true interpretation of time integration in equilibrium passive sampling for PCBs in ambient water?

Limited theoretical understanding of mass transfer dynamics of HOCs in PS under fluctuating ambient concentrations in surface water.

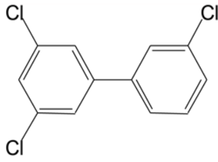
- Perturbation timings
- Hydrophobicity of PCB compounds
- Polyethylene (PE) sampler thickness
- Comparison of Diffusion and First Order Model for time integrative measurement



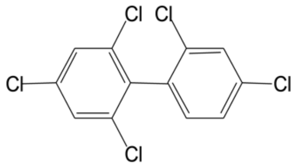




PCB4
(Dichlorinated, *Ortho*-substituted)



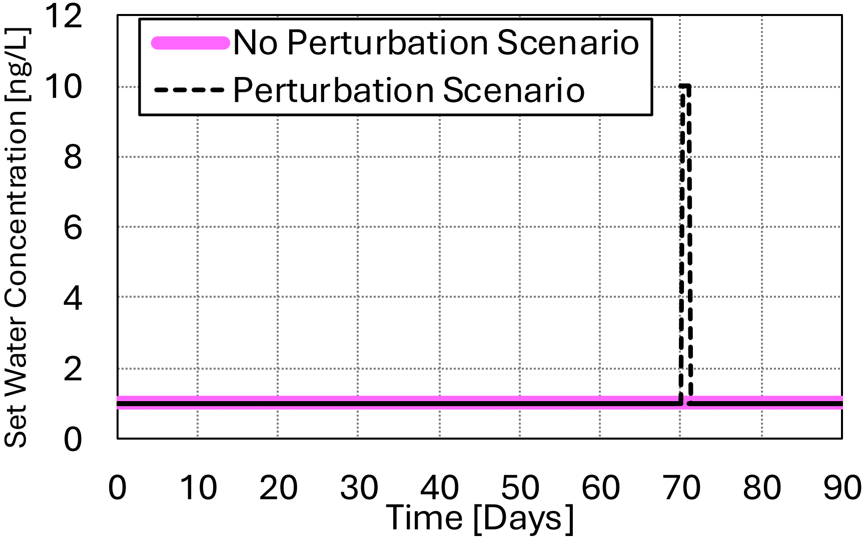
PCB36
(Trichlorinated, *Meta*-substituted)



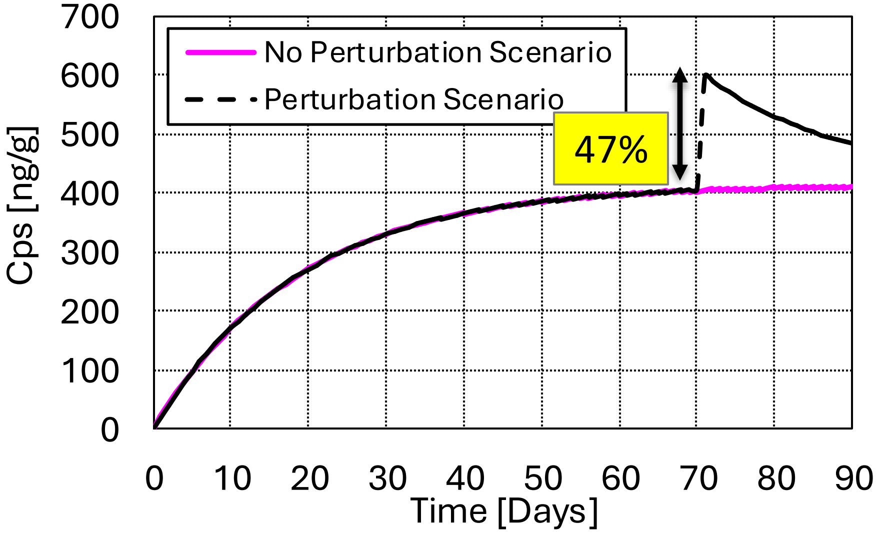
PCB100
(Pentachlorinated, *Ortho*-substituted)

METHODS

Set Water Concentration



Modeled uptake of PCB 37 in 25 µm thick PE over 90 days

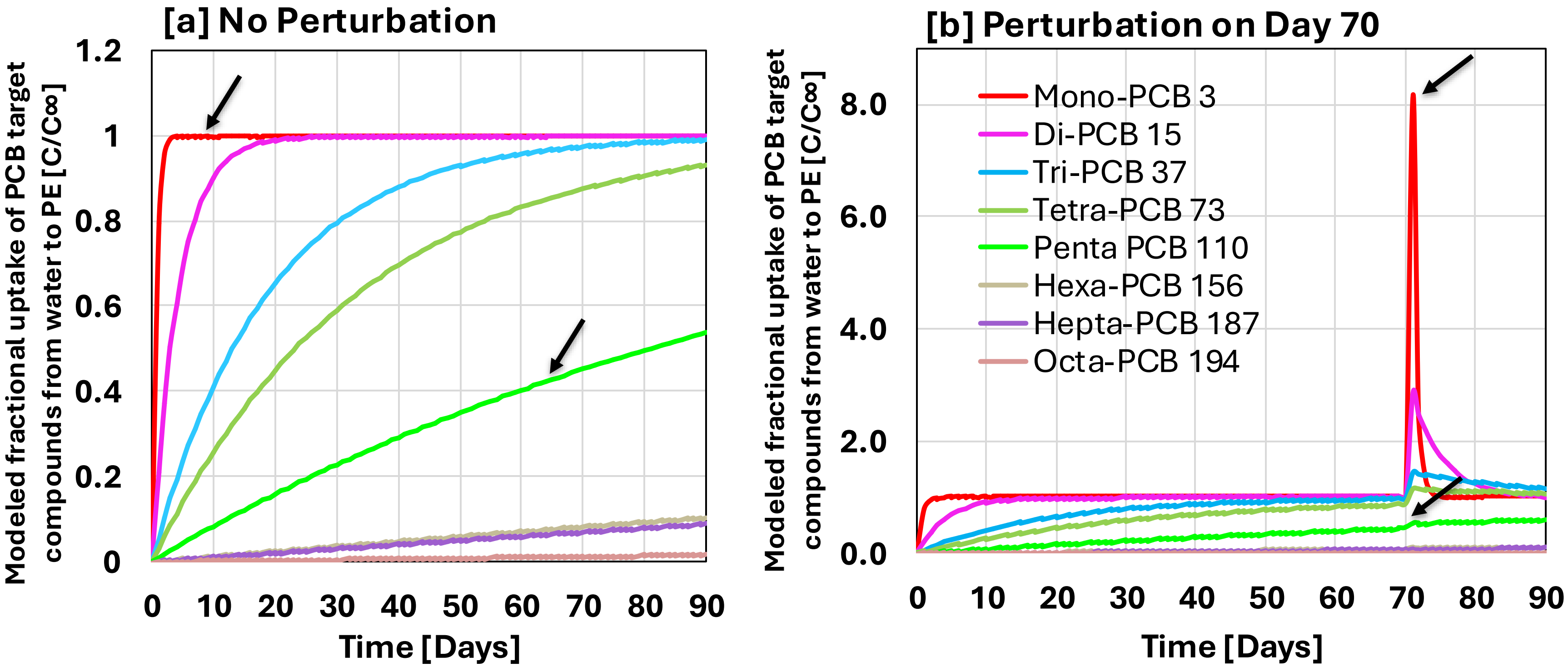


How sensitive is the sampler-chemical system to the single-day pulsed perturbation in concentration? → **SENSITIVITY TO PERTURBATION**

How long does the system take to recover from the perturbation to provide the correct estimation of time-averaged concentration? → **SAMPLING TIME-SCALE OF INTEGRATION (TSI)**

RESULTS: SENSITIVITY TO PERTURBATION

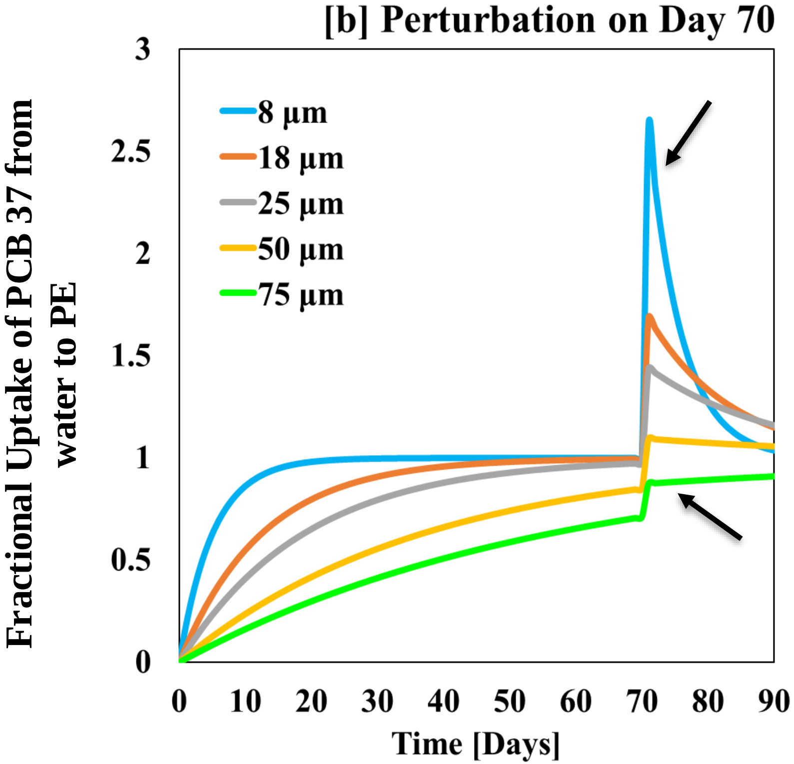
- Less hydrophobic compounds are more sensitive to the ambient perturbation than more hydrophobic compounds.

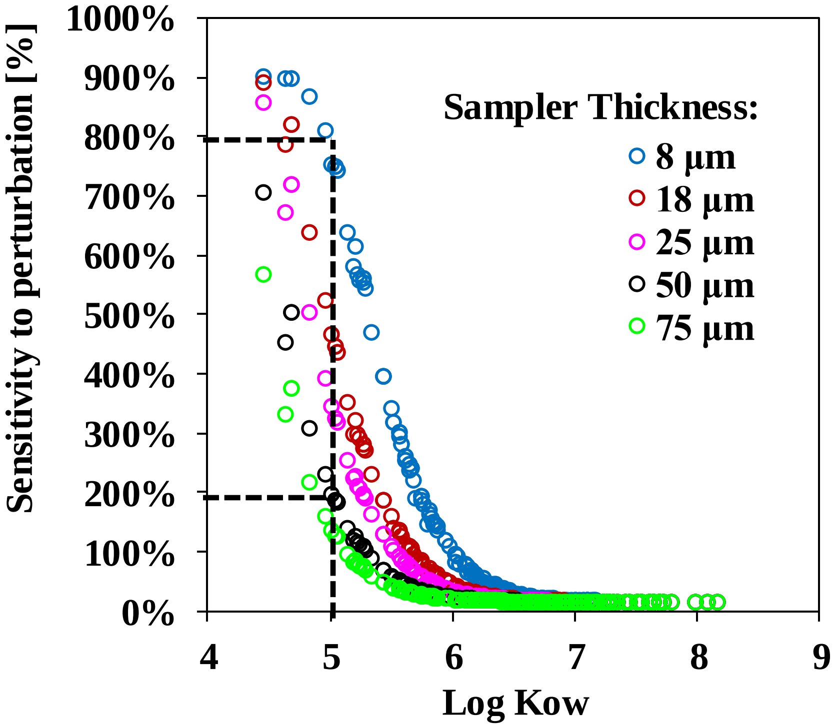


RESULTS: SENSITIVITY TO PERTURBATION

Thinner PE more sensitive to the ambient perturbation than thicker PE.

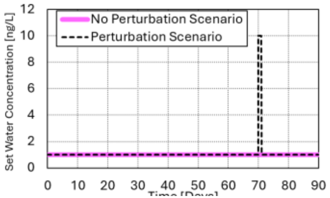
For PCB compound with <u>Log K_{ow} = </u>5, **8 um PE** is **800%** sensitive to the ambient perturbation while **50 um PE** is **200%** sensitive.

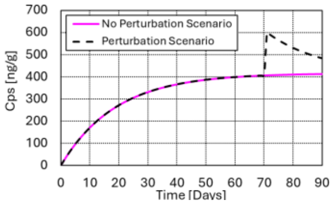




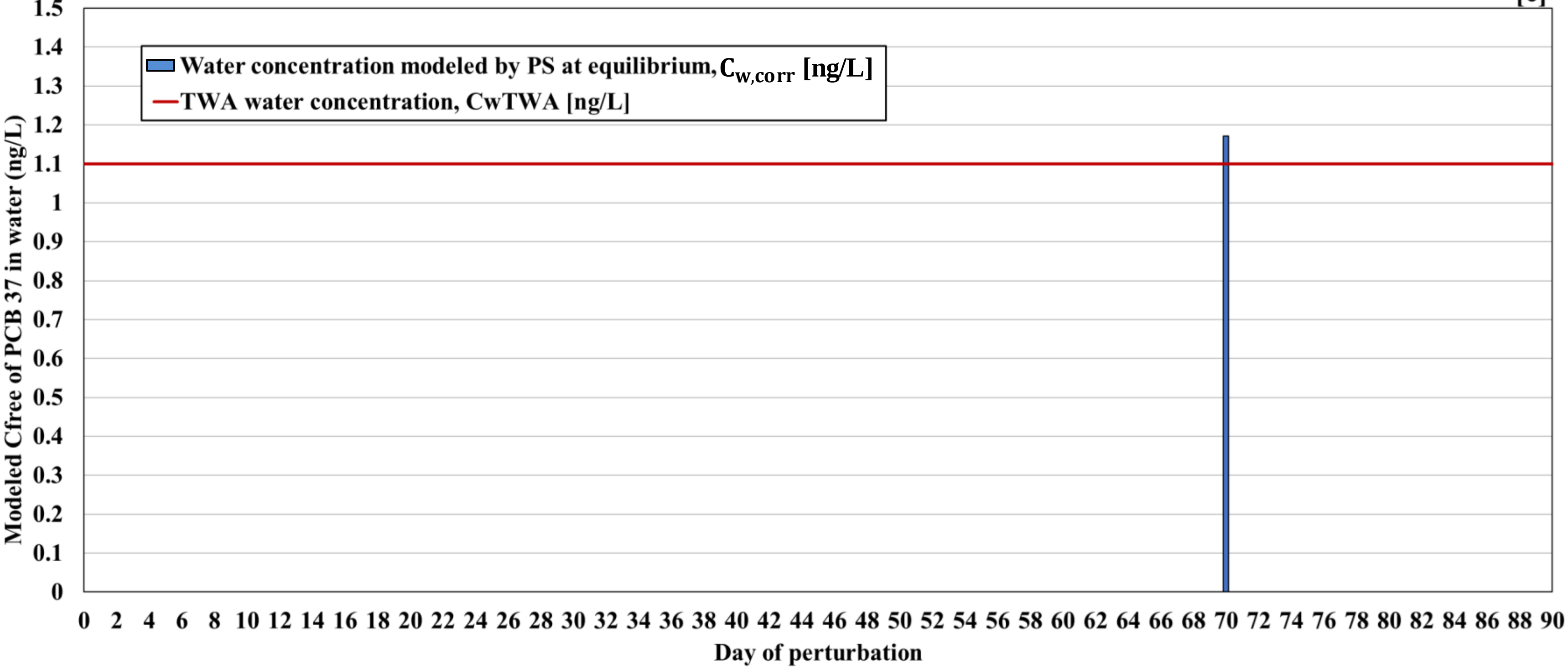
METHODS: SAMPLING TIME-SCALE OF INTEGRATION (TSI)

$$C_{w,TWA} = \frac{(C_w^{np} \times t^{np}) + (C_w^{p} \times t^{p})}{t}$$





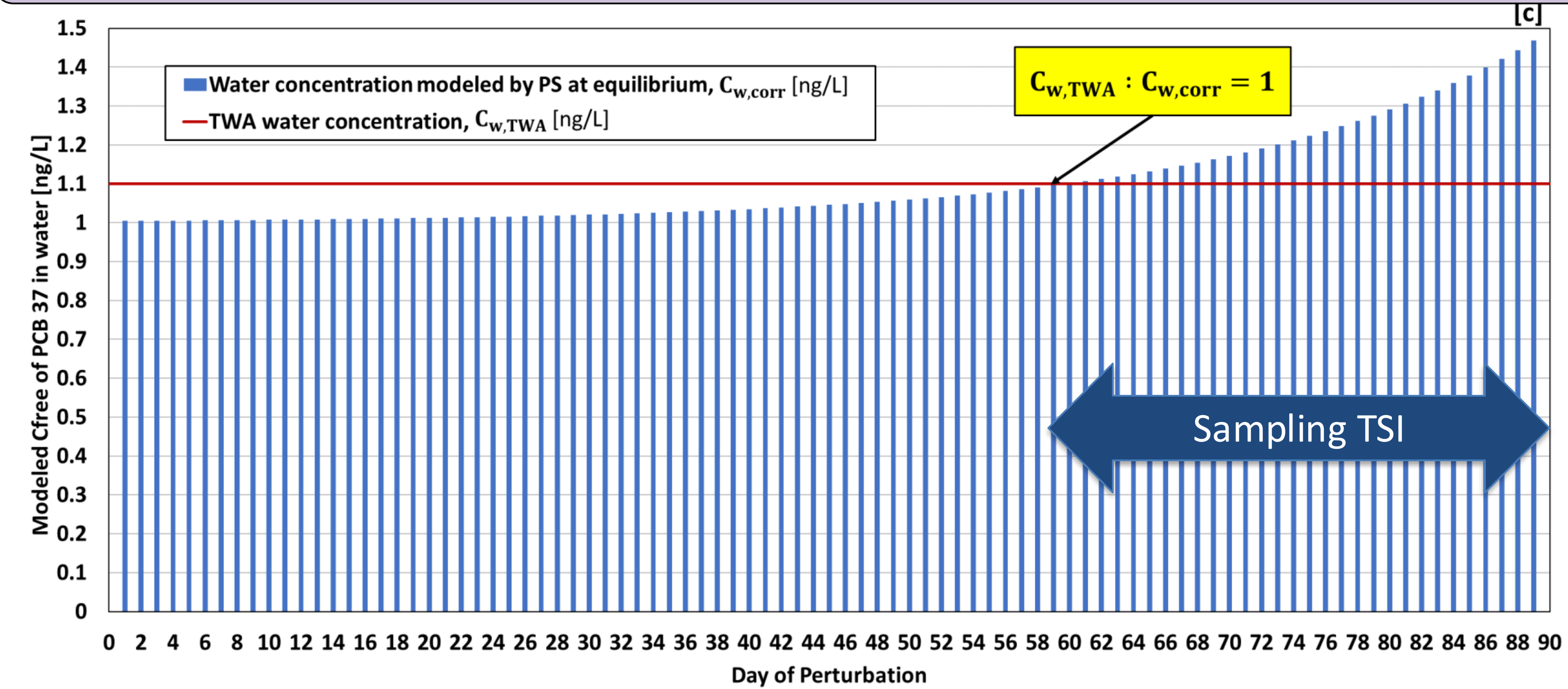
$$C_{w,Eqlb} = \frac{C_{PS,corr}}{K_{psw}}$$



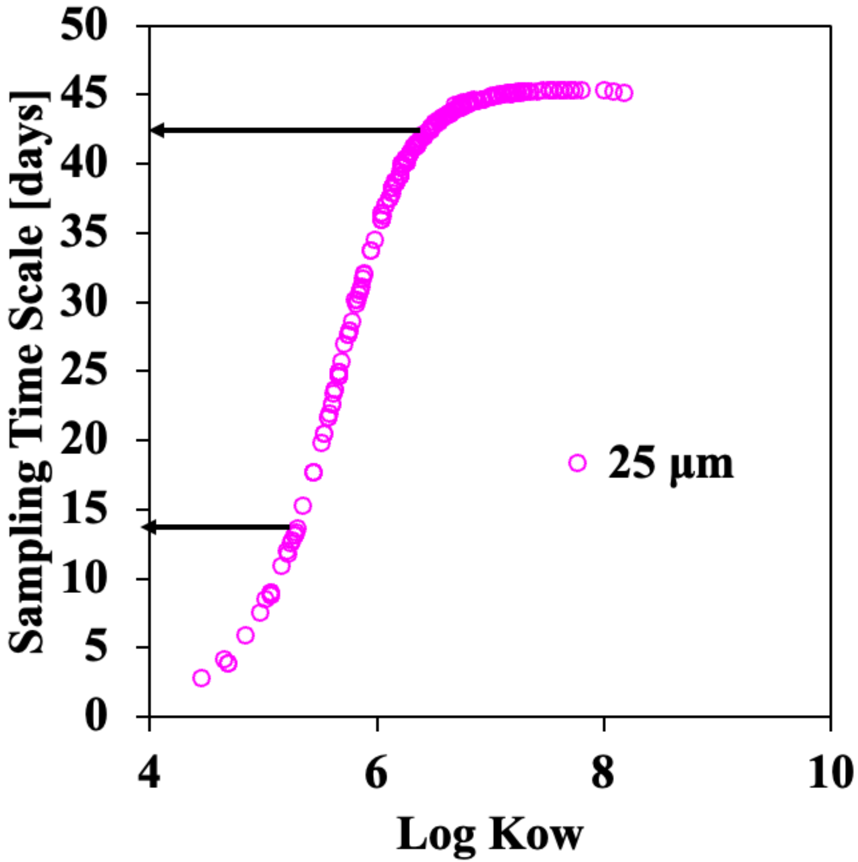
METHODS:

SAMPLING TIME-SCALE OF INTEGRATION (TSI)

Time (days) required by the PS to recover from a 1-day pulsed perturbation to provide the correct estimation of C_{TWA}

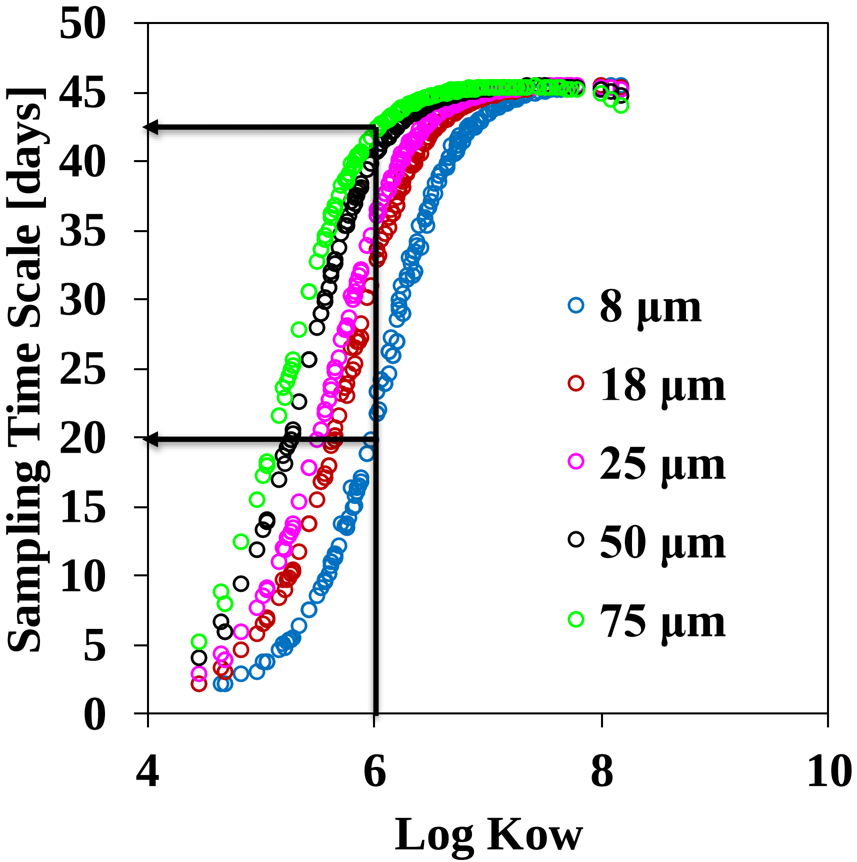


RESULTS: SAMPLING TIME-SCALE OF INTEGRATION (TSI)



- Sampling TSI increases with increasing hydrophobicity of PCB compounds.
  14-15 days for a di-chloro-biphenyl to 43-45 days for a hexa-chloro-biphenyl.

RESULTS: SAMPLING TIME-SCALE OF INTEGRATION (TSI)

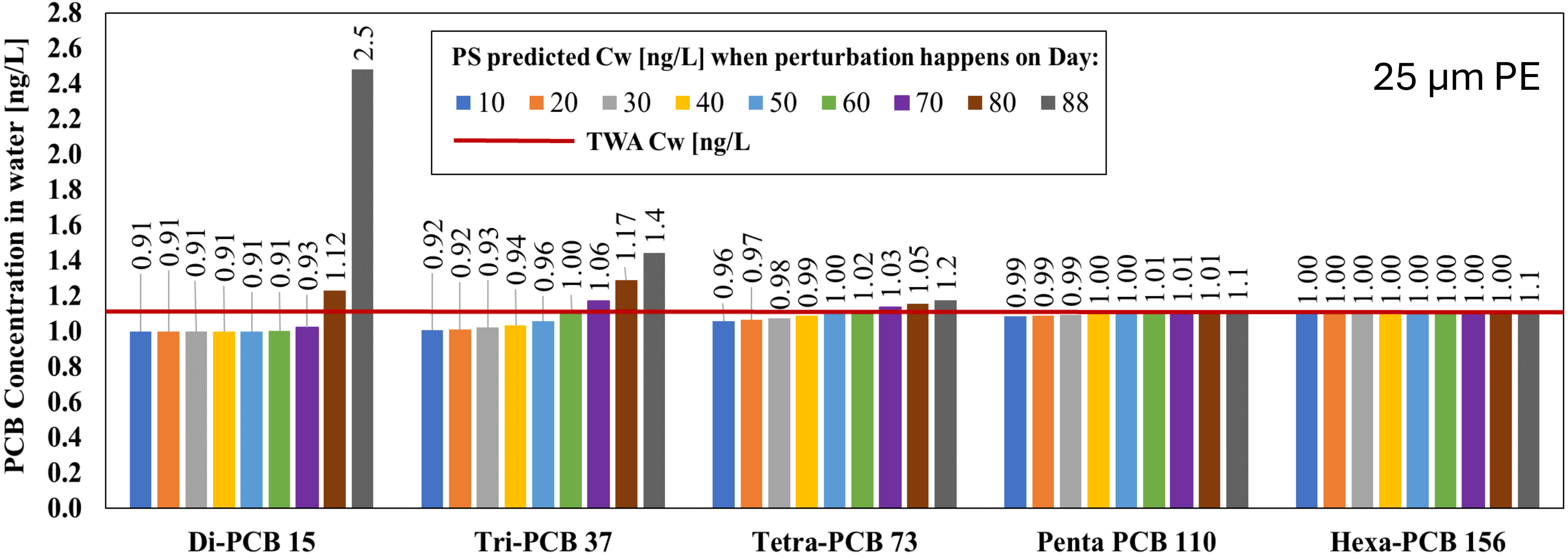


- Sampling TSI increases with increasing hydrophobicity of PCB compounds.
  - 14-15 days for a di-chloro-biphenyl to 43-45 days for a hexa-chloro-biphenyl.

- Sampling TSI increases with increasing sampler thickness.
  - 42 days for 75 um thick PE, 20 days for 8 um thick PE for Log Kow=6.

RESULTS: SAMPLING TIME-SCALE OF INTEGRATION (TSI)

- **90-day deployment** for a **25 µm PE** works well to **provide a TWA concentration of tetra and higher** chlorinated PCB compounds.
- **Sampling TSI** is much **smaller for di- and tri-** (high deviations) → underpredicted when perturbation is early, overpredicted if too close to the retrieval.



CONCLUSION

1. Time-Scale of Integration (TSI) : time in days for which the sampler should be deployed to achieve the true time-averaged concentration.
    - pattern and timing of perturbation
    - hydrophobicity of the analytes
    - thickness of the PS
2. Thick sheet sampler and heavier, more hydrophobic compounds: higher mass-transfer resistance - lower sensitivity - longer TSI.
    - ↘ The sampling TSI for a typical 25 µm PE sheet ranged widely from 14-15 days for a di-chloro-biphenyl to 43-45 days for a hexa-chloro-biphenyl.
3. Longer field deployments do not necessarily lead to longer-term integrated measurements for all congeners. Less hydrophobic compounds are prone to reflecting near-term fluctuations from perturbation events.
4. Mechanistic understanding of mass transfer kinetics in PS → optimize more targeted sampler design strategies

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THANK YOU

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Project Sponsors and Collaborators

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BATTELLE
It can be done

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Extra Slides

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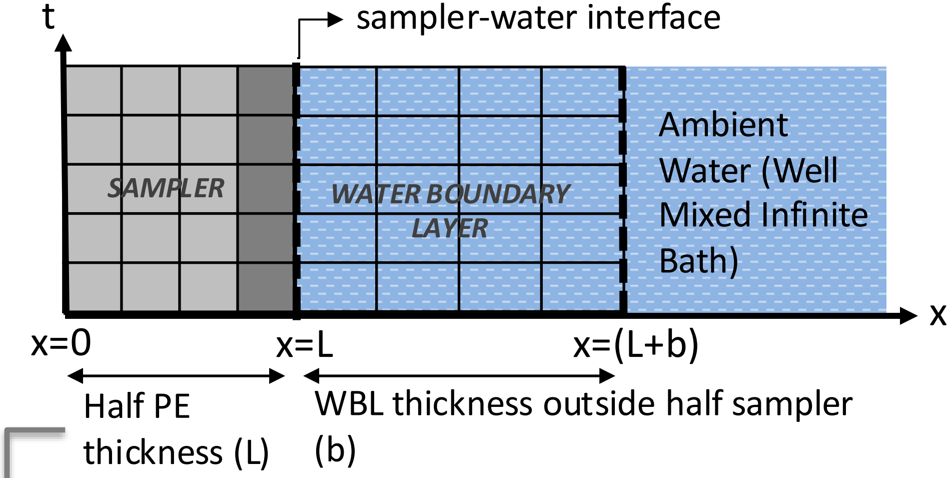
NUMERICAL MODELS

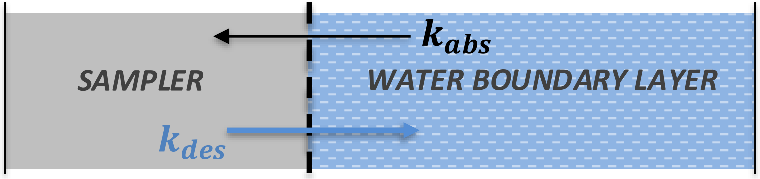
Diffusion Model



$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2}$$
when $-L < x < L$

$$\frac{\partial C_W}{\partial t} = D_W\frac{\partial^2 C_W}{\partial x^2}$$
when $-L > x > -(L+b)$ and $L < x < (L+b)$

First-Order Model



Overall flux of the chemical into sampler:

$$\frac{dC_{PE}}{dt} = k_{abs}C_W - k_{des}C_{PE}$$

(Assumption: $k_{abs} = k_{des} = k_e$)

Analytical solution is given by:

$$C_{PE} = C_W K_{PE-w}[1 - e^{-k_e t}]$$

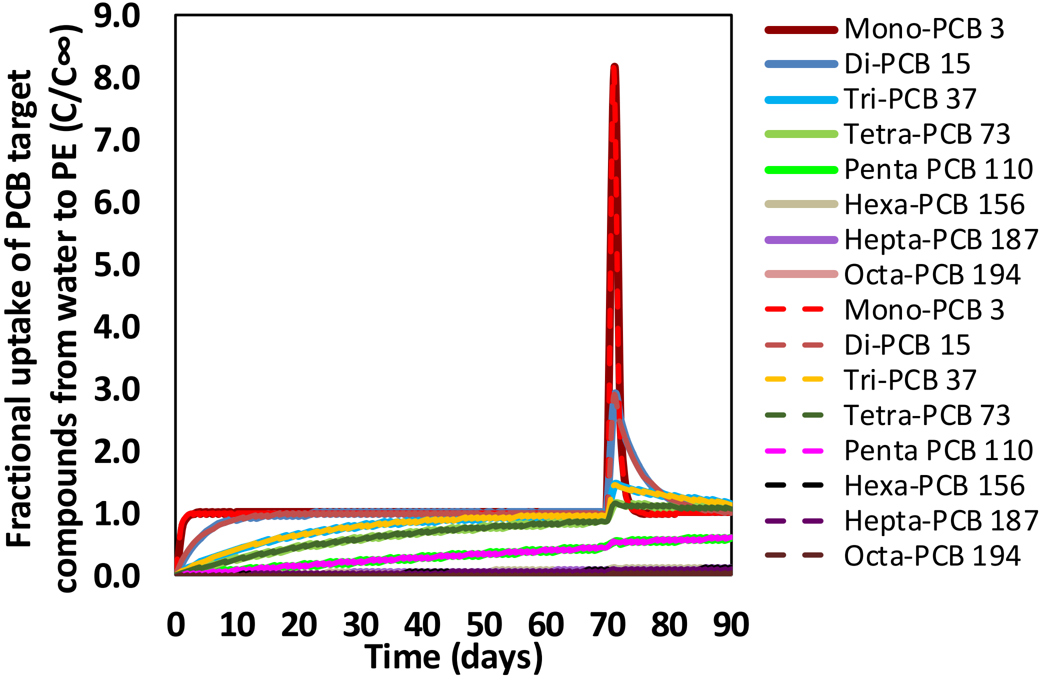
Exchange rate coefficient, k_e is calculated as:

$$k_e = \frac{1}{t}\ln\frac{C_{PE,PRC}^{t=0}}{C_{PE,PRC}^{t=90}}$$

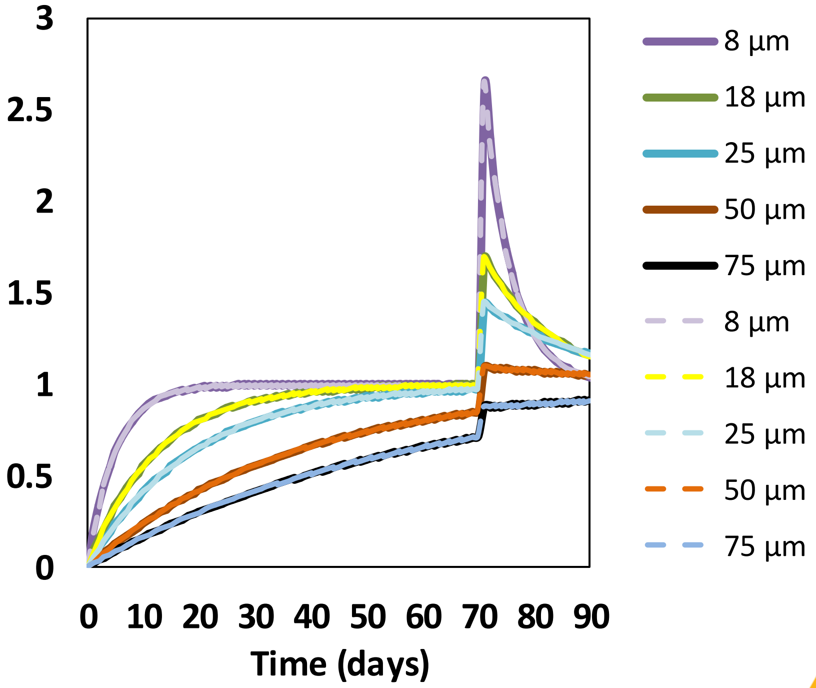
From diffusion model

RESULTS: DIFFUSION VERSUS FIRST-ORDER MODELS

Response of PCB compounds of varying hydrophobicity



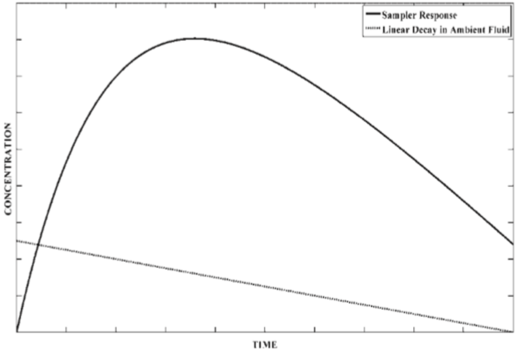
Response of different PE thicknesses



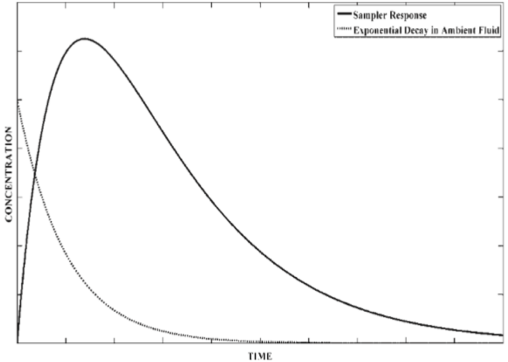
Knowledge gaps for Objective 1: Hawker et al., 2010

Hawker et al., 2010

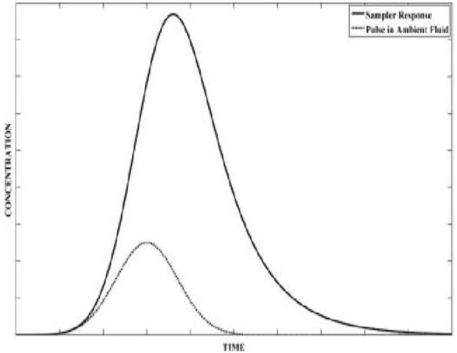
Linear Decay



Exponential Decay



Pulse



- A theoretical study by Hawker using a **first order exchange model** showed that the **time course of accumulation** in a sampler reflects the changing ambient concentration with a **measurable time lag**.
- They suggested the **use of multiple measurements to determine changing ambient concentrations** but **did not analyze sampling TSI**.
- Sampling rate model used: no solid mechanistic interpretation about **partial WBL-PS control of mass transfer** could be drawn for compounds of **varying hydrophobicity**.

INTRODUCTION

NUMERICAL MODELS