Time-Integration in Equilibrium Passive Samplers: A Mathematical Modeling Approach

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Chemical Biochemical and Environmental Engineering

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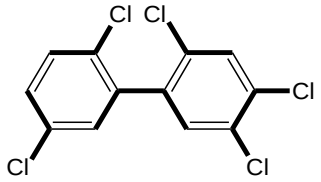
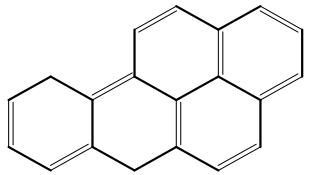
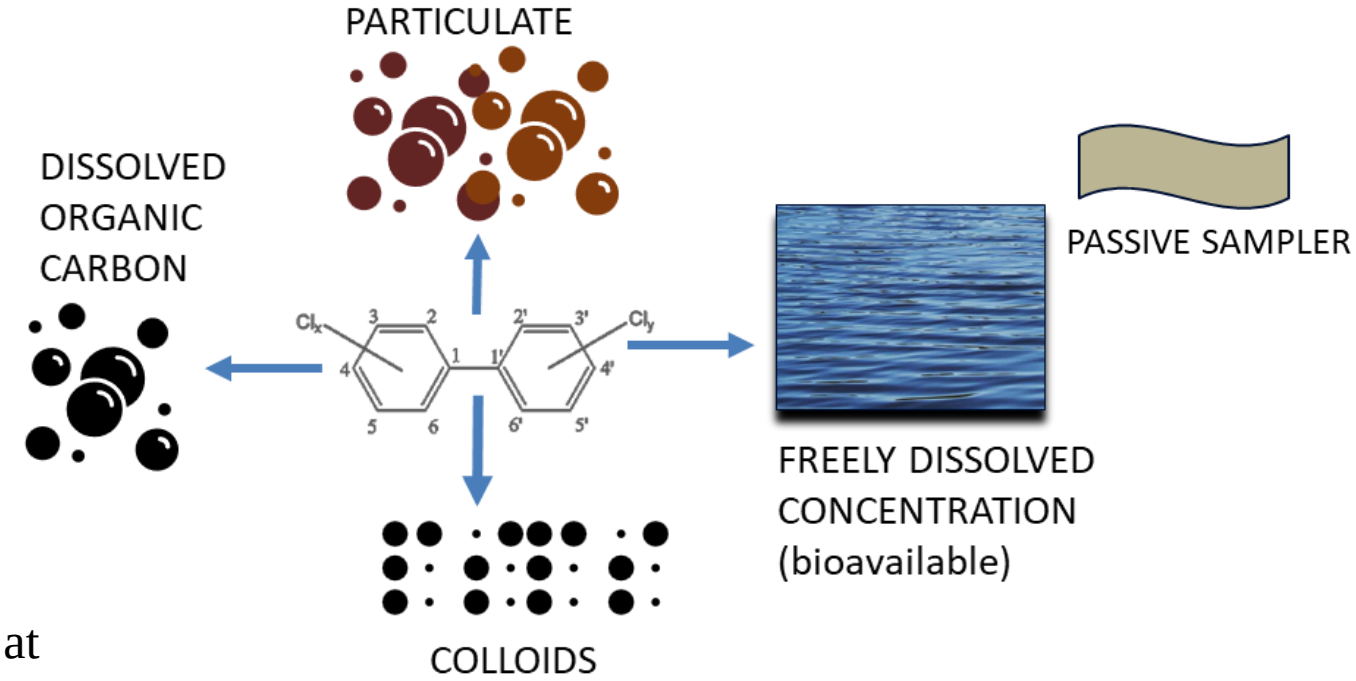
Introduction

Polychlorinated Biphenyls (PCBs)



Polycyclic Aromatic Hydrocarbons (PAHs)



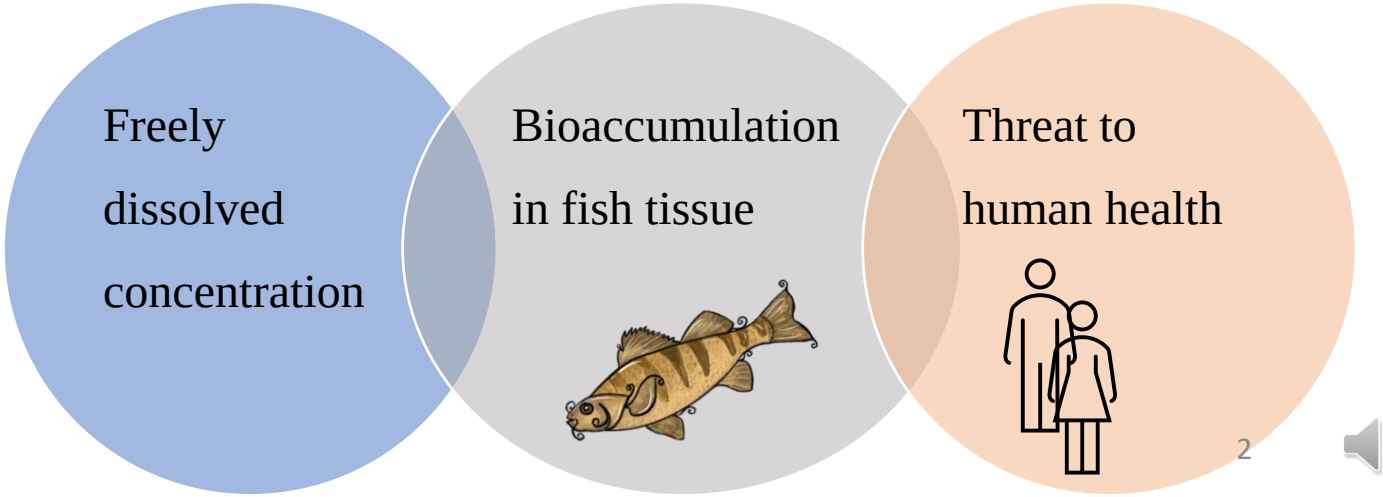


Hydrophobic organic contaminants (HOC):

- Partition among different environmental phases - persist in the environment
- Strong bioaccumulation potential
- Pose threats to human and ecological health even at trace concentrations of pg-ng/L.

Passive sampling:

- Allows measurement of the freely dissolved concentrations (thermodynamic driving force for bio uptake).
- Time averaged measurement.



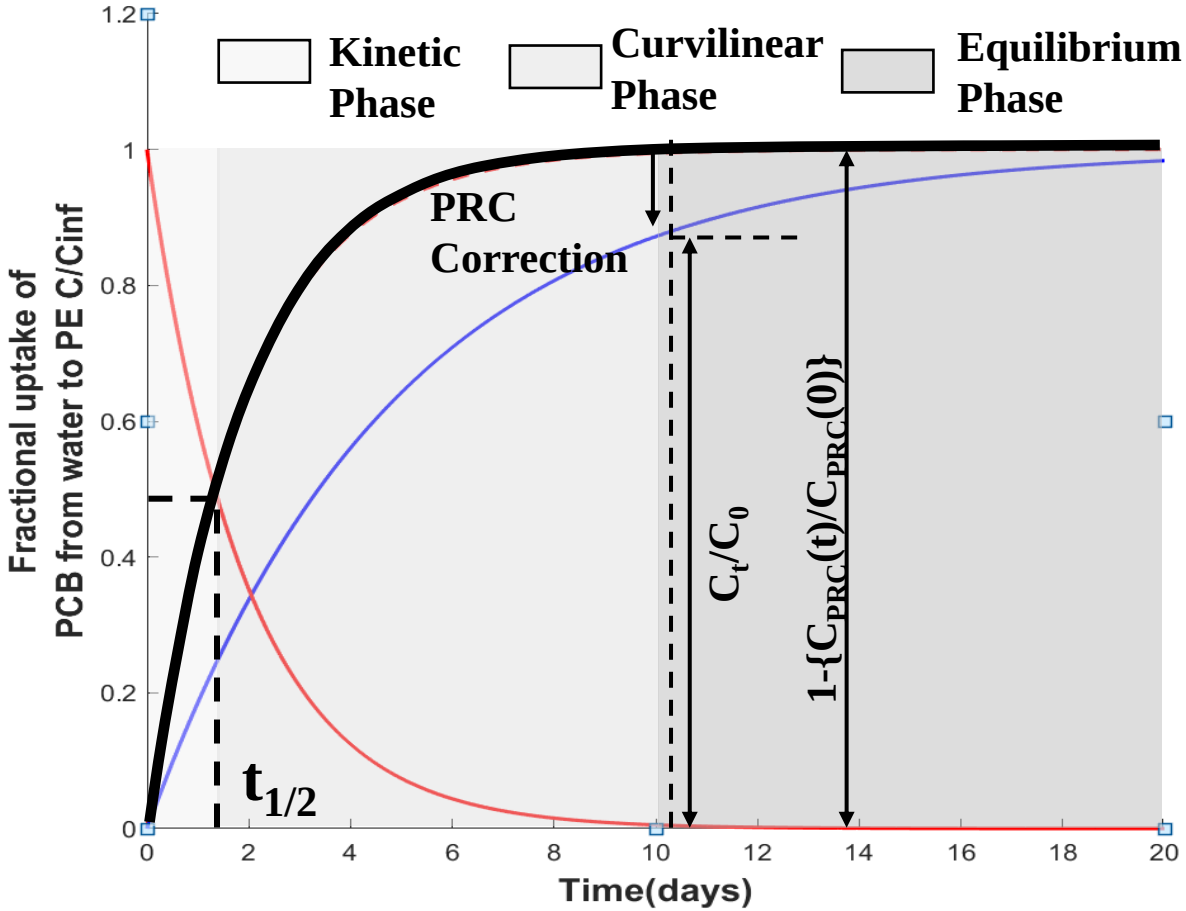
Equilibrium Passive Samplers and PRC Correction

Polyethylene (PE)

Polydimethylsiloxanes (PDMS)

Polyoxymethylene (POM)

$$C_{ps}(t\infty) = K_{ps-w}C_w$$

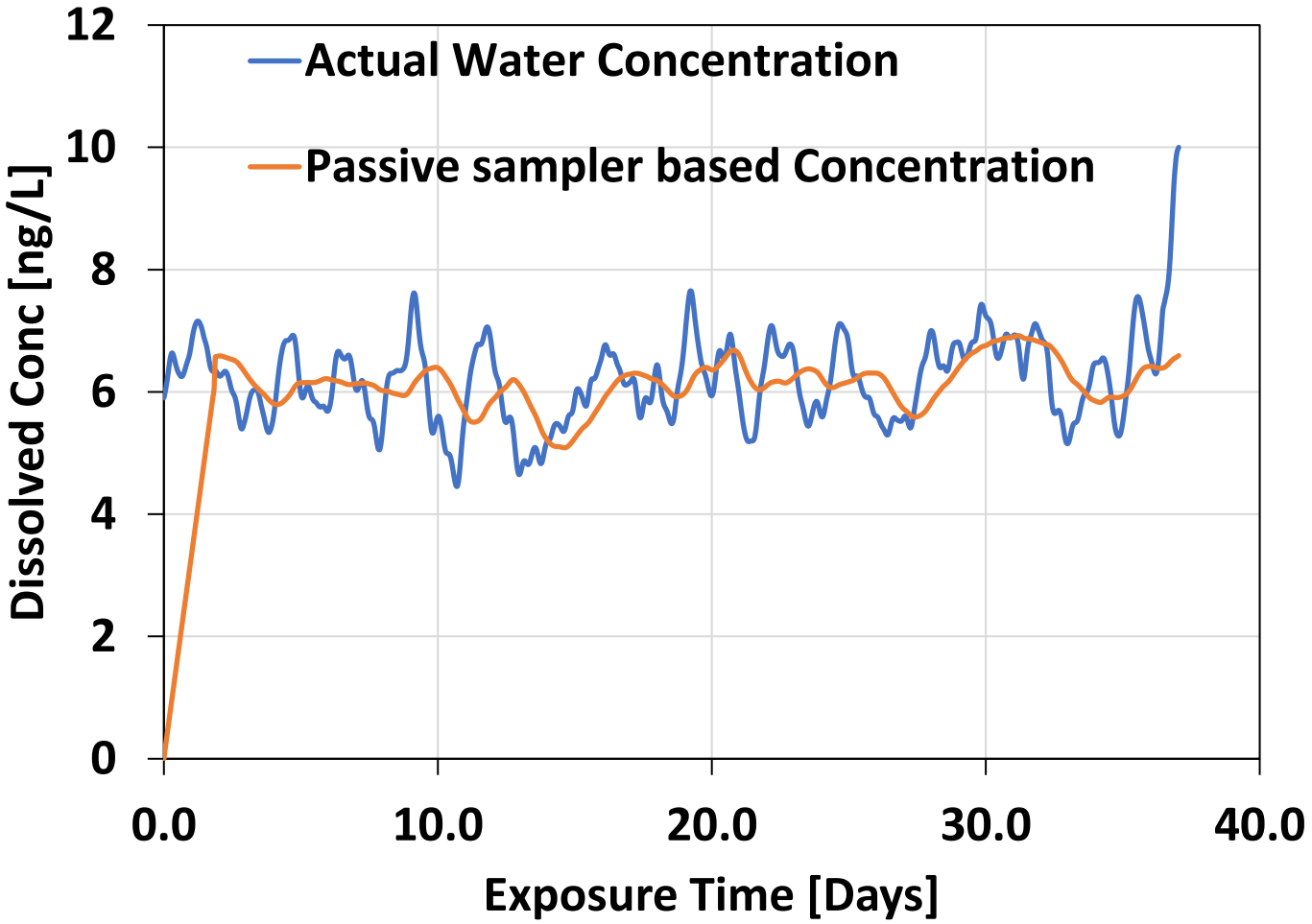


Fractional loss of Performance Reference Compound (PRC) from passive sampler to surrounding medium

Actual fractional uptake of target PCB analyte from surrounding medium to passive sampler

Fractional uptake of target analyte corrected for non-equilibrium (1-fractional PRC loss)

Existing Knowledge Gaps



Limited **theoretical understanding** of mass transfer dynamics in equilibrium passive samplers under **fluctuating ambient concentrations** in surface water.

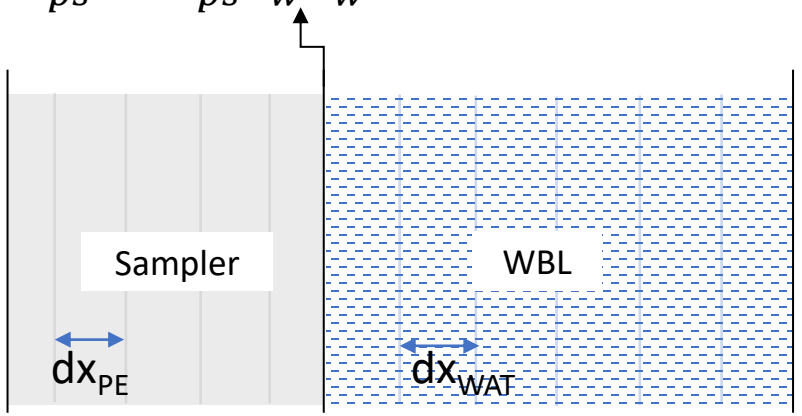
Comparison of **Diffusion** and **First Order Model** for understanding the mass transfer dynamics in a single-phase **equilibrium passive sampler** like PE for **time integrative measurement** for surface water measurements.

Models to simulate exchange kinetics

Fick's Diffusion

$$D_{ps}\frac{\partial C_{ps}}{\partial x} = D_W\frac{\partial C_W}{\partial x}$$

$$C_{ps} = K_{ps-w}C_w$$



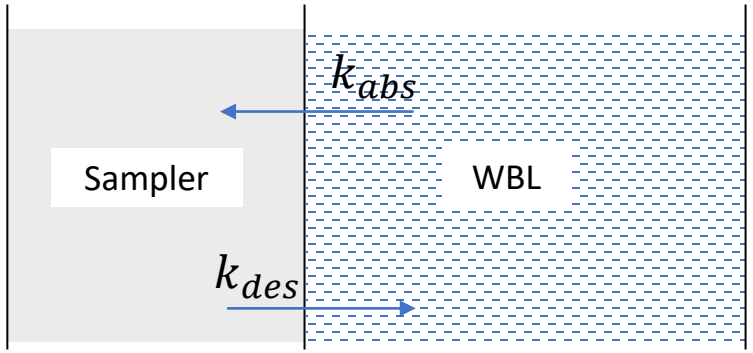
x=0 x=L x=L+b

$$\frac{\partial C_s}{\partial t} = D_{ps}\frac{\partial^2 C_{ps}}{\partial x^2}$$

$$\frac{\partial C_W}{\partial t} = D_W\frac{\partial^2 C_W}{\partial x^2}$$

First-Order

$$\frac{dC'_{ps}}{dt} = k_{abs}C_w - k_{des}C_{ps}$$



Assumption:

$k_{abs} = k_{des} = k_e$ (empirical term)

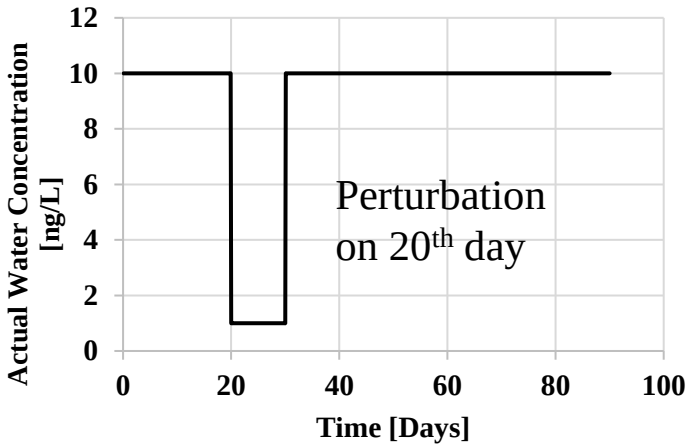
Research Objective

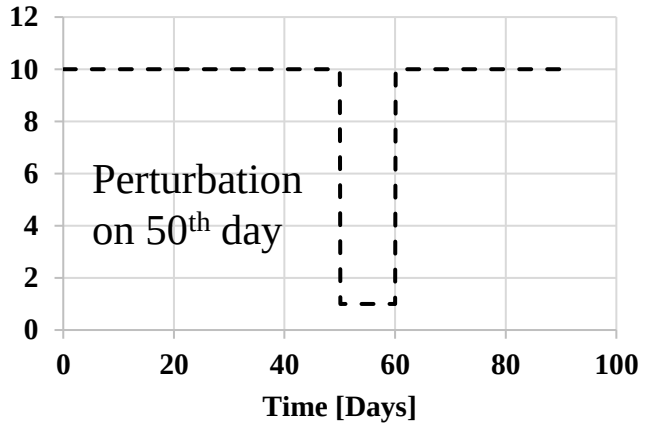
Develop the modeling framework of exchange kinetics in passive samplers when there is perturbation in the ambient concentration .

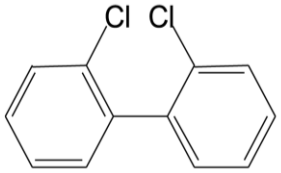
Knowledge gaps addressed:

- Theoretical understanding of mass transfer in PE
- Consistency of Diffusion & First-Order models.

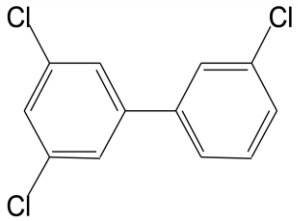
Methodology and Approach



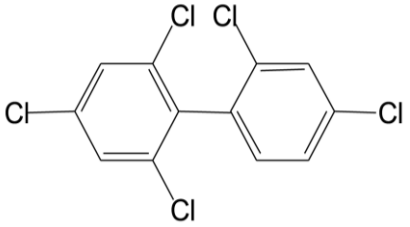




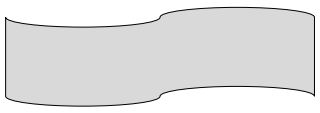
PCB4
(Dichlorinated, *Ortho*-substituted)



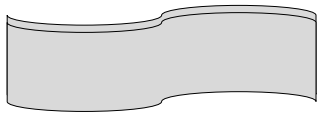
PCB36
(Trichlorinated, *Meta*-substituted)



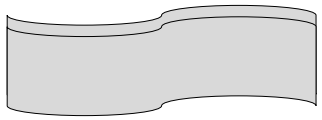
PCB100
(Pentachlorinated, *Ortho*-substituted)



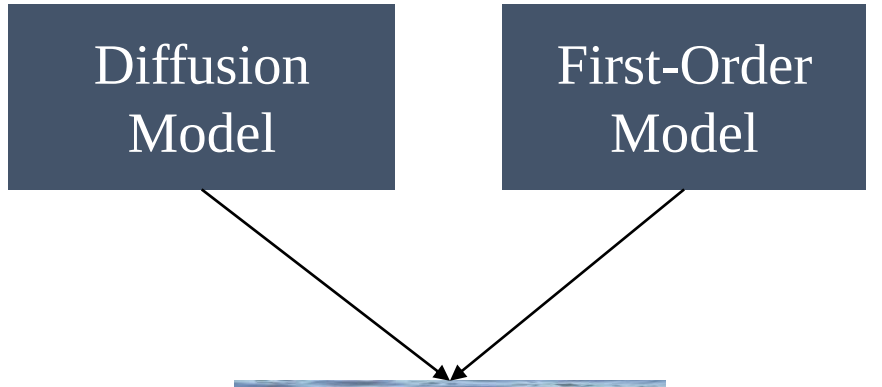
1mil=
25µm

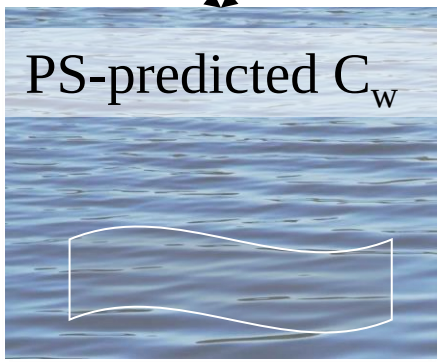


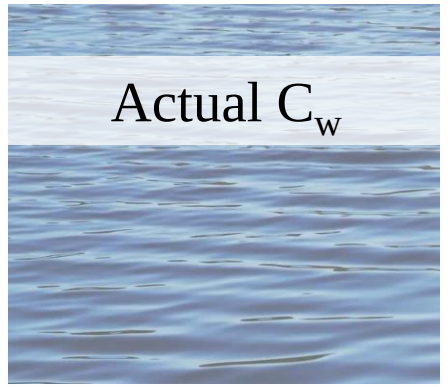
2mil=
50µm



3mil=
75µm

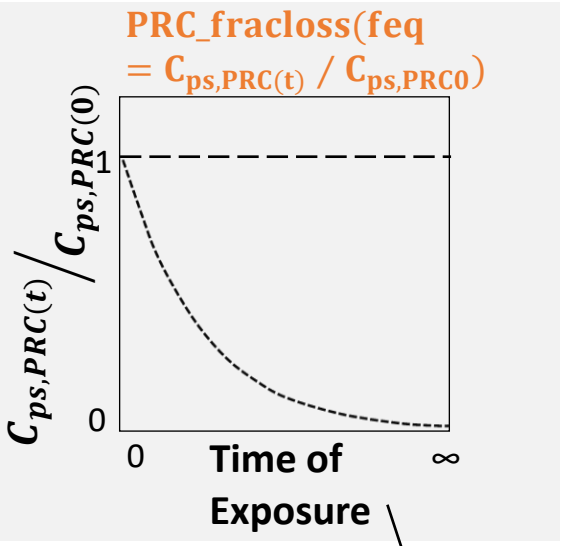


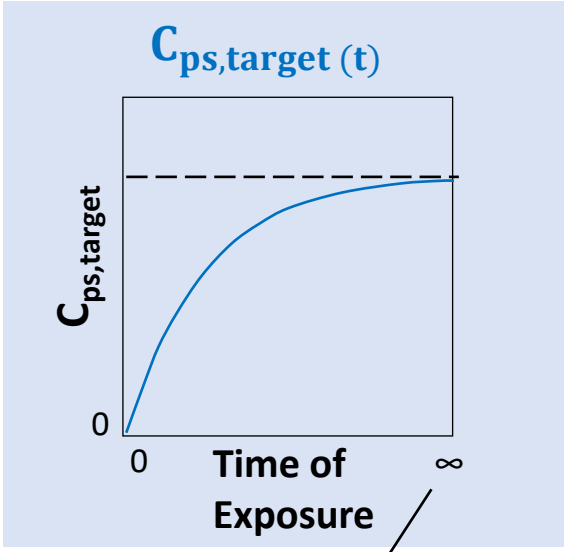




Methodology and Approach

Fick's Diffusion





$$C_{w,Eqlb} = \frac{C_{ps,target}(t)}{(1 - feq)K_{ps-w}}$$

First-Order

$$k_e = \frac{1}{t}\ln\left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)}\right)$$

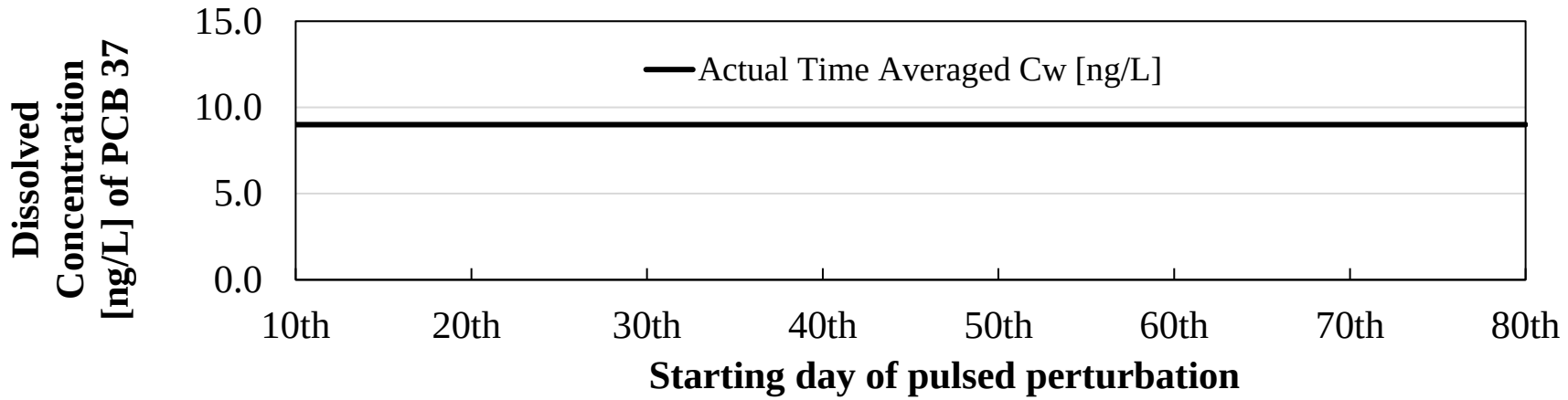
From diffusion model

$$C'_{w,Eqlb} = \frac{C'_{ps,target}}{K_{sw}(1 - e^{-k_e t})}$$

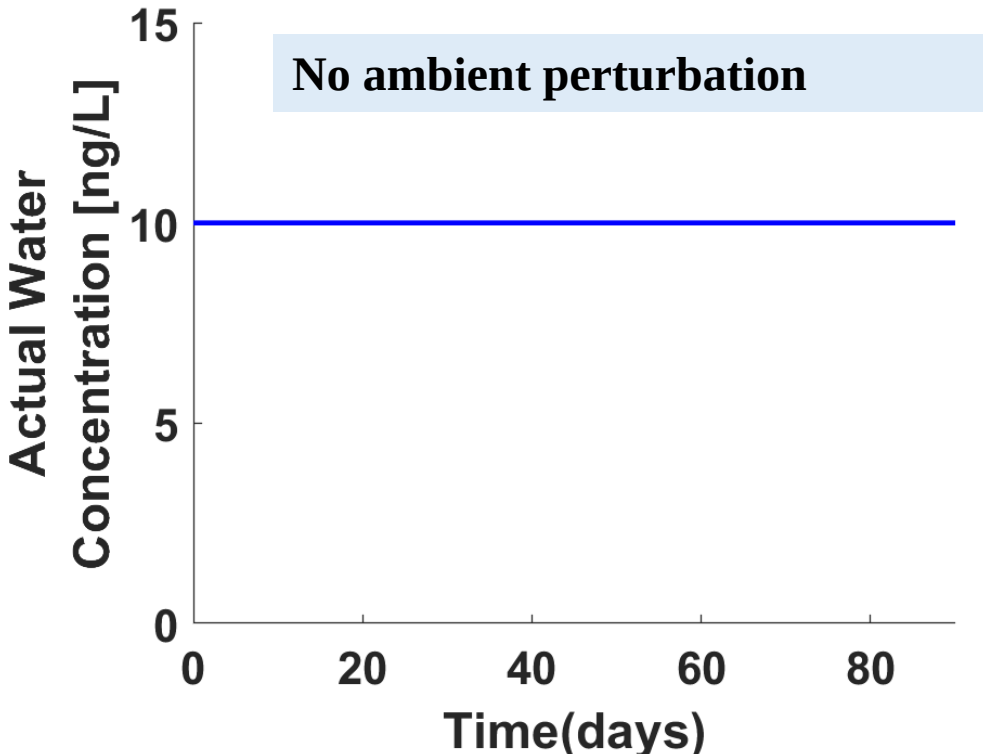
Actual Time Averaged Water Concentration (90 days):

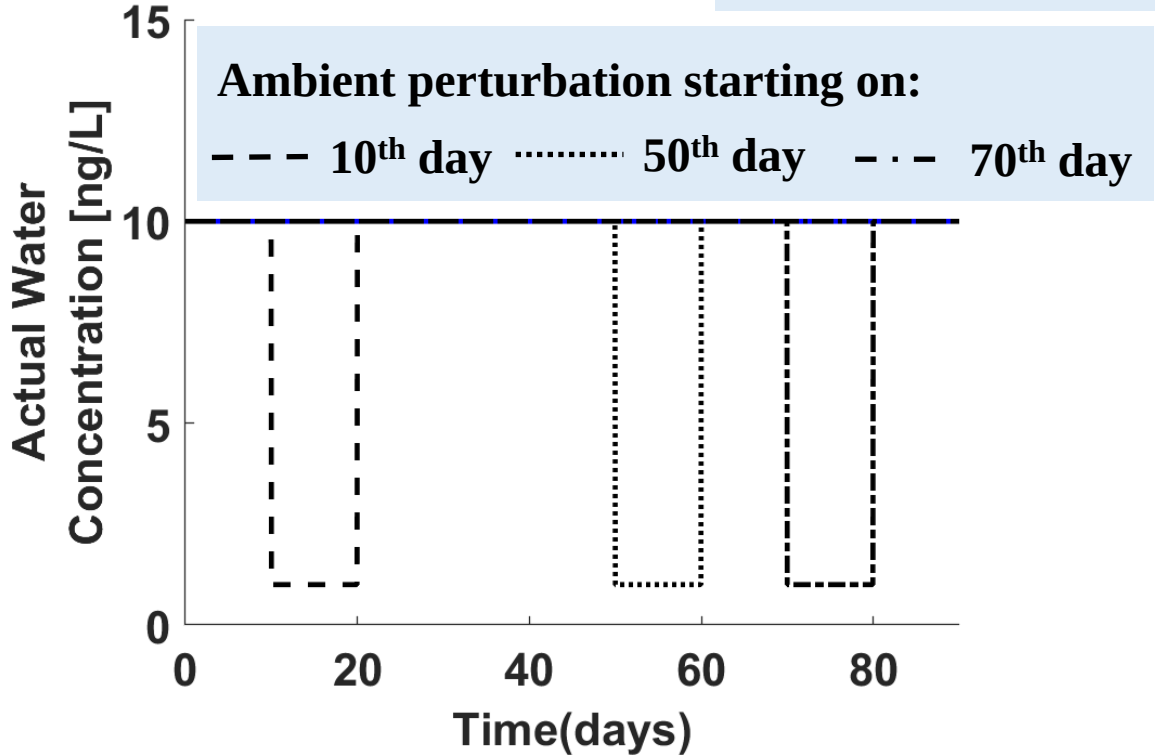
$$C_{w,Actual} = \frac{\left(C_w^{np} \times t^{np}\right) + \left(C_w^{p} \times t^{p}\right)}{t}$$

Results: Timing of Perturbation (PCB 37)



$$C_{w,Actual} = \frac{\left(C_w^{np} \times t^{np}\right) + \left(C_w^{p} \times t^{p}\right)}{t} = \frac{(10 \times 80) + (1 \times 10)}{90} = 9ng/L$$





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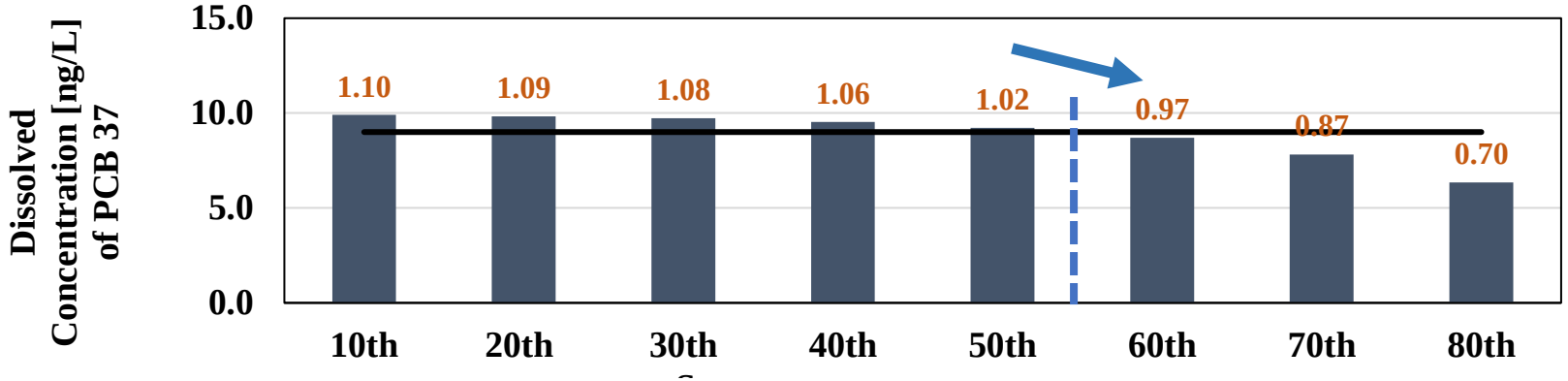
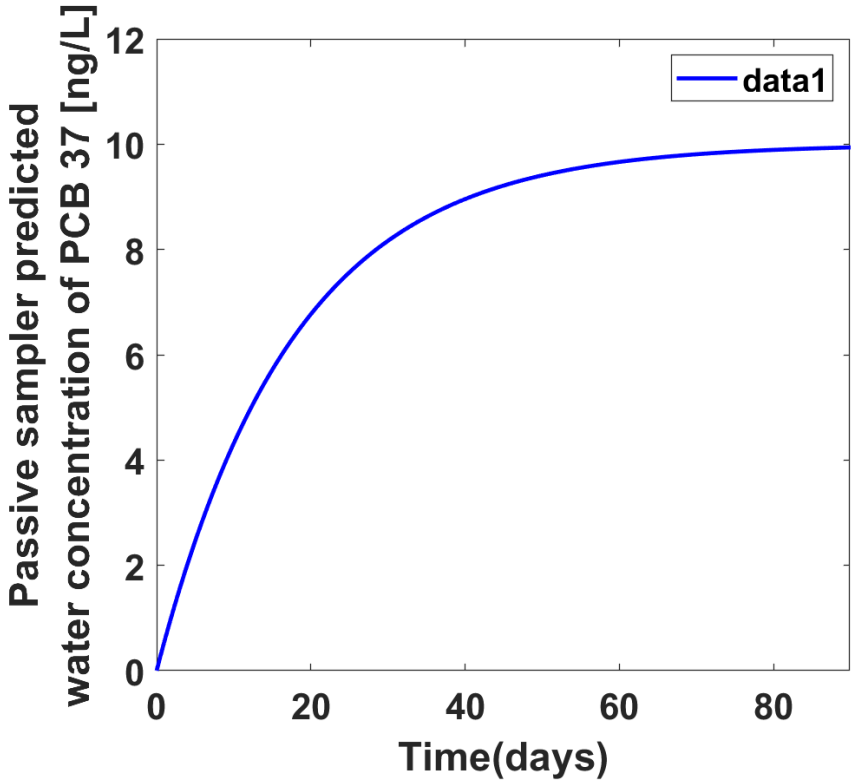
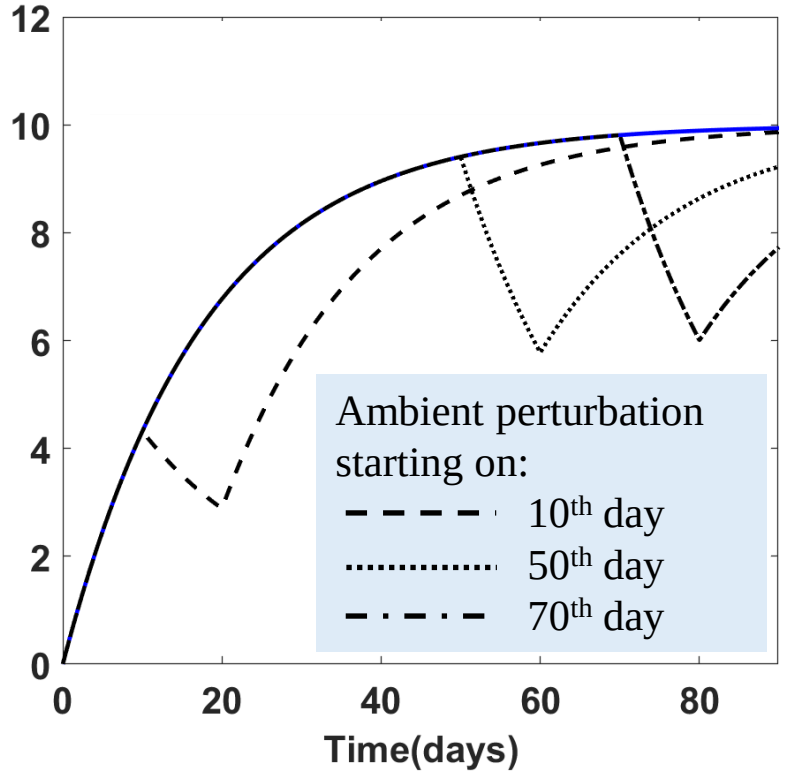






Time period of Integration:
Approximate time after a **known pattern of fluctuation**, when a **sampler** should be retrieved to correctly estimate the actual time-averaged concentration
[PCB 37: 90-60=30 days]

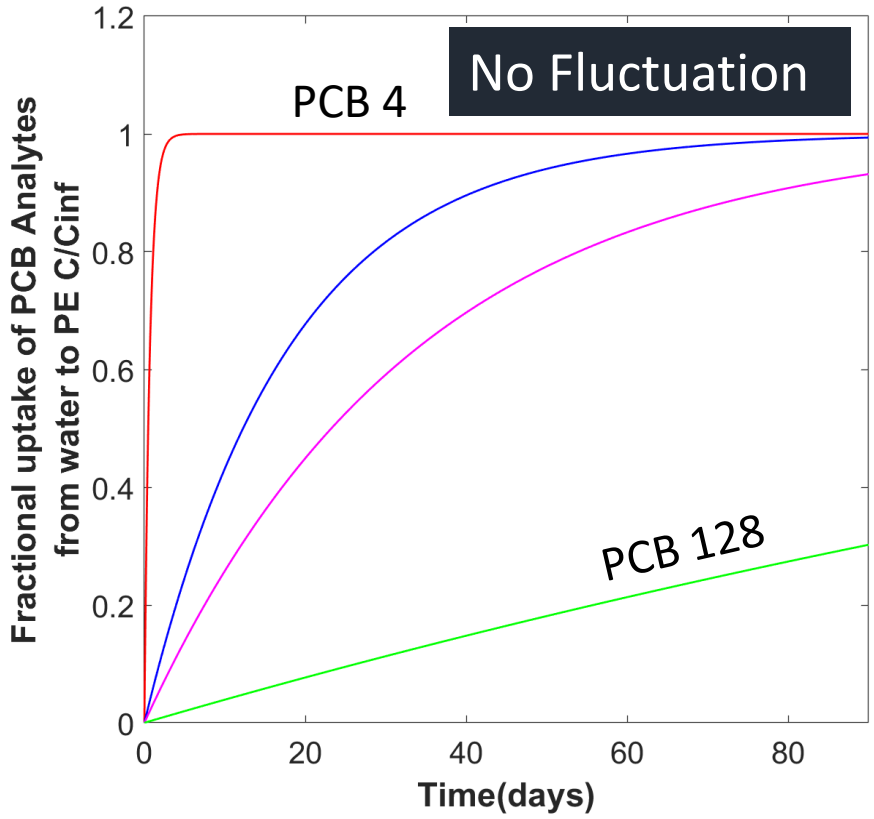
Fractional Accuracy (over/under-prediction):

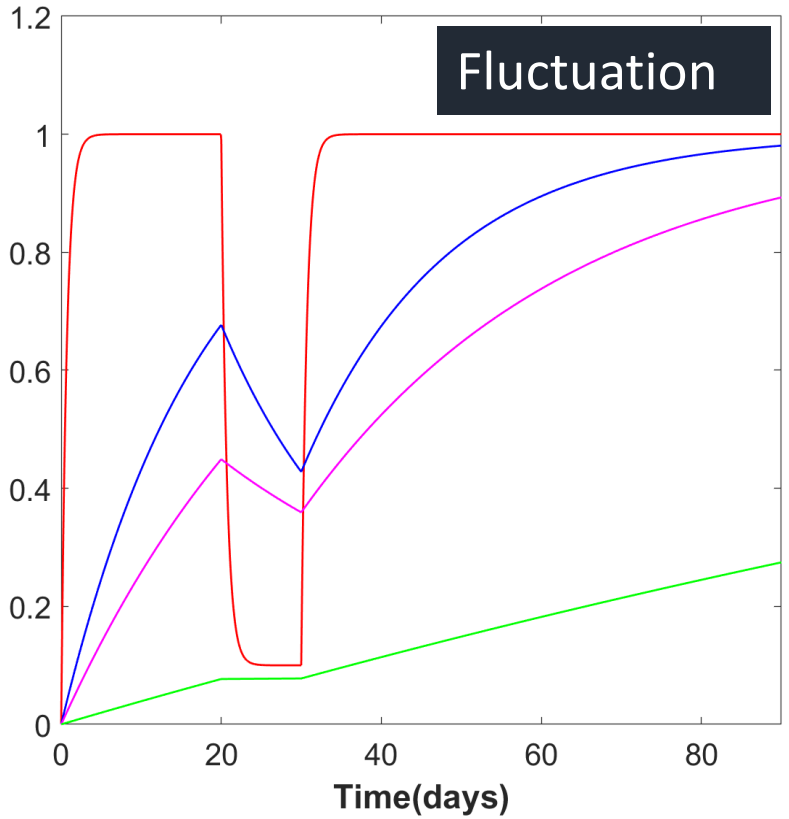
$$\frac{\text{PS based predicted water concentration}}{\text{Actual time-averaged concentration}}$$

% cross-over/ degree of sensitivity:
sum of % deviation around the day of cross-over **[For PCB 37:**
$((1.02-1)+(1-0.97))\times 100 = 6\%)]$

Results: Hydrophobicity of the analyte

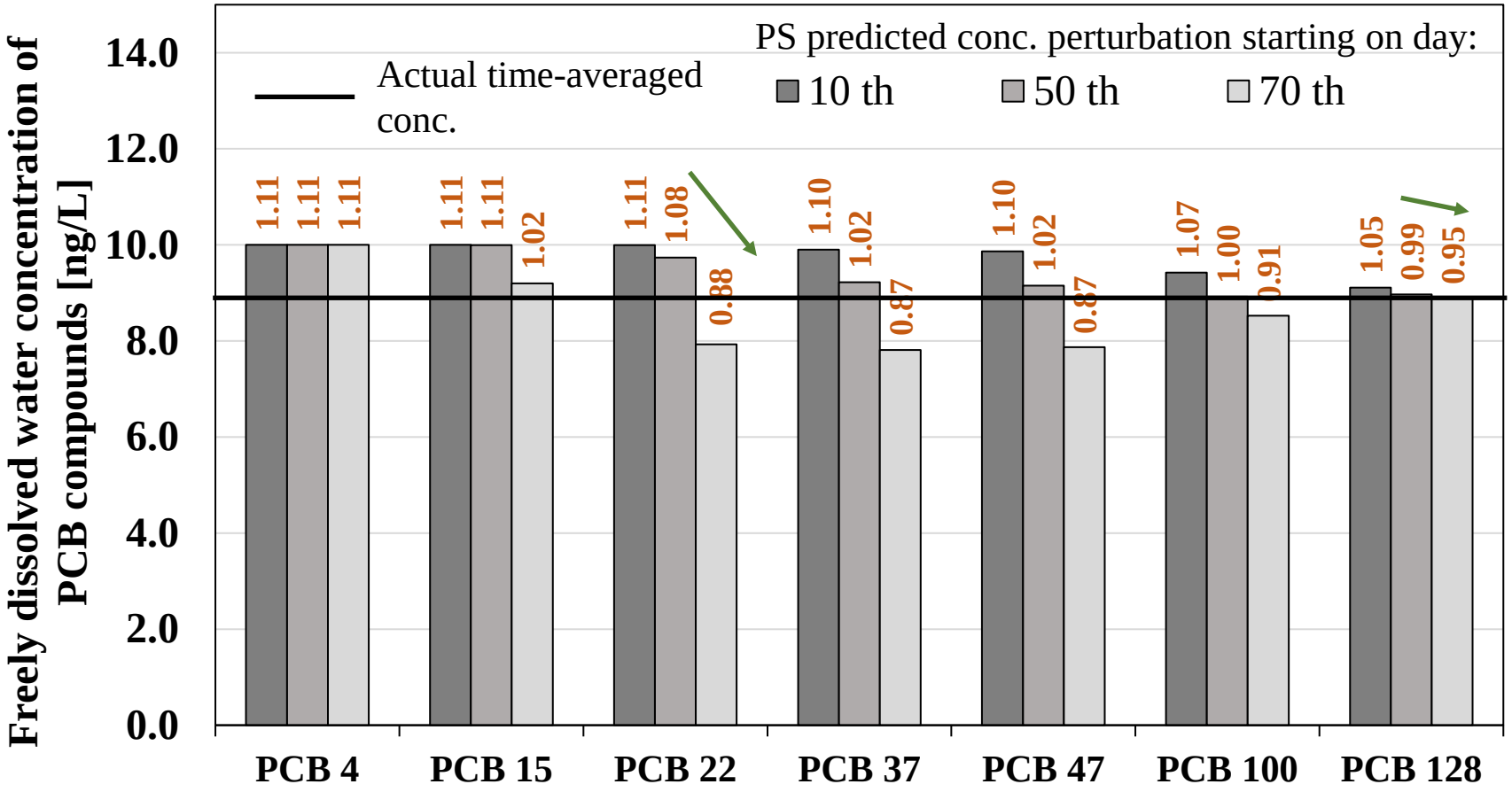
Homolog Group	PCB compd.	Molecular Weight [g/mol]	Log D_{pe} (cm^2/s)	Log K_{ow}
Di	PCB 4	223.1	-8.64	4.65
Tri	PCB 37*	257.54	-8.81	5.83
Tetra	PCB 73	291.99	-8.98	6.04
Hexa	PCB 128	360.88	-9.33	6.74





PCB 4 (di)
PCB 37 (tri)
PCB 73 (tetra)
PCB 128 (hexa)

Results: Hydrophobicity of the analyte



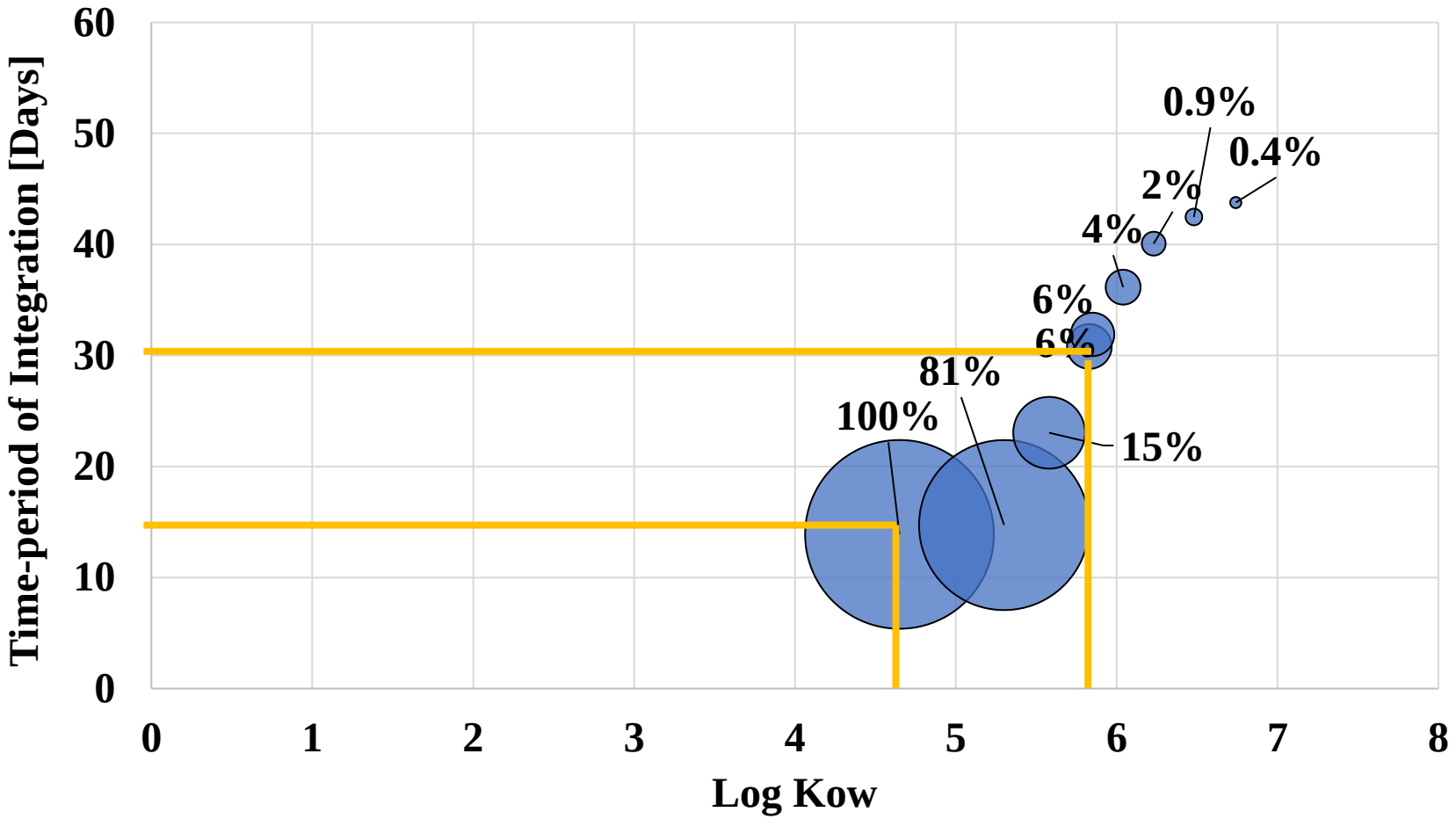
Fractional Accuracy (over/under-prediction):

$$\frac{\text{PS based predicted water concentration}}{\text{Actual time-averaged concentration}}$$

Congeners have varying levels of over or underprediction trends:

- function of their hydrophobicity and
- consequent sensitivity to fluctuations in ambient concentrations.

Results: Hydrophobicity of the analyte



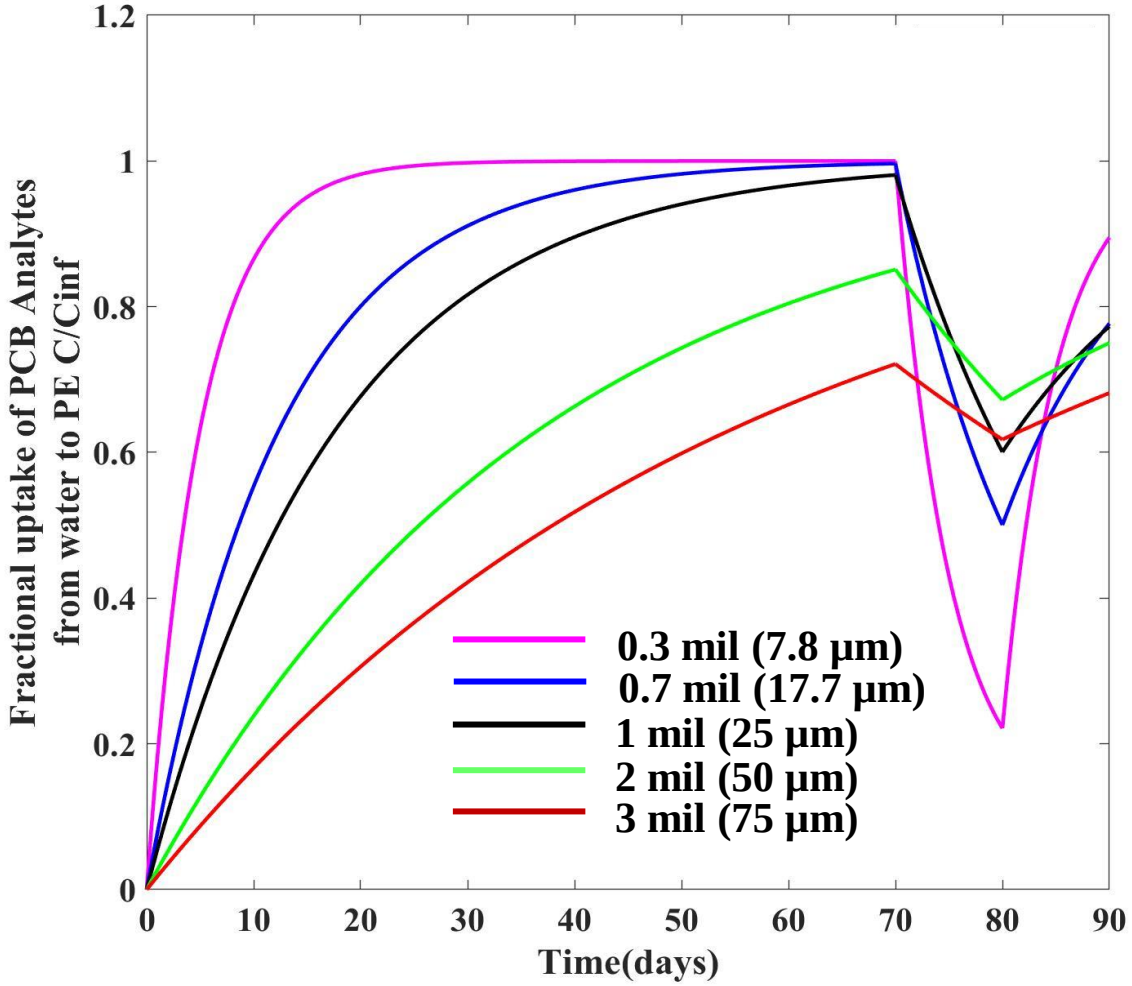
Time period of Integration:
Approximate time after a **known pattern of fluctuation**, when a **sampler** should be retrieved to correctly estimate the actual time-averaged concentration **[PCB 37: 90-60=30 days]**

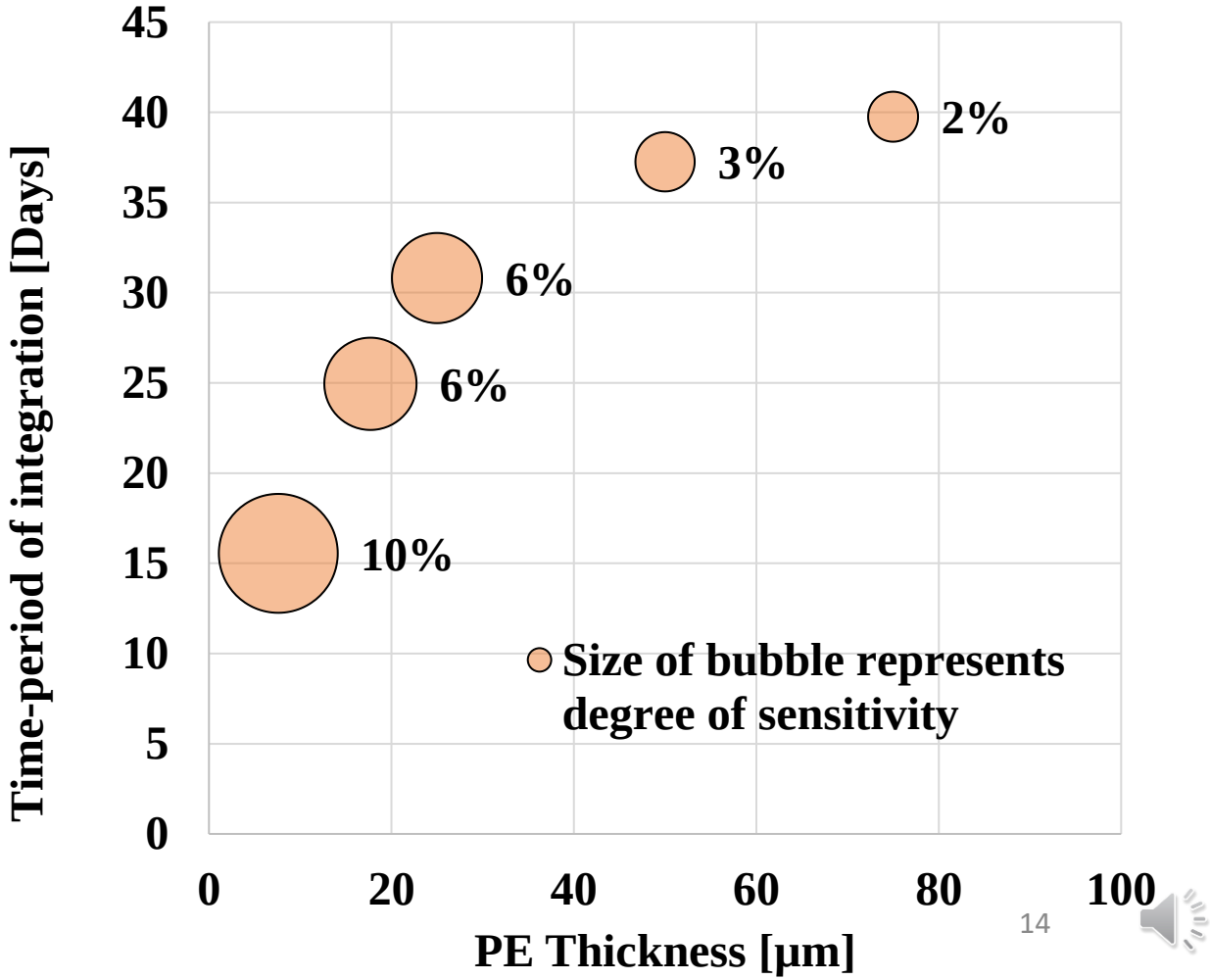
% cross-over/ degree of sensitivity:
sum of % deviation around the day of cross-over **[For PCB 37:** $((1.02-1)+(1-0.97))\times 100 = 6\%$**)]**

- The percentage cross-over for each congener: estimate of the sensitivity of the congener to the pulse (Size of Bubbles)
- Increasing hydrophobicity -> increasing time-period of integration -> decreasing sensitivity

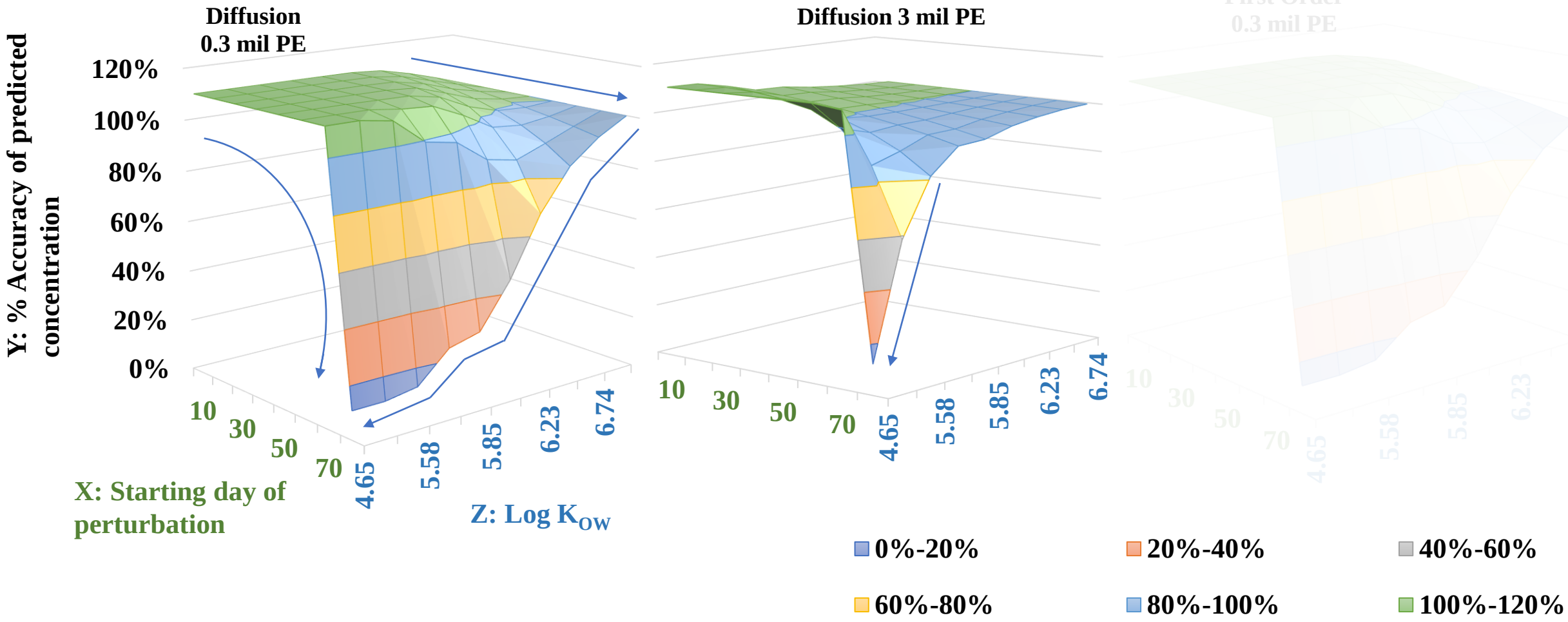
Results: Sampler thickness (PCB 37)

A thicker polymer is more resistive to perturbations in the ambient concentration.





Results: Comparison of mathematical models



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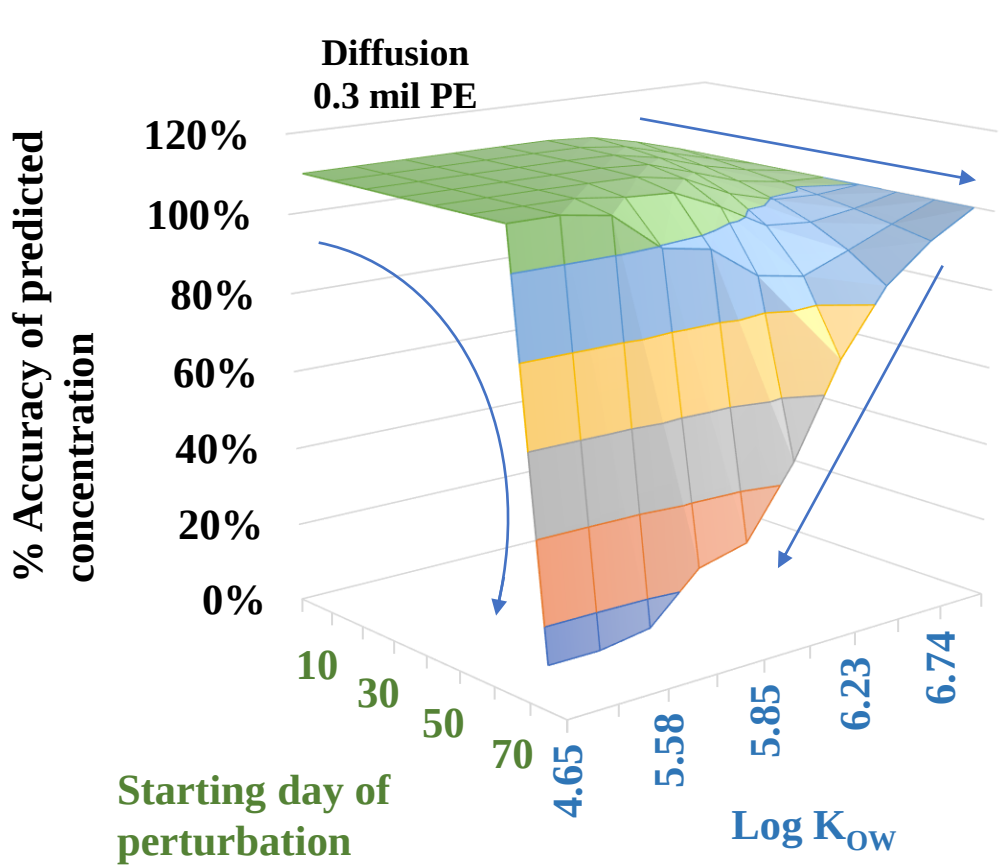
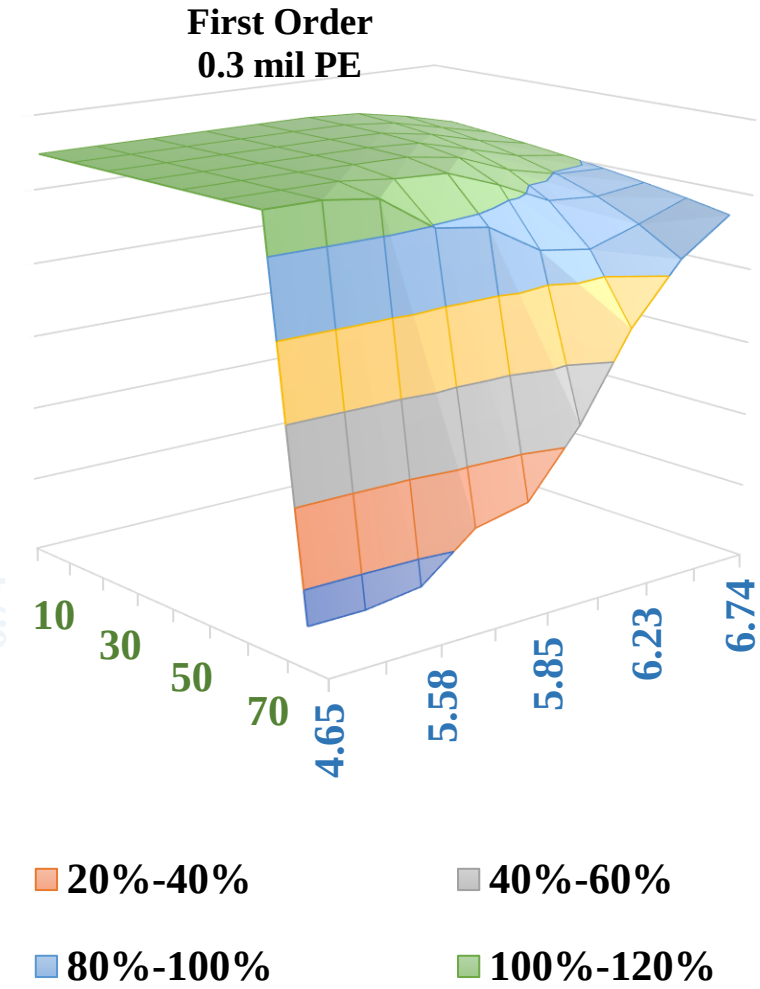
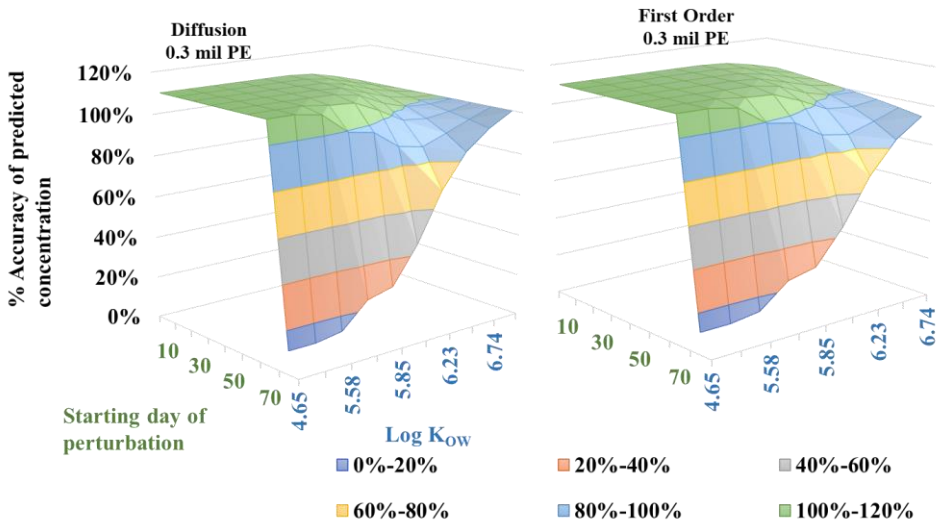




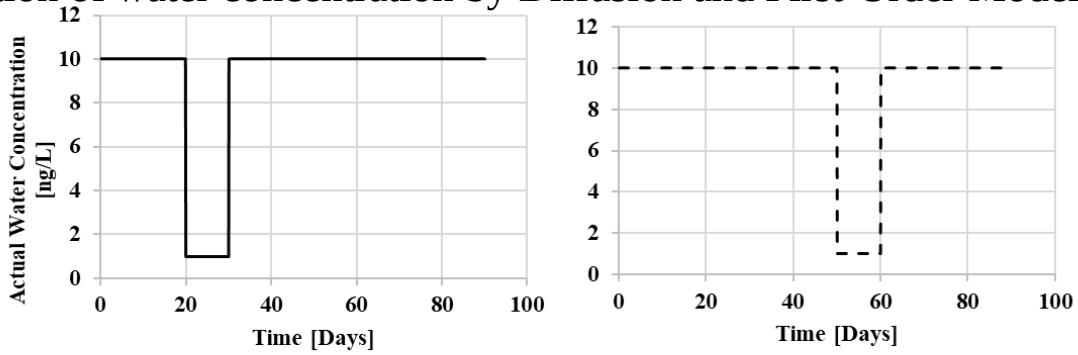
Diffusion and First-Order produce consistent predictions of perturbed ambient water concentration.

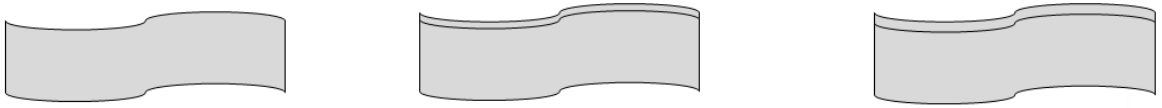
Conclusion

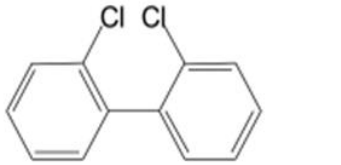
- Determination of time-period of integration of PCB compounds (minimum amount of time required by a compound to represent true ambient water concentrations: 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl while using a 1 mil PE):
  - Nature of perturbation
  - Hydrophobicity of congener
  - Thickness of passive sampler



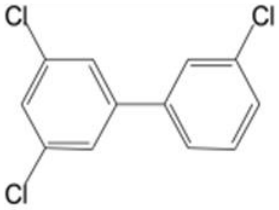
- Consistent prediction of water concentration by Diffusion and First-Order Models.



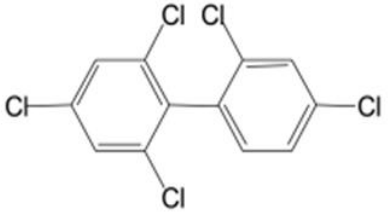




PCB4
(Dichlorinated, *Ortho*-substituted)



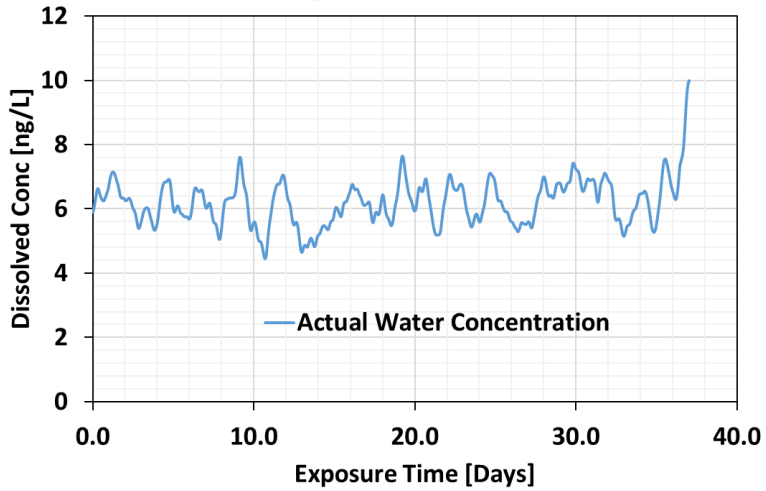
PCB36
(Trichlorinated, *Meta*-substituted)

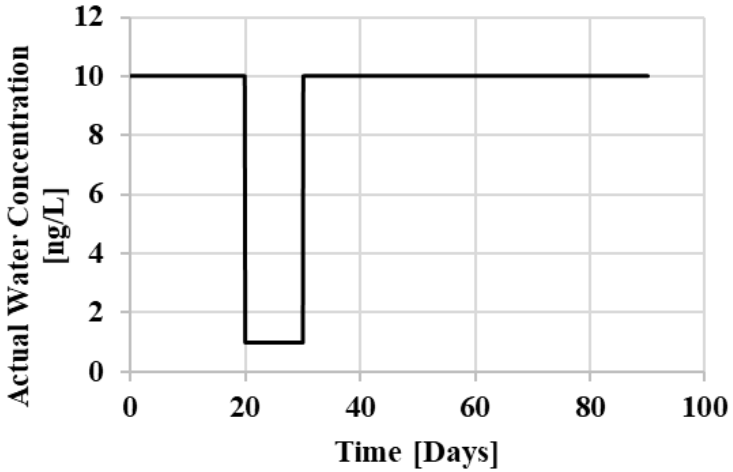


PCB100
(Pentachlorinated, *Ortho*-substituted)

Conclusion

- Determination of time-period of integration of PCB compounds (minimum amount of time required by a compound to represent true ambient water concentrations: 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl while using a 1 mil PE):
  - Nature of perturbation
  - Hydrophobicity of congener
  - Thickness of passive sampler
- Consistent prediction of water concentr





- **Assumptions to keep in mind:**
  - Real-time perturbations last for a few hours. An exaggerated version chosen for this study.
  - Real measurements involve errors from correction for equilibrium and calculation of exchange rate coefficients (ke)
- **Future Implications:**
  - Optimize choice of passive sampler properties for monitoring compounds of interest in surface water or sediment porewater, within a desired time frame.

Thank You

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