Optimization of Passive Sampling Applications Using Mass Transfer Modeling

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Chemical
Biochemical and
Environmental
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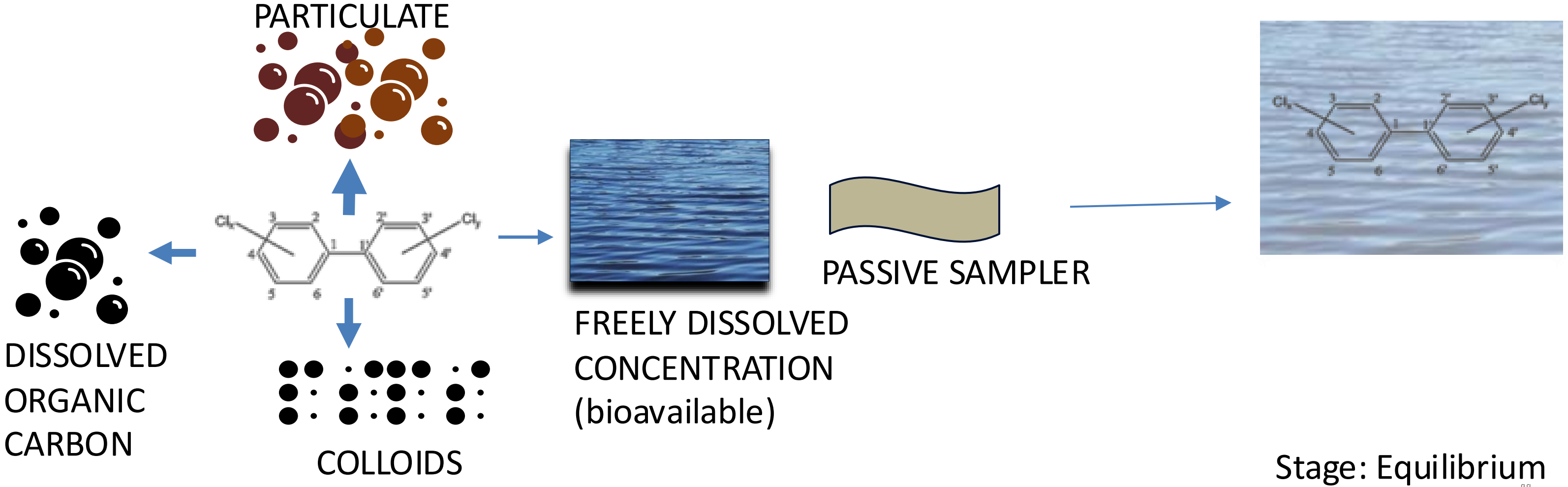
PASSIVE SAMPLING



PARTICULATE

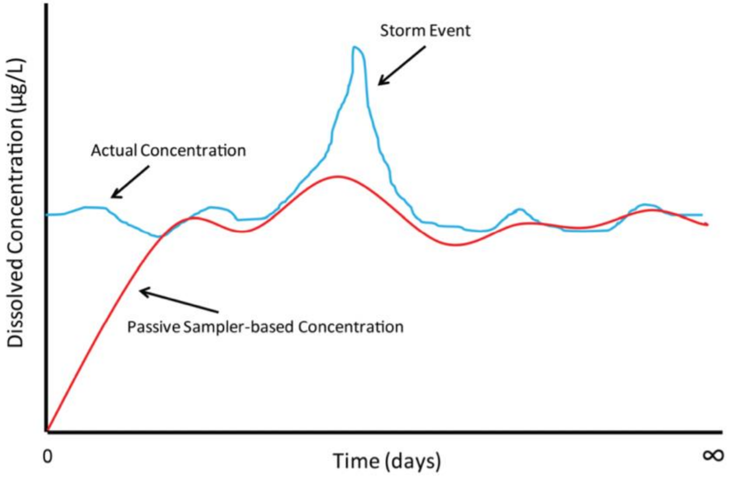
DISSOLVED ORGANIC CARBON

COLLOIDS

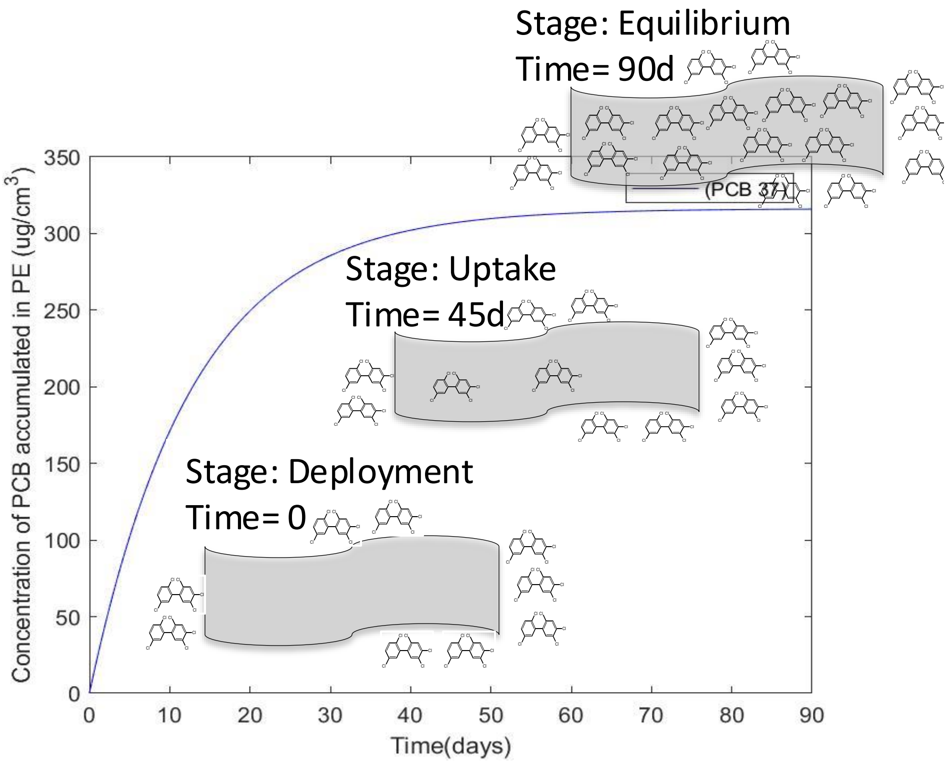
FREELY DISSOLVED CONCENTRATION (bioavailable)

PASSIVE SAMPLER

Freely dissolved conc. of contaminant in water column/ interstitial water (ug/L) [Ghosh et al., 2014]



Burgess, R. M. (2012).



Stage: Equilibrium
Time= 90d

Stage: Uptake
Time= 45d

Stage: Deployment
Time= 0

Part 1: What does Time Integration mean for Passive Sampling?

Part 2: Can we capture the true water concentration of PCBs within a day?

Aims: UNDERSTANDING TIME-PERIOD OF INTEGRATION

How does the **Time-Period of Integration** vary in Passive Sampling:

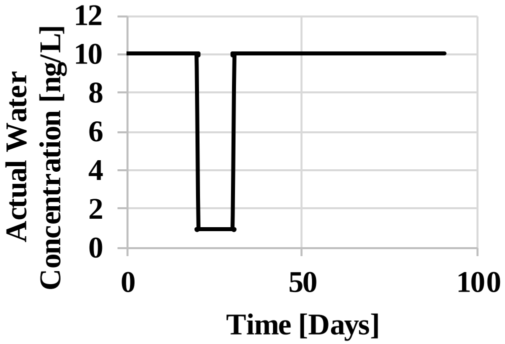
- With **varying day** of introduction of perturbation in ambient water concentration
- With PCB congeners as a function of their varying **hydrophobicity**
- With varying **sampler thickness**

Consistency of predicted results across models in use.

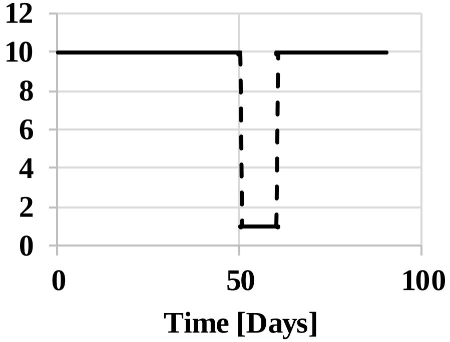
Fick's Diffusion Model

First Order Model

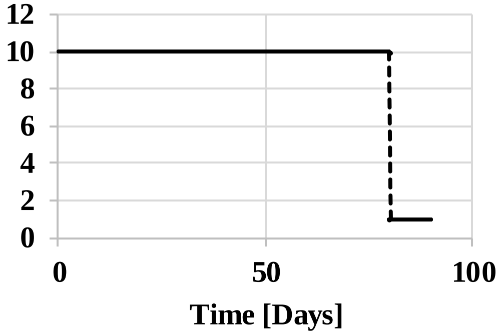
Storm (20-30)



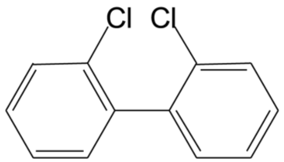
Storm (50-60)



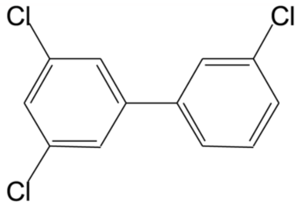
Storm (80-90)



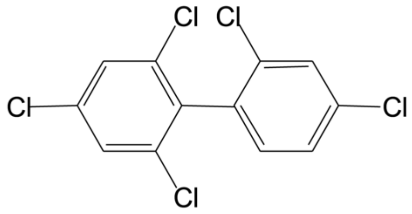
10-day long perturbation when C_w is diluted by 10 times



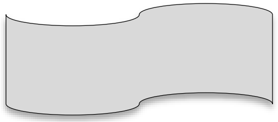
PCB4
(Dichlorinated, *Ortho*-substituted)



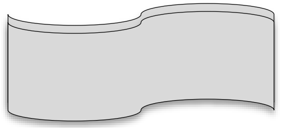
PCB36
(Trichlorinated, *Meta*-substituted)



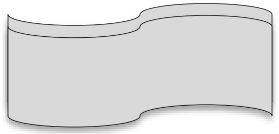
PCB100
(Pentachlorinated, *Ortho*-substituted)



1mil= 25µm



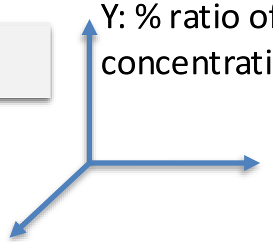
2mil= 50µm



3mil= 75µm

Results: UNDERSTANDING TIME-PERIOD OF INTEGRATION

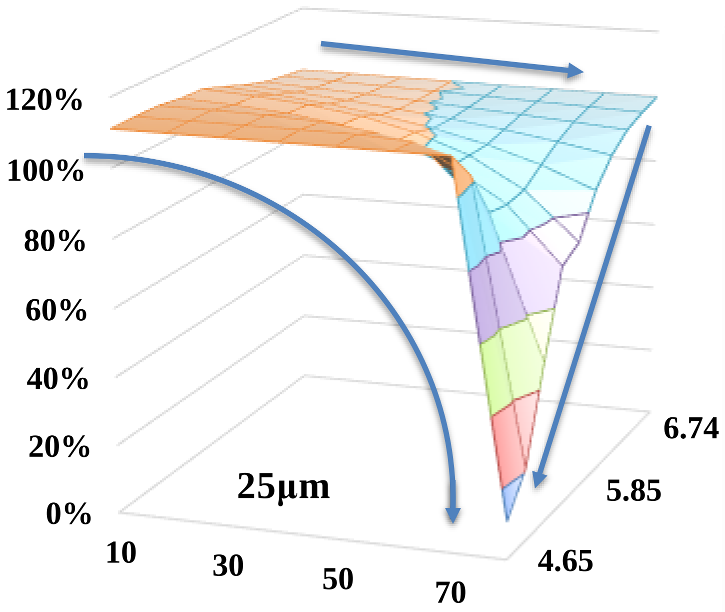
Fick’s Diffusion Model

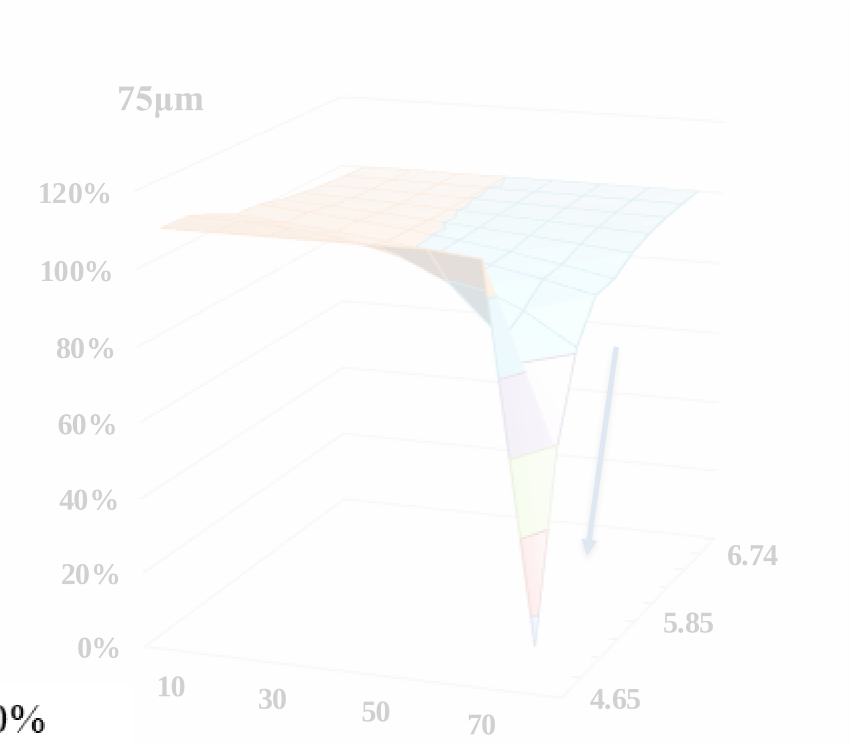


Y: % ratio of the PS based predicted water concentration : actual time-integrated concentration

X: starting day of the 10-day long perturbation the ambient fluid

Z: Log Kow of the PCB congeners

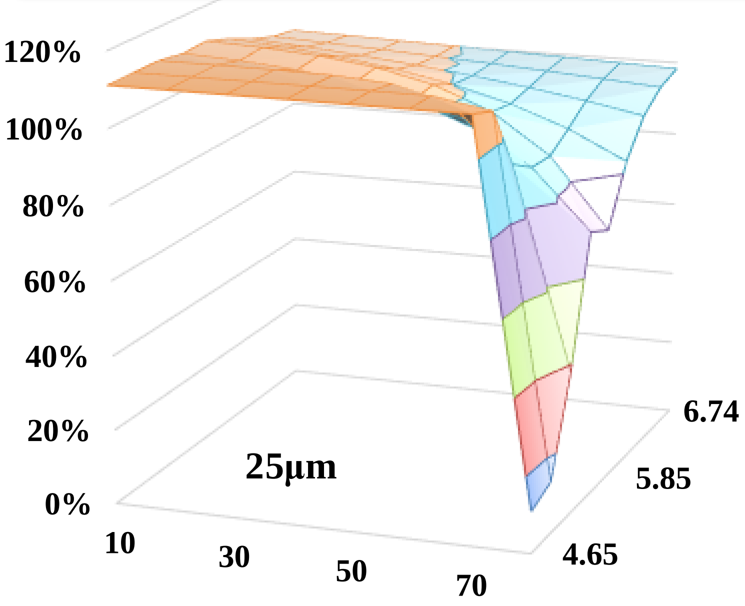




🟦 0%-20% 🟥 20%-40% 🟩 40%-60%

🟪 60%-80% 🟦 80%-100% 🟧 100%-120%

First Order Model



Aims: MODELING SHORT-TERM UPTAKE IN PASSIVE SAMPLERS

Governing Equation: System of well mixed infinite water bath

$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2} \qquad \text{when } -L < x < L \qquad (1)$$

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

Boundary Conditions:

At the interface of the PE and water, the diffusive fluxes match so that mass is conserved

$$D_{PE}\frac{\partial C_{PE}}{\partial x} = D_W\frac{\partial C_W}{\partial x} \qquad \text{when } x = L \text{ and } x = -L \quad (3)$$

local equilibrium distribution

$$C_{PE} = K_{PEW}C_W \qquad \text{when } x = L \text{ and } x = -L \qquad (4)$$

Initial Conditions:

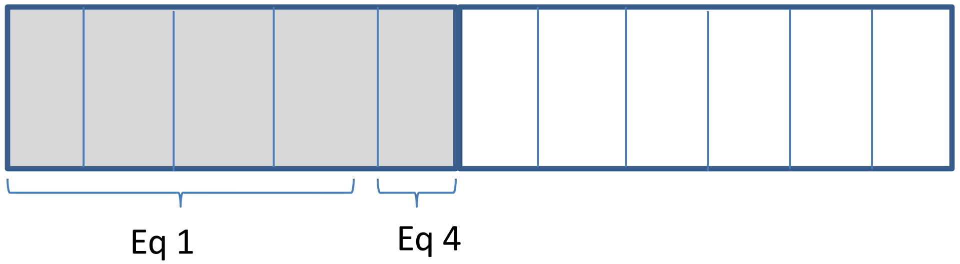
```
CoinPE=100;% Initial conc. of PCB analyte in PE (ug/cm^3)
CoinW=0;% Initial conc. of PCB analyte in WATER (ug/cm^3)
```

$$fractional\ lossof\ PRC = \frac{MinPE}{MinPEinit}$$

$$fractional\ uptake\ of\ target\ analyte = 1 - \frac{MinPE}{MinPEinit}$$

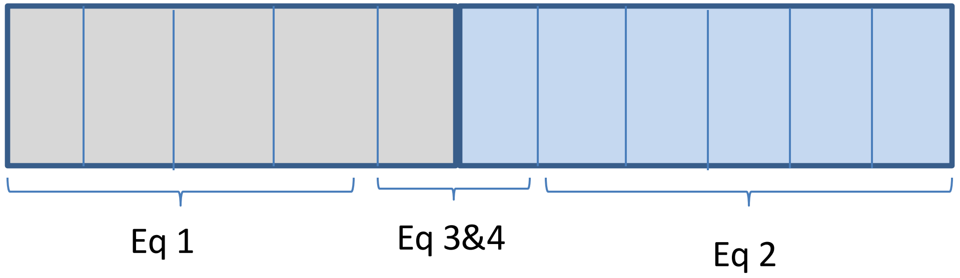
Scenario 1:Fully-sorbent controlled kinetics

WBL=0



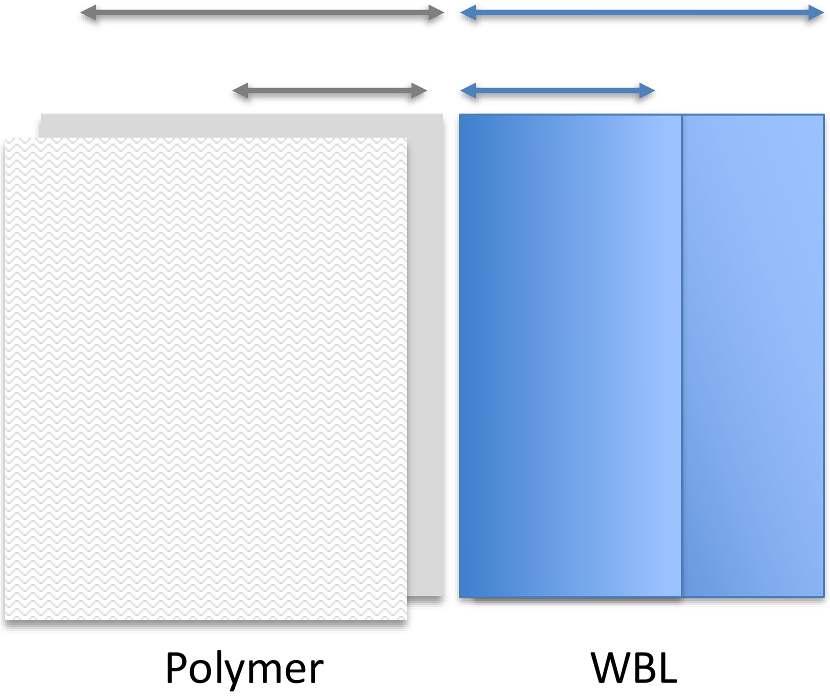
Scenario 2: Partial sorbent-WBL controlled kinetics

WBL≠0



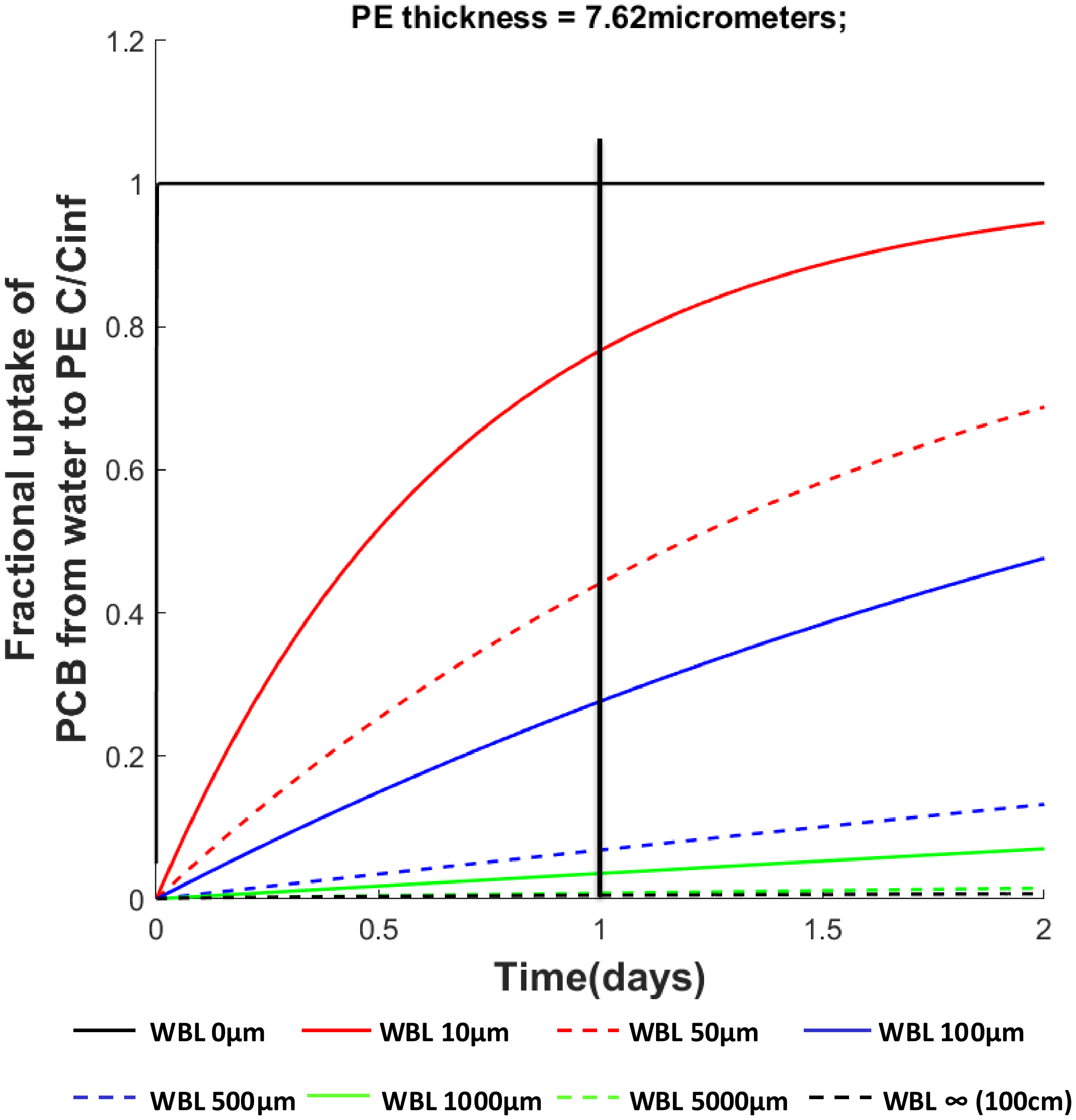
Aims: MODELING SHORT-TERM UPTAKE IN PASSIVE SAMPLERS

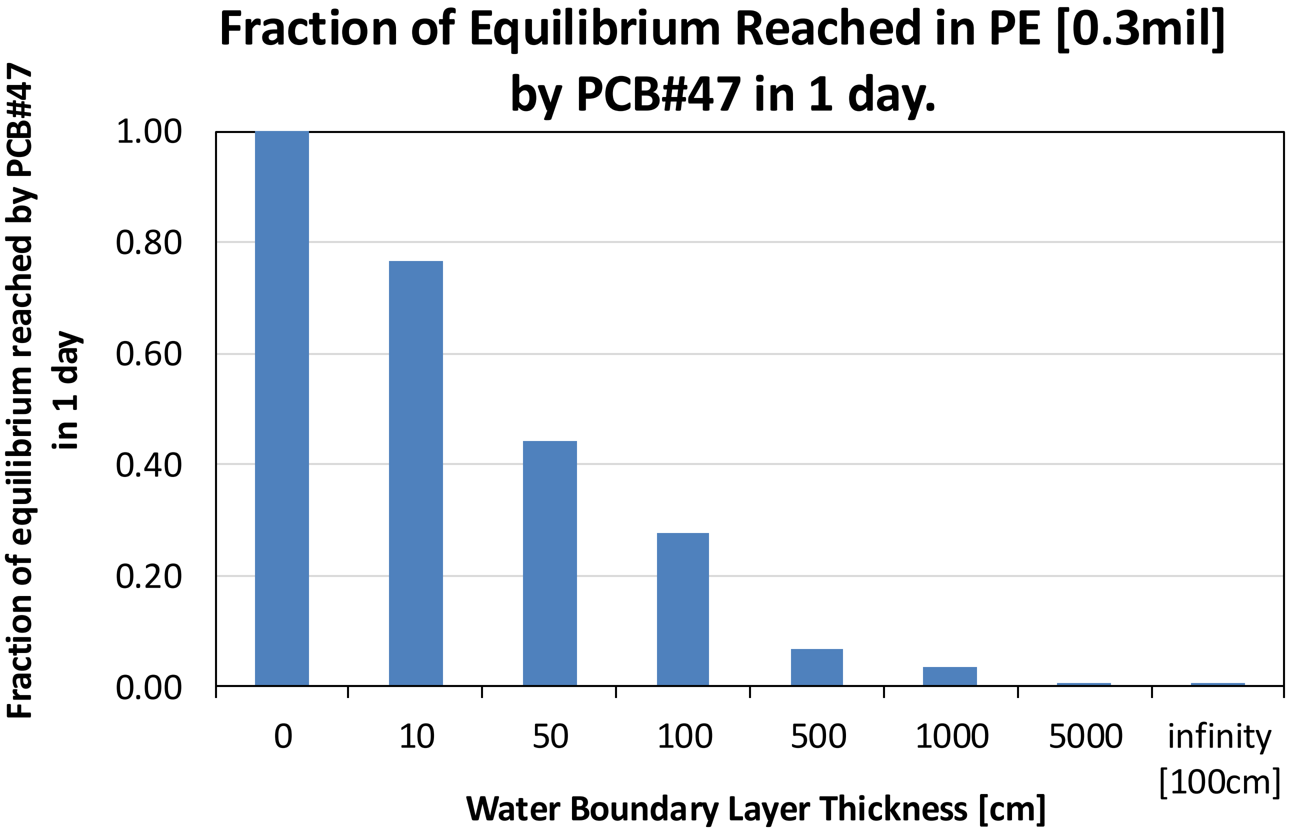
1. Typical WBL thicknesses we might face in the real world? [10µm -500µm, Lohmann 2012]
2. Optimizing PE thickness [0.3,1,2,3 mil] for a range of WBL.
3. Optimizing choice of polymer like Polydimethylsiloxane; PDMS? (Ongoing…)



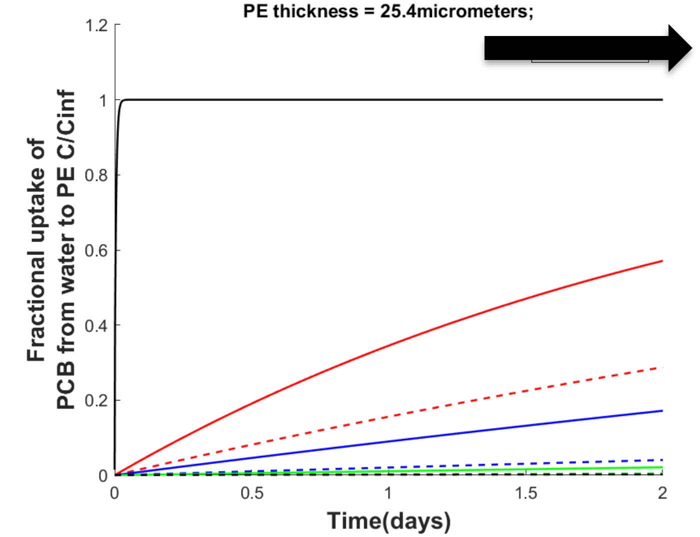
UMBC

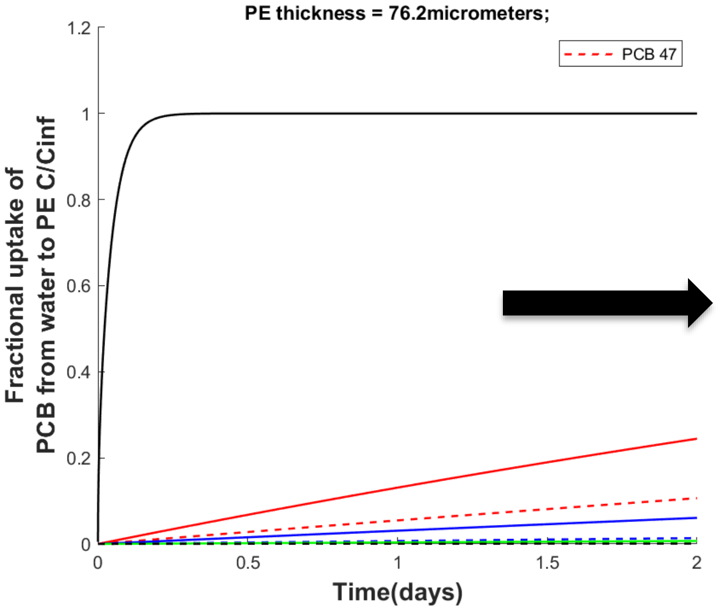
Results: MODELING SHORT-TERM UPTAKE IN PASSIVE SAMPLERS

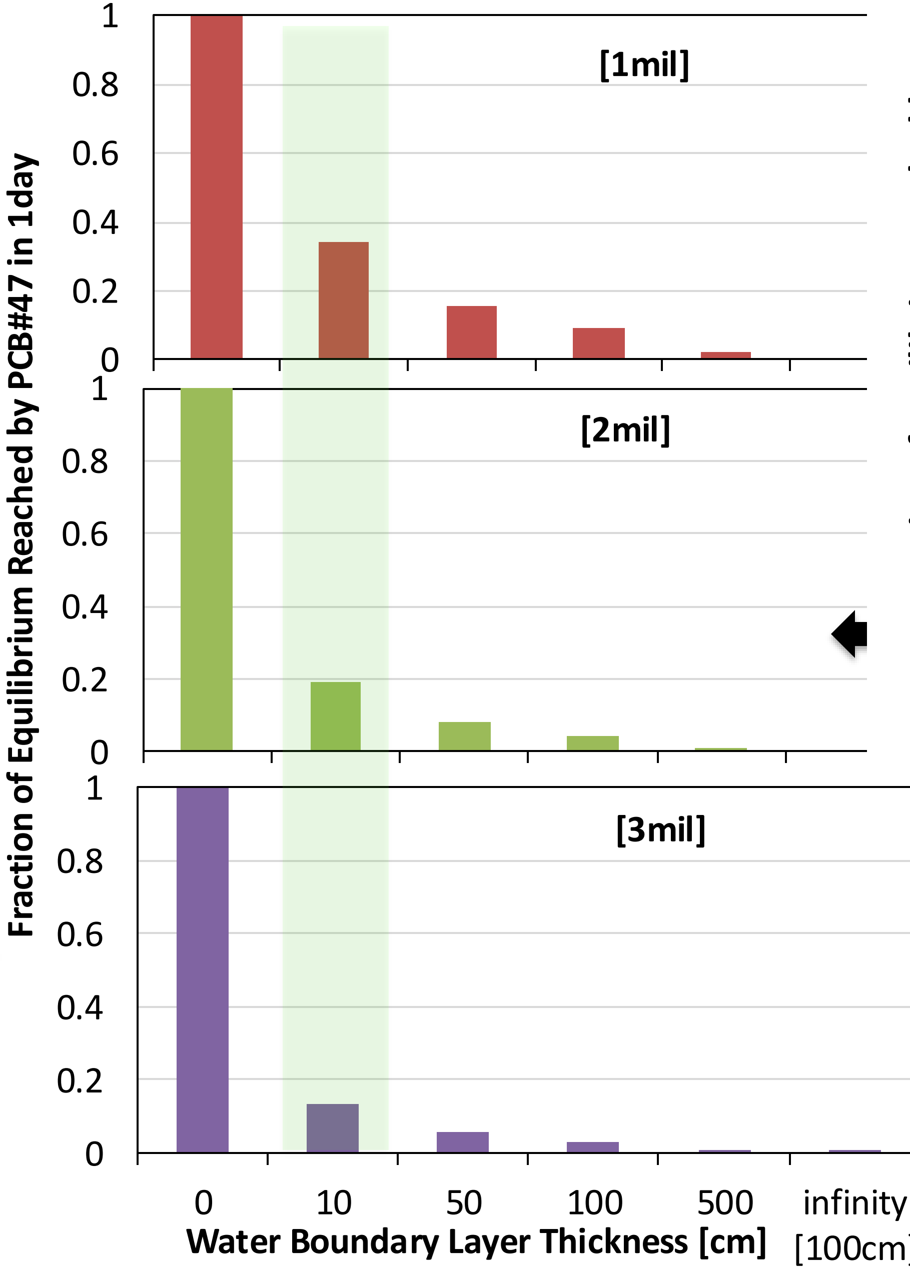


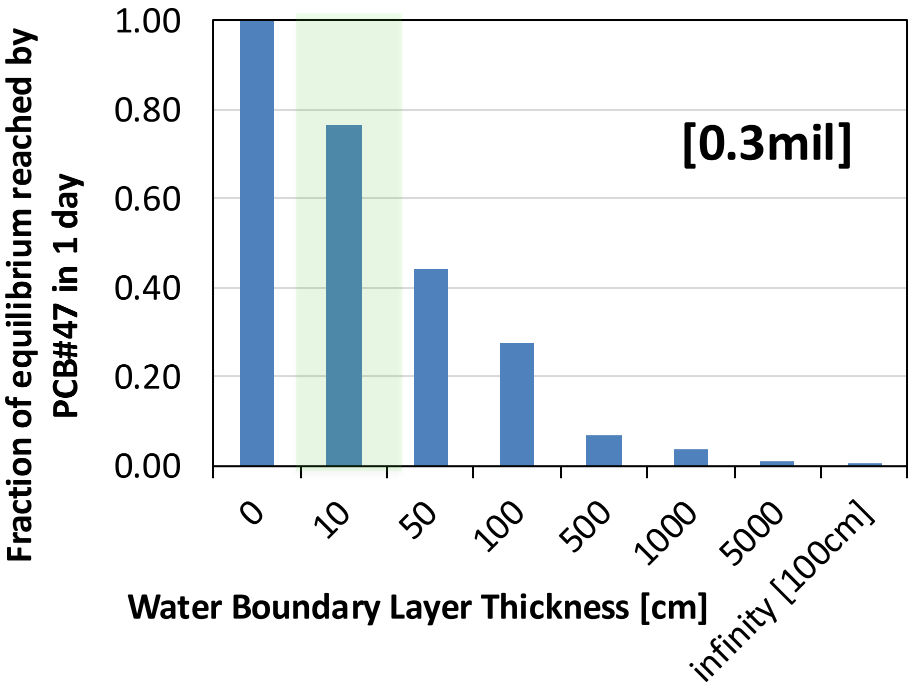


WBL 0µm — WBL 10µm — WBL 50µm — WBL 100µm
WBL 500µm — WBL 1000µm — WBL 5000µm — WBL ∞ (100cm)









Optimizing choice of Polymer: PE vs PDMS

Scenario 1:Fully-sorbent controlled kinetics :

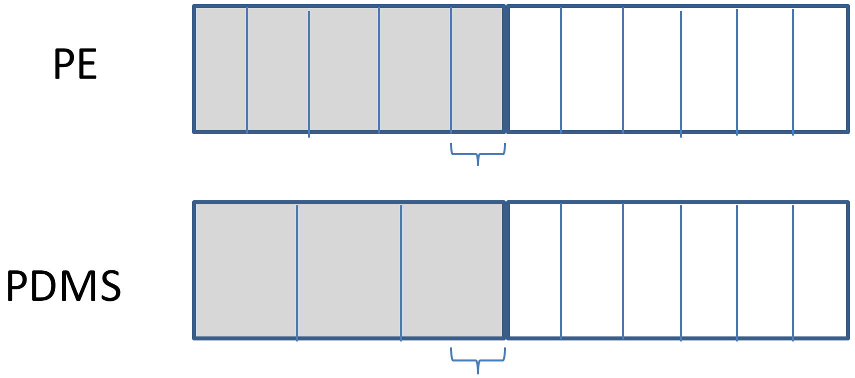
WBL=0

- No interactive fluxes going on at the polymer-water interface.
- Concentration at interface is constant with local equilibrium distribution
- Instant Equilibrium

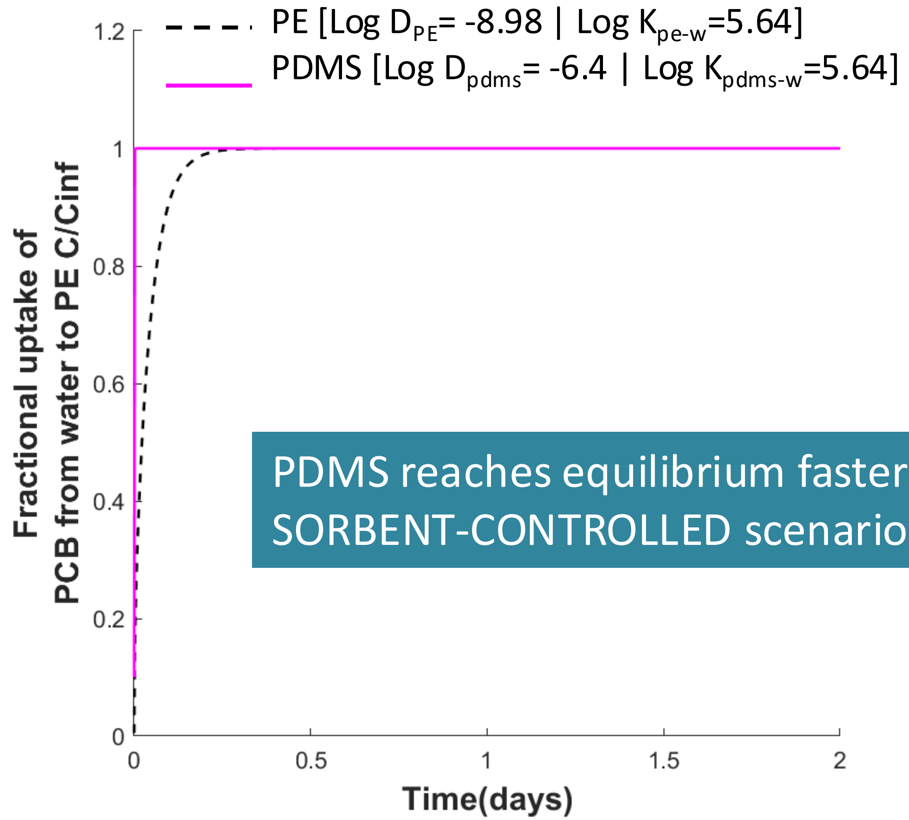
when $x = L$ and $x = -L$

$$\cancel{D_{PS}\frac{\partial C_{PE}}{\partial x} = D_W\frac{\partial C_W}{\partial x} \qquad (3)}$$

$$C_{PS} = K_{PEW}C_W \qquad (4)$$



Polymer Thickness	No. of PE sections [Log D_{PE}= -8.98 for PCB#47]	No. of PDMS sections [Log D_{pdms}= -6.4 for PCB#47]
3mil [76.2µm]	204	10



PDMS reaches equilibrium faster in FULLY-SORBENT-CONTROLLED scenario.

Conclusions

Part 1: What does Time Integration mean for Passive Sampling?

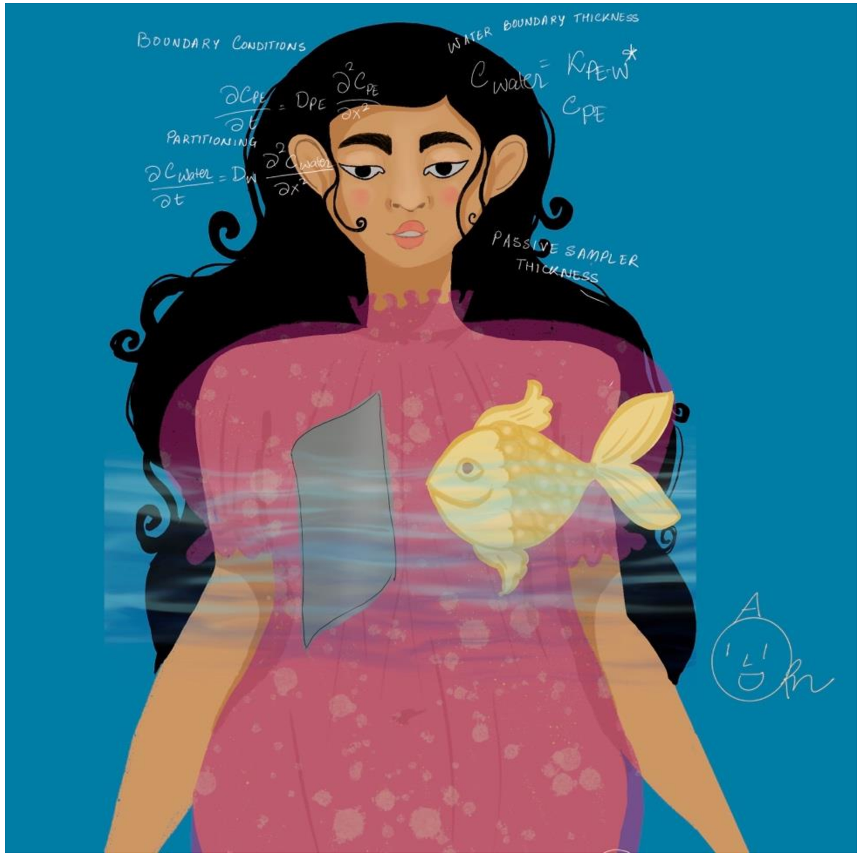
- **Time Period of Integration:** Minimum amount of time required by a congener to represent true ambient water concentrations
  - **Nature of ambient perturbation** (concentration fluctuation, duration) : 10-day pulsed perturbation
  - **Hydrophobicity of congener** : 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl
  - **Thickness of passive sampler :** thicker polymer is more resistive to ambient perturbation.

- Consistent results for Diffusion and 1st order models

Part 2: Can we capture the true water concentration of PCBs within a day?

- Typical WBL thicknesses : 10µm -500µm, Lohmann 2012
- Thinner polymer - turbulent conditions –faster equilibrium represents true water concentration.
- 0.3mil PE |WBL 10µm : 10% equilibrium achieved for upto LogK_{ow} 6.74 (hexa)
- **Fully sorbent-controlled** scenario, WBL=0, PDMS performs better than PE.

Thank You


BOUNDARY CONDITIONS
WATER BOUNDARY THICKNESS
$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2}$
$C_{water} = K_{PE\text{-}W}^{*} C_{PE}$
PARTITIONING
$\frac{\partial C_{water}}{\partial t} = D_W \frac{\partial^2 C_{water}}{\partial x^2}$
PASSIVE SAMPLER THICKNESS