What Does Time-Integration Really Mean for Passive Sampling?

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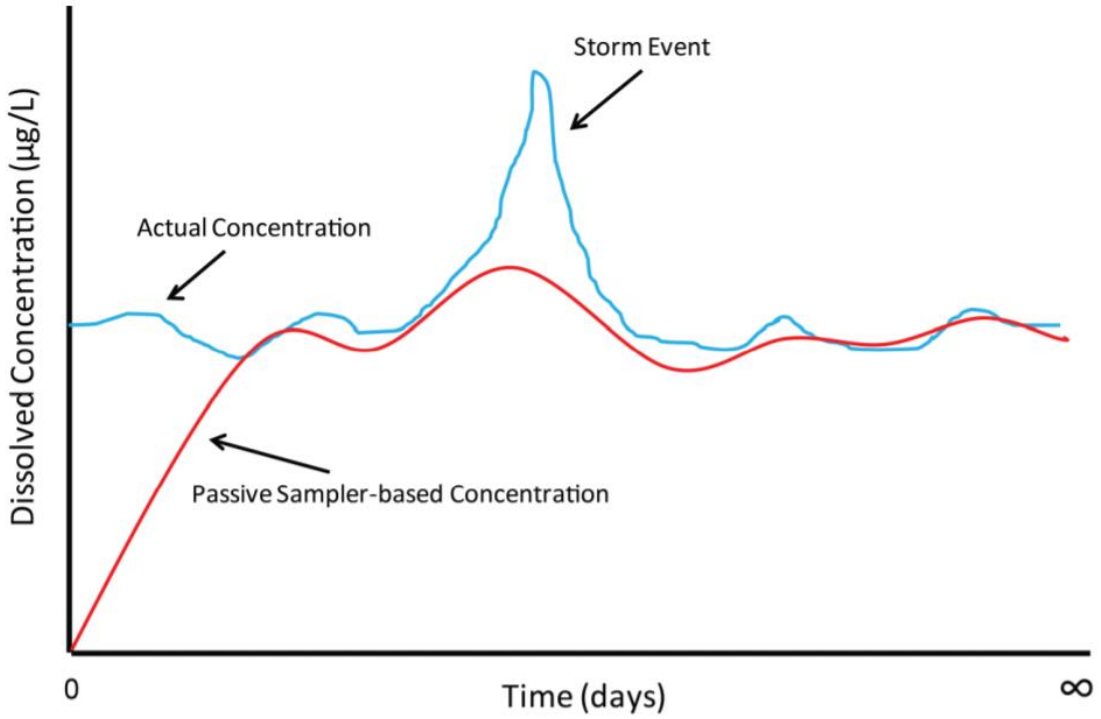
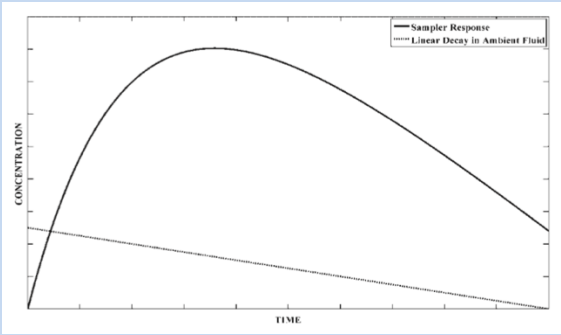
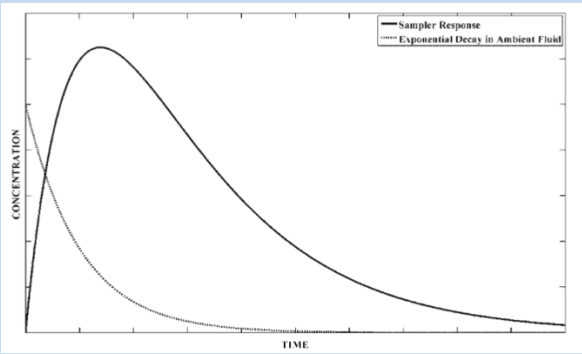
LITERATURE REVIEW & AIMS



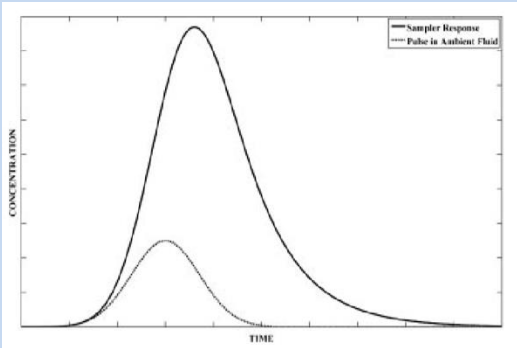
Linear Decay



Exponential Decay



Pulse



- Characteristic of ambient concentration
- Passive sampler-based water concentration (Analytical solution)

Hawker et al., 2009

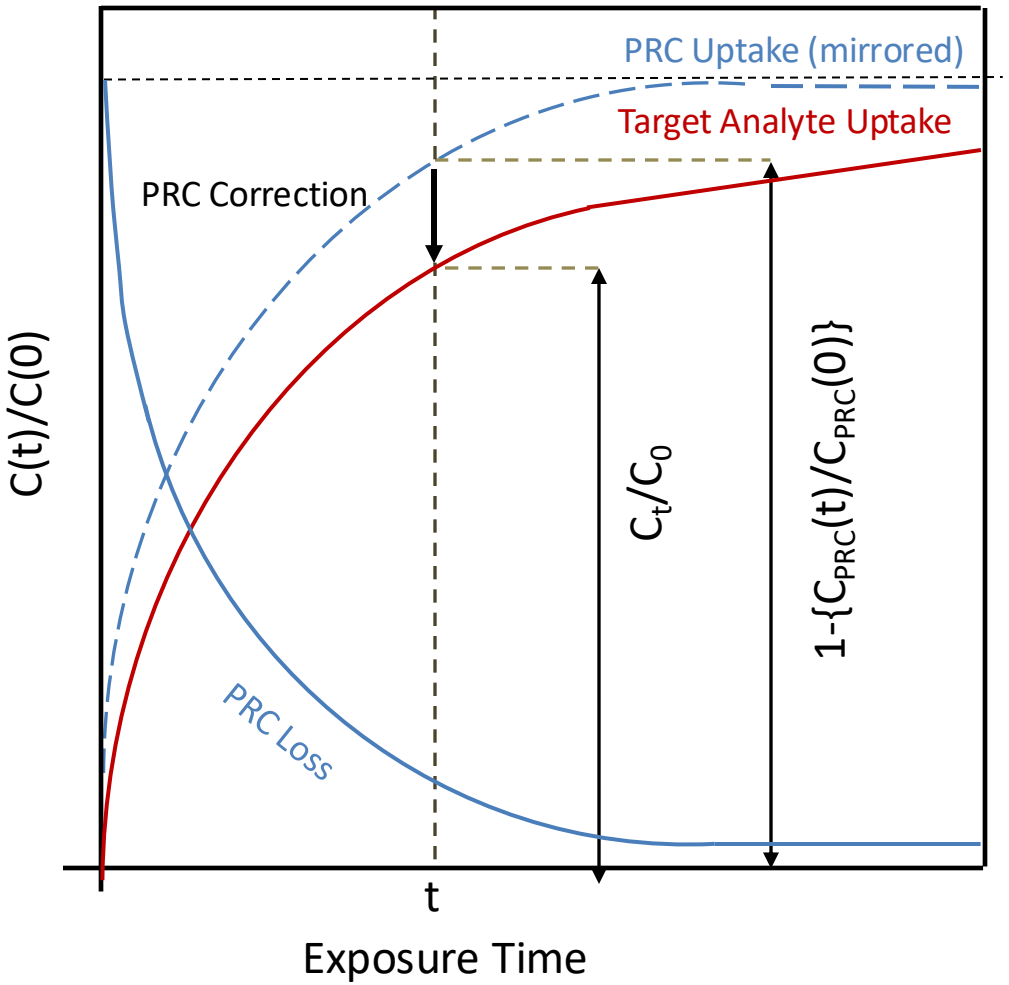
AIM

- In the real environment, water concentrations of these HOCs vary temporally.
- Important for ecological exposure assessment.
- **How well passive sampler concentrations represent the time-averaged concentration over an entire deployment period?**

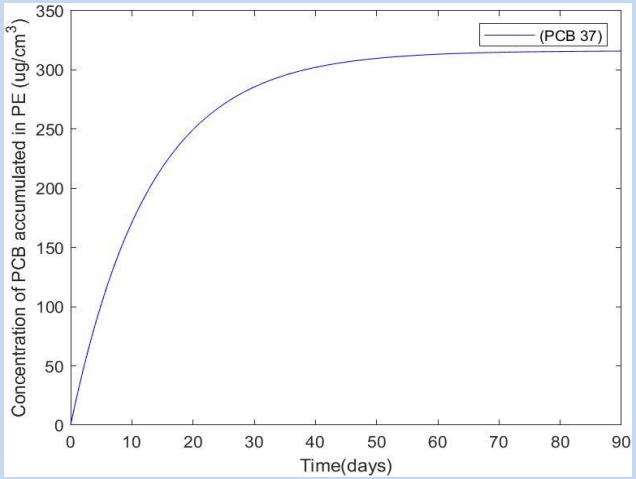
INITIAL CONDITIONS: Water concentration varies from 10ng/L to 1ng/L.

METHOD: PRC CORRECTION

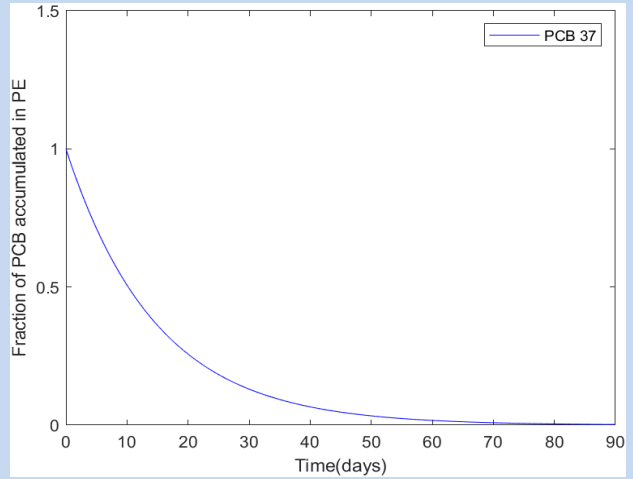
PERFORMANCE REFERENCE COMPOUND CORRECTION FOR EQUILIBRIUM



Gain Function = Actual Mass Gained



Loss Function = Fraction of Loss



$$Corrected\ Mass\ of\ PCB\ Uptake = \frac{Actual\ Mass\ Gained}{Fraction\ of\ Loss}$$

$$C_w = \frac{Corrected\ Mass\ of\ PCB\ Uptake}{K_{PEW}}$$

METHOD

FICK'S DIFFUSION MODEL

Governing Equation: System of well mixed infinite water bath

Eq 1 $$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{for } -l < x < l$$

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

Boundary Conditions:

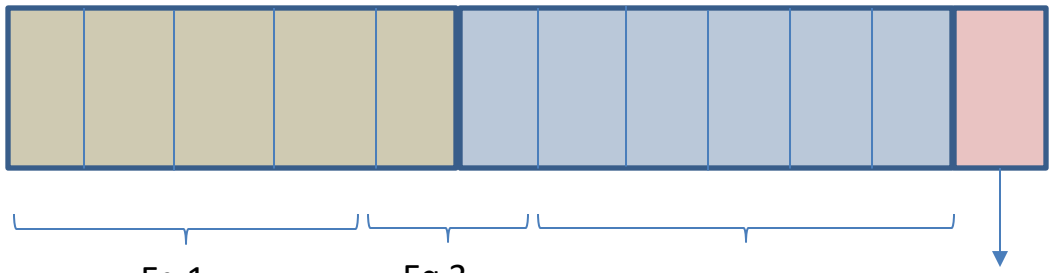
At the interface of the PE and water, the diffusive fluxes match so that mass is conserved

$$D_{PE}\frac{dC_{PE}}{dx} = D_W\frac{dC_W}{dx} \quad \text{for } x = l \text{ and } x = -l$$

local equilibrium distribution

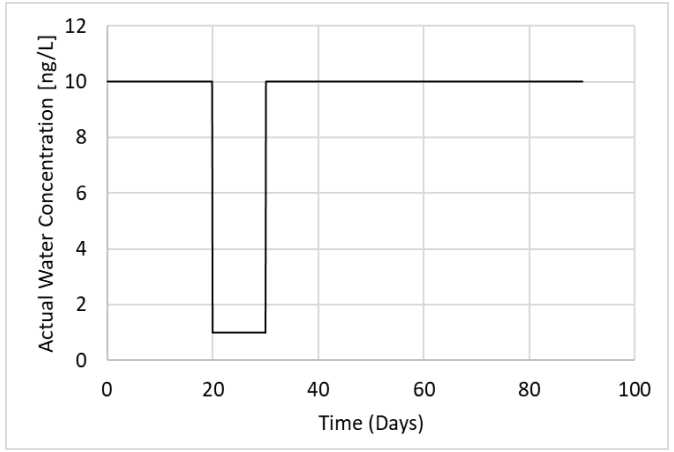
$$C_{PE} = K_{PEW}\,C_W \quad \text{at } x = l \text{ and } x = -l$$

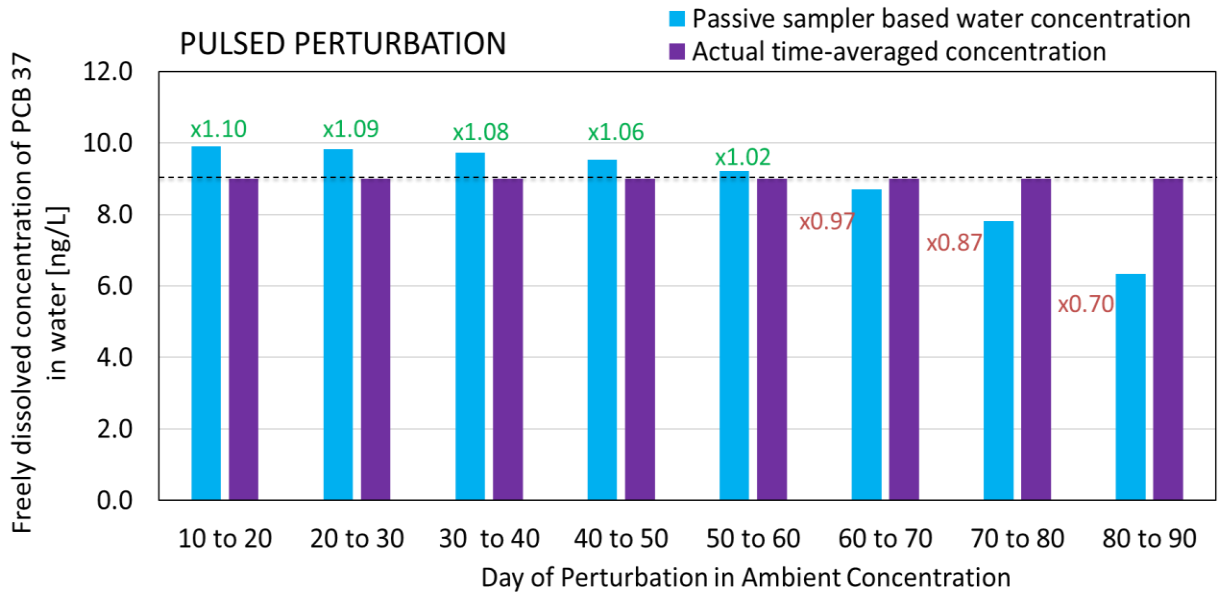
Eq 3

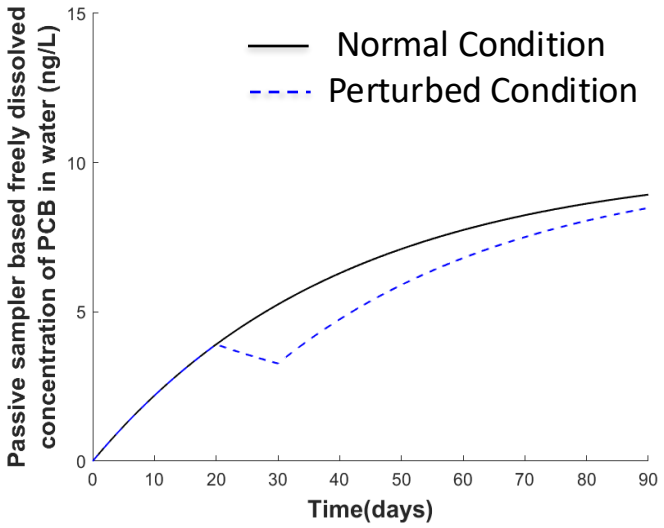


RESULTS

Impact of **varying day of introduction of perturbation** in ambient water concentration.







- Time-averaged C_w stays constant
- Crossover from overestimation to underestimation
- Time period of Integration, PCB 37: 31 days.

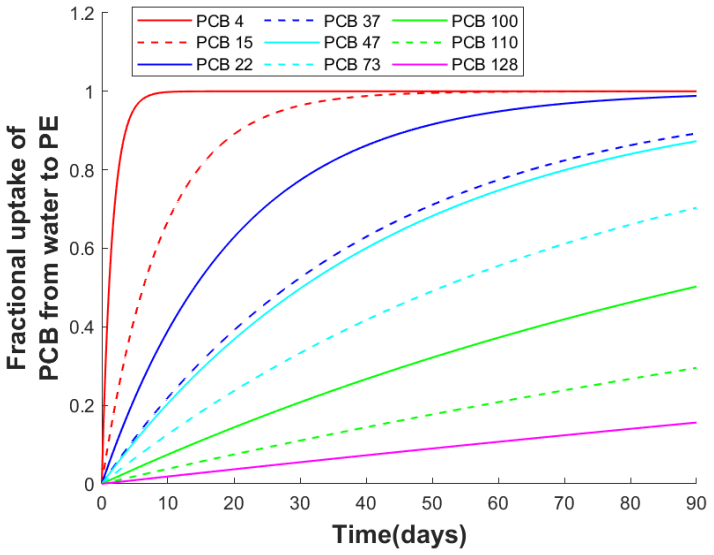
RESULTS

Impact of **varying congener hydrophobicity** under perturbed ambient water concentration.

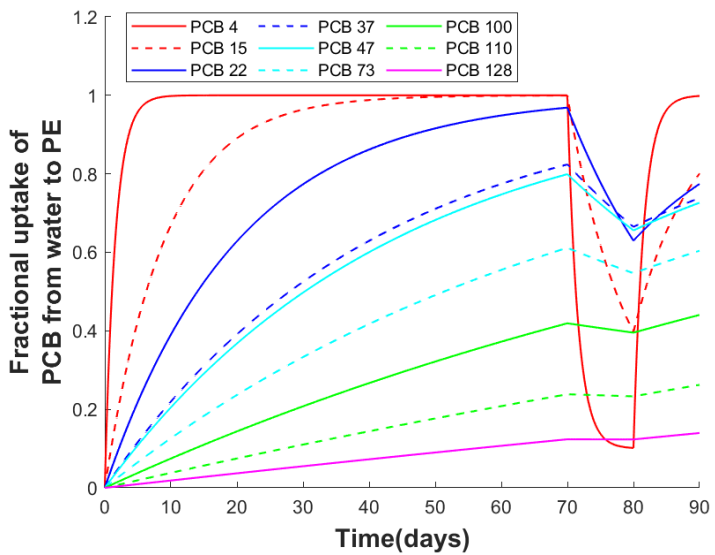
Serial No.	# Cl atoms	PCB congener	Molecular Weight [1]	Log D_{PE} (cm^2/s) [1]	D_W (cm^2/s) [2]	Log K_{OW} [3]	Log K_{PE-W} [4]
1	2	PCB 4	223.1	-8.64	5.81E-06	4.65	4.23
2	2	PCB 15	223.1	-8.64	5.81E-06	5.3	4.99
3	3	PCB 22	257.5	-8.81	5.24E-06	5.58	5.32
4	3	PCB 37	257.5	-8.81	5.24E-06	5.83	5.62
5	4	PCB 47	291.9	-8.98	4.80E-06	5.85	5.64
6	4	PCB 73	291.9	-8.98	4.80E-06	6.04	5.87
7	5	PCB 100	326.4	-9.16	4.43E-06	6.23	6.09
8	5	PCB 110	326.4	-9.16	4.43E-06	6.48	6.39
9	6	PCB 128	360.8	-9.33	4.13E-06	6.74	6.69

- K_{OW} , K_{PW} is function of hydrophobicity.
- D_{PE}, D_W of same homolog group congeners are same.
- lower homologs reach equilibrium faster.
- lower homologs are more sensitive to the ambient perturbations.

NO PERTURBATION

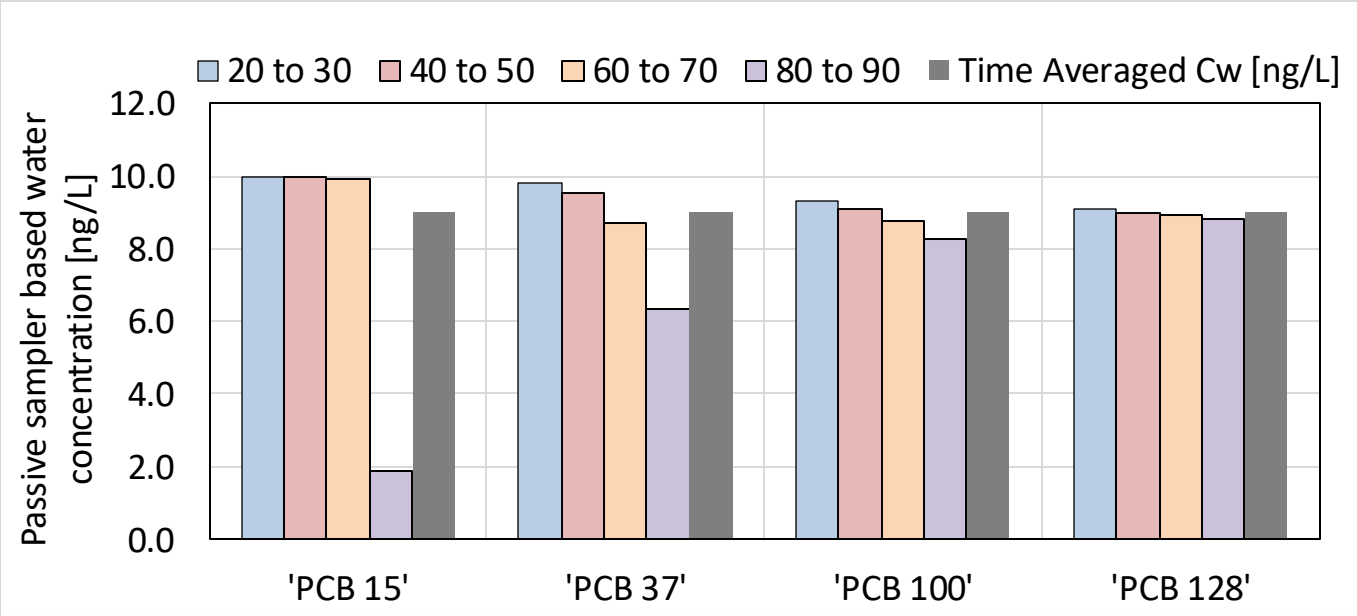


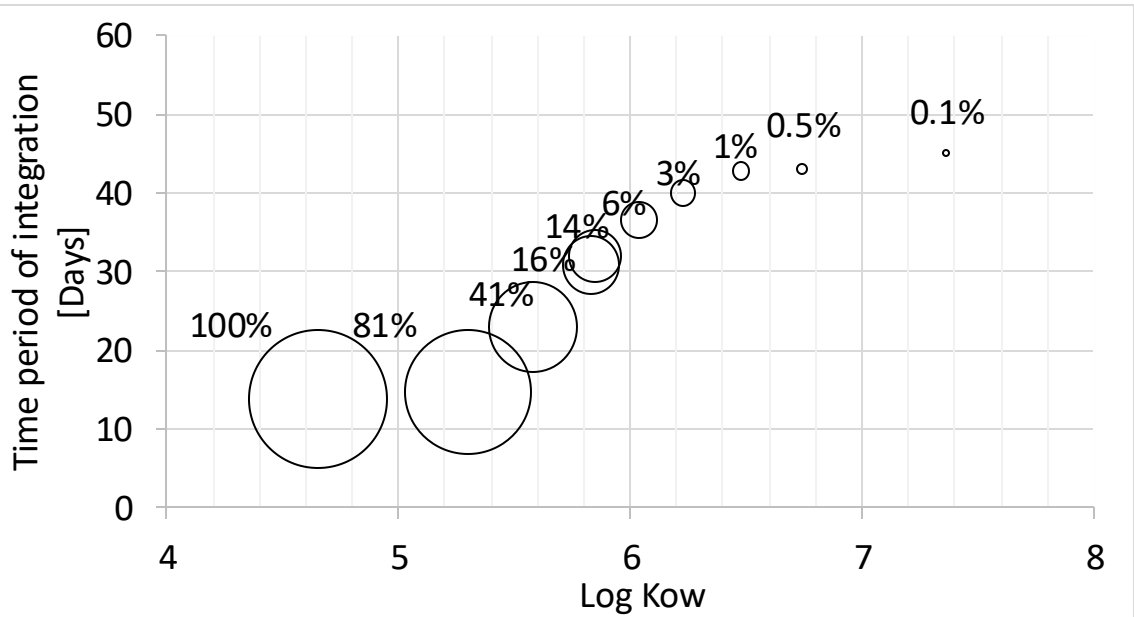
PULSED PERTURBATION ON DAY 70



RESULTS

Impact of **(varying congener hydrophobicity+ varying day of introduction of perturbation)**





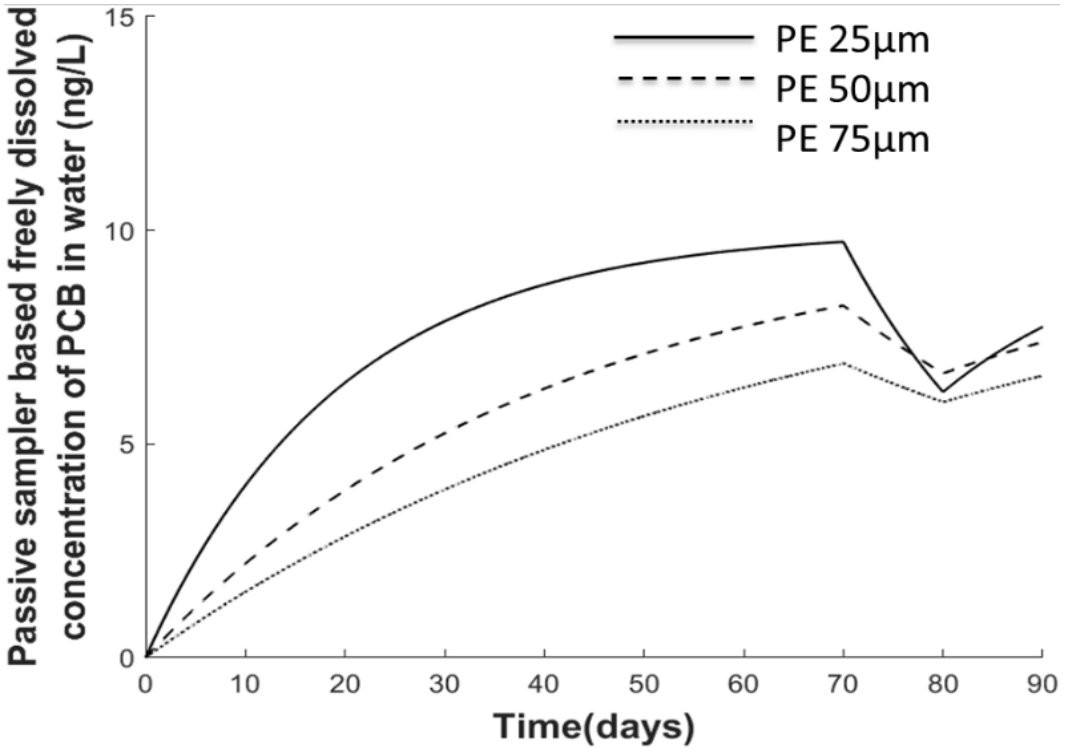
Congeners have varying levels of over or underprediction trends:

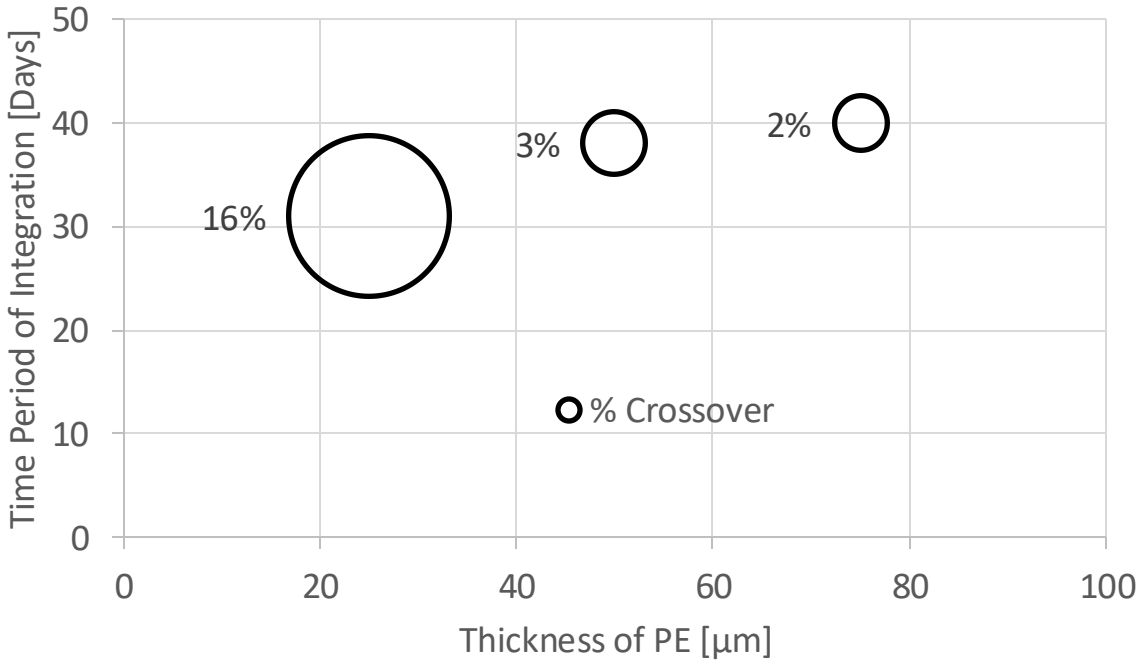
- function of their hydrophobicity and
- consequent sensitivity to fluctuations in ambient concentrations.

- 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

Impact of **varying PE thickness** on the uptake of PCB 37





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

CONCLUSION

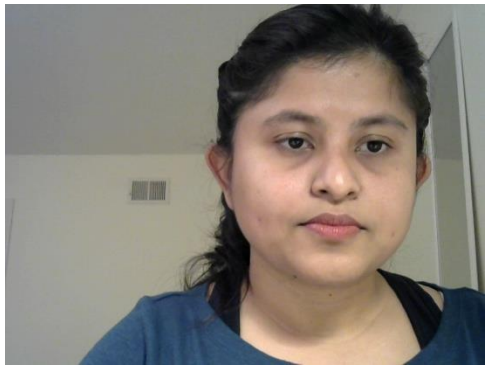
- Time period of integration for passive samplers under fluctuating ambient concentrations of PCBs in water.

- Minimum amount of time required by a congener to represent true ambient water concentrations:
  - Hydrophobicity of congener
  - Thickness of passive sampler

- Range: 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl.

- Perturbations can be multiple and of varying intensities. A simple case chosen for this study.

- Real measurements involve errors from correction for equilibrium.



THANK YOU