

# Mass transfer model for interpreting concentrations in passive samplers used in sediments

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## Report Documentation Page

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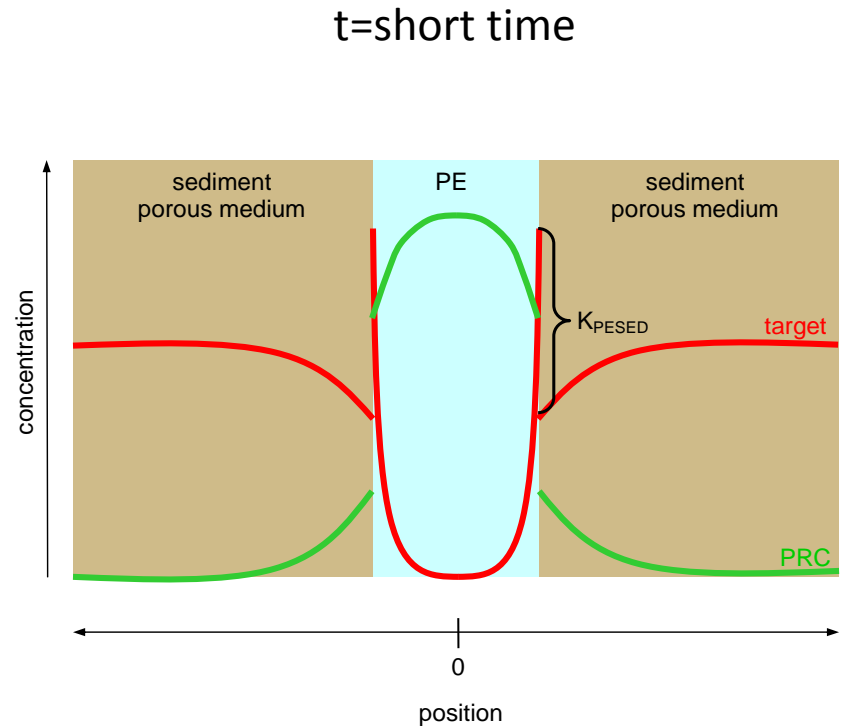
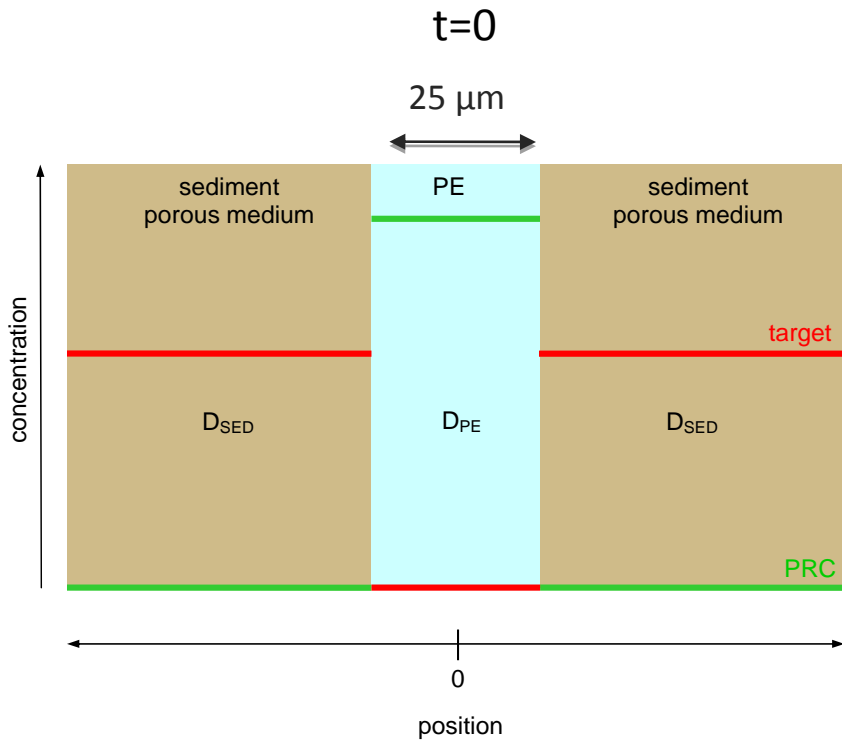
## USING A DIFFUSIVE MASS TRANSFER MODEL TO INTERPRET CONTAMINANT UPTAKE BY POLYMERIC PASSIVE SAMPLERS FROM ENVIRONMENTAL POROUS MEDIA

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(Massachusetts Institute of Technology)

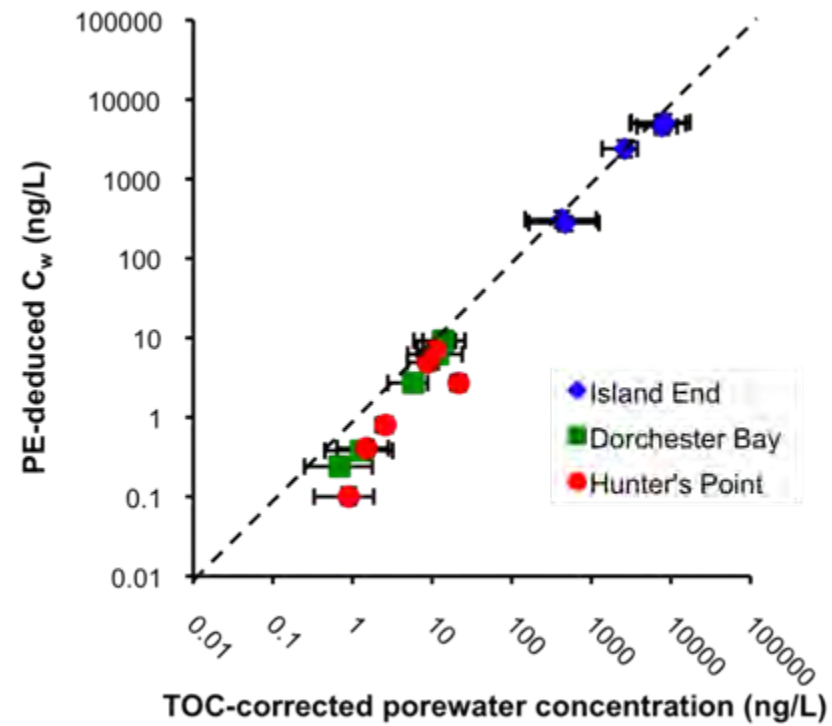
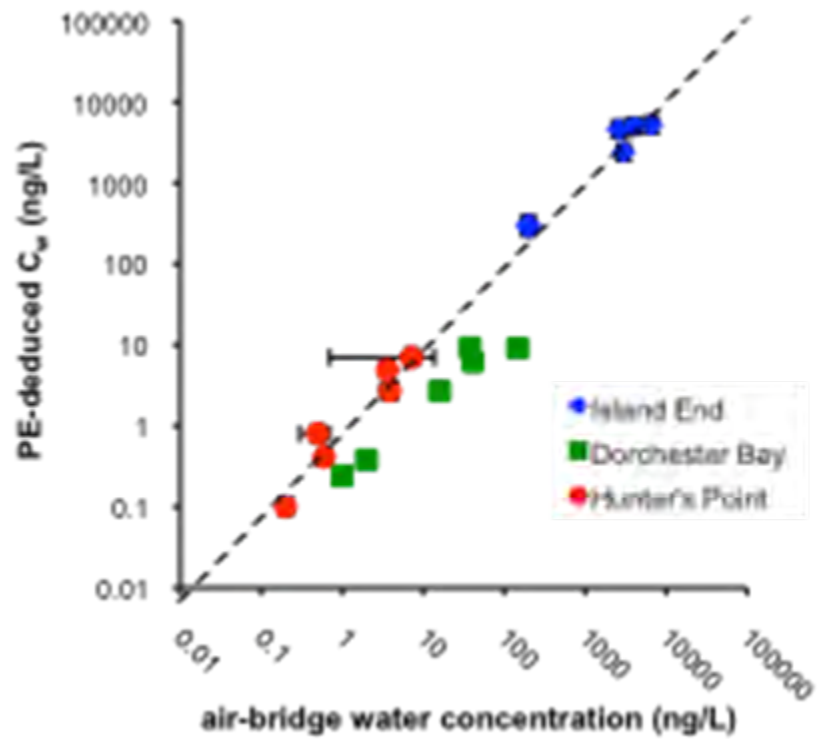
Performance reference compounds (PRCs) are often used in passive sampling devices in order to allow sampler deployment for times shorter than would be required for full equilibration. They are especially important for in situ passive sampling of sediment beds, where equilibration of sampler and sediments could take years. In order to translate sampler concentration data, for both PRCs and target chemicals, into useful information such as water concentrations or chemical activities, an accurate mass-transfer model for the system is necessary. Here, a two-phase diffusion model for a polymer sheet in porous media is described and its use demonstrated. A method for calibrating sampler/site-specific mass transfer behavior using three PRCs and the model is described. The accuracy of such results are compared to measured porewater concentrations of seventeen target polycyclic aromatic hydrocarbons in a test sediment. Finally, the diffusion model is exercised to predict how air-filled pores would affect deployment times when using polyethylene to sample contaminants in soils.

# PE sampler in sediment

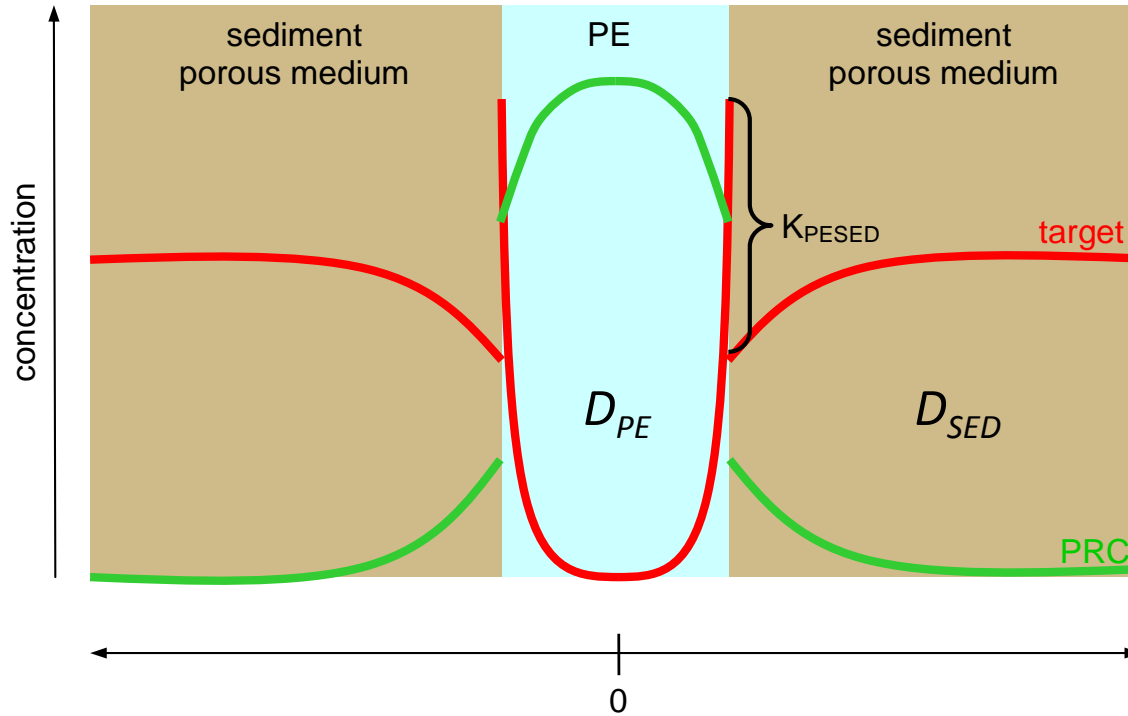


$$M_{target}(t) = k \frac{C_{targetSED}^0}{K_{SEDPE}}$$

$$M_{PRC}(t) = k C_{PRC,PE}^0$$



# PE sampler in sediment

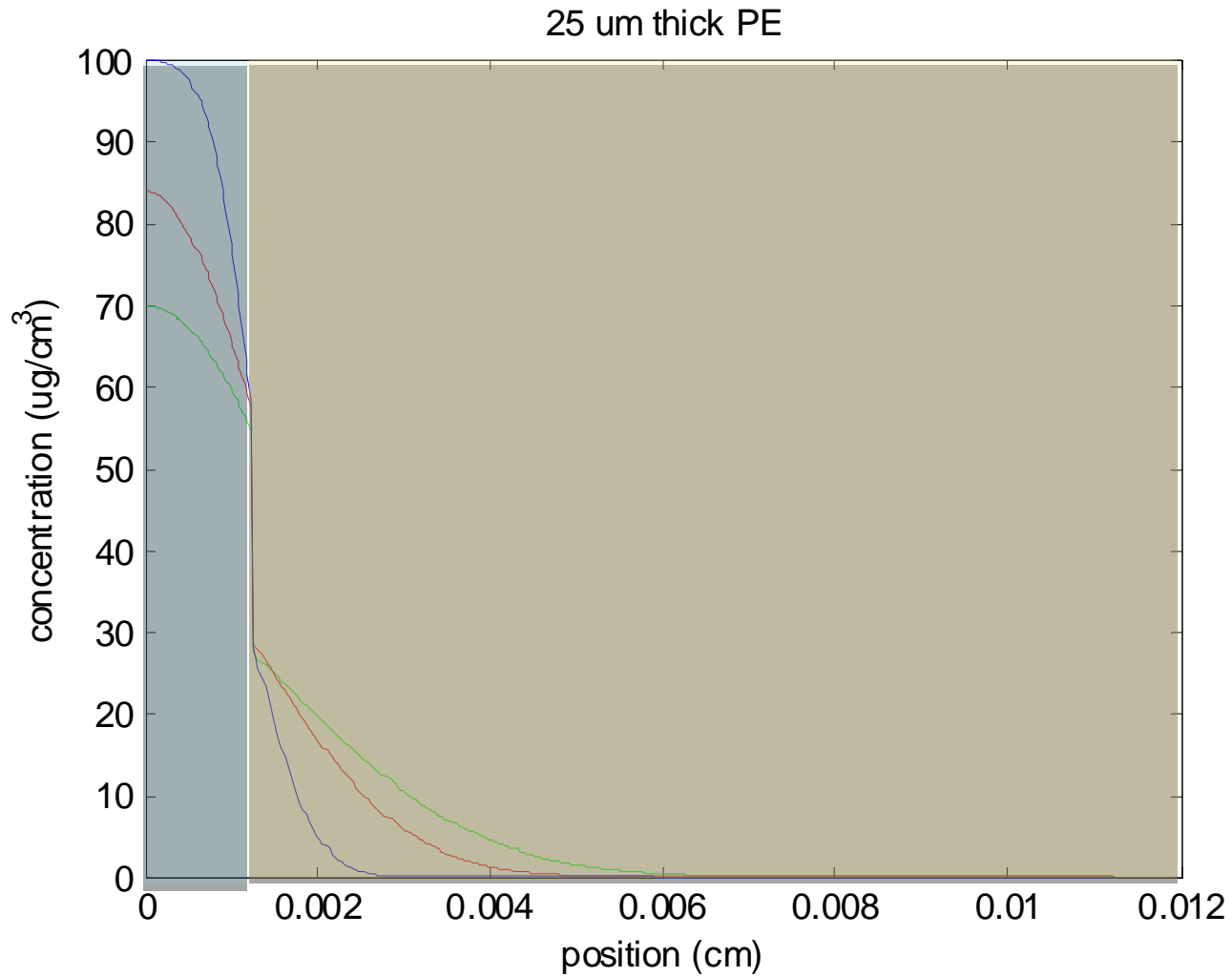


$$D_{SED} = \frac{D_W}{(1 + r_{sw} K_d) \tau}$$

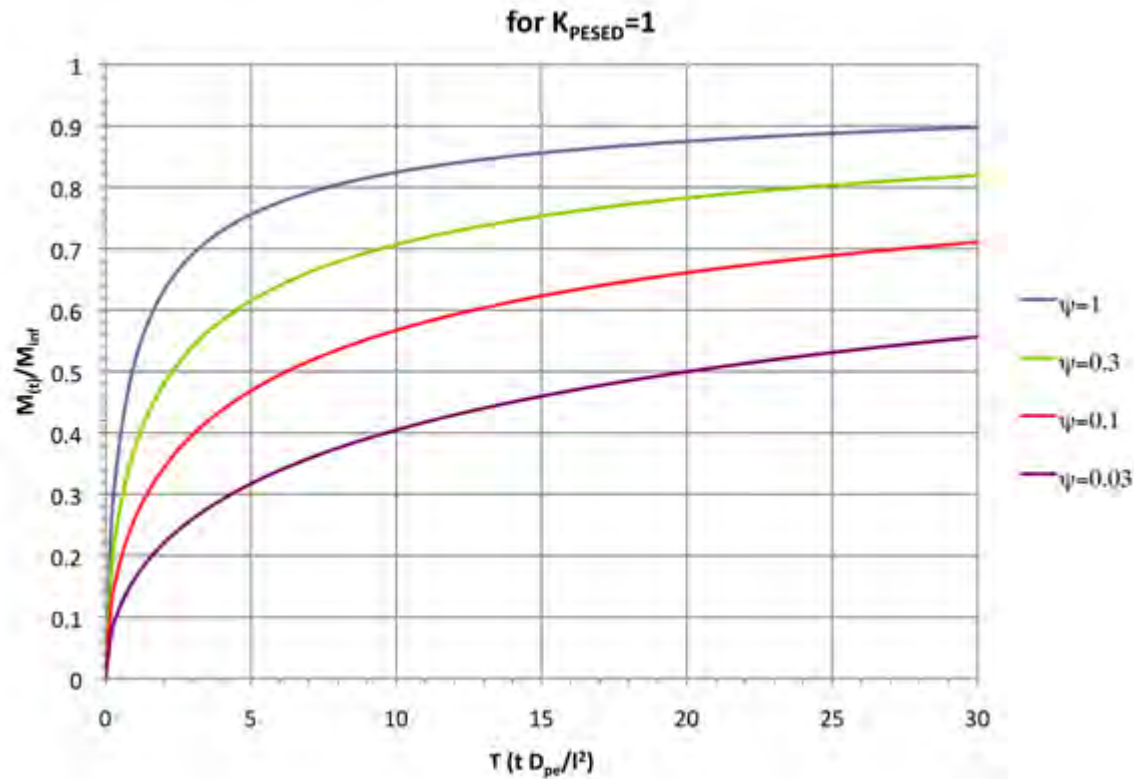
position

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \qquad \frac{\partial C_{SED}}{\partial t} = D_{SED} \frac{\partial^2 C_{SED}}{\partial x^2}$$

# Numerical model of mass transfer



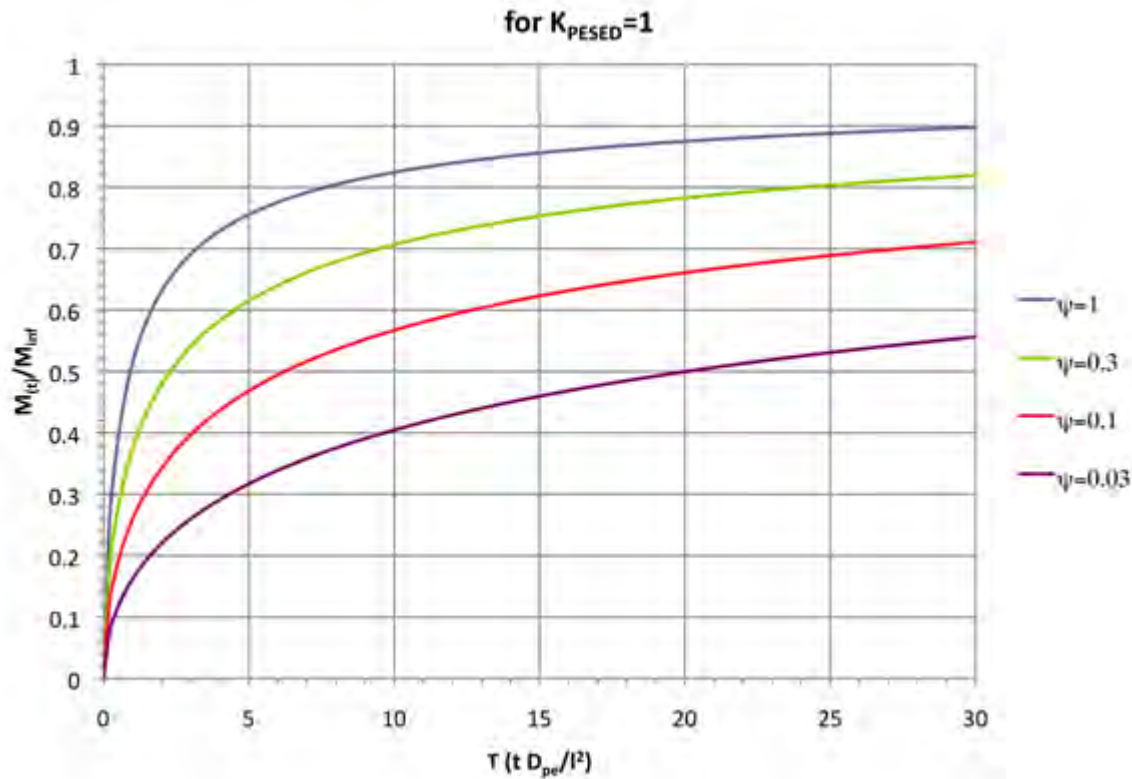
# Laplace space solution to mass-transfer model



$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d) \tau D_{PE}} \approx \frac{D_W}{r_{sw} K_d \tau D_{PE}}$$

$$K_{PESED} = \frac{K_{PEW}}{K_d}$$

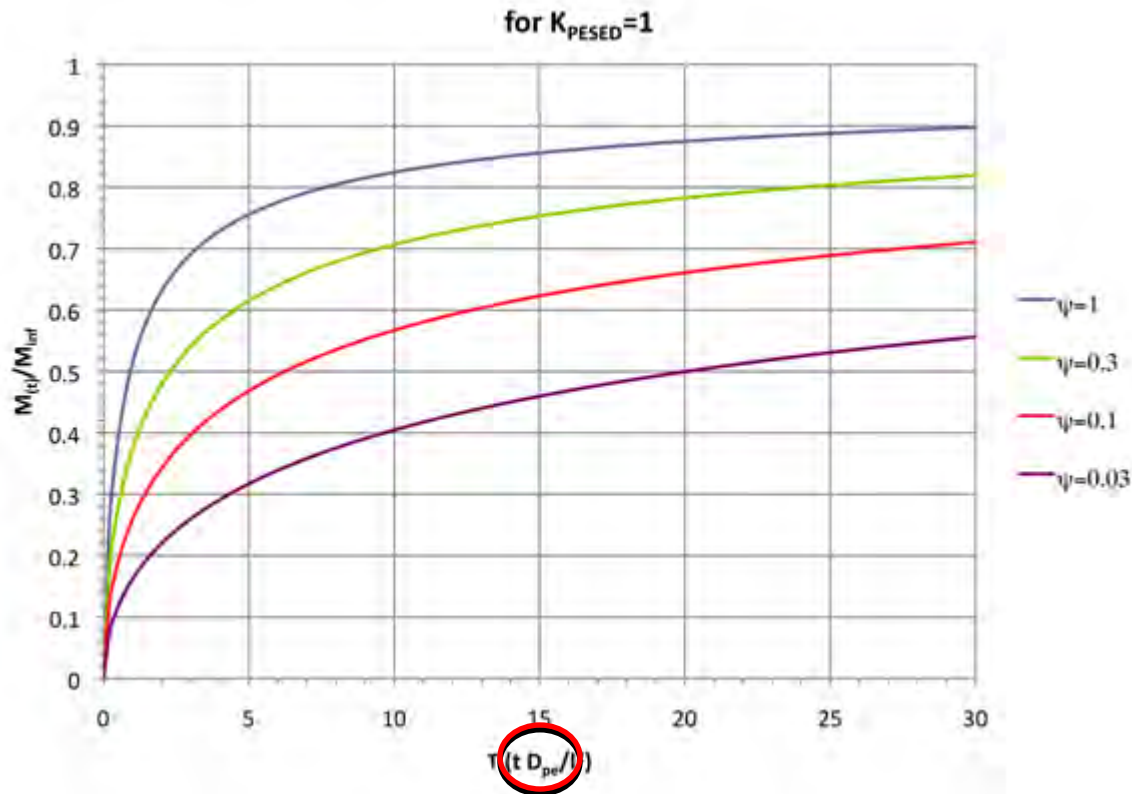
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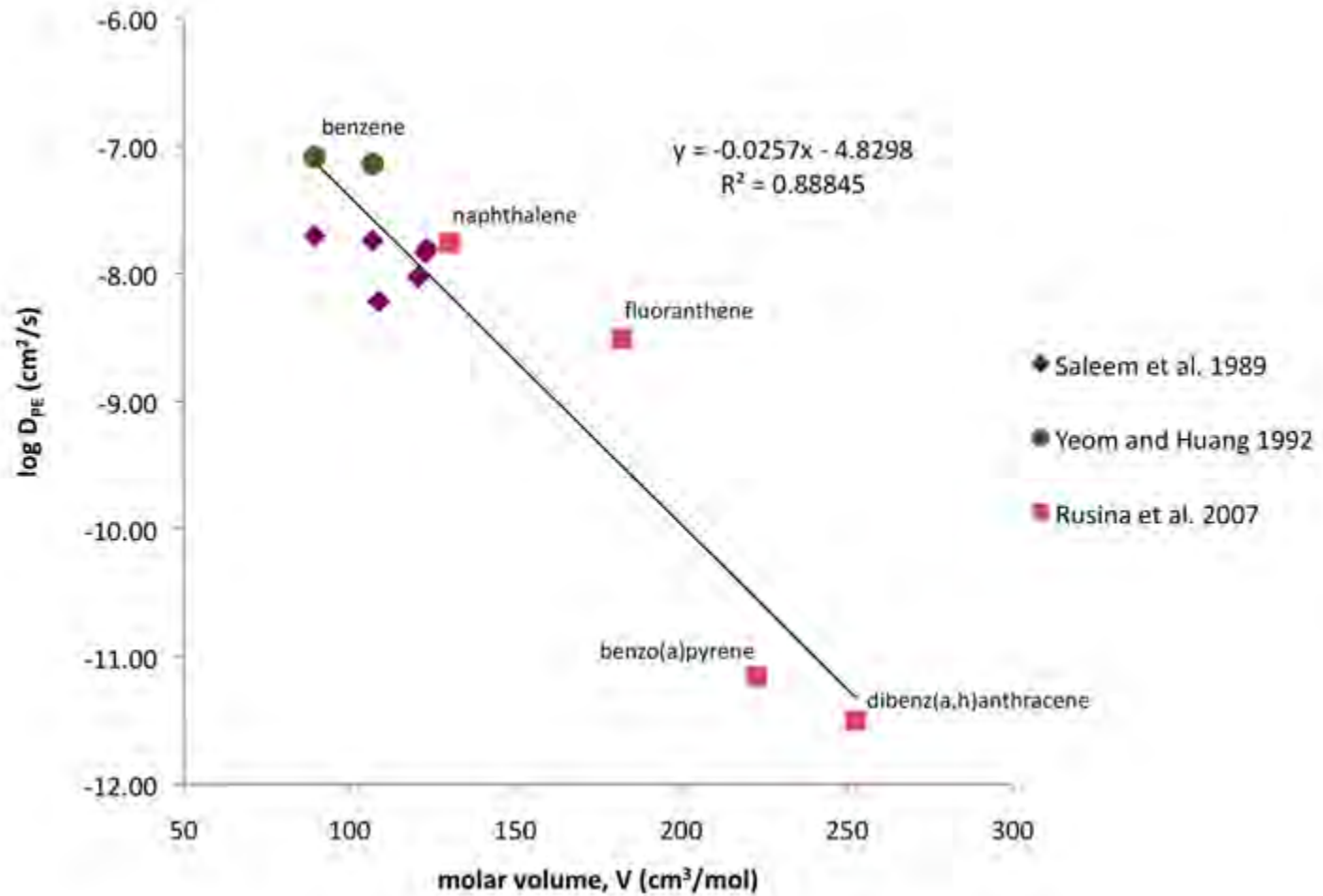
# Laplace space solution to mass-transfer model



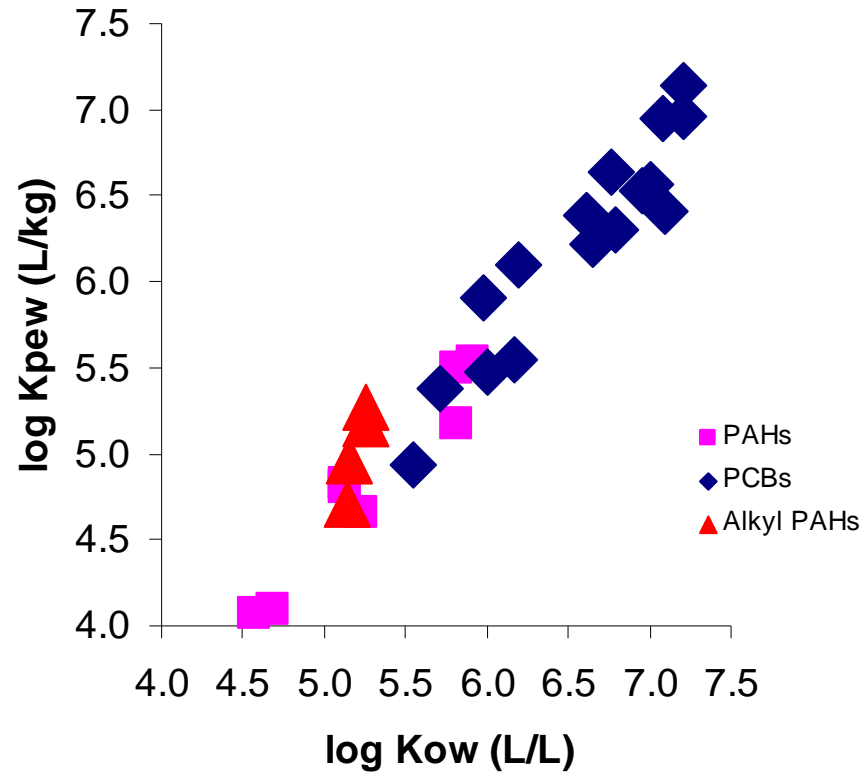
$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d) \tau D_{PE}} \approx \frac{D_W}{r_{sw} K_d \tau D_{PE}}$$

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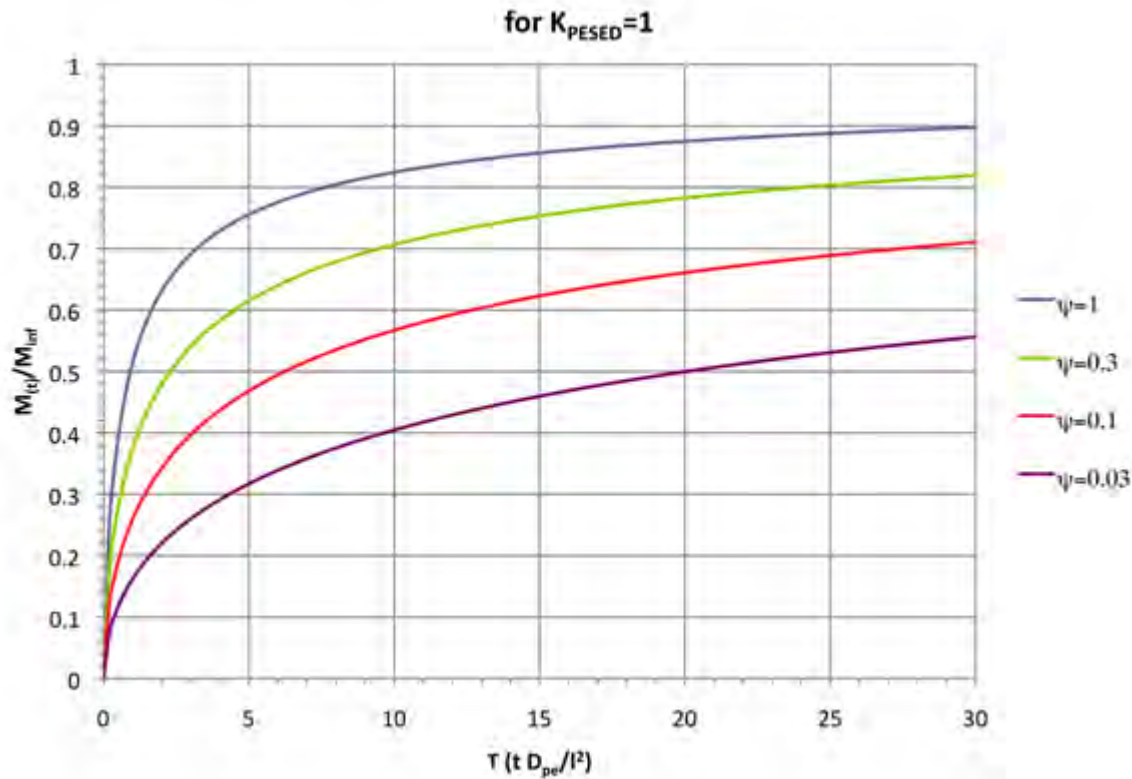
# Relationship between $\log D_{PE}$ and molar volume



# Relationship between $\log K_{PEW}$ and $\log K_{OW}$



# Laplace space solution to mass-transfer model



$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d) \tau D_{PE}} \approx \frac{D_W}{r_{sw} K_d \tau D_{PE}}$$

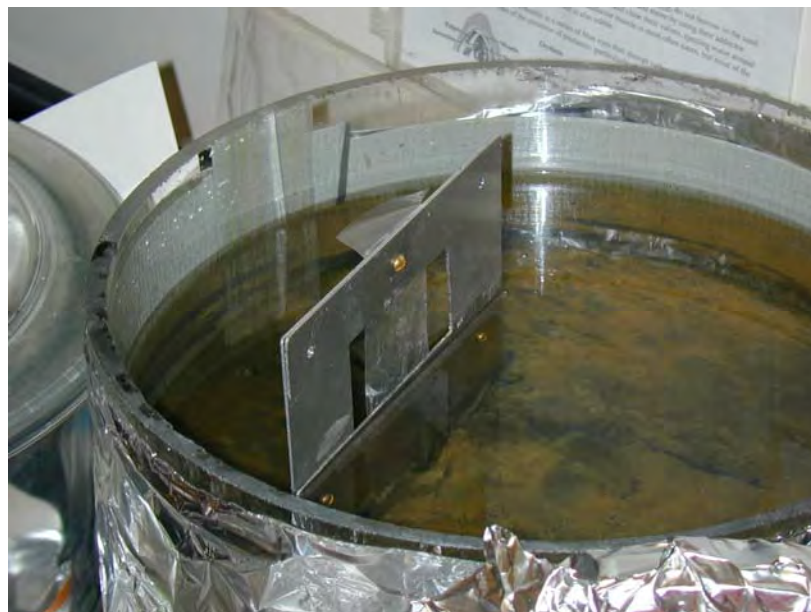
$$K_{PESED} = \frac{K_{PEW}}{K_d}$$



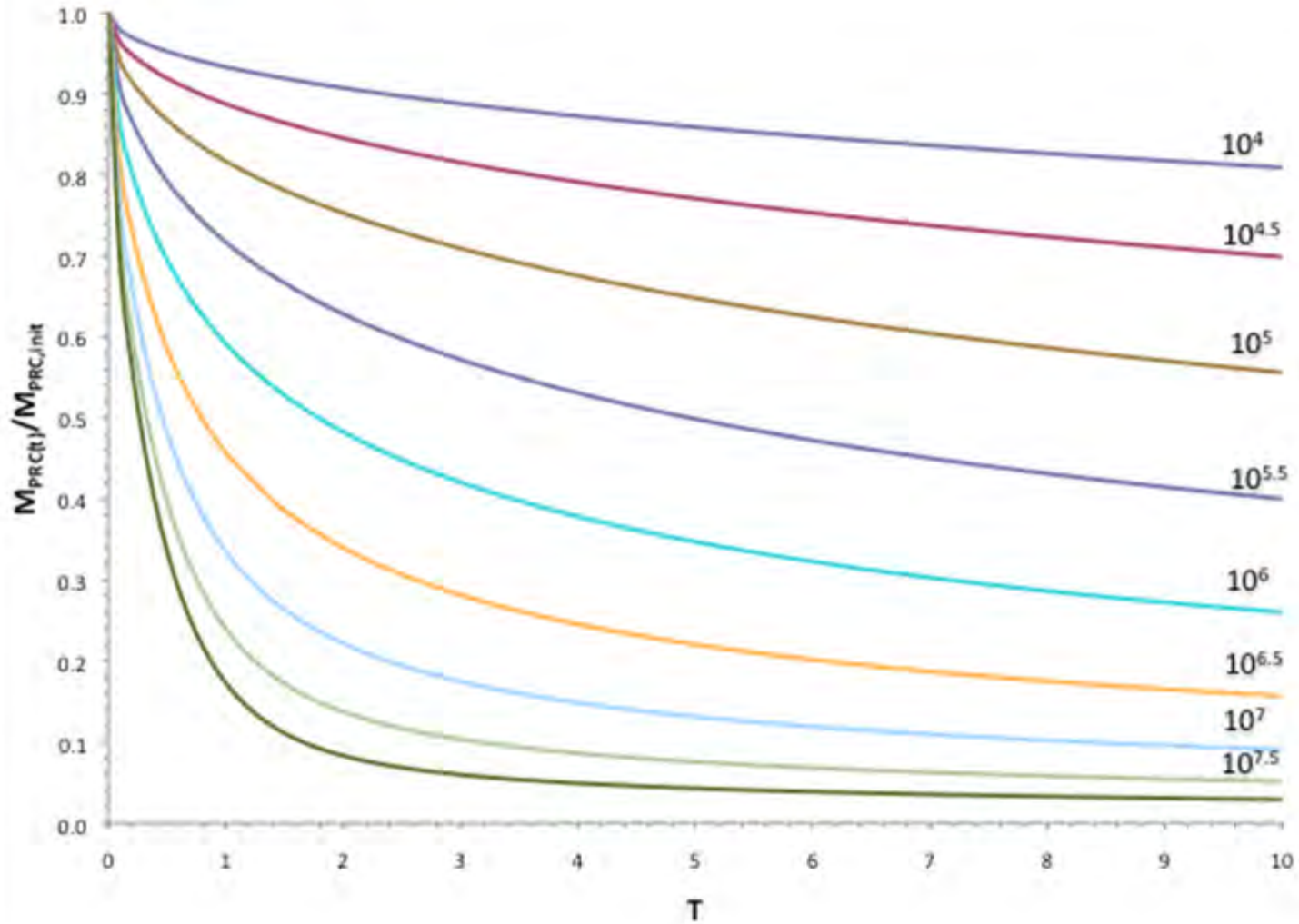
sediment collection

homogenized sediments





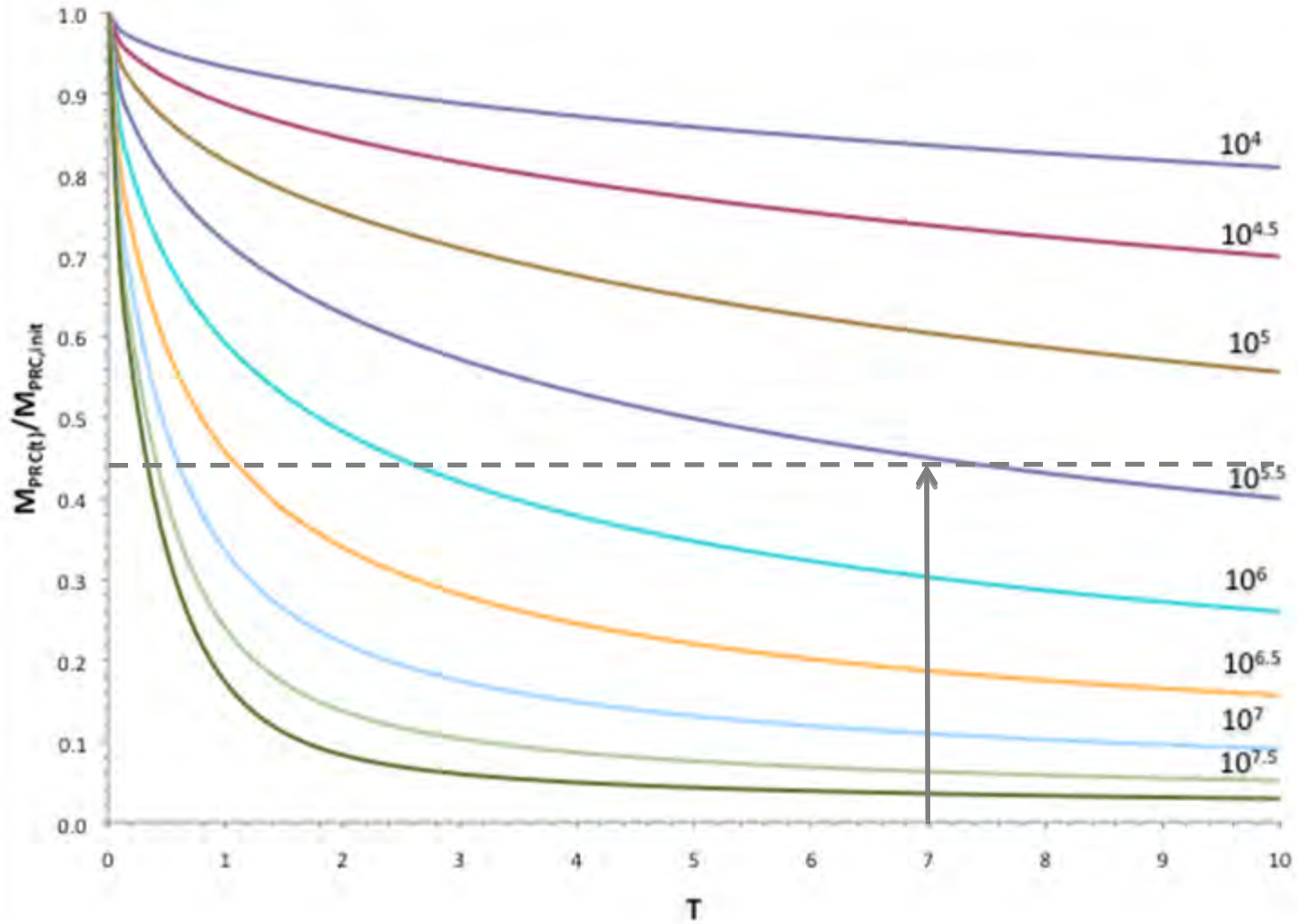
# d12-chrysene



51  $\mu\text{m}$  PE  
10 day exposure ;  $T=7$

25  $\mu\text{m}$  PE  
3 day exposure ;  $T=8.5$

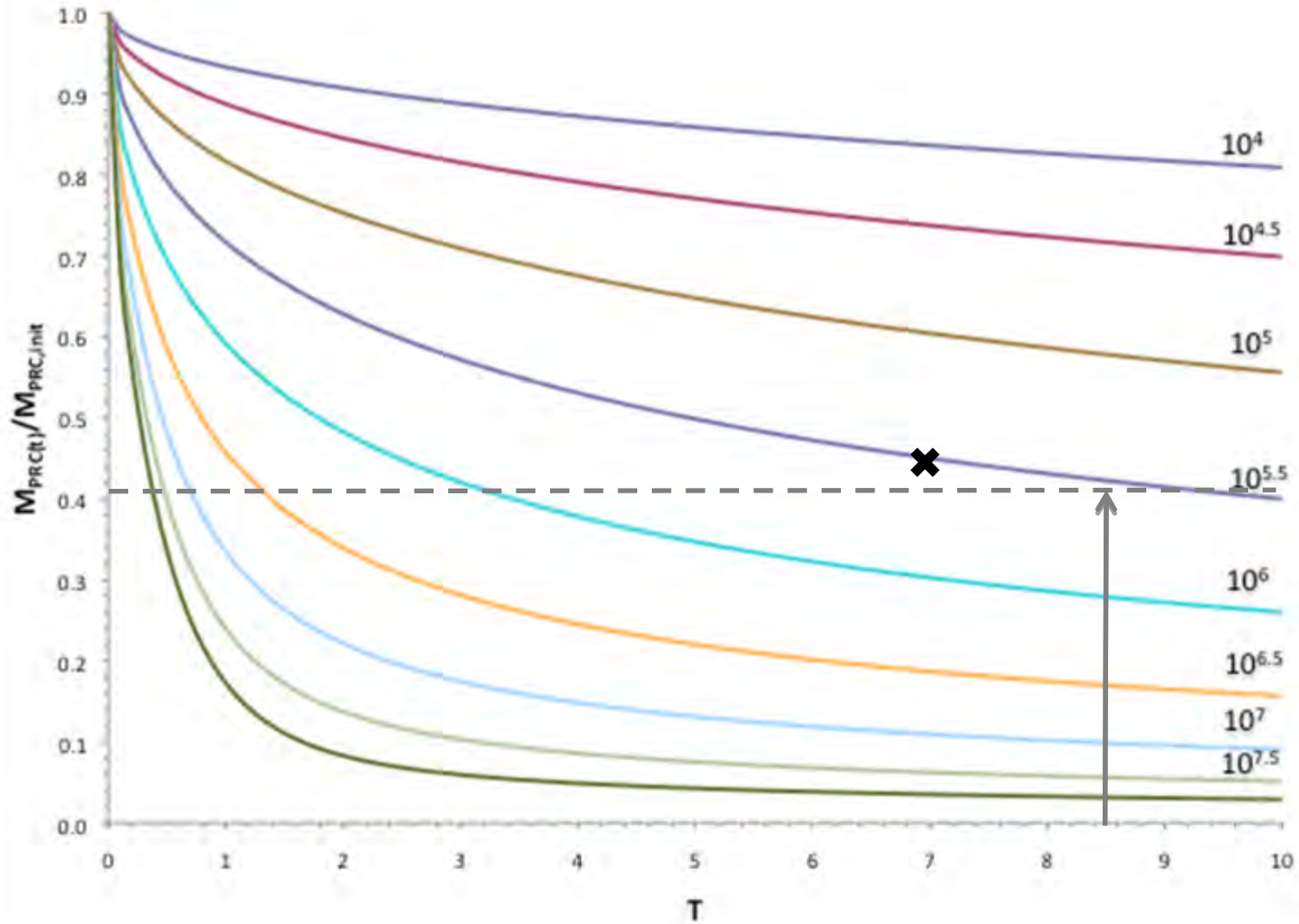
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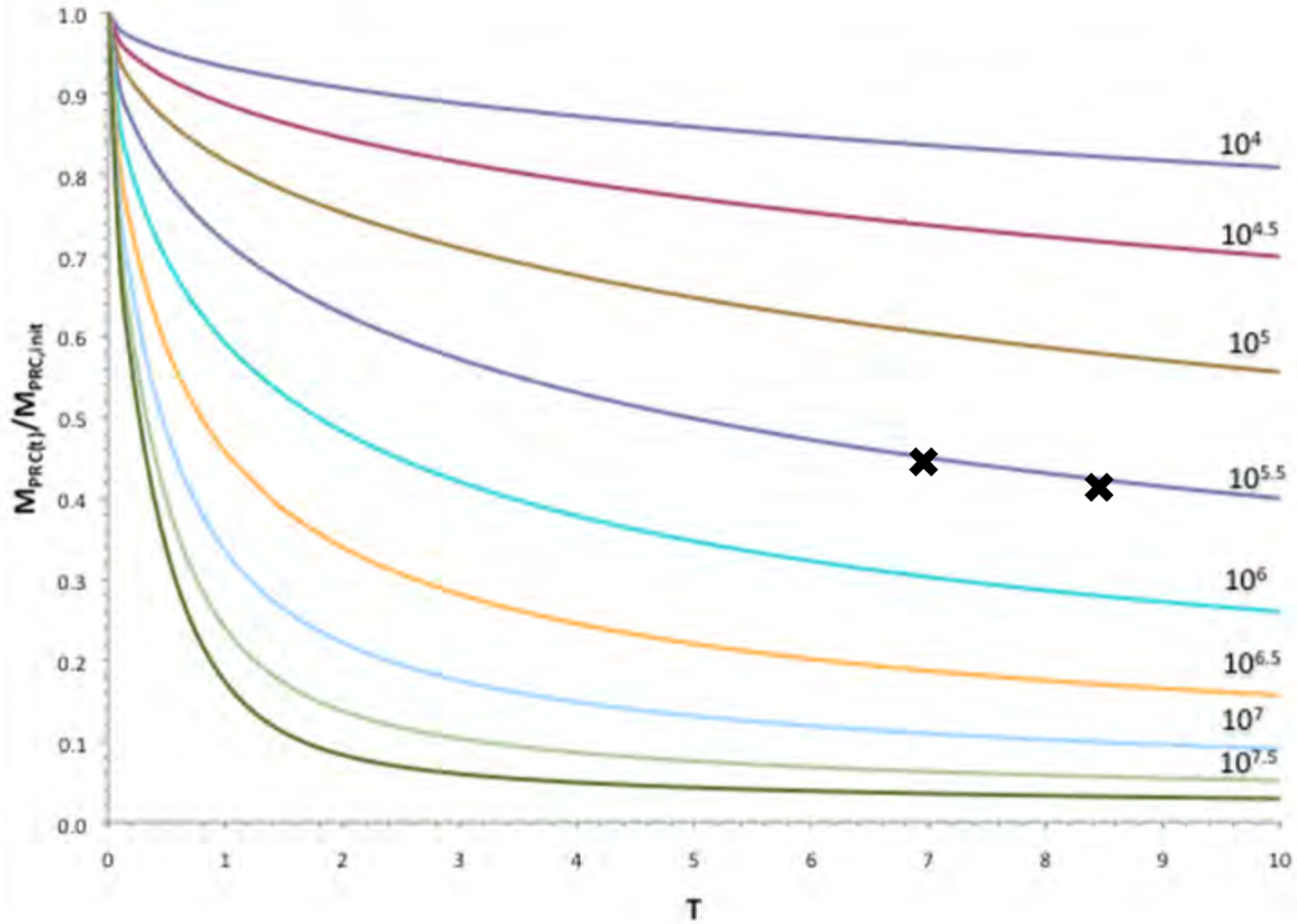
# d12-chrysene



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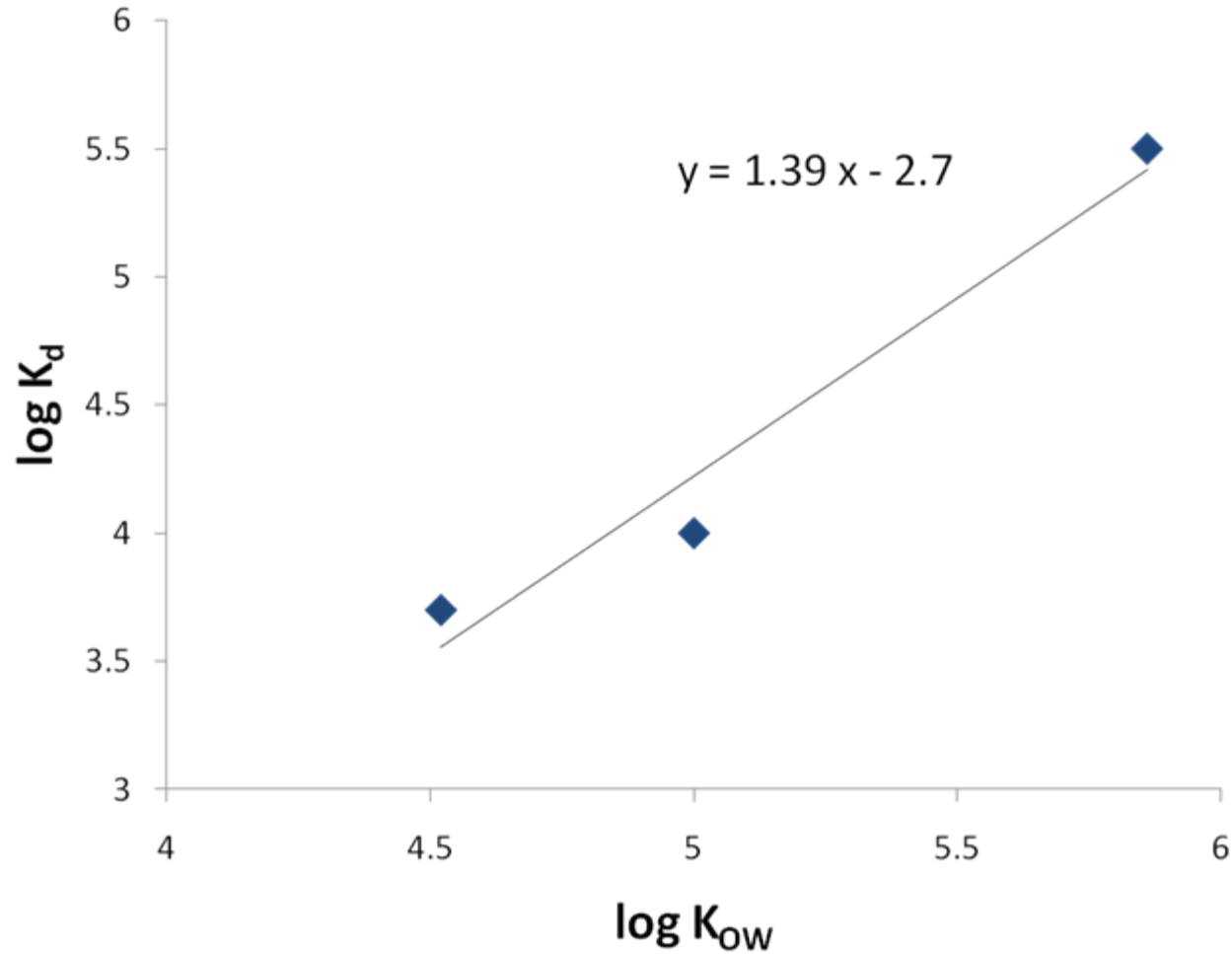
# d12-chrysenene



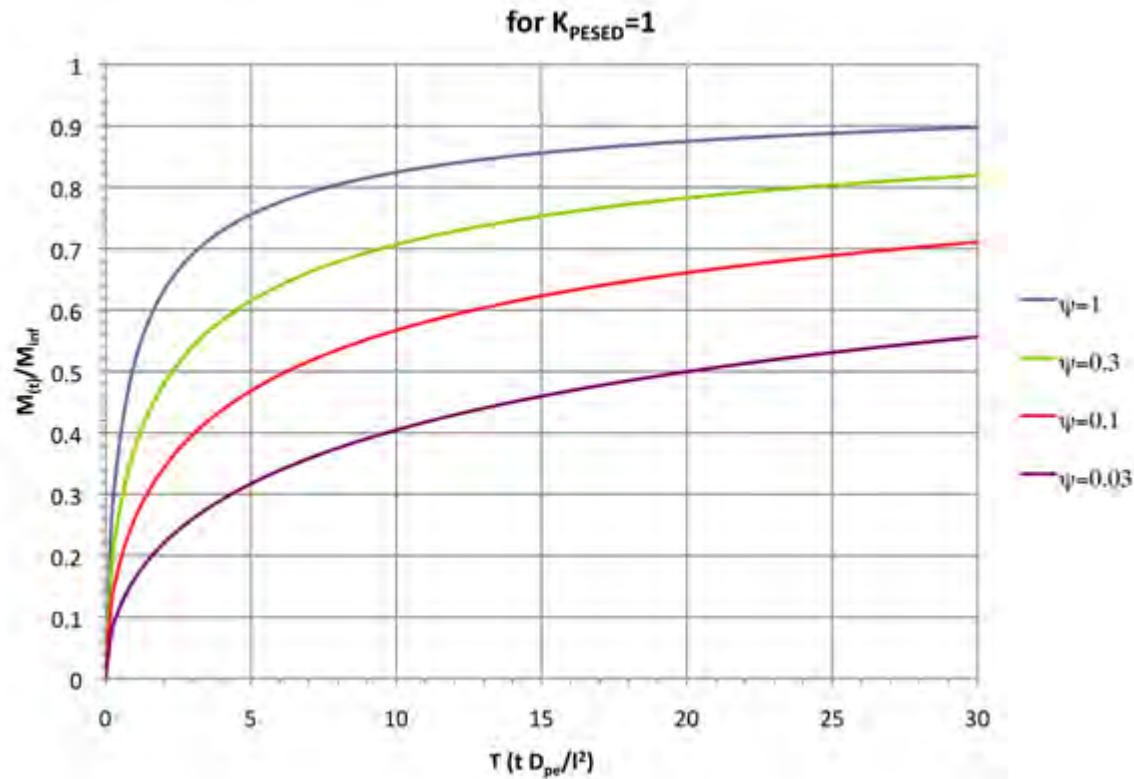
51  $\mu$ m PE  
10 day exposure ;  $T=7$

25  $\mu$ m PE  
3 day exposure ;  $T=8.5$

Use PRCs to find relationship between  $\log K_d$  and  $\log K_{ow}$



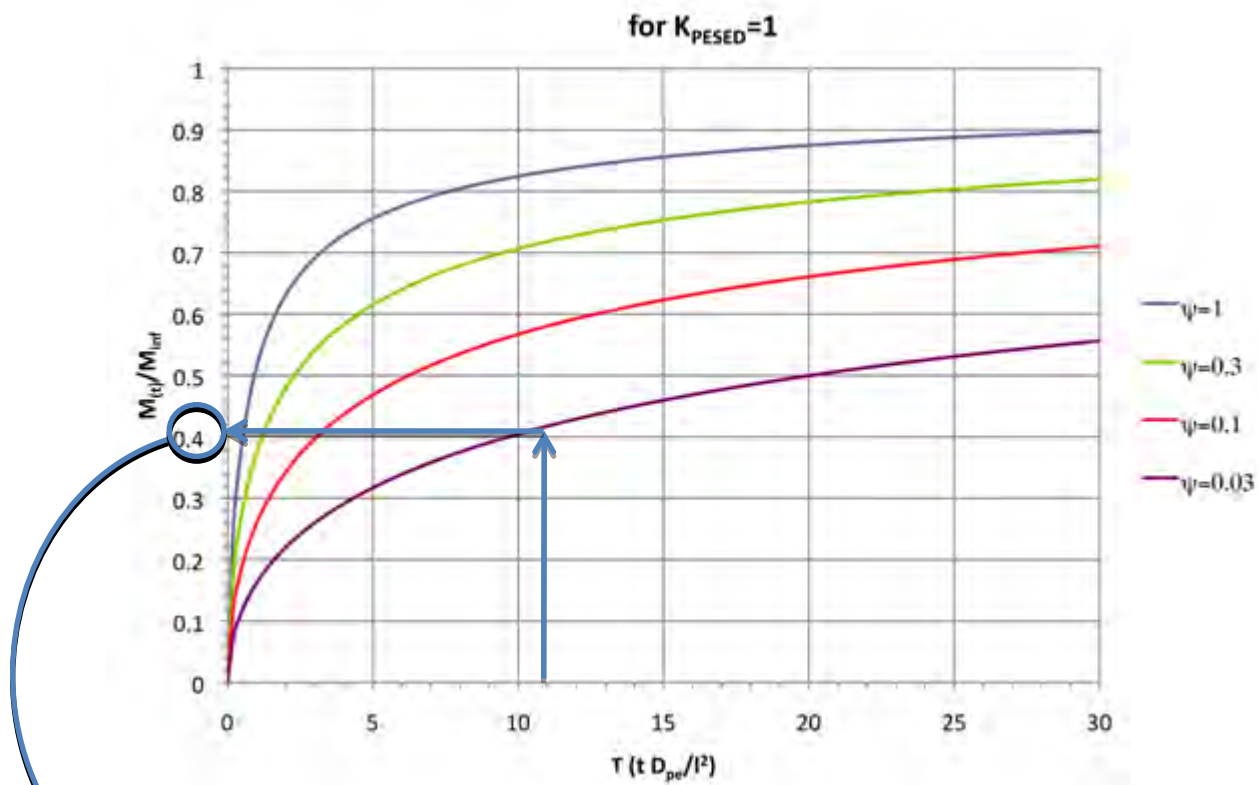
# Laplace space solution to mass-transfer model



$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d) \tau D_{PE}} \approx \frac{D_W}{r_{sw} K_d \tau D_{PE}}$$

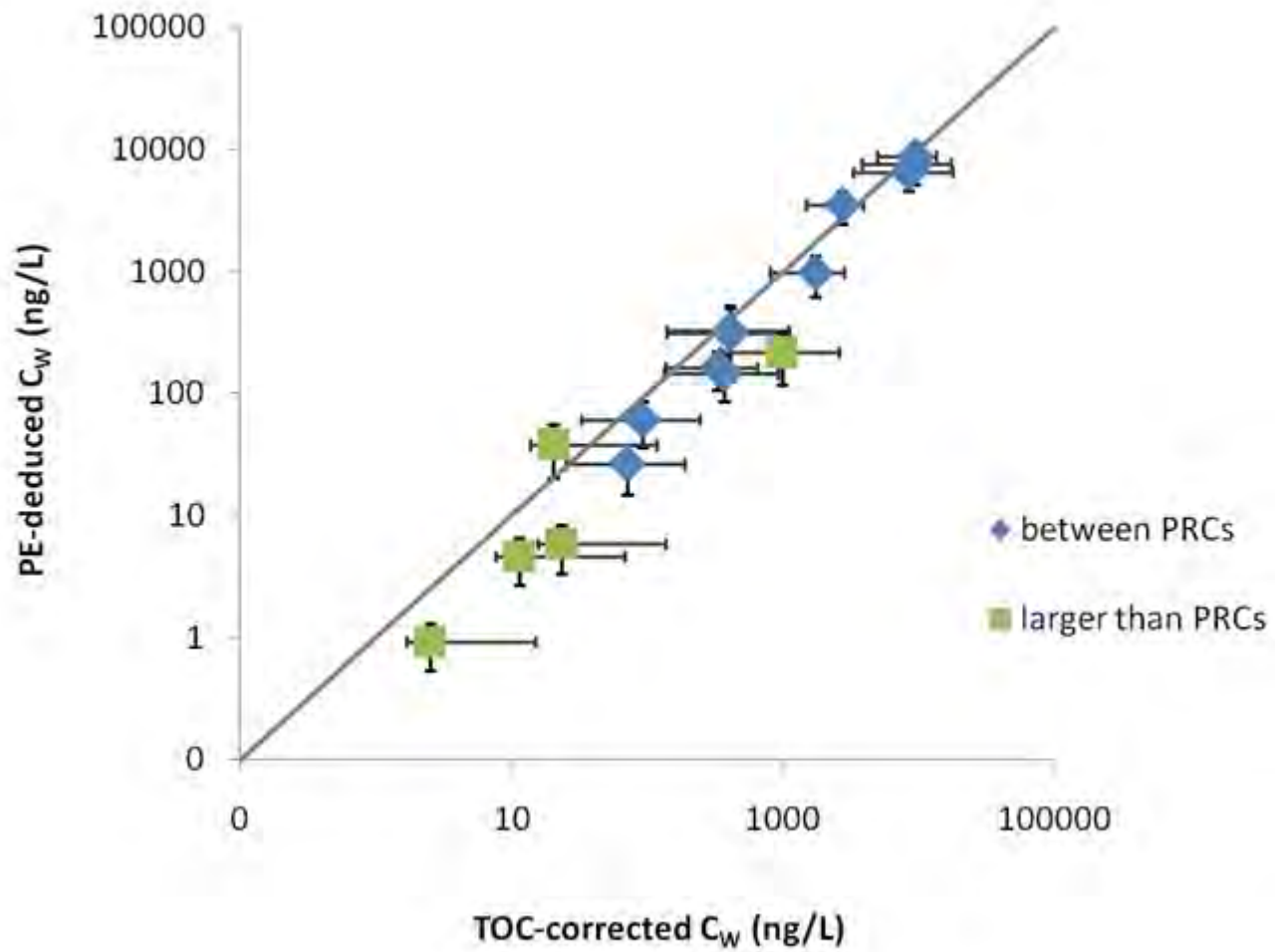
$$K_{PESED} = \frac{K_{PEW}}{K_d}$$

# Laplace space solution to mass-transfer model

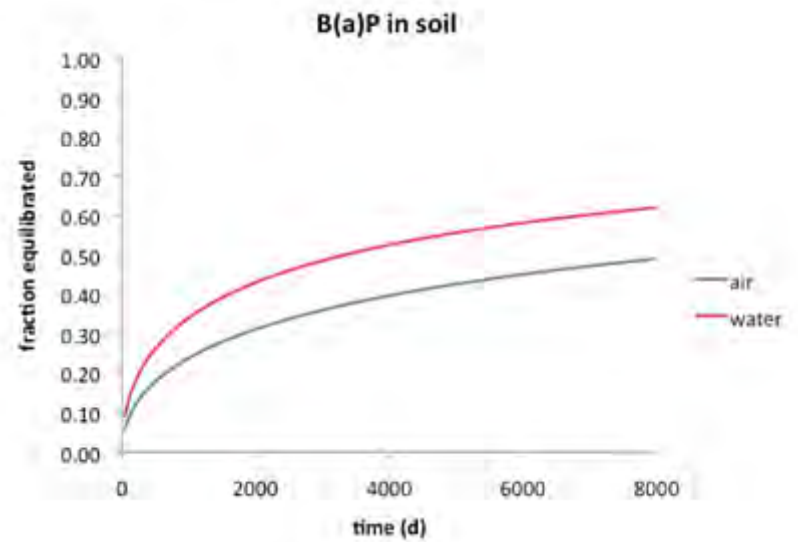
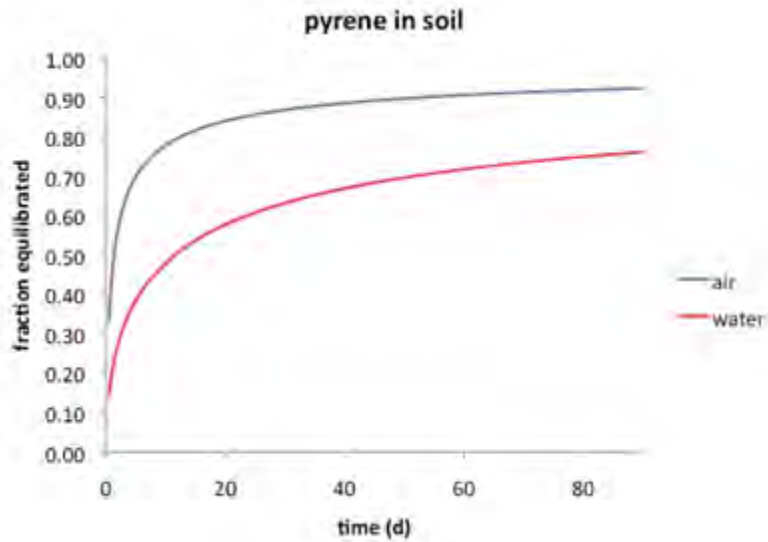
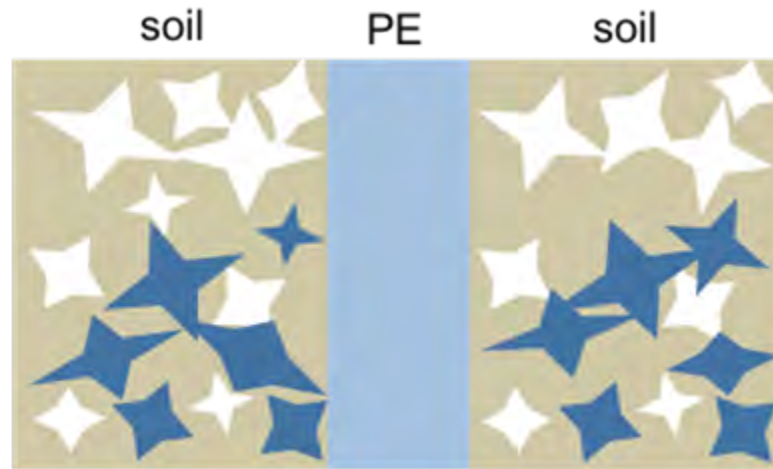


$$\frac{M_{inPE}(t)}{\text{fraction to equilibrium}} = M_{inPE} \text{ at equilibrium}$$

$$\frac{M_{PE} \text{ at equilibrium}}{\text{Mass of sampler}} = C_{PE} \text{ at equilibrium} \quad \Rightarrow \quad \underline{\underline{C_W \text{ or } a}}$$

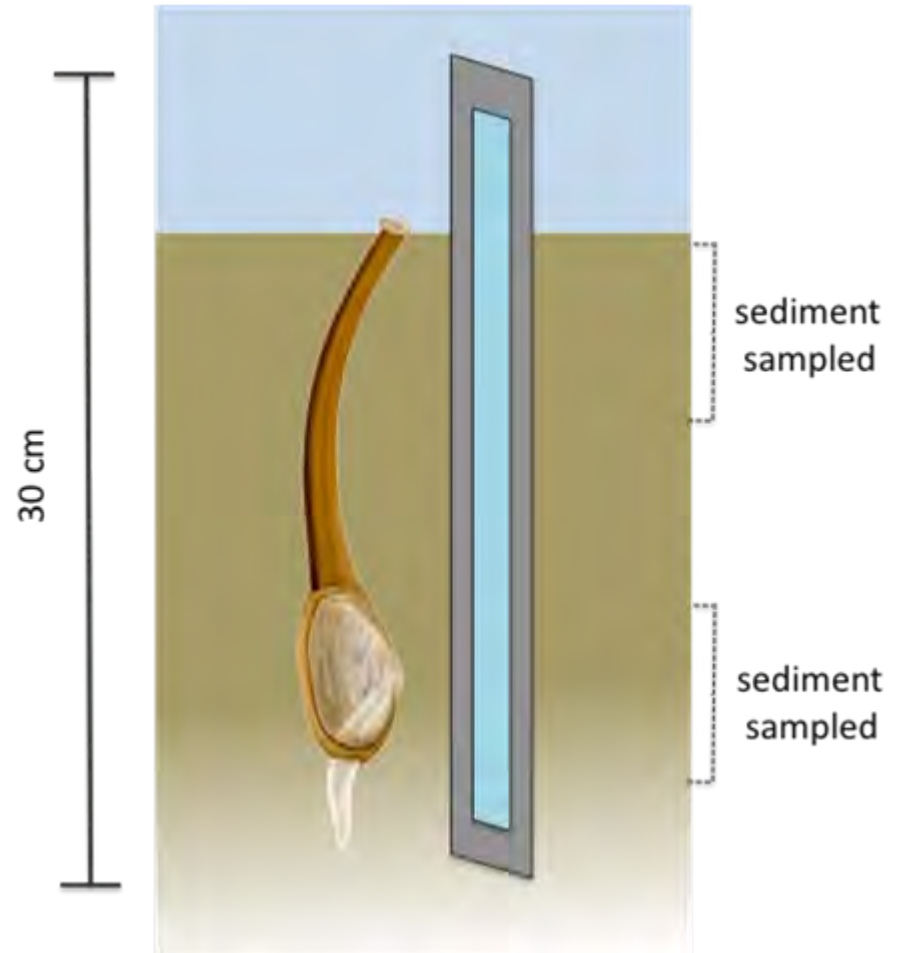
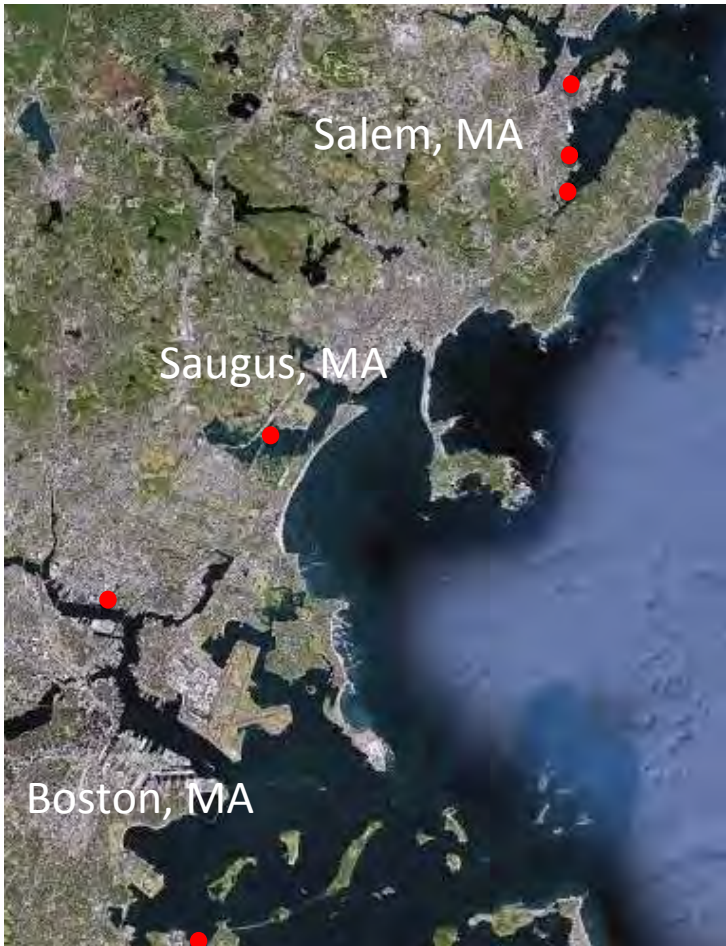


# mass transfer model for polymer in soils

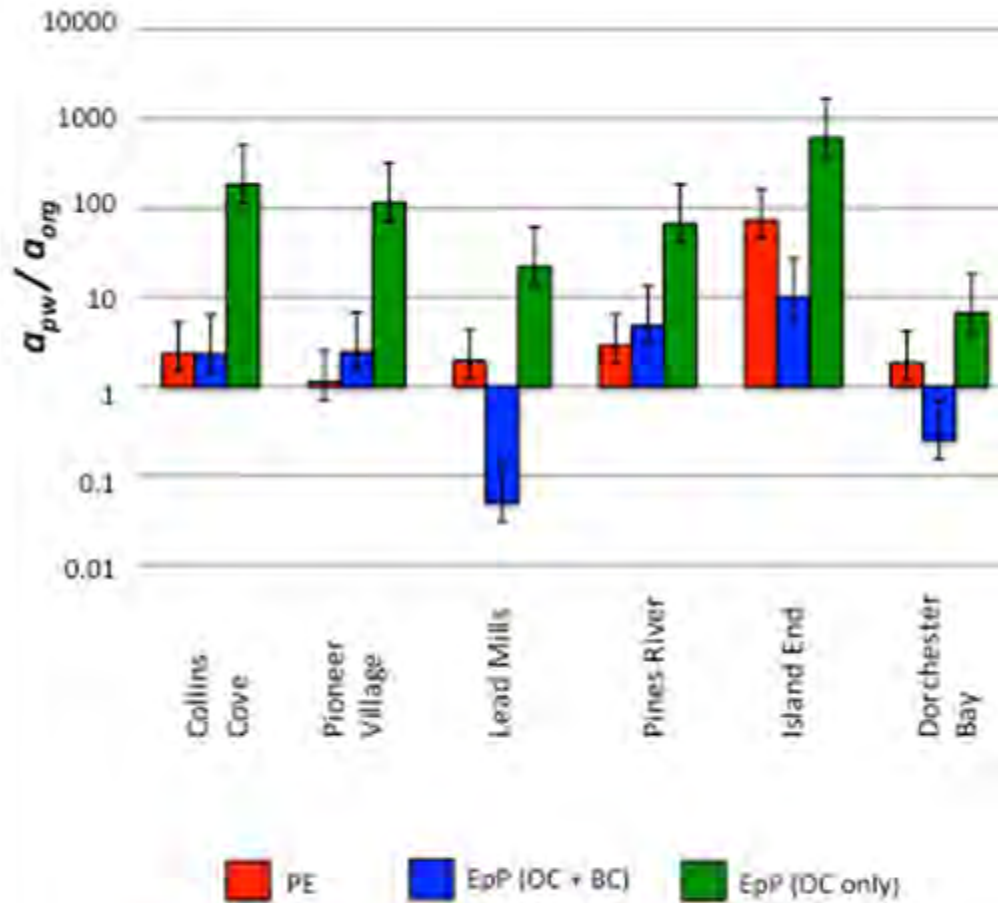


Can we measure  $C_w$  or  $a$  directly in porewaters and do they correlate with organism concentrations?

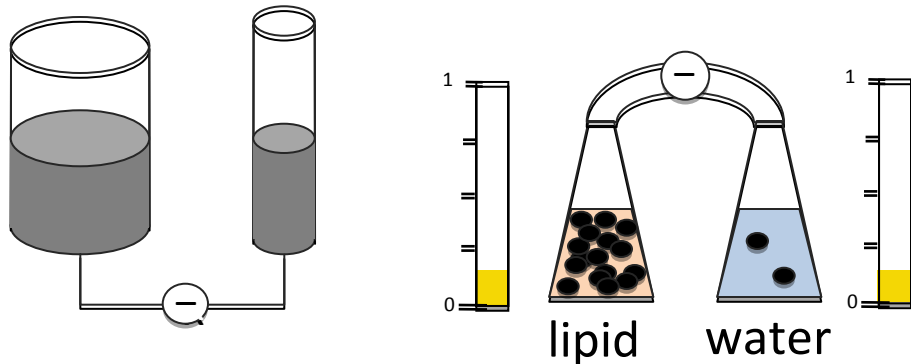
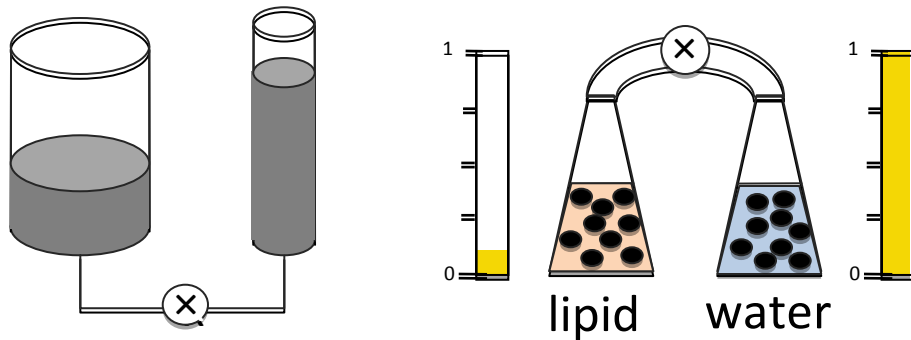
“availability”  $\longrightarrow$   $a$  or  $C_w$



# pyrene



# HOC chemical activity (fugacity) in sediments



$$a_{phase} = \frac{(C_{phase} / K_{phase-w})}{C_w^{sat}(L)}$$

reference concentration

$$C_w = a C_w^{sat}(L)$$