

Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals

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1. Derivation of Laplace solution for diffusion model

The following is the derivation of the Laplace space expression for the fractional PRC mass lost from a polymer film to an infinite bed of sediment porous medium. First we expressed concentrations, distance and time in non-dimensional terms.

$$\hat{C}_{PE} = \frac{C_{PE}}{C_{PE,init}} \quad (S1)$$

$$\hat{C}_{SED} = \frac{C_{SED} K_{PESED}}{C_{PE,init}} \quad (S2)$$

$$\hat{x} = \frac{x}{l} \quad (S3)$$

$$T = \frac{t D_{PE}}{l^2} \quad (S4)$$

At the boundary of the polymer film and the sediment ($\hat{x} = 1$), $\hat{C}_{PE} = \hat{C}_{SED}$ for all $t > 0$, and Eqn. 5 may be expressed as

$$\frac{\partial \hat{C}_{PE}}{\partial \hat{x}} = \frac{\psi}{K_{PESED}} \frac{\partial \hat{C}_{SED}}{\partial \hat{x}} \quad \text{at } \hat{x} = 1 \quad (S5)$$

where $\psi = D_{SED}/D_{PE}$ and K_{PESED} is the polymer-sediment partition coefficient ($\text{cm}^3 \text{ sediment}/\text{cm}^3 \text{ polymer}$) .

Fick's 2nd Law for diffusion in the polymer and in the sediment may also now be expressed in non-dimensional terms

$$\frac{\partial^2 \hat{C}_{PE}}{\partial \hat{x}^2} = \frac{\partial \hat{C}_{PE}}{\partial T} \quad \hat{x} < 1 \quad (S6)$$

$$\frac{\partial^2 \hat{C}_{SED}}{\partial \hat{x}^2} = \frac{1}{\psi} \frac{\partial \hat{C}_{SED}}{\partial T} \quad \hat{x} > 1 \quad (S7)$$

By symmetry, a zero-flux boundary may be placed in the center of the sampler:

$$\frac{d\hat{C}_{PE}}{d\hat{x}} = 0 \quad \text{at } \hat{x} = 0$$

The remote boundary in the sediment is:

$$\frac{d\hat{C}_{SED}}{d\hat{x}} = 0 \quad \text{at } \hat{x} = \text{infinity}$$

The initial condition is:

$$\hat{C}_{PE,init} = 1 \text{ and } \hat{C}_{sed,init} = 0, \quad \text{at } T = 0$$

Taking the Laplace transform, the diffusion expressions become:

$$\frac{\partial \bar{\bar{C}}_{PE}}{\partial \hat{x}} = \frac{\psi}{K_{PESED}} \frac{\partial \bar{\bar{C}}_{SED}}{\partial \hat{x}}, \quad \hat{x} = 1 \quad (S8)$$

$$\frac{d^2 \bar{\bar{C}}_{PE}}{d\hat{x}^2} = s \bar{\bar{C}}_{PE} - 1, \quad \hat{x} < 1 \quad (S9)$$

$$\frac{d^2 \bar{\bar{C}}_{SED}}{d\hat{x}^2} = \frac{s}{\psi} \bar{\bar{C}}_{SED}, \quad \hat{x} > 1 \quad (S10)$$

and the boundary conditions become:

$$\frac{d\bar{\bar{C}}_{PE}}{d\hat{x}} = 0, \quad \text{at } \hat{x} = 0$$

$$\frac{d\bar{\bar{C}}_{SED}}{d\hat{x}} = 0, \quad \text{at } \hat{x} = \text{infinity}$$

The following expressions for $\bar{\bar{C}}_{PE}$ and $\bar{\bar{C}}_{SED}$ satisfy Equations S8, S9 and S10, and the boundary and initial conditions:

$$\bar{\bar{C}}_{PE} = A \cosh(\hat{x}\sqrt{s}) + \frac{1}{s} \quad (\text{S11})$$

$$\bar{\bar{C}}_{SED} = B e^{-\sqrt{\frac{s}{\psi}} \hat{x}} \quad (\text{S12})$$

where

$$A = - \left(s \cosh(\sqrt{s}) + \frac{\sinh(\sqrt{s}) K_{PESED}}{\sqrt{\psi}} \right)^{-1} \quad (\text{S13})$$

and

$$B = \frac{-A \sinh(\sqrt{s}) K_{PESED} e^{\sqrt{\frac{s}{\psi}}}}{\sqrt{\psi}} \quad (\text{S14})$$

Integrating $\bar{\bar{C}}_{PE}$ from $\hat{x} = 0$ to $\hat{x} = 1$ gives the Laplace-domain mass of PRC in the polymer section:

$$\bar{\bar{M}}_{PRC} = \left(\frac{1}{s} - \frac{\sqrt{\psi}}{s^{3/2} \left(K_{PESED} + \sqrt{\psi} \coth(\sqrt{s}) \right)} \right) \quad (\text{S15})$$

By integrating over half the thickness of the film, $\bar{\bar{M}}_{PRC}$ gives the fraction of initial mass remaining in the sampler, as $\bar{\bar{M}}_{PRC,init} = 1$, and the two halves are mirror images of each other.

A similar derivation was followed for the case where target chemical is present only in the porous medium initially and diffuses into the polymer section. In this case Eqns. S9 and S10 become

$$\frac{d^2 \bar{\bar{C}}_{PE}}{d\hat{x}^2} = s \bar{\bar{C}}_{PE}, \quad \hat{x} < 1 \quad (\text{S16})$$

$$\frac{d^2 \bar{\bar{C}}_{SED}}{d\hat{x}^2} = \frac{s}{\psi} \bar{\bar{C}}_{SED} - \frac{1}{\psi}, \quad \hat{x} > 1 \quad (\text{S17})$$

Eqns. S11 and S12 become

$$\bar{\bar{C}}_{PE} = D \cosh(\hat{x}\sqrt{s}) \quad (\text{S18})$$

$$\bar{\bar{C}}_{SED} = B e^{-\sqrt{\frac{s}{\psi}} \hat{x}} + \frac{1}{s} \quad (\text{S19})$$

where

$$D = \left(s(\cosh(\sqrt{s}) + \frac{\sinh(\sqrt{s}) K_{PESED}}{\sqrt{\psi}}) \right)^{-1} \quad (\text{S20})$$

Now integrating $\bar{\bar{C}}_{PE}$ from $\hat{x} = 0$ to $\hat{x} = 1$ gives the Laplace-domain mass of target chemical in the polymer section (Eqn. 7):

$$\bar{M}_{target} = \frac{\sqrt{\psi}}{s^{3/2} \left(K_{PESED} + \sqrt{\psi} \coth(\sqrt{s}) \right)} \quad (\text{S21})$$

Again, this is the fraction of the equilibrium mass of target chemical in the section, as

$\bar{M}_{target,inf} = 1$, and the two halves are mirror images of each other. Equation S15 for the PRC

contains the result above for the target, so it may be written:

$$\bar{M}_{PRC} = \left(\frac{1}{s} - \bar{M}_{target} \right) \quad (S22)$$

2. Matlab functions and scripts for numerically inverting Eqns. 7 and 8 to real-space values

A. Mass_in.m

```
% Laplace-domain expression for the mass of target chemical taken up by
% polymer from porous medium
% K12 is partitioning coefficient between phase 1 (polymer) and phase 2
% (porous medium)
% Y is ratio of diffusivities (D(porous medium)/D(polymer))
% s is the Laplace parameter

function F = Mass_in(s,Y,K12);
global K12;
global Y;
F = (Y.^0.5)./((s.^1.5).*(K12+(Y.^0.5).*coth(sqrt(s))));
```

B. Mass_out.m

```
% Laplace-space expression for the mass of PRC transferred from
% polymer to porous medium
% K12 is partitioning coefficient between phase 1 (polymer) and phase 2
% (porous medium)
% Y is ratio of diffusivities (D(porous medium)/D(polymer))
% s is the Laplace parameter

function F = Mass_out(s,Y,K12);
global K12;
global Y;
F = (1./s)-((sqrt(Y))./(s.^(3/2).*(K12+sqrt(Y).*coth(sqrt(s)))));
```

C. Deffective.m

```
% calculates effective diffusivity, Deff
% given MW, porosity, and tortuosity for Kd input in units of vol water/vol
% sediment

function F=Deffective(Kd);

%clear all

MW=276; % MW=molar mass (g/mol)
Dw=(2.7*10^-4)/(MW^0.71); % Dw=diffusivity in water (cm^2/s)
phi=0.6; % porosity
rsf=1/phi; % ratio of sediments to fluid
```

```

f=1/(1+rsf*Kd); %fraction in fluid assuming Kd in (Lw/Lsed)
tau=3; % tortuosity
Dpm=Dw/tau; % diffusivity in porous medium

F=f*Dpm; %(cm^2/sec)

```

D. Script for creating plots of fractional PRC loss vs. T (2)

```

% Script used to create plots of fractional PRC loss vs. T for various Kd

hold on
clear all;
T=1:1:150;
global Y;
global K12;
for n=1:9
    Kpew=10^4.3*0.92; %polymer-water partition coefficient for PRC (cm^3/cm^3)
    Kd=10^(0.5+n*0.5);
    K12=Kpew/Kd;
    Dsed=Deffective(Kd);
    Dpe=5.3*10^-10; %diffusivity of PRC in polymer (cm^2/s)
    Y=Dsed/Dpe;
for i=1:150
    M(i)=invlap('Mass_out', [T(i)]); % invlap.m (2, 3)
    Data(i,n)=M(i);
end
plot(T,M,'r')
xlabel('non-dimentional time,(t*D1/L^2)')
ylabel('M(t)/Minit')

end
hold off

```

E. Script for finding fractional equilibration of target chemical in polymer sampler

```

% Script used to find the fraction equilibration of target chemical in polymer
% exposed to porous medium for a given non-dimensional time, T

clear all;
T=1.62; % non-dimensional time of deployment

global Y;
global K12;

Kpew=10^6.7*0.92; % Kpew for target chemical (Lw/Lpe)
Kd=10^6.8; %Kd of porous medium (Lw/Lpm)
K12=Kpew/Kd;
Dsed=Deffective(Kd);
Dpe=1.22*10^-11; %diffusivity of target chemical in polymer (cm^2/s)

```


$Y = D_{sed} / D_{pe};$

```
M=invlap('Mass_in', [T]); % invlap.m (2,3)
fraction_equilibrated=M
```

3. References

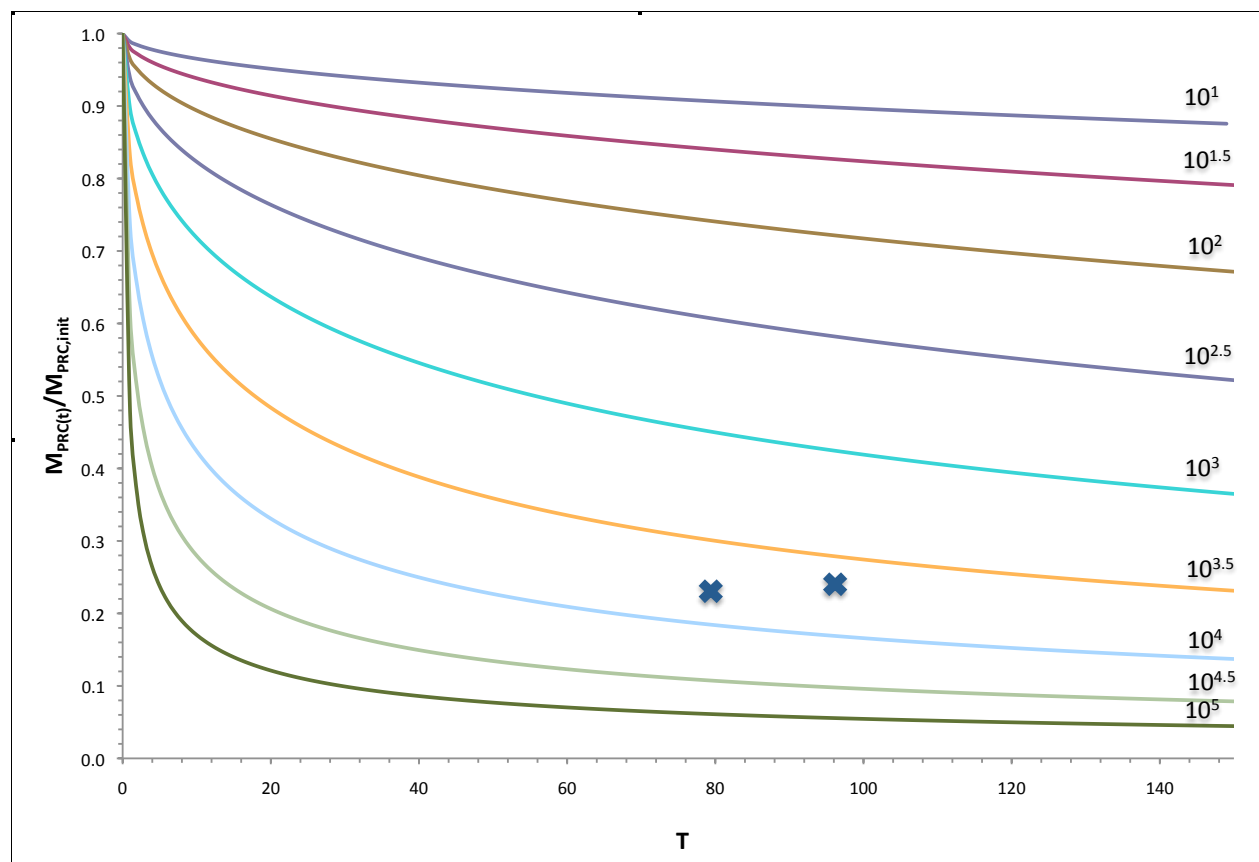
- (1) Ruelle, P. The n-octanol and n-hexane/water partition coefficient of environmentally relevant chemicals predicted from mobile order and disorder (MOD) thermodynamics. *Chemosphere* **2000**, 40, 457.
- (2) Hollenbeck, K. J. INVLAP.M: A matlab function for numerical inversion of Laplace transforms by the de Hoog algorithm.
cambridge.org/us/engineering/author/nellisandklein/downloads/invlap.m
- (3) Hollenbeck, K. J.; Harvey, C. F.; Haggerty, R.; Werth, C. J. A method for estimating distributions of mass transfer rate coefficients with application to purging and batch experiments. *J. Contam. Hydrol.* **1999**, 37 (3-4), 367-388.

Tables

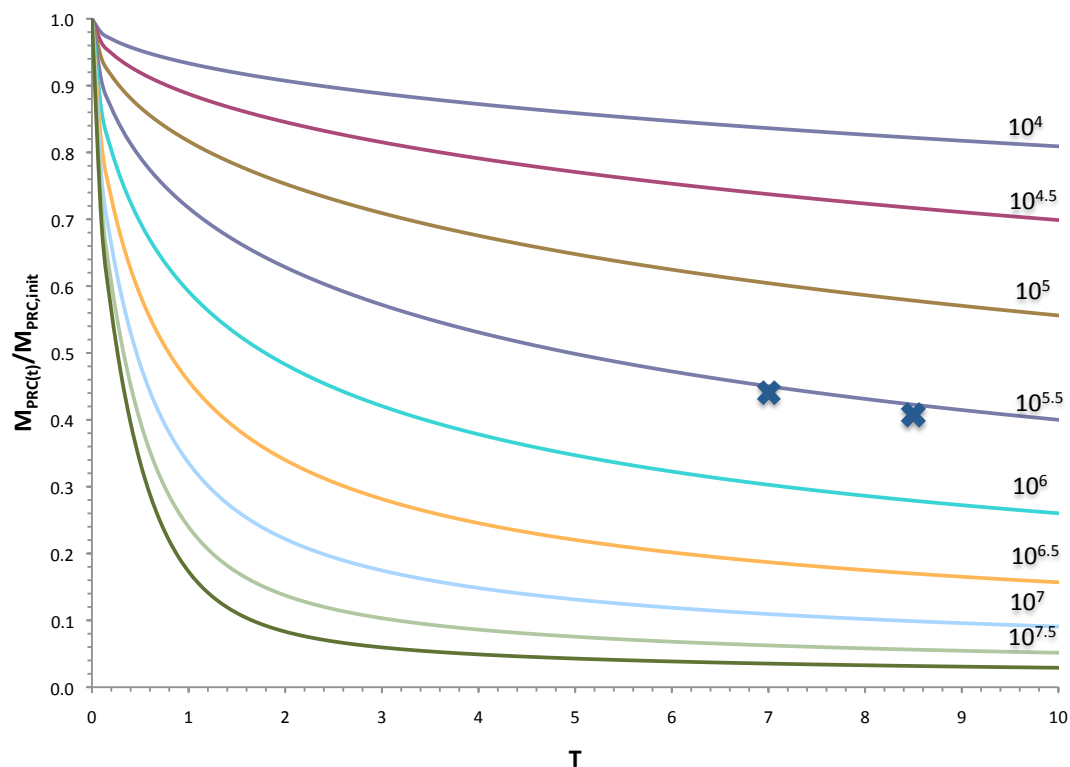
Table S1. Estimated ψ and K_{PESED} for six example compounds in low OC and high OC sediments and a soil. Low OC sediments assumed to have $f_{\text{OC}} = 0.005$, and $f_{\text{BC}} = 0.0005$. High OC sediments and soil assumed to have $f_{\text{OC}} = 0.05$, and $f_{\text{BC}} = 0.005$. Diffusion in soil is assumed to occur through both air and water phases.

Compound	low OC sed ψ	high OC sed ψ	soil ψ	low OC sed K_{PESED}	high OC sed and soil K_{PESED}
phenanthrene	10	1	9,000	20	2
benzo(a)pyrene	1	0.1	600	3	0.3
2,2',5,5'-PCB	40	4	30,000	300	30
2,2',3,4,4',5,5'-PCB	50	5	40,000	400	40
atrazine	7,000	900	7,000,000	100	20
p,p'-DDT	6	1	5,000	3	0.3

Figures



Figures S1. Fractions remaining for a PRC, d10-phenanthrene, vs. non-dimensional exposure time in sediments like those from IE (60% porosity) for a wide range of K_d s. With 25 μm thick PE exposed for 3 days ($T=96$) 24% remained, while 51 μm thick PE exposed for 10 days ($T=79$) had 23% remaining. The intersections of these loss data and the dimensionless times indicated two estimates of d10-phenanthrene K_d of $10^{3.6}$ and $10^{3.8}$, respectively, for this site's sediment.



Figures S2. Fractions remaining for a PRC, d12-chrysene, vs. non-dimensional exposure time in sediments like those from IE (60% porosity) for a wide range of K_d s. With 25 μm thick PE exposed for 3 days ($T=8.5$) 41% remained, while 51 μm thick PE exposed for 10 days ($T=7.0$) had 44% remaining. The intersections of these loss data and the dimensionless times indicated an estimate of d12-chrysene K_d of $10^{5.5}$ for this site's sediment.

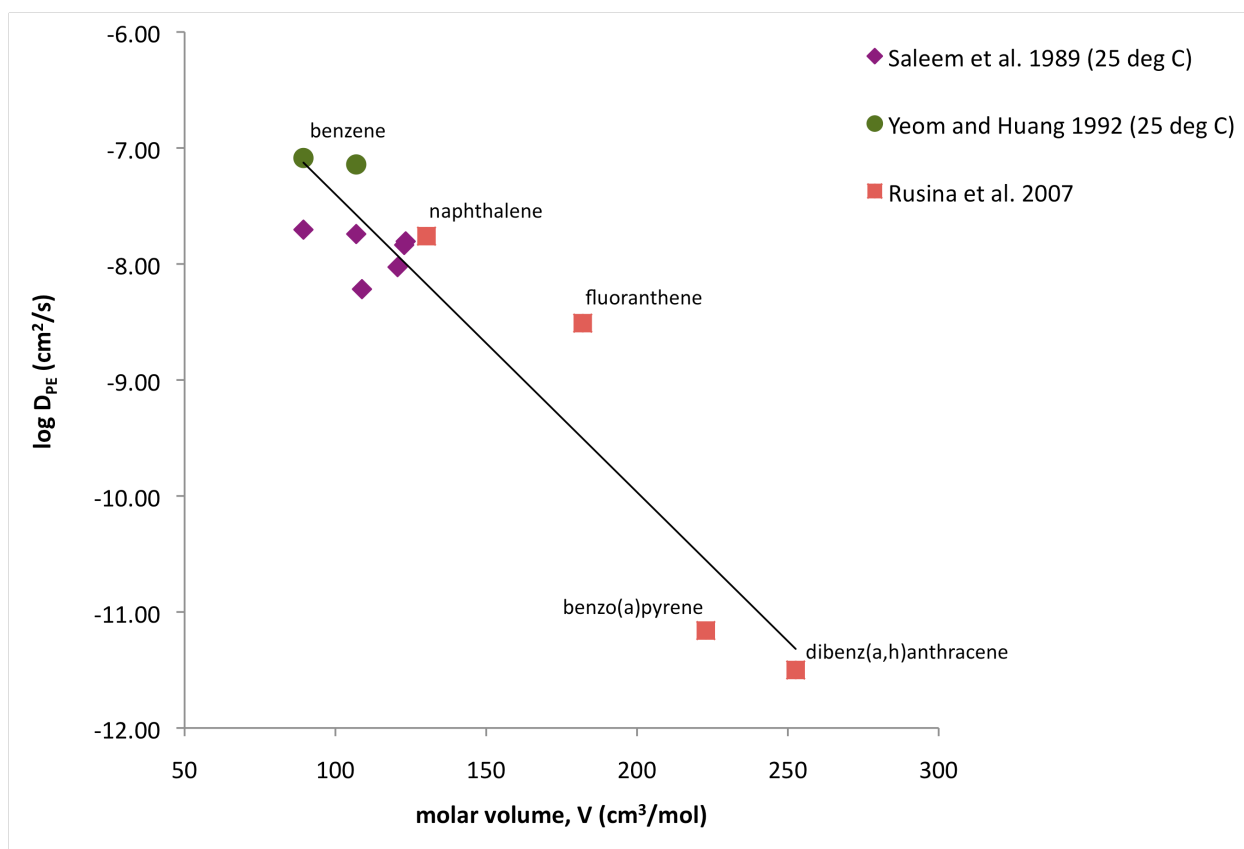


Figure S3. Published $\log D_{PE}$ values versus molar volumes (V) for ten aromatic compounds. The best-fit log-linear relationship, $\log D_{PE} = -0.026 \times V - 4.8$, was used to estimate D_{PE} for PAHs in this study.

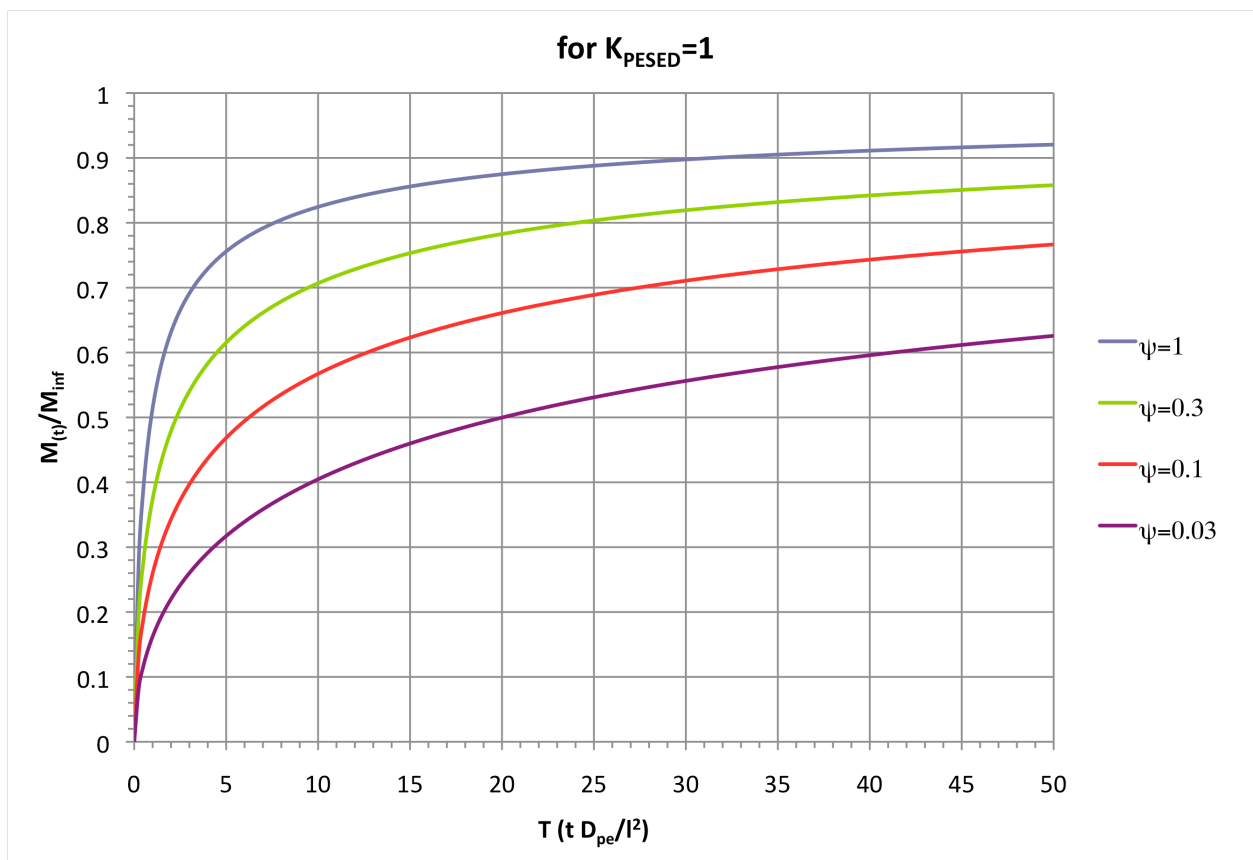


Figure S4. Curve describing target chemical uptake to sampler Figure S3. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 1$ and ψ from 0.03 to 1.

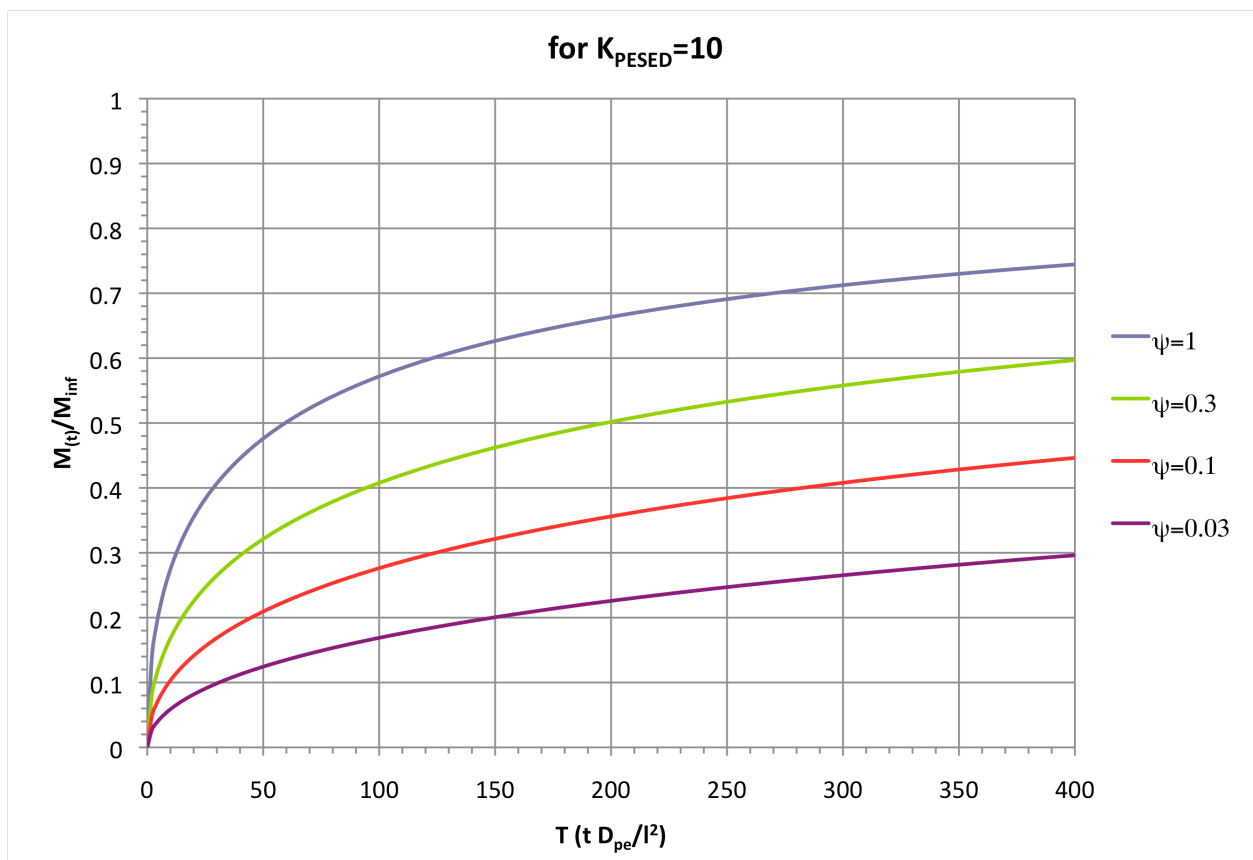


Figure S5. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 10$ and ψ from 0.03 to 1.

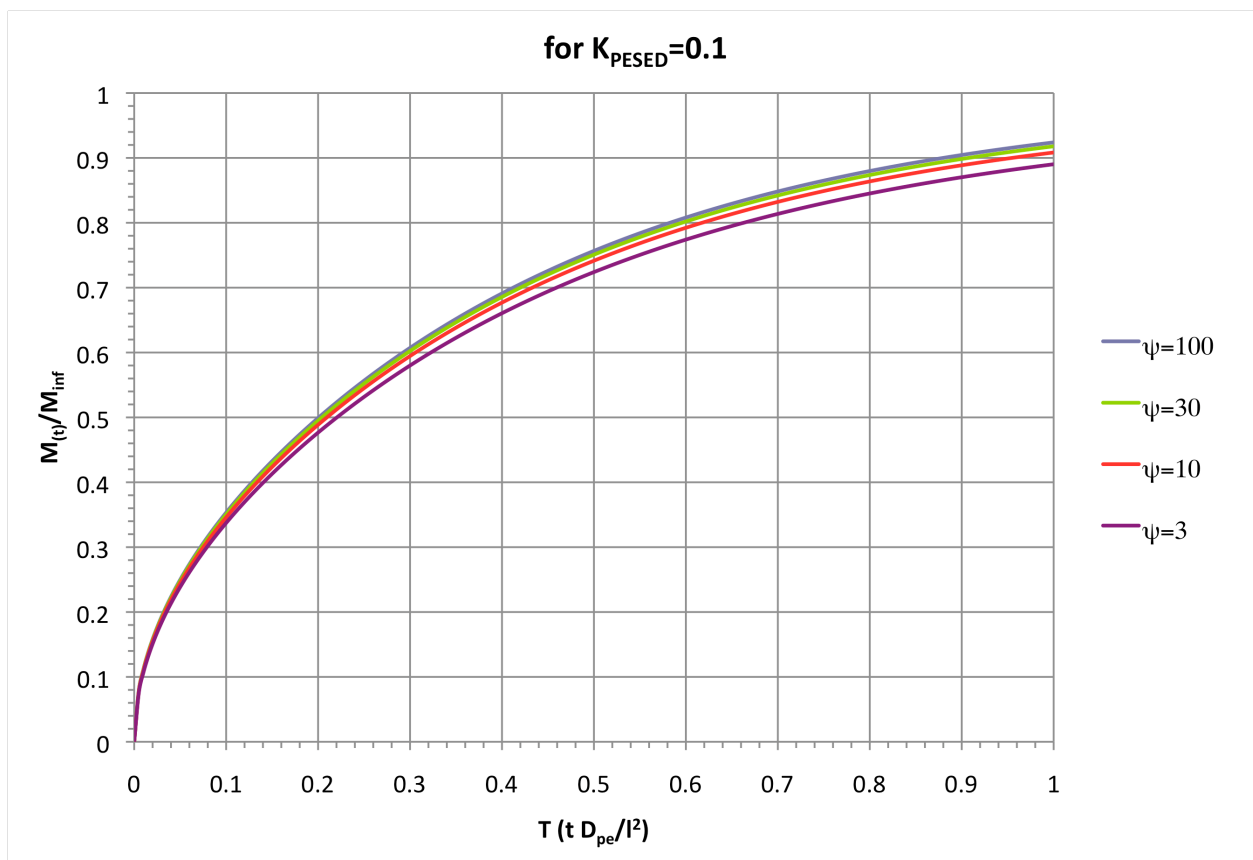


Figure S6. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 0.1$ and ψ from 3 to 100.

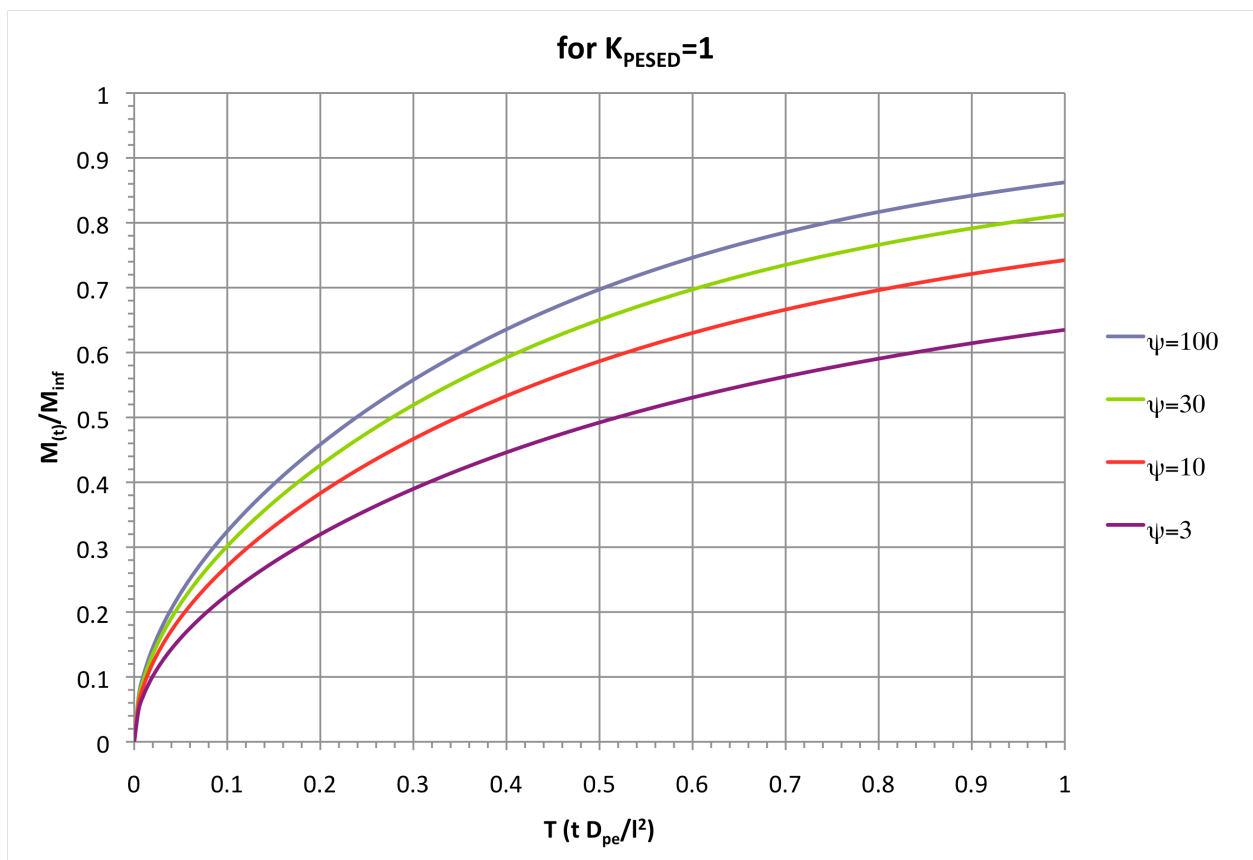


Figure S7. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 1$ and ψ from 3 to 100.

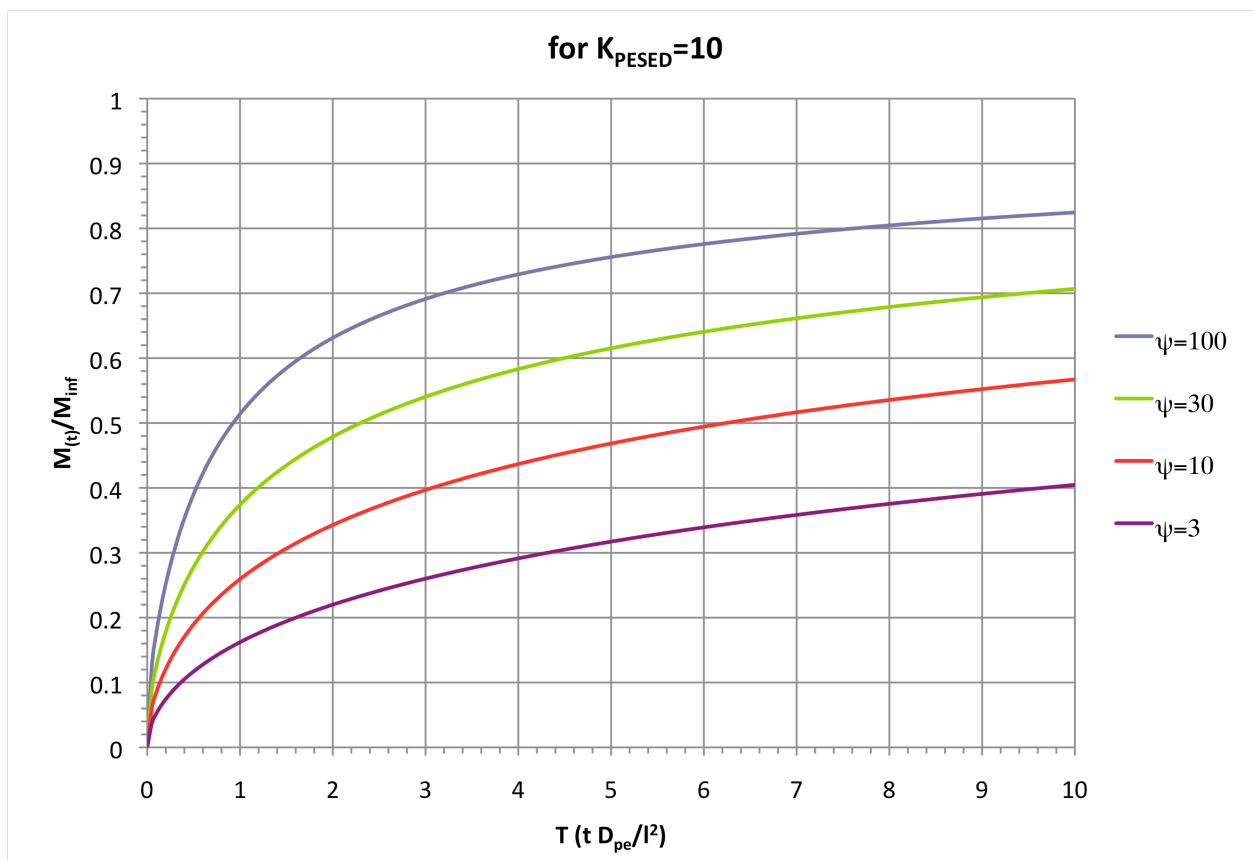


Figure S8. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 10$ and ψ from 3 to 100.

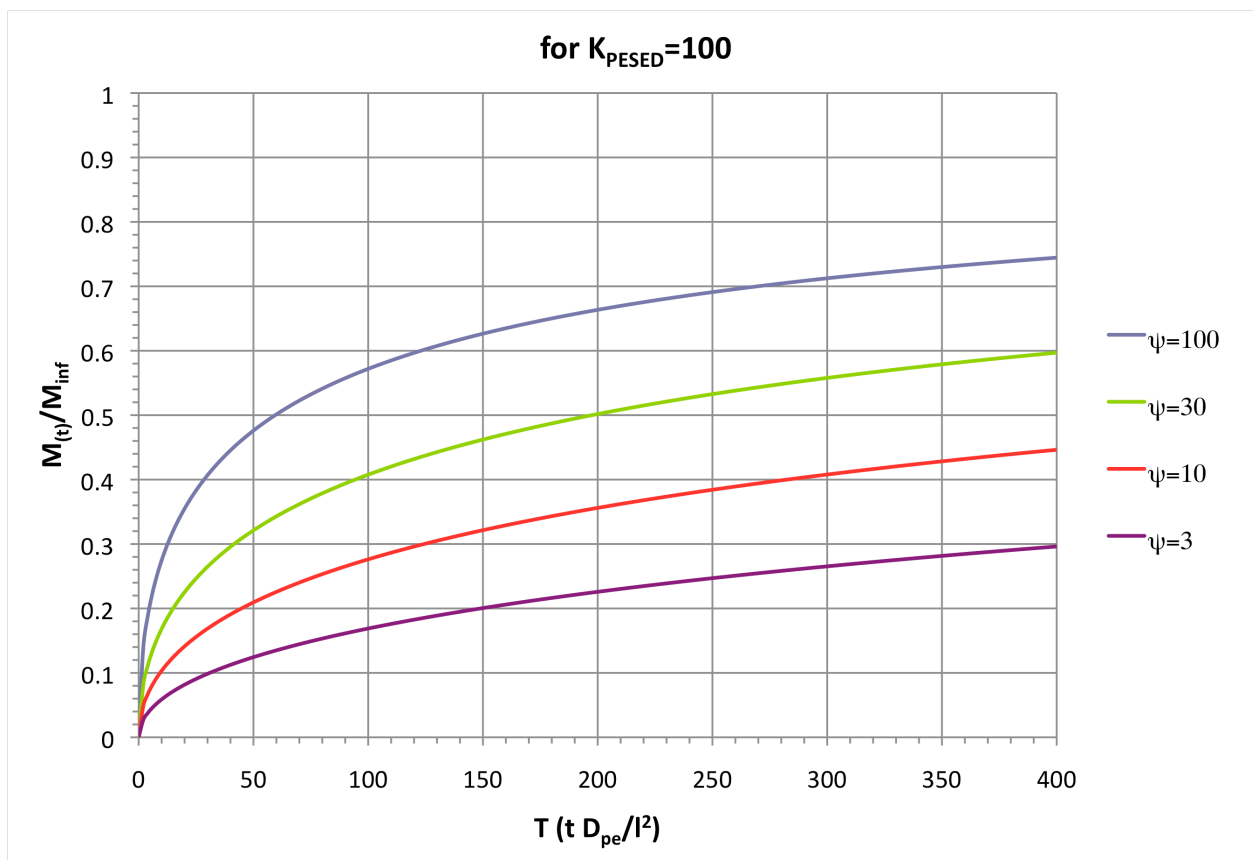


Figure S9. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 100$ and ψ from 3 to 100.

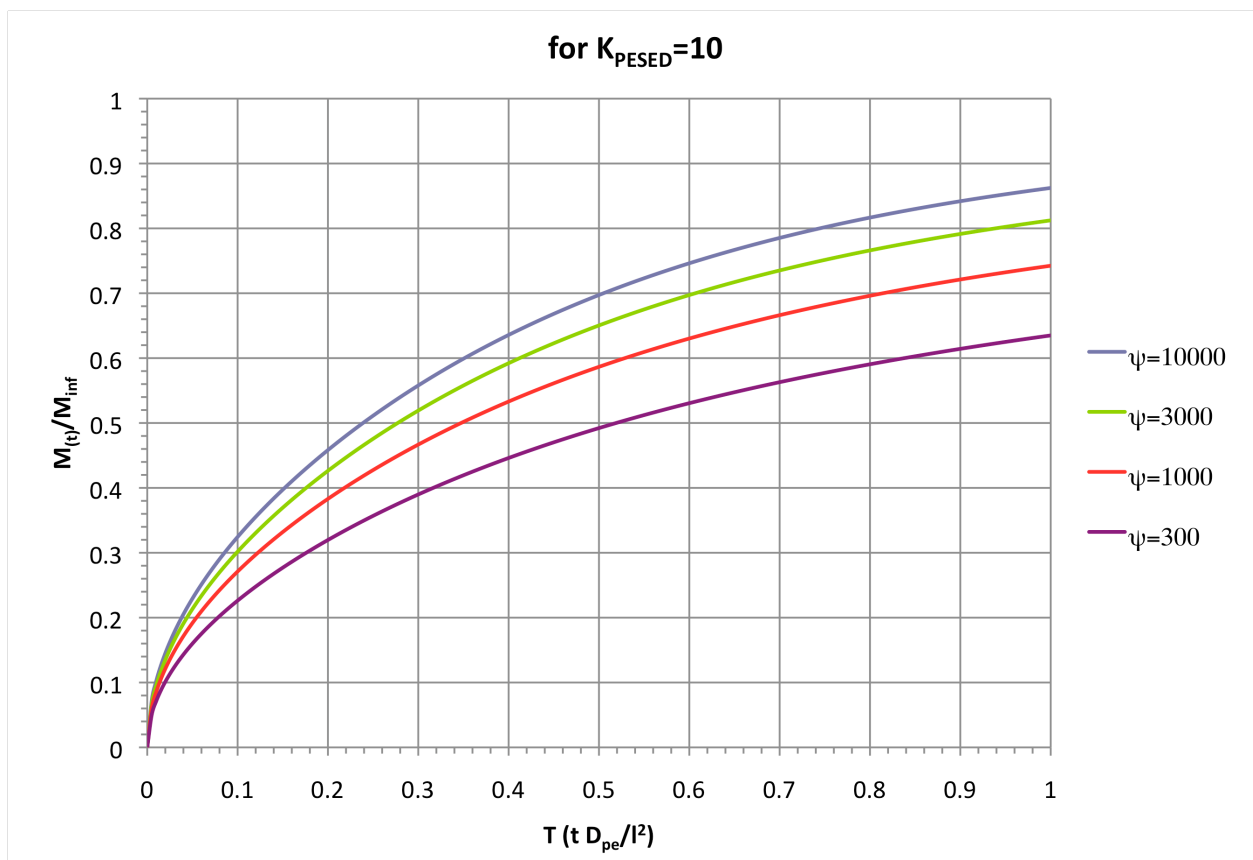


Figure S10. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 10$ and ψ from 300 to 10,000.

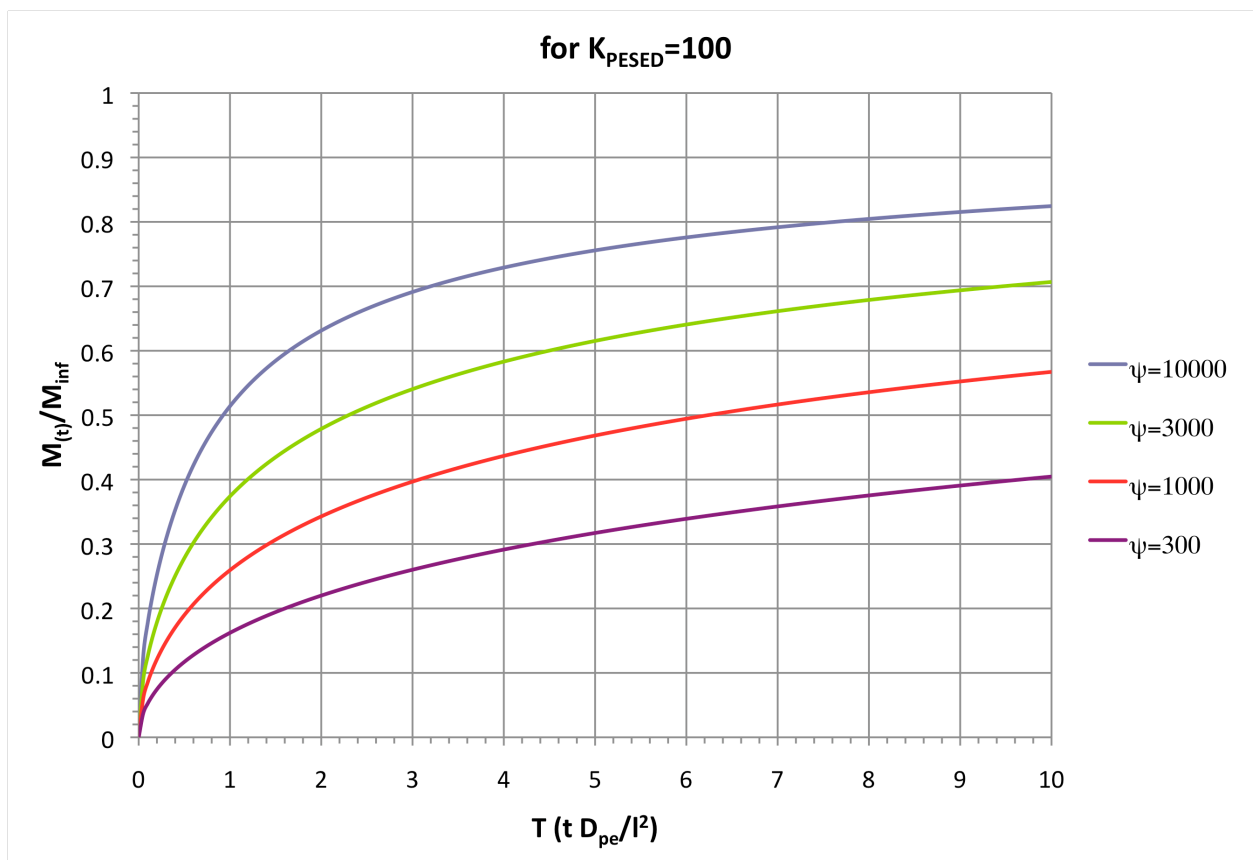


Figure S11. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 100$ and ψ from 300 to 10,000.

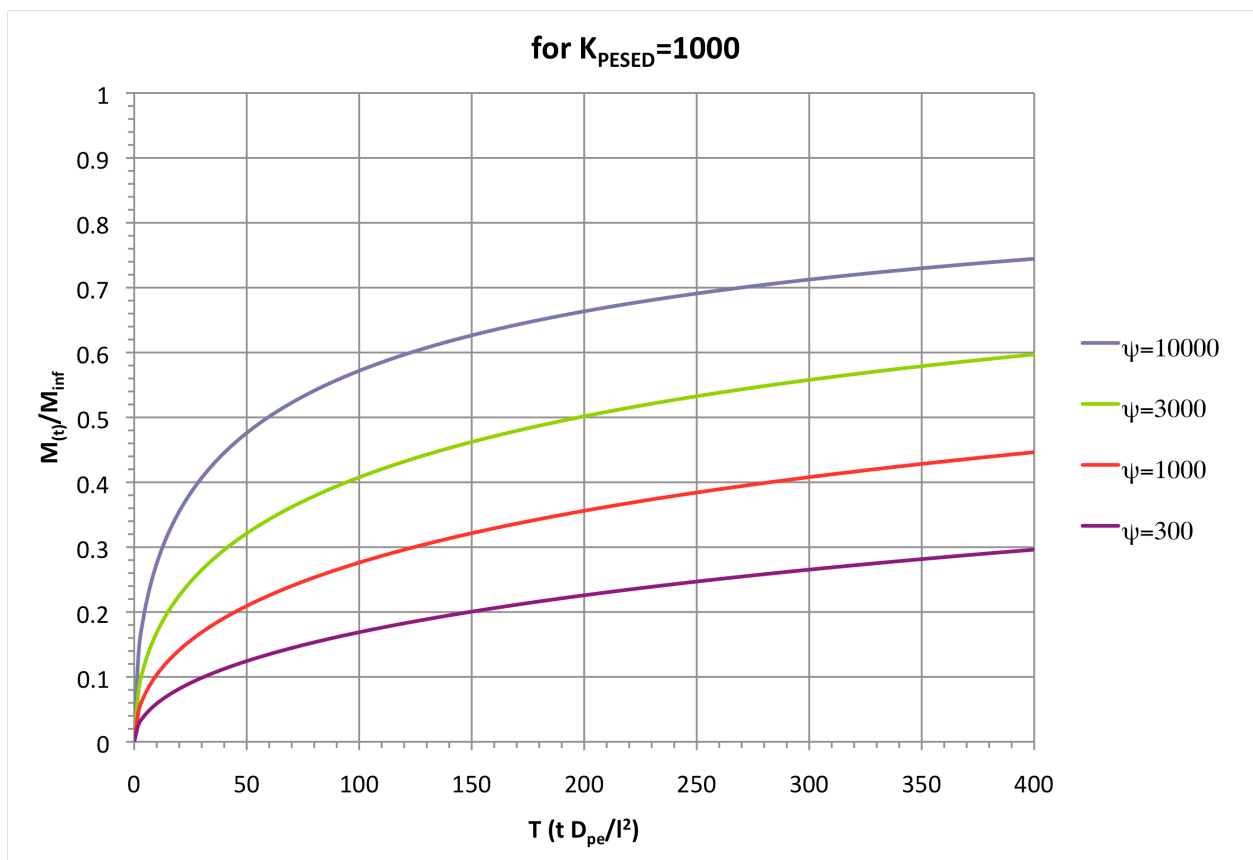


Figure S12. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 1,000$ and ψ from 300 to 10,000.

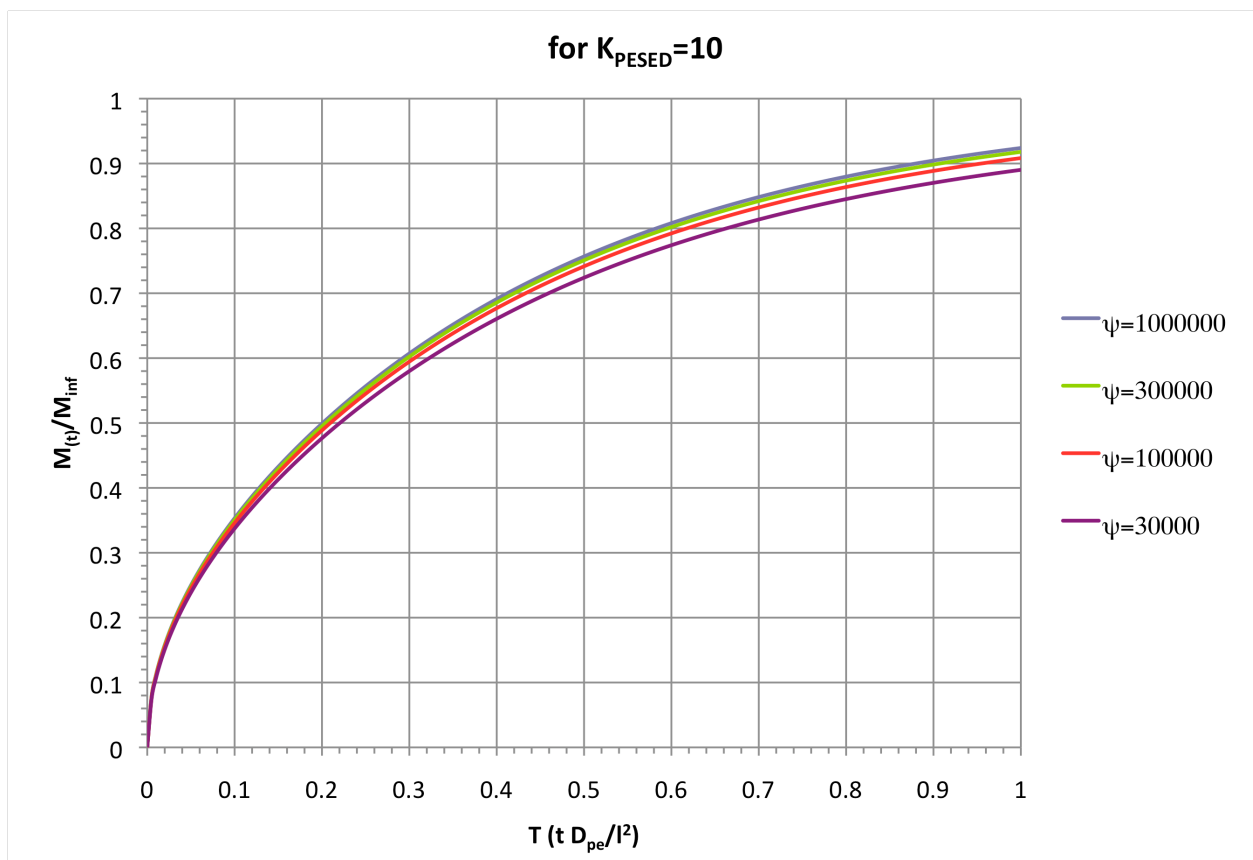


Figure S13. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 10$ and ψ from 30,000 to 1,000,000.

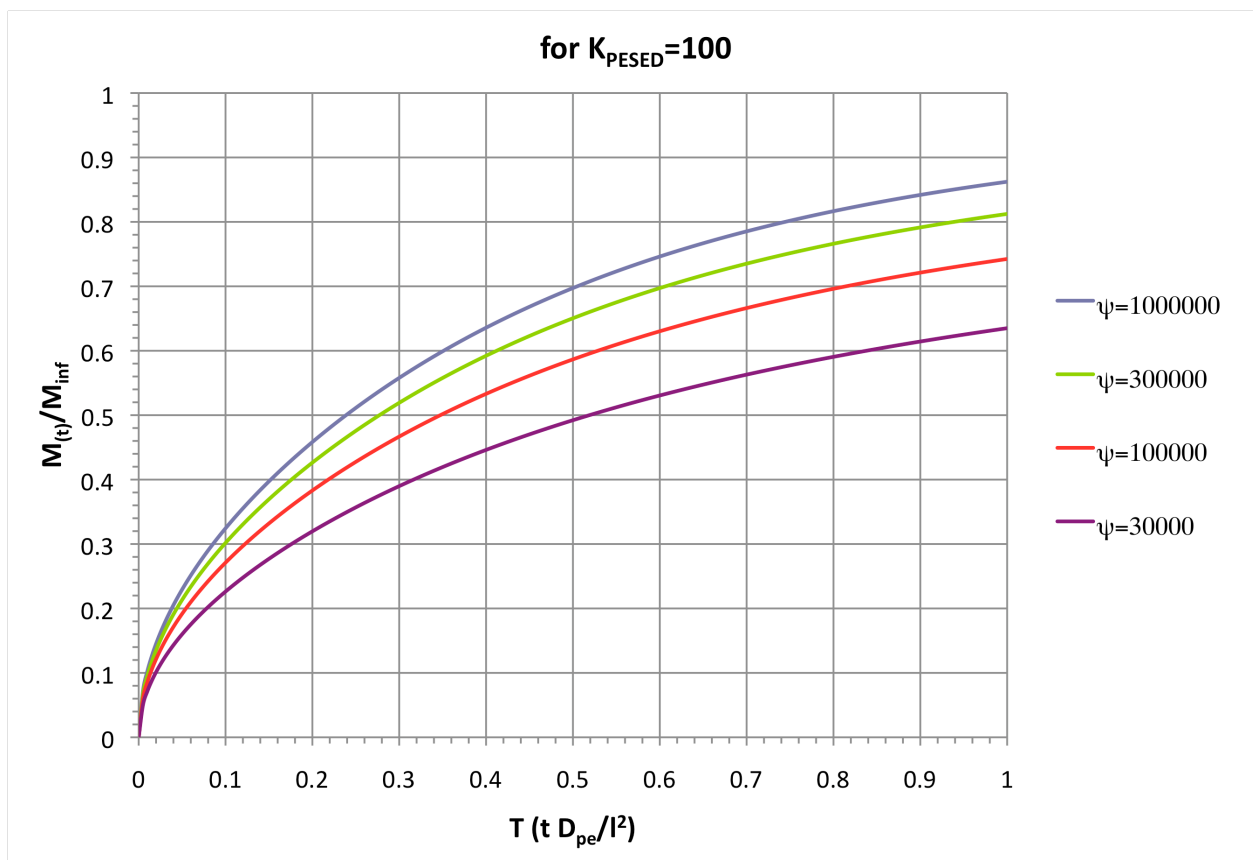


Figure S14. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for $K_{PESED} = 100$ and ψ from 30,000 to 1,000,000.