5.1 Mass Transport of Contaminants in Subsurface

5.1.1 Mechanisms of Mass Transport

Principal mechanisms for mass transport
- Advection
- Dispersion/Diffusion
- Reactions: degradation, precipitation, adsorption, partitioning, ion exchange, etc.

$$J_{advection} =$$
$$J_{diffusion} =$$

where C = concentration of a contaminant [M/L^3];
v_z = seepage velocity (or average linear velocity) [L/T];
D = diffusion coefficient of the contaminant [L^2/T]; and
z = travel distance [L].

$$D_h = D_m + D'$$

where D_h = hydrodynamic dispersion coefficient;
D_m = molecular diffusion coefficient; and
D' = mechanical dispersion coefficient.

$$D' = \alpha \cdot v_z$$

where α = dispersivity [L].

5.1.2 Mass Transport Model

Overall Mass Transport = Mass Transport due to Advection
+ Mass Transport due to Diffusion/Dispersion

Mass Transport due to Advection

$$J_{x,i} = \frac{M_{x,i}}{(\triangle y \cdot \triangle z)}$$

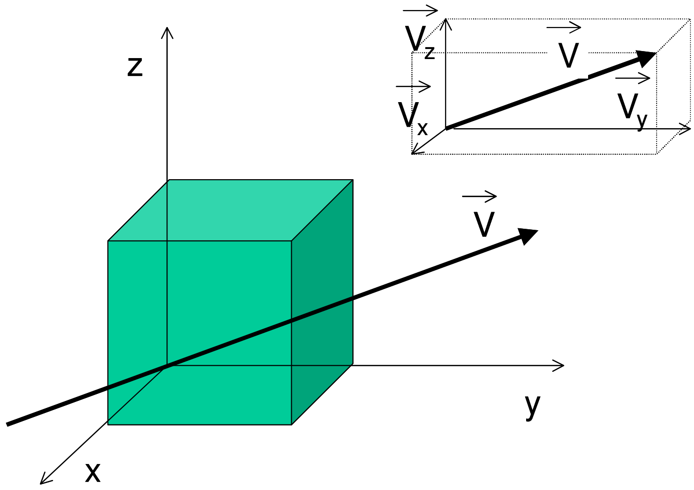

Fig. 5.1 Elemental control volume for mass transport

$$M_{x,i} =$$

where $M_{x,i}$ = mass flux into the unit volume along x direction

$$M_{x,out} =$$

$$= \{ q_{x,i} \cdot C_i + \triangle(q_x \cdot C) \} \cdot (\triangle y \cdot \triangle z)$$

$$\cong (q_{x,i} \cdot C_i + \frac{\partial q_x \cdot C}{\partial x} \cdot \triangle x) \cdot (\triangle y \cdot \triangle z)$$

where $M_{x,o}$ = mass flux out from the unit volume along x direction

$$M_{x,i} - M_{x,out} = -\frac{\partial}{\partial x}(q_x \cdot C \cdot \triangle x \cdot \triangle y \cdot \triangle z)$$

$$M_{y,i} - M_{y,out} = -\frac{\partial}{\partial y}(q_y \cdot C \cdot \triangle x \cdot \triangle y \cdot \triangle z)$$

$$M_{z,i} - M_{z,out} = -\frac{\partial}{\partial z}(q_z \cdot C \cdot \triangle x \cdot \triangle y \cdot \triangle z)$$

$$\therefore M_i - M_{out} = -$$

$$M_i - M_{out} =$$

where, n_e = effective porosity.

$$\therefore \frac{\partial C}{\partial t} = \frac{1}{n_e} \cdot \left\{ \frac{\partial}{\partial x}(q_x \cdot C) + \frac{\partial}{\partial y}(q_y \cdot C) + \frac{\partial}{\partial z}(q_z \cdot C) \right\}$$

or

$$n_e \cdot \frac{\partial C}{\partial t} = - \nabla \cdot (q \cdot C)$$

$$v =$$

$$\frac{\partial C}{\partial t} = - v \cdot \nabla C$$

Mass Transport due to Dispersion/Diffusion

$$M_{x,i} =$$

$$M_{x,out} =$$

$$= \left\{ - D_h \cdot \left(\frac{\partial C}{\partial x}\right)_i - \frac{\partial}{\partial x}\left(D_h \cdot \frac{\partial C}{\partial x}\right) \cdot \triangle x \right\} \cdot (n_t \cdot \triangle y \cdot \triangle z)$$

$$= - D_h \cdot \left(\frac{\partial C}{\partial x}\right)_i \cdot (n_t \cdot \triangle y \cdot \triangle z) - \frac{\partial}{\partial x} \cdot \left(D_h \cdot \frac{\partial C}{\partial x}\right) \cdot (n_t \cdot \triangle x \cdot \triangle y \cdot \triangle z)$$

$$\therefore M_{x,i} - M_{x,out} = \frac{\partial}{\partial x}\left\{ \left(D_h \cdot \frac{\partial C}{\partial x}\right) \cdot (n_t \cdot \triangle x \cdot \triangle y \cdot \triangle z) \right\}$$

$$\therefore M_{y,i} - M_{y,out} = \frac{\partial}{\partial y}\left\{ \left(D_h \cdot \frac{\partial C}{\partial y}\right) \cdot (n_t \cdot \triangle x \cdot \triangle y \cdot \triangle z) \right\}$$

$$\therefore M_{z,i} - M_{z,out} = \frac{\partial}{\partial z}\left\{ \left(D_h \cdot \frac{\partial C}{\partial x}\right) \cdot (n_t \cdot \triangle x \cdot \triangle y \cdot \triangle z) \right\}$$

$$M_i - M_{out} = (n_t \cdot \triangle x \cdot \triangle y \cdot \triangle z) \cdot \left\{ \frac{\partial}{\partial x}\left(D_h \cdot \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_h \cdot \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_h \cdot \frac{\partial C}{\partial z}\right) \right\}$$

$$M_i - M_{out} = \frac{\partial C}{\partial t} \cdot (n_t \cdot \triangle x \cdot \triangle y \cdot \triangle z)$$

Overall Mass Transport

$$\frac{\partial C}{\partial t} = D_h \cdot \nabla^2 C - v \cdot \nabla C \quad (\nabla C = \text{Divergence of C})$$

for one-dimensional case

$$\frac{\partial C}{\partial t} = D_h \cdot \frac{\partial^2 C}{\partial z^2} - v_z \cdot \frac{\partial C}{\partial z}$$

5.1.3 Mitigation Mechanisms

(1) Biodegradation

(2) Ion Exchange

(3) Precipitation

5.1.4 Estimation of Mass Transport Parameters

Seepage velocity

$$v = \frac{Q}{A} =$$

where v = specific discharge [L/T];

Q = flow rate [L^3/T];

A = cross-sectional area [L^2];

K_h = hydraulic conductivity or permeability [L/T];

Δh = hydraulic head difference [L];

Δl = distance along the fluid flowing direction [L]; and

i = hydraulic gradient.

Effective porosity

Total porosity (n_t) is readily measurable.

Relationship between effective porosity and total porosity is case-dependent.

Typical compacted clay liner, n_e = 90% of n_t (Kim, et al., 2001).

Using the olumn test with tracers, effective porosity can be estimated.

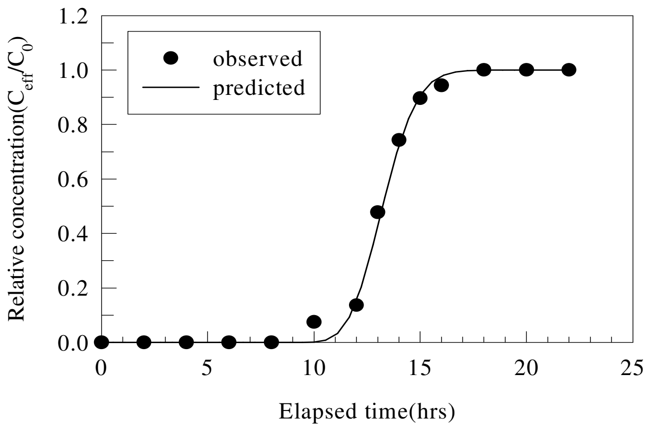

Fig 5.2 Breakthrough concentration data and mathematical breakthrough curve

Partition Coefficient

- Many previous studies have reported that the partition coefficients estimated from batch tests and column tests are significantly different.
- Partition coefficient estimation is also affefted by the water chemistry (e.g., pH, DOM, temperature, etc.)
- The effect of solid:liquid ratio in batch test on the estimated partition coeffi차ent

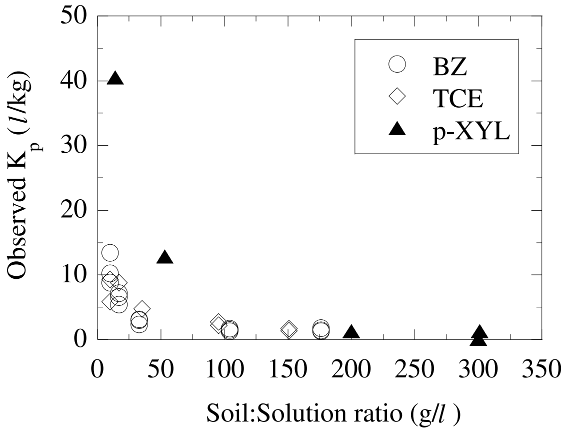

Fig. 5.3 Effect of soil:solution ration on the observed partition coefficient of between soil and water (Kim, et al., 2003)

5.1.5 Prdiction of Contaminant Movement

$$\frac{\partial C}{\partial t} = D_h \cdot \frac{\partial^2 C}{\partial z^2} - v_z \cdot \frac{\partial C}{\partial z}$$

Ogata and Banks (1961)

Initial condition:

$$C(z,0) = 0 \qquad 0 < z < \infty$$

Boundary conditions:

$$C(0,t) = C_o \qquad 0 < t; \text{ and}$$
$$C(\infty,t) = 0 \qquad 0 < t.$$

$$C(z,t) = \frac{C_o}{2} \cdot \left[erfc\left\{ \frac{z - v_z \cdot t}{2\sqrt{D_h \cdot t}} \right\} + \exp\left(\frac{v_z \cdot z}{D_h} \right) \cdot erfc\left\{ \frac{z + v_z \cdot t}{2\sqrt{D_h \cdot t}} \right\} \right]$$

$$erfc(x) = \frac{2}{\sqrt{\Pi}} \cdot \int_x^\infty \exp(-u^2) du$$

where *erfc* = complementary error function; and
exp = exponential function.

Table 5.1 Sorption isotherm models and their corresponding retardation equations

Isotherm	Isotherm model	Retardation equation
Linear model	$C_s = K_p \cdot C_l$ where C_s = solid phase concentration; K_p = partition coefficient (or distribution coefficient); and C_l = liquid phase concentration.	$R_f = 1 + \frac{(1-n_t)}{n_t} \cdot \rho_s \cdot K_p$ where ρ_s = soil solid density.
Freundlich model	$C_s = K_f \cdot C_l^{\,n_f}$ where K_f *and* n_f = Freundlich constant.	$R_f = 1 + \frac{(1-n_t)}{n_t} \cdot \rho_s \cdot n_f \cdot K_f \cdot C_l^{\,n_f - 1}$
Langmuir model	$C_s = \frac{Q_o \cdot K_l \cdot C_l}{1 + K_l \cdot C_l}$ where Q_o = saturation constant; and K_l = Langmuir constant.	$R_f = 1 + \frac{(1-n_t) \cdot \rho_s \cdot Q_o \cdot K_l}{n_t \cdot (1 + K_l \cdot C_l)^2}$

linear isotherm model (Vermeulen and Hiester, 1952).

$$\frac{\partial C}{\partial t} = \frac{D_h}{R_f} \cdot \frac{\partial^2 C}{\partial z^2} - \frac{v_z}{R_f} \cdot \frac{\partial C}{\partial z}$$

where R_f = Retardation factor (Hashimoto et al., 1964).

Initial condition:

$$C(z,0) = 0 \qquad 0 < z < \infty$$

Boundary conditions:

$$C(0,t) = C_o \qquad 0 < t; \text{ and}$$
$$C(\infty,t) = 0 \qquad 0 < t.$$

$$C(z,t) = \frac{C_o}{2} \cdot \left[erfc\left\{ \frac{R_f \cdot z - v_z \cdot t}{2\sqrt{R_f \cdot D_h \cdot t}} \right\} + \exp\left(\frac{v_z \cdot z}{D_h} \right) \cdot erfc\left\{ \frac{R_f \cdot z + v_z \cdot t}{2\sqrt{R_f \cdot D_h \cdot t}} \right\} \right]$$

Lindstrom et al., 1967; Gershon and Nir, 1969; and van Genuchten and Alves, 1982

Initial condition:

$$C(z,0) = C_i$$

Boundary conditions:

$$v \cdot C(0^+, t) - D \cdot \frac{dC(0^+, t)}{dz} = v \cdot C_o \ ;$$

$$\frac{dC(\infty, t)}{dz} = 0$$

$$\frac{C(z, t) - C_i}{C_o - C_i} = \frac{1}{2} \cdot \left[erfc(\xi_1) + 2 \cdot \sqrt{\frac{\xi_4}{\pi}} \cdot \exp(\xi_1^2) - (1 + \xi_2 + \xi_4) \cdot \exp(\xi_2) \cdot erfc(\xi_3) \right]$$

$$\xi_1 = \frac{R_f \cdot z - v_z \cdot t}{2 \cdot \sqrt{R_f \cdot D_h \cdot t}}$$

$$\xi_2 = \frac{v_z \cdot z}{D_h}$$

$$\xi_3 = \frac{R_f \cdot z + v_z \cdot t}{2 \cdot \sqrt{R_f \cdot D_h \cdot t}}$$

$$\xi_4 = \frac{v_z^2 \cdot t}{D_h \cdot R_f}$$

$$Peclet \quad number = \frac{v_z \cdot d}{D_m}$$ (Perkins, et al., 1963)

where d = mean particle diameter.

Peclet number > 6 : dispersion dominant zone; and
Peclet number < 0.02 : diffusion dominant zone.

Shackelford (1994)

$$P_c = \frac{v_z \cdot L}{D_m}$$

where P_c = column Peclet number; and
L = travel distance [L].

P_c > 50 : advection dominant zone; and
P_c < 1 : diffusion dominant zone.

5.2 Mass Transport through Geomembranes

5.2.1 Mechanisms of Mass Transport

(i) Partitioning between leachate and geomembrane;

(ii) Diffusion within the geomembrane;

(iii) Partitioning between geomembrane and groundwater.

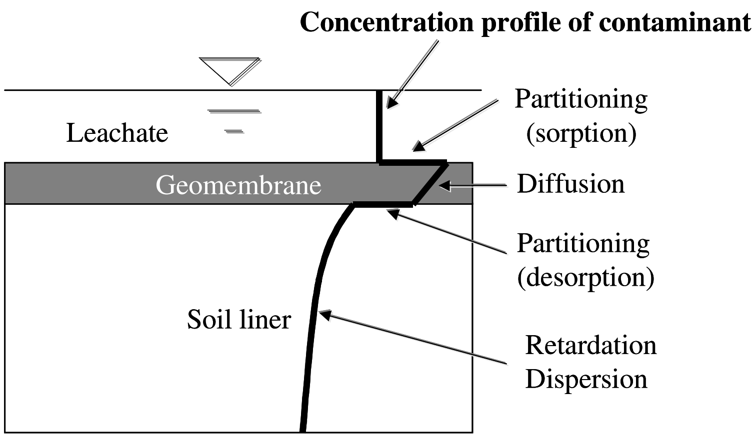

Fig. 5.3 Contaminant transport mechanisms through a composite liner system consist of geomembrane and compacted soil liner

(1) Partitioning

$$K = \rho_{GM} \cdot \frac{C_{GM}}{C_l}$$

where K = partition coefficient [dimensionless];

ρ_{GM} = density of geomembrane [M/L^3];

C_{GM} = concentration of a solute in geomembrane [M/M]; and

C_l = concentration of the solute in the solution [M/L].

(2) Diffusion

Fick's law

$$J_{diffusion} = -D \cdot \nabla C_{GM}$$

and

$$\frac{\partial C_{GM}}{\partial t} = \nabla^2 C_{GM}$$

where D = diffusion coefficient [L^2/T].

Permeation

$$P \equiv D \cdot K$$

where P = permeability coefficient.

(3) Physical Damage on Geomembranes
Giroud and Bonaparte (1989)
- High QA/QC 1 hole/acre (= 247 holes/km^2)
- Low QA/QC 10 holes/acre.

Pin holes ($d \ll t_g$): Poiseuille's equation for flow through a capillary tube.

$$Q = \frac{\pi \cdot \rho_w \cdot g \cdot h_w \cdot d^4}{128 \cdot \eta_w \cdot t_g}$$

where Q = leakage rate through a geomembrane hole [L^3/T];
ρ_w = density of water;
h_w = water height on the top of geomembrane;
d = diameter of hole;
η_w = dynamic viscosity of water; and
t_g = thickness of geomembrane.

Holes ($d > t_g$): Bernoulli's equation for free flow through an orifice.

$$Q = C_B \cdot a \cdot \sqrt{2 \cdot g \cdot h_w}$$

where C_B = dimensionless coefficient (= 0.6 for sharp edge); and
a = hole area.

For composite liner system

In the case of good contact;

$$Q = 0.21 \cdot h_w^{0.9} \cdot a^{0.1} \cdot k_s^{0.74}$$

In the case of poor contact;

$$Q = 1.15 \cdot h_w^{0.9} \cdot a^{0.1} \cdot k_s^{0.74}$$

where Q = (m^3/sec);

h_w = (m);

a = (m^2); and

k_s = hydraulic conductivity of underlying soil liner (m/sec)

Assumptions:

(i) $i < 2$;

(ii) T = 20°C (or $Q_T = \frac{\eta_{w,20}}{\eta_{w,T}} \cdot Q_{20}$);

(iii) 1×10^{-10} m/sec < k_s < 1×10^{-6} m/sec; and

(iv) 합성수지차수막의 상부의 매질 혹은 상부 토사의 투수계수 > k_s.

5.2.2 Estimations for mass Transport Parameters

(1) Batch test

$$K = \frac{\rho_{GM} \cdot (C_{l,o} - C_{l,e}) \cdot V_l}{M_{GM} \cdot C_{l,e}}$$

where ρ_{GM} = density of geomembrane (g/cm^3);

$C_{l,o}$ = initial concentration of a solute in the solution (mg/L);

$C_{l,e}$ = equilibrium concentration of the solute in the solution (mg/L);

V_l = volume of liquid contacting with geomembrane (mL); and

M_{GM} = mass of geomembrane applied (g).

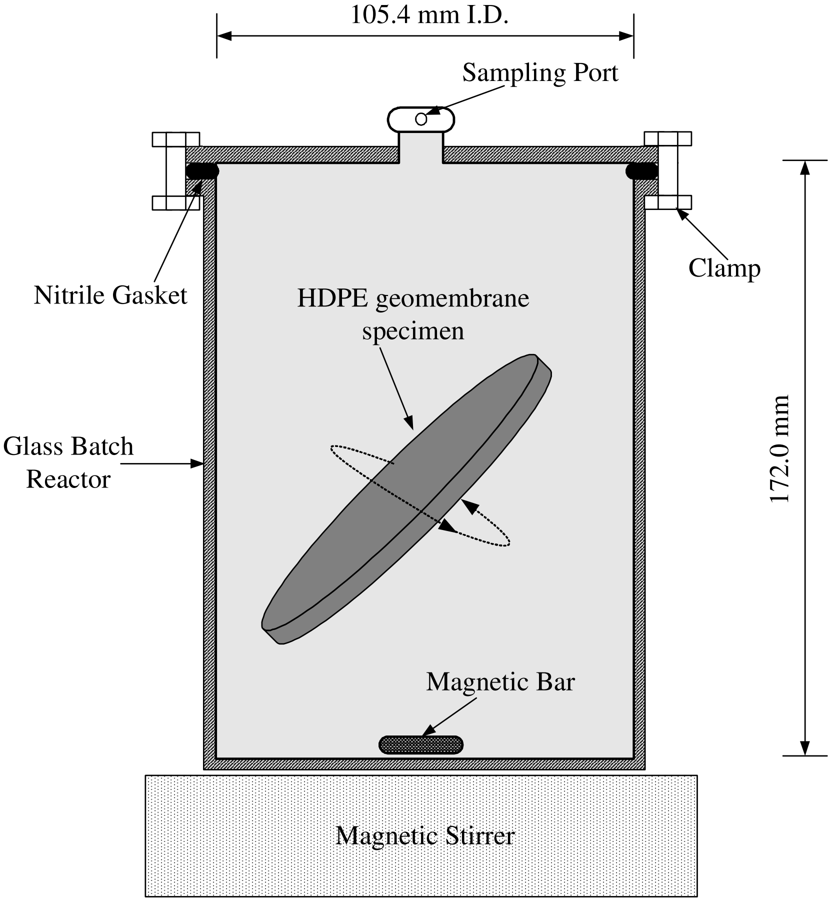

Fig. 5.4 A batch test apparatus for measurement of partition and diffusion coefficients of geomembranes.

$$\frac{\partial C_{GM}}{\partial t} = D \cdot \frac{\partial^2 C_{GM}}{\partial x^2}$$

Initial condition:

$$C_{GM}(x,0) = 0 \qquad -l < x < l$$

Boundary conditions:

$$a \cdot \frac{\partial C_l}{\partial t} = \mp D \cdot \frac{\partial C_{GM}}{\partial x} \quad \text{or} \quad \frac{a}{K} \cdot \frac{\partial C_l}{\partial t} = \mp D \cdot \frac{\partial C_{GM}}{\partial x} \qquad x = \pm l,\ t > 0$$

where $a = \dfrac{V_l}{2 \cdot A}$

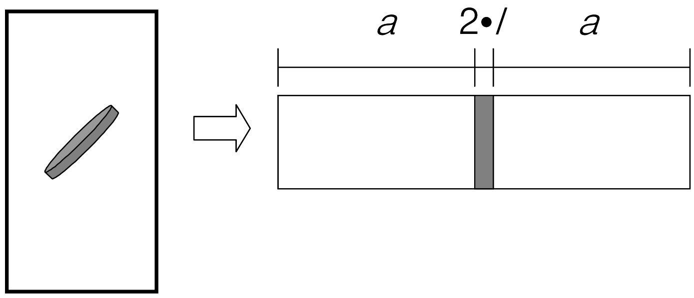

Figure 5.5 Schematic diagram of diffusion model from a well mixed solution of limited volume.

An analytical solution for small values of time (before solute reaches at the center of geomembrane):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2 \cdot \alpha \cdot (1+\alpha)}{1+\alpha+\alpha^2 \cdot q_n^2} \cdot e^{-D \cdot q_n^2 \cdot t/l^2}$$

where M_t = amount of solute in geomembrane at time t [M];

M_∞ = amount of solute in geomembrane in the inifinite time (at equilibrium) [M];

$\alpha = a / (K \cdot l)$ [dimensionless]; and

q_n = non-zero positive roots of $\tan(q_n) = -\alpha \cdot q_n$.

An alternative solution,

$$\frac{M_t}{M_\infty} = (1+\alpha) \cdot [1 - e^{T/\alpha^2} \cdot erfc\sqrt{T/\alpha^2}]$$

$$T = D \cdot t/l^2$$

In terms of concentration in solution at time, t, (Reynolds et al., 1990)

$$\frac{C_{l,t}}{C_{l,o}} = e^{T/\alpha^2} \cdot erfc\sqrt{T/\alpha^2}$$

and

$$t_{1/2} = 0.585 \cdot \frac{a^2}{K^2 \cdot D}$$

where $t_{1/2}$ = time for $C_{l,t}/C_{l,o}$ = 0.5.

Numerical Analysis

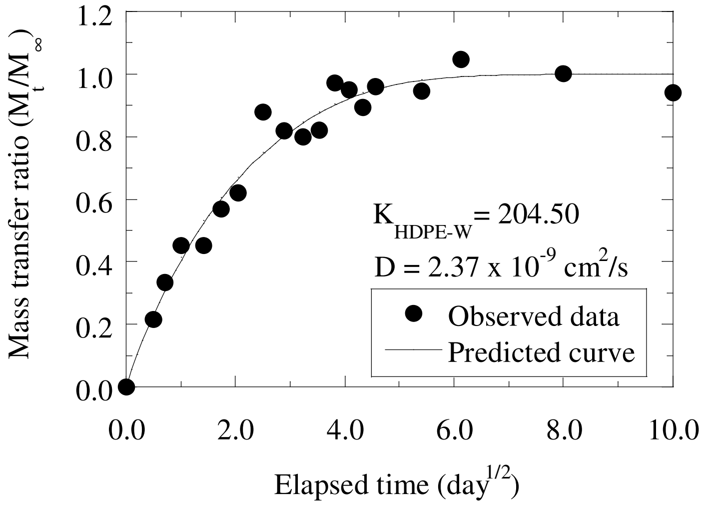

Fig 5.6 An example of partition and diffusion coefficient estimation using mathematical model and observed data from batch test (Joo et al., 2004)

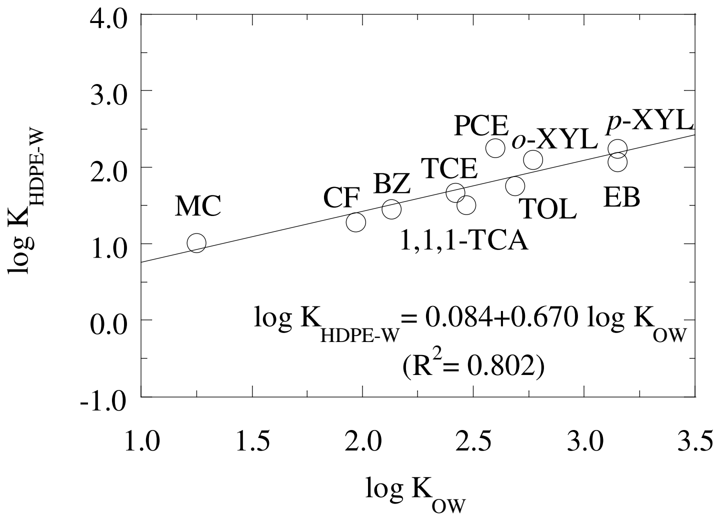

Fig 5.7 Relationship between the octanol-water partition coefficients (K_{OW}) and the HDPE-water partition coefficients ($K_{HDPE\text{-}W}$) of various organic compounds in dilute aqueous solutions (Joo, et al. 2004)

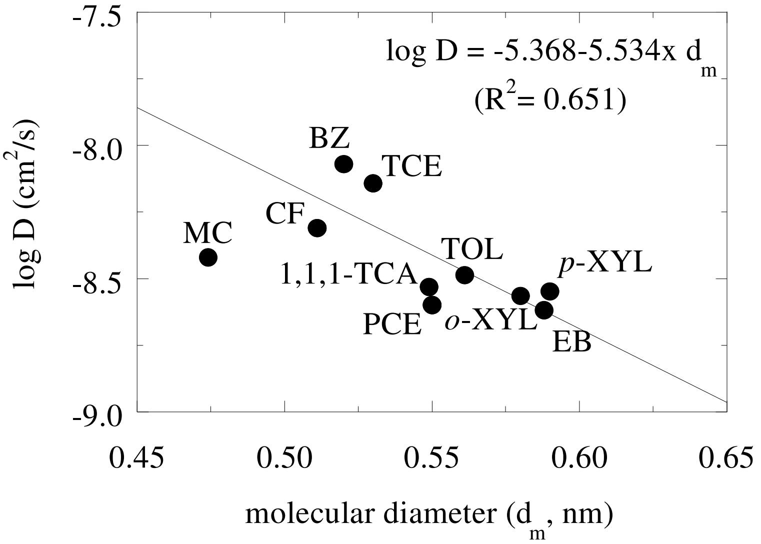

Fig. 5.8 Relationship between the diffusion coefficients (D) and molecular diameter (d_m) of organic compounds for dilute aqueous organic compound

(2) Compartment test

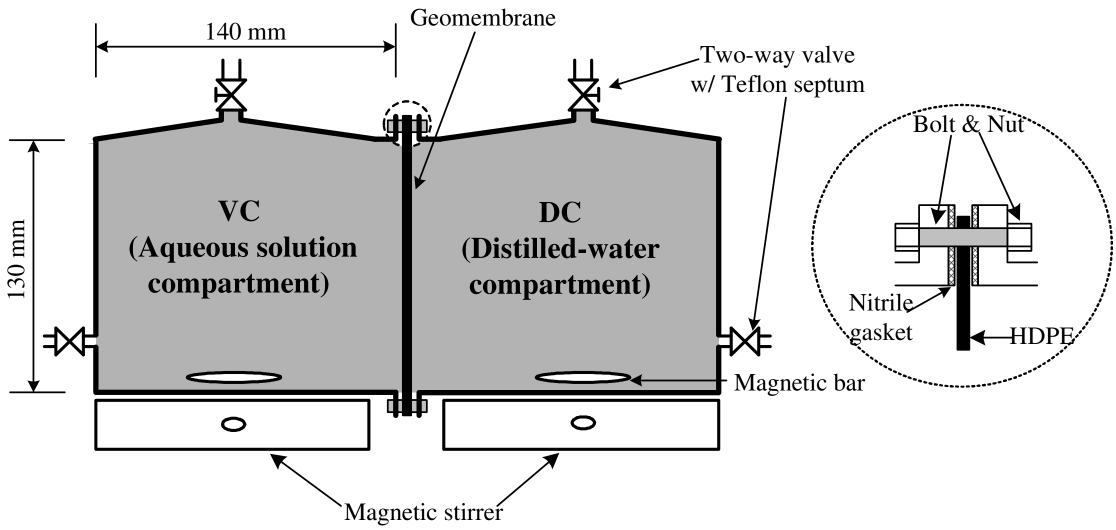

Fig. 5.9 Example of schematic of confined double-compartment apparatus.

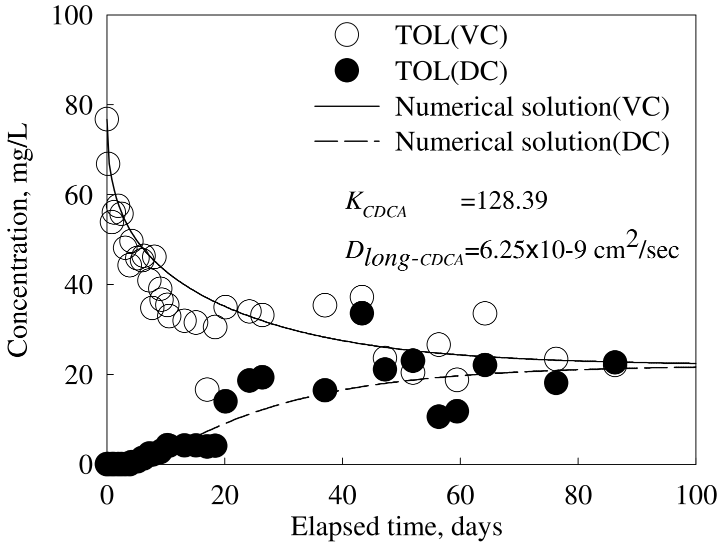

Fig. 5.10 An example of partition and diffusion coefficient estimation using mathematical model and observed data from compartment test

5.2.3 Prediction of Mass Transport in Composite Liner System

Kim (1997)

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