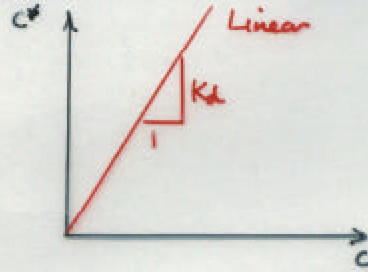
6.2 EQUILIBRIUM SURFACE REACTIONS

Linear Isotherm

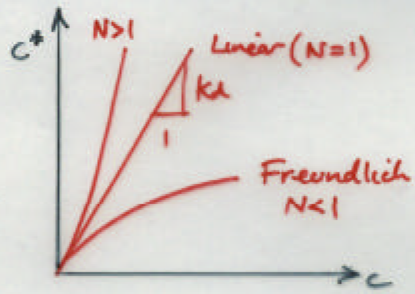
$$C^* = K_d C$$

C^* (mg/kg) solute sorbed onto surface
c (mg/L) concentration of solute in equilibrium with solid
K_d (L/kg) distribution coefficient.

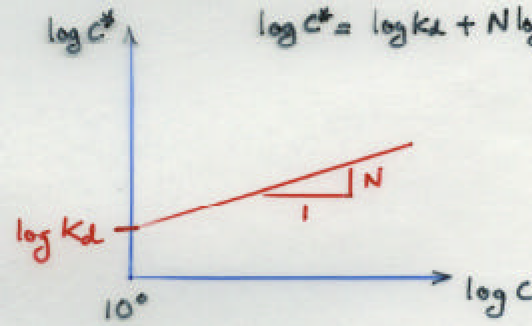


Freundlich Isotherm

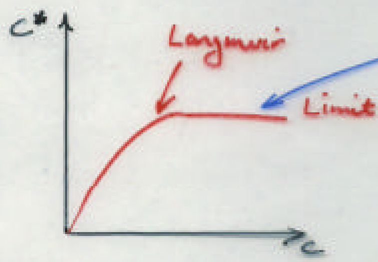
$$C^* = K_d C^N$$



$$\log C^* = \log K_d + N \log c$$



Langmuir Isotherm



Represents a finite no. of sorption sites

$$\frac{c}{C^*} = \frac{1}{\alpha\beta} + \frac{c}{\beta} = \frac{\alpha\beta c}{1+\alpha c}$$

α = absorption coefficient related to binding energy (L

β = max amount of solute that may be absorbed to solid (mg/kg)

Why interested in Isotherms

Recall:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x} - \frac{\rho_d}{\theta}\frac{\partial c^*}{\partial t} + \left(\frac{\partial c}{\partial t}\right)_r \rightarrow 0$$

$$\frac{\partial c^*}{\partial t} = \frac{\partial c^*}{\partial c}\left(\frac{\partial c}{\partial t}\right) = K_d \frac{\partial c}{\partial t}$$

Move retardation term to L.H.S.

$$\frac{\partial c}{\partial t} + \frac{\rho_d}{\theta}\underbrace{\left(\frac{\partial c^*}{\partial c}\right)}_{K_d}\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x}$$

$$\underbrace{\left[1 + \frac{\rho_d}{\theta} K_d\right]}_{\text{Retardation coefficient, } R}\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x}$$

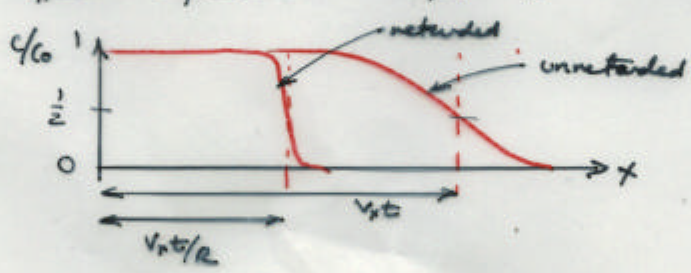
$$\frac{\partial c}{\partial t} = \frac{D_L}{R}\frac{\partial^2 c}{\partial x^2} - \frac{v_x^a}{R}\frac{\partial c}{\partial x}$$

Effective (retarded) parameters.

Effect:

1. Retards velocity as $V_{effective} = v_x^a/R$
2. Reduces effective dispersion as D_L/R

} Apply these to all previous expressions.



DISTRIBUTION COEFFICIENTS

Form	Relation	$K_d = \partial c^*/\partial c$	
Linear	$c^* = K_d c$	$\frac{\partial c^*}{\partial c} = K_d$	$R = [1 + \rho_d/\theta \, K_d]$
Freundlich	$c^* = K_d c^N$	$\frac{\partial c^*}{\partial c} = N K_d c^{N-1}$	$R = [1 + \rho_d/\theta \, N K_d c^{N-1}]$
Langmuir	$c^* = \frac{\alpha \beta c}{1 + \alpha c}$	$\frac{\partial c^*}{\partial c} = \frac{\alpha \beta}{(1 + \alpha c)^2}$	$R = 1 + \frac{\rho_d}{\theta} \frac{\alpha \beta}{(1 + \alpha c)^2}$

Typical magnitudes of R

K_d in the range 0 to 10^3 ml/g

$$\rho_d = 2500 \text{ kg/m}^3 \longrightarrow 2.5 \text{ g/ml}$$
$$\theta = 0.2 \text{ to } 0.4$$

$$R \doteq \left(1 + \frac{2.5}{.25} K_d\right) \qquad R \doteq (1 + 10 K_d) \Rightarrow 1 \text{ to } 10^4$$

Range.

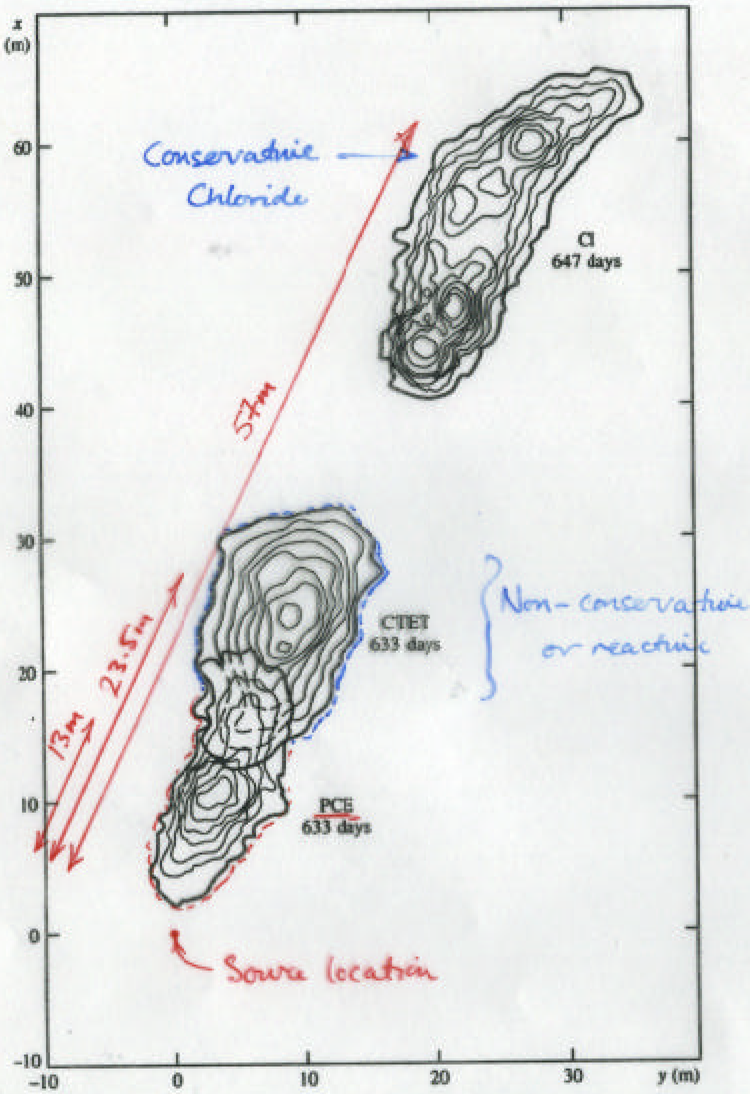


FIGURE 3.16 Plumes of chloride, carbon tetrachloride, and tetrachloroethylene at the end of the experimental period. The plumes are based on depth-averaged values. Source: P. V. Roberts, M. N. Goltz, and D. M. Mackay, *Water Resources Research* 22, no. 13 (1986):2047–59. Copyright by the American Geophysical Union.

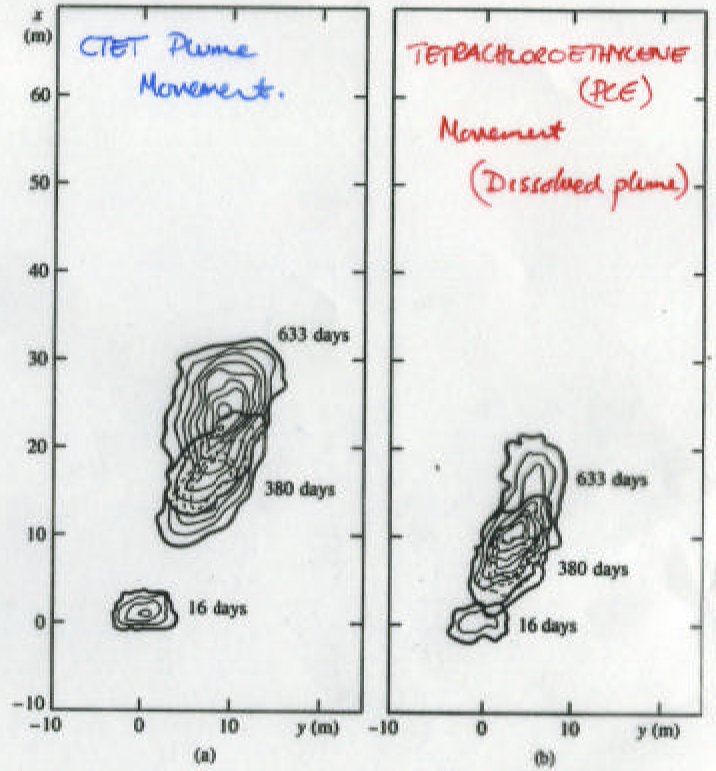


FIGURE 3.17 (a) Growth of carbon tetrachloride plume with time; (b) growth of tetrachloroethylene plume with time. Source: P. V. Roberts, M. N. Goltz, and D. M. Mackay, *Water Resources Research* 22, no. 13 (1986):2047–59. Copyright by the American Geophysical Union.

Why are different compounds differentially mobile ??

Assuming Cl is unretarded: $R = \frac{V^a_{cl}}{V^a} = \frac{l_{cl}}{t}\frac{t}{l}$

CTET => $R = 2.42$

PCE => $R = 4.38$

$$2000\ Kg/m^3 = 2000 \frac{Kg}{m^3} \frac{1m^3}{1000L} = \frac{2Kg}{L} = 2\frac{g}{mL}$$

$1m^3 = 1000L$

$$\frac{\theta}{\rho_b} = \frac{.3}{2}\frac{L}{Kg} = .15$$

Rearranging

$$R = [1 + \frac{\rho_b}{\theta} K_d]$$

$$(R-1)\frac{\theta}{\rho_b} = K_d$$

Solute	$(R-1)$	$(R-1)\frac{\theta}{\rho_b} = K_d$ (L/kg or mL/g)	
CTET	1.62	.213	
PCE	3.38	.507	(tetrachloroethylene)
		K_d	

(Note can also check dispersion)

Note: organic content very low ~ 0.02%

∴ absorption limited

Estimates

	Solute	Solubility	log Kow (octanol-water partition)
	CTET	805 mg/l @ 30°C	2.7
(Tetrachloroethylene)	PCE	1503 mg/l @ 25°C	2.6