

7.1.1 Diffusive Transport

Fick's first law

$$q_D = \Theta_g D_g^* \frac{\partial c_g}{\partial x}$$

q_D = diffusive mass flux

c_g = Concentration of VOC
in gas phase

Θ_g = Volumetric gas content

D_g^* = "Effective" diffusion
coefficient of gas.

Fick's second law

Mass continuity/Conservation of mass equation.

$$R \frac{\partial c_g}{\partial t} = D_g^* \frac{\partial^2 c_g}{\partial x^2}$$

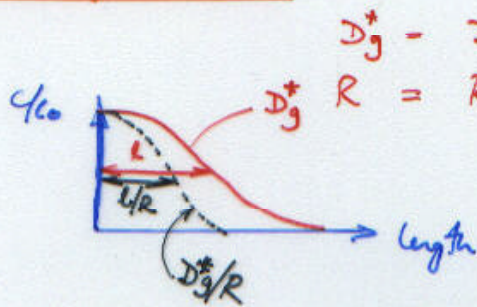
R = Retardation factor

- accounts for sorption
between phases

This ignores:

1. Advection of vapors due to pumping (vacuum stripping)
2. Advection due to density/temperature effects
3. Infiltration due to rain/etc.

Controlling Parameters



D_g^* - Diffusive transport

R = Retardation of the diffusive transport.

At same time, t_1

□ Note the physical meaning of these parameters.

Effective Diffusion Coefficient, D_g^*

$$D_g^* = \tau D_g$$

τ = tortuosity

D_g = "Free" diffusion coefficient (L^2/T)

Tortuosity

1. Experimental Measurement



$$\tau = \left(\frac{L}{L_0}\right)^2$$

2. Empirical estimates

eg. $\tau = \frac{\theta_g^{2/3}}{\theta_c}$

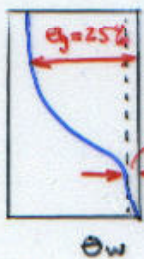
(Millington and Quirk, 1961)

Total porosity (i.e. Saturated)

Estimates of D_g^*

TCE @ 20°C $D_g = 8.1 \times 10^{-6} \text{ m}^2/\text{s}$ (typical for chlorinated solvent).

Assume $\theta_c = 35\%$



Residual water zone: $\theta_g = 25\%$ $\tau = 0.32$

$$D_g^* = 2.6 \times 10^{-6} \text{ m}^2/\text{s}$$

Transition zone: $\theta_g = 5\%$

$$\tau = 0.0075$$

$$D_g^* = 6.1 \times 10^{-8} \text{ m}^2/\text{s}$$

D^* in water (saturated)

$$D^* = 2 \times 10^{-9} \text{ m}^2/\text{s}$$

PARTITIONING BEHAVIOR

Retardation results from two mechanisms $\left\{ \begin{array}{l} \text{Gas} \rightarrow \text{Water partitioning} \text{ ①} \\ \text{Water} \rightarrow \text{Solid partitioning} \text{ ②} \end{array} \right.$

① Gasous/Aqueous Partitioning

Described by Henry's Law.

$$H = \frac{C_g}{C_w}$$

C_w = water concentration (in same units as C_g)

H = "Dimensionless" Henry law coeff.

Alternate (usual) form of Henry's Law

$$H' = \frac{C_g'}{C_w'} = \frac{P_v}{S}$$

i.e. $P = H' C_w$

P_v = vapor pressure

S = saturation of "solvent" in water, Max value = Solubility

H' units of $\text{atm} \cdot \text{m}^3/\text{mol}$

② Aqueous/Solid Partitioning

- Identical to saturated zone.

i.e.

$$K_D = K_{oc} \cdot f_{oc}$$

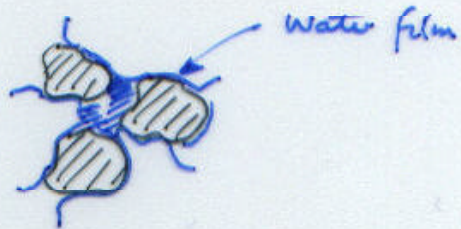
RETARDATION FACTOR

Assume equilibrium partitioning between phases $\begin{cases} \text{water} \\ \text{solid} \end{cases}$

$$R = 1 + \underbrace{\frac{\theta_w}{\theta_g} \cdot \frac{1}{H}} + \underbrace{\frac{\rho_b \cdot k_d}{\theta_g \cdot H}}$$

Partitioning to
Water

Partitioning to solid
via water



Note: H adjusts the proportion present in
the water as a function of concentrations
in the gas phase i.e.

$$H = \frac{C_g}{C_w}$$

This is the non-dimensional Henry's constant.

RETARDATION FACTOR MAGNITUDES

Magnitudes are dependent on the two retardation mechanisms $\left\{ \begin{array}{l} \text{gas} \rightarrow \text{water} \\ \text{gas} \rightarrow \text{solid} \\ \text{(via water)} \end{array} \right.$

TCE @ 20°C

$$H = 0.3$$

$$K_{oc} = 126 \text{ ml/g.}$$

Assume: $\theta_w = 10\%$

$$\text{and } \rho_b = 1.65 \text{ g/cm}^3$$

$$\theta_g = 25\%$$

Contrast low and high organic content soils.

$$f_{oc} = 0.01\% \quad f_{oc} = 1\%$$

f_{oc}	$\frac{\theta_w}{\theta_g} \cdot \frac{1}{H}$	$\frac{\rho_b \cdot K_{oc}}{\theta_g \cdot H}$	R
0.01%	1.33	.27	2.61
1%	1.33	27.7	30.1

∴ As expected, higher f_{oc} has proportionately greater sorption of vapor
a Note vapor sorbed to f_{oc} is sorbed via water.
i.e. gas \rightarrow water \rightarrow solid

DIFFERENTIAL RETARDATION - o Gas movement

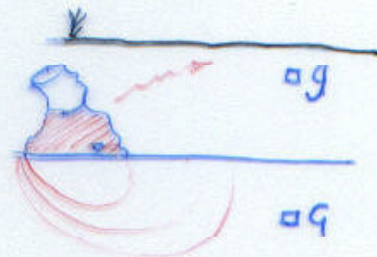
o Aqueous dissolution and movement

Aqueous. Effective velocity, $= \frac{v}{R_a}$

$$R_a = \left[1 + \frac{\rho_b \cdot K_d}{\theta_{w \text{ sat.}}} \right]$$

Gas. Retardation, $R_g = \left[1 + \frac{\theta_w}{\theta_g} \cdot \frac{1}{H} + \frac{\rho_b}{\theta_g} \cdot \frac{K_d}{H} \right]$

Implication of these two different retardation coeffs is that the order of arrival @ a "vadose" monitoring location and a "groundwater" monitoring location may be different.



Dimensionless Henry's coeff.

Table 5-2. Parameters and values used to calculate the relative order of transport velocity for TCA, TCA, and MC and Chapter 5.3.15 (reprinted from ACS, 1992)

Chemical	K_{oc} (ml/g)	K_d (ml/g)	R_a	H	R_g	Relative Order of Movement in Groundwater	Relative Order of Movement in Vapor
1,1,1-Trichloroethane (TCA)	152	2.58	16.9	0.599	55.8	3	2
Trichloroethene (TCE)	126	2.14	14.2	0.379	73.3	2	3
Methylene Chloride (MC)	8.8	0.15	1.93	0.084	34.9	1	1

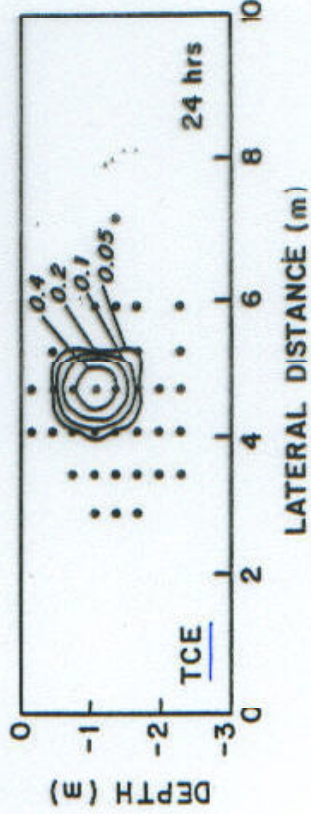
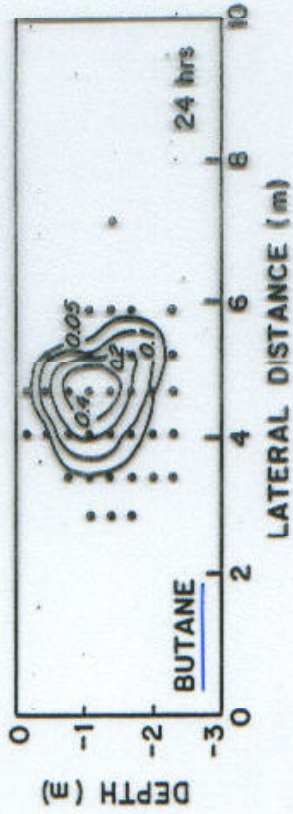
VARIABLE EXPERIMENT (09-1)

Methane
Butane
Trichloroethylene (TCE) } + Nitrogen carrier gas

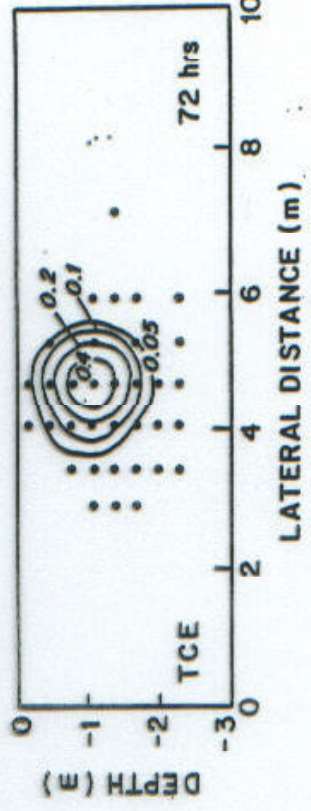
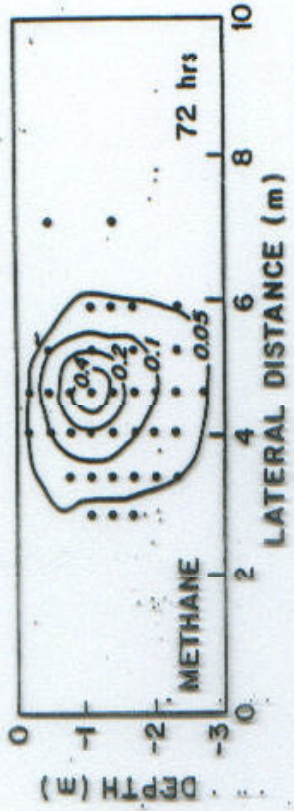


Monitoring @ 60 cm x 25 cm centers.

Residual m/c. & Low fee



[RELATIVE CONCENTRATIONS]



[RELATIVE CONCENTRATIONS]

FOR EXPERIMENTAL RESULTS

Henry's Law Coeffs.

Methane	~ 8
Butane	~ 12
TCF	$\sim .4$

$$\therefore H_{\text{meth}} \approx H_{\text{but}} > H_{\text{TCF}}$$

$$\therefore \text{since } R = 1 + \frac{\rho_w}{\rho_g} \frac{1}{H} + \frac{\rho_b}{\rho_g} \frac{k_d}{H}$$

$$R_{\text{meth}} ; R_{\text{but}} < R_{\text{TCF}}$$

and TCF vapors migrate more slowly.

HENRY'S LAW COMPARISONS

Two forms:

$$H = \frac{C_g}{C_w}$$

$$H' = \frac{P_v}{C_w}$$

Ideal gas law: $P_v = \rho \frac{\bar{R}}{M} T$

\bar{R} = universal gas const

$$= 8.20575 \times 10^{-5} \text{ [(atm} \cdot \text{m}^3)/(\text{mol} \cdot \text{K})]$$

$$T = \text{K} = \text{C} + 273.16 \text{ K}$$

M = mass of 1 mole

is. Atomic wt.
(mass/mole)

Substituting:

$$H' = \frac{P_v}{C_w} = \frac{\rho \bar{R} T}{M C_w}$$

$$H' = \left(\frac{\rho}{M C_w} \right) (\bar{R} T) = H (\bar{R} T)$$

Correspondingly:

$$H = \frac{H'}{(\bar{R} T)}$$

Check form of H :

$$H = \frac{\rho}{M C_w} \quad \text{and} \quad \frac{\rho}{M} = C_g$$

since $\frac{\text{grams}}{\text{m}^3} \cdot \frac{1}{\text{Molec. Wt.}} = \frac{\text{moles}}{\text{m}^3}$

i.e. $\frac{\rho}{M} = C_g !! \therefore \text{ok.}$

Example for TCE @ $20^\circ\text{C} = 293 \text{ K}$

$$H'_{\text{air}}(\text{K}_H) = 9.1 \times 10^{-3} \text{ atm} \cdot \text{m}^3/\text{mol}$$

$$H = \frac{9.1 \times 10^{-3}}{(8.2 \times 10^{-5}) 293} \left[\frac{\text{atm} \cdot \text{m}^3}{\text{mol}} \frac{\text{mol} \cdot \text{K}}{\text{atm} \cdot \text{m}^3 \cdot \text{K}} \frac{1}{\text{K}} \right]$$

$$H \cong 0.38$$

Table 4-6. Vapor concentration and total gas density data for selected DNAPLs at 25°C (from Fatah et al., 1989).

Chemical	Molecular Weight, M g/mole	Vapor Pressure kPa (@25°C)	Saturated Vapor Concentration (kg/m ³)	Total Gas Density kg/m ³
Trichloroethene	131.4	9.9	0.52	1.58
Chloroform	119.4	25.6	1.23	2.11
Tetrachloroethene	165.8	2.5	0.17	1.31
1,1,1-Trichloroethane	133.4	16.5	0.89	1.87
Methylene Chloride	84.9	58.4	2.00	2.50
1,2-Dichloroethene	96.9	43.5	1.70	2.37
1,2-Dichloroethane	99.0	10.9	0.44	1.48
Chlorobenzene	112.6	1.6	0.07	1.23
1,1-Dichloroethane	99.0	30.1	1.20	2.03
Tetrachloromethane	153.8	15.1	0.94	1.93
Air at 1 atm, 25°C	28.6	(101.3)		1.17

25°C

Check Results

TCE: $C_{g,max} = .52 \text{ kg/m}^3 = 520 \text{ mg/l}$

$C_{w,max} @ 20^\circ\text{C} = 1100 \text{ mg/l}$

$H = \frac{520}{1100} \approx 0.47$

This compares with .38 previously since vapor data at 25°C. ∴ different temperature.

CONCENTRATIONS

Vapor Concentrations : C_g

Variety of units :
molar basis \rightarrow mol/m³
weight basis \rightarrow mg/l
volume basis \rightarrow ppmv or %
pressure basis \rightarrow atm., Pa or mmHg.

All are related through ideal gas law $P = \rho \frac{\bar{R}}{M} T$

Aqueous Concentrations : C_w

Related to C_g by Henry's Law. $H = \frac{C_g}{C_w}$

Max C_w will be solubility.

Note that vapor concentration depends on mixture in liquid containing it

Equilibrium concentration : $C_g = X_i \frac{P_v}{RT} = X_i \frac{P_v}{T} \frac{M_i}{\bar{R}}$

gas const \rightarrow RT Universal gas const \rightarrow $\frac{\bar{R}}{M}$

C_g has units of mol/m³
 X_i = mole fraction of compound i in liquid

$R = \frac{\bar{R}}{M}$

Non-equilibrium:

- slow vaporization kinetics
 - dispersed or isolated residual DRAPL
- } same as water!!