Partitioning Between Phases

The Answer

NAPL ←→ Water	Raoult's equation	$\rho_{aq_i} = \gamma_i \rho_{aq_i}^{Pure\_NAPL} x_{NAPL_i}$ **(1)**
NAPL ←→ Soil Gas	Ideal Gas equation	$\rho_{gas_i} = \dfrac{\gamma_i P_{gas_i}^{Pure\_NAPL} x_{NAPL_i} MW_i}{RT}$ **(2)**
Water ←→ Soil Gas	Henry's Equation	$\rho_{gas_i} = K_{HD_i} \rho_{aq_i}$ **(3)**
Water ←→ Sorbed	Instantaneous equilibrium and a constant proportionality	$\omega_{sorbed_i} = f_{oc} K_{oc_i} \rho_{aq_i}$ **(4)**

SEE TABLES PARAMETERS IN CANVAS HANDOUTS

Where:

ρ_{aqi} = Mass per volume water of constituent i … (M/L^3)

γ_i = Activity of constituent i … generally 1 in dilute solutions… (dimensionless)

$\rho_{aq_i}^{Pure\_NAPL}$ = Concentration of a NAPL constituent in water in equilibrium with a pure NAPL … aqueous solubility (e.g. benzene) … (M/L^3)

x_{NAPL_i} = Fraction of a given NAPL in a mixed multiple component NAPL on a molar basis… (dimensionless)

ρ_{gas_i} = Mass per volume gas of constituent i… (M/L^3)

$P_{gas_i}^{Pure\_NAPL}$ = gas pressure above a pure NAPL … (M/LT^2)

$$\frac{kg \cdot \frac{m}{sec^2}}{m^2} = 1\ Pa$$

R = Gas constant (8.31 kg m^2 s^{-2} K^{-1} mol^{-1}) (ML^2/T^2 Kelvin mole)

T= Tempertature (Kelvin)

K_{HD_i} = Dimensionless Henry's constant for constituent i

ω_{sorbed_i} = Mass of constituent i on solids per mass dry solids

f_{oc} = Fraction of organic carbon in soil on a weight basis… (dimensionless)

K_{oc_i} = Partitioning coefficient to organic carbon for compound I (L^3/M)

Building Blocks

http://www.legacy.com/obituaries/deseretnews

Willard Lindsay (1979) Chemical Equilibria in Soils


CHEMICAL EQUILIBRIA IN SOILS

WILLARD L. LINDSAY

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Colorado State University, Fort Collins

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS, New York • Chichester • Brisbane • Toronto

DYNAMIC EQUILIBRIA IN SOILS

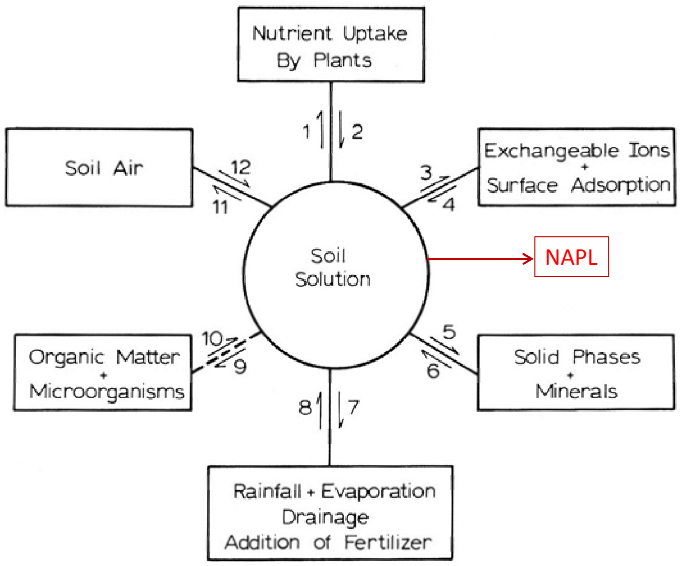
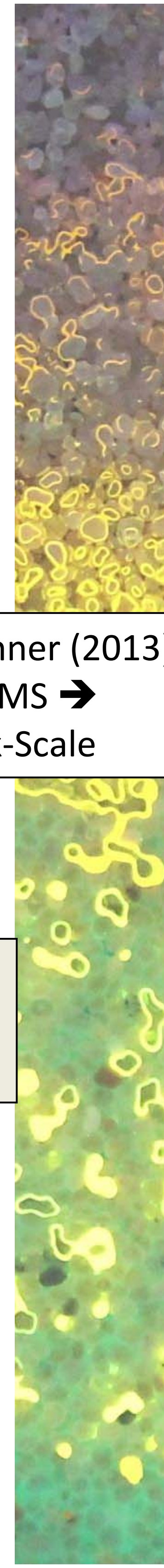


Fig. 1.1 The dynamic equilibria that occur in soils.

Mercer and Cohen 1990
Pore-scale



Anna Skinner (2013)
CSU MS ➔
Tank-Scale

Journal of Contaminant Hydrology, 6 (1990) 107–163
Elsevier Science Publishers B.V., Amsterdam

Review Paper

A REVIEW OF IMMISCIBLE FLUIDS IN THE SUBSURFACE: PROPERTIES, MODELS, CHARACTERIZATION AND REMEDIATION

JAMES W. MERCER and ROBERT M. COHEN
GeoTrans, Inc., Herndon, VA 22070 (U.S.A.)

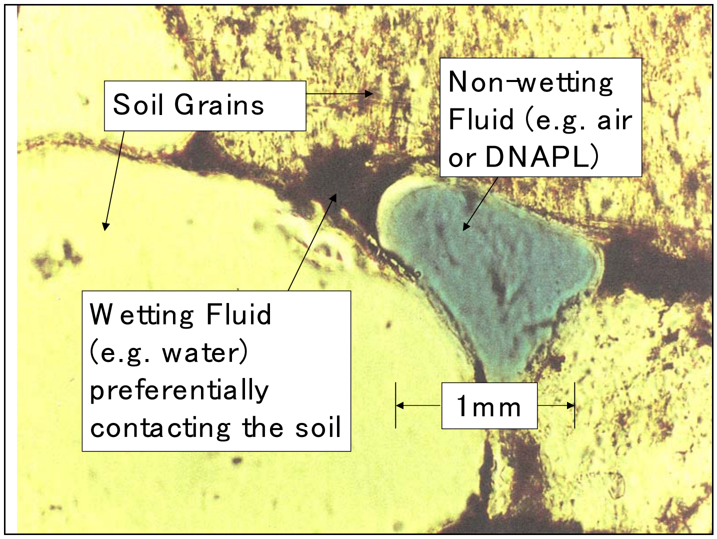
(Received February 5, 1990; revised and accepted May 8,

Posted to Handouts … good list of physical properties

ABSTRACT

Mercer, J.W. and Cohen, R.M., 1990. A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation. *J. Contam. Hydrol.*, 6: 107–163.

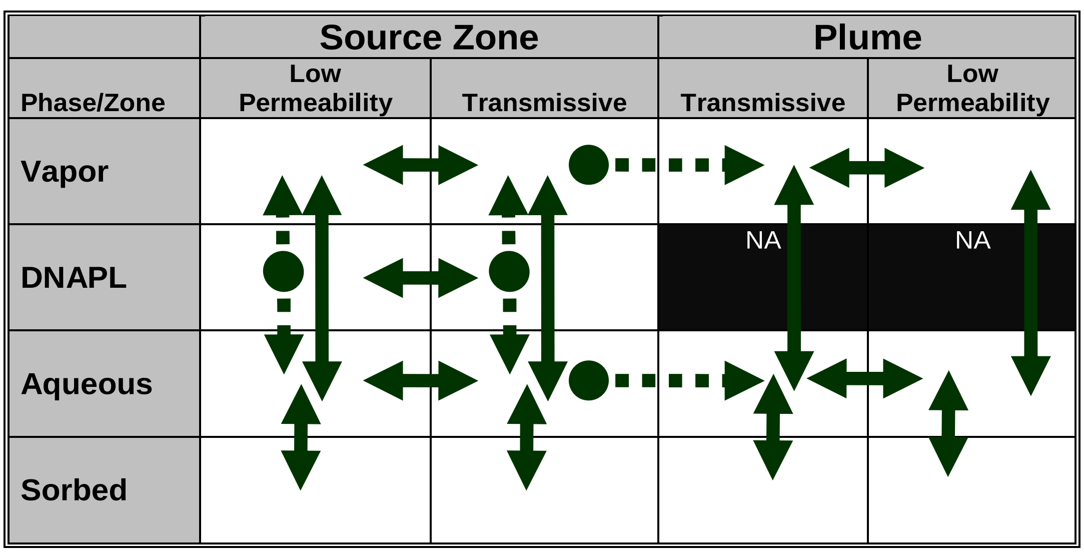
In the past few years, as hazardous waste sites have been studied more often and in more detail, immiscible fluids have been encountered in the subsurface with greater frequency. These nonaqueous phase liquids (NAPL's) behave differently than dissolved solutes in the subsurface. This behavior depends on fluid properties such as interfacial tension, viscosity and density. In addition, mass transfer produces vapor transport in the vadose zone and solute transport in groundwater. Mass transfer depends on properties associated with volatilization and aqueous solubility. As a consequence, characterization techniques as well as remediation efforts must be modified at sites where NAPL's are present. Although considerable research is necessary before NAPL problems are well understood, sufficient work has been performed to permit a review of NAPL properties and behavior in the subsurface.



Immiscible fluids in the pore space of a granular porous media
(after Wilson et al., 1990 - + Labels per Sale 2001 API 4711)

Sale and Newell (2012)
Macro-Scale

Table 1 – 14 subsurface compartments potentially containing chlorinated solvents. Arrows show mass potential transfer links between compartments. Dashed arrows indicate irreversible fluxes.



Derivation Follows D.B. McWhorter AG638 1994

NAPL ←→ Water

Raoult's equation (1882) for vapor pressure above a liquid at equilibrium

$$P_{gas\_Total} = \sum_{i=1}^{n} P_{gas_i}^{Pure\_liquid} x_{liquid_i}$$

or

$$P_{gas\_partial_i} = P_{gas_i}^{Pure\_liquid} x_{liquid_i}$$

P = Pressure in gas

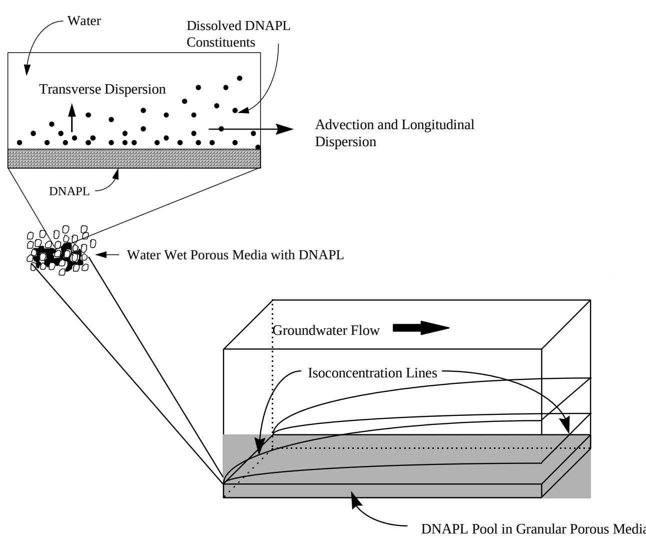
x_i = mole fraction of x in liquid

Analogously… put water in place of the gas assume …typically assume activity coefficient γ is 1

$$\rho_{aq_i} = \gamma_i \rho_{aq_i}^{Pure\_NAPL} x_{NAPL_i} \quad (1)$$

ρ = mass /volume

An example



NAPL ←→ Soil Gas

Ideal Gas Equation (Law) $PV = nRT$

First stated by Émile Clapeyron in 1834

(Assumes $R = \dfrac{PV}{nT}$ constant for all gases)

$$\rho_{gas_i} = \frac{n_i MW_i}{V_i} \text{ therefore } \rightarrow n_i = \frac{\rho_{gas_i} V_{gas_i}}{MW_i}$$

Substituting the definition of n into $PV = nRT$ and solving for ρ_{gas_i}

$$P_{gas_i} V_{gas_i} = \frac{\rho_{gas_i} V_{gas_i}}{MW_i} RT \rightarrow \rho_{gas_i} = \frac{P_{gas_i} MW_i}{RT}$$

Recall $P_{gas_i} = P_{gas_i}^{Pure\_NAPL} x_{NAPL_i} \gamma_{NAPL_i}$ by substitution

$$\boxed{\rho_{gas_i} = \frac{P_{gas_i}^{Pure\_NAPL} x_{NAPL_i} \gamma_{NAPL_i} MW_i}{RT}} \quad (2)$$

Water ←→ Soil Gas

Henry's Equation (Law - 1803) $K_H = \dfrac{P_{gas_i}}{[C_{aq_i}]}$

Recall $\left[C_{aq_i}\right] = \dfrac{\rho_{aq_i}}{MW_i}$ and

$$\rho_{gas_i} = \frac{P_{gas_i} MW_i}{RT} \quad \rightarrow \quad P_{gas_i} = \frac{\rho_{gas_i} RT}{MW_i}$$

By substitution

$$K_H = \frac{\dfrac{\rho_{gas_i} RT}{MW_i}}{\dfrac{\rho_{aq_i}}{MW_i}} \quad \text{or} \quad \frac{K_H}{RT} = \frac{\rho_{gas_i}}{\rho_{aq_i}}$$

Defining a dimensionless Henry's coefficient

$$K_{HD} = \frac{K_H}{RT} \quad \ldots \qquad \rho_{gas_i} = K_{HD}\,\rho_{aq_i} \quad (3)$$

Water ←→ Sorbed

Assume a linear-instantaneous-equilibrium between the aqueous mass density and sorbed mass per unit dry weight soils (ω_{sorbed_i})

$$K_d = \frac{\omega_{sorbed_i}}{\rho_{aq_i}} \quad \ldots\ldots \; K_d \text{ units of volume/mass}$$

Note K_d can be estimated as the product of the fraction of organic carbon f_{oc} and organic carbon - water partitioning coefficients K_{oc}

$$K_d = f_{oc} K_{oc}$$

By substitution $$\omega_{sorbed_i} = f_{oc} K_{oc} \rho_{aq_i} \quad (4)$$

Examples

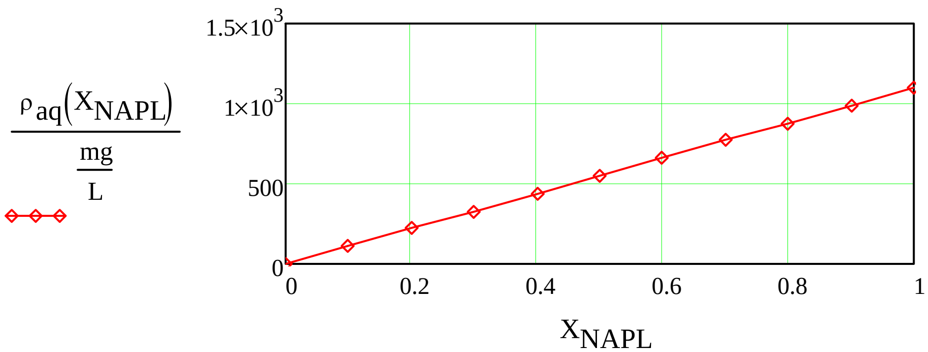
(1) NAPL←→Water

Inputs

$\rho_{Pureaq} := 1100 \cdot \frac{mg}{L}$ $\quad X_{NAPL} := 0, .1 .. 1$ $\quad \gamma := 1$

Solutions

$\rho_{aq}(X_{NAPL}) := \gamma \cdot \rho_{Pureaq} \cdot X_{NAPL}$ $\quad \rho_{aq}(0.1) = 110 \frac{mg}{L}$



Trichlorethene (TCE)

(2) NAPL ←→ Soil Gas

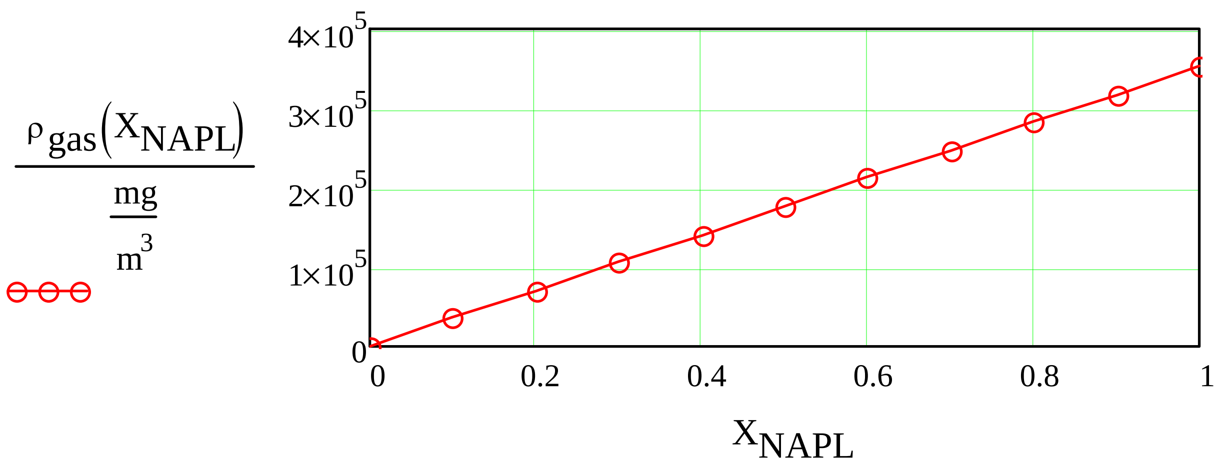
Inputs

$X_{NAPL} := 0, .1 .. 1$ $\quad P_{gaspure} := 50 \cdot torr$ $\quad MW := (2 \cdot 12 + 3 \cdot 35 + 1) \cdot \frac{gm}{mole}$

$R := 8.314 \cdot \frac{J}{mole K}$ $\quad T := (21.7 + 273) \cdot K$

Solutions

$\rho_{gas}(X_{NAPL}) := \frac{P_{gaspure} \cdot X_{NAPL} \cdot \gamma \cdot MW}{R \cdot T}$ $\quad \rho_{gas}(0.5) = 1.768 \times 10^{5} \frac{mg}{m^3}$



(3) Water ←→ Soil Gas

Inputs

$i := 1 .. 7$

$\rho_{aq_i} :=$

$0.001 \cdot \frac{mg}{L}$
$0.01 \cdot \frac{mg}{L}$
$0.1 \cdot \frac{mg}{L}$
$1 \cdot \frac{mg}{L}$
$10 \cdot \frac{mg}{L}$
$100 \cdot \frac{mg}{L}$
$1000 \cdot \frac{mg}{L}$

$$R := 8.314 \cdot \frac{J}{mole \cdot K}$$

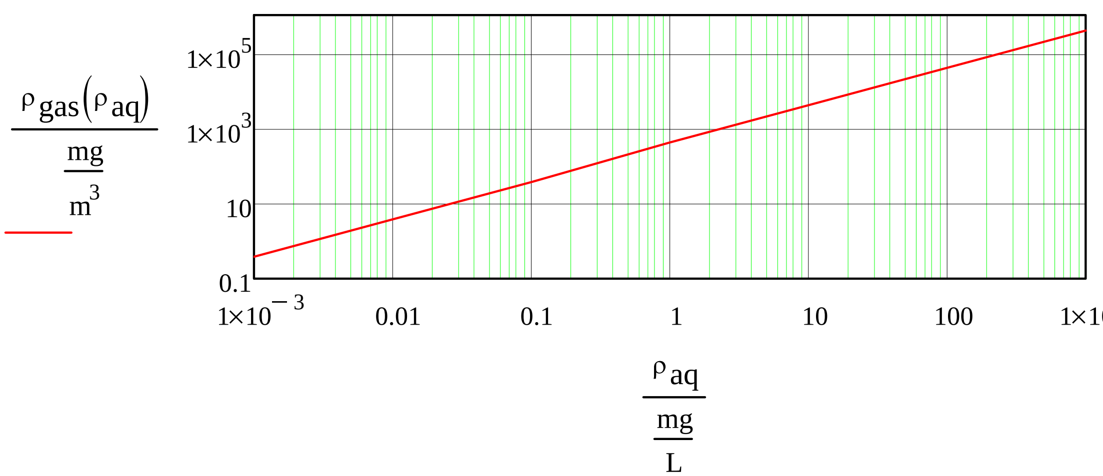
$$T := (21.7 + 273) \cdot K$$

$$K_H := 0.00937 \cdot \frac{atm \cdot m^3}{mole}$$

$$K_{HD} := \frac{K_H}{R \cdot T} = 0.387$$

Solutions

$$\rho_{gas}(\rho_{aq}) := K_{HD} \cdot \rho_{aq} \qquad \rho_{gas}\left(0.01 \cdot \frac{mg}{L}\right) = 3.875 \frac{mg}{m^3}$$



(4) Water ⇐⇒ Sorbed

Inputs $j := 1..7$ $K_{oc} := 126 \cdot \frac{mL}{gm}$

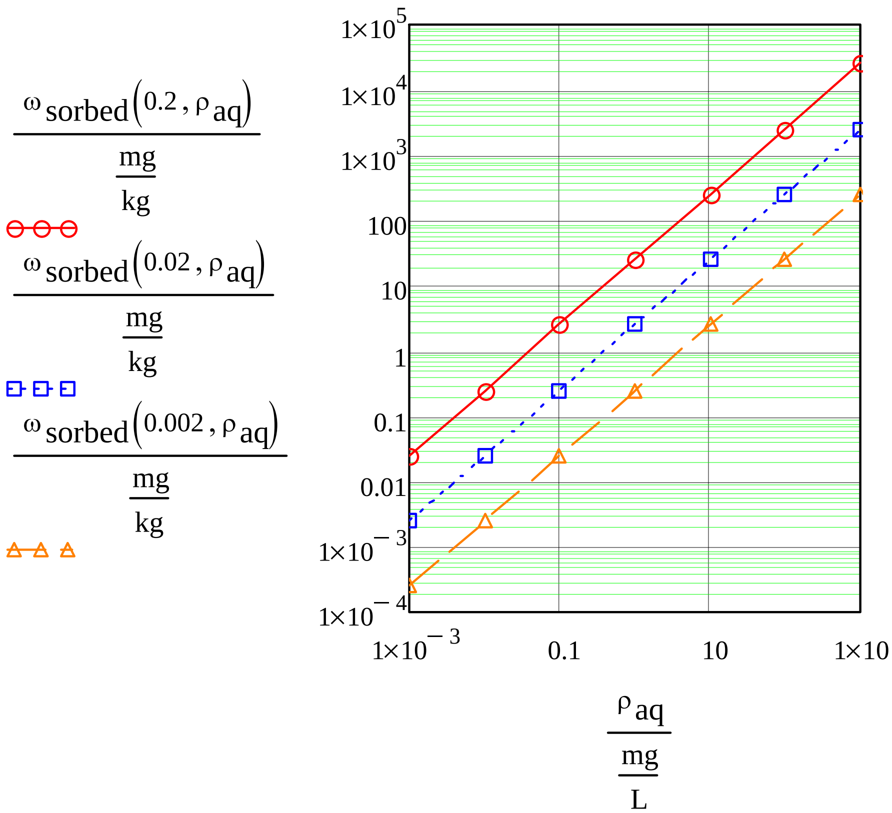
$\rho_{aq_j} :=$

$0.001 \cdot \frac{mg}{L}$
$0.01 \cdot \frac{mg}{L}$
$0.1 \cdot \frac{mg}{L}$
$1 \cdot \frac{mg}{L}$
$10 \cdot \frac{mg}{L}$
$100 \cdot \frac{mg}{L}$
$1000 \cdot \frac{mg}{L}$

Solutions

$$\omega_{sorbed}(f_{oc}, \rho_{aq}) := f_{oc} \cdot K_{oc} \cdot \rho_{aq}$$

$$\omega_{sorbed}\left(0.01, 100 \cdot \frac{mg}{L}\right) = 126 \frac{mg}{kg}$$



NEXT – Add up all of the pieces to get to a total