3.7 BEHAVIOR OF LNAPLS

3.7.1 Migration of LNAPLS

Surface spill: 1. Penetrate vadose zone under gravity with influence of capillary forces.

Vadose zone water wet.

NAPL is non-wetting.

Capillary Fringe: Holds water as continuous phase with residual air saturation

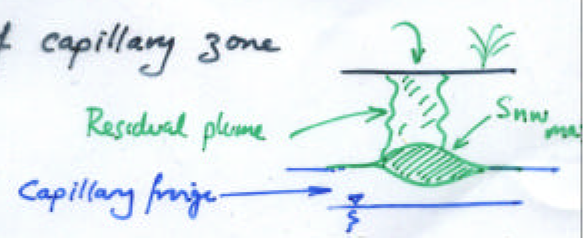
$h_c \uparrow$ with $\downarrow$ grain size $\rightarrow \downarrow$ pore size

$$\left\{ \text{i.e. } h_c = \frac{4\sigma}{d\gamma} \right\}$$

Example usual capillary rise

	Grain size (mm)	Rise (cm)
Fine gravel	2-5	2.5
Medium sand	0.2-0.5	24.6
Fine silt	0.02-0.05	200+

LNAPL will penetrate down to top of capillary zone (if enough volume)



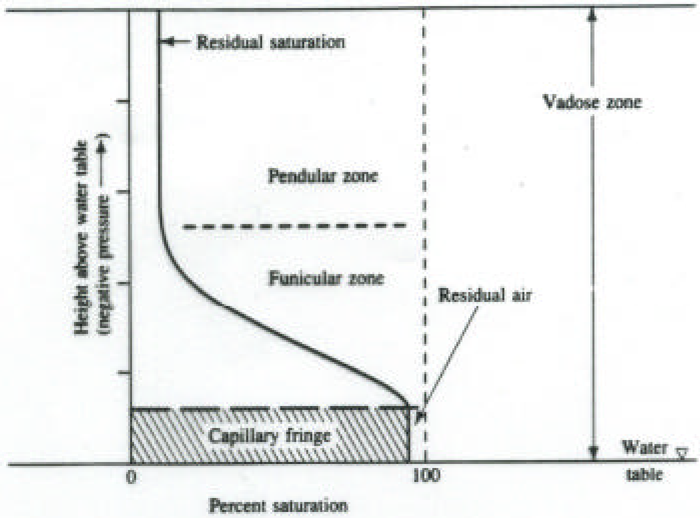


FIGURE 5.13 Vertical distribution of water in the vadose zone in the absence of nonaqueous phase liquids. Source: A. S. Abdul, *Ground Water Monitoring Review* 8, no. 4 (1988):73–81. Copyright © 1988 Water Well Journal Publishing Co.

TABLE 5.1 Visual capillary rise in unconsolidated materials (porosity of all samples is about 41%).

Material	Grain Size (mm)	Capillary Rise (cm)
Fine gravel	2–5	2.5
Very coarse sand	1–2	6.5
Coarse sand	0.5–1	13.5
Medium sand	0.2–0.5	24.6
Fine sand	0.1–0.2	42.8
Silt	0.05–0.1	105.5
Fine silt	0.02–0.05	200 +

Source: Lohman (1972).

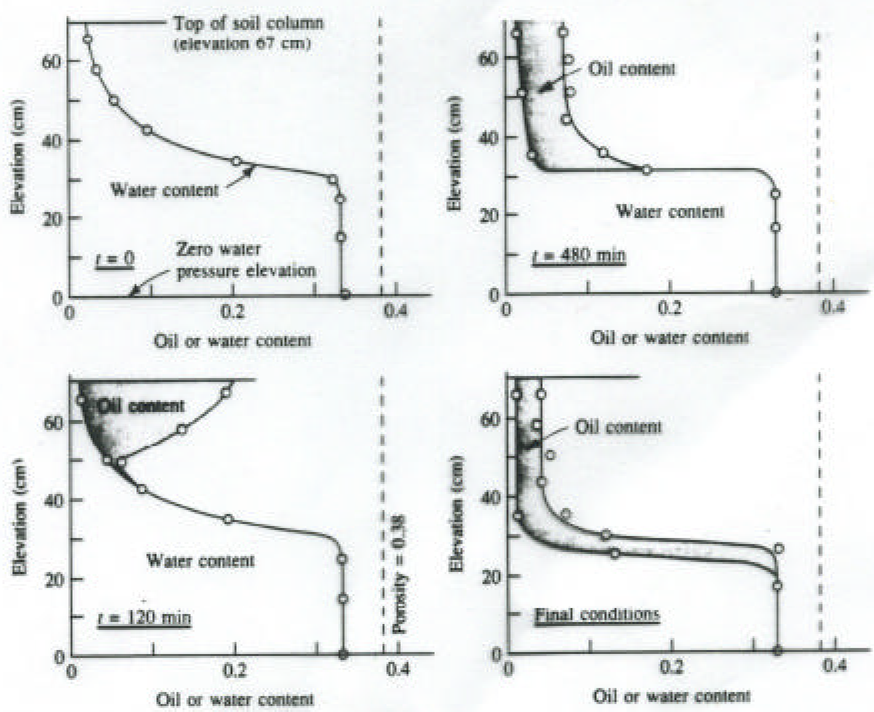
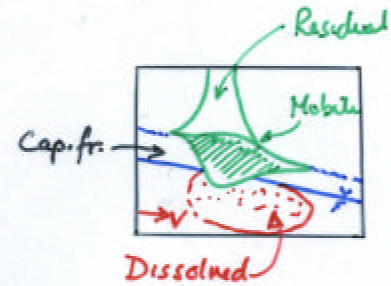


FIGURE 5.14 Changes in the vertical distribution of oil with time after a slug of oil is added to the top of a column of sand. Oil content and water content are expressed as a fraction of the total volume of the porous media. Source: D. K. Eckberg and D. K. Sunada, *Water Resources Research* 20, no. 12 (1984):1891–97. Copyright by the American Geophysical Union.

DEVELOPMENT OF AN OIL TABLE (Abdul, 1988)

Add oil incrementally to a) → b) develop oil fringe
b) → c) develop oil table
c) → d) remove capillary fringe and create oil table.

Mobile oil product may migrate "free" product



3 Components

- Residual column
  - What is saturation? – Since free phase moved through zone, residual saturation must be greater than irreducible.
  - Re-mobilized as rain fall from surface ⇣
    Partitioning → 1. Vapor phase → volatilization.
    2. Dissolves in aqueous phase.
- "Free" product – May mobilize with rising/falling water table. May flow down steep water table

- Dissolution into groundwater
  Gasoline → Benzene, Toluene, Ethylbenzene & Xylene (BTEX) soluble fractions.
  Degree of partitioning depends on volatility of fractions

Which fractions will partition in → air, → water } Henry's Law

What is partitioning rate?

→ Transport processes (aqueous/gaseous).

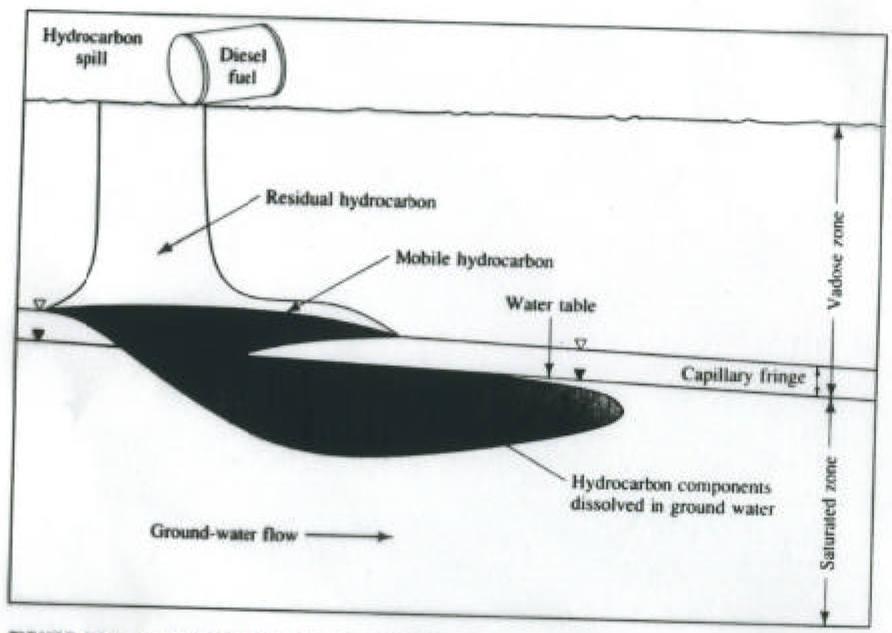


FIGURE 5.16 Subsurface distribution of an LNAPL spill.

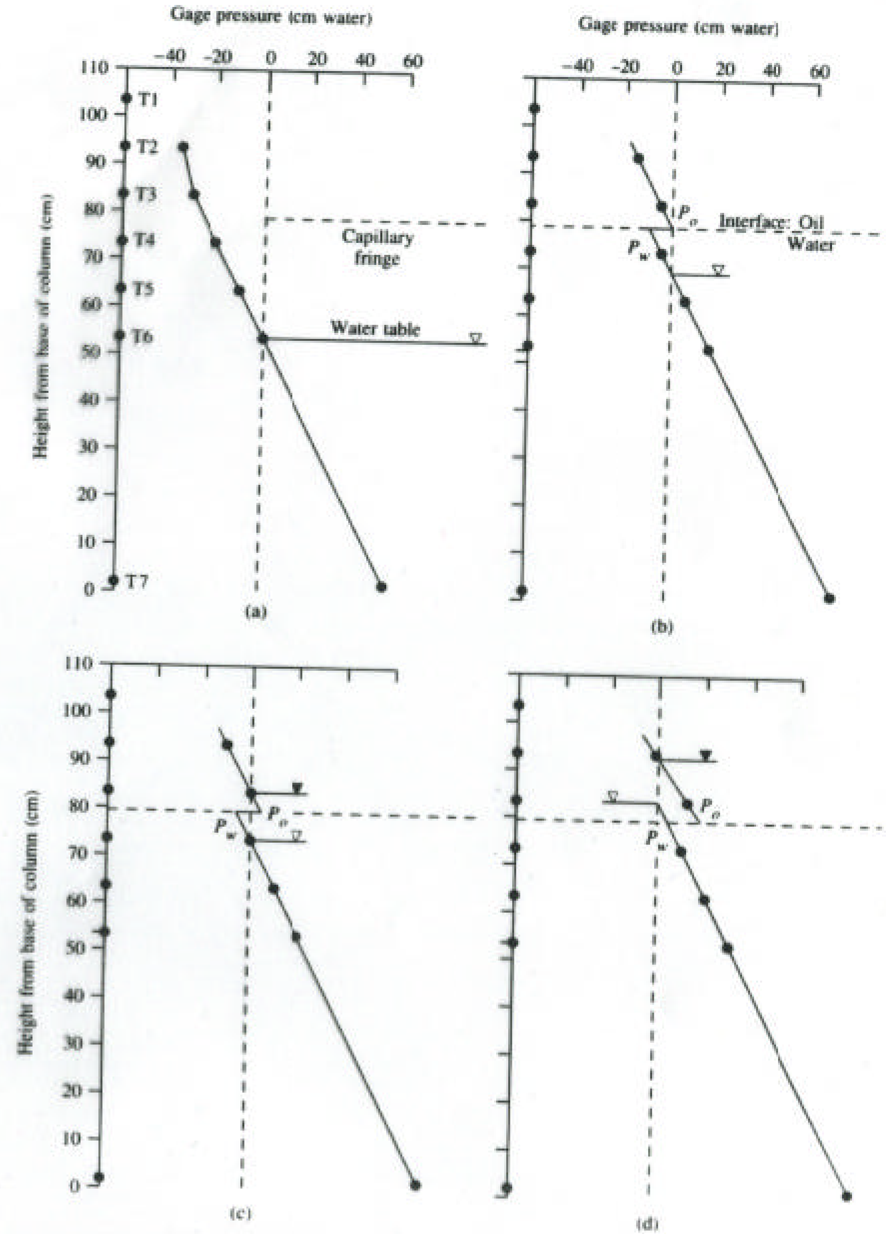


FIGURE 5.15 Hydrostatic pressure head/tension distribution in a sand column to which oil is being added to the top of the column. (a) Before the addition of the oil, (b) after addition of the oil showing the development of an oil fringe, (c) after addition of sufficient oil for an oil table to form, and (d) after sufficient mobile oil has accumulated to eliminate the water capillary fringe. Source: A. S. Abdul, *Ground Water Monitoring Review* 8, no. 4 (1988):73–81. Copyright © 1988 Water Well Journal Publishing Co. Used with permission.

Henry's Law

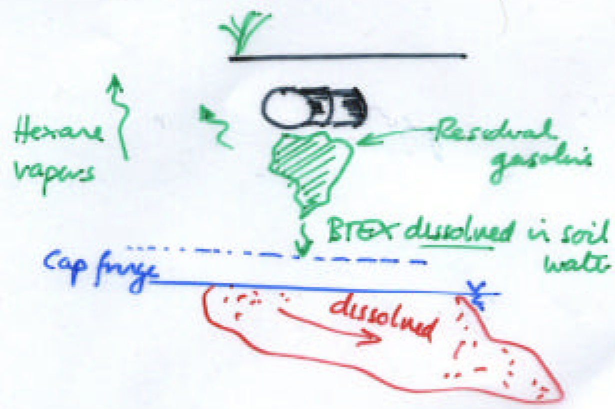
Linear relationship between vapor pressure of a solute and its aqueous solution and the concentration of the solution.

Proportionality coefficient ≡ Henry's Law constant.

Also applicable to partitioning in air.

Low water-air partition coefficients (alkanes) -> favor vapor phase
High water-air " " (benzene) -> favor aqueous phase

Different time of release for different materials:



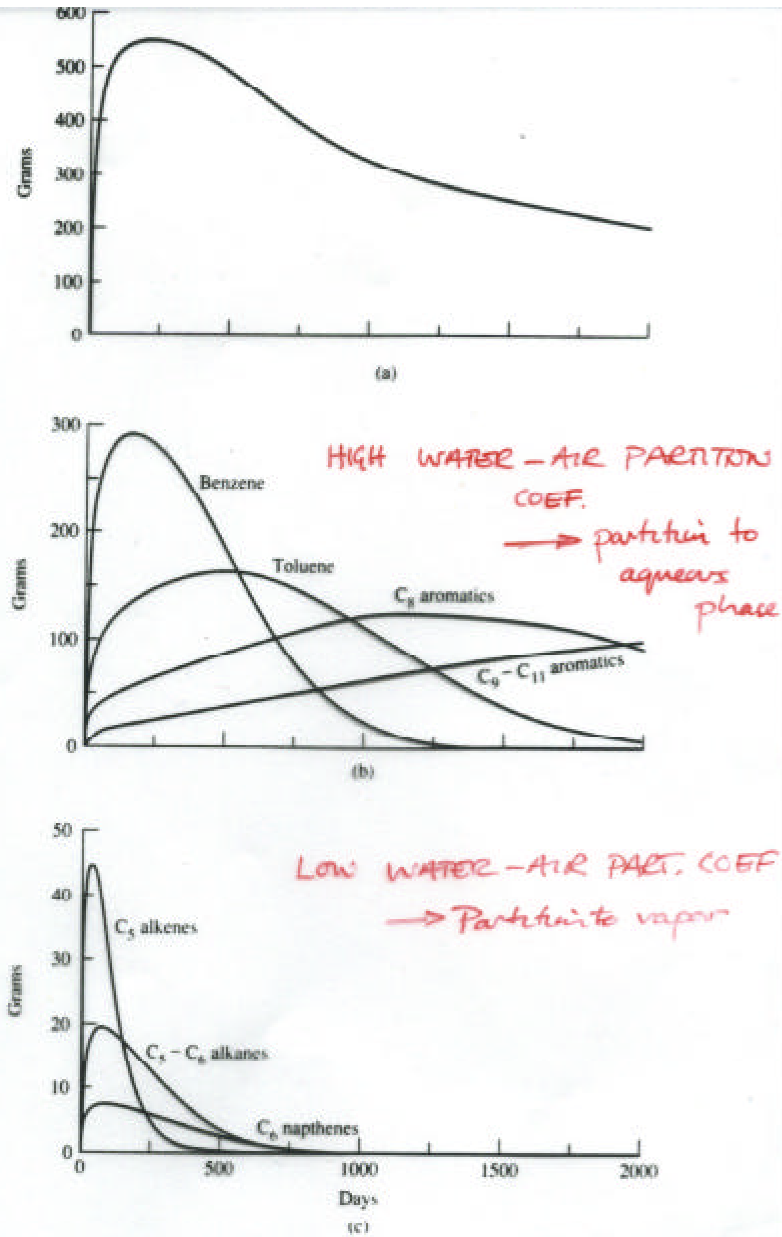


FIGURE 5.17 Mass of residual hydrocarbon in vadose zone partitioning into capillary water as a function of time, with (a) total hydrocarbons, (b) aromatic constituents, and (c) nonaromatic constituents. *Source:* A. L. Baehr, *Water Resources Research* 23, no. 10 (1987): 1926–38. Copyright by the American Geophysical Union.

TABLE 5.2 Water-air partition coefficients for selected organic compounds.

Compound	Formula	Molecular Weight	Water-Air Partition Coefficient
Aromatics			
Benzene	C_6H_6	78	5.88
Toluene	C_7H_8	92	3.85
o-Xylene	C_8H_{10}	106	4.68
Ethylbenzene	C_8H_{10}	106	3.80
Nonaromatics			
Cyclohexane	C_6H_{12}	84	0.15
1-Hexene	C_6H_{12}	84	0.067
n-Hexane	C_6H_{14}	86	0.015
n-Octane	C_8H_{18}	114	0.0079

Source: A. L. Baehr. *Water Resources Research* 23, no. 10:1928. Published 1987 by American Geophysical Union. Used with permission.