

Note that the relative permeability goes to zero well before the saturation goes to zero. This is a reflection of the second consequence of partial saturation. Any liquid will tend to wet the media to some degree. These surface tension forces cause some of the liquid to be retained and a *residual saturation* of that liquid is observed. The suction of the surface tension forces cause the liquid in the unsaturated zone to have a negative pressure head, $h_p < 0$. Thus, $h_p > 0$ below the water table and in Artesian aquifers, $h_p = 0$ at the water table (relative to atmospheric pressure) and $h_p < 0$ above the water table. The negative pressures above the water table give rise to capillary rise and the presence of a *capillary fringe* above the water table.

To understand the causes of the negative pressures in the liquid that wet a porous medium, consider an isolated water droplet in air. Surface tension is an indicator of the amount of work required to change the surface area of the bubble. Consider the force that must be applied across the surface of the bubble to change its radius from r to $r + dr$ and area from $4\pi r^2$ to $4\pi(r + dr)^2$ if the bubble surface tension is σ is given by

$$\text{Work} = \text{Force} \cdot \text{distance} = F dr = \sigma[4\pi(r + dr)^2 - 4\pi r^2]$$

$$F = \frac{\sigma}{dr} 4\pi(r^2 + 2r dr + dr^2 - r^2) \quad (8.39)$$

$$F \approx 8\pi r \sigma$$

At equilibrium this must be balanced by a difference in pressures (forces per unit area) across the surface of the bubble.

$$\sum F = 0$$

$$4\pi r^2 P_m = 4\pi r^2 P_{out} + 8\pi r \sigma \quad (8.40)$$

$$P_m - P_{out} = \frac{2\sigma}{r}$$

This means that the inside pressure of the curved surface is always greater than the pressure on the outside of the curved surface. If we consider the water wetting the sides of an individual capillary, as in Figure 8.6, the air in the region above the interface is *inside* the curved surface and Equation 8.40 suggests that the pressure in the air phase is greater than the pressure in the water. Because the air pressure is atmospheric this means that the pressure in the water is below atmospheric or a negative gage pressure.

Let us evaluate this phenomenon as it applies to capillary rise. To do so, we must consider the point of contact between the liquid and a solid. The effect of interfacial tensions is to minimize surface area. The forces per unit width of surface are as shown in Figure 8.7 where σ_{gs} is the interfacial tension at the gas-solid interface, σ_{sl} is the interfacial tension at the solid-liquid interface, and σ_{lg} is the interfacial tension at the gas-liquid interface. The angle that the water makes with the solid surface is termed the *contact angle*, θ_c . The component of the gas-liquid interfacial tension that is along the solid surface is then $\sigma_{lg} \cos \theta_c$ and a balance of forces gives

$$\sigma_{gs} = \sigma_{sl} + \sigma_{lg} \cos \theta_c \quad (8.41)$$

or

$$\cos \theta_c = \frac{\sigma_{gs} - \sigma_{sl}}{\sigma_{lg}}$$

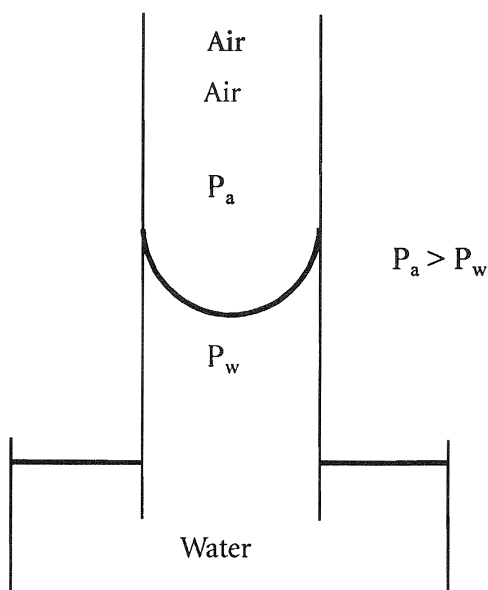


FIGURE 8.6 Capillary rise and pressure in a single capillary. Note that the diameter of the capillary is greatly expanded relative to the water in the bottom tray for purposes of illustration.

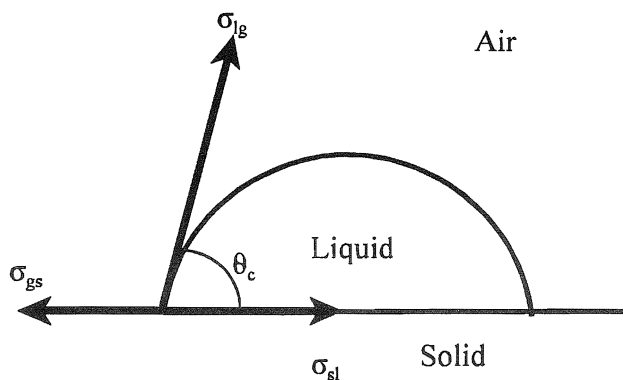


FIGURE 8.7 Contact angle and equilibrium forces acting on a droplet on a solid.

If the water completely wets the surface, the contact angle is 0° and the radius of curvature of the water interface is identical to the capillary radius. In the capillary of Figure 8.6, the water is then at a negative pressure (relative to the atmospheric pressure air) of

$$P_w - P_a = -\frac{2\sigma}{r} \tag{8.42}$$

This suction is available to pull water up the capillary against the force of gravity. At equilibrium, the capillary rise, h_c , is

$$h_c = \frac{2\sigma}{(\rho_w - \rho_a)gr} \tag{8.43}$$

If the contact angle is other than 0° , σ in Equations 8.42 and 8.43 must be replaced by $\sigma \cos\theta_c$. If the contact angle is 90° , there is no capillary rise and if the contact angle were 180° , the liquid would be completely non-wetting and there would be a capillary depression rather than a rise. The liquid phases of interest in soil, however, water and oil or other organic liquids, all tend to wet the

surface to some degree. In soils, water tends to be more wetting than an oil or organic phase which, in turn, tends to be more wetting than an air phase.

Equation 8.42 can be generalized to deal with the interface between any wetting (e.g., water) and non-wetting fluid (e.g., oil or air).

$$P_w - P_{nw} = -\frac{2\sigma}{r} \quad (8.44)$$

where σ now represents the interfacial tension between the wetting and non-wetting phase. Note that the pressure difference across the interface, and therefore the capillary suction that gives rise to retention of the wetting liquid and capillary rise, is proportional to the inverse of the capillary radius. That is, the smaller the radius of the capillary, or the smaller the pore space, the greater the curvature and pressure difference across the interface. This causes the more wetting fluid to tend to fill the finer capillaries of a soil and be retained there at greater saturations after drainage. Thus, in the unsaturated zone, water tends to be trapped in the finest capillaries, an organic phase, if present, tends to be in the next largest capillaries, and air is left to the remainder of the pore space. If the soil contains a fine-grained lens, the residual saturations of the liquid phases will tend to be greatest in this zone.

Similarly, if an organic phase is found beneath the water table a pressure difference will occur at the interface between the two liquids depending on the size of the capillaries where they come in contact. Water will again tend to be held in the finest pore spaces since it is the more wetting fluid. An organic phase will tend to be excluded from the fine pore spaces because the pressure difference tends to resist displacement of the water and will, instead be found preferentially in coarser media and pore spaces. After an oil spill to the surface, an organic phase will tend to collect in the finer grained soil regions in the unsaturated zone because it is typically more wetting than air and in the coarser regions in the saturated zone because it is less wetting than water.

As with permeability, the distribution of pore sizes complicates the situation. The capillary rise associated with a uniform pore size is like that shown in Figure 8.8a while in a broad distribution of pore sizes the capillary rise looks more like that in Figure 8.8b. In fine pores, the water rises to a great height while in more coarse pores the capillary rise is less. The capillary rise, of course, is directly related to the magnitude of the negative pressure which is, in turn, inversely related to the size of the pores in the media. The negative pressure where air first begins to enter the media and saturation drops below 100% is called the air entry pressure head, h_a . The height of the bulk of the capillary fringe in a soil is thus characterized by the height associated equivalent to the air entry pressure head.

For a given soil, there is a relationship between the capillary suction pressure head and the water content as shown in Figure 8.9. The relative permeability is a function of fluid saturation and therefore also a function of capillary pressure. As indicated earlier, a residual water exists (or other liquid content) below which it is not possible to reduce the saturation by hydraulic forces. In Figure 8.9 these are indicated by the saturations which remain even at very large negative pressures or when the conductivity is effectively zero. In summary, the effect of pore size distribution and capillary effects is that the water saturation, ϕ_w , and hydraulic conductivity, K_p , take on the following functional forms.

$$\begin{aligned} \phi_w &= \phi_w(h_p) & h_p < h_a \\ \phi_w &\approx 1 & h_p \geq h_a \\ k_{eff} &= \kappa_r(h_p)k_p & h_p < h_a \\ k_{eff} &\approx k_p & h_p \geq h_a \end{aligned} \quad (8.45)$$

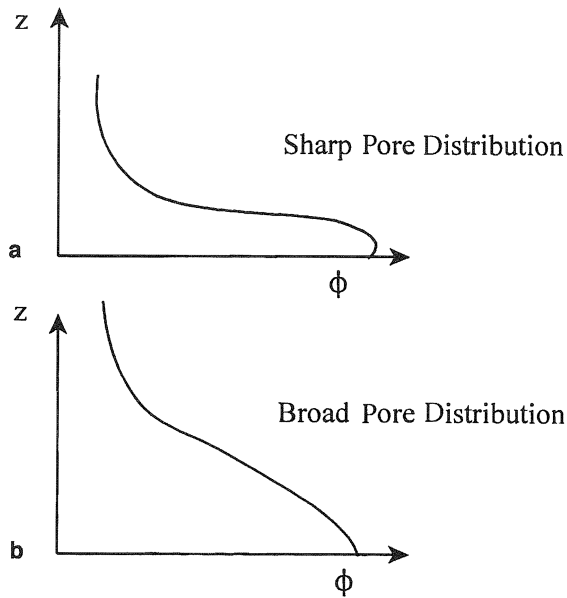


FIGURE 8.8 Capillary head vs. height (coarse and fine soil).

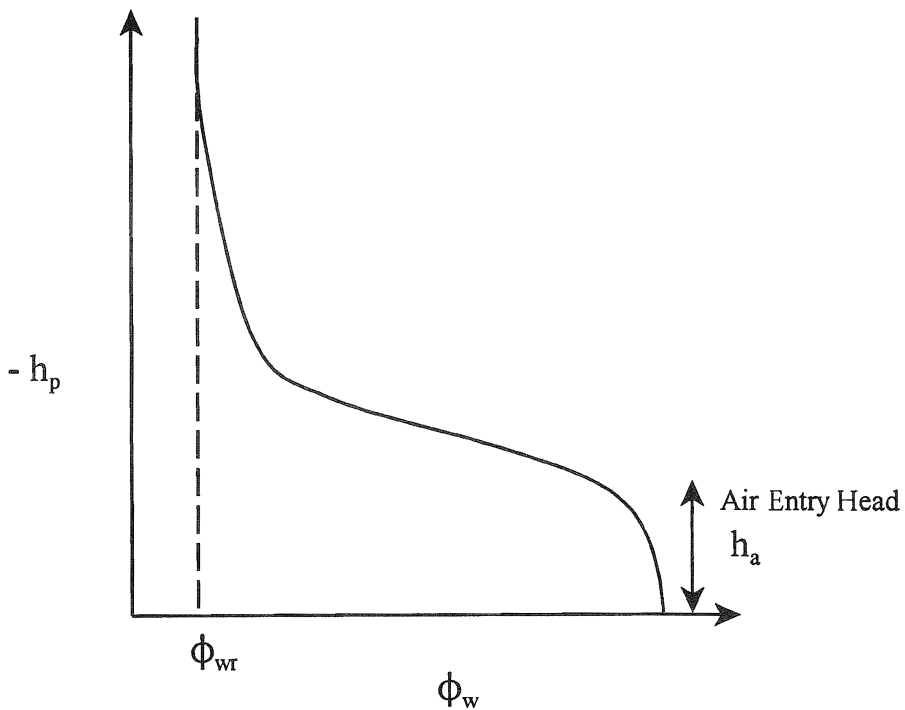


FIGURE 8.9 Capillary pressure as a function of saturation indicating air entry head or displacement pressure.

It is now possible to understand the behavior of water infiltrating after a rainfall. Immediately after a rainfall the upper soil layers are saturated. In a relatively short time the water-filled pores will drain to the soil's field capacity. The combination of low relative permeability and the high capillary suction at low moisture contents limits any further water drainage. Vegetation and evaporation, however, will continue to remove water from the system. Vegetation can continue to

remove water until the content approaches the *wilting point*, at which point the water is held so tightly by the soil that it is not possible for vegetation to absorb this water. At the wilting point, the negative pressures exhibited by the water phase cannot be overcome by the suction associated with the uptake by the root systems of vegetation. Because plants can provide suctions of 15 atm, the wilting point represents residual water held very tightly by the soil. Even at these moisture contents water tends to wet the surface of most soil particles and this surface will remain covered with water. Typically, the moisture content must be reduced below 1 to 3% before dry soil surface is exposed. Values of field capacity and wilting point for various types of soils can be found in Table 8.2.

TABLE 8.2
Typical Values of Unsaturated Zone Parameters

Soil	Porosity (ϵ)	Field Capacity (ϵ_w)	Wilting Point (ϵ_w)	h_a (cm of H ₂ O)	k_p (cm/min)
Sand	0.35–0.45	0.1–0.15	0.05	10	1
Sandy loam	0.38–0.45	0.12–0.15	0.07–0.08	20	0.2
Loam	0.40–0.45	0.15–0.25	0.1	50	0.04
Silty loam	0.42–0.48	0.22–0.30	0.1–0.12	80	0.01
Clay loam	0.45–0.50	0.25–0.35	0.15	60	0.015
Clay	0.48–0.52	0.25–0.35	0.20	40	0.008

Note: Porosity, field capacity, and wilting point shown in volume voids or water per total volume. (Adapted from Clapp, R.B. and G.M. Hornberger (1978) *Water Resour. Res.*, 14 (4): 601–604, and Dunne, T. and L.B. Leopold (1978) *Water in Environmental Planning*, W.H. Freeman and Co., New York.)

8.3 CONTAMINANT TRANSPORT IN SOILS

We are now in a position to evaluate contaminant transport in soils. Let us consider the contamination of a soil by a spill or leak of an organic or oily phase to the surface of the soil. In recognition that this phase is only sparingly soluble in water and remains as a separate phase, it is often referred to as a nonaqueous phase liquid (NAPL). A separate NAPL is sometimes separated into a dense NAPL (DNAPL) if its density is greater than that of water and a lighter than water NAPL (LNAPL). Most chlorinated organics exhibit densities greater than one and are, therefore, DNAPLs in soil while almost all hydrocarbon mixtures such as gasoline, kerosene, most oils, and diesel exhibit a density less than that of water and are LNAPLs.

After a spill or leak of a NAPL, there are four zones of contamination with very different behavior governed by the principles discussed in the preceding section. These include:

1. Bulk NAPL contaminating vadose zone.
2. Vapor phase contaminant from NAPL contaminating vadose zone.
3. Bulk NAPL contaminating initially water-saturated zone.
4. Dissolved phase contaminant from NAPL contaminating aquifer.

The development of these four zones is depicted in Figure 8.10 as a result of a spill or leak of a nonaqueous phase liquid to the surface. Initially the NAPL moves through the unsaturated zone, driven by gravity and capillary forces. Because there is normally always water present in the soil, the finest pore spaces tend to be unavailable to the NAPL. The NAPL is more wetting than the air

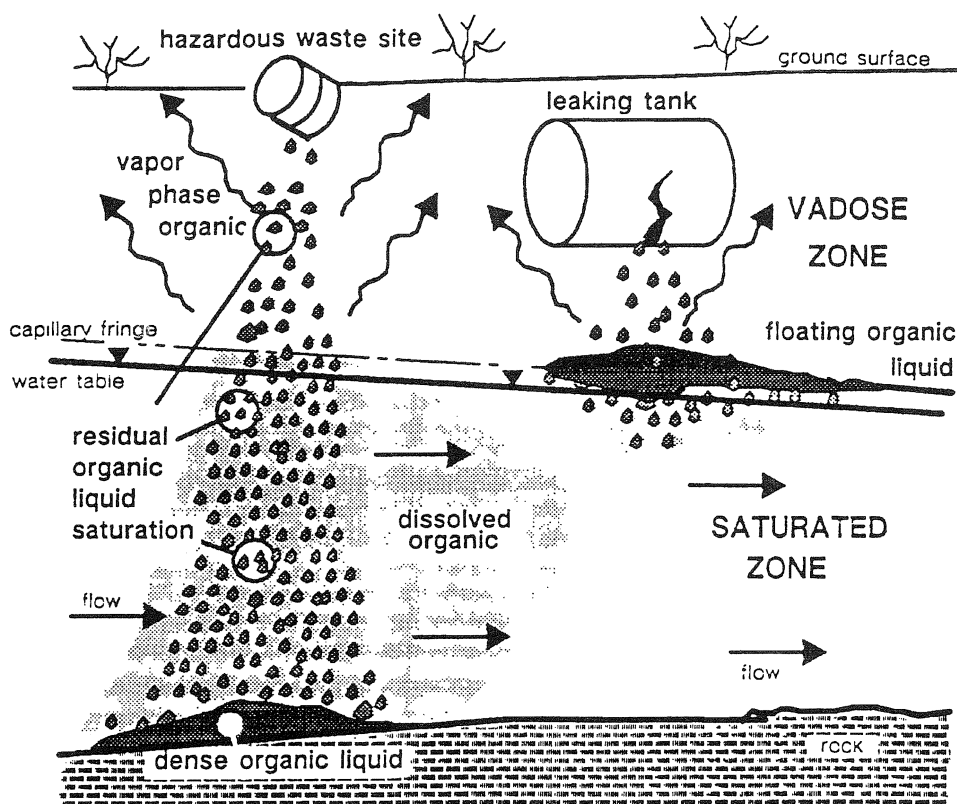


FIGURE 8.10 Migration pattern for an organic liquid more dense than water (left), and less dense than water (right). (From Wilson, J.L., et al. (1990) Laboratory Investigation of Residual Liquid Organics, EPA/600/6-90/004.)

phase, however, and will therefore leave a residual typically representing a saturation of 10 to 20% of the pore space. This largely immobile separate phase residual is the first zone of contamination. Although the bulk liquid phase is largely immobile, the residual can evaporate into the soil vapor space and move as a vapor throughout the vadose zone. The contaminated vapor in the vadose zone is a second zone of contamination.

If there is a sufficient volume of the NAPL, it will ultimately migrate downward to the water table. For a small volume spill or a long distance to the water table, the capillary entrapment of NAPL in the water-unsaturated zone may reduce the flowing volume to the extent that the water table is not reached. This is sometimes referred to as capillary exhaustion of the infiltrating NAPL. If the water table is reached, however, very different behavior is observed with an LNAPL vs. a DNAPL. The LNAPL will tend to spread on the surface of the water table and any further migration might be in the direction of the slope of the water table. The DNAPL, however, will tend to penetrate the water table. As it moves through the originally water-saturated zone, a residual is left behind due to capillary entrapment (although again left to the larger pore spaces due to the typically more wetting behavior of the water). Ultimately, if a sufficient volume of DNAPL is introduced to the subsurface, the phase may progress all the way through the water table aquifer until its motion is arrested by the presence of a low permeability strata. The fine pore spaces in this low permeability strata holds water tightly and typically the nonaqueous phase cannot displace this water and penetrate the strata. As a result, it tends to collect and pool on the surface of the low permeability material. If the strata is tilted, the DNAPL may migrate downslope, regardless of the direction of

the groundwater flow. The state of the nonaqueous phase in the originally water-saturated zone, whether pooled at the water table as with the LNAPL or spread as a residual and pooled on low permeability strata at the base of the water table aquifer, as in a DNAPL, is the third zone of contamination.

Ultimately, the motion of the NAPL ceases, either due to pooling on an essentially flat water table or strata or due to “capillary exhaustion” from the residual held by capillary forces. Subsequent contaminant movement is the result of dissolution into the groundwaters and transport by their motion. This is the fourth zone of contamination.

The nature and form of the contamination defines the mobility of the contaminants and appropriate remedial approaches. The quantitative description of contaminant transport in each zone of contamination and the effects of these zones on selecting appropriate remedial options will be discussed in the subsequent sections.

8.3.1 FIRST ZONE OF CONTAMINATION — NAPL RESIDUAL IN THE VADOSE ZONE

As indicated in the above discussion, a NAPL introduced to the soil via a spill or leak first migrates via gravity and capillary forces through the vadose zone leaving behind a residual. To understand the process that results in the residual, largely immobile contamination of the vadose zone, we must first explore the infiltration of the NAPL. Let us consider the situation in Figure 8.11 in which a body of contaminant liquid is spilled to the surface of the soil where it exhibits a “ponded depth” of height h . This is the depth of the pool of liquid and therefore its elevation head above the surface. Let us assume that the penetration into the soil can be modeled by consideration of the media as a bundle of capillary tubes, a single example of which is shown in Figure 8.11. Note that due to the wetting characteristics of the invading contaminant liquid and the curvature of the liquid-air interface, the pressure in the NAPL is less than the pressure in the air phase being displaced. The pressure head in the liquid is thus negative near the location of the advancing front and increases to zero (gauge) at the free surface of the spilled liquid. This is also depicted in Figure 8.11. Because the air is being displaced from the soil pores and is being pushed downward by the advancing front of the penetrating liquid, it also exhibits a pressure gradient but because of the low viscosity of air and the typically slow rate of infiltration of liquid, this is generally negligible. Thus, the hydraulic head (the sum of the pressure and elevation heads) at the advancing front of the penetrating liquid (position, z_f) is

$$\begin{aligned} h(z_f) &= h_p + h_c \\ &= -h_c - z_f \end{aligned} \quad (8.46)$$

where h_c is the effective head of the capillary suction at the infiltrating front and is approximated by Equation 8.43 for pores of uniform radius r . In a real soil, capillary pressures are strongly saturation dependent and not so easily characterized by a single effective capillary suction. In a relatively uniform sand or in a medium in which the finer pores have been filled with the typically more wetting water, the air-entry pressure provides a reasonable estimate of this parameter. Note that this air-entry pressure would be associated with the liquid phase being displaced (i.e., the NAPL) and not the more commonly measured air-entry pressure into water-filled pores.

The hydraulic head at the soil surface assuming a pooled liquid of height h is

$$h(0) = h \quad (8.47)$$

assuming again that the pressure head in the atmosphere is 0 gauge pressure. Substituting into Darcy’s Law for unsaturated flow taking the saturation of the infiltrating NAPL as ϕ_n ,

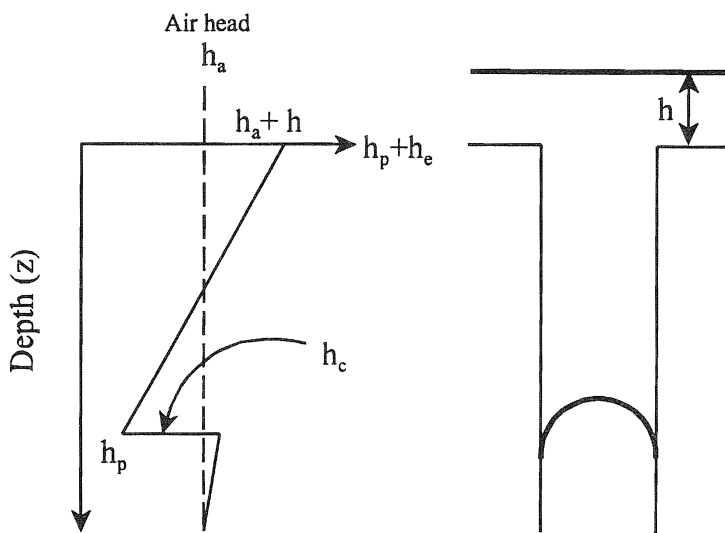


FIGURE 8.11 Model of infiltration illustrated by movement into a single pore assuming a ponded depth h at the surface. The total head, the sum of the pressure head (h_p), and elevation head (h_c) are also shown. The effective capillary pressure (h_c) is the difference in head between air and liquid at the infiltrating liquid front.

$$\frac{Q}{A} = q = \kappa_r(\varphi_n)k_p \frac{z_f + h_c + h(0)}{z_f} \tag{8.48}$$

Remembering that the Darcy velocity is the interstitial velocity, $u_i = dz_f/dt$ times the porosity, or that fraction of the porosity filled by the infiltrating NAPL, $\phi_n \varepsilon$, this can be rewritten

$$q = \varepsilon \phi_n \frac{dz_f}{dt} = \kappa_r(\varphi_n)k_p \frac{z_f + h_c + h(0)}{z_f} \tag{8.49}$$

This is a differential equation that describes the rate of penetration of the infiltrating liquid. It is only useful if the capillary suction head, h_c , can be approximated as a constant or known function. Variations in pore sizes and liquid saturation may cause this to vary significantly with position. Often the basic features of the infiltration are reasonably well described by a simple constant, however. The infiltrating liquid phase will generally fill all the pore space available to it. Because water is normally present at field capacity or higher levels and filling the finer pore spaces, an infiltrating nonaqueous phase is normally limited to the larger pores of the media. This serves to reduce the effects of capillarity and improve the accuracy of the model. The model has also been used to describe water infiltration after a rainfall (a so-called Green and Ampt model after the first to propose such a model). Reible et al. (1990) describe various solutions to the model. Let us consider here only the condition that the effects of capillarity and the ponded head can be neglected, for example, due to a spill on a coarse sand. Under these conditions, the model reduces to

$$q = \varepsilon \phi_n \frac{dz_f}{dt} = \kappa_r(\varphi_n)k_p \frac{z_f}{z_f} = \kappa_r(\varphi_n)k_p$$

$$z_f = \frac{\kappa_r(\varphi_n)k_p}{\varepsilon \phi_n} t \tag{8.50}$$

and the rate of penetration of the infiltrating liquid is a constant as long as the saturation is essentially uniform.

After the liquid infiltrates completely into the soil, the soil will begin to drain leaving a residual saturation behind the main body of liquid. If the effective capillary suction in this partially saturated region is the same as the effective capillary suction at the leading edge of the liquid, Equation 8.50 would also govern the drainage rate. Penetration at this constant velocity would continue until the entire volume of the infiltrating liquid phase was contained within the largely immobile residual. If V_n is the volume and ϕ_{nr} is the residual saturation with respect to the nonaqueous phase, the maximum penetration is given by

$$z_f|_{\max} = \frac{V_n}{\phi_{nr} \varepsilon A} \quad (8.51)$$

This is the depth to which the liquid will infiltrate before being exhausted by capillary retention. If this depth is greater than the depth to the water table, then interactions with the water table must be considered. For an LNAPL, the remaining liquid will spread in the form of a thick “pancake” on the water table surface. For a DNAPL, further penetration of the water table is likely as discussed further in the third zone of contamination.

The value of the residual nonaqueous phase saturation, ϕ_{nr} , should be related to the interfacial tension since the pressure resulting in capillary retention is $2\sigma/r$. Because water is always present, the appropriate interfacial tension is the tension between the nonaqueous phase and water. This can be crudely estimated if we assume that water and the nonaqueous phase are pure and mutually insoluble by replacing the solid phase in Figure 8.7 with a water phase. The nonaqueous phase droplet tends to wet the water suggesting $\cos \theta_c = 1$ and therefore

$$\sigma_{aw} = \sigma_{wn} + \sigma_{an} \cos \theta_c \quad (8.52)$$

or

$$\sigma_{wn} = \sigma_{aw} - \sigma_{an}$$

where the subscripts a, w, and n reflect the air, water and nonaqueous phases, respectively. Thus, the interfacial tension between the water and the nonaqueous phase is simply the difference between liquid-air surface tensions. Because the capillary retention should scale with the interfacial tension, an estimate of the residual NAPL saturation can be deduced from the residual water saturation in an otherwise air-filled soil (field capacity) by

$$\phi_{nr} \approx \phi_{wr} \frac{\sigma_{nw}}{\sigma_{aw}} \approx \phi_{wr} \frac{\sigma_{aw} - \sigma_{an}}{\sigma_{aw}} \quad (8.53)$$

Benzene, for example, exhibits a surface tension with air of 28.8 dyn/cm. Water exhibits a surface tension of 72 dyn/cm. The interfacial tension between water and air can then be estimated as 43.2 dyn/cm and the residual saturation of benzene in a water-wetted soil would be expected to be of the order of 60% of the residual water saturation. This approach neglects the effect of the different pore sizes that would be filled by the benzene vs. the residual water, so it should be considered a crude approximation at best. Organic residual saturations, however, do tend to be less than observed field capacities or residual saturations of water.

The same basis could be used to estimate the effective capillary suction or air-entry pressure into a porous medium filled with an NAPL rather than water. That is,

$$(h_c)_{nw} \approx (h_a)_{nw} \approx (h_a)_w \frac{\sigma_{nw}}{\sigma_{aw}} \approx (h_a)_w \frac{\sigma_{aw} - \sigma_{an}}{\sigma_{aw}} \quad (8.54)$$

where the subscript nw represents the nonaqueous phase values and the subscript w represents the corresponding quantities in water-filled pores.

The form and distribution of the residual NAPL and not just its volume or average saturation also is important to its subsequent mobility. For example, a finely divided residual exhibits more surface area to volume than large “blobs” and is thus more likely to evaporate or dissolve in infiltrating rainwater. This would be especially important for soluble or volatile components of a largely insoluble or nonvolatile mixture. These contaminants must diffuse to the surface of the bulk mixture before they are available for dissolution/vaporization. The larger the blobs of the bulk mixture the longer the diffusion path and the slower the process of release.

The calculation of the infiltration of a nonaqueous liquid phase is illustrated in Example 8.3. Example 8.4 illustrates some approximate characteristics of the residual ganglia or blobs left behind.

Example 8.3: Rate and extent of infiltration of an organic phase in the unsaturated zone

Estimate the rate of infiltration of 1000 L of benzene over 10 m² of soil with a water conductivity of 1 cm/min. The residual water saturation is 30%.

The saturated conductivity of benzene is given by

$$(k_p)_{Bz} = (k_p)_w \frac{\rho_n \mu_w}{\mu_n \rho_w} = 1 \text{ cm/min} \frac{0.88 \text{ g/cm}^3}{0.0064 \text{ g/(cm} \cdot \text{s)}} \frac{0.01 \text{ g/(cm} \cdot \text{s)}}{1 \text{ g/cm}^3} = 1.375 \text{ cm/min}$$

The residual benzene saturation is estimated to be

$$\phi_n = \phi_{wr} \frac{\sigma_n}{\sigma_w} = 0.3 \frac{43.2 \text{ dyn/cm}}{72 \text{ dyn/cm}} = 0.18$$

The relative permeability of the benzene is then

$$\kappa_r = \left(\frac{0.7 - 0.18}{1 - 0.18} \right)^{\frac{2+3(2.8)}{2.8}} = 0.184$$

The maximum infiltration rate is $\kappa_r K_p = 15.2 \text{ cm/h}$. The position of the infiltrating benzene as a function of time is then

$$z_f(t) = \frac{qt}{\epsilon \phi_n} = \frac{15.2 \text{ cm/h}}{(0.4)(0.7)} t = (54 \text{ cm/h})t$$

The maximum infiltration depth (assuming a homogeneous soil) is

$$z_{\max} = \frac{V_n}{\epsilon \phi_n A} = \frac{1 \text{ m}^3}{0.4 \cdot 0.18 \cdot 10 \text{ m}^2} = 13.9 \text{ m}$$

Example 8.4: Ganglia size in the unsaturated zone

Estimate the maximum size of the residual nonaqueous phase ganglia (or blobs) in the unsaturated zone

The maximum size of a ganglion is dependent on a balance between the capillary forces ($2\sigma/R$ per unit area) stabilizing the ganglia vs. the gravitation or buoyancy forces per unit area ($\rho_n g L$) destabilizing the ganglia. Setting these two forces per unit area equal, solving for the ganglia size L , and evaluating for benzene in a 0.1-mm pore radius (fine sand),

$$L \approx 2 \frac{\sigma_{nw}}{R\rho_n g} = 2 \frac{43.2 \text{ dyn/cm}}{(0.01 \text{ cm})(0.88 \text{ g/cm}^3)(9800 \text{ cm/s}^2)} = 1 \text{ cm}$$

For a pore radius more consistent with silt or clay this would increase by an order of magnitude or more. As this suggests the size of these ganglia can be quite large, slowing transport to and from the residual nonaqueous phase. Actual ganglia tend to occur in a range of sizes smaller than this.

8.3.2 SECOND ZONE OF CONTAMINATION — CONTAMINANT VAPORS IN VADOSE ZONE

The residual that remains after penetration of the NAPL through the subsurface can serve as a source of vapors that can then migrate rapidly through the subsurface. At any location where free NAPL exists, the local pore space is likely saturated with vapors from the NAPL. If the NAPL were a pure organic phase, the pore space would exhibit a vapor concentration associated with the pure component vapor pressure of the organic phase. If the NAPL were a mixture, the pore space would exhibit a vapor concentration of a particular compound associated with the vapor pressure of the compound above that mixture. If the NAPL were an ideal mixture of organic compounds, Raoult's Law would hold and the pore space would exhibit a partial pressure of a particular compound equal to the product of the pure component vapor pressure and the mole fraction abundance of that compound in the mixture. Thus the partial pressure in the pore space adjacent to a residual NAPL under the two most common scenarios are given by

$$p_i = \begin{cases} P_v & \text{pure NAPL} \\ x_i P_v & \text{ideal NAPL mixture} \end{cases} \quad (8.55)$$

These contaminant vapors will then migrate away from the zone of liquid residual contamination.

The primary mechanism whereby vapors travel in the subsurface is via diffusion. There are some advective processes but they are generally only important under specialized situations. If the NAPL introduced to the subsurface is extremely volatile (vapor pressures greater than 1 atm), for example, its evaporation could significantly increase the vapor density in the pore space and cause an advective flow away from the point of evaporation. Methyl bromide, for example, is a soil fumigant that is introduced to soil as a liquid under pressure. Rapid vaporization of this compound would likely increase local vapor phase pressures causing a pressure driven flow away from the point of injection. For lower but still high volatility compounds (vapor pressures between 0.1 and 1 atm), the concentration of the vapors in the pore space could be sufficient to cause a buoyancy-driven flow. Air containing 10% or more of a compound with a molecular weight different than that of air, 29 g/mol, would cause such buoyancy-driven flows. For low vapor pressure compounds present in the vapor space at low concentrations, there may still be effects of advective processes if there are significant local variations in pressure. For example, a buried cavity could equilibrate with a high pressure atmosphere and then pressure-driven advective flow could result if the atmo-

spheric pressure was reduced as the result of frontal passage. Finally advective flow could be driven by imposing a pressure gradient across the unsaturated zone, as might be attempted in certain remedial approaches such as soil vacuum extraction.

Under most situations of interest, however, the primary mechanism for vapor transport in soils is diffusion. Repeating Fick's first and second laws of diffusion in one dimension,

$$\begin{aligned} \text{Fick's First Law} \quad q_m &= -D_{sv} \frac{dC_{sv}}{dz} \\ \text{Fick's Second Law} \quad \frac{\partial C_T}{\partial t} &= -D_{sv} \frac{\partial^2 C_{sv}}{\partial z^2} \end{aligned} \quad (8.56)$$

where C_{sv} is the concentration of a volatile contaminant of interest in the soil vapor phase within the soil pores and D_{sv} is an effective diffusion coefficient for the vapors in the soil media. The term C_T is the total concentration of the contaminant in the soil including contaminant on the soil and water phases. C_T is the total concentration — sum of mass of contaminant in all soil phases divided by the volume of the soil.

In a porous medium, the effective diffusion coefficient is the product of the diffusivity in the fluid filling the pore spaces, in this case, air, and a correction for the fraction of void space available to diffusion, ϵ or ϵ_a , and the effective length of the diffusion path, the tortuosity, τ .

$$D_{sv} = D_a \frac{\epsilon}{\tau} \quad (8.57)$$

The Millington and Quirk (1961) model is a commonly used predictor of the effective diffusion coefficient and it has the form, in a partially saturated medium, of

$$D_{sv} = D_a \frac{\epsilon_a^{10/3}}{\epsilon^2} \quad (8.58)$$

where ϵ_a is the air-filled porosity and ϵ is the total porosity in the soil. This model suggests that the effective diffusion coefficient in the soil vapors is significantly affected by the presence of residual water as shown in Example 8.5. It should be emphasized that there is no generally reliable model of effective diffusion coefficients in the soil media. The Millington and Quirk model is completely employed, simple, and has been shown to be at least approximately correct in granular media such as sands.

Example 8.5: Soil-vapor diffusivity — the effect of moisture content

Estimate the diffusivity of a vapor in a 40% porosity soil with varying water contents. The diffusivity of the compound in air is 0.1 cm²/s.

Let us consider water saturations of 20, 40, 60, and 80%. The effective diffusivity at 20% water saturation is given by

$$D_{sv} = D_a \frac{[\epsilon(1 - \phi_w)]^{10/3}}{\epsilon^2} = 0.1 \text{ cm}^2/\text{s} \frac{[(0.4 \cdot (1 - 0.2))]^{10/3}}{0.4^2} = 0.014 \text{ cm}^2/\text{s}$$

The diffusivity at all water saturations are given below.

ϕ_w	$D_{sw}, \text{cm}^2/\text{s}$
0	0.029
0.2	0.014
0.4	0.0054
0.6	0.0014
0.8	0.00014
1	0 (diffusion in water phase only)

The flux of a contaminant through the pore space is a function of the effective diffusion coefficient. The time required for complete evaporation and recovery of a contaminated zone, however, depends upon the portion of the contaminant that is mobile vs. that which is sorbed to the soil. As indicated previously the ratio of the total concentration to the mobile phase concentration is the retardation factor. Here

$$\frac{C_T}{C_{sv}} = R_f = \epsilon_a + \frac{\epsilon_w}{K_{aw}} + \frac{\rho_b K_{sw}}{K_{aw}} \quad (8.59)$$

the air-water partition coefficient, K_{aw} , is assumed to relate vapor and water phase concentrations and if sorption onto only the residual water and onto the soil surface is considered. The first term in Equation 8.59 represents the portion of the contaminant in the vapor space, the second the portion of the contaminant in the residual water, and the third the portion sorbed to the solid in contact with the residual water.

The accumulation in the phases other than the vapor is important when transient, or time-dependent diffusion occurs. Often, however, the time required to set up a steady-state concentration profile and therefore a steady-state diffusive flux is small compared to the time required to deplete the liquid contaminant. Keep in mind that a liquid is typically 1000 times more dense than a vapor phase. As a result, steady-state diffusion in the vapor phase is applicable which implies, in one dimension,

$$\begin{aligned} \frac{d^2 C_a}{dz^2} &= 0 \\ \frac{dC_a}{dz} &= \alpha \quad (\text{Flux is constant}) \\ C_a &= \alpha z + \beta \quad (\text{linear in } z) \end{aligned} \quad (8.60)$$

The amount of that flux is given by Fick's first law in Equation 8.56 with an estimate of D_s given by Equation 8.58. Example 8.6 examines steady-state vapor transport in the unsaturated zone of a soil.

Example 8.6: Vapor diffusion through a clean soil cap

Consider a clean soil "cap" 50 cm thick over a contaminated soil containing 100 mg/kg benzene. The average moisture content in the cap is 20%, its total porosity is 40%, bulk density of 1.5 g/cm³, and organic carbon content of 3%.

The concentration in the soil water and soil vapor at the bottom of the cap are in equilibrium with the contaminated soil with $K_{sw} = K_{oc} \omega_{oc} = 2.61 \text{ L/kg}$, and $K_{aw} = 0.224$ (for benzene).

$$C_{sw} = \frac{W_s}{K_{sw}} = \frac{100 \text{ mg/kg}}{2.61 \text{ L/kg}} = 38.2 \text{ mg/L}$$

$$C_{sv} = C_w K_{aw} = 38.2 \text{ mg/L} \cdot 0.224 = 8.6 \text{ mg/L}$$

From Example 8.5, the diffusivity in the 20% saturated soil is about 0.14 times the free air diffusivity ($D_B = 0.088 \text{ cm}^2/\text{s}$) or $0.012 \text{ cm}^2/\text{s}$. The steady-state flux through the soil cap, assuming the air is effectively free of benzene is

$$q_m = \frac{D_{sv}}{h} C_{sv} = \frac{0.012 \text{ cm}^2/\text{s}}{50 \text{ cm}} (8.6 \text{ mg/L}) = 75.9 \frac{\text{mg}}{\text{m}^2 \cdot \text{h}}$$

The time required to reach this steady-state is dependent upon the retardation factor defined by Equation 8.59.

$$R_f = (0.32) + \frac{0.08}{0.224} + (1.5 \text{ g/cm}^3) \frac{2.61 \text{ L/kg}}{0.224} = 18.2$$

Thus, at any location in the soil cap the mass of benzene in the vapor phase is only $1/18.2$ of the total mass. This significantly delays the onset of steady conditions which can be demonstrated by examining the characteristic time to reach steady conditions at the top of the cap.

$$\tau_{diff} = h^2 \frac{R_f}{D_{sv}} = \frac{(50 \text{ cm})(18.2)}{0.012 \text{ cm}^2/\text{s}} = 42.8 \text{ day}$$

Whether this time period is important or not depends upon the amount of benzene in the subsurface (that is, for a large spill, a delay of 42 days to reach steady conditions is insignificant). If the cap material were less sorbing, for example, contained less water or less organic material in the soil, the delay to steady state would be much less. The characteristic time to reach steady state in a dry non-sorbing cap ($R_f = \epsilon_a = 0.4$) is only 0.9 days.

8.3.3 THIRD ZONE OF CONTAMINATION — NAPL RESIDUAL IN INITIALLY WATER-SATURATED ZONE

That portion of the NAPL that ultimately reaches the water table forms the third zone of contamination. If the NAPL is lighter than water, the liquid will tend to pool on the water table surface, although some depression of the water table is likely to occur due to the static head of the NAPL. This pooled NAPL may migrate down the groundwater gradient and impact other locations if the initial spill or leak was of sufficient volume.

If the NAPL is a DNAPL, it will tend to penetrate the water table and progress downward until impeded by low permeability geological strata. The NAPL is generally less wetting of the media than water and thus displacement of water from fine-grained strata is unlikely to occur. The low permeability of such a strata would further reduce the rate of any penetration that is likely to occur.

The residual nonaqueous phase left behind is similar in many respects to that left behind in the vadose zone. The residual nonaqueous phase saturation tends to be somewhat higher than in the vadose zone in large part due to the tendency of the nonaqueous phase to coalesce into larger blobs beneath the water table. As with the vadose zone, the form and distribution of the nonaqueous phase is as important to the subsequent migration of the contaminant as the absolute volume of residual. The particular distribution of the residual is a strong function of the details of the soil heterogeneities and is almost impossible to predict or even measure even with numerous wells and