

coring of the soils. Unlike the vadose zone, the nonaqueous phase shows a strong preference for coarse-grained media. Due to the difference in wetting characteristics, the nonaqueous phase can only displace water from the coarser media, and then it is effectively trapped there since further migration would require displacement of water from finer-grained media.

If the spill is of sufficient volume, enough NAPL may penetrate to the bottom of the water table aquifer so that a pool of liquid occurs on the underlying strata. This pool is subject to further migration due to the negative buoyancy of the liquid in the direction of the downhill tilt of the water table. This migration downslope may occur regardless of the direction of ground water flow, potentially causing contamination to migrate “up-gradient.” This is especially difficult to understand if the presence of the nonaqueous phase pool has not been identified. Developing a conceptual model of the form and distribution of the contamination at a site can be an incredibly daunting task requiring a great deal of sampling and interpretation. At many sites, this site is never completed to the satisfaction of the investigators and surprises in the form of unexpected contamination in a new sample is always possible. Example 8.7 compares the stable size of the ganglia or blobs left behind in the saturated zone to those calculated in Example 8.4 for the unsaturated zone. The stability of the nonaqueous phase residual during water flushing is illustrated in Example 8.8.

Example 8.8: Ganglia size as a function of key parameters in the saturated zone

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

The maximum size of a ganglia in the saturated zone is dependent on a balance between the capillary forces ($2\sigma/R$ per unit area) stabilizing the ganglia vs. the pressure gradient forces destabilizing the ganglia. From Darcy’s Law, the pressure difference across a ganglia of size L is given by

$$q = \frac{\kappa_p}{\mu_w} \frac{dP}{dz} \Rightarrow \Delta P = \frac{qL\mu_w}{\kappa_p}$$

Setting these two forces per unit area equal and solving for the ganglia size L , a relationship can be found between the ganglia size and the flow and soil parameters. If a fine sand or sandy loam is assumed with a pore radius of the order of 0.01 cm with benzene as the NAPL, the following estimate for ganglia size can be made.

$$L \approx 2 \frac{\sigma_{nw} \kappa_p}{Rq\mu_w} = 2 \frac{(43.2 \text{ dyn/cm})(3.4 \cdot 10^{-8} \text{ cm}^2)}{(0.01 \text{ cm})(0.2/60 \text{ cm/s})(0.01 \text{ g/(cm} \cdot \text{s)})} = 9 \text{ cm}$$

This estimate assumes a hydraulic conductivity of 0.2 cm/min which corresponds to a medium permeability of $3.4 (10)^{-8} \text{ cm}^2$. The estimate also assumes unit hydraulic gradient such that the groundwater velocity is equal to the hydraulic conductivity. The estimated size is larger than that expected in the unsaturated zone and if a lesser hydraulic gradient were applied such that $q < K_p$, an even larger stable size would result. Again the size of a ganglion can significantly slow mass transport between the NAPL and water

Example 8.8: Volume of water required to dissolve a nonaqueous phase residual

Consider a soil with a residual nonaqueous phase liquid saturation of 20% and a total porosity of 40%. Estimate the pore volumes of water required to completely dissolve the liquid if the liquid is (1) 1,2-

dichloroethane, (2) pure benzene, or (3) a 1% mixture of benzene in an essentially insoluble bulk NAPL with density 0.8 g/cm^3 with an average molecular weight of 140.

Let us employ a basis of 1 m^3 of soil. The total mass of NAPL to be removed from the soil is then

$$M_n = \rho_n \phi_n \epsilon (1 \text{ m}^3) \quad \rho (\text{g/cm}^3) = \begin{bmatrix} 1.25 \\ 0.88 \\ 0.8 \end{bmatrix} \quad M_n (\text{kg}) = \begin{bmatrix} 100 \\ 70.4 \\ 64 \end{bmatrix}$$

The volume of water required depends upon the solubility in water of 1,2-dichloroethane and benzene (5500 and 1780 mg/L, respectively) and the solubility times mole fraction benzene for the mixture (assuming Raoult's Law or an ideal nonaqueous phase). The mole fraction and solubility of benzene in the mixture is

$$x_B = \frac{0.01/78}{0.01/78 + 0.99/140} = 0.018 \quad C_B = x_B S_w = (0.018)(1780 \text{ mg/L}) = 31.7 \text{ mg/L}$$

The minimum volume of water required to remove the contaminants from the soil and the minimum volume divided by the pore volume in the soil (i.e., the number of pore volumes) are

$$V_w = \frac{M_n}{C_w} \quad V_w (\text{m}^3) = \begin{bmatrix} 18.2 \\ 39.6 \\ 3600 \end{bmatrix}$$

$$V_p = \frac{V_w}{\epsilon \text{ l m}^3} \quad V_p = \begin{bmatrix} 45.5 \\ 98.9 \\ 8990 \end{bmatrix} \begin{array}{l} \text{1,2-dichloroethane} \\ \text{Benzene} \\ \text{1\% mixture of benzene} \end{array}$$

Thus, very large flushing volumes of water are required to dissolve the nonaqueous phase ganglia, especially for dilute mixtures which reduces the dissolved phase concentration even below the solubility limit.

8.3.4 FOURTH ZONE OF CONTAMINATION — DISSOLVED CONTAMINANT IN SUBSURFACE WATER

The nonaqueous phase residual or pools present in, on, or beneath the water column serve as a subsequent source of contamination to the aqueous phase. It is this contamination that is generally of most interest in terms of risk to potential users of the ground water. The contamination can migrate to surface waters fed by the groundwater or to drinking water wells leading to exposures by contact or ingestion. If the nonaqueous phase is largely immobile, this migration and exposure results from dissolution and *miscible displacement* of the contaminant.

At any location where NAPL exists, the local pore space is likely saturated with dissolved constituents. If the NAPL were a pure organic phase, the pore space would exhibit a dissolved concentration equal to the solubility of the contaminant. If the NAPL were a mixture, the pore space would exhibit a dissolved concentration according to the partitioning of the compound from that mixture. If the NAPL were an ideal mixture of organic compounds, Raoult's Law would hold. For a hydrophobic organic, the mole fraction of the component times the pure component solubility

would be observed in the water in the local pore space. The dissolved concentration in the pore space adjacent to a residual NAPL under the two most common scenarios are given by

$$C_w = \begin{cases} S_w & \text{pure NAPL} \\ x_n S_w & \text{NAPL mixture} \end{cases} \quad (8.61)$$

where S_w is the tabulated solubility of the contaminant in water and x_n is the mole fraction of the component in the nonaqueous phase. Equation 8.61 estimates only the purely dissolved contaminant. Any dissolved or suspended particulate organic carbon can increase the amount of hydrophobic organic contaminant contained in the porewater. Using the models for estimating the proportion on dissolved or suspended particulate organic carbon discussed in Chapter 3, the total porewater concentration is given by

$$\begin{aligned} C_{sw} &= C_w + C_{oc} \\ &= C_w + \rho_{oc} K_{oc} C_w \\ &= C_w (1 + \rho_{oc} K_{oc}) \end{aligned} \quad (8.62)$$

Here we are differentiating between the total concentration, the total soil water (sw) or porewater concentration, and the dissolved concentration. The definition of these are as follows:

- C_T — Total concentration is the sum of mass on soil, dissolved and other suspended contaminant per unit volume of soil (as above).
- C_{sw} — Soil water concentration is the sum of contaminant dissolved or otherwise suspended in pore water per volume of pore water.
- C_w — Dissolved concentration is the sum of dissolved contaminant per volume of porewater.

The dissolved and suspended contaminants will migrate away from the zone of nonaqueous residual. The primary mechanism whereby these contaminants migrate is generally advection. Unlike vapor transport in the vadose zone, diffusive transport in the groundwater is quite slow (vapor diffusivities are of the order of 10,000 times larger than liquid diffusivities). In addition, there is usually a significant groundwater transport rate. The ratio of the advective transport to the diffusive transport is governed by the Peclet number,

$$N_{Pe} = \frac{QL}{AD_{sw}} = \frac{qL}{\left(D_w \frac{\epsilon}{\tau}\right)} \quad (8.63)$$

Again the effective diffusion coefficient is again often estimated using the model of Millington and Quirk which for a water-saturated medium becomes

$$D_{sw} = D_w \epsilon^{4/3} \quad (8.64)$$

Using the Millington and Quirk estimate of effective diffusion coefficient in a water-saturated medium with a porosity of 40% for a compound with a water diffusivity of 10^{-5} cm²/s, $D_{sw} = (10^{-5}$ cm/s) $0.4^{4/3} = 0.29 \cdot 10^{-5}$ cm/s. For even transport distances of 1 m, the Peclet number exceeds unity and advection is dominant for Darcy velocities as low as $0.29 \cdot 10^{-7}$ cm/s = 0.91 cm/year. Thus, diffusion is negligible for most groundwater flow velocities of interest.

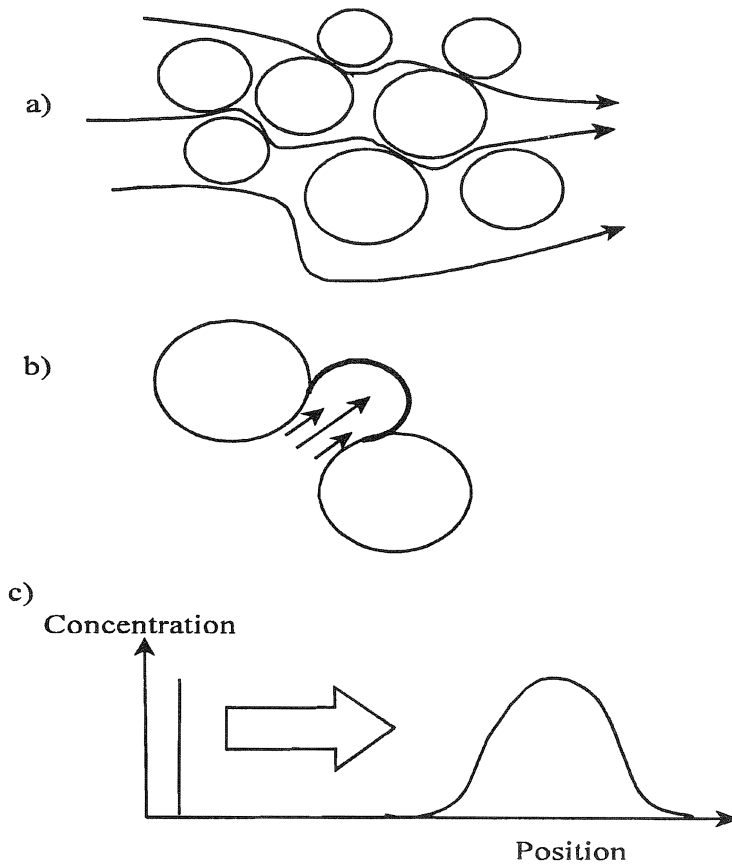


FIGURE 8.12 Mechanism and effect of microscale dispersion: (a) tortuous path fluid takes through media; (b) variations in velocity within a pore; and (c) spreading due to these processes.

This does not mean that diffusive-like processes can be neglected, however. The groundwater flow is limited to moving through the interstitial pore space and as a result follows a tortuous path as shown in Figure 8.12a. In addition, the velocity within the interstitial space is variable with effectively zero velocities at the soil grains and a maximum velocity in the center of the pores, also as shown in Figure 8.12b. As a result of these differences in path and velocity, parcels of fluid are spread in a manner similar to that caused by diffusion during their progress through any porous media. If we examine fluid marked with a tracer entering a sequence of pore spaces, for example, the fluid moves at different velocities and along different paths through the pore spaces. As a result the arrival of the tracer at the exit of the pore sequence is blurred and spread as shown in Figure 8.12c. The spread of the contaminant concentration with distance is referred to as *dispersion*. It is a microscale phenomenon that results from a coupling of advection and diffusion processes causing spreading on the macroscale.

Just as heterogeneities at the pore level cause dispersion, macroscale heterogeneities associated with large scale variations in pore or grain sizes and permeabilities also cause a similar dispersion process in that again, fluid moves at different velocities and along different paths through the media. This is illustrated in Figure 8.13. A finite zone of low permeability material behaves in much the same way as a single soil grain acts at the microscale. Two layers of differing permeability result in spreading the time of arrival of a tracer in a withdrawal well.

Note that in all cases, dispersion is associated directly with the motion of the fluid through the media. Because the effect is associated with spreading in a diffusion-like manner, dispersion is

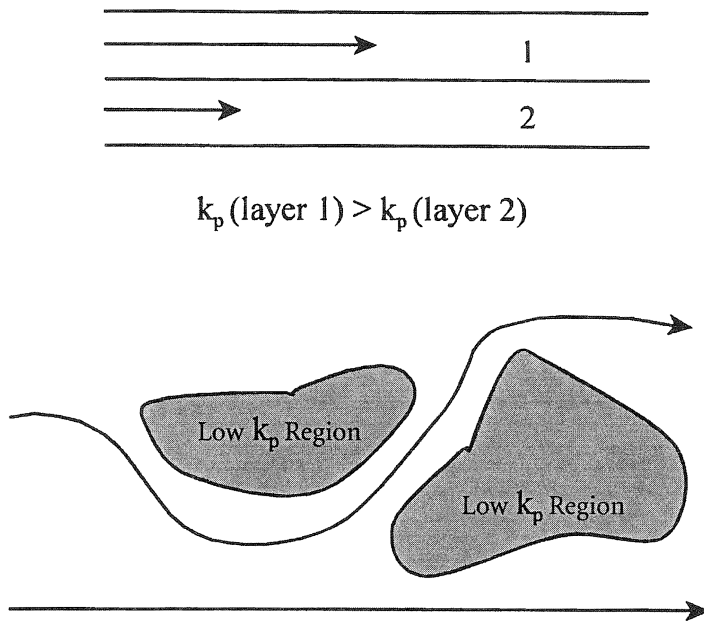


FIGURE 8.13 Illustration of enhanced lateral spreading or dispersion associated with macroscale heterogeneities.

normally modeled with an effective diffusion coefficient, or dispersion coefficient, that depends on the fluid velocity. At the low Darcy velocities observed in most soils, the effective diffusion coefficient resulting from dispersion, or *dispersion coefficient*, K_D , is often observed to exhibit a relationship with velocity of the following form

$$K_D = D_w \frac{\varepsilon}{\tau} + \alpha_D q \quad (8.65)$$

where α_D is termed the dispersivity. Unfortunately, some authors prefer to refer to what we have here identified as K_D as the dispersivity. We will hold to the usage that the quantity referred to as K_D is a dispersion coefficient and that α_D is a dispersivity. The dispersivity is a measure of the scale of the heterogeneities in a medium and has units of length.

For a uniform bed of packed spheres, α_D is approximately equal to the particle diameter in the direction of flow and approximately $1/10$ of that in the direction normal to the flow. In a real soil, the transverse dispersivity is still of the order of 10% of that in the direction of flow, but the values of both tend to be much greater than in laboratory columns filled with sand. The largest heterogeneities encountered by the flow tend to grow with distance traveled and as a result the observed dispersivity under field conditions also tends to grow with distance. A commonly used approximation is to assume that the dispersivity is of the order of 5 to 10% of the travel distance. Thus, if the distance from a contaminated soil zone to a drinking water well is 1 km, the effective dispersivity over that distance is 50 to 100 m. A similar approach was suggested by Neumann (1990) based on field observations of dispersivity. He proposed the relationship

$$\alpha_D \approx 0.017 L^{1.5} \quad L, \alpha_D \text{ in m} \quad (8.66)$$

where L is the travel distance of the contaminant in meters. Again the dispersivity in the transverse direction perpendicular to the groundwater flow direction is typically about 10% of this value.

Example 8.9 compares the dispersivity and the dispersion coefficient suggested by this relationship to molecular diffusion. It should be emphasized that the actual dispersivity may vary greatly from this prediction due to variations in local geology.

Example 8.9: Values of the dispersivity and dispersion coefficient

Estimate the dispersivity and dispersion coefficient for groundwater flow between a contaminant source area and a water well potentially at risk 100 m downgradient. Assume a soil porosity of 40%, a molecular diffusivity of 10^{-5} cm²/s, and a Darcy velocity of 10 m/year.

By the Millington and Quirk model the effective molecular diffusion coefficient in the soil is

$$D_{sw} = D_w \epsilon^{4/3} = 2.95 \cdot 10^{-6} \text{ cm}^2/\text{s}$$

Estimating the dispersivity by Equation 8.66

$$\alpha_D = 0.017 L^{1.5} = 0.017 (100)^{1.5} = 17 \text{ m}$$

$$\begin{aligned} K_D &= D_{sw} + \alpha_D q = 2.95 \cdot 10^{-10} \text{ m}^2/\text{s} + (17 \text{ m})(10 \text{ m/year}) \\ &\approx 170 \text{ m}^2/\text{year} = 0.054 \text{ cm}^2/\text{s} \end{aligned}$$

The effect of molecular diffusion on horizontal transport is clearly negligible compared to the dispersion. The Peclet number **based upon the dispersion coefficient** is

$$N_{Pe} = \frac{qL}{K_D} = \frac{(10 \text{ m/year})(100 \text{ m})}{170 \text{ m}^2/\text{year}} = 5.9$$

Although advection is the more significant process ($N_{Pe} > 1$), it does not completely dominate and significant mixing via dispersion occurs. If only molecular diffusion were operable, advection without any significant mixing would be observed.

Describing miscible displacement or contaminant migration as a result of groundwater movement requires solution of an advection-diffusion equation. The equations for flux and the concentration equivalent to Fick's first and second laws are thus

$$\begin{aligned} q_m &= qC_{sw} - K_D \frac{dC_{sw}}{dz} \\ \frac{\partial C_T}{\partial t} + q \frac{dC_{sw}}{dx} &= K_D \frac{\partial^2 C_{sw}}{dz^2} \end{aligned} \quad (8.67)$$

Where K_d is the dispersion coefficient as described above.

For movement in groundwater with linear, reversible sorption onto the solid organic carbon fraction as well as sorption onto suspended or particulate organic matter, the total concentration is given by

$$\begin{aligned} C_T &= (\epsilon + \rho_b K_{sw}^{obs}) C_{pw} \\ &\approx (\epsilon + \rho_b \omega f_{oc} K_{oc} + \rho_{oc} K_{oc}) C_w \end{aligned} \quad (8.68)$$

In the first relationship the observed partition coefficient between the porewater and the solid phase is employed. This is defined by

$$K_{sw}^{obs} = \frac{W_s}{C_{sw}} \quad (8.69)$$

The second relation of Equation 8.68 attempts to estimate this partition coefficient through the assumption that the dissolved fraction of the hydrophobic organic partitions onto the solid organic carbon and fine suspended particulate organic carbon according to the organic carbon based partition coefficient. Often simply measuring the partition coefficient (Equation 8.69) might be more useful in indicating what is sorbed to the immobile solid phase since even filtered water samples normally include the quantity of contaminant sorbed to the suspended fine particulate fraction and not just the truly dissolved. The corresponding definitions of the retardation factor, the ratio of the total concentration to the mobile phase concentration is given by

$$\begin{aligned} \frac{C_T}{C_{sw}} &= R_f = \varepsilon + \rho_b K_{sw}^{obs} \\ &\approx (\varepsilon + \rho_p \omega_{oc} K_{oc} + \rho_{oc} K_{oc}) \frac{C_w}{C_{sw}} \\ &\approx \frac{\varepsilon + \rho_p \omega_{oc} K_{oc} + \rho_{oc} K_{oc}}{1 + \rho_{oc} K_{oc}} \end{aligned} \quad (8.70)$$

The last relationship recognizes that by the linear partitioning to the suspended organic carbon model that $C_{sw} = C_w(1 + \rho_{oc} K_{oc})$. Using this definition of the retardation factor, Equation 8.67 becomes

$$\begin{aligned} q_m &= qC_{sw} - K_D \frac{dC_{sw}}{dz} \\ \frac{\partial C_{sw}}{\partial t} + \frac{q}{R_f} \frac{dC_{sw}}{dx} &= \frac{K_D}{R_f} \frac{\partial^2 C_{sw}}{dz^2} \end{aligned} \quad (8.71)$$

Note that the flux is not different while the transient advection-diffusion equation is changed by the addition of the quantity sorbed onto the immobile soil fraction. Effectively the retardation factor reduces the speed of the contaminant's migration in the porewater. The effective velocity and dispersion coefficient is given by

$$\begin{aligned} u &= \frac{q}{R_f} \\ K_D &= D_w \frac{\varepsilon}{R_f \tau} + \frac{\alpha_D q}{R_f} \\ &= D_w \frac{\varepsilon}{R_f \tau} + \alpha_D u \end{aligned} \quad (8.72)$$

and both are reduced by the retardation factor. Example 8.10 illustrates the effective dispersion coefficient and velocity as reduced by retardation.

Example 8.10: Transit time for advective transport with sorption-related retardation

Estimate the transit time for contaminants between a source area and a water well 100 m away through soil of bulk density 1.5 g/cm³, porosity of 40%, and organic carbon of 1%. Consider the contaminants (1) chloride ion (nonsorbing), (2) benzene (log K_{oc} = 2.1), (3) hexchlorobutadiene (log K_{oc} = 3.67), and (4) pyrene (log K_{oc} = 5.0). The groundwater velocity is 10 m/year.

Based upon the given data the soil-water partition coefficient and retardation factor is given by

$$K_{sw} = K_{oc} \omega_{oc} = \begin{bmatrix} 0 \\ 1.3 \\ 46.8 \\ 1000 \end{bmatrix} \text{L/kg} \quad R_f = \varepsilon + \rho_b K_{sw} = \begin{bmatrix} 0.4 \\ 2.29 \\ 70.6 \\ 1500 \end{bmatrix}$$

The time required to reach the well by advection only is then given by

$$\tau_{adv} = \frac{L}{q_{eff}} = \frac{LR_f}{q} = R_f \cdot 10 \text{ year} = \begin{bmatrix} 4 \\ 22.9 \\ 706 \\ 1500 \end{bmatrix} \text{year}$$

Chloride ion
Benzene
Hexachlorobutadiene
Pyrene

Clearly the more sorbing compounds, such as pyrene, move very slowly through the subsurface due to the retardation associated with sorption. Note, however, that the chloride ion moves faster than the Darcy velocity, that is at an average velocity of 25 m/year. This is due to the previously recognized fact that the interstitial velocity in the pore spaces is greater than the Darcy or superficial velocity based upon the entire area of the soil.

Note that since the retardation factor arises from the time-dependent term in the advection-diffusion equation, there is no retardation of steady-state transport. The differences between transient and steady-state processes are explored in the examples. Note that the fate and transport of contaminants is an especially important part of evaluating the exposure and risk associated with contaminated soils in that without migration processes contaminated soils generally exhibit no risk. Based upon the release and transport processes, however, it may be important to remediate soils, that is, restore them to an effectively pristine state.

Example 8.11 illustrates the application of the miscible transport models developed above to indicate the rate of subsurface movement of sorbing contaminants.

Example 8.11: Concentrations at a well with advection and dispersion

Employing the dispersion coefficients from Example 8.9 and the retardation factors from Example 8.10, estimate the time required for the well to reach 10% of the concentration at the source area for each of the compounds in Example 8.10.

Assuming a simple one-dimensional advection-diffusion problem, the concentration as a function of time and distance away from the source area can be estimated with Equation 5.136 with K_D replacing D and q replacing U . In addition, $C_0 = 0$.

$$\frac{C_f(z,t)}{C_f(0)} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{R_f z - qt}{\sqrt{4K_D R_f t}} \right) + \exp \left(\frac{qz}{K_D} \right) \operatorname{erfc} \left(\frac{R_f z + qt}{\sqrt{4K_D R_f t}} \right) \right]$$

We are using $z = 100$ m, $q = 10$ m/year, and $K_D = 170$ m²/year (assumed constant). R_f is given by the preceding examples. The time required to reach 10% of the source concentration (in the water, i.e., $C_f(z,t)/C_f(0) = 0.1$) is summarized in the table below. The calculation is conducted iteratively by guessing a time and then calculating concentration and continuing this process until the concentration is 10% of that at the source.

Compound	R_f	τ_{adv} Example 8.10	t for $C_f/C_f(0) = 0.1$ Equation 5.136
Chloride ion	0.4	4	1.7 year
Benzene	2.29	22.9	9.8 year
Hexachlorobutadiene	70.6	706	302 year
Pyrene	1500	15000	6430 year

The contaminant also disperses laterally and vertically which significantly reduces the concentration progressing toward the well and increases the time required to achieve any particular concentration at a downwind location. Equation 5.136 is still useful, however, to provide an indication of rate of travel. Equation 5.143 can be used to estimate the steady concentration achieved at the well (which is not subject to retardation). The effective lateral and vertical dispersion coefficients might be 10% of that in the direction of groundwater flow (17 m²/year). For a constant concentration source, the flux at the source is $q C(0)$ and $Q_m = q C(0) A$. Thus, the concentration at the well (assumed along x or directly downgradient) as a percentage of the concentration at the source and per unit area of source is

$$\frac{C}{C(0)A_s} = \frac{q}{4\pi\sqrt{D_y D_z} x}$$

For the conditions of this problem, the steady-state concentration at the well is 0.047% of that at the source per m² of source area.

8.3.5 NATURAL ATTENUATION OF CONTAMINANTS IN SOILS

It is important to recognize that transport processes do not always control the exposure to contaminants in groundwaters. Many subsurface contaminants undergo natural attenuation processes, generally microbial degradation processes, that render them harmless before they can migrate to a possible exposure point. It has become increasingly clear that we are generally unable to intervene in contaminated soil sites and return them to a pristine, precontamination state. This has caused increased attention to be focused on the natural degradative pathways that might, given sufficient time and appropriate enhancements, allow these sites to ultimately return to a pristine state after the conclusion of whatever human interventions were feasible.

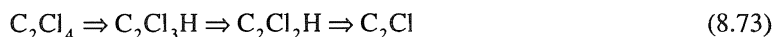
Aerobic degradation of petroleum hydrocarbons and light aromatic compounds has long been recognized and has been discussed previously in aqueous environments. In soil, these processes are generally much slower due to a variety of factors including:

- Presence of soil phase and sorption of degrading compounds onto that phase
- Limited quantities of water, oxygen and nutrients in the subsurface environment

- Trace soil or water components that might cause inhibition or toxicity among the microorganisms
- Presence of separate phase contaminants of limited solubility, slowing degradation which must generally take place in the soil water, and the high contaminant concentrations can lead to inhibition or toxicity effects

More recently it has become clear that chlorinated organics also undergo natural attenuation processes, generally via anaerobic pathways. These processes occur via a more interesting and difficult chemistry, but in many cases they appear to hold the only significant promise for ultimately achieving a return to a near pristine state for soils contaminated with these materials. The mechanisms whereby chlorinated aliphatic compounds including the common solvent contaminants — the chlorinated ethenes and ethanes — are degraded include:

Reductive dehalogenation — In reductive dehalogenation, the chlorinated compound is not used as food by the organism (i.e., as a carbon source) as are the petroleum hydrocarbons in an aerobic degrading environment. Instead the chlorinated compound serves as an electron acceptor, giving up a chlorine atom for a hydrogen atom. Generally this process occurs sequentially, with tetrachlorinated ethane (PCE) dechlorinating to trichloroethylene (TCE), to dichloroethylene (DCE), and finally to vinyl chloride.



The rate of dechlorination slows as the number of chlorine atoms remaining decreases. This means that vinyl chloride tends to be a relatively stable product of reductive dechlorination, a result that is unfortunate in that vinyl chloride is the most mobile of these compounds and has been demonstrated to be a potent human carcinogen.

Electron Donor Reactions — It is possible to degrade some chlorinated organic compounds aerobically during which the less oxidized chlorinated compounds, such as vinyl chloride, serve as electron donors and food for the microorganisms. Under the right conditions, it is possible to achieve complete mineralization of the vinyl chloride to carbon dioxide. The difficulty of course is that these are not the same conditions that give rise to the dehalogenation of the more chlorinated compounds.

Cometabolism — The final mechanism for the degradation of chlorinated organic compounds is during the degradation of other compounds. Enzymes or other substances are produced to enable the microbe to degrade one compound, but this same enzyme or factor also enables the degradation of the chlorinated compound. In such a situation, the microorganisms appear to gain no benefit from the coincidental degradation of the chlorinated compound.

Although reactive dechlorination will occur with only natural organic carbon available as a food source for the microbial population, the most rapid degradation occurs when there is more readily degradable anthropogenic carbon available. This is, of course, commonly the case in a contaminated site where residual petroleum hydrocarbons may coexist with the chlorinated contaminants. The ideal situation is rapid dechlorination in an anaerobic zone with significant anthropogenic carbon followed by movement of the contaminant plume into a region with less natural or anthropogenic carbon and oxygen concentrations greater than 1 mg/L. Then aerobic degradation pathways will take over and the partially reduced chlorinated contaminants such as vinyl chloride will be utilized as food via electron donor reactions.

In this manner the chlorinated solvent contaminant may be eliminated prior to arrival at a potential exposure site. It is also possible, at least in principle, to encourage this transition from reductive dechlorination to aerobic mineralization by the addition of dissolved oxygen to the migrating contaminant plume. Active remediation efforts to remove subsurface contamination are the subject of the next section.

8.4 REMEDIATION OF CONTAMINATED SOILS

Until about 20 years ago contaminated soil was largely ignored as an environmental concern. Only when demonstrated migration to points of contact, ingestion, or inhalation led to human and ecological risks was this problem identified and addressed. The first responses to acknowledged soil contamination issues, and still a widely used response, is removal and placement in a more secure landfill environment. Although this simply moves contaminated soil from one place to another, it can be of significant benefit due to improvements in landfill design. Often early landfills were sited in wetlands or adjacent to rivers and encouraged contaminant migration and ultimately exposure to at-risk populations. Wastes could be stabilized after removal and before or during placement to further reduce mobility after placement. Stabilization might include solidification with concrete or a similar material or direct chemical treatment of certain contaminants.

In certain cases, incineration or thermal treatment of the contaminated soil could be used to eliminate organic contaminants susceptible to destruction or removal by these means. Because these processes also necessarily entail vaporization of water and treatment or destruction of certain innocuous organic materials in the soil, the processes are energy-intensive and expensive. As a result, the approach is generally only appropriate and cost effective in soils that cannot be remediated by other means. These approaches are generally not applicable to inorganic contaminated soils.

A variety of other processes have been employed to treat contaminated soils once excavated and removed from a site. Included among these are biological degradation in dedicated bioreactors and sophisticated extraction schemes, for example, supercritical extraction, followed by the application of destruction processes to the effluent. All such options are hindered by the need to remove the soils, with its associated costs, potential disruption of surface activities, and habitat destruction.

An alternative to removal options of remediating soil is the use of *in situ* means that do not require soil removal. These are generally the options of choice if they can be demonstrated effective at reducing the volume, toxicity, or exposure to the wastes. Unfortunately, *in situ* treatments are necessarily less subject to engineering controls that can be implemented quite effectively on above-ground treatment and destruction processes. For deep contamination, contamination beneath sensitive land uses, and some other contamination issues, *in situ* treatment may be the only viable remedial approach.

Let us examine both removal and nonremoval options for soil remediation in more detail.

8.5 REMOVAL OPTIONS FOR SOIL REMEDIATION

8.5.1 INCINERATION

Incineration of solid wastes and contaminated soils are very affective means of destroying organic wastes. Efficiencies of destruction of much greater than 99% of most organic compounds are routinely observed by maintaining temperatures above 2000°F and residence times in excess of 2 s. The effectiveness of incineration is generally measured in terms of the destruction removal efficiency (DRE), measured by

$$DRE = \frac{(Q_m)_{in} - (Q_m)_{out}}{(Q_m)_{in}} \times 100 \quad (8.74)$$

where Q_m is the mass flowrate of the particular component for which destruction is desired. A reference to “four nine’s” refers to a DRE of 99.99%.

A number of problems are often cited for incineration, however, including:

- Products of incomplete combustion (PICs)
- Generation of toxic emissions due to the presence of other contaminants

- Residue of non-combustible contaminants (e.g., metals)
- High cost of soil treatment

Incomplete combustion generally occurs when the residence time and temperature of the combustion chamber are insufficient to completely convert organic compounds to carbon dioxide and water. Some starting and intermediate compounds, however, are inherently difficult to burn completely, especially in the complex soil matrix which places severe demands upon furnace design.

Generally of more concern is the presence of other contaminants, e.g., sulfur or chlorine, that can produce toxic contaminants in the stack gases. For example, 95% or more of the sulfur will oxidize to sulfur dioxide in a combustion chamber, requiring desulfurization of the flue gases or release of additional sulfur dioxide into the environment. Since the amount of sulfur dioxide produced in a small waste or soil incinerator is very little compared to a coal-fired power plant, this may not be of significant concern. The presence of chlorinated wastes in the soil means that combustion will release chlorine in the form of other chlorinated contaminants and hydrochloric acid (HCl). The HCl can cause severe corrosion problems in the incinerator system, but the release of other chlorinated compounds, such as dioxin (2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin, TCDD) is generally more troubling to the broader community. Some dioxin can always be found in the incinerator flue gases when chlorinated compounds are burned. Since dioxin is considered to be one of the most potent carcinogens known, this problem has significantly hindered the application of incineration to many wastes.

Incinerators also are of little use for dealing with noncombustible contaminants such as metals. The metals typically remain with the ash residue that requires landfilling or some other treatment method. If there is a significant reduction in volume of the material being burned, the metals in the residual could be concentrated significantly, making disposal more difficult.

Finally, the cost of incineration means that it is viable only in a few situations. Clearly incineration of a produced NAPL is appropriate because the residual volume is small, mass transfer limitations associated with a solid phase are not present, and the high heating value of such a waste means that additional fuel usage can be minimized or eliminated. For a soil containing small amounts of combustible material and large amounts of water to vaporize, however, incineration can be extremely expensive due to additional fuel requirements.

8.5.2 LANDFILLING

Isolating contaminated soil and wastes in a landfill is the oldest means of reducing exposure. Unfortunately, an insecure landfill simply moves the problem and does not reduce the volume or toxicity of the contaminated material. Most of the contaminated soil sites of greatest concern are poorly designed treatment sites. Some of the initial efforts to deal with wastes responsibly have been found in retrospect to be wanting.

The primary goal of an acceptable landfill system is elimination of opportunities for contaminants in the landfilled materials to be released to the air and water and migrate offsite. Figure 8.14 illustrates some of the techniques designed to achieve this. The landfill is lined with liners which exhibit low permeability to the percolation of water from the landfill mass. Liners may be constructed from clay, commercial stabilizers such as concrete, or soil-additive mixtures such as bentonite, or synthetic fabrics or geomembranes. Clay liners are placed by applying thin layers, providing compaction, and then adding additional layers up to a total depth of about 1 m. Soil-additive liners are prepared in a similar manner with a stabilizing additive such as bentonite being added to thin layers and providing mixing and compaction before adding additional layers. The total thickness is typically similar to that for a clay liner. Geomembranes, such as high density polyethylene, are extremely thin (e.g., 30 mils, 0.76 mm) and placed at one time. Care must be taken to avoid puncturing the thin membrane or its water retention properties are lost. All liners are typically placed with a layer of protective soil above.

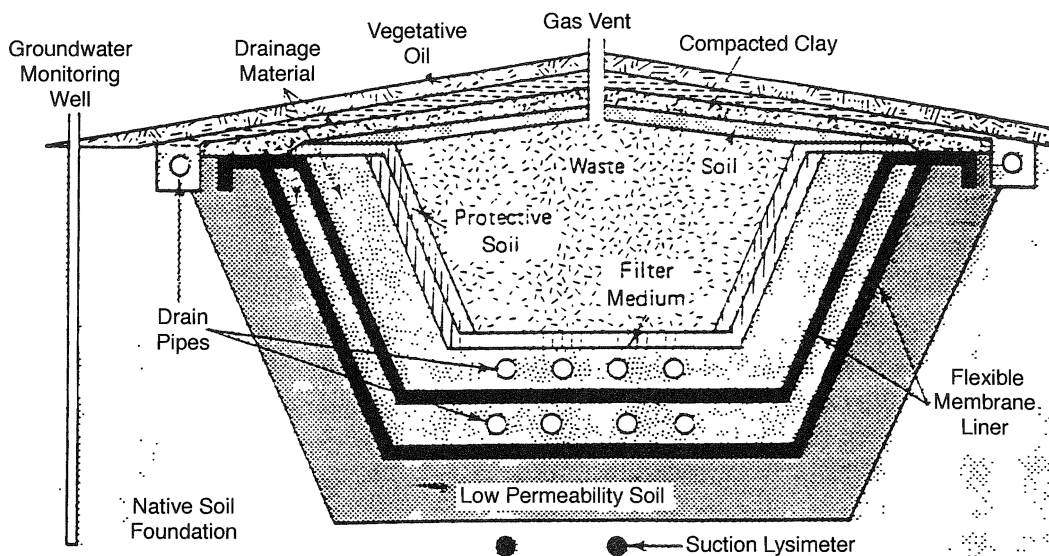


FIGURE 8.14 Schematic of a hazardous waste landfill. (From Masters, G.M. (1994) *Introduction to Environmental Science and Engineering*, Prentice-Hall, Upper Saddle River, NJ. With permission.)

The permeability of the liner is such that water should require significant time to penetrate. A water collection system, referred to as a leachate collection system, is placed above the liner to remove any water before that penetration can occur. The water collected in such a system has percolated through the waste leaching contaminants and therefore treatment of the produced waters is necessary. The type of treatment depends upon the contaminants present in the leachate waters.

In order to minimize the demands placed upon the leachate collection system, wastes are no longer placed in landfills in liquid form and a landfill cover is normally used to reduce infiltration of rainwater into the landfill. The characteristics of the cover are generally very similar to a liner — a layer of low permeability clay or similar material designed to eliminate water penetration. The landfill cover has the additional advantage of reducing vapor migration out of the landfill as illustrated previously in Example 8.6.

8.5.3 STABILIZATION/SOLIDIFICATION

Prior to landfilling solid wastes or soil in a landfill, solidification/stabilization processes are often used to further guard against contaminant release. This is especially true if the waste is primarily in the form of liquids or if the landfilled solids have a high water content. A wide variety of solidification/stabilization processes exist, but they all attempt to solidify the waste or soil and make associated contaminants less available to a leaching water phase. Portland cement, in combination with soluble silicate or fly ash, lime, and fly ash or cement of lime kiln dust, are all used to solidify and stabilize wastes. All of these reagents contain silica (SiO_2), oxides of calcium and magnesium ($\text{CaO} + \text{MgO}$), and alumina and iron oxide ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) in varying proportions. Portland cement is the result of the reaction of silica and quicklime (calcium oxide, CaO) to form calcium orthosilicates, Ca_2SiO_4 . The Portland cement reduces the mobility of any contaminants contained within its solidified matrix.

Often a bulking agent is added to the mixture to reduce the volume of cementing agent needed to perform a particular solidification. This reduces costs and in some cases a bulking agent exhibits pozzolanic activity. A pozzolan is defined as a material that exhibits cementing ability when mixed with other materials. A pozzolan will encourage solidification as well. The cementing agents that

are appropriate for a solidification process and the effectiveness of the solidified product must be evaluated by experimentation with the actual contaminated materials requiring solidification.

The effectiveness of a stabilization system is dependent upon the cementing materials employed and the nature of the contaminants in the soil. The desired reduction in contaminant availability is dependent upon the formation of a tight matrix that keeps water out and provides little exposure of the contaminant. Large amounts of organic materials such as oil and grease may deter the solidification reactions and reduce the effectiveness of the product. Soluble salts of magnesium, tin, zinc, copper or lead may cause swelling or cracking and increase the availability of the contaminants. Soluble sulfates may lead to deterioration of the cement and release of the contaminants. In addition a variety of constituents may retard setting leading to exposure to leachate water, for example, before the solidification process is complete. Finally, the setting reactions evolve significant amounts of heat and this will tend to drive volatiles out of the system. The solidified system or leachate water may show low levels of contaminants, but this may be due simply to vaporization during the solidification process. Several inventors have promoted solidification treatment processes, which upon closer investigation have proven to simply be vaporization processes.

8.5.4 *EX SITU* BIOREMEDIATION

The final *ex situ* treatment option that we mention here is off-site bioremediation. In principle this is no different from a wastewater treatment system in that the process is generally operated with sufficient water to generate a slurry. Biological activity is entirely within the aqueous phase and the presence of soil simply slows the process by reducing the amount of contaminant available in the aqueous phase. By processing the soil in an above-ground facility careful control of nutrients, oxygen, and mixing requirements can be maintained. In principle, it is possible to provide sufficient mixing to maintain the aqueous slurry at equilibrium with the soil phase. For a hydrophobic organic exhibiting a partition coefficient of K_{sw} with the soil, the concentration in the aqueous phase which is available for biodegradation can be written

$$C_w = \frac{C_{w0}}{(\epsilon + \rho_b K_{sw})} \quad (8.75)$$

where C_{w0} is the concentration that would be in the aqueous phase if none of the contaminant were sorbed to the solid fraction and ρ_b is the bulk density of the solid phase. As we have employed previously, ϵ represents the void fraction, here likely to be much greater than the 30 to 45% porosity observed *in situ*. Thus, the presence of the slurry reduces the rate of a first order reaction by the retardation factor, $\epsilon + \rho_b K_{sw}$. In reality, the reduction may be much greater due to the inability to reach equilibrium saturation with respect to the sorbing chemical.

8.6 *IN SITU* SOIL REMEDIATION PROCESSES

In situ processes avoid the costs and exposure associated with removal of the contaminated soil. Treating the soil *in situ*, however, limits the range of remedial options available and their ultimate effectiveness. Two general options exist for *in situ* remedial processes — extraction of the contaminants or destruction in-place. Extraction below the water table can take place by pumping groundwater and treatment at the surface for the removal of contaminants followed by reinjection of the water. This extraction can be enhanced by thermal or chemical means (with surfactants) to increase the solubility of the contaminants in the extracting water phase. Above the water table, extraction is normally conducted by creating a vacuum to remove vapors from the unsaturated zone. With this vapor comes the volatilized contaminants. This has proven to be an especially useful process for the hazardous components of gasolines and other light hydrocarbon fuels. These components,