

primarily benzene, toluene, ethyl benzene, and xylene (BTEX) are volatile and easily removed by this process. The remaining constituents pose a much reduced hazard to groundwater and to direct exposure by vapor inhalation than the BTEX compounds. For specific contaminants other extractive technologies also exist. For ionic species, for example, voltage placed across the soil will result in migration of charged species to a collecting cell.

In situ destruction methods typically focus on bioremediation. Microbes exist in large numbers in near-surface soils and it becomes simply a question of encouraging the right microbes and making nutrients and oxygen available to provide the desired contaminant-degrading environment. Some abiotic processes also exist to destroy certain contaminants *in situ* including *in situ* vitrification, which uses electrical power to vitrify, or convert to a glassy state, the soil and its contaminants. This process also tends to drive off volatile species due to the high temperatures that are generated.

Let us examine both extractive and destructive *in situ* remedial processes in more detail.

8.6.1 PUMP AND TREAT EXTRACTION OF CONTAMINATED GROUNDWATER

Groundwater pump and treat refers to the effort to remove contaminated groundwater or separate contaminant phases (NAPL) via withdrawal wells for above-ground treatment. In this manner the mobile component of the subsurface contaminants could be treated directly and without removal and treatment of the surrounding soil. Direct removal of a nonaqueous contaminant phase always leaves a residual that can be difficult to locate and may serve as a continuing source of contamination of groundwater. In addition, the vast majority of sparingly soluble contaminant resides in the soil phase and vast volumes of contaminated water must typically be removed to eliminate the subsurface contamination. The cleanup of a site via pump and treat technology was generally expected to require years to decades of pumping of marginally contaminated water. Even these estimates of the required time, however, proved overly optimistic. A variety of problems including site heterogeneity, the presence of long term contaminant sources, and low concentrations of contaminant in the withdrawn water combined to slow the rate of soil and groundwater recovery. It soon became clear that the cleanup of aquifers by simply pumping and treating groundwater to levels approaching that required of drinking water was generally not feasible.

Even though the objective of soil and groundwater remediation was soon recognized as unachievable, groundwater removal often resulted in reversal of groundwater gradients and thus the direction of groundwater flow. Because the primary route of exposure and risk to the ecosystem and humans was generally the result of off-site migration of contaminated liquids, reversal of the groundwater flows could eliminate or minimize these risks. Containment of off-site migration and risk became the primary objective at many pump and treat sites. Unfortunately, this commits a cleanup to operate indefinitely unless some fate processes render the contaminant harmless over time.

The contaminant processes during pump and treat remediation can be conveniently divided into (1) contaminant release from a source area (typically the NAPL residual) and (2) contaminant migration from the source area to the withdrawal point. It is important to recognize that the second of these processes emphasizes that the limitations of pump and treat remediation are not solely associated with release from the NAPL residual. In those occasions where all of the contaminant exists in the aqueous phase and no NAPL residual remains, pump and treat remediation is still limited by the ability of the withdrawn water to carry the contaminant. Contaminants of interest typically sorb to the soil phase, reducing the fraction of contaminant that can be removed by displacing the water from the pore space.

It is often assumed that the soil and the adjacent porewaters are in a state of chemical equilibrium. For the hydrophobic, or sparingly soluble, organic contaminants of interest here, the capacity of the solid phase is governed by the organic carbon fraction of the soil as discussed previously. The equilibrium relations allow one to predict the water or mobile phase concentration that can be swept toward a withdrawal well based on the loading on the soil. Linear partitioning gives a reasonable approximation of the concentration of contaminant in the adjacent water as long

as that predicted concentration is well below the compound's solubility. The water concentration cannot exceed the compound's solubility and the soil loading corresponding to this maximum water concentration is sometimes referred to as the critical mass. If the volumetric withdrawal rate from a well is Q , the maximum rate of removal of mass is then given by

$$\begin{aligned} Q_m &= QC_w \\ &= Q \frac{W_s}{\omega_{oc} K_{oc}} \quad \text{if } W_s < W_{critical} \\ &= QS_w \quad \text{if } W_s > W_{critical} \end{aligned} \quad (8.76)$$

These relations continue to assume that suspended or colloidal organic carbon does not contribute significantly to the total water concentrations. Colloidal organic carbon can cause the total water concentration to exceed the water solubility which is only a dissolved concentration.

The ratio of the total concentration in a soil system to that in the mobile phase is the retardation factor

$$R_f = \frac{C_{sw} \varepsilon + \rho_b W_s}{C_{sw}} = \varepsilon + \rho_b K_{sw} \quad (8.77)$$

This retardation factor indicates the additional mass that must be transported in the mobile phase (the porewater) to fill the immobile phase. In a transient transport process it indicates the ratio of the actual time required for a contaminant to travel between the source area and the withdrawal well and the time that would be required for a non-sorbing tracer. The minimum volume of water that must be removed to extract a non-sorbing tracer from a volume of contaminated groundwater is the same as the volume of water between the source area and the withdrawal well, or one pore volume (V_p). The minimum volume of water (V_e) or time (T_e) required to extract a sorbing contaminant (V_e) is then

$$\begin{aligned} V_e &= R_f V_p \\ \tau_e &= R_f \tau_p \end{aligned} \quad (8.78)$$

Thus, a sorbing contaminant can require significantly more water to be extracted before the contaminant can be eliminated from the system. This was explored previously in Example 8.8. Consider a soil with a porosity of 40%, a bulk density of 1.5 g/cm³, and containing 1% organic carbon. Benzene has an organic carbon based partition coefficient of 83 cm³/g. The retardation factor for benzene in this soil is estimated to be

$$\begin{aligned} R_f &= \varepsilon + \rho_b K_{sw} = \varepsilon + \rho_b \omega_{oc} K_{oc} \\ &= 0.4 + (1.5)(0.01)(83) \\ &= 1.645 \end{aligned} \quad (8.79)$$

A minimum of 1.645 pore volumes of water is required to flush water contaminated with benzene from the subsurface in this example. Note, however, that this is valid only as long as the soil phase concentration of benzene is less than the critical loading or, given a water solubility for benzene of 1780 g/m³,

$$W_{critical} = S_w f_{oc} K_{oc} = 1480 \text{ mg/kg} \quad (8.80)$$

The actual number of pore volumes or time is considerably greater than given by the above equations in any real soil environment due to two considerations

1. Not all of the contaminant (perhaps only a very small fraction of the total) is present in the porewater at the initiation of flushing. The material that is sorbed or not in contact with the mobile porewater must first be released from the source areas.
2. Uncontaminated water also is withdrawn from the well diluting the effluent and increasing the total volume of water that must be removed before cleanup of the porewater.

In practice, the initial concentrations observed in a groundwater extraction well is due to water that has long been in contact with the contaminated source areas and is equilibrated with those areas. The initial concentrations measured in a withdrawal well are relatively high. Once this water has been removed, however, the subsequent water is generally not in contact with the contaminants sufficiently to reach equilibrium and the effluent concentration decreases. This is shown in Figure 8.15. Ultimately, the concentration drops so low that the pumping is stopped. At one time, it was assumed that the aquifer had been completely remediated when this occurred. Experience has now shown us that if pumping is restarted after a period of no operation once again high concentrations will be observed because the withdrawn water will have had an opportunity to equilibrate once again with the contaminants. Continued pumping will once again result in reduction of the concentration as before. This increase upon the reinitiation of pumping is termed the rebound effect. The inability to achieve lasting low concentration groundwater as a result of pump and treat remediation is the reason that the process is considered appropriate for containment of groundwater, but not for full remediation of the aquifer and adjacent soils.

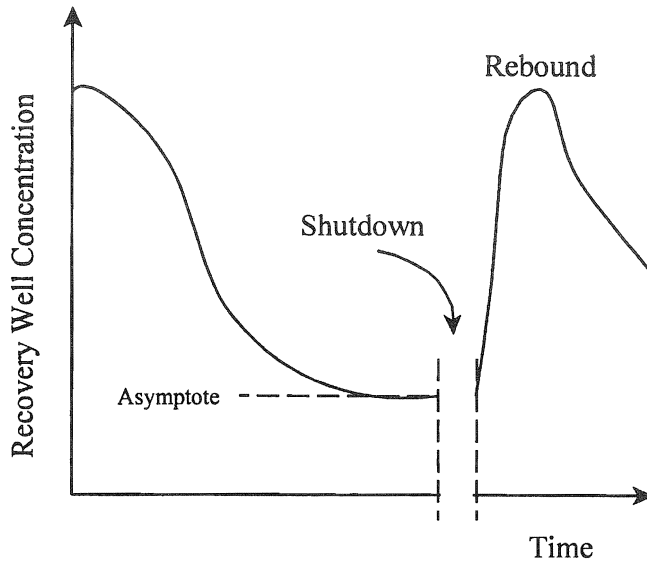


FIGURE 8.15 Concentrations in recovery well as a function of time during a groundwater removal effort. The concentration often approaches an asymptote whereupon the cleanup limit might be assumed to be reached and the recovery operation shutdown. Later restarting of the recovery operation may find a rapid rebound to near the initial well concentrations due to recontamination of the groundwater by previously inaccessible contaminants.

8.6.2 ENHANCEMENT OF PUMP AND TREAT PROCESSES

Pump and treat methods of remediation of soils are of limited usefulness when significant quantities of NAPLs exist. Due to the low solubility of most soil contaminants, large volumes of water are required to remove contaminants present in a separate phase even if it were possible to maintain the water at saturation. Because the solubility of organic compounds in water increases significantly with temperature, however, the use of steam or other sources of heating has been proposed to encourage soil remediation. As with incineration, it is necessary to raise the temperature of a large volume of inert soil and water in order to heat the contaminants. The process is energy intensive although generally the vaporization of soil water is generally avoided easing the energy demands to some extent.

Surfactants, or surface-active agents, are similarly used to increase the solubility of contaminants in the groundwater. Surfactants present at concentrations of 1 to 5% can increase the solubility of hydrophobic organic compounds by several orders of magnitude. Surfactants also reduce interfacial tension between an oily phase and the adjacent water, however. Because of the Laplace relationship

$$\Delta P = \frac{2\sigma}{r} \quad (8.81)$$

the reduction in interfacial tension translates directly into a reduction in the pressure required to mobilize the NAPL from a pore of a given radius. Thus, surfactants not only contribute to dissolution of the contaminants but also to their mobilization. The mobilization must be controlled through the application of an appropriate hydraulic gradient or by the presence of low permeability supporting strata. Any uncontrolled mobilization which results in further downward contaminant phase migration or migration toward a sensitive receptor is undesirable. As a result of this phenomenon, surfactant-enhanced remediation has received much attention and study but it has only been applied under field conditions at very few sites. Heat addition in the form of steam injection also can increase the mobility of a residual nonaqueous phase to some extent due to the corresponding reduction in viscosity of the contaminant phase. This means that a reduced pressure gradient can be applied to achieve significant mobilization.

8.6.3 VACUUM EXTRACTION IN THE UNSATURATED ZONE

A process that is similar conceptually to pump and treat of groundwater is soil vacuum extraction (SVE) in the water-unsaturated zone. In this process, a vacuum is applied to the unsaturated zone by placing a vacuum pump on a well screened in the unsaturated zone. This pulls vapors through the soil, removing any volatile components that have volatilized in the subsurface. Because the viscosity of air is low and the relative capacity of many volatile contaminants in air is quite high (the capacity of atmospheric pressure air for benzene is 0.125 atm or 12.5% at 25°C), the process is potentially quite effective. Just as we did with pump and treat of groundwater, it is possible to make some simple estimates, at least providing a minimum time required to clean a contaminated unsaturated zone via vacuum extraction. Example 8.12 considers the evaporation of a volatile organic into the flushing air phase.

Example 8.12: Volume of air required to evaporate a nonaqueous phase residual

Consider a soil with a residual NAPL saturation of 20% and a total porosity of 40%. Estimate the pore volumes of air required to completely evaporate 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/cm³ with an average molecular weight of 140.

Let us employ a basis of 1 m³ of soil as in Example 8.8. The total mass of NAPL to be removed from the soil is then

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

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

The volume of air required depends upon the partial pressure in air of pure 1,2-dichloroethane ($P_v = 0.24 \text{ atm}$), benzene ($P_v = 0.125 \text{ atm}$), and benzene from the mixture ($p_B = 0.018 \cdot 0.125 \text{ atm} = 0.00222 \text{ atm}$). The minimum volume of air 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

$$V_w = \frac{M_n}{C_a} = \frac{M_n}{\frac{P_a \cdot MW}{RT}} \quad V_w(\text{m}^3) = \begin{bmatrix} 103 \\ 177 \\ 9030 \end{bmatrix}$$

$$V_p = \frac{V_w}{\epsilon \cdot 1 \text{ m}^3} \quad V_p = \begin{bmatrix} 258 \\ 442 \\ 22600 \end{bmatrix} \quad \begin{array}{l} \text{1, 2-dichloroethane} \\ \text{Benzene} \\ \text{1\% mixture of benzene} \end{array}$$

Note that an even larger volume of air is required to flush the NAPL from the pore space than for water in Example 8.8. The difference is that it is much easier (and cheaper) to pump large volumes of low viscosity and low density air through soil than water, as is shown in Example 8.13.

A model of the dynamics of soil vacuum extraction can also be developed. That the air moves as a plug through the soil as used in groundwater pump and treat is even less likely to be an appropriate assumption. Higher air flowrates and mixing and lack of control over the entry point of the air suggests that it is more appropriate to consider the vacuum extraction of a volume of soil as though it were taking place in a zone of approximately uniform concentration. The initial contaminant mass in the soil is M , which is assumed to be distributed in the local air, water, non-aqueous, and soil phases via equilibrium relationships. If ϵ_a represents the air-filled porosity, ϵ_w , and ρ_b the bulk density of the soil, the relationship between the air concentration and the total mass of contaminant in a volume of soil, V , is

$$\begin{aligned} \frac{M}{V} &= \epsilon_a C_a + \epsilon_w C_w + \epsilon_n C_n + \rho_b W_s \\ &= \epsilon_a C_a + \epsilon_w \frac{C_a}{K_{aw}} + \epsilon_n K_{nw} \frac{C_a}{K_{aw}} + \rho_b K_{sw} \frac{C_a}{K_{aw}} \end{aligned} \quad (8.82)$$

where K_{nw} is the partition coefficient between the NAPL and water and all other terms have been defined previously. K_{nw} can be estimated by

$$K_{nw} = \frac{C_n}{C_w} = \frac{\rho_n}{S_w} \quad (8.83)$$

A material balance on the assumed well-mixed soil zone then gives

$$\begin{aligned} \frac{d(MV)}{dt} &= -QC_a \\ \frac{d}{dt} \left(\epsilon_a + \frac{\epsilon_w}{K_{aw}} + \epsilon_n \frac{K_{nw}}{K_{aw}} + \rho_b \frac{K_{sw}}{K_{aw}} \right) C_a V &= -QC_a \\ \frac{dC_a}{dt} &= -\frac{Q}{VR_f} C_a \end{aligned} \quad (8.84)$$

where

$$R_f = \left(\epsilon_a + \frac{\epsilon_w}{K_{aw}} + \epsilon_n \frac{K_{nw}}{K_{aw}} + \rho_b \frac{K_{sw}}{K_{aw}} \right)$$

This equation has the solution

$$C_a = C_a(0) e^{-\frac{Qt}{VR_f}} = \frac{M_0}{VR_f} e^{-\frac{Qt}{VR_f}} \quad (8.85)$$

Alternatively, solving for the time of remediation

$$t = -V \frac{R_f}{Q} \ln \left(\frac{C_a}{C_a(0)} \right) \quad (8.86)$$

Thus, for 99% remediation of the site gives $\ln(C_a/C_a(0)) = -4.605$ and the time is given by

$$t_{99} = 4.605 V \frac{R_f}{Q} = 4.605 V \frac{\left(\epsilon_a + \frac{\epsilon_w}{K_{aw}} + \epsilon_n \frac{K_{nw}}{K_{aw}} + \rho_b \frac{K_{sw}}{K_{aw}} \right)}{Q} \quad (8.87)$$

For the movement of the incompressible groundwater through the soil in an pump and treat system, the volumetric flowrate can be found from Darcy's Law recognizing that the head gradient is linear. For a compressible phase such as air, however, the equivalent of the pressure is governed, in one dimension, by

$$\begin{aligned} \frac{d^2(P^2)}{dx^2} &= 0 \\ P &= \left(P_0^2 - \frac{P_0^2 - P_1^2}{L} x \right)^{1/2} \end{aligned} \quad (8.88)$$

Thus, the square of the pressure driving the vapor flow is linear. Taking Darcy's Law in terms of pressure and solving for the volumetric gas flow at the withdrawal well,

$$\begin{aligned}
 q &= -\kappa_r \frac{\kappa_p}{\mu} \frac{dP}{dx} \\
 &= \frac{\kappa_r \frac{\kappa_p}{\mu} (P_0^2 - P_1^2)}{2LP_1}
 \end{aligned}
 \tag{8.89}$$

The relative permeability of the air in the soil, κ_r , is in general different from the relative permeability defined by Equation 8.38. Equation 8.38 defines the relative permeability for a wetting phase such as water displacing oil or air or oil displacing air from a medium. Air, however, is always a non-wetting phase and the Brooks and Corey model for such a phase, **in terms of the wetting phase saturation and residual saturation**, is given by

$$(\kappa_r)_a = \left[\frac{1 - (\phi_w - \phi_{wr})}{1 - \phi_w} \right]^2 \left\{ 1 - \left[\frac{\phi_w - \phi_{wr}}{1 - \phi_{wr}} \right]^{\frac{2+b}{b}} \right\}
 \tag{8.90}$$

The wetting fluid can be either water or an NAPL.

In this model, note that only the volumetric flowrate at the exit well is required by our assumption of well mixedness in the soil. The loss of contaminant from the soil is based solely on the exit concentrations and flowrate. Example 8.13 explores this model for benzene.

Example 8.13: Dynamics of remediation via soil vacuum extraction

Consider remediation of benzene-contaminated soil in the unsaturated zone via soil vacuum extraction. The saturations of water and benzene are each 25%. Assume that the residual water saturation is 5% and the organic fraction is 3%. $K_{aw} = 0.224$ and $K_{sw} = 2.61$ L/kg as in Example 8.6. Assume a soil with an intrinsic permeability of 10^{-8} cm² and a parameter $b = 2.8$. Assume the contaminated zone is 1 m² in area and 10 m in length. Then 1 atm pressure is held at one end of the contaminated zone and a vacuum well at the other end applies a pressure of 0.2 atm (0.8 atm vacuum).

The NAPL-water partition coefficient can be defined by considering the pure benzene phase-water equilibrium

$$K_{nw} = \frac{\rho_n}{S_w} = \frac{0.88 \text{ g/cm}^3}{1780 \text{ } \mu\text{g/cm}^3} = 494$$

From Equation 8.84, the retardation factor is then

$$R_f = 0.4(1 - 0.25) + \frac{(0.4)(0.25)}{0.224} + (0.4)(0.25) \frac{494}{0.224} + (1.5 \text{ gm/cm}^3) \frac{2.61 \text{ L/kg}}{0.224} = 239$$

The relative permeability from Equation 8.90 is 0.58. The air flow is given by Equation 8.89 to be 67 m/day. The time required to remove 99% of the contamination is then

$$t_{99} = 4.605 \frac{R_f V}{qA} = 4.605 \frac{(239)(10 \text{ m}^3)}{(67 \text{ m/day})(1 \text{ m}^2)} = 163 \text{ days}$$

This is quite a rapid rate of removal compared to what can be accomplished by water flushing below the water table. For this and economic reasons, soil vacuum extraction has become the standard response to volatile contaminated unsaturated soils.

Soil vapor stripping can also be enhanced by thermal means. Because the change in vapor pressure of a compound with temperature is generally much greater than an increase in water solubility with temperature, Henry's Law constant increases with temperature and the effect of retardation by sorption into the water and soil phases decreases. Thus, more of the contaminant becomes available in the vapor phase for removal by the stripping process. As with thermally enhanced contaminant removal by pumping groundwater, the additional cost of the energy supplied may offset any benefit gained. The relative merits of heating depend, as with thermally enhanced groundwater pumping, on the particular compound and soil setting.

8.6.4 *IN SITU* BIOREMEDIATION OF SOILS

Perhaps the most desirable of all treatment processes is *in situ* biodegradation to render the soil harmless and to naturally recycle the contaminants. This desirable goal has proved elusive. There are a number of compounds that undergo detoxification by microbial processes at rates that are sufficient to justify natural recovery of contaminated soils. That is, the rate of recovery of the soil by these processes is such that the contaminant will not have traveled sufficiently far off-site to pose a risk to human or ecological health before being rendered harmless by natural degradative processes. In other cases, the addition of nutrients, such as nitrogen or phosphorus or an oxygen source, may provide the enhancement needed to achieve acceptable rates of degradation. This has proven the case for many petroleum hydrocarbons that are degraded by a variety of natural microorganisms under aerobic conditions. In other cases, the presence of easily degradable compounds can lead to *cometabolism* and the resulting destruction of other more refractory compounds. This is the case with high molecular weight polycyclic aromatic hydrocarbons in the presence of lower molecular 2- and 3-ring polycyclic aromatics. Although biodegradation of these petroleum hydrocarbons is routinely accomplished, it is important to recognize that the rate of degradation depends upon a number of factors that are not easily quantified including temperature, desorption rates from the soil for soil-sorbed contaminants, and the concentration and degree of acclimation of microorganisms. Field trials and monitoring must supplement any efforts to predict the rate of the biological degradation processes.

Chlorinated solvents generally pose more difficult problems for *in situ* bioremediation than petroleum hydrocarbons. As discussed previously, dechlorination, the first steps in degradation, typically occurs via anaerobic pathways. Anaerobic microbial processes typically occur at a slower rate than aerobic processes and, in addition, the dechlorination of chlorinated ethanes can lead to the formation of vinyl chloride as discussed previously. This is a serious problem in that vinyl chloride is more mobile than its more chlorinated precursors, and more toxic. Vinyl chloride is a known human carcinogen and its presence in groundwater can lead to significant concerns about the health and safety in exposed populations. This is one of the few examples where biodegradation leads to contaminants that are more toxic than the parent compounds. Generally biodegradation leads to lower molecular weight, less toxic compounds, and under aerobic conditions, more oxidized compounds.

A recent development in the *in situ* treatment of contaminated groundwater overcomes this problem by combining both anaerobic treatment for the dechlorination of multichlorinated organic compounds followed by aerobic degradation of vinyl chloride and other aerobically degraded contaminants. This process is conducted via a process in which contaminated groundwater is forced via a gate into the treatment zone as shown in Figure 8.16. Iron filings are often used to create anaerobic, reducing conditions in the first layers of the gate for the reductive dechlorination of the multichlorinated organic species. This is followed by a zone where oxygen



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12. Plot the Brooks and Corey relative permeability function for various values of b between sand ($b = 2.8$) and a fine clay ($b \sim 10$). How does the soil type cause this function to vary?
13. If a fine sand has a capillary fringe of 20 cm above the water table, what is the effective capillary diameter to which this would correspond? Does this seem reasonable given the actual size of pores in such a media?
14. If the fine sand in Problem 13 has an intrinsic permeability of 10^{-8} cm², what is the conductivity of an oil with a viscosity of 1000 cp and a specific gravity of 0.8? What is the expected capillary rise and an estimate of the residual oil saturation if the surface tension of the oil is about 20 dyn/cm? The field capacity (or residual water saturation) of the soil is 20% of the total soil volume.
15. If the oil of Problem 14 ($\sigma_{an} = 20$ dyn/cm and $\mu_n = 1000$ cp) is spilled onto the surface of the fine sand, estimate the rate of infiltration into the soil as a function of time neglecting the effect of any ponded depth at the surface. If the total spill is 10,000 L over a 10 m² area and the soil porosity is 40%, estimate the depth to which the spill will penetrate.
16. If a soil contains a gasoline with a vapor pressure of 0.3 atm at 25°C, estimate the initial rate of evaporation immediately after a spill, assuming the air-side mass transfer coefficient is 3000 cm/h. Estimate the reduction in this rate of evaporation if the gasoline is covered with a 25-cm layer of sand with a total porosity of 40% if the sand is dry, i.e., contains no water, if the sand contains 20% water by volume (water saturation of 50%), and if a sprinkler system at the surface maintains the sand at close to 90% saturation.
17. In the situation of Problem 16, the gasoline also contains 5% benzene. Estimate the benzene evaporation rate immediately after the spill and for a sand cap with each of the moisture conditions evaluated in Problem 16.
18. Estimate a characteristic time ($T_{diff} \approx h^2 R_f / D_{iv}$) for benzene vapors to penetrate a newly placed soil cap 25 cm thick (h) under the following conditions: (1) dry sand cap with 40% porosity; (2) moist sand cap with a volumetric content of 20% (water saturation of 50%), and moist sand cap (as in condition 2) with 5% organic carbon added to increase sorption. The bulk density of the cap soil is 1.5 g/cm³.
19. The gasoline spill referred to in the preceding problems has migrated to the water table. Estimate the maximum concentration of benzene that would be found in the water in contact with the floating pool of gasoline (benzene is 5% of the gasoline).
20. If 100 L of 1,2-dichloroethane (EDC) is distributed over a cubic region 10 m on a side and the average groundwater flow through this region is 30 m/year, estimate the minimum amount of time required to completely dissolve the trichloroethylene.
21. If the soil through which the groundwater moves in Problem 20 is 40% porosity sand with essentially no sorption potential, estimate the time required for the EDC to be detected at concentrations exceeding 1 µg/L at a drinking water well located 100 m downgradient. Repeat the calculation if the soil contains 5% organic carbon (i.e., if sorption cannot be neglected).
22. Compare the various disposal options for organic-contaminated soil after removal from a contaminated site. How might the feasibility of these options change if the contaminant is a metal?
23. Under the conditions of Problem 19, plot the minimum removal time as a function of groundwater flowrate.
24. Is it feasible to remove the EDC discussed in Problem 19 by placement of withdrawal and injection water wells and increasing the local groundwater flow? Fully support your answer.
25. If 100 L of gasoline ($P_v = 0.3$ atm at 25°C) is trapped within an unsaturated zone of a cubic soil region 10 m on a side, estimate the minimum time required for removal if a vacuum system applies a pressure differential of 0.25 atm across this region. Make the calculation for each of the following soils. In each soil the total porosity is 40%. Sandy soil with $\kappa_p = 10^{-8}$ cm², $b = 2.8$, $\phi_w = 0.2$. Silty soil with $\kappa_p = 10^{-10}$ cm², $b = 5$, $\phi_w = 0.4$. Silty, clayey soil with $\kappa_p = 10^{-12}$ cm², $b = 10$, $\phi_w = 0.6$.
26. If 100 L of gasoline containing 5% benzene is trapped within an unsaturated zone of a cubic soil region 10 m on a side, estimate the minimum time required for removal of the benzene if a vacuum system applies a pressure differential of 0.25 atm across this region. Make the calculation for each of the following soils. In each soil the total porosity is 40%. Sandy soil with $\kappa_p = 10^{-8}$ cm², $b = 2.8$, $\phi_w = 0.2$. Silty soil with $\kappa_p = 10^{-10}$ cm², $b = 5$, $\phi_w = 0.4$. Silty, clayey soil with $\kappa_p = 10^{-12}$ cm², $b = 10$, $\phi_w = 0.6$.

27. If 100 L of EDC is trapped within an unsaturated zone of a cubic soil region 10 m on a side, estimate the minimum time required for removal if a vacuum system applies a pressure differential of 0.25 atm across this region. Make the calculation for each of the following soils. In each soil the total porosity is 40%. Sandy soil with $\kappa_p = 10^{-8} \text{ cm}^2$, $b = 2.8$, $\phi_w = 0.2$. Silty soil with $\kappa_p = 10^{-10} \text{ cm}^2$, $b = 5$, $\phi_w = 0.4$. Silty, clayey soil with $\kappa_p = 10^{-12} \text{ cm}^2$, $b = 10$, $\phi_w = 0.6$.

28. Estimate a characteristic time for the transport of EDC to an air withdrawal well located 10 m away from the contaminated region. Consider each of the following soils. The total porosity is 40% and the bulk density is 1.5 g/cm^3 of each soil. Sandy soil with $\kappa_p = 10^{-8} \text{ cm}^2$, $b = 2.8$, $\phi_w = 0.2$, $\omega_{oc} = 0.005$. Silty soil with $\kappa_p = 10^{-10} \text{ cm}^2$, $b = 5$, $\phi_w = 0.4$, $\omega_{oc} = 0.02$. Silty, clayey soil with $\kappa_p = 10^{-12} \text{ cm}^2$, $b = 10$, $\phi_w = 0.6$, $\omega_{oc} = 0.05$.

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