Unsaturated Zone Hydrology for Scientists and Engineers

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Soil Remediation Techniques

INTRODUCTION

Corrective-action objectives for remediating soil contamination can be achieved by a large number of technologies. Numerous remedial-action alternatives that have proved to be effective in contaminated soil cleanups are reviewed here, and discussed as having potential implementation. Alternative remediation techniques discussed do not include free-product recovery. This chapter presents techniques for determining corrective-action criteria, and provides brief descriptions and analyses of potential alternative remediation techniques that can be applicable to contaminated soil. Site-specific differences need to be taken into account when selecting a preferred alternative.

15.1 SOIL CORRECTIVE-ACTION CRITERIA

Background

While many different kinds of contaminants can be remediated in soils, the most common are hydrocarbons and other organics. The question then, is "how clean is clean?" when considering practical conditions for making a given contaminated site available for public or other uses. The U.S. Environmental Protection Agency (EPA 1989a) has studied soilresponse action levels based on potential contaminant migration to the underlying ground water. In general, EPA considers that a remediation level in soil does not have to be as clean as the ground water, because ground water is a drinking source. A general rule-of-thumb is that soil remediation levels may have 100 times more contaminants than ground water. Thus, if there were 100 milligrams (mg) of total petroleum hydrocarbons (TPH) in one kilogram (kg) of soil, and that contaminant level were acceptable to a regulator, the ground water would have to be 100 times cleaner, or about 1 mg per liter (mg/L) to be acceptable to the same regulator. In the United States, some individual states have the authority to set remediation levels for both soil and water. For soil, there is a very large range of remediation levels in considering TPH. This range varies from background (or ambient) TPH concentrations to over 1,000 parts per million (ppm) TPH. Figure 15.1 shows TPH remediation levels for all 50 of the United States. Several orders of magnitude separate the recommended TPH soil remediation levels. For example, New Hampshire has a 1-ppm remediation level for TPH, whereas California has a 1,000-ppm TPH soil remediation level. In light of this large TPH remediation level difference from state to state, and because certain remediation technologies work well for cleaning soil to certain levels, it is probably best to know what the remediation

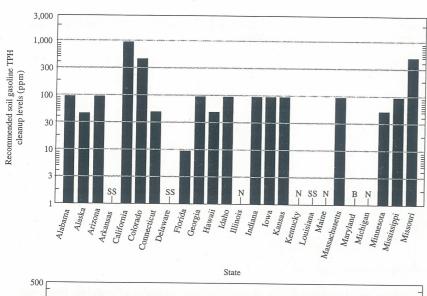
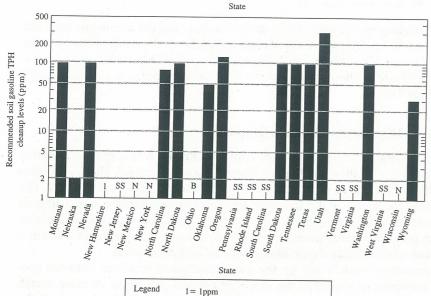


Figure 15.1 Recommended soil TPH remediation levels (data from Marencik 1991)



SS = Site-specific standard N = No TPH standard established

B = Background

level for a soil will be before selecting a remediation technology. Additionally, it is best to negotiate a remediation level with the regulator prior to attempting remediation; it might even be advantageous to negotiate a remediation level with the option of changing the level if the technology cannot meet the negotiated soil remediation level. States in figure 15.1 that do not have established TPH remediation levels must negotiate the soil-remediation level prior to acceptance of the remediation plan.

General Principles of Application

The level of remediation required depends on many site-specific factors, as well as the hazardous substances involved, and the degree of public exposure at a given site. The methods and models used as tools in the analysis of contaminant migration to ground water vary from

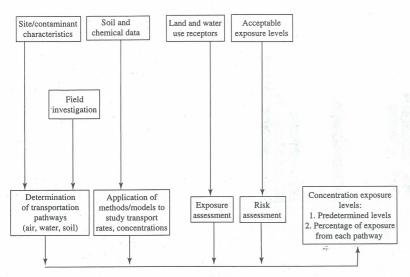


Figure 15.2 Process for determining soil cleanup levels

one site to another, depending on the unique site characteristics and the chemicals involved. In general, the milestones in the determination of cleanup levels are depicted as shown in figure 15.2 (EPA 1989a). The aspects of figure 15.2 discussed here deal only with fate and transport of contaminants from soil to the ground water. Other aspects in figure 15.2 are treated in other documents (EPA 1989b).

Fate and Transport Models for Evaluating Migration to Ground Water

The fate and transport factors affecting subsurface contaminant-migration processes within the environment are broadly classified as physical, chemical, and microbial. These processes and the factors affecting their relative significance at a given site are listed in table 15.1. The variety and quantity of such factors make the exposure-route determination more difficult for ground water than for other exposure pathways. Consequently, arriving at an acceptable cleanup level based on potential contaminant migration to the ground water can warrant a detailed characterization of the site, and careful selection of analytical tools.

Transport and speciation models rely on the quantification of relations between specific parameters and variables to simulate the effect of natural processes. A close match between the natural processes at the site and those of the selected model has to exist if the modeling exercise is to provide a satisfactory result. Transport processes strongly depend upon chemical speciation. The simplest approach to estimating the concentration of a hazardous constituent is to assume it behaves as a conservative substance (i.e., it does not react with its surroundings). The inclusion of degradative processes required (e.g., biodegradation and hydrolysis) to model the fate of a given compound considerably increases the chemical and environmental data needed. Where such degradative processes are suspected, a more sophisticated assessment is necessary.

The prediction of contaminant transport and transformation involves the following six steps (EPA 1989a):

- **Step 1** Determination of fate-influencing processes such as transport parameters and partition coefficients
- Step 2 Delineation of environmental compartments
- Step 3 Representation of soil/hydrogeologic processes
- **Step 4** Mathematical representation of speciation processes such as acid-base and sorption

TABLE 15.1	Fate and Transport Processes Affecting Subsurface
Contaminant	Migration

Category	Process	Factors affecting process
Physical	Advection Dispersion Flow in fractures Diffusion Precipitation Dissolution	Topography Climate Precipitation Soil type Vegetative cover Depth to ground water Soil-hydraulic conductivity Soil-void ratio Soil-moisture characteristics Geology Hydrology Morphology
Chemical	Partitioning	Physical, chemical properties of contaminants Geology
	Equilibrium speciation acid/base equilibration organic complexation inorganic complexation	
	Abiotic transformation hydrolysisoxidation/reduction	
Microbial	Oxidation/reduction and hydrolysis	Geology Contaminants Microbial environment

Source: Data from EPA (1989a)

Step 5 Mathematical representation of transport and transformation processes such as precipitation, degradation, dissolution, advection, and solubility

Step 6 Determination of contaminant load and mode of entry into the environmental media.

The following fate and transport methods can be considered for use in estimating soil levels for contaminated sites. These models are analytical, and include techniques appropriate for both organics and inorganics. These methods include: the Freundlich equation; allowable concentration model; Summers model; modified Summers model; Single Pathway Preliminary Pollutant Limit Values (SPPPLV) model; contaminant profile model; decision-tree process; and the Regulatory and Investigative Treatment Zone (RITZ) model. Additional models are also available and are presented in more detail in EPA (1989a). Depending on the complexity of the site and the desires of the regulator, other models can also be appropriate.

Freundlich equation The Freundlich method is designed for use with organic compounds. It is used to determine a dry-soil contaminant concentration that would elevate the ground-water contaminant levels above a given ground water quality goal, such as a maximum contaminant level (MCL), set by a regulator. A dry-soil contaminant level is calculated for each individual or group of organic contaminants of concern. The Freundlich equation is:

$$Q_e = (K_d)(C_e)^{(1/n)} (15.1)$$

where Q_e is the dry-weight concentration of the nonionic organic compound in the soil (mg/kg), C_e is the equilibrium pore-space aqueous concentration (mg/L), n is an experimentally derived exponential adjustment factor to the adsorption isotherm (unitless), and K_d is the soil:water partition coefficient [(mg/kg)/(mg/L)].

The soil:water partition coefficient K_d is usually normalized to the organic-carbon content of the mixture (K_{oc}) , which can be given as:

$$K_d = (K_{\rm oc})(f_{\rm oc}) \tag{15.2}$$

where $K_{\rm oc}$ is the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil to the concentration of the chemical in solution at equilibrium and $f_{\rm oc}$ is the fraction of organic-carbon content of the soil. Equation 15.2 is valid for carbon contents above about 0.1 percent. $K_{\rm oc}$ has been related to the aqueous solubility (S) and the octanol:water partition coefficient ($K_{\rm ow}$) of a chemical. The relations usually take the form of

$$\log K_{\rm oc} = (c) \log (S \qquad \text{or} \qquad K_{\rm ow}) + d \tag{15.3}$$

where c and d are empirical regression coefficients. Table 15.2 lists the selected equations which use either S or $K_{\rm ow}$ to estimate $K_{\rm oc}$. The valid use of the equations in table 15.2 requires that the medium of interest possess the organic contents that fall within the range of those used to develop the equations. It is important to recognize that these equations are not universally applicable to all organic chemicals in all soil systems and should, therefore, be used with caution (Dragun 1988). Table 15.3 is a summary of selected octanol:water partition coefficients $K_{\rm ow}$, and water solubility S for organic and inorganic chemicals (Dragun 1988; Cohen, Mercer, and Matthews 1993). These values can be used with the equations in table 15.2 to estimate values of $K_{\rm oc}$ in order to compute values of K_d for use in the Freundlich equation.

In order to use the Freundlich equation, a value of C_e has to be derived; this requires several calculations. The first involves using the following equation (CH₂M-Hill 1985):

$$\frac{C}{C_o} = \operatorname{erf}\left[\frac{Z}{2(D_t X)^{1/2}}\right] \cdot \operatorname{erf}\left[\frac{Y}{4(D_t X)^{1/2}}\right]$$
(15.4)

where C_o is the original ground water concentration at the source area $(\mu g/L)$, C is the concentration at the receptor well or compliance area (soil) $(\mu g/L)$, Z is the saturated-zone thickness (m), X is the distance of the compliance point from the source (m), Y is the width of the lateral extent of the source (m), D_t is the transverse dispersivity (m), and erf is the error function.

By using a health-based level or ground water quality value (e.g., an MCL for C), the desired concentration in the ground water directly beneath the contaminant source C_o that correlates with this source can be calculated. After the original source concentration C_o is obtained, the percolation rate through the unsaturated zone is calculated.

$$PR = (p)(A) \tag{15.5}$$

where PR is the percolation rate (m^3/yr) , p is the percolation (amount of rainfall per year at the site) (m/yr), and A is the total area of the site contaminated with a specific contaminant (m^2) .

The next calculation required to estimate migration is the lateral ground water flow (LGWF):

$$LGWF = (Z)(v)(L)$$
 (15.6)

where LGWF is the lateral ground water flow (m^3/yr) , Z is the aquifer saturated thickness (m), V is the ground water velocity (m/yr), and L is the lateral source length (m).

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TABLE 15.2 Predictive Equations for K_{oc}

Equation: $\log K_{\rm oc} = -0.54 \log S + 0.44$

S = water solubility (mole fraction)

 $\log K_{\rm oc} = \log K_{\rm ow} - 0.21$

Reference: Karickhoff, Brown, and Scott (1979)

Soil percent-organic-carbon range: 0.09 to 3.29

Organic chemicals utilized to develop K_{oc} :

anthracine 2-methylnaphthalene benzene naphthalene

hexachlorobiphenyl phananthrene methoxychlor pyrene 9-methylanthracene tetracene

Equation: $\log K_{\rm oc} = -0.557 \log S + 4.277$

S = water solubility (micromoles/liter)

Reference: Chiou, Peters, and Freed (1979)

Soil percent-organic-matter content (one soil): 1.6

Organic chemicals utilized to develop K_{oc} :

DDT 1,2-dichloroethane 1,2-dibromo-3-chloropropane 1,2-dichloropropane

1,2-dibromomethane 2,2',4,4',5,5'-hexachlorobiphenyl parathion 1,1,2,

2-tetrachloroethane

1,2-dichlorobenzene lindane 2,2',5,5'-tetrachlorobiphenyl tetrachloroethene 2,4'-dichlorobiphenyl

1,1,1-trichloroethane

 $\log K_{\rm oc} = 0.937 \log K_{\rm ow} - 0.006$ Equation:

Brown and Flagg (1981) Reference:

Sediment organic carbon content (one sediment): 0.033

Organic chemicals utilized to develop K_{oc} :

atrazine simazine cyanazine trietazine ipazine trifluralin

propazine trifluralin photodegradation products

Equation: $\log K_{\rm oc} = 1.029 \log K_{\rm ow} - 0.18$

Reference: Rao and Davidson (1980)

Soil organic carbon range: not specified

Organic chemicals utilized to develop K_{oc} :

atrazine DDT diuron methylparathion bromacil dicamba lindane simazine carbofuran dichlobenil malathion terbacil

2,4-D

Equation: $\log K_{\rm oc} = 0.524 \log K_{\rm ow} + 0.855$

Reference: Briggs (1973)

Soil percent-organic-matter range: 1.0 - 4.0

TABLE 15.2 Predictive Equations for K_{oc} (continued)

Organic chemical utilized to develop K_{oc} :

3-(3-bromophenyl)urea 3-(4-bromophenyl)urea

3-(3-chlorophenyl)urea

3-(3-chloro-4-methoxyphenyl)urea

3-(3,4-dichlorophenyl)urea

1,1-dimethyl-3-(4-chlorophenyl)urea 1,1-dimethyl-3-(3-chloro-4-methoxyphenyl)urea

1,1-dimethyl-3-(3,4-dichlorophenyl)urea

1,1-dimethyl-3-(3-trifluoromethylphenyl)urea

3-(3-fluorophenyl)urea 3-(4-fluorophenyl)urea

3-(3-hydroxyphenyl)urea

Equation:

 $\log K_{\rm oc} = -0.82 \log S + 4.07$ S = water solubility (ppm)

Reference:

Means et al. (1980)

Soil percent-organic-carbon range:

0.11 to 2.38

Organic chemicals utilized to develop K_{oc} :

debenzanthracene

3-methylcholanthrene

1-methyl-3-(3-chlorophenyl)urea

1-methyl-3-(3,4-dichlorophenyl)

3-(3-trifluoromethylphenyl)urea

chlorophenyl)urea

3-(4-sulfophenyl)urea

phenylurea

1-methyl-1-methoxy-3-(4-bromo-3-

1-methyl-3-(3-chloro-4-methoxyphenyl)urea

1-methyl-1-methoxy-3-(4-bromophenyl)urea 1-methyl-1-methoxy-3(4-chlorophenyl)urea

1-methyl-1-methoxy-3-(3,4-dichlorophenyl)urea

7,12-dimethylbenz[a]anthracene pyrene

Equation:

 $\log K_{\rm oc} = 0.72 \log K_{\rm ow} + 0.49$

Reference:

Schwartzenback and Westall (1981)

Soil percent-organic-matter range:

< 0.01-33.0

Organic chemicals utilized to develop K_{oc} :

n-butylbenzene

1,2,4,5-tetramethylbenzene

chlorobenzene

toluene

1,4-dichlorobenzene 1,4-dimethylbenzene

1,2,3-trichlorobenzene 1,2,4-trichlorobenzene 1,2,3,4-tetrachlorobenzene 1,2,3-trimethylbenzene

1,2,4,5-tetrachlorobenzene 1,3,5-trimethylbenzene tetrachloroethylene

Equation:

 $\log K_{\rm oc} = -0.594 \log S - 0.197$

S = water solubility (mole fraction)

 $\log K_{\rm oc} = 0.989 \log K_{\rm ow} - 0.346$

Reference: Karickhoff (1981)

Soil percent-organic-carbon range:

Organic chemicals utilized to develop K_{oc} :

anthracene phenanthrene

benzene pyrene

naphalene

Equation:

 $\log K_{\rm oc} = -0.55 \log S + 3.64$

S = water solubility (mg/L)

 $\log K_{\rm oc} = 0.544 \log K_{\rm ow} + 1.377$

Reference: Kenega and Goring (1980)

Soil percent-organic-matter range:

not specified

(continued)

Organic chemicals utilized to develop K_{oc} :

aldrin dinitramine norfluorazon ametryn dinoseb oxadiazon anthracene dipropetryn parathion asulam disulfoton pebulate atrazine diuron 2,2',4,5,5'-pentachlorobiphenyl benefin **EPTC** pentachlorophenol benzene ethion phenanthrene bromacil ethylene bromide phenol sec-bumeton fenuron picloram butralin fluchloralin phorate carbaryl fluometuron profluralin carbophenothion 2,2',4,4',5,5'-hexachlorobiphenyl prometon chloramben hexachlorobenzene prometryn chloramben methyl ester ipazine pronamide chlobromuron isocil propachlor chloroneb isopropalin propazine 6-chloropicolinic acid leptophos propham chloroxuron lindane pyrazon chlorpropham linuron pyrene chlorpyrifos methaxole pyroxychlor chlorpyrifos-methyl metobromuron silvex chlorthiamid methomyl simazine crotoxyphos methoxychlor 2,4,5-T cyanazine 2-methoxy-3,5,6-trichloropyridine tebuthiuron cycloate 9-methylanthracene terbacil 2,4-D acid methyl isothiocyanate terbutryn DDT 2-methylnaphthalene tetracene diallate methyl parathion thiabendazole diamidaphos metribuzin triallate ibromochloropropane monolinuron 3,5,6-trichloro-2-pyridinol dicamba monuron triclopyr dichlobenil naphthalene trietazine 3,6-dichloropicolinic acid napropamide trifluralin cis-1,3-dichloropropene neburon trans-1,3-dichloropropene nitralin diflubenzuron nitrapyrin

The LGWF is then added to the percolation rate to obtain the total flow in the saturated zone underlying the contaminated area.

$$Q_t = LGWF + PR (15.7)$$

where Q_t is the total flow (m³/yr), LGWF is the lateral ground water flow (m³/yr), and PR is the percolation rate (m³/yr). Next, to determine the annual mass of contaminant (X) leaching from the unsaturated zone, the following relation is used:

$$\frac{X}{Q_t} = C_o \tag{15.8}$$

where X is the annual mass of contaminant leaching from the unsaturated zone (mg/yr) and Q_t is the total flow in the saturated zone underlying the site (m³/yr). Thus, to cause a contaminant level of C_o in the saturated zone underlying the contaminated area requires:

$$X = (C_o)(Q_t) \tag{15.9}$$

mass of contaminant leaching from the unsaturated zone annually.

TABLE 15.3 Solubility and Octanol-Water Partition Coefficients for Selected Organic and Inorganic Constituents

Compound	Solubility in water at 25 °C (mg/L)	Log ₁₀ Octanol-water partition coefficient	Compound	Solubility in water at 25 °C (mg/L)	Log ₁₀ Octanol–water partition coefficient
Ethers			Polynuclear aromatic		
Bis(chloromethyl)	22,000	-0.38	hydrocarbons		
Bis(2-chloroethyl)	10,200	1.58	2-Chloronaphthalene	6.74	4.12
	1,700	2.58	Benzo(a)anthracene	0.014	5.16
Bis(2-chloroisopropyl)	15,000	1.28	Benzo(b)fluoranthene	6.75	3.10
2-chloroethyl vinyl	3.3	4.08	Benzo(k)fluoranthene	0.00055	6.84
4-chlorophenyl phenyl	3.3	5.15		0.0033	6.04
4-Bromophenyl phenyl	91 000		Benzo(a)pyrene		7.66
Bis(2-chloroethoxy)methane	81,000	1.26	Indeno(1,2,3-cd)pyrene	0.62	
Phthalates			Dibenzo(a,h)anthracene	0.0005	5.97
Dimethyl	4,300	2.12	Benzo(ghi)perylene	0.00026	7.23
Diethlyl	1,000	3.22	Acenaphthene	3.42	4.33
	13	5.2	Acenaphthylene	3.93	4.07
Di-m-butyl	3	9.2	Anthracene	0.073	4.45
Di-n-octyl	0.4	9.2 8.73	Chrysene	0.002	5.61
Bis(2-ethylhexl)			Fluoranthene	0.26	5.33
Butyl benyl	2.9	5.8	Fluorene	1.98	4.18
Nitrogen compounds			Naphthalene	34.4	3.37
N-nitrosodimethylamine	miscible	0.06	Phenanthrene	1.29	4.46
	IIIIscible	2.57	Pyrene	0.14	5.32
N-nitrosodiphenylamine		1.31			
N-nitroso-di-n-propylamine	400		PCBs and related compounds		
Benzidine	400	1.81	Aroclor 1016	0.42	4.38
3,3'-Dichlorobenzicine	224	3.02	Aroclor 1221	15	2.8
1,2-Diphenylhydrazine	221	3.03	Aroclor 1232	1.45	3.2
Acrylonitrile	73,500	-0.14	Aroclor 1242	0.24	4.11
Pl1-			Aroclor 1248	0.054	5.75
Phenols	67,000	1.46	Aroclor 1254	0.012	6.03
Phenol		2.17	Aroclor 1260	0.0027	7.14
2-Chlorophenol	28,500		71100101 1200	0.0027	7.11
2,4-Dichlorophenol	4,500	2.75	Halogenated hydrocarbons		
2,4,6-Trichlorophenol	800	3.38		6,450–7,250	0.91
Pentachlorophenol	14	5.01	Methylene chloride	16,700	1.25
2-Nitrophenol	2,100	1.76	Chloroform	9,600	1.97
4-Nitrophenol	16,000	1.91	Carbon tetrachloride	800	2.64
2,4-Dinitrophenol	5,600	4.09	Chloroethane	5,740	1.54
2,4-Dimethylphenol	17,000	2.50			
p-Chloro-m-cresol	3,850	2.95	1,1-Dichloroethane 1,2-Dichloroethane	5,500	1.79 1.48
4,6-Dinitro-o-cresol	250	2.85		8,300	
. 75 3.			1,1,1-Trichloroethane	950	2.17
Aromatics	4.000	2.12	1,1,2-Trichloroethane	4,500	2.17
Benzene	1,800	2.13	1,1,2,2-Tetrachloroethane	2,900	2.56
Chlorobenzene	472	2.84	Hexachloroethane	50	3.34
1,2-Dichlorobenzene	145	3.38	Vinyl chloride	1.1	0.60
1,3-Dichlorobenzene	123	3.38	1,2-Dichloropropane	2,700	2.28
1,4-Dichlorobenzene	79	3.39	1,3-Dichloropropene	2,700	1.98
1,2,4-Trichlorobenzene	30	4.26	Hexachlorobutadiene	2	3.74
Hexachlorobenzene	6	6.18	Hexachlorocyclopentadiene	0.805	3.99
Ethylbenzene	206	3.15	Methyl bromide	900	1.1
Nitrobenzene	1,900	1.85	Dichlorobromomethane		1.88
Toluene	535	2.69	Chlorodibromomethane		2.09
2,4-Dinitrotoluene	270	2.01	Bromoform	3,190	2.30
2,6-Dinitrotoluene		2.05	Dichlorodifluoromethane	280	2.16
					(continued

TABLE 15.3 Solubility and Octanol-Water Partition Coefficients for Selected Organic and Inorganic Constituents (continued)

Compound	Solubility in water at 25 °C (mg/L)	Log ₁₀ Octanol-water partition coefficient †	Compound	Solubility in water at 25 °C (mg/L)	Log ₁₀ Octanol–water partition coefficient [†]
Trichlorofuoromethane	1,100	2.53	Selected metal compounds	SoftElm	
Trichloroethylene	1,100	2.29	Antimonic acid and oxides	Very slightly soluble	
1,1-Dichloroethylene	5,000	1.48	Arsenic oxide @ 16 °C	1.5×10^{6}	
1,2-Trans-dichloroethylene	6,300	1.48	Arsenic oxide @ 20 °C	3.7×10^{6}	
Tetrachloroethylene	150	2.88	Beryllium oxide @ 30 °C	0.2	
Pesticides			Cadmium chloride @ 20 °C Cadmium sulfide @ 18 °C	1.4×10^6 1.3	
α -Endosulfan	0.53	3.55	Cadmium hydroxide @ 25 °C	2.6	
β -Endosulfan	0.28	3.62	Chromium oxide		
α -BHC	2.0	3.81	(as H ₂ CrO ₄) @ 0 °C	6.17×10^{5}	
β-BHC	0.24	3.80	Copper chloride @ 0 °C	7.06×10^{5}	
δ-ΒΗС	31.4	4.14	Lead oxide @ 20 °C	17	
gamma-BHC	7.5	3.72	Lead chloride @ 20 °C	9.9×10^{3}	
Aldrin	0.011	5.17	Mercuric oxide @ 25 °C	53	
Dieldrin	0.20		Mercuric sulfide (α) @ 18 °C	0.01	
4,4'-DDE	0.12	5.69	Mercuric sulfide	Insoluble	
4,4'-DDT	0.006	3.98	Mercuric chloride @ 20 °C	6.9×10^{4}	
4,4'-DDD	0.02	5.98	Nickel sulfide @ 18 °C	3.6	
Endrin	0.26	5.6	Nickel chloride @ 20 °C	6.42×10^{5}	
Heptachlor	0.056	4.40	Selenium dioxide @ 14 °C	3.84×10^{5}	
Heptachlor epoxide	0.35	3.65	Selenium trioxide Silver oxide @ 20 °C	Very soluble	
Chlordane	1.85	2.78	Silver chloride @ 10 °C	0–13	
Toxaphene	1.75	3.3	Thallium sulfide @ 20 °C	0.89	
Oxygenated compounds			Thallium chloride @ 16 °C Zinc oxide @ 29 °C	2.0×10^{2} 2.9×10^{3}	
Acrolein	400,000	-0.090	Zinc oxide @ 29 °C Zinc chloride @ 25 °C	1.6 4.32×10^{6}	

†Not available for metals.

The next step in the procedure is to determine the average unsaturated pore-space aqueous concentration C_e that causes the C_o in the saturated zone directly beneath the site to exceed the calculated C_o from equation 15.4. This is estimated by dividing the annual mass of the contaminant X escaping from the unsaturated zone by the percolation rate PR, or:

$$C_e = \frac{X}{PR} \tag{15.10}$$

Using a literature K_d value or K_d calculated from equation 15.2 and an estimated value for 1/n gives an estimate of Q_e . The resultant dry-soil concentration is the suggested level of cleanup that derives a contaminant concentration in compliance with a ground water quality goal or a health-based value at a receptor well.

The basic limitations of the Freundlich isotherm method include the assumptions that adsorption is completely reversible, and that the rates of adsorption and desorption result in instantaneous equilibrium. These assumptions are probably not correct, thus may never be achieved. Also, it is often assumed that the (n) value used to obtain the adjustment factor is unity, making the isotherm linear. In reality, values of n are experimentally derived and are different for different ranges of the Freundlich isotherm. The time investment required to derive n is often a constraint on using this method.

QUESTION 15.1

Find the original groundwater concentration C_o at a source area for a Polynuclear Aromatic (PNA), whose health-based level C is 0.029 $\mu g/L$ (10^{-6} unit cancer-risk factor direct-ingestion level) if the saturated-zone thickness Z is 16 feet; the distance of the compliance point from the source X is 1,000 feet; the width of the lateral extent of the source Y is 2,400 feet; and the transverse dispersivity D_t is 13 feet.

QUESTION 15.2

Find the equilibrium pore-space aqueous concentration for the PNA value of C_o in Question 15.1 if the annual precipitation at the site is 11.15 in/yr, the site area is 28 acres, and the saturated ground water velocity of the underlying soil is 60 ft/yr.

Allowable concentration model This method estimates the allowable cleanup concentration of a soil contaminant that corresponds to the maximum allowable contaminant level in the underlying ground water at some down-gradient receptor. The maximum allowable contaminant level in ground water is usually available from local regulators.

To use this method, the initial source concentration C_o is calculated from equation 15.4. After calculating the initial source concentration, the next step is to convert the maximum allowable ground water contamination concentration (assumed to be C in equation 15.4) to an allowable soil-contaminant concentration. This is done by using the partition coefficient K_d , defined by the following, where C_o is assumed to be C_{water} :

$$K_d = \frac{C_{\text{soil}}}{C_{\text{water}}} \tag{15.11}$$

Methods for determining K_d are available from EPA (1989a) or from sources in the literature. The required soil-cleanup concentration level can be determined by multiplying the allowable concentration in the ground water directly beneath the site by the partition coefficient:

$$C_{\text{soil}} = (C_{\text{water}})(K_d) \tag{15.12}$$

Summers model The Summers model (Summers, Gherini, and Chen 1980) was developed to estimate the point at which contaminant concentrations in soil produce ground water contaminant concentrations at acceptable levels. The resultant soil-contaminant concentration can then be used to specify a cleanup goal. The model assumes that a percentage of the rainfall at a given site infiltrates the surface and desorbs contaminants from the soil, based on equilibrium K_d values. The model also assumes that this contaminated infiltration mixes completely with the ground water beneath a given contaminant site, resulting in an equilibrium ground water concentration.

The model begins by estimating the concentration of the contaminant infiltration that results in ground water concentrations at or below target level. The mixing rates of uncontaminated ground water with contaminated infiltration, and the resultant concentrations in ground water can be calculated from:

$$C_{gw} = \frac{(Q_p C_p)(Q_A C_A)}{Q_p + Q_A}$$
 (15.13)

where: C_{gw} is the contaminant concentration in the ground water $(\mu g/L)$; $Q_p = (VD_z)(A_p)$ is the volumetric flow rate of infiltration (pore water) into the aquifer (m^3/day) ; $VD_z = (V_s)(e)$ is the Darcian velocity in the downward direction (m/day); V_s is the ground water seepage velocity (m/day); e is the void ratio (ground water volume: volume of solid); A_p is the horizontal area of the spill (m^2) ; C_p is the concentration of pollutant in the infiltration at the

unsaturated-, saturated-zone interface $(\mu g/L)$; $Q_A = (V_D)(h)(w)$ is the volumetric flow rate of ground water (m^3/day) ; V_D is the Darcian velocity of the aquifer (m/day); h is the thickness of the aquifer (m); w is the spill-width perpendicular to the flow direction of the aquifer (m); and C_A is the initial (or background concentration of) contaminant in the aquifer $(\mu g/L)$. The maximum allowable contaminant concentration in the infiltration that does not result in a ground-water concentration exceeding a water-quality goal (i.e., an MCL) can be calculated by using this water-quality goal for C_{gw} in equation 15.13, and solving for the infiltration contaminant concentration C_p , or:

$$C_{p} = \frac{C_{gw}(Q_{p} + Q_{A}) - Q_{A}C_{A}}{Q_{p}}$$
 (15.14)

Once the maximum allowable contaminant concentration in the leachate is calculated, the contaminant concentration in the soil can be calculated. This is the soil-cleanup level that needs to be attained in order to protect the ground water, and can be obtained from the soil:water partitioning equation

$$C_s = (K_d)(C_p) \tag{15.15}$$

where C_s is the soil concentration ($\mu g/kg$), C_p is the concentration in the infiltration, from equation 15.14 ($\mu g/L$), and K_d is the equilibrium partition coefficient [($\mu g/kg$)/(μ/L)].

Modified Summers model The modified Summers model (EPA 1989a) is a variation of the Summers model, developed to derive soil-cleanup criteria using established ground water regulatory and health-based levels, coupled with an equilibrium partitioning approach. Soil cleanup levels are calculated for saturated and unsaturated media, assuming equilibrium between dissolved and adsorbed phases for each contaminant. The following relation is used

$$S_{\text{sat}} = (K_d)(C_{\text{sat}}) \tag{15.16}$$

where $S_{\rm sat}$ is the concentration of contaminant adsorbed to the soil in the saturated zone $(\mu g/kg)$, K_d is the partition coefficient $[(\mu g/kg)/(\mu g/L)]$, and $C_{\rm sat}$ is the concentration of contaminant in the ground water in the saturated zone $(\mu g/L)$. The desired contaminant concentration for ground water is determined using established health-based criteria (e.g., MCLs or cancer risk values). The cleanup criteria is calculated using equation 15.16.

Calculations to derive unsaturated soil-cleanup criteria include the assumption that dissolved contamination in the ground water recharge reaches equilibrium with the adsorbed phase on unsaturated soils, and that such recharge is fully diluted into the entire water column upon reaching the water table. Cleanup criteria for unsaturated soils are established using equation 15.16 as well as a dilution equation for calculating the contaminant concentration in the ground water in the saturated zone $C_{\rm sat}$:

$$C_{\text{sat}} = \frac{(C_{\text{unsat}})(q)}{(q+Q)} \tag{15.17}$$

where $C_{\rm unsat}$ is the contaminant concentration of the ground water recharge ($\mu g/L$), q is the volumetric flow rate of recharge flowing downward through a unit area (m^3/day), and Q is the volumetric flow rate of ground water in the saturated zone throughout the unit (m^3/day). The equilibrium assumption

$$S_{\text{unsat}} = (K_d)(C_{\text{unsat}}) \tag{15.18}$$

combined with equation 15.17 yields the equation used to calculate the cleanup criteria for soil in the unsaturated zone:

$$S_{\text{unsat}} = \frac{(S_{\text{sat}})(e+Q)}{e} \tag{15.19}$$

where $S_{\rm unsat}$ is the concentration of contaminant adsorbed to the soil in the unsaturated zone $(\mu g/kg)$ and Q is the ground water volumetric flow rate (m^3/day) in the saturated zone from Darcy's law

$$Q = (K)(i)(A) \tag{15.20}$$

where K is the saturated hydraulic conductivity (m/day), i is the hydraulic gradient (m/m), and A is the cross-sectional area of flow (unit width \times the saturated thickness of the aquifer) (m²).

SPPPLV model The Single Pathway Preliminary Pollutant Limit Values (SPPPLV) and Preliminary Pollutant Limit Values (PPLV) methods were developed by the U.S. Army (1987) to determine site-specific cleanup levels. They require the identification and measurement of contaminants that are present; pathways of exposure; and the determination (or estimation) of an acceptable daily dose (D_t) for each contaminant to a receptor.

SPPPLVs for all pathways and contaminants are calculated from measured levels of contaminants at a particular site. The acceptable daily intake for each contaminant; distance to the receptor; rate of off-site migration; and rates of dilution and degradation are used in the model. Assuming that contaminants are in equilibrium along all exposure pathways from source to receptor, partition coefficients can be used to determine levels of contaminants in different media along the exposure pathways. Critical pathways are selected for each contaminant, and a preliminary pollutant limit value (PPLV) is then derived for each medium by normalization of the SPPPLV using the following equation (U.S. Army 1987):

$$PPLV = \frac{1}{\left(\frac{1}{\sum_{i=0}^{n} (SPPPLV)_i}\right)}$$
(15.21)

In order to establish PPLVs, the best available toxicological information is used to estimate an acceptable daily dose D_t for human exposure to each compound. A PPLV is derived from consideration of the D_t , along with the probable exposure level. For example: for soil, two exposure pathways (ingestion and skin absorption) are considered for a given site. The equations for these two pathways are written as:

Soil Ingest (SPPPLV) =
$$\frac{(D_t) \text{ (body weight)}}{\text{daily amount of soil ingested}}$$
 (15.22)

Skin Absorption (SPPPLV) =
$$\frac{(D_t) \text{ (body weight)}}{\text{weight of soil per day}}$$
 (15.23)

The PPLV for soil when considering both ingestion and skin absorption is then calculated by:

Soil PPLV =
$$\frac{1}{\frac{1}{\text{Soil Ingestion (SPPLV)}} + \frac{1}{\text{Skin Absorption (SPPPLV)}}}$$
 (15.24)

Contaminant profile model The contaminant profile model method (Williams et al. 1988) was developed as a tool for estimating the transport and fate of chemicals from sites where initial concentrations of contaminants are known as a function of depth. One of the objectives of the model is to provide an estimate of the amount of contaminant that leaves the unsaturated zone and enters the ground water. Transport of contaminants through the following five phases is considered: water; stationary inorganic; immobile organic; mobile organic; and vapor. In certain disposal or spill situations, the mobile organic phase—in addition

to the water phase—flows through soil, thereby enhancing the mobility of potentially hazardous chemicals which are adsorbed to the mobile organic phase. The contribution from all five phases is described by the following relation:

$$C_T = (1 - n)(\rho_s)(C_s) + (\phi_i)(\rho_i)(C_i) + (\theta_a)(\rho_a)(C_a) + (\phi_m)(\rho_m)(C_m) + (\eta_v)(\rho_v)(C_v)$$
(15.25)

where C_T is the initial total concentration of the contaminants in the soil sample (kg/kg); n is the total pore fraction (porosity) of the system (m³/m³); C are the concentrations of the contaminant (kg/kg) in the solids s, water a, immobile organic i, mobile organic m, and vapor v phases; ρ are the densities of the solids s, water a, immobile organic i, mobile organic m, and vapor v phases (kg/m³); ϕ are the volume fractions of the immobile i and mobile i organic phases in the total sample (m³/m³); θ_a is the volume fraction of the water phase in the total sample (m³/m³); and η is the volume fraction of the vapor phase (m³/m³).

Independent relations (R) must be obtained between each of the phases and the total concentrations, allowing independent calculation of the concentration of each contaminant in each phase. This can be done by defining five new terms:

$$C_T = (R_s)(C_s) = (R_i)(C_i) = (R_a)(C_a) = (R_m)(C_m) = (R_v)(C_v)$$
 (15.26)

Assuming linear partitioning and local equilibrium, the *R* terms can be defined in terms of partition coefficients. Another assumption is that the interface between each of the phases is water and the other phases do not contact each other. Therefore, contaminant transfer from one phase to another must include transfer through the water phase. The partition coefficients can be defined as follows:

$$C_s = (K_s)(C_a) \qquad C_m = (K_m)(C_a)$$
$$C_i = (K_i)(C_a) \qquad C_v = (K_v)(C_a)$$

where K_s is the solid:water partition coefficient, K_i is the immobile organic:water partition coefficient, K_m is the mobile, immiscible organic:water partition coefficient, and K_v is the vapor:water partition coefficient.

Now the equation can be rewritten in terms of the partition coefficients and the respective phase concentrations. For example, the total soil concentration and the R terms can be expressed as:

$$C_{T} = C_{s} \left[(1 - n)\rho_{s} + \frac{(\phi_{i}\rho_{i}K_{i} + \theta\rho_{a} + \phi_{m}\rho_{m}K_{m} + \eta_{v}\rho_{v}K_{v})}{K_{s}} \right]$$
(15.27)

$$R_{s} = (1 - n)\rho_{s} + \frac{(\phi_{i}\rho_{i}K_{i} + \theta\rho_{a} + \phi_{m}\rho_{m}K_{m} + \eta_{v}\rho_{v}K_{v})}{K_{s}}$$
(15.28)

Decision tree process This method (State of California 1986) evaluates the movement of chemicals through the unsaturated zone, and is used to estimate the concentrations of organic chemicals in the saturated zone as water percolates through the unsaturated soil column. The concentration in the ground water depends on the residual concentration in the soil prior to percolation. The decision tree process incorporates a retardation factor based on the carbon and clay content in the soil. It is assumed that the unsaturated zone usually has a higher retardation factor than the saturated zone.

The equations following were developed to analyze a "batchwise" extraction of chemicals by percolating water from a soil column divided into several cells of equal size. Cell size is determined by factors such as the location of the cell (saturated or unsaturated zone) and the limitations of the computer used to run the model. The equations assume that mobile

water is replaced by clean water and the system reaches equilibrium with each successive percolating cycle. The concentration of chemicals leaving the first cell can be expressed as:

$$C_w = \left(\frac{C_s}{K_d}\right) \left(\frac{(K_d)(M_s) + (M_w)(\alpha)}{(K_d)(M_s) + (M_w)}\right)$$
(15.29)

where C_w is the concentration of chemicals in the water after wetting (mg/L); C_s is the chemical concentration in the soil (mg/kg); K_d is the partition coefficient [(mg/L)/(mg/kg)]; M_s is the mass of solids per unit volume of soil (kg), M_w is the mass of water per unit volume of soil, assuming 50-percent water content (kg); and α is the fraction of immobile water. The chemical concentration in the water leaving the second cell can be expressed as:

$$C_{w2} = \frac{C_{w2} * (M_s K_d + M_w) - C_{w1} M_w (1 - \alpha)}{M_s K_d + M_w \alpha}$$
(15.30)

where C_{w2} is the concentration of chemicals in water leaving cell 2 (mg/L); C_{w1} is the concentration of chemicals in water entering cell 2 from cell 1 (mg/L); and C_{w2*} is the concentration of chemicals in water in cell 2 after one pore-volume flush (mg/L).

Water leaving cell 2 enters cell 3; this methodology uses a batchwise extraction of chemicals from the soil column. The resulting chemical concentration leaving the last cell is the concentration at the unsaturated–saturated boundary. Upon entering the saturated zone, the chemical concentrations are attenuated by the higher flow rates. The method also assumes that total mixing of chemicals occurs as water is leached out of the unsaturated zone. The amount of attenuation is calculated by using relative flow rates and chemical concentrations entering and leaving a control volume:

$$C_{H!} = \frac{(Qin)_{H}C_{H} + (Qin)_{v}C_{v}}{(Qin)_{H} + (Qin)_{v}}$$
(15.31)

where $C_{H!}$ is the resulting attenuated soil chemical concentration in the saturated zone (mg/kg); C_H is the initial soil chemical concentration in the saturated zone (mg/kg); $(Qin)_H$ is the flow rate entering the control volume in the horizontal direction from the saturated zone (L^3/T) ; $(Qin)_v$ is the flow rate entering the control volume in the vertical direction from the unsaturated zone (L^3/T) ; and C_v is the soil chemical concentration entering the control volume vertically from the unsaturated zone (mg/kg).

Two additional calculations are needed—the percolation rate and the dilution factor—to complete the evaluation of the chemical concentration in the unsaturated zone, compared to the estimated chemical concentration in the aquifer. The percolation rate is a fraction of the precipitation and is the principle contributor to chemical leaching from the unsaturated zone. The equation to calculate the monthly water balance (or mean percolation) is:

$$PERC = P - RO - \Delta S - \Delta ET$$
 (15.32)

where PERC is the monthly percolation rate (m/mo); P is the mean monthly precipitation (m); RO is the mean monthly runoff (m); ΔS is the monthly change in soil-moisture storage (m); and ΔET is the monthly actual evapotranspiration (m). The dilution factor is defined as:

$$DF = \frac{(Qin)_v}{(Qin)_H + (Qin)_v}$$
(15.33)

where $(Qin)_v = (A_v)(PERC)$ and A_v is the horizontal cross-sectional area of the control volume in the saturated zone (m^2) . The flow rate entering the control volume in the horizontal direction from the saturated zone, $(Qin)_H$, is given by Darcy's Law as:

$$(Qin)_{H} = (A_{H})(K_{H})(i)$$
 (15.34)

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where A_H is the cross-section area of the aquifer (m²), K_H is the aquifer hydraulic conductivity (m/T), and i is the aquifer hydraulic gradient (m/m). After obtaining the dilution factor and the chemical concentration at the unsaturated–saturated boundary, the predicted concentration of the chemical in the aquifer can now be calculated as:

Aquif Conc = (Conc at the Unsaturated – Saturated Boundary)
$$(DF)$$
 (15.35)

Equation 15.35 is an estimate of the resultant chemical concentration at the point of exposure, given the initial chemical concentration in the soil in the unsaturated zone. This method has limitations that include: extensive (and sometimes difficult to obtain) field measurements; assumed vertical movement of water through the unsaturated zone into the ground water; assumed total mixing of chemicals leaving the unsaturated zone; and the assumption that the soil column is flushed with clean water.

RITZ model The Regulatory and Investigative Treatment Zone Model (RITZ) was originally developed and published by Short (1985). Nofziger and Williams (1988) subsequently published a user guide that incorporated microcomputer hardware and software, input guidance, and graphical and tabular output. The model incorporates the influence of oil in sludge applied to land areas, water movement, volatilization, and degradation upon the transport and fate of a hazardous chemical. This model is one of many models that can be used to assess the fate and transport of contaminants in the unsaturated zone, in order to calculate soil remediation levels. Chapter 13 gives a more complete listing of the available models for fate and transport of contaminants in the unsaturated zone.

Short (1985) makes several assumptions in developing the RITZ model. These include:

- Waste material is uniformly mixed in the plow zone;
- The oil in the waste material is immobile and never leaves the plow zone; only the contaminant moves with the soil water;
- The soil properties are uniform from the ground surface to the bottom of the treatment zone;
- The flux of water is uniform throughout the treatment site and throughout time;
- Hydrodynamic dispersion is insignificant and can be neglected;
- Linear isotherms describe the partitioning of the contaminant between the liquid, soil, vapor, and oil phases, and local equilibrium between phases is assumed;
- First-order degradation of the contaminant and oil is assumed and degradation constants do not change with soil depth or time;
- The contaminant partitions between the soil, oil, water, and soil vapor and does not partition to the remaining fractions of the sludge;
- The sludge does not measurably change the properties of the soil water or the soil, so the pore liquid behaves as water; and
- The water content of the soil is related to the hydraulic conductivity as described by Clapp and Hornberger (1978):

$$\frac{K}{K_s} = \left(\frac{\theta}{\theta_s}\right)^{2b+3} \tag{15.36}$$

where K is the hydraulic conductivity at a volumetric water content of θ , K_s is the saturated hydraulic conductivity (or the conductivity of the soil) at the saturated water content, (θ_s) , and b is the Clapp and Hornberger constant for the soil.

The User's Guide and RITZ program are available from EPA (Nofziger and Williams 1988). The user of the model is cautioned to consider the assumptions in the model, and to apply the model only where appropriate. The model presents results for the specific parameters

entered without any measure of uncertainty in the calculated values. The user is encouraged to compare results for a series of simulations using parameters in the expected ranges for the site, in order to obtain an estimate of the uncertainty. Layered soils cannot be handled by the model, although if the site contains two layers, the user can run the simulation twice, one for the soil properties of each layer.

15.2 ALTERNATIVE TECHNOLOGIES FOR SOIL REMEDIATION

Corrective-action objectives for remediating soil can be achieved by a large number of technologies. Numerous remedial-action alternatives that have proven to be effective in contaminated-soil cleanups are available, and selected potential implementation technologies are discussed below; the alternatives discussed here do not include free-product recovery. Table 15.4 lists some of the soil (and ground water) treatment technologies for site remediation. Selected technologies are described in more detail below.

No Action

Under this alternative, no remedial action is undertaken. Two possible no-action subalternatives include passive bioremediation and monitoring. Effectiveness of both of these no-action sub-alternatives assumes that steps are taken to ensure that any further handling of products causing the contamination at a given site is conducted so as to prevent any further impact on the environment. If the contamination was caused by a leaking tank or other source, this source must be removed in order to implement these two sub-alternatives effectively.

Passive bioremediation Many regulators permit use of passive bioremediation to reduce contaminant plumes naturally and to complete eventual cleanup. In order to use such a technique, several conditions usually need to be met: (1) the contaminant can be metabolized and degraded by naturally occurring microorganisms; (2) the plume must have stabilized that is, it is no longer moving; and (3) the source of the plume has been removed. Hydrocarbons and similar organic substances are most readily amenable to passive bioremediation. Generally, metals are not as effectively treated using passive bioremediation; however, bacteria are known to "take up" metals as part of their metabolic processes, as well as removed in soils by the processes of adsorption, precipitation, ion exchange, and complexation (EPA 1981).

Physical treatment	Biological treatment	Chemical treatment	Thermal treatment
Coagulation/flocculation	Activated sludge	Neutralization	Incineration
Oil-water separation	Activated sludge with PAC	Precipitation	Thermal desorption
Air and steam stripping	Aeration tank	Ion exchange	Vitrification
Carbon adsorption	Aerobic and anaerobic fixed film	Chemical oxidation	
Filtration	Anaerobic digester/tank	Chemical reduction	
Reverse osmosis	Fluidized bed	Photolysis (ultraviolet light)	
Sedimentation	Rock-reed filter	Wet-air oxidation	
Evaporation and distillation	Sequencing batch reactor	Stabilization	
Solvent extraction	Trickling filter	Dechlorination	
Freeze crystallization	Composting	Soil washing	
Centrifugation	In-situ biodegradation	egadini i bio qari) në 2 t	
Sonic treatment	Land treatment		
Soil venting	Liquid/solid systems		
Air sparging	Wetlands treatment		

If the contaminant source is removed and the contaminant is resident in the soil at residual saturation, both aerobic and anaerobic microorganisms act to reduce the plume mass and complete cleanup (LLNL 1995). A contaminant spreads in unsaturated soil due primarily to the influence of gravity, until the point is reached at which the fluid no longer holds together as a single, continuous phase, but rather occurs in isolated, residual globules. At this point, the contaminant has largely become immobile under the usual soil-potential conditions and can migrate further only: (1) in water according to its solubility; or (2) in the gaseous phase within the unsaturated zone (Schwille 1988). Evaluation of over 1,500 leaking underground fuel tanks in California indicates that, in general, plume lengths change slowly and tend to stabilize in relatively short distances from the release site (LLNL 1995). The evaluation also indicates that once contaminant sources are removed and the plume is stabilized, hydrocarbons (at least in ground water) appear to degrade naturally at rates as high as 50 to 60 percent per year. Therefore, passible bioremediation is a potentially effective and low-cost method for final cleanup of selected organic contaminants in both the unsaturated and saturated zones.

Monitoring A long-term ground water monitoring program needs to be established to identify and assess any potential contaminant migration. Existing boreholes and monitoring wells used in the site investigation should be used as a component of the ground water monitoring network. It may be necessary to install additional ground water monitoring wells both up- and down-gradient of the observed contamination to assess contaminant migration trends, and to document contamination levels at the site boundaries.

By sampling existing and new wells, this alternative establishes a mechanism for identifying any changes in ground water flow patterns, contaminant levels, and contaminantplume migration. A monitoring program also provides an early warning of increases in contaminant levels. For the short term, this alternative is not protective of human health and the environment. Contaminated soil stays in place and there are not any mitigative measures taken to decrease the concentration of the contaminants in soil. The existing environmental impacts remain. For long-term effectiveness, the risks that exist without cleanup continue.

The residual risks—as a result of the no-action alternative—may prove to be acceptable to regulators, and this alternative is not to be overlooked as a possible solution if there are no potential receptors within a given site. Although there are no capital costs associated with the no-action alternatives, there are annual (or more frequent) monitoring costs. Relative to the costs for other alternatives presented below, this cost is low.

Capping

Capping is designed to minimize contact and infiltration of precipitation, thereby reducing the potential for leachate generation from contaminants in the soil. Capping also helps to eliminate erosion and storm-water transport of contaminants into local surface-water collection areas. The capping process requires a relatively impermeable barrier overlying the contaminated area. A variety of cap designs and capping materials are available, ranging from a single-layered synthetic type, to a multilayered, that supports a soil cover to protect the barrier and allow the growth of vegetation. The capping materials considered in practice include clay, synthetic membranes, asphalt or concrete, and multilayer combined media.

Historically, clay has been the most extensively used capping material in landfills or surface impoundments. However, exposed clay can shrink and crack when it dries. Additionally, clay caps have a low tolerance for heavy surface loads that can be expected at some sites. Consequently, consideration of clay as a capping material needs to take these parameters into account. Both bituminous asphalt and concrete have been demonstrated to perform as effective barriers for precipitation and surface-water infiltration.

Synthetic membranes can also be used as a capping construction material. The factors influencing the use of synthetic membranes include chemical compatibility, prevention of tears and punctures, and proper overlapping of seams and seam sealing; without proper protection from surface loads, synthetic membranes are subject to punctures and tearing.

Current environmental regulations require that the design of most caps conform to the performance standards in 40 CFR Part 264.310, which addresses Resource Conservation and Recovery Act (RCRA) landfill-closure requirements. Most cap designs are multilayered to conform to these standards. A typical multilayered cap design (see figure 15.3) includes an upper vegetative layer, underlain by a drainage layer and two low-permeability layers. The vegetation is supported by the loam layer; the drainage layer is composed of sand or a geosynthetic drainage net; and the low-permeability layer is formed by the combined synthetic liner and clay system. An additional layer of stone and gravel is often placed immediately above the contaminated soil, as structural backfill to support the cap. Prior to capping the fill must be graded and compacted, in order to enhance the stability of the cap and reduce settlement. The use of capping technology also necessitates compliance with local regulations. Closure considerations deal primarily with cover materials and designs, while post-closure concerns involve site maintenance and monitoring.

The effectiveness of a cap in reducing the potential for leachate generation is dependent on ground water levels. Ground water coming into contact with contaminated soil—more likely when the local water table is elevated—can produce leachate despite the existence of a well-designed cap. Capping can be combined with ground water extraction or other containment technologies, to prevent or reduce the movement of a contained plume. Therefore, capping with asphalt/concrete or a multimedia layer in conjunction with other technologies, is often an effective remedial-action method.

Capping is effective for the short-term time frame, since the contaminated soil remains in place and direct exposure to it is minimal. Occupational risks to workers are no greater

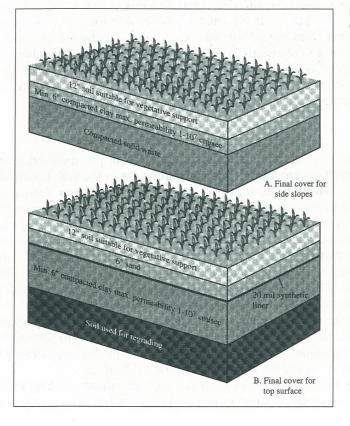


Figure 15.3 Typical multilayer cap design (data from McAneny et al. 1985)

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than those normally experienced in construction of this type. The risk to nearby, off-site people is negligible, because exposure to the contaminated soil does not occur if these soils are covered by a cap. The capping alternative is not effective for the long term, although the cap does prevent direct contact with the contaminated soil. If ground water intersects the contaminated soil, causing contaminates to be continuously washed (flushed) from it to ground water, then the cap would not prevent migration of contaminants and would not protect human health and the environment. The costs associated with this alternative would be in the low cost range compared to other alternative technologies.

Soil Venting

In situ soil venting implements a vacuum extraction system (VES) that removes volatile organic compounds (VOCs) from the soil matrix via vapor-phase pathways. In soil venting, VOCs are removed and can be further treated, either to completely degrade the compound or transfer it to another medium. The transfer to another medium does not destroy the contaminant, but does remove it from the soil. In addition to extracting contaminants directly, the pumping action draws a continuous supply of air through the soil, enhancing in situ biodegradation of the pollutant by naturally occurring aerobic bacteria. A soil venting system consists of the installation of wells and/or trenches in the contaminated area, with a pump to draw air out of the wells (see figure 15.4). In turn, air moves through the soil and into the wells, thus providing a continuously renewed oxygen source for the aerobic bacteria. A wide variety of environmental and soil factors determine whether this alternative is applicable to a given site; these factors include water content; porosity and permeability; clay content; as well as other factors. However, a VES pilot study can determine the feasibility of this type of alternative, and is encouraged at any site for which this alternative is considered.

The Superfund Innovative Technology Evaluation (SITE) Program (EPA 1991a) indicates that VES is the most widely used innovative technology for National Priorities List (NPL) sites. VES has proved successful in remediating petroleum-contaminated soils at many sites. Both horizontal and vertical VESs have proved successful in removing benzene, toluene, ethylene, and xylene (BTEX) contaminants from soils (EPA 1991b). If the water table is near the surface, the high vacuum required for vertical wells at some sites can cause the water table to be lifted into the extraction system, thus diminishing the effectiveness of the treatment system; horizontal VES requires less vacuum to achieve a greater radius of influence. Using either the vertical or horizontal design, the volatiles extracted are processed

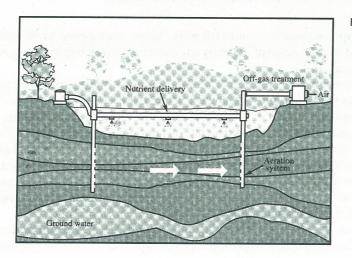


Figure 15.4 Typical soil venting system



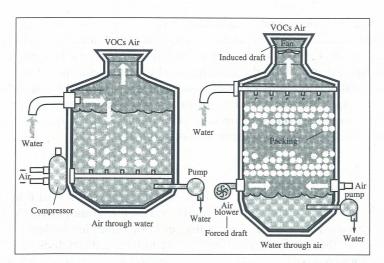


Figure 15.5 Air stripping system

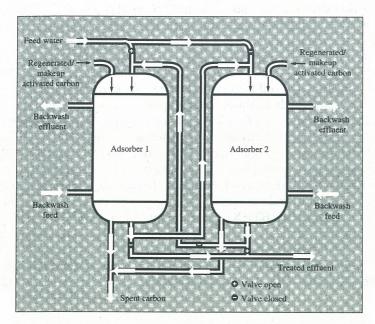


Figure 15.6 Carbon adsorption system

through a liquid-vapor separator or air stripping system (see figure 15.5), and the vapor is treated by activated-carbon adsorption or by catalytic converter, before being released to the atmosphere (see figure 15.6).

The effectiveness of a VES system depends on the contaminant vapor pressure—that is, the pressure of its vapor in equilibrium with its pure liquid (or solid) phase. The temperature at which the vapor pressure of a liquid is equal to atmospheric pressure, is the boiling point of the contaminant. For a fixed-flow rate of venting air, the maximum rate at which a contaminant is extracted from the soil is derived by assuming that the partial pressure of the contaminant in the vented vapor is equal to the vapor pressure of the contaminant. The molar density of the contaminant in the vapor phase is equal to its partial pressure, assuming an ideal vapor behavior. The vapor pressure at 40 °F and the maximum extraction rates of some common VOCs are shown in table 15.5.

This alternative is protective of human health and the environment during the short term, because the vapors are treated prior to release. Vacuum extraction provides permanent

TABLE 15.5 Maximum Vapor Extractability ¹			
Compound	Vapor pressure at 40 °F (mm Hg)	lb/100 ft ³	lb/day at 100 SCFM
Benzene	28.0	7.9	1134
Chlorobenzene	3.8	1.5	221
Chloroform	77.0	33.2	4782
1,1 DCA	89.0	31.7	4564
Methylene chloride	198.9	59.9	8622
Naphthalene	0.1	0.05	7
PERC	7.5	4.49	646
1,1,1 TCA	4.6	21.9	3154
TCE	28.0	13.1	1891
Toluene	9.0	3.0	430
Xylenes	3.0	1.1	165

¹Assumes continuous vapor saturation

removal of the contaminants from the soil, for long-term effectiveness; therefore, the mobility and volume of contaminants is greatly decreased. Vacuum extraction has proved effective in controlling fugitive emissions from contaminated sites, and it is the most commonly used in situ remedial technology. Proper implementation of this technology does require a pilot test to determine the trench size; pump capacities; flow rates; well spacing; and operating pressures. Excavation of trenches and subsequent laying of pipe is also required to implement the alternative. Once flow paths are established, the vapor extraction is usually rapid. The more-volatile contaminants are removed the fastest, with the less-volatile contaminants being removed at a slower rate. However, old spills—where many of the volatiles have escaped—may not respond as well to the VES technology.

The cost of this alternative is a fraction of the cost for other innovative remedial-action technologies, such as on-site thermal treatment. The cost of VES is in the medium-cost range compared to the no-action or capping alternatives.

Air Sparging

Essentially, air sparging (see figure 15.7) creates a crude air stripper in the subsurface, with the saturated-soil column acting as the packing (Angell 1992). Injected air flows through the water column over the packing, and air bubbles contacting dissolved/adsorbed-phase contaminants cause the VOCs to volatilize. The entrained organics are then carried by the air bubbles into the unsaturated zone, where they are captured by a vapor extraction system—or if permissible—allowed to escape through the ground surface into the air. As a bonus, the sparged air maintains high dissolved oxygen, which enhances natural biodegradation.

The key to successful air sparging is good contact between the injected air and contaminated soil and ground water. Beneath the water table, the air bubbles have to travel vertically through the aquifer in order to strip the VOCs. Additionally, a permeability differential above the air-injection zone reduces the effectiveness of air sparging. As a consequence, low permeability or heterogeneities push the dissolved contamination concentrically from the injection point, thereby resulting in spread of contaminants, rather than cleanup. Thus, there are two primary concerns with air sparging: (1) the spread of dissolved contaminants; and (2) the acceleration of vapor-phase transport and subsequent accumulation of vapors in buildings (or other closed spaces). Because air sparging increases the pressure in the unsaturated zone, exhausted vapors from the ground water are drawn into the basement of buildings. In areas with potential vapor receptors, air sparging needs to be evaluated with a concurrent-vent system.

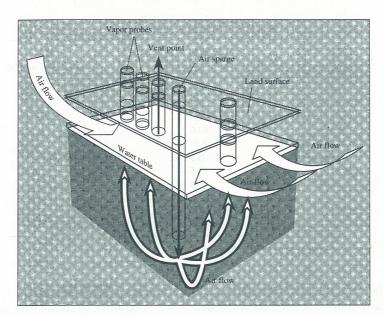


Figure 15.7 Air sparging system

Two factors are critical to the effective design and operation of an air sparging system: (1) the extraction system itself; and (2) the vapor-abatement system. The extraction system includes the number, spacing, and location of extraction wells; manifold layout; and the size (and type) of blowers. A properly designed extraction system operates with minimal adjustment; a poorly designed system requires the repeated installation of additional wells, piping, and blowers. Vapor-abatement systems—often required by regulatory agencies—consist of carbon or thermal treatment. Carbon is generally easy and inexpensive to install and permit, but is likely expensive to use for high VOC concentrations. Thermal systems, on the other hand, require higher capital costs and take more time to permit, but are relatively inexpensive to operate. The maximum venting efficiency occurs in a soil venting system when the following factors occur (Angell 1992):

- The induced-air flow directly contacts the contaminated soil;
- The radius of influence of the vent wells matches the area of contamination; and
- The correct size vacuum blower is chosen, based on site-specific soil-permeability conditions such as water content, texture, and mineralogy.

The information needed for an effective air sparging system design is as follows (Angell 1992):

- The location of potential ground water and vapor receptors;
- The geological conditions of the site (e.g., permeability, lithology, heterogeneity);
- The contaminant-mass distribution within the area, to be treated in both soil and ground water; and
- The radius of influence of the sparge wells at various flow rates/pressures.

A typical air sparging system design requires a field test that includes monitoring the following (Angell 1992):

- Pressure versus distance (indicator of radius of influence);
- VOC concentrations in ground water (indicator of what is being removed and should be done before, during, and after the test);

- CO₂ and O₂ concentrations in soil vapor (indicators of biological activity and should be done before, during, and after the test, and under both static and pumping conditions);
- Dissolved oxygen levels in the water (indicator of the effectiveness of the sparging, with changes being slower than for air flow); and
- Water levels before and during the test (air flow causes some rise in the water table and thus needs to be measured).

The cost of an air sparging system is similar to that for a VES system, and generally falls into the medium-cost range when compared to the no-action and capping alternatives. This alternative also is protective of human health and the environment in both the long- and short-term, as long as appropriate precautions are undertaken relative to venting and treatment of vapors from the sparge system.

Soil Flushing

In situ chemical treatment consists of flushing contaminants from soil through injection of a flushing agent (see figure 15.8). Organic and inorganic contaminants can be washed from contaminated soil by an extraction process called "soil flushing," "ground leaching," or "solution mining." Water (or an aqueous solution) is injected or sprayed into the area of contamination; the contaminated elutriate is collected and pumped to the surface for removal, recirculation, or on-site treatment and reinjection. During elutriation, the flushing solution mobilizes the sorted contaminants by dissolution or emulsification.

Soil flushing has been specified in the Records of Decision (RODs) for as many as 10 NPS sites. Studies have been conducted to determine the appropriate solvents for mobilizing various classes and types of chemical constituents. The difficulty in implementing this technology depends on the ability to flood the soil with the flushing solution, and to install collection wells or subsurface drains to recover all of the applied liquids; provision also must be made for disposal of the elutriate. The achievable level of treatment varies, dependent on the contact of the flushing solution with the contaminants, the appropriateness of solutions for the contaminants, and the hydraulic conductivity of the soil.

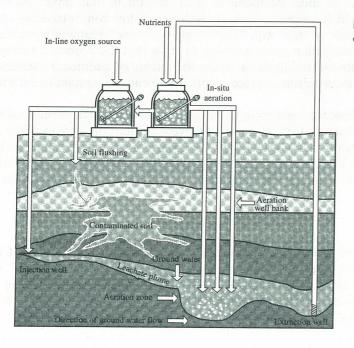


Figure 15.8 Flushing and bioreclamation of soil and ground water

A slight variation to soil flushing—an air stripping technology—has been developed. This method involves injecting superheated, compressed air into and below the zone of contamination, via vertical or horizontal perforated piping. Most volatiles go out with the soil water by evaporation, opening up void paths, thus increasing the permeability of the soil to air flow. As the water evaporates, it also removes volatile hydrocarbons by steam distillation. Air-injection rates increase as the soil permeability increases.

The advantages of using soil flushing for site remediation are that removal of contaminants is permanent and no additional treatments are necessary if the process is successful. Also, the technology can be easily applied to permeable areas. However, implementation of the process may be moderately expensive depending upon the flushing solution chosen. Soil flushing also introduces potential toxins (the flushing solution) into the soil system. An effective collection system is required to prevent contaminant migration.

Biological Treatment

In situ biological treatment (enhanced bioremediation) is the provision of nutrients and oxygen to enhance the rate of microbial biodegradation of volatile organic contamination in the soil (see figure 15.8). Biological remediation consists of the use of microbiological organisms to degrade the organic contaminant compounds to carbon dioxide and water. The system supplies nutrients and oxygen to the indigenous bacteria and fungi to stimulate their growth and reproduction, enabling them to use the contaminants as a substrate. As the contaminants are broken down, they are incorporated into the microorganisms' biochemical cycles, and transformed from toxic to nontoxic substances. Care should be taken to investigate the possibility that biological treatment does not produce intermediate products that are more toxic than the original contaminant.

Bioremediation has proved effective in the degradation of certain types of contaminated soil; however, certain conditions must exist for the microorganisms to achieve this effectiveness. These conditions pertain primarily to providing a suitable environment based on temperature, pH, moisture and nutrient contents, oxygen availability, and biodegradability of the contaminated soil constituents. Minimal permeability requirements must be met; sandy materials are far more amenable to in situ treatment than clayey materials. It should be noted that very high concentrations—as well as very low concentrations—of organic contaminants are difficult to treat with the biological process. Treatability studies are required prior to any bioremediation process design, to show that the proposed bioremediation will not accelerate contaminant migration, cause the release of additional contaminants without adequate capture mechanisms in place, or otherwise cause a contaminated site to become a greater hazard.

Bioremediation, if properly implemented, provides permanent removal of the contaminants from the soil media for long-term effectiveness. Therefore, the mobility and volume of contaminants is greatly decreased and this alternative is protective of human health and the environment, after any corrective action has been implemented. The cost of this alternative is in the medium to low range in comparison to all other alternatives except the no-action alternative.

Soil Excavation

Excavation involves the physical removal of the contaminated portion of the soil, using standard excavation practices and technology. Excavation is performed extensively in contaminated-soil site remediation, and satisfies the objective of preventing any future release of contaminants to the ground water. Typical equipment used in this alternative include backhoes, drag lines, and front-end loaders.

Materials handling is a major concern that affects the implementation of excavation; staging areas are necessary. These areas are used to prepare contaminated soil for disposal or treatment; graded to prevent ponding; lined with clay (or other liners) to prevent groundwater contamination; and bermed to prevent runoff. Backfilling, grading, and revegetation after excavation are necessary to prevent large, open areas that could trap precipitation and cause runon. Sampling of remaining soil confirms the removal of all contaminants. The excavated area is backfilled with clean soil obtained from off-site. The subsequent transportation of contaminated soil resulting from excavation must meet federal, state, and local shipping and manifesting regulations.

Excavation and removal of contaminated soil eliminates the environmental and health concerns associated with leachate production and subsequent ground water contamination. However, consideration must be given to the health and safety of remedial workers. Contaminated soil at the site can contain VOCs, and workers could be subject to exposure to these vapors. On-site air monitoring and dust-, vapor-, and odor-control provisions are necessary during all excavation operations. Excavation activities can also result in the release of fugitive dusts and runoff from disturbed areas. Dust controls include water sprays or application of chemical dust suppressants; surface-water controls might also be required. Excavation, in conjunction with other soil treatment technologies (e.g., incineration, soil washing, etc.), is an effective remedial alternative for many sites.

Soil Washing

Soil washing (see figure 15.9) is the extraction of contaminants from excavated soil by mixing them with water, solvents, surfactants, and chelating agents; the contaminated mixture is then treated for removal of contaminants. Heavily contaminated soil is commonly treated several times in a multistage, countercurrent treatment system. Soil washing technology has been developed independently by the U.S. EPA and by ECOVA Corporation. Soil washing is most effective on materials with less than 35 percent fine-grained materials. Soil washing is not particularly effective for remediation of contaminated fill, because of the heterogeneous mixture of materials and particle sizes.

Soil washing has demonstrated its effectiveness in removing various gasoline components, solvents, pesticides, phenols, and trace-metals to regulatory levels. The EPA's demonstration unit has concentrated on remediation of gasoline-contaminated soil; ECOVA's unit has demonstrated successful treatment of pesticides, phenols, and trace metals.

Treatability testing is required in advance to determine the appropriate solvents, surfactants, or acid washes that are required for a prototype soil washing operation. Additionally, permitting and regulatory acceptance is needed prior to implementation of remedial activities. Costs associated with this alternative are very high compared to other in situ alternatives.

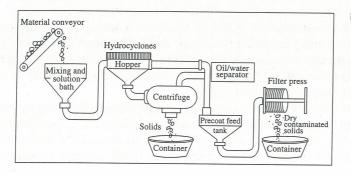


Figure 15.9 Soil washing system

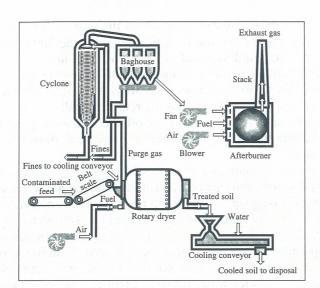


Figure 15.10 Thermal desorption system

On-Site Thermal Treatment

On-site (but not in situ) thermal treatment is carried out in conjunction with excavation, to address soil contamination (see figure 15.10). On-site thermal processes include rotary kiln, fluidized bed, and circulating-bed incineration. All of these processes are potentially acceptable to regulators, and are available from numerous vendors; different vendors provide different treatment processes. A treatability study/test burn is needed in order to select the appropriate treatment process for contaminated soil at a given site.

Incineration involves the thermal destruction of organic compounds, to a nonhazardous product. This process is completed using either an incinerator erected on-site, or a commercial facility located off-site. In general, the major technical considerations for effective incineration are: the ability to handle the physical properties of the contaminated soil involved; adequate size for a reasonable contaminated-soil throughput rate; and an ability to effectively destroy the soil contaminants, based on the chemical properties of the contaminated soil.

Cleanup of off-gases generated is required in order to meet pertinent air-quality standards. Gas cleanup technologies currently in use include: bag houses for particulate removal; various designs of scrubbers for particulate sulfur and chloride removal; and precipitators for particulate removal. Gas treatment, in turn, requires treatment of the resulting aqueous- and solid-waste streams by filtration, physical/chemical treatment, or land disposal.

Construction of a new on-site incineration facility requires compliance with all federal, state and local regulations, including RCRA and the Clean Air Act; RCRA design and permitting standards are listed under Subpart C, 40 CFR Part 264. The preferred alternative is an on-site mobile incinerator, since control of such an incinerator is possible.

New incinerator construction typically meets with strong public opposition, creating time-consuming siting and permitting problems. The entire process of siting, permitting, design, and construction can take several years. The capital cost for such a project is relatively high compared with other alternatives. For these reasons, construction of an on-site incinerator is not the best alternative for many sites.

Incineration technologies are capable of thermally destroying organic hazardous materials. Ash and sludge remaining from the incineration process have to be disposed of using an appropriate secondary technology; disposal of these treatment by-products needs to conform to all requirements of RCRA, most notably the Land Disposal Restrictions.



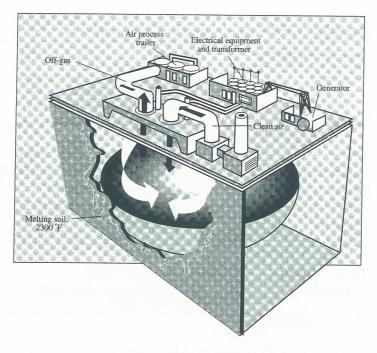


Figure 15.11 In-situ vitrification

Incineration effectively destroys the soil volatile contaminants that are contributing to ground water contamination. Because the contaminated soil is excavated, the risk of exposure of workers to contaminated material is higher than for in situ alternatives during the short term; however, these risks are considered to be minimal and temporary. During the burning of contaminated soil, the public and environment are protected, because equipment is installed for particulates and gas treatment. In the long term, this alternative provides protection to the public and the environment, because the soil is removed and then incinerated. Removing the soil reduces the mobility—and volume—of contaminants into the ground water. Incineration is a proven technology for use in hazardous-waste applications, and is commercially available from various vendors. For on-site treatment, fixed and mobile rotary kiln incineration are available. The capital and operating costs of on-site incineration are much higher than the costs of other alternatives we have considered, so far.

In-situ Vitrification

A much more complicated and expensive system is in-situ vitrification (figure 15.11) or other solidification or stabilization techniques. Generally, in-situ vitrification is used for inorganic wastes and metals, although it has been tested in some organic compounds. The principle is to physically hold the contaminant or solidify the contaminant into a soil matrix. It has little effect on the chemistry of the contaminant when used for inorganic metals, but does increase the solubility and, hence, the toxicity of the contaminant. In-situ vitrification may cause future leaching potential as a result of its use. The cost of this alternative treatment technology is the highest of those considered.

SUMMARY

Table 15.6 is a summary of the types of wastes that can be treated with a given remediation technology; additional details on the applications of each technology can be found in EPA (1991c). Most of the technologies presented primarily treat organic wastes, although some—

Remediation technology	Application		
No action	Soils containing residual concentrations of soluble organics, sludges, oily wastes, inorganics and radioactive wastes		
Capping Soils containing soluble organics, incaping and radioactive wastes			
Venting	Soils containing volatile organic compounds		
Air Sparging	Soils containing volatile organic compounds		
Flushing	Organic and inorganic compounds		
Biological treatment	Soils or soil water containing soluble organics		
Excavation	All types of contaminants		
Washing	Soils containing organic and/or inorganic compounds		
Thermal treatment	Soils containing organics		
In-situ vitrification	Soils containing organics, inorganics, and radioactive wastes		

Sources: Data from EPA (1991c)

TABLE 15.7 Qualitative Soil Remediation Technology: Costs and Effectiveness			
Remediation technology	Qualitative cost	Effectiveness	
No action	Low (monitoring)	Some long-term contamination risks	
Capping	Low	Some long-term contamination risks	
Venting	Medium	Long-term effectiveness	
Air sparging	Medium	Long-term effectiveness	
Flushing	Medium to high	Long-term effectiveness	
Biological treatment	Low to medium	Long-term effectiveness	
Excavation	Low to medium	Long-term effectiveness	
Washing	Very high	Long-term effectiveness	
Thermal treatment	Very high	Long-term effectiveness	
In-situ vitrification	Very high	Long-term effectiveness	

such as no action, capping, flushing, soil washing, carbon adsorption, and in-situ vitrification can be used to treat inorganics, including metals.

The costs and effectiveness of alternative soil remediation technologies are highly sitespecific. Table 15.7 presents a qualitative summary of the remediation costs for the technologies described above.

ANSWERS TO QUESTIONS

15.1. First find the arguments to be used in the error function (erf) terms. The two arguments are calculated by substituting the values into the variables of equation 15.4. $A = Z/[2(D_t X)^{1/2}] = 16 \text{ ft/}$ [2(13 ft × 1,000 ft)^{1/2}] = 0.0702. $B = Y/[4(D_t X)^{1/2}] = 2,400$ ft/[4(13 ft × 1,000 ft)^{1/2}] = 5.262. Evaluating the value of C_o : $C_o = C/[\text{erf}(A) \times \text{erf}(B)] = 0.029 \ \mu\text{g/L/[erf}(0.0702) \times \text{erf}(5.262)] =$ $0.367 \mu g/L$.

15.2. Using equations 15.5 through 15.10 we calculate the following: $PR = p \times A = 11.15$ in/yr \times 28-ac \times 1 ft/12 in \times 43,560 ft³/ac-ft \times 28.32 L/ft³ = 32,094,660 L/yr; LGWF = $Z \times v \times Y = 16$ ft \times 60 ft/yr \times 2,400 ft = 2,304,000 ft³/yr = 65,249,280 L/yr; $Q_t = \text{LGWF} + PR = (32,094,660 + 65,249,280)$ L/yr = 97,343,940 L/yr; $X = Q_t \times C_o = 97,343,940$ L/yr \times 0.367 μ g/L = 35.7 g/yr; and $C_e = X/PR = (35.7 \text{ g/yr})/(32,094,660 \text{ L/yr}) = 1.11 \mu$ g/L.

ADDITIONAL QUESTIONS

- 15.3. Find the dry-weight concentration of the PNA Benzo(a) anthracene in the soil for the site defined in Questions 15.1 and 15.2, using the Freundlich method and assuming that the percentage of organic carbon in the soil is 0.10 percent and n = 1.
- **15.4.** Find the soil cleanup criteria for the site described in Questions 15.1 and 15.2 and in question one, above, using the Allowable Concentration Model.