

CONTAMINATED SITE REMEDIATION STRATEGIES

Part I - Evaluation of Site Characteristics

Course Content

1.0 THE IMPORTANCE OF SITE CHARACTERISTICS

The objective of a contaminated site remediation is to achieve the established concentration limits (cleanup target levels) for the chemicals of concern (COC) in the affected environmental media, and thereby bring the cleanup process to a closure. The cleanup target levels (CTLs) are established on the basis of preventing adverse impacts (or minimizing the exposure risks) on human health and the environment. Risk-Based Corrective Action (RBCA) for cleanups at contaminated sites (e.g., petroleum, drycleaning and brownfield sites) has three tier remediation goals (site closure options) or risk management levels. Tier 1 remediation goals generally represent generic CTLs, based on conservative default assumptions. Tier 2 and Tier 3 provide site-specific media cleanup limits based on the site's characteristics or conditions. These characteristics include the soil and groundwater properties, the nature and extent of the contamination, and the current or projected use of groundwater in the vicinity of the site.

In developing RBCA program requirements, many states have adopted broad categories of site closure options: No Further Action (NFA) with or without controls (engineering or institutional) based on the generic CTLs or site-specific risk-based CTLs and/or site-specific contaminant characteristics. Some states have provisions allowing the use of site-specific CTLs for Tier 1 closure option or risk management. In general, the cleanup actions at a site may involve one or a combination of the following: No Action, Risk Assessment, Source Removal, Treatment of the impacted media and Monitored Natural Attenuation.

Site characteristics are the primary factors in determining whether a particular remediation process is feasible or effective for the cleanup of the contaminated media. Many site remediation projects fail due to inadequate site characterization and/or poor evaluation of the site characteristics, leading to the selection and implementation of ineffective remedial action. Other reasons for failure include lack of proper operation and maintenance (O&M) of the remedial systems. The decision to implement any remediation technology at a site should be made on case-by-case basis, considering site-specific factors. Site characteristics are critical in evaluating and recommending alternative site closure options, as well as screening and selecting alternative cleanup processes. The selected site closure option and cleanup actions, and the sequence and timing of the actions constitute the site's remediation strategy.

To illustrate the importance of site characteristics, consider the following soil/water partition equation for determining soil cleanup target levels (SCTLs) based on groundwater leachability. The SCTL of a chemical is calculated using the groundwater cleanup target level (GCTL) for the chemical and site-specific parameters. The equation assumes that SCTL (mg/kg) of soil contaminant would produce a groundwater leachate of GCTL ($\mu\text{g/L}$), under a given set of site conditions. The values of soil characteristics shown on the table are the default (assumed) values for the entire state of Florida and used to calculate the default SCTLs in that state. Different

default values may apply in other states. However, site-specific soil properties may be used to calculate alternative SCTLs (see table).

$$SCTL = GCTL \times CF \times DF \times \left[K_{oc} \times f_{oc} + \left(\frac{\theta_w + \theta_a H}{\rho_b} \right) \right]$$

Parameters for Leachability Based SCTL Calculation				
Parameter Type	Parameter	Definition (Units)	Default Values	Site-Specific Values for Calculating Alternative SCTL
Site-Specific Parameters	DF	Dilution Factor (unitless)	20	Lower DF value if site is larger than 0.5 acres or water table is shallow
	f _{oc}	Fraction of organic carbon in soil (g/g)	0.002	Site-Specific Soil Property - e.g., clay is associated with more natural organic matter
	θ _w	Water-filled porosity w x ρ _b (unitless)	0.3	Site-Specific Soil Property - depends on moisture content.
	θ _a	Air-filled porosity n - θ _w (unitless)	0.134	Site-Specific Soil Property - depends on the total porosity and water content
	ρ _b	Dry soil bulk density (g/cm ³)	1.5	Site-Specific Soil Property - depends on the dry bulk density (soil lithology)
	w	Average soil moisture content (unitless)	0.2	Site-Specific Soil Property - depends on the moisture content
	n	Total soil porosity 1 - (ρ _b /ρ _s)	0.434	Site-Specific Soil Property - depends on the soil porosity (soil lithology)
	ρ _s	Soil particle density (g/cm ³)	2.65	Site-Specific Soil Property - depends on the soil lithology
Chemical-Specific Parameters	K _{oc}	Soil-organic carbon partition coefficient (L/kg)		
	H	Henry's Law constant (atm-m ³ /mol)		
	H'	Henry's Law constant H x 41 (unitless)		
Table-Specific Parameter	GCTL	Groundwater Cleanup Target Level (µg/L)		
Conversion Factor	CF	Conversion factor (mg/µg)	0.001	

Example 1-1

Which of the following factors can potentially cause the failure of a contaminated site cleanup process?

- a. Inadequate site characterization.
- b. Poor evaluation of the site characteristics.
- c. Selection of remedial action based on site-specific conditions.
- d. a, b and c.
- e. a and b.

Answer: e.

Example 1-2

Henry's Law constant is a site-specific soil property (or parameter) and it can be used to calculate a site-specific soil cleanup target levels (SCTLs), different from the generic (default) cleanup target level.

- a. True
- b. False

Answer: b. (Henry's Law constant is a chemical-specific parameter; site-specific Parameters, such as porosity, are used to calculate site-specific CTLs.)

2.0 SITE HISTORY, LOCATION AND LAND USE

2.1 Physical Setting, Drainage Features and Land Use

The physical setting, drainage features and land use of a site and the adjoining areas include the following: topography and surface water bodies; potable and irrigation water supply wells; zoning and land use designation (e.g., residential or industrial); and the current and projected use of the site, the adjacent properties, surface water and groundwater. These site characteristics are useful in determining potential off-site sources of contamination, current and future receptors, exposure scenarios and site-specific human risk exposure factors, potential site closure alternatives (e.g., applicable residential or industrial CTLs), and the possibilities of implementing institutional (e.g., deed restrictions) or engineering controls.

Depending on other site conditions, the land use may become a critical factor in determining if a long term site monitoring, as opposed to an active remediation, is a viable remedial option at a site. The following is a summary of the relevance of physical setting, drainage features and land use to developing effective contaminated site remediation strategies.

Relevance: Risk Assessment
Site Closure Alternatives
Remediation Process Selection

Risk Assessment: Source – Pathway - Receptor Analysis

The risk assessment of contaminated sites consists of an analysis of contaminant source, pathways and receptors. The source analysis includes the contaminant release information (location and history), quantities and concentrations, as well as the chemical, physical and toxicological properties. The pathway analysis identifies exposure scenarios and pathways; and determines the contaminant distribution, transport and fate, that may result from the processes of volatilization, sorption, degradation and migration, in order to quantify exposure concentrations. The receptor analysis identifies current and future receptors and assesses the human and environmental hazards using the exposure concentrations and toxicological data.

2.2 Past and Current Facility Activities

The current site conditions and the activities that have occurred in the past are critical for evaluating and recommending remedial action alternatives for contaminated sites. Historical information regarding the use and activities of a facility is available by means of facility and regulatory agency file review, personnel interview and database searches. Knowledge of the facility operations, including chemical storage and handling, waste treatment, disposal processes, and previous remediation activities is useful for determining existing and potential on-site sources of contamination, as well as the nature and extent of the contamination. With the information, one can identify potential and benefits for source removal, and the areas requiring active or passive remediation.

A facility may be classified as active or closed, depending on whether or not it is in operation. The operations of an active facility may impose limitations to the use of certain remediation processes. Construction activities may interrupt the business, while site safety and human exposure risk may become critical considerations. Also, source removal may not be a viable option if the active chemical or fuel storage system is located in the source area.

Relevance: Risk Assessment
Remediation Process Selection

2.3 Surface Cover

The land surface of a contaminated site may be uncovered (e.g., grassy areas) or paved with asphalt or concrete. Existing pavements provide less permeable surfaces, compared to uncovered surfaces, and act as surface seals to limit the flow of air or contaminant vapor in and out of the subsurface environment. This is of particular consideration in the design of vacuum extraction, air sparging and vapor phase injection systems.

Pavements may also limit direct human exposure to subsurface contaminants and thus affect the pathway and receptor exposure analysis. Similarly, surface cover can affect the amount of organic residues that deposited on and/or incorporated into the subsurface environment.

Relevance: Risk Assessment
Remediation Process Selection

2.4 Structures and Utilities

The location of buildings, utilities and buried objects can limit site access and construction activities and hence influence the choice of remediation. The site construction activities include treatment system installation, trenching and piping, excavation and drilling. Staging and loading areas for equipment and soil are needed during excavation. Buildings, storage tanks, overhead electrical and telephone lines are the most commonly encountered above ground structures and utilities.

In addition to limiting site construction, underground structures and utilities (fiber optic cables, petroleum and gas pipelines, water and sewer lines, manholes and culverts, storage tanks and basements) may provide preferential pathways for the migration and/or accumulation of contaminants. Use of air sparging should be avoided or carefully evaluated (with additional engineering safety considerations) at nearby subsurface confined spaces, such as basements and sewers, to avoid vapor accumulation.

Relevance: Contaminant Transport
Construction Limitations
Remediation Process Selection

Example 2-1

Surface cover, underground structures, drainage features and land use are examples of risk assessment parameters that affect Source-Pathway-Receptor analysis.

- a. True
- b. False

Answer: a.

Example 2-2

Which of the following site conditions should be considered in selecting a remediation process that requires site construction activities?

- a. The on-going business activities at the site.
- b. Aboveground and underground structures and utilities.
- c. The location of buildings, chemical and fuel storage systems.
- d. a, b and c.
- e. b and c only.

Answer: d.

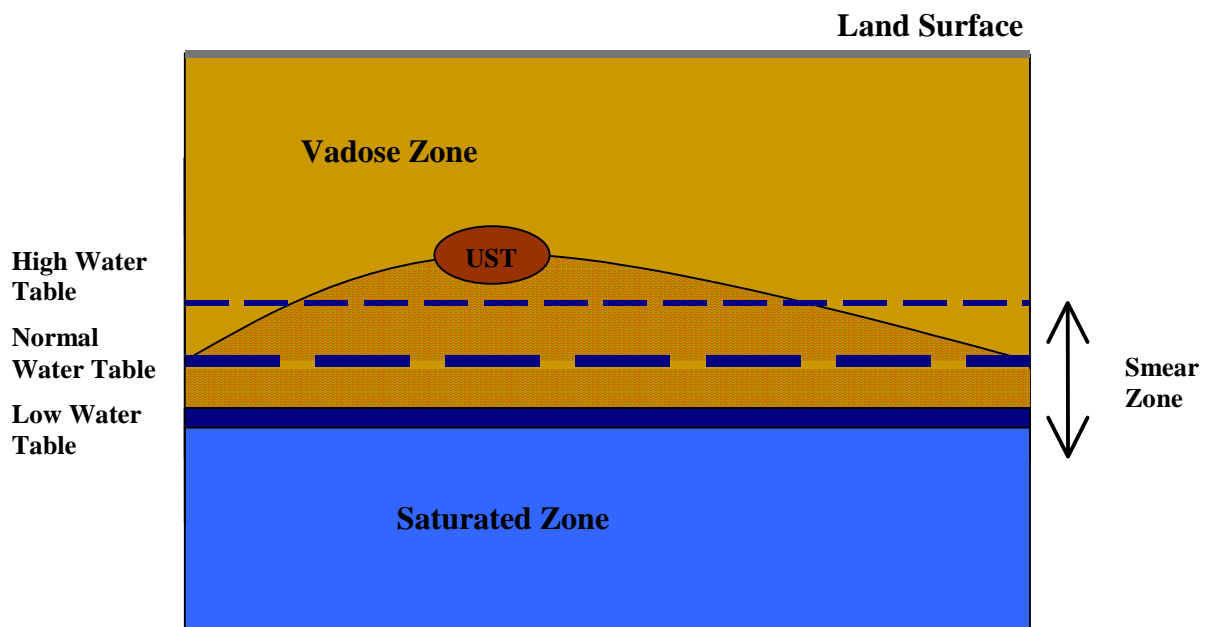
3.0 SITE GEOLOGY AND HYDROGEOLOGY

3.1 Groundwater Depth and Water Table Fluctuations

The subsurface between the land surface and the water table is the vadose zone, which consists of the unsaturated zone (directly below the land surface) and a capillary fringe (directly above the water table). The pore (void) spaces are filled with air or soil gas. Soil moisture is normally present as a small percent of the void space. Due to seasonal water table fluctuations, the thickness of the vadose zone is variable. The nature of contaminant migration generally restricts soil contamination in the vadose zone to the source areas.

The groundwater saturated zone is below the water table. The pore spaces are almost completely filled with groundwater and dissolved contaminants, free product or liquid phase and suspended solids with small amounts of air. The top of the saturated zone will vary depending upon seasonal water table fluctuations, and may be overlain with free product.

The smear zone is the area of soil contamination that may exist, at varying extents, within the zone of water table fluctuations that have occurred since the time of a discharge. For example, petroleum product floating on top of the water table can become sorbed onto the soil within this zone (as the water table fluctuates); potentially leaving a large amount of petroleum product mass adhered (adsorbed) to the soil grains. This product may remain trapped below the water table as the water table rises. Soil Cleanup Target Levels (SCTLs) apply to the vadose zone (above the water table), but due to water table fluctuations the SCTLs may or may not apply to the smear zone.



Although the vadose zone contamination may be restricted to a small area around the source, the bulk of the contaminant mass could potentially exist within this small area and the smear zone. Therefore, in many cases, source removal by excavation of the vadose and smear zones is desirable. However, the depth to the water table, the potential for dewatering, the stability of excavations, and lithology can be limiting factors. It may be necessary to dewater in order to excavate down to the smear zone during high water table conditions.

Depth to water table also affects the choice use of other remediation processes, such as soil vacuum extraction (SVE), multiphase extraction (MPX) and air sparging. At sites with shallow groundwater, vertical air flow in the immediate vicinity of extraction wells may lead to air flow short circuiting. This can be prevented by the use of natural barriers or engineered surface seals. Special design provisions must be made if significant water table fluctuations are anticipated. For example, liquid-gas interface moves according to groundwater level fluctuations, making it difficult to keep vacuum extraction tubes in the optimal position for extraction of the air/droplet stream. The depth to water table and water table fluctuations must also be considered in designing groundwater monitoring wells. The shallow or surficial aquifer groundwater monitoring wells must be properly screened to intercept both the high and lower water table levels. The groundwater sample analytical results must be interpreted with caution, where smear zone contamination exists and water table fluctuation is drastic.

Relevance: Site Closure Options
Site Monitoring
Remediation Process Selection

3.2 Soil Lithology

Soil lithology is a description of the soil types (gravel, sands, silts and clay): mineral composition, structure and stratigraphy; color, porosity and density; and particle (grain) size. They affect the ease with which fluids flow through or adsorb to soil; fine-grained soils (clays and silts) have lower permeability than coarse-grained soils (sands and gravels). Soil is heterogeneous and soil properties may change dramatically over very short distances, both vertically and horizontally across a site.

Characterization of site-specific soil properties (composition and texture, pore network, capillary pressure, wettability, saturation, residual saturation and relative permeability) are critical for the interpretation of the direction and preferential pathways for the migration of contaminants (both NAPL, dissolved and vapor phases) through the subsurface environment, and the development of appropriate cleanup strategies. Finer-grained soils (e.g., clayey soil) typically have a higher organic matter than the coarse grained soils, and have a stronger adsorption potential for organic contaminants. In-situ air sparging and soil vacuum extraction systems are highly affected by soil stratification and require closely spaced wells in heterogeneous formations. Vertically nested wells are critical in a stratified medium.

Relevance: Contaminant Transport
Remediation Process Selection

3.3 Porosity and Pore Volume

Porosity is the volume fraction of the subsurface material that is porous (void). Fluids move through the interconnected voids between the grains of soil. The total pore volume represents the volume of the subsurface zone that can be filled with fluids (water, air and contaminants), and it is the product of the bulk volume (V) and the total porosity (ϕ).

$$\text{Pore Volume} = \phi V$$

The migration of non-wetting phase fluids, such as free product and vapor, occurs primarily through the interconnected fluid-filled pore spaces. The water-filled porosity is important in determining the potential for leaching of contaminants from the soil to the groundwater, and it is a factor in determining site-specific CTLs. The air-filled porosity, on the other hand, is the basic determinant of the volume available for vapor transport, and the extent to which soil gas diffusion can take place.

Relevance: Site Closure Options
Contaminant Transport
Remediation Process Selection

3.4 Groundwater Velocity and Flow Direction

Hydraulic conductivity combined with hydraulic gradient determines groundwater velocity. Flowing groundwater transports dissolved contaminants, and the flow velocity affects the rate of natural attenuation. Thus, flow velocity and the direction of flow (relative to potential receptors) affect the choice of active remediation processes (aggressive or passive) and groundwater monitoring plans (monitoring locations and frequency).

It is important to differentiate between the actual velocity (v_s) of groundwater (also called the average, seepage or interstitial velocity) from the Darcy velocity (v) of groundwater (also called apparent velocity). The actual velocity is larger than the Darcy velocity. The Darcy velocity (see Section 3.4) assumes that flow occurs through the entire portion of the porous medium. However, the effective cross-sectional area available for flow is smaller; and the actual groundwater velocity varies from point to point due to porosity, tortuosity of the flow paths, and the absence of flow in some (dead) pores. If Q [L^3T^{-1}] is the volumetric flow rate of groundwater, A [L^2] the cross-sectional area and ϕ [dimensionless] the porosity of the porous medium, respectively, then the actual or seepage velocity (v_s) is related to the Darcy velocity (v) as follows;

$$v_s = \frac{Q}{\phi A} = \frac{v}{\phi}$$

Relevance: Contaminant Transport
Site Monitoring
Remediation Processes Selection

3.5 Intrinsic Permeability and Hydraulic Conductivity

Darcy's law states that the velocity of a homogeneous fluid in a porous medium is directly proportional to the driving force and inversely proportional to the fluid viscosity. Fluid flow velocity is dependent on the fluid density and viscosity. Density is dependent on pressure for compressible fluids (e.g., gases) and independent of pressure for incompressible fluids (e.g., water). For a horizontal, linear flow of an incompressible fluid, Darcy's law can be expressed as:

$$v = -\frac{k\rho g}{\mu} \frac{dh}{dl} \quad \text{or} \quad v = -K \frac{dh}{dl}$$

$$\text{where } k = K * \left(\frac{\mu}{\rho * g} \right)$$

v = Darcy fluid flow velocity [L/T]	l = length [L]
k = absolute (intrinsic) permeability [L ²]	h = hydraulic head [L]
ρ = fluid density [M/L ³]	g = acceleration due to gravity [L/T ²]
μ = fluid viscosity [M/LT]	K = hydraulic conductivity [L/T]

The constant, k, called absolute permeability (also known as specific or intrinsic permeability) is a measure of the ability of the porous medium (soil) to transmit fluids. Intrinsic permeability is solely dependent on the porous medium provided the latter is completely saturated (100 percent) with a single fluid. Thus, absolute permeability has the same value, irrespective of the nature of the fluid. Absolute permeability values are high for sand and gravel and low for clay and most rocks. It has the dimensions of area and units of cm². In the petroleum industry, the "darcy" has been defined as a unit of permeability.

Hydraulic conductivity has the dimensions of velocity, and it is a function of the porous medium and the fluid flowing through it. It has high values for sand and gravel and low values for clay and most rocks. The unit of gal/day/ft² (gpd/ft²) is widely used for hydraulic conductivity in the water well industry.

The following consistent units may be used in determining hydraulic conductivity from absolute permeability values, and vice versa.

k = absolute (intrinsic) permeability (cm ²)
μ = fluid viscosity (g/cm*sec)
ρ = fluid density (g/cm ³)
g = acceleration due to gravity (cm/sec ²)
K = hydraulic conductivity (cm/sec)

Conversion: At 20°C: μ/ρg = 1.02*10⁻⁵cm/sec.
To convert absolute permeability from cm² to darcy, multiply by 10⁸.

Saturations, Multi-Phase Flow and Relative Permeabilities

Absolute (or intrinsic) permeability is a property of a porous medium, irrespective of the nature of the fluid flowing through the pores (with the exception of gas flow at low pressures or high rates), as long as the porous medium is completely saturated (100 percent) with the flowing fluid. If two or more fluids, such as oil, water and/or air, flow simultaneously through a porous medium, then each fluid has its own, so-called effective permeability (k_o , k_a and k_w for oil, air and water, respectively). These permeabilities are dependent on the saturation (fraction of the pore volume occupied by the fluid) of each fluid. The sum of all the fluids' saturations is always equal to one (1), and the sum of the effective permeabilities is always less than the absolute permeability. The fluid saturation is designated as S_o , S_a and S_w for the oil, air and water phases, respectively. The effective permeability of each fluid increases with the fluid's saturation.

The relationship between fluid saturation and relative permeability to the fluid phases can be used to predict subsurface flow regimes of multiphase systems and develop appropriate cleanup strategies at sites contaminated with light non-aqueous phase liquids (LNAPLs), such as the petroleum products. The relative permeability of the porous medium to each fluid phase (water, oil or air) is defined as the ratio of the effective permeability of the fluid phase to the absolute permeability of the porous medium. Similar to effective permeability, the relative permeability increases with the fluid's saturation. There is an irreducible or residual saturation at which a fluid will not flow, and the relative permeability (and effective permeability) is zero (0). Water will only flow at saturation values above the irreducible water saturation. Oil is immobile at the residual oil saturation and the effective permeability to oil is zero. Similar observations have been made for water-air filled surface and subsurface soils, and the effective permeability to air shown as a function of water content (saturation). At the residual air saturation the effective permeability to air is zero.

At high LNAPL saturation (low water saturation), LNAPL is mobile and flows in a continuous phase. At intermediate saturation, both LNAPL and water occur as continuous phases; they both flow, but do not share the same pores. At low LNAPL saturation (high water saturation), flow is almost exclusively the movement of water, not LNAPL, and LNAPL is discontinuous and trapped as a residual phase in isolated pores. Wettability (see Section 4.4), the preferential attraction of a fluid phase to a solid surface (when two immiscible phases are placed in contact with the solid surface), influences the pore distribution of fluid phases and hence affects the relative permeability-saturation functions and multiphase flow.

Fluid flow velocities and the effectiveness of "pump and treat" and multiphase extraction systems that remove NAPL, vapors and groundwater simultaneously are particularly dependent on the saturation of the fluid phases.

Relevance: Contaminant Transport
Remediation Process Selection

Example Problem 3-1

The depth to water table, seasonal water table fluctuations and soil lithology affect the design of soil vapor extraction (SVE), multiphase extraction (MPX) and air sparging systems, and surficial (shallow) aquifer groundwater monitoring wells.

- a. True
- b. False

Answer: a.

Example 3-2

Which of the following statements is incorrect?

- a. Fine-grained soils (clays and silts) generally have lower permeabilities than coarse-grained soils (sands and gravel).
- b. Hydraulic conductivity is a function of the porous medium and the fluid flowing through it, whereas, intrinsic permeability is solely a function of the porous medium.
- c. Actual or groundwater seepage velocity (v_s) is larger than the Darcy velocity (v).
- d. Multiphase fluid flow (e.g., the extraction of liquid and vapors using a single pump) is unaffected by the saturation of each fluid (liquid and vapors) phase.
- e. The “darcy” and “ cm^2 ” are units of permeability.

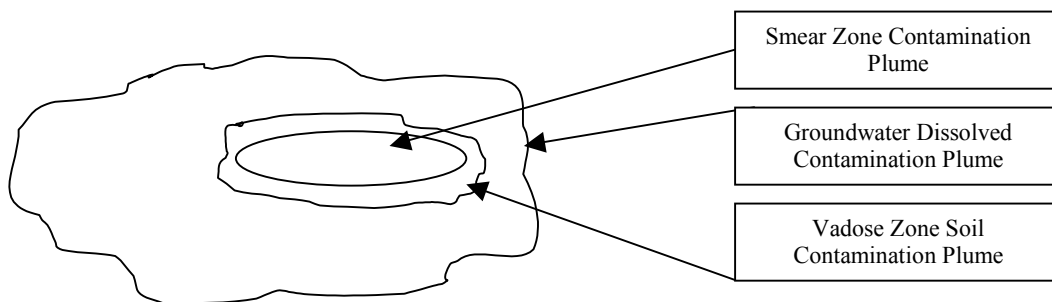
Answer: d.

Example 3-3

Below is a plan view of contamination distribution at a site. Which contamination plume(s) most likely contain(s) the least amount of contaminant mass?

- a. Vadose and Smear Zones combined
- b. Groundwater Saturated Zone

Answer: b.



4.0 CONTAMINANT TYPE AND DISTRIBUTION

4.1 Chemical Composition

The chemical composition of a contaminant affects the likelihood of success of the contaminant removal by active treatment and natural attenuation processes. Mechanical removal of contaminants by stripping (e.g., air sparging and soil vapor extraction), for example, depends on the volatility of the organic compounds which is directly related to the chemical composition. Biodegradability and chemical oxidation are also dependent of the chemical nature of the contaminant. Contaminants vary widely in chemical nature and their impacts; oxygen-depleting organics and nutrients, metals, radioactives, nuisance substances and toxic organics.

Toxic organic chemicals associated with petroleum products and chlorinated solvents are the most frequently occurring contaminants in soil and groundwater in the United States. These products are composed of a mixture of compounds (constituents); the properties of the constituents and the mole fraction of each individual constituent in the mixture determine the characteristics of the bulk product.

Relevance: Contaminant Transport
Remediation Process Selection

Petroleum Products

Petroleum products are complex mixtures of petroleum hydrocarbons and hydrocarbon additives. They can be broadly classified into three types on the basis of their composition and physical properties: gasolines, middle distillates and heavy fuel oils.

Gasolines: Gasolines consist mainly of branched-chain paraffins, cycloparaffins, and aromatics. The components of gasolines have lower molecular weights than components of middle distillates and heavy fuels. As a result, gasolines have lower viscosity, higher volatility, moderate water solubility, and hence higher mobility. Fresh gasolines have higher percentages of light aromatic hydrocarbons, for example, benzene, toluene, ethylbenzene and xylenes (BTEX).

Middle Distillates: The Middle Distillates include diesel fuel, kerosene, jet fuel and lighter jet fuels. They contain compounds, such as the polycyclic aromatic hydrocarbons, that are denser, less volatile, less water soluble and less mobile than the compounds found in gasolines. The polycyclic aromatic (or polyaromatic) hydrocarbons (PAHs) are light molecular weight, easily adsorbed, moderately soluble, low volatility compounds, e.g., naphthalene. Lighter aromatics, such as BTEX, are generally found in trace impurities in middle distillates.

Heavy Fuel Oils: The heavy fuel oils and lubricants are similar in composition and characteristics to the middle distillates. The heavy fuels are relatively viscous and insoluble in groundwater, and are therefore more immobile in the subsurface.

Additives: Chemical additives include 1, 2-dibromethane (EDB); and gasoline oxygenates (hydrocarbons containing one or more oxygen atoms), such as methyl tert-butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME). The most common inorganic additive is lead.

Chlorinated Solvents

Halogenated volatile organic compounds (VOCs) are the most frequently occurring type of contaminant in soil and groundwater at Superfund and other hazardous waste sites in the United States. The chlorinated aromatic hydrocarbons (CAHs) consist of hydrocarbon constituents and chlorine, used as solvents, degreasers and the manufacture of raw materials. Chlorinated solvents are commonly used for drycleaning.

CAHs include tetrachloroethene (PCE), trichloroethene (TCE) and carbon tetrachloride. As the number of substituted chlorine atoms on the CAH increases, molecular weight and density generally increase, and vapor pressure and aqueous solubility generally decrease.

4.2 Volume of Contaminant Released and Contaminant Phase Distribution

In the subsurface environment, petroleum hydrocarbons and chlorinated aliphatic hydrocarbons (CAHs), may exist in any four phases: non-aqueous phase liquids (NAPLs), dissolved phase (groundwater and/or soil moisture), gaseous phase (vadose zone and the capillary fringe) and solid phase (adsorbed to soil and/or aquifer particles). Liquid hydrocarbon or non-aqueous phase liquid (NAPL) is also known as free product and it exists as a separate (immiscible) phase when in contact with water and/or air. Upon release into the subsurface, NAPLs tend to move downward under the influence of gravity and capillary forces, the effect being greater for heavy weight or dense non-aqueous phase liquids (DNAPLs), such as CAHs, than for the lighter weight or light non-aqueous phase liquids (LNAPLs), such as the petroleum products.

The extent of surface migration is a function of the volume of contaminant released, the area over which the release occurs, the duration of the release, and the chemical and physical properties of the contaminant and the subsurface environment. In soil, the hydrocarbon constituents are transported by the flow of the NAPL or diffusion in soil-gas vapor. If the volume of free product released into the subsurface is small, relative to the retention capacity of the soil, then the hydrocarbons will tend to sorb to soil particles and essentially the entire mass will be immobilized. In groundwater, advective transport (the movement of contaminants by flowing groundwater) is the predominant factor in the transport of the dissolved constituents. Dissolution, volatilization and sorption determine the partitioning between phases. The typical phase distribution, equilibrium process and predominant physicochemical characteristics for each of the processes are summarized in the following “Phase Distribution Figure and Equilibrium Process Table.” The physicochemical characteristics are described in Section 4.4.

In general, the greater the impacted area and depth, resulting from the release of a contaminant, the greater the cleanup cost, regardless of the remediation approach. The phase distribution of the contaminant constituents in the subsurface environment is critical for the selection of the remediation process. For example, the dissolved (aqueous) phase contaminants are more readily available for biodegradation than NAPLs. Also the product mix may need to include surface active agents for the mobilization of soil adsorbed phase constituents into the groundwater dissolved phase.

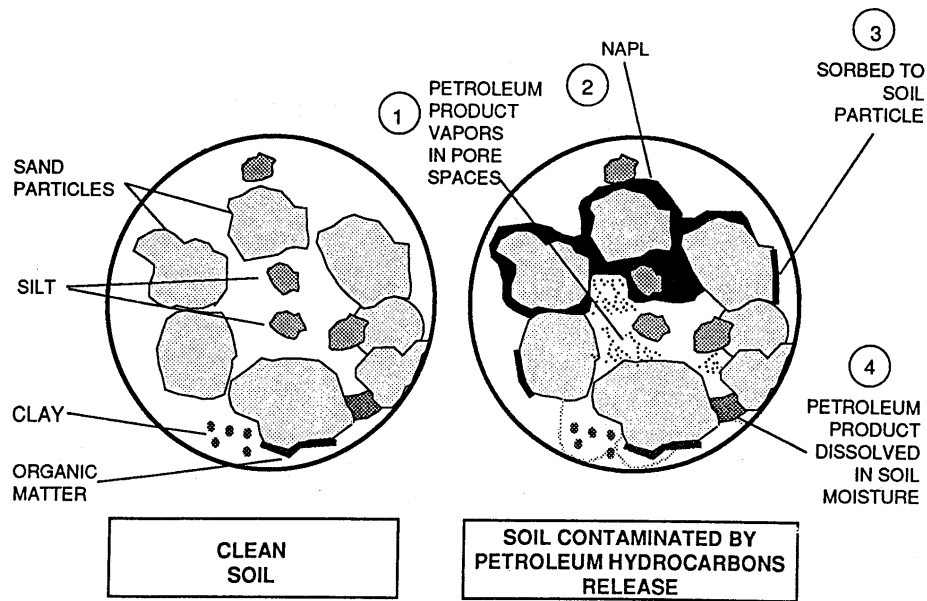
Relevance: Contaminant Transport
Site Monitoring
Site Closure Options
Remediation Process Selection

4.3 Chemicals of Concern (Contaminant Concentrations)

The horizontal and vertical extent of the chemicals of concern (COC) and the maximum concentration for each chemical in the impacted media are critical for selecting and designing a remedial action. The plume concentration maps are useful in determining or confirming the source(s) of contamination, identifying imminent offsite migration and selecting target areas (or media and/or zones) for active treatment, passive remediation or monitoring. The historical analytical data provide information concerning the occurrence of natural attenuation at the site.

The current concentrations (and historical trend) of the COC and the geochemical properties of the site should be used to evaluate alternative site closure options and remedial approaches. The current concentrations of the COC are used for estimating the existing contaminant mass, designing the remedial system and preparing a monitoring plan. It directly affects the cleanup time and costs. The goal of a remedial system is to remove the COC to concentration levels below the cleanup target levels (CTLs) or levels required for alternative closure options, in all the applicable media. The physical and chemical properties of selected COC are tabulated in Section 4.4 for chlorinated solvents and petroleum products.

Relevance: Contaminant Transport
Site Monitoring
Site Closure Options
Remediation Process Selection and Design Criteria



Phase Distribution (Figure Above) and Equilibrium Process (Table Below)

<i>Contaminant Phase</i>	<i>Phase Distribution (Equilibrium Process)</i>	<i>Predominant Factor</i>
Non-Aqueous Phase Liquid (NAPL)	Dissolution to Groundwater	Solubility
	Dissolution to Soil Matrix	Partition Coefficient
	Volatilization to Soil Gas	Vapor Pressure
Soil Gas Phase	Dissolution to Groundwater	Henry's Constant
	Adsorption to Soil Matrix	Vapor Pressure
Soil Adsorbed Phase	Dissolution to Groundwater	Partition Coefficient
	Volatilization to Soil Gas	Vapor Pressure
Groundwater Dissolved Phase	Adsorption to Soil Matrix	Partition Coefficient
	Volatilization to Soil Gas	Henry's Constant

4.4 Physicochemical Properties

The physicochemical properties of contaminants (composition, solubilities, density and viscosity, vapor pressure and partitioning coefficient) affect how the contaminants are distributed and transport in the subsurface environment. The phase distribution and equilibrium processes are summarized in the previous figure and table. The following describes pertinent physicochemical properties and their relevance to contaminant transport and remediation processes.

Chemical and Physical Properties

Selected Chemicals of Concern

Chemicals of Concern	Molecular Weight (g/mole)	Liquid Density (g/ml @ 4°C)	Aqueous Solubility (mg/L @ approx 25°C)	Vapor Pressure (mm Hg @ 25°C)	Log Kow (Octanol/Water Partition Coefficient)	Henry's Law Constant (atm·m ³ /mol)
<i>Drycleaning (Chlorinated) Solvents</i>						
Tetrachloroethene (PCE)	165.8	1.62	150	17.8	2.6	0.0153
Trichloroethene (TCE)	131.4	1.46	1100	57.9	2.38	0.0091
cis-1,2-Dichloroethene (cis-DCE)	96.9	1.28	3500	208	0.7	0.0037
chloroethene (Vinyl chloride)	62.5	gas	2670	2660	1.38	0.315
1,1,1-Trichloroethane (1,1,1-TCA)	133.4	1.34	1500	123	2.5	0.008
Chloroethane (Ethyl chloride)	64.5	gas	5700	1064	1.52 to 2.16	0.0085
Tetrachloromethane (Carbon tetrachloride)	153.8	1.59	757	90	2.64	0.0304
Dichloromethane (Methylene chloride)	84.9	1.33	20000	362	1.3	0.00268
Chloromethane (Methyl chloride)	50.5	gas	6500	4310	0.95	0.0452
<i>Petroleum Solvents or Products</i>						
Acenaphthene	154	1.069	3.42	2.04E-06	4.33	9.02E-05
Anthracene	178	1.25	4.50E-02	2.56E-07	4.45	1.02E-03
Naphthalene	128.16	1.145	34.4	1.14E-04	3.37	4.26E-04
Benzene	78.12	0.879	1780	1.00E-01	2.13	4.40E-03
Ethylbenzene	106.17	0.867	152	9.00E-03	3.15	6.00E-03
Toluene	95.15	0.866	515	2.90E-02	2.69	5.20E-03
Xylenes, total	106.17	0.867	186.7	8.00E-03	3.04	4.70E-03

Density

The density of a substance refers to the mass per unit volume of the substance, and it may be presented as specific gravity (the ratio of a substance's density to that of some standard substance, usually water for liquids and air for gases, at a specified temperature). The density of most fluids generally decreases with increase in temperature.

Density affects the buoyancy of a contaminant; it determines whether gases are heavier than air, or whether liquids will float or sink. Light non-aqueous phase liquids (LNAPLs), such as gasoline, fuel oil and non-halogenated solvents, have densities less than the density of water (specific gravity less than 1.0), and they float when in contact with water. Dense non-aqueous phase liquids (DNAPLs), such as the halogenated solvents, have densities greater than the density of water (specific gravity greater than 1.0), and they sink when in contact with water. Density also affects the subsurface mobility of fluids. As noted in Section 3.5, hydraulic conductivity is a function of the absolute permeability of the porous medium and the density and viscosity of the flowing fluid. The hydraulic conductivity of a porous medium, with respect to a fluid, increases with increase in density.

Viscosity

Viscosity describes a fluid's resistance to flow. It is temperature dependent and generally decreases with increase in temperature.

Viscosity is used to determine the ability to pump a fluid through pipes and the subsurface, and the rate of flow into and through injection and extraction wells; the lower the fluid's viscosity, the less the energy required for the fluid to flow through pipes and porous media. Also, the hydraulic conductivity of a porous medium, with respect to a fluid, increases as the viscosity of the fluid decreases.

Water Solubility

The aqueous solubility of a constituent is a measure of the maximum weight of the constituent that can be dissolved in water at a given temperature; it is a component of the vapor/dissolved phase partitioning behavior of the constituent. Contaminants have a broad range of aqueous solubility. For example, ethylamine is miscible with water, where as, dichloromethane, benzene, tetrachloroethene, naphthalene and anthracene have solubilities of 20000, 1780, 150, 34 and 0.045 mg/L, respectively, at 25 °C.

Solubility controls the amount of solute that can partition into the aqueous phase and thus be transported. In general, the more soluble the compound, the further it will be transported in the subsurface via groundwater.

Insolubility and sorption may limit the bioavailability of an organic contaminant, the interaction between the contaminant and the microbes responsible for its biodegradation. Microbes may

degrade some insoluble hydrocarbons in aqueous solution by direct contact with the surface of the hydrocarbon. For others, however, some hydrocarbons must be dissolved in the aqueous phase before appreciable biodegradation can occur. For example, the biodegradation of PAHs is often limited because the contaminants are not available to the biomass.

Interfacial Tension

Interfacial tension is the energy required to enlarge the interface (surface of separation) between two phases by one unit area. The surface phase separating two bulk phases (two liquids or a liquid and a vapor) may be a few molecules thick, and it occurs because forces of molecular attraction in the same phase are much greater than the forces between the molecules in different phases. Temperature, changes in pH and the presence of surfactants and dissolved gases affect interfacial tension.

Interfacial tension between an organic liquid and water affects such processes as the formation of stable emulsions, the resistance to flow through capillaries, the dispersion of droplets and liquid-liquid entrapment in porous media. The low interfacial tension between a NAPL phase and water allows the NAPL to enter easily into small fractures and pore spaces, facilitating deep penetration into the subsurface. Low interfacial tension also contributes to the low retention capacities of soils for chlorinated solvents. The presence of surfactants in liquid/vapor phase systems can lead to the generation of foam; and this may drastically impact the flow behavior and mobility of both phases, especially in a heterogeneous porous medium.

Wettability

Wettability is the preferential attraction of a fluid phase to a solid surface, when two immiscible phases are placed in contact with the solid surface. As a result, the fluid phase (wetting phase) spreads on (adheres to, coats or wets) the solid surface. In a subsurface multiphase system, the wetting phase fluid forms a thin film around the rock matrices, while the non-wetting phase occupies the interconnected pore spaces. The composition of NAPL aqueous phase (dissolved); the presence of organic matter and surfactants; the mineralogy and the saturation history of the porous medium affect the wettability of the medium.

In the vadose zone, where air, water and LNAPL are present, liquids (usually water), preferentially wet the solid (soil) surfaces. Where only air and NAPL are present, the NAPL will wet the surface. In the saturated zone, with only water and NAPL present, water will generally be the wetting fluid and will displace LNAPL from pore spaces.

Vapor Pressure

Vapor Pressure is the pressure exerted by the vapor of a compound at equilibrium with its pure condensed phase (liquid or solid) at a given temperature. Vapor pressure is a measure of a compound's tendency to volatilize and partition into the gas phase (vapor/dissolved phase

partitioning). It increases with temperature, and for a pure compound will equal 1 atmosphere at its boiling point temperature.

In the subsurface, vapor pressure is an indication of the tendency of a compound to volatilize from the adsorbed, liquid and aqueous (dissolved) phases. Constituents with higher vapor pressure are generally more likely to convert from the dissolved phase to the vapor phase. Vapor pressure and Henry's law constant are the critical indicators of the volatility of a constituent. Constituents with higher vapor pressures are generally more amenable for extraction by soil vacuum extraction (SVE) than constituents with lower vapor pressures.

Henry's Law Constant (Vapor/Dissolved Phase Partitioning)

Henry's law states that the ratio of the partial pressure of a constituent in the vapor phase to the concentration of the constituent in the dissolved phase is constant, for ideal gases and solutions under equilibrium conditions.

$$P_a = H_a X_a \quad \text{where: } P_a = \text{partial pressure of constituent } a \text{ in air (atm)}$$
$$H_a = \text{Henry's law constant (atm)}$$
$$X_a = \text{solution concentration of constituent (mole fraction)}$$

Solubility and vapor pressure interact to control the air-water partitioning of volatile organic compounds; and Henry's law constant (or air-water partition constant) can be expressed as the ratio of saturated vapor density to solubility. The Henry's law constant quantifies the relative escaping tendency of a compound to exist as vapor molecules as opposed to being dissolved in water. Thus, it is an index of the partitioning of a chemical (equilibrium distribution) between the dissolved and gaseous phases. Vapor/dissolved phase partitioning is a function of both vapor pressure (a measure of volatility) and solubility; the most important characteristic to evaluate it is Henry's law constant, and solubility is the least important.

Compounds with larger H_a values are more likely to move by vapor diffusion as opposed to liquid diffusion. High vapor pressure and low solubility compounds will partition appreciably from water to air. High vapor pressure, very high solubility compounds (e.g., acetone), do not partition easily from water to air. The Henry's law constant is used to evaluate partitioning of compounds from soil moisture and groundwater into soil gas. It is also used in the design of air strippers. Constituents with greater Henry's law constants are generally more amenable for extraction by SVE than constituents with lower Henry's law constants.

Example 4-1

In general, lower molecular weight petroleum organic compounds have lower viscosity, higher volatility, moderate water solubility, and hence higher mobility.

- a. True
- b. False

Answer: a.

Example 4-2

The magnitude of the effect of gravity and capillary forces on LNAPLs and DNAPLs are the same, and one would expect no differences in the subsurface phase distribution of the two.

- a. True
- b. False

Answer: b.

Example 4-3

Which of the following statements is incorrect?

- a. The current and historical trends of the concentrations of the chemicals of concern are both important in evaluating alternative remedial actions at contaminated sites.
- b. Interfacial tension affects the formation of stable emulsions in organic liquid/water systems and foams in liquid/vapor phase systems.
- c. The volume or mass of a subsurface discharge, and the resulting area and depth of impact do not affect the cost of cleanup.
- d. Dissolved (aqueous) phase contaminants are more readily available for biodegradation than NAPLs.

Answer: c.

5.0 GEOCHEMICAL PROPERTIES

Geochemical properties affect the fate and transport of contaminants in the subsurface environment, and may indicate changes resulting from biological, chemical and physical processes. Geochemical properties should be evaluated at the unaffected or background (upgradient), contaminant source and plume areas.

5.1 Temperature and pH

Physicochemical properties, such as density, viscosity, solubility, interfacial tension and vapor pressure are dependent on temperature and/or pH, among other factors. Biochemical processes operate best within optimum ranges of pH and temperature. These are site and process-specific. The optimum temperature range is 10 to 40°C (50 – 104°F) and the optimum pH range is 6 to 8 for many applications. Temperature and pH can be used to determine if conditions are beneficial for microbial growth; most bacteria prefer pH of 6.5-7.5. Aerobic biodegradation of petroleum products produces carbon dioxide and organic acids, resulting in a region of lower pH and increased alkalinity. Anaerobic biodegradation may result in increased pH.

5.2 Dissolved Oxygen and Oxidation-Reduction (Redox) Potential and Other Electron Acceptors

The dissolved oxygen (DO) and the oxidation-reduction potential (ORP) measure the oxidizing (aerobic) and reducing conditions (anaerobic) of the contaminant environment; different microbial processes and terminal electrons are used under these conditions. In general, biodegradation rates tend to be much lower under reducing conditions than under oxidizing conditions. In-Situ bioremediation may be limited by the rate at which oxygen is transferred to the degrading microorganism; dissolved oxygen becomes limiting at concentrations between 0.1 and 1.0 mg/L for aerobic conditions. Depending on other factors, anaerobic conditions will be induced if DO is less than 0.5 mg/L in groundwater.

The ORP or redox potential generally ranges from +800 to -400 millivolts in groundwater, and it identifies microbes that are likely to be present. A redox potential greater than zero is commonly interpreted to be an oxidizing environment. The change in redox potential can be used as an indication of the amount of biodegradation that may have occurred in a contaminated site.

When oxygen supply is depleted, facultative anaerobic microorganisms will utilize nitrates as electron acceptor. Once available oxygen and nitrate are depleted microorganisms may use ferric iron (insoluble) as an electron acceptor. The ferric iron [Fe^{3+}] is reduced to ferrous iron [Fe^{2+}]. This is soluble. When the redox potential is further reduced, sulfate may act as electron acceptor. Under significantly lower redox conditions, methanogenic conditions will exist and the microorganisms can degrade the petroleum contaminants using water as electron acceptor. Reduced forms of iron (Fe^{2+} , soluble) and other metals may be oxidized during in-situ remediation by processes, such as soil venting, air sparging and multi-phase extraction, that involve the movement of air through the contaminated media. The normal oxidized form of iron

in water is approximately 0.1 to 0.3 ppm, depending on the pH of formation water. Deposition of biomass (resulting from biological activities) and oxides of iron can reduce the permeability of the contaminated porous medium.

5.3 Organic Content of Soil

The soil solids contain organic and inorganic components; the organic matter serves a critical role in the sorption of contaminants. The organic content of soil determines the extent to which contaminants may adsorb to soil, rather than migrate with groundwater; and provides a source of carbon for biodegradation. The tendency to adsorb (retard) organic compounds increases with organic content. However, natural organic matter that consumes oxidants can have an adverse impact on a chemical oxidation process.

Finer-grained soils (e.g., clayey soil) typically have a higher organic matter than the coarse grained soils, and have a stronger adsorption potential for organic contaminants. The fraction of organic carbon (f_{oc}) typically ranges from 1 to 3.5 per cent in surficial soils, and an order of magnitude lower in subsurface soils. The adsorption coefficient (K_d), the tendency of a constituent to remain adsorbed on soil, is given by the product of f_{oc} and the organic carbon partition coefficient (K_{oc}). The latter is considered as the partition coefficient for the organic compound with hypothetical pure organic carbon phase.

$$K_d = f_{oc} \times K_{oc}$$

5.4 Nutrients and Soil Minerals

The primary reason to determine nutrient availability in contaminated media is for the consideration of monitored natural attenuation and/or active remediation by bioremediation. The microbial requirements for nutrients are almost the same as their cell composition. The chemical structure of microorganisms is often expressed as “ $C_5H_7O_2N$ ” or $C_{60}H_{87}O_{32}N_{12}P$. Hydrogen and oxygen are supplied by water. The maximum amount of major nutrients (carbon, nitrogen and phosphorus) that should be required is a ratio of 100:10:1 or 2 of C:N:P for microbial degradation of organic contaminants. Ammonia, nitrate and nitrite are the most biologically available forms of nitrogen; and ortho-phosphate is the most biologically available form of phosphorus. Caution should be exercised in interpreting nutrient measurements and correlating the results with biological activity, since organic forms of the nutrients exist.

Besides the major nutrients, minor nutrients such as potassium, sulfur, magnesium, calcium, sodium, chlorine are important as trace elements that are part of the building blocks of microorganisms. These microelements are present in most soil and aquifer systems.

5.5 Microbes and Microbial Activities

Heterotrophic bacteria and fungi derive the carbon and energy for growth from organic compounds, and are the primary agents of bioremediation. The presence of microorganisms

capable of degrading the contaminants, in sufficient numbers should be evaluated. Heterotrophic plate counts, specific degrader counts and *in-situ* respiration tests can be utilized to perform this evaluation. Microbial populations in the range of 10^5 – 10^7 colony forming units per gram (cfu/gm) of soil may be considered healthy for bioremediation.

Bioavailability, discussed in Section 4.4 (Aqueous Solubility), is another factor that determines microbial activity.

Biodegradability of Contaminants

The chemical nature of a contaminant affects its biodegradability. Simple hydrocarbons, C₁-C₁₅, are easier to biodegrade than the more complex compounds, such as the PAHs. Preferential degradation results in a sequential attack where the higher energy yielding compounds are degraded first. In a petroleum product contaminated site, for example, benzene will be degraded at a faster rate than naphthalene under aerobic conditions. Also, the reaction (biodegradation) pathways may determine whether the contaminant is utilized as a primary substrate or whether cometabolic reactions are necessary. Due to the kinetics of enzyme induction and substrate binding, there is a substrate concentration below which biodegradation rates will be negligible. Thus, contaminants initially at very low concentrations may not be degraded at all.

Example 5-1

A dissolved oxygen (DO) value of less than 0.5 mg/L at any portion of a contaminated site most likely indicates which of the following?

- a. An oxidizing environment.
- b. A reducing environment.
- c. None of the above.

Answer: b.

Example 5-2

Which of the following statements is incorrect?

- a. Reduced forms of iron and other metals may be oxidized during in-situ remediation, if it involves the movement of air through the contaminated media.
- b. Redox potential greater than zero is commonly interpreted to as an indication of oxidizing environment.
- c. Natural organic matter that will consume oxidants most likely would not have an adverse impact on a chemical oxidation process.
- d. Simple hydrocarbons, C₁-C₁₅, may be easier to biodegrade than the more complex compounds, such as the PAHs.
- e. Heterotrophic plate counts, specific degrader counts and *in-situ* respiration tests can be used to evaluate the presence of contaminant degrading microorganisms.

Answer: c

Example 5-3

Temperature, pH and Specific Conductance are common indicator parameters of changes resulting from active remediation or naturally occurring biological and chemical processes.

- a. True
- b. False

Answer: a.

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