



Ground Water Issue

FUNDAMENTALS OF SOIL SCIENCE AS APPLICABLE TO MANAGEMENT OF HAZARDOUS WASTES

David S. Burden* and Judith L. Sims**

INTRODUCTION

The Regional Ground Water Forum is a group of ground-water technical specialists, representing EPA's Regional Offices, organized to exchange up-to-date information related to ground-water remediation at hazardous waste sites. Proper site characterization has been identified by the EPA Regional Ground Water Forum as a major issue of concern for decision-makers at many hazardous waste sites. In order to have a thorough understanding of the processes involved in remediating the subsurface, a working knowledge of the major physical, chemical, and biological factors which affect the fate of contaminants in the vadose zone must be achieved. This paper summarizes the basic concepts of soil science as related to the management of hazardous wastes and serves as a foundation from which to build a thorough understanding of soil processes.

For further information contact Dr. David S. Burden, 580-436-8606, at the Subsurface Protection and Remediation Division of the National Risk Management Research Laboratory, Ada, Oklahoma.

Soil as a Waste-Receiver System

A thorough soil characterization of a contaminated terrestrial system is essential to the development of an accurate assessment of the extent of problems associated with the specific contamination as well as identification and

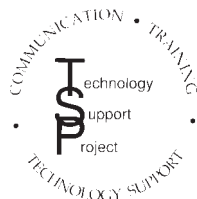
implementation of remedial actions. Characterization efforts will define potential means and routes of exposure to human populations and the environment in order to develop appropriate site modification and management procedures for protection of public health and the environment. The goal of an effective soil characterization process is the identification and measurement of specific soil factors that affect the behavior and fate of specific waste constituents at a specific contaminated site so that an effective remedial action can be developed and implemented.

Figure 1 depicts possible degradation and immobilization/transport processes influencing the behavior and fate of waste constituents in a soil system. In a soil, residual waste constituents may pose public and environmental health hazards through their ability to contaminate the atmosphere through volatilization or resuspension as airborne particles and the hydrosphere through leaching and runoff (Dawson and Brown 1981).

Human exposure via atmospheric pathways may occur directly through dermal contact and inhalation of particles or gas or indirectly through deposition on crops or bioaccumulation in grazing game and agricultural animals, either or both of which may be ingested by humans. Waste constituents may reach surface waters in runoff, either dissolved or suspended in water or adsorbed to eroding soil particles. Movement of waste constituents through the soil may occur as a liquid or gas or dissolved in soil water. Movement may be in both lateral and vertical directions to ground and surface waters. Human contact may occur through ingestion of the contaminated water. Detoxification of some waste constituents may be accomplished by the growth of plants or removed from the site in vegetation.

* Hydrologist, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Subsurface Protection and Remediation Division

** Soil Scientist, Utah Water Research Laboratory, Utah State University



Superfund Technology Support Center for Ground Water

National Risk Management Research Laboratory
Subsurface Protection and Remediation Division
Robert S. Kerr Environmental Research Center
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency
Response, US EPA, Washington, DC

Walter W. Kovalick, Jr., Ph.D.
Director

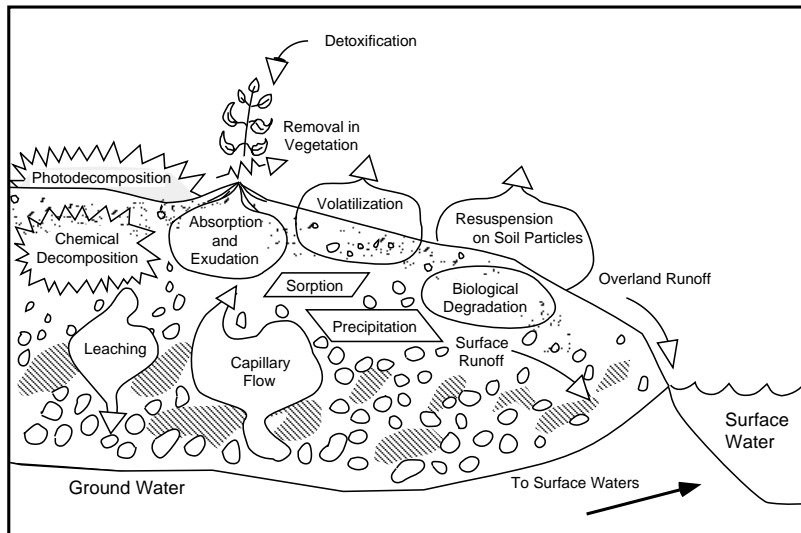


Figure 1. Processes influencing fate and behavior of waste constituents in the soil environment (Sims et al., 1984).

Behavior and Fate of Waste Constituents in a Soil System

Degradation and Detoxification

The term *degradation* may refer to complete mineralization of hazardous constituents to carbon dioxide, water, inorganic compounds, and cell mass. In the natural environment, a constituent may not be completely degraded, but transformed to intermediate products that may be less, equally, or more hazardous than the parent compound, as well as less or more mobile in the environment. The goal of using degradation as a remedial process is the formation of products that are no longer hazardous to human health and/or the environment. Degradation processes in a contaminated soil system may include biotic and abiotic reactions. The ultimate products of aerobic metabolism are carbon dioxide and water. Under anaerobic conditions (i.e., in the absence of oxygen), metabolic activities result in the formation of incompletely oxidized simple organic substances such as organic acids as well as other products such as methane or hydrogen gas.

Both microbial populations and higher plants may be active in the breakdown of waste constituents. In most bioremediation management processes at the present time, the use of microbial degradation is the primary focus, though research is being conducted to evaluate the use of plants to degrade waste constituents (e.g., Walton and Anderson 1990; Aprill and Sims 1990).

Abiotic degradation reactions in soil systems often do not result in complete degradation of waste constituents, but may alter them sufficiently so that they are more susceptible to further degradation by biotic processes. Abiotic mechanisms that may account for loss of waste constituents include (Sims et al., 1984; Dragun, 1988):

- (1) *hydrolysis*- a chemical reaction in which a waste chemical reacts with water or hydroxide ions;
- (2) *photochemical degradation*- use of incident solar reaction to accomplish degradation. Two processes may be involved in photodegradation: (1) direct photodegradation, in which

each particle of light, or quanta excites one substrate molecule; and (2) sensitized photodegradation, in which a sensitizing molecule absorbs light in the visible region and then returns to ground state by transferring its excess energy to molecular oxygen, forming singlet oxygen, a highly reactive species of oxygen that readily oxidizes organic substrates.

- (3) *substitution and elimination*- processes where other chemicals in the soil react with a waste constituent by substituting for reactive groups or eliminating reactive groups;
- (4) *oxidation*- a reaction resulting in the removal of electrons from a chemical. This removal generally occurs by two different pathways: (a) heterolytic or polar reactions (an electrophilic agent attacks a molecule and removes an electron pair, resulting in the formation of an oxidized product); or (b) homolytic or free radical reaction (an agent removes only one electron to form a radical that undergoes further reaction); and
- (5) *reduction*- a reaction that results in a net gain of electrons.

Immobilization/Transport

Waste constituents may be immobilized in a soil system by sorption or partitioning to soil particles (e.g., organic materials, such as humus, or inorganic materials, such as the clays montmorillonite, vermiculite, or the hydrous oxides). Other mechanisms of immobilization are chemical precipitation or polymerization processes. Transport of constituents through the soil may be as volatile materials, sorbed to mobile soil particles (i.e., facilitated transport (Huling 1989)), or leached with soil liquids (water or organic waste liquids). Transport may also occur as dissolved or sorbed constituents move with runoff waters or as constituents move into the atmosphere as volatile materials or are sorbed to suspended airborne soil particles.

The ultimate fate of waste constituents immobilized in a soil system is dependent upon the long-term stability of immobilized waste constituent/soil complexes and reversibility of the

immobilization reactions. The effectiveness of soil remedial technologies such as soil flushing will also be dependent upon the strength and reversibility of immobilization processes.

DESCRIPTION OF THE SOIL AND VADOSE ZONE

Definition and Description of Soils

A soil is defined by the Soil Science Society of America (1987) as "the unconsolidated mineral matter on the immediate surface of the earth that (1) serves as a natural medium for the growth of land plants; and (2) has been subjected to and influenced by genetic and environmental factors of parent material, climate (including moisture and temperature effects), macro- and microorganisms, and topography, all acting over a period of time and producing a product -soil- that differs from the material from which it was derived in many physical, chemical, biological, and morphological properties and characteristics."

The soil is a complex system, consisting of three phases: (1) soil gases; (2) soil water; (3) organic and inorganic solids. For a soil impacted by wastes, a fourth phase, nonaqueous phase liquids (NAPLs), may also be present. Gases and water, which are found in the pore spaces of a soil, together comprise about 25 to 50 percent (by volume). A waste constituent, depending upon solubility and tendency to volatilize, may be found in varying proportions in these two phases. Pore sizes, continuity, and relative proportions of water and air in the pores are examples of factors that affect the mobility of contaminants (both vertically and horizontally) in a specific soil.

Soil solids include both organic and inorganic components. The inorganic components are comprised of sparingly soluble constituents known as minerals, which are composed of primarily quartz, feldspars, iron and aluminum hydrous oxides, kaolinite, smectites, and micaceous minerals distributed in sand, silt, and clay size fractions in most soils. The solids may contain highly reactive charged surfaces that play an important role in immobilizing waste constituents in a specific soil. Certain types of clay minerals such as the smectites are especially high in negative charges, thus exhibiting what is termed as a high exchange capacity. Clays and hydrous oxides may also contain positively charged surfaces and act as anion exchange media for negatively charged constituents.

Soil organic matter also has many highly reactive charged surfaces and may aid in retaining waste constituents in a soil system. The term *humus* refers to the relatively stable portion of soil organic matter that remains in soil after plant and animal residues have decomposed. Hydrophobic organic constituents may be sorbed onto soil organic matter and thus become less mobile in the soil system. Immobilization of organic waste constituents may result in additional time for degradation, reducing bioavailability to microorganisms.

Soil Profiles and the Vadose Zone

Surface soils are a portion of the vadose zone, which is the part of the earth extending from the ground surface to the upper surface of the principal water-bearing formation (Lehr 1988). In the vadose zone, water in pore spaces generally coexists with air, though saturated regions may occur if perched water tables develop at interfaces of layers with different textures and permeabilities. Prolonged infiltration may also result in transient saturated conditions. Topsoils are weathered geological materials arranged in more or less well-developed layers (referred to as soil horizons). The depth of a soil horizon is site specific. Water movement in topsoils is unsaturated, with soil

water held in the soil at less than atmospheric pressure. Weathered topsoil materials usually gradually merge with underlying earth materials, which may include residual or transported solids. Topsoil differs from the material lying below it in that it is often more weathered, contains organic matter and biological life associated with organic matter, and is the zone of maximum plant-root growth. The entire vadose zone may be hundreds of feet thick, and the transport time of pollutants to the ground water hundreds or thousands of years, while in other regions, the vadose zone may be underlain by shallow, potable aquifers that are especially susceptible to contamination due to short transport times and presence of soil materials that have low potential for pollutant attenuation.

Soil horizons are designated A, E, B, and C to represent surface soil, subsoil, and substratum, respectively. The A and B horizons are formed by weathering and other soil-forming factors. The C horizon, relatively unchanged by soil forming processes, is usually composed of slightly altered parent material or undifferentiated geological deposits from which the A and B horizons developed (e.g., sediment from ancient sea and lake beds, loess), rocks and rock powder released from melting glaciers, and alluvium from flooding streams). The E horizon is the horizon of maximum eluviation of silicate clays, iron, and aluminum oxides. The E horizon is also generally lighter in color than the A horizon. Not all soils have all four horizons, while many soils show variations within each master horizon.

Each horizon within a specific soil can have significantly different characteristics such as depth, texture, bulk density, mineral composition, and chemical properties that may result in differing waste transport and attenuative characteristics. Horizon boundary characteristics can adversely affect vertical movement (percolation) of soil liquids. Such boundary characteristics include abrupt changes in texture or structure, such as clay or sand layers or the presence of hard pans (i.e., a hardened soil layer in the lower A or in the B horizon caused by cementation of soil particles with organic matter or with materials such as silica, sesquioxides, or calcium carbonate and whose hardness does not change appreciably with changes in water content). Horizontal flow may also result from such discontinuities, resulting in contamination of adjacent areas. In general, deeper soil horizons result in more potential attenuation of waste constituents and greater protection against transport of constituents to ground water.

Soil Physical Properties

Soil Texture and Textural Classes

Soil texture is a term that reflects the relative proportions of the various particles (commonly referred to as soil separates) in a soil. Size classes of soil separates, as defined by the U.S. Department of Agriculture (USDA) and the Unified Soil Classification System (USCS), are presented in Table 1.

The analytical procedure that is used to separate soil separates is called particle-size analysis (Brady and Weil 1999). Sieves are used to mechanically separate the very fine sand and larger separates from the finer particles. Silt and clay contents are then determined by measuring the rate of settling of these two separates from suspension in water. Stones and gravel are separated from a soil sample before particle-size analysis. Organic matter is usually also removed, by oxidation reactions, before analysis. The results of the analysis are used to assign a soil to a textural class.

Soil textural classes are used to provide information concerning soil physical properties. The proportions of sand, silt, and clay

Table 1. U.S. Department of Agriculture (USDA) and Unified Soil Classification System (USCS) Particle Sizes (Fuller 1978)

| USDA | | USCS | |
|------------------|-----------------|--------------------|-----------------|
| Particle | Size Range (mm) | Particle | Size Range (mm) |
| Cobbles | 76.2 - 254 | Cobbles | >76.2 |
| Gravel | 2.0 - 76.2 | Gravel | 4.76 - 76.2 |
| Coarse gravel | 12.7 - 76.2 | Coarse gravel | 19.1 - 76.2 |
| Fine gravel | 2.0 - 12.7 | Fine gravel | 4.76 - 19.1 |
| Sand | 0.05 - 2.0 | Sand | 0.074 - 4.76 |
| Very coarse sand | 1.0 - 2.0 | Very coarse sand | |
| Coarse sand | 0.5 - 1.0 | Coarse sand | 2.0 - 4.76 |
| Medium sand | 0.25 - 0.5 | Medium sand | 0.42 - 2.0 |
| Fine sand | 0.1 - 0.25 | Fine sand | 0.074 - 0.42 |
| Very fine sand | 0.05 - 0.1 | Very fine sand | |
| Silt | 0.002 - 0.05 | Fines ^a | <0.074 |
| Clay | <0.002 | (Silt and clay) | |

^a USCS silt and clay designations are determined by response of the soil to manipulation at various water contents rather than by measurement of size.

in a specific soil are used to define the textural class, using a textural triangle (Figure 2). The triangle is used by locating the percentage of one of the soil separates and projecting inward in the direction of the arrow. The same procedure is used for one of the other separates. The point at which the two projections cross identifies the class name.

Three broad groups of textural class names are often used to classify soil texture (Table 2). These general terms are also used to provide indications of physical and chemical properties of soils. Finer-textured soils have a greater surface area and greater intensities of physical and chemical properties, such as adsorption and swelling, as shown in Figure 3. Soil textural classes are not easily subjected to modification in the field. Texture of a specific soil can only be changed by mixing with soil of a different textural class.

K. W. Brown and Associates (1980) developed a summary of the advantages and disadvantages of the use of various textured soils for the treatment of hazardous industrial wastes (Table 3). In general, loam, silt loam, clay loam, sandy clay loam, silty clay loam, silty clay, and sandy clay soils were identified as best suited for land treatment of hazardous wastes.

Soil Structure and Aggregation

Soil structure refers to the aggregation of primary soil separates (sand, silt, and clay) into peds or aggregates. Aggregates, separated by surfaces of weakness or open planar pores, are often seen as cracks in the soil. Structure exhibited in the different horizons of a soil profile are essential characteristics of the profile, similar to texture or chemical composition. Soils may also have no structure: coarse soils with no structure are referred to as possessing single grain structure, while fine soils are called massive (soil material clings together in large uniform masses). Ped formation is thought to result from the cementing action of soil colloidal matter (colloidal-sized clay minerals, colloidal oxides of iron and manganese, and colloidal organic matter). Peds may vary in stability, changing in response to moisture content, chemical content, chemical composition of the soil solution, biological activity, and management practices.

Structure may modify the influence of texture in regard to moisture and air relationships. Interpedal pores are often larger and more continuous compared to pores among the primary particles within the peds. For example, a soil with a content of shrink-swell clays would exhibit only limited permeability if it did not have a well-developed structure to facilitate water and air movement. Aggregation in coarse soils stabilizes the soil surfaces and increases water retention in the soil, and can also restrict infiltration.

The type of structure also determines the dominant direction of the pores and thus the direction of water movement. Platy structures restrict vertical percolation, prismatic and columnar

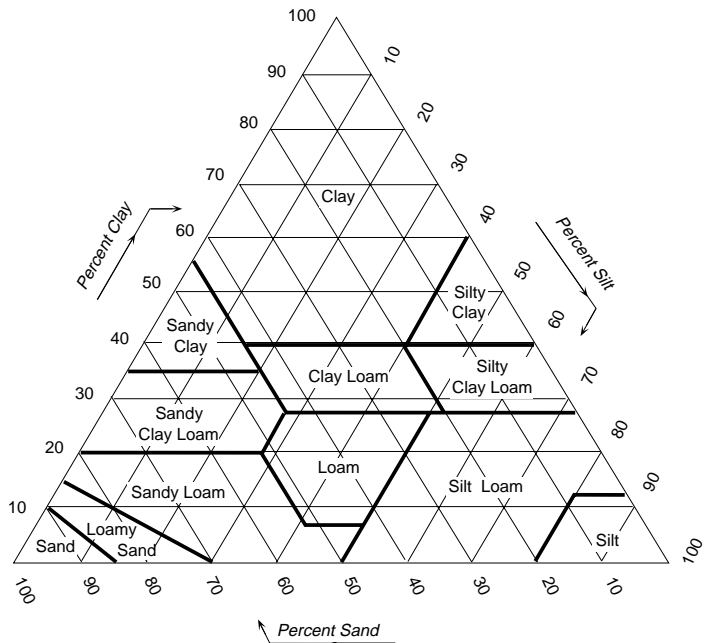


Figure 2. USDA Soil Textural Triangle.

Table 2. General Terms Used to Describe Soil Texture in Relation to the Basic Soil Textural Class Names

| U.S. Department of Agriculture Classification System | | |
|--|-------------------|---------------------------------|
| General Terms | | |
| Common names | Texture | Basic soil textural class names |
| Sandy soils | Coarse | Sands |
| | Moderately coarse | Loamy sands |
| | | Sandy loam |
| Loamy Soils | Medium | Fine sandy loam |
| | | Very fine sandy loam |
| | | Loam |
| | Moderately fine | Silt loam |
| | | Silt |
| | | Sandy clay loam |
| | | Silty clay loam |
| Clayey soils | Fine | Clay loam |
| | | Sandy clay |
| | | Silty clay |
| | | Clay |

structures enhance vertical percolation, and blocky and granular structures enhance percolation both vertically and horizontally (Otis 1983). Structural units that can withstand mechanical disturbance without disintegrating provide better soil hydraulic properties.

Soil Consistence

Soil consistence is a term used to describe the resistance of a soil to deformation or rupture, which is determined by the degree of cohesion and adhesion of the soil mass. Structure reflects the shape, size, and distinctness of soil peds, while consistence reflects the strength and nature of the forces between particles. Consistence is measured by feeling and manipulating a soil or by pulling a tillage instrument through it (Brady and Weil 1999).

Particle Density, Bulk Density, and Porosity

Two methods are commonly used to express soil mass: particle density and bulk density (Figure 4). Particle density is defined as the mass of a unit volume of soil solids. Particle density is not affected by the size of soil particles, the arrangement of the soil solids, or the pore space, but is dependent on the chemical composition and crystal structure of the mineral particles.

Particle densities for most mineral soils range from 2.60 to 2.75 g/cm³, since the major portion of soils is usually comprised of quartz, feldspar, micas, and colloidal silicate clays, with particle densities in the same range. If a soil contains minerals with high particle densities (e.g., magnetite, garnet, or hornblende), the particle density may exceed 2.75 g/cm³. Organic matter has a lower particle density, ranging from 1.1 to 1.4 g/cm³. Surface soils, with higher contents of organic matter, usually have lower particle densities than subsurface soils. However, for general calculations, the average soil with 3 to 5 percent organic matter may be considered to have a particle density of 2.65 g/cm³ (Brady and Weil 1999).

Bulk density is the mass of oven dry soil per unit bulk volume. This volume includes both solids and pores. Soils with a high

proportion of pore space to solids have lower bulk densities than those that have less pore space. Density and distribution of pore sizes determine the ease and amount of air and water stored in and moving through pore spaces. Of soils with the same texture, those with higher bulk densities are more dense, have less pore volume and are less permeable. Soil bulk densities usually increase with depth due to less organic matter, less aggregation, and compression from the weight of the overlying soil (K.W. Brown and Associates 1980). Sandy soils, with particles lying close together and low contents of organic matter, exhibit high bulk densities, ranging from 1.2 to 1.8 g/cm³. Finer textured soils have more pore space, organic matter, and lower bulk densities, generally ranging from 1.0 to 1.6 g/cm³ (Brady and Weil 1999). Root growth is impaired at bulk densities greater than 1.6 g/cm³.

A useful soil characteristic utilizing soil bulk density for determining such values as the mass of a waste constituent present at a contaminated site is calculation of the mass of a unit volume of soil. A volume commonly used is an acre-furrow slice (AFS); i.e., the volume of soil over one acre to a plow depth of 6 to 7 inches. If an average acre-furrow slice is considered to have a bulk density of 1.3 g/cm³, the soil to a depth of 7 inches would weigh approximately 2,000,000 pounds. In metric units, the weight of a hectare of soil 20 cm deep and with a bulk density of 1.3 g/cm³ would weigh approximately 2,600,000 kg/HFS. On this basis, a soil containing 1 percent (10,000 ppm) of a waste constituent would contain 20,000 pounds of the constituent per AFS.

The ratio of bulk density to particle density is a measure of the soil volume occupied by solids. For example, a soil with a bulk density of 1.56 g/cm³ and a particle density of 2.6 g/cm³ would contain 60 percent solids and 40 percent pore space.

Soil Color

Color and color patterns in soil can often be used as indicators of soil drainage characteristics of soil. Soil colors can be described in general terms (e.g., brown, gray, yellow, etc.), although the use of the Munsell color system, which characterizes soil color in quantitative descriptive terms of hue (the dominant wavelength or color of the light), value (brilliance of the light), and chroma (purity of the dominant wavelength of the light), is preferred (Foth 1984). Soil colors are determined by comparing a soil sample to the Munsell Color Chart, which

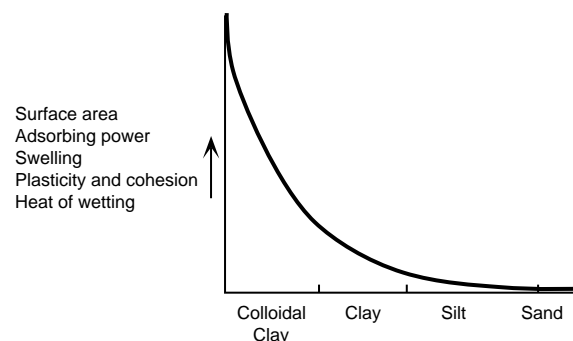


Figure 3. Relationship between soil texture and selected soil physical properties. (Reprinted from *Nature and Properties of Soils*, 12/E, 1999, by N. C. Brady and R. R. Weil with permission of Prentice-Hall, Inc. New Jersey.)

Table 3. Suitability of Various Textured Soils for Land Treatment of Hazardous Industrial Wastes (K.W. Brown and Associates 1980)

| Texture | Advantages | Disadvantages |
|-----------------|---|--|
| Sand | Very rapid infiltration; usually oxidized & dry; low runoff potential | Very low cation exchange capacity; very high hydraulic conductivity rate; low available water; little soil structure |
| Loamy sand | High infiltration; low to medium runoff | Low cation exchange capacity; moderate to high hydraulic conductivity rate; low to medium available water |
| Loam | Moderate infiltration; fair oxidation; moderate runoff potential; generally accessible; good cation exchange capacity | Fair structure |
| Silt loam | Moderate infiltration; fair oxidation; moderate runoff potential; generally accessible; good cation exchange capacity | Some crusting; fair to poor structure |
| Silt | Low infiltration; fair to poor oxidation; good cation exchange capacity; good available water | High crusting potential; poor structure; high runoff |
| Silty clay loam | Medium to low percolation; fair structure; high cation | Medium to low infiltration; some crusting potential |
| Silty clay | Good to high available water | Moderate runoff; often wet; fair oxidation |
| Clay loam | Medium-low percolation; good structure; medium to poor aeration; high cation exchange capacity; high available water | Medium to low infiltration; moderate to high runoff; often wet |
| Clay | Low percolation; high cation exchange capacity; high available water | Low infiltration; often massive structure; high runoff; sometimes low aeration |
| Sandy clay | Medium to low percolation; medium to high cation exchange capacity | Fair structure; moderate to high runoff |
| Sandy clay loam | Medium to high available water; good aeration | Medium infiltration |

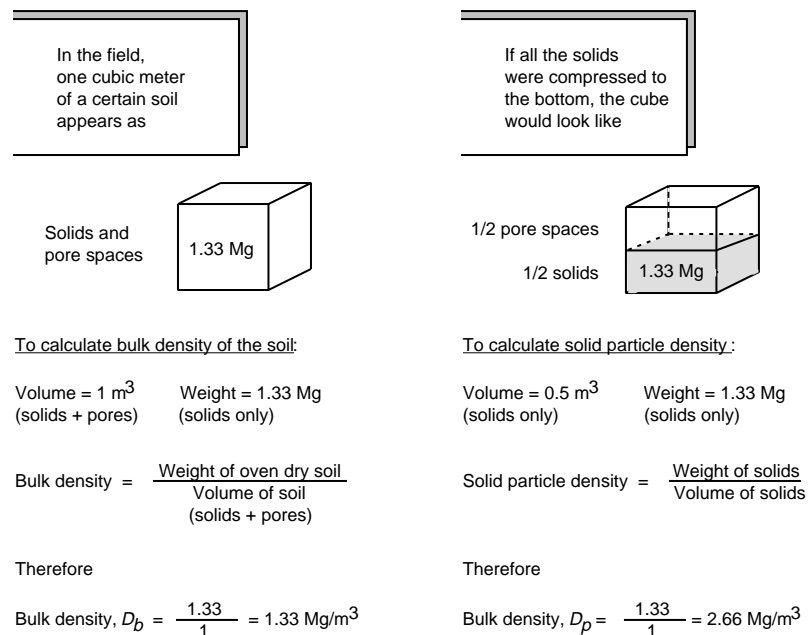


Figure 4. Calculation of soil bulk density and particle density. (Reprinted from *Nature and Properties of Soils*, 12/E, 1999, by N. C. Brady and R. R. Weil with permission of Prentice-Hall, Inc. New Jersey.)

consists of color chips arranged systematically on charts according to hue, value, and chroma. The Munsell notation of color is a numerical and letter designation of each of the three properties of color. For example, in the Munsell notation 10YR 6/4, 10YR refers to the hue, 6 refers to the value, and 4 refers to the chroma.

Uniform red, yellow, or brown colors indicate that a soil is well-drained and is seldom or never saturated with water (Foth, 1984). Organic matter is an important coloring agent in soils and is most often highest in content in surface soil layers. Organic matter is usually brown to black, depending upon the degree of decomposition. In areas where conditions are unfavorable for plant growth and accumulation of organic matter, soils may be light gray or nearly white, colors inherited from parent materials such as quartz or marl. In arid regions, surface soils may be white due to the accumulation of soluble salts after the evaporation of water, while subsoils may be white due to limited leaching and the accumulation of calcium carbonate. A red color in soil is generally produced by unhydrated and oxidized iron oxide, while yellow soil colors are produced by hydrated iron oxide. A yellow color in the subsoil is an indication of imperfect drainage but not of water saturation.

Gray or blue colors indicate that the soil is saturated continuously or for extended periods. Soils with spots or streaks (mottles) of red, yellow, or black in a gray matrix (referred to as "mottled" soils) are usually periodically saturated with water. Mottles result from chemical and biological reactions when saturated conditions, organic matter, and temperatures above 4° C occur together in the soil (Otis 1983). Bacteria utilizing organic matter deplete oxygen present in the soil. Other bacteria continue organic decomposition using insoluble oxidized iron and manganese compounds in their metabolism. The iron and manganese are reduced to soluble forms, causing a soil to lose its red, yellow, and brown colors and to turn it gray. When water moves through the soil, the soluble iron and manganese are transported to larger pores in the soil. When they contact air-filled pores, they are re-oxidized, forming insoluble compounds that accumulate as red, yellow or black mottles near pore surfaces. The soil from which the compounds were removed remains gray. Examination of a soil profile for the presence of

mottles may provide an indication of the depth of the seasonal high water table at that location.

PROPERTIES OF SOIL CLAYS, COLLOIDAL CLAYS, AND ORGANIC MATTER

Colloidal Materials in Soils

The colloidal fraction of a soil is of primary importance in sorption and immobilization of both organic and inorganic waste constituents in a soil system. The colloidal fraction, composed of organic and inorganic particles with a maximum size of 0.001 mm, is the most chemically active portion of a soil. These particles are characterized by large exposed surfaces (both outer and inner surfaces), a capacity to sorb and immobilize solids, gases, ions, and polar compounds, and a tendency to hasten (catalyze) or retard chemical reactions (Anderson et al., 1982). Of the mineral (inorganic) portion of soils, only clay particles are colloidal in size, and even some clay particles are too large to be classified as colloidal. However, recognizing the exceptions, the term "clay" is often used to refer to the inorganic colloidal portion of soils. The organic colloidal fraction is composed of amorphous humus, derived from organic materials during their breakdown by microorganisms.

Clay Minerals in Soils

Silicate Clay Minerals

The layer silicate clays have a planar, layer-like, crystalline geometry, large specific surface areas, and high residual negative charge densities that are neutralized by a large external swarm of cations, thus resulting in a capacity for strong sorption of and catalytic action towards waste constituents (Allrichs 1972).

Two basic sheet-like molecules compose the structure of silicate clays. A tetrahedral sheet is comprised of a series of tetrahedrons with four oxygen atoms surrounding a central cation, which is usually silicon (Si^{4+}), but may also be aluminum (Al^{3+}), in a close-packed arrangement (Figure 5a). An octahedral sheet is comprised of a series of octahedrons, with six oxygen atoms forming the corners around a cation, which is usually Al^{3+} (referred to as a dioctahedral sheet), but may be magnesium

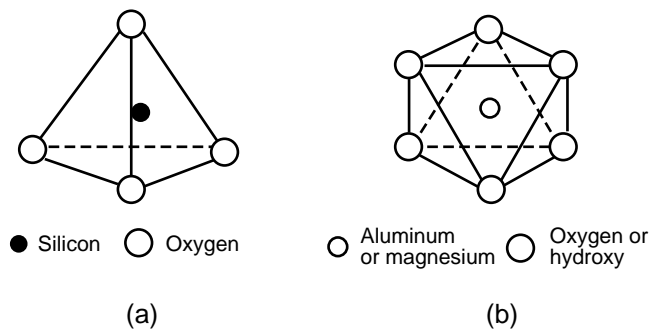


Figure 5. Basic molecular and structural components of silicate clays: (a) a tetrahedron, and (b) and octahedron. (Reprinted from *Nature and Properties of Soils*, 12/E, 1999, by N. C. Brady and R. R. Weil with permission of Prentice-Hall, Inc. New Jersey.)

(Mg²⁺) (referred to as a trioctahedral sheet) or iron (Fe²⁺ or Fe³⁺). The sheets are formed by the sharing of corner oxygens (Figure 5b).

The sheets may be joined in two ways, either in a 1:1 or 2:1 arrangement. In 1:1 arrangements, one tetrahedral layer is connected to one octahedral layer by sharing a common oxygen. Layers of these 1:1 units produce clays such as kaolinite. The 2:1 arrangement has single tetrahedral layers joined to each side of the octahedral layer by sharing of oxygen atoms. This 2:1 unit produces the basic layer that when formed into multi-layers forms such clays as montmorillonite, vermiculite, and mica.

Source of Charge in Clay Minerals

Some clays exhibit high negative charges due to substitution of lower valency cations for higher valency cations within normally neutral crystals. This process is referred to as isomorphous substitution. During formation, ions of similar radii, such as Al³⁺ for some Si⁴⁺ in the tetrahedral layer, and Mg²⁺ or Fe²⁺ for Al³⁺ or Fe³⁺ in the octahedral layer, may be substituted. The lower valency of the substituting cation results in a residual negative charge, which must be balanced by a cation external to the layer unit, either on its edge or in the interlayer surfaces.

Additional negatively charged adsorptive sites occur on the edges of clay minerals, as well as on humus, allophane, and iron and aluminum hydroxides. Because these charges are dependent on soil pH, they are termed variable or pH-dependent, compared to the more permanent charges resulting from isomorphous substitution (Brady and Weil 1999).

One mechanism of pH-dependent charge is associated with the hydroxyl (OH⁻) groups on the edges and surfaces of the inorganic and organic colloids. Inorganic colloids with pH dependent charge include 1:1 clays and Fe and Al hydrous oxides. Under moderately acid conditions, there is little or no charge on these colloids, but as the pH increases, the hydrogen dissociates, reacting with OH⁻ ions in the soil solution to form water, and resulting in a negative charge. These reactions are reversible. As the pH increases, the negative charge on the particle surfaces increases, as the pH is lowered, the negative charge is reduced.

A second source of increased negative charge with increasing pH is the removal of positively charged aluminum hydroxy ions, such as Al(OH)₂⁺, from silicate clays. As pH is raised, Al(OH)₂⁺ ions react with OH⁻ ions in the soil solution to form insoluble Al(OH)₃, thus freeing the negatively charged exchange site.

The surface geometry of the silicate clays is important in the attenuation of waste constituents. The interlayer surfaces provide most of their surface area (Allrichs 1972). The source of the charge deficit in a clay is important in determining the bonding action between layers and consequently the amount of swelling. Marshall (1964) suggested that tetrahedral sources of charge deficit provide larger bonding energies than octahedral sources, since the distance from the cause of charge deficiency is closer to the planar surface in the tetrahedra.

The size of the interlayer spacing may determine which compounds may enter the interlayer of a clay mineral. For example, montmorillonite will allow larger size molecules or compounds to enter if there is an attraction for them, while the interlayer surfaces of vermiculite with a smaller swelling potential than montmorillonite are small enough to prevent the entrance of many compounds.

Anion exchange on colloidal materials (especially on iron and aluminum oxides, some 1:1-type clays, and allophane) also occurs, but to a much lesser extent than that of cation exchange because it occurs at pH values less than 3. Anions may replace hydroxy groups and other anions in colloidal materials. Some anions, such as phosphates, molybdates, and sulfates, react with protonated hydroxy groups and are held tightly by the soil solids.

Soil Chemical Properties Associated with Charged Soil Solids

Cation exchange capacity (CEC) is a measure of the number of cation sorption sites per unit weight of soil, which is a result of both the negative charges from isomorphous substitution and from pH-dependent edge charges. CEC is defined as the sum total of exchangeable cations adsorbed, expressed in SI units as centimoles of positive charge per kilogram of soil (cmol/kg). If a soil has a CEC of 12 cmol/kg, one kg of this soil can adsorb 12 cmol of K⁺, and can exchange the K⁺ with 12 cmol of another monovalent cation, such as H⁺ or Na⁺, or with 6 cmol of a divalent cation such as Ca²⁺ or Mg²⁺. The 12 cmol of negative charge associated with one kg of soil is attracting 12 cmol of positive charges (Brady and Weil 1999).

CEC was formerly expressed in milliequivalents per 100 grams of oven dry soil (meq/100 g). One milliequivalent per 100 grams of soil is equal to one centimole per kilogram of soil, so soil data using either of these methods of expression are comparable. CEC values of typical soils range from 1-10 cmol/kg for loam soils, 12-20 cmol/kg for clay loam soils, and greater than 20 cmol/kg for clay and organic soils.

The proportion of the cation exchange capacity of a specific soil satisfied by a given cation is referred to as the percentage saturation for that cation. For example, if 25 percent of the CEC were satisfied by Mg²⁺ ions, the exchange complex has a percentage magnesium saturation of 25. The percentage saturation with H⁺ and Al³⁺ provides an indication of the acidity in a soil (i.e., exchangeable acidity), while the percentage saturation due to nonacid cations (e.g., Ca²⁺, Mg²⁺, K⁺, Na⁺), referred as percentage base saturation, provides an indication of alkalinity and neutrality in a soil.

Physical Characteristics of Soil Colloidal Clays

Dispersion of clay particles in a soil can occur due to the repulsion of negatively charged particles for each other. Sodium in its hydrated state is much larger than other common cations and is not tightly held, and does not reduce the electronegativity of clay particles; thus the presence of large quantities of sodium in a soil tends to keep clay particles dispersed, thus reducing water infiltration and percolation into the soil. If sufficient salts are added, the effective electronegativity of the clay particles will be reduced so that the clay particles can flocculate. However, the required salt concentration may be so high as to restrict microbial activity and degradative processes in the soil. The sodium absorption ratio (SAR) is a measurement of the relationship between soluble sodium and soluble divalent cations, which can be used to predict the exchangeable sodium percentage of soil equilibrated with a given solution. SAR is defined as follows:

$$SAR = (Na)/[(Ca + Mg)/2]^{1/2}$$

where concentrations, denoted by parentheses, are expressed in meq per liter.

As a general rule, an SAR of 15 or greater is considered unacceptable and may result in reductions in permeability. However, there is a difference in acceptable SAR values, depending on the dominant clay type in a particular soil. For example, with kaolinite, the SAR may be as high as 20 before serious swelling problems occur. However, in soils in which montmorillonite is dominant, SAR values of 8-10 may cause serious swelling problems and reduction in permeability. In terms of exchangeable sodium percentage (ESP), an ESP of less than 5 percent is satisfactory, greater than 10 percent can result in reduced permeability in fine-textured soils, and greater than 20 percent can result in reduced permeability in coarse-textured soils.

The tendency of some silicate clays to swell and shrink can result in soils with wide, deep cracks when the soils are dry, but the soils can become impervious due to swelling when water is added. Swelling results from the penetration of water between the crystal layers, from water attracted to both the clay colloids and to the ions adsorbed by them, and from air bubbles entrapped as water moves into the small pores of these soils. Soils high in smectite clays are especially susceptible to shrink-swell conditions.

Types of Silicate Clays and Other Clay Minerals

There are a number of silicate clays, but most are variations of a few major types. Kaolinite is the most common type of 1:1 type clay. The 1:1 units are bonded together by hydrogen bonding between hydroxyl groups, thus there is no interlayer surface area, and kaolinite does not swell with the addition of water. There is also little substitution within the tetrahedral or octahedral layers, resulting in a low charge deficit. Kaolinite, therefore, has low reactivity and sorptive capacity for cations. Kaolinite contains more surface hydroxyl groups than other silicate clays, and is considered to be primarily responsible for anion exchange in temperate or arid region soils.

Montmorillonite, a member of the smectite group of clays (a group noted for interlayer expansion), is a common 2:1 type clay that has a negative charge of 80 to 100 cmol/kg and swells and shrinks as water moves freely between the weakly bonded 2:1 units. Water is attracted to the oxygen surface of the clay and to the neutralizing cations in the interlayers. The swelling caused by the water exposes the large surface area and the large charge deficit, which is available for cation adsorption. Bentonite, commonly used to construct clay liners at waste sites, is a type of clay composed of primarily smectite minerals produced by the alteration of volcanic ash in situ.

Fine-grained mica possesses the same 2:1 structure as montmorillonite but differs in that adjacent 2:1 units are tightly bonded by potassium bridges. Fine-grained mica, therefore, does not swell in water, and most of its charge is neutralized by potassium ions. Fine-grained mica does not exhibit large potentials for shrinking, swelling, and plasticity. Fine-grained micas are expected to exhibit minimal interactions with waste constituents present in soil systems (Allrichs 1972).

Vermiculite, considered a limited-expansion clay mineral, is similar to the fine-grained micas, except that potassium is not present. Vermiculite usually has hydrated magnesium (Mg^{2+}) or calcium (Ca^{2+}) in the interlayers neutralizing the charges and acting as bridges to hold the units together. The degree of swelling is less than that of the smectites but more than kaolinite. The CEC of vermiculite is the highest of the silicate clays, due to the high negative charge in the tetrahedral sheet.

Soils also contain colloidal clays that are amorphous (lacking crystalline structure) that can be detected by x-ray diffraction. Allophane is an amorphous silicate colloidal clay that is developed from volcanic ash and is commonly found in the northwestern part of the U.S. Soils containing allophane lack discrete mineral particles and are like a gel (Foth 1984). Features of soils high in allophane content include high organic matter content, large amounts of surface area, and high water-holding capacity. Allophane also has a high cation exchange capacity and can adsorb anions.

The hydrous oxide clays are oxides containing associated water molecules. They are formed by intense weathering, after silicon has been removed from the silicate clays, leaving iron and aluminum hydroxides in a highly colloidal state. Aluminum and iron hydroxides are protonated in the acid environments that are common in highly weathered tropical soils and thus are important in anion exchange reactions.

Organic Colloids

Soil contains many organic compounds in various stages of decomposition. Soil organic matter is derived from: (1) plant material; (2) animal matter; (3) microorganisms, both living and dead; (4) synthesized and secreted products of living plants and microorganisms; and (5) decomposition products of organic debris (Anderson 1982).

Schnitzer (1978) estimated that 65 to 75 percent of organic matter in mineral soils consists of humic materials; i.e., humic acid (HA), fulvic acid (FA), and humin. They are amorphous, dark-colored, hydrophilic, acidic, partly aromatic, chemically complex substances ranging in molecular weight from hundreds to several thousand, with large surface areas (500-800 m^2/g) and high cation exchange capacities (200-500 cmol/kg)(primarily pH-dependent). These colloidal-sized humus particles are composed of carbon, hydrogen, and oxygen, likely in the form of polyphenols, polyquinones, and polysaccharides (Brady and Weil 1999). Humus is involved in the formation of structural aggregation in soils and imparts a characteristic black or brown color to soils. It also reduces physical properties due to the presence of silicate clay minerals, such as plasticity and cohesion.

The remainder of the organic matter is composed primarily of polysaccharides and protein-like substances (Flaig et al. 1975). These include substances with still recognizable physical and chemical characteristics, such as carbohydrates, proteins, peptides, amino acids, fats, waxes, alkanes, and low molecular weight organic acids (Schnitzer 1978). They are readily decomposed by microorganisms and have a short lifetime in soils. Schnitzer (1978) identified the following important characteristics of all humic materials:

- (1) ability to form water-soluble and water-insoluble complexes with metal ions and hydrous oxides; and
- (2) ability to interact with minerals and a variety of organic compounds, including alkanes, fatty acids, dialkyl phthalates, pesticides, herbicides, carbohydrates, amino acids, peptides, and proteins.

The formation of water soluble complexes with metals and organics can increase concentrations of these constituents in soil solutions and natural waters to levels greater than their calculated solubilities.

The oxygen-containing functional groups are important for the reactions of humic materials with metals, minerals, and organic

compounds. Humic matter is somewhat organophilic, which may be important for sorption of some nonionic organic waste constituents. The oxygen-containing functional groups contribute to the high cation exchange capacity, thus acting similarly to clays in preventing cations from leaching from a soil. Humus can account for 20-90 percent of the adsorbing power of mineral soils (Brady and Weil 1999). Research has been conducted to determine if waste constituents bound to organic matter through abiotic sorption processes or through biological incorporation into soil organic matter (i.e., humification) through oxidative coupling and polymerization reactions will result in long-term detoxification and binding of the constituents (Bollag and Bollag 1990).

Humus also increases the ability of a soil to hold and retain water, since it swells when wet and can adsorb 2-6 times its own weight in water (which is 4-5 times the capacity of silicate clays). However, it only rewets slowly if thoroughly dried.

Humus and other organic materials, because of their chemical composition, can add to the nutrient status of a soil, thus increasing microbial activity that may be responsible for degradation of waste constituents present in the soil. Nitrogen, phosphorus, and minor nutrients such as sulfur, zinc, and boron can be supplied by organic matter.

The amount of nitrogen relative to the amount of carbon (referred to as the C:N ratio) in decomposing organic matter is an especially important characteristic, for insufficient nitrogen may limit rates of degradation of organic waste constituents. The C:N ratio in the upper 15 cm of agricultural soils ranges from 8:1 to 15:1, with an average value of 10:1 to 12:1. Organic matter with a low nitrogen content (or wide C:N ratio) is often associated with a slow rate of decomposition. Materials that contain more than 1.5 to 1.7 percent nitrogen probably do not need additional fertilizer or soil nitrogen to meet the requirements of microorganisms during degradative processes. This corresponds to a threshold carbon-nitrogen ratio of 25 to 30 (Taylor et al. 1980). However, C:N ratios should be used with caution, for the ratio does not indicate availability of the carbon or nitrogen to microorganisms.

In summary, humified soil organic material, because of its surface area, surface properties, and functional groups, can serve as a buffer, an ion exchanger, a surfactant, a chelating agent, and a general sorbent, all of which are important in the attenuation of waste constituents in soil systems (Allrichs 1972).

Additional Soil Chemical Properties

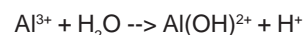
Soil pH: Acidity and Alkalinity

Soil pH determines in part the degree of surface charge on colloidal-sized soil particles. At high pH values, negatively charged surfaces develop, while at low pH values, positively charged surfaces occur. The tendency for sorption of anions or cations is thus dependent on the soil water pH.

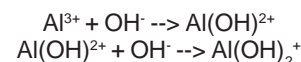
Soil pH also has major effects on biological activity in a soil. Some organisms have small tolerances to variations in pH while others can tolerate a wide pH range. The optimum range for degradation of most waste constituents is pH 6.5 to 8.5. Bacteria and actinomycetes have pH optima near neutrality and do not compete effectively with fungi under acidic conditions (Taylor et al. 1980). Soil pH also affects availability of nutrients.

There are several sources of hydrogen (H⁺) and hydroxyl (OH⁻) ions in soil solutions. The hydrolysis of exchangeable bases

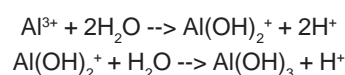
(Ca²⁺, Mg²⁺, Na⁺, and K⁺) that dissociate from cation exchange sites contribute OH⁻ ions. Exchangeable H⁺ in moderately acid and acid soils that has been released from exchange sites contributes H⁺ to the soil solution. When the pH of the soil is below 5.5, aluminum becomes soluble and is adsorbed as exchangeable aluminum. Adsorbed aluminum is in equilibrium with aluminum ions in the soil solution. Upon hydrolysis, each aluminum ion becomes the source of H⁺ ions. At pH levels less than 5.0 (strongly acid soils), aluminum ions are hydrolyzed, thus releasing H⁺ ions:



At pH levels of 5.0 to 6.5 (moderately acid soils), aluminum is converted to hydroxy ions:



These hydroxy ions are hydrolyzed to release H⁺ ions:



In neutral to alkaline soils, with pH values 7.0 and above, neither hydrogen nor aluminum dominate the exchange sites. The exchange sites are occupied by calcium, magnesium, and other base-forming cations.

Total soil acidity can be characterized into three types. Active acidity is a measure of the H⁺ activity in the soil solution. The quantity of H⁺ due to active acidity is very low, but this is the concentration of H⁺ in the environment to which biological life in the soil is exposed.

Exchangeable acidity is associated with exchangeable aluminum and hydrogen ions, present in large quantities in acid soils and in lesser quantities in moderately acid soils. However, even in moderately acid soils, the amount of limestone required to neutralize this type of acidity is 100 times that required for active acidity. At a given pH, exchangeable acidity is highest for smectites, intermediate for vermiculites, and lowest for kaolinite.

Potential acidity is the acidity remaining in the soil after active and exchangeable acidity have been neutralized. Potential acidity is associated with aluminum hydroxy ions and with hydrogen and aluminum ions that are held in nonexchangeable forms by organic matter and silicate clays. Potential acidity is estimated to be 1000 times greater than the active and exchangeable acidity in a sandy soil and 50,000 to 100,000 times greater in a clayey soil high in organic matter. The amount of limestone required to neutralize potential acidity in an average mineral soil usually ranges from 4 to 8 metric tons per hectare-furrow slice (1.8 to 3.6 tons per acre-furrow slice), while the amount required to neutralize the active acidity in a hectare-furrow slice would be only 2 kilograms.

If a soil has a high CEC (i.e., has high clay and/or organic matter contents), more potential acidity must be neutralized in order to achieve an increase in percentage base saturation; thus the soil has a high buffering capacity and high resistance to change in pH.

Neutral and alkaline soils of arid and semiarid regions that are high in salts (e.g., chlorides and sulfates of calcium, magnesium, sodium, and potassium) may exhibit detrimental effects on biological activity in soils (Brady and Weil 1999). If soils contain sodium salts, additional deleterious effects on soil physical properties may be present. Salt content of soils is

determined by measuring the electrical conductivity (EC) of a soil solution; i.e., the ability of the salt in the soil solution to conduct electricity.

Salt-affected soils are classified as saline, sodic, and saline-sodic. Saline soils are high in soluble salts. Plant growth and microbial activity may be impaired due to the osmotic pressure of the soil solution restricting water uptake. Saline soils have pH values less than 8.5 because the salts present are neutral. Saline salts may be reclaimed by leaching out the salts with water low in sodium.

A soil high in sodium (sodic soil) has a high pH due to the hydrolysis of sodium carbonate and the formation of the strong base, sodium hydroxide. A sodic soil does not contain large quantities of soluble salts. When the cation exchange capacity of a soil is 15 percent or more saturated with sodium, or a significant amount of sodium carbonate exists in a soil, pH values may range from 8.5 to 10 or higher. Sodic soils are usually in an unsatisfactory physical condition, with reduced water infiltration and aeration due to the dispersion of clay minerals.

Saline-sodic soils contain large quantities of both neutral soluble salts and sodium ions. The pH is usually 8.5 or less because of the presence of neutral salts. To reclaim these soils, especially if the soils are low in calcium and magnesium salt concentrations, irrigation water should be high in calcium or magnesium to prevent an increase in pH due to the hydrolysis of exchangeable sodium, which may result in dispersion of soil colloids.

The pH of a calcareous (containing CaCO_3) soil or a calcareous soil horizon ranges from 6.8 to 8.3. The presence of a calcareous soil horizon may affect transport of waste constituents by an abrupt change in soil pH, which may affect solubility or ionization states of the constituents.

Soil pH can be adjusted by using agricultural management techniques. To decrease soil acidity, agricultural limes, which include carbonates, oxides, or hydroxides of calcium and magnesium, are used. The amount of a particular liming material required is dependent on: (1) the change in pH required; (2) the buffer capacity of the soil; (3) the chemical composition of the liming materials used; and (4) the fineness of the liming materials (Brady and Weil 1999).

Oxidation-Reduction (Redox) Potential

A measurement of the oxidation-reduction potential, or Eh, of a soil solution, in conjunction with measurement of soil pH, may be useful in understanding the form and mobility of waste constituents in a soil system. Eh is an expression of the electron density of a system. As a system becomes reduced, there is a corresponding increase in electron density, resulting in a progressively increased negative potential (Taylor et al. 1980). With Eh and pH known, Eh-pH diagrams can be constructed, showing stability fields for major dissolved chemical species and solid phases.

The maximum rate of decomposition of degradable organic compounds is correlated with a continuous supply of oxygen. Excessive levels of degradable materials may lead to depletion of O_2 in soil and the creation of anaerobic conditions, which usually slows the rate and extent of decomposition and may produce some reduced compounds that are odorous and toxic to microorganisms and plants.

However, the degradative pathways for some waste constituents may involve several essential reductive steps. For example, an important initial step in the degradation of DDT is a reductive dechlorination, which involves anaerobiosis (Guenzi and Beard 1967). Parr and Smith (1973,1976) have shown that toxaphene and trifluralin degrade more rapidly under anaerobic conditions. Recent research has shown that anaerobic dehalogenation reactions specifically involving reductive processes can effectively degrade a wide variety of soil and ground-water organic halogenated waste constituents, including polychlorinated biphenyls, and carboxylated, oxygen-substituted, nitrogen-substituted, cyano-substituted, methylene-substituted, and chlorinated benzenes (Vogel et al. 1987; Kuhn and Suflika 1989).

An engineering management tool to maximize detoxification and degradation of compounds subject to reductive dechlorination may be alternation of aerobic/anaerobic conditions (Guenther 1975) by adjusting Eh. Anaerobic conditions may be created and maintained by flooding (with appropriate runoff and leaching control) or by addition of readily degradable organic matter. Regular cultivation of soil is a possible means of maintaining aerobic conditions.

Nutrient Status of Soils

The biological degradation of organic waste constituents requires the presence of nutrients for optimum biological growth. Three of the major nutrients, nitrogen, phosphorus, and potassium, can be supplied in common inorganic fertilizers. Calcium deficiencies usually occur only in acid soils and can be corrected by liming. If the soil is deficient in magnesium, the use of dolomitic lime (i.e., calcium-magnesium carbonate) is advised. A high level of exchangeable bases (calcium, magnesium, sodium, and potassium) on the exchange surface sites of the soil is also desirable for good microbial activity and to prevent excessively acid conditions.

Though sulfur levels in soils are typically sufficient, sulfur is usually added as a constituent of most inorganic fertilizers. Micronutrients also occur in adequate amounts in most soils. At sites contaminated with waste constituents, a primary danger may be in overloading the soil with one of these elements that may have been present in the waste, thus causing toxicity and leaching problems.

The pH of the soil is also important for some elements. The pH affects their solubility and biological availability, and thus their toxicity and leaching potential.

HYDRAULIC PROPERTIES OF THE SOIL PROFILE

Introduction

Soil/water relationships and associated soil hydraulic properties affect both the movement of waste constituents through the soil as well as soil processes acting within the soil to effect attenuation (i.e., degradation, detoxification, and/or immobilization) of the waste constituents. Biodegradation requires water for microbial growth and for diffusion of nutrients and by-products during the degradation process. Soil hydraulic properties are those properties whose measurement involves water flow or retention of water within the soil profile (U.S. EPA 1977).

Soil Water Content and Soil Water Energy Concepts

The total volume of a soil consists of about 50 percent pore space and 50 percent solid matter. Water entering the soil (i.e., infiltration) fills the pore spaces until they are full. The water continues to move down into the subsoil, displacing air as it travels; this flow, when the soil is at maximum retentive capacity, is said to be saturated. After water input to the soil ceases, the water drains from the pores, and the soil becomes unsaturated. Water in the soil below the saturation level in the soil is held against the force of gravity. The forces that hold the water in the soil result from cohesion of water molecules to each other and adhesion of water molecules to soil surfaces, a phenomenon referred to as capillarity (Figure 6). Capillarity can result in water movement in the horizontal direction as well as in the vertical direction.

Soil water content (measured gravimetrically as the amount of water lost from a soil upon drying to a constant weight at 90° C), expressed as either the weight of water per unit weight of dry soil (mass basis) or as the volume of water per unit bulk volume of soil (volumetric basis), can be determined at saturation or at any degree of unsaturation. Indirect methods of measuring soil water content in the field include the resistance method and neutron scattering.

The movement of soil water is an energy-related process (Brady and Weil 1999). All materials, including water have a tendency to move or change from a state of higher energy to a state of lower energy; i.e., in soils, water will move from an area where the free energy of the water is high, which is a wet soil, to an area where its free energy is lower, or to a dry soil. The differences in energy levels in a soil profile determine the direction of water movement.

Three forces act upon soil water to affect its free energy level (Brady and Weil 1999). Adhesion, or the attraction of soil solids for water, provides a matric force (responsible for adsorption and capillarity) that reduces the free energy of adsorbed water molecules and even some of those held by cohesion. The attraction of ions and other solutes for water, i.e., osmotic forces, also reduces the free energy of soil water. Osmotic potential is usually not important in mass flow of water in a soil, but may be important in the uptake of water into biological cells. Since both osmotic and matric forces reduce the free energy of

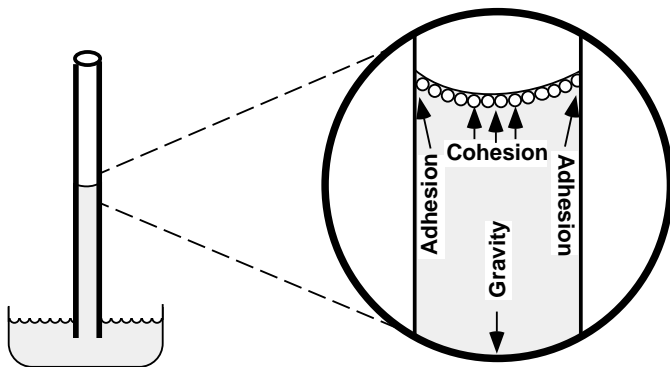


Figure 6. Phenomenon of capillarity in a fine glass tube placed in water. (Reprinted from *Nature and Properties of Soils*, 12/E, 1999, by N. C. Brady and R. R. Weil with permission of Prentice-Hall, Inc. New Jersey.)

water, their expression in energy terms, or potential, are negative. Gravity also acts on soil water, tending to pull water downward. The free energy of water at a higher elevation in a soil profile is higher than pure water at a lower elevation, so water flows downward.

The term *soil water potential* is used to describe the difference between the free energy of soil water and that of pure water in a standard reference state. Soil water potential is comprised of matric potential, osmotic potential, and gravitational potential. The free energy level of water at a single point in a soil is not as important in describing water movement and behavior in a soil as differences in free energy levels at different points in a soil.

Soil water energy may be described in terms of the height in centimeters of a unit water column whose weight equals the potential of the soil water, or in terms of standard atmospheric pressure at sea level (i.e., 14.7 lb/in², 760 mm Hg, or 1020 cm of water). A bar is approximately equal to a standard atmosphere, and 10 bars is equal to the SI unit megapascal (MPa). All of these terms are negative quantities, since water at less than saturation is held in soil pores at less than atmospheric pressure. The term *soil suction* is also used to describe the energy of soil water, but is reported as a positive quantity. Soil water potential can be measured in the field using tensiometers, which are fine porous cups filled with water that is held in equilibrium with water in the adjacent soil.

The force by which water is held in soil pores is approximately inversely proportional to the pore diameter. As water evaporates or drains, the larger pores (macropores) drain first, while the smaller pores (micropores) are still filled with water. Therefore, as soil water content decreases, the absolute value of the matric potential increases. A graphical representation of such a relationship is referred to as a soil water characteristic curve and is illustrated in Figure 7 for three different soil textures. The shape of the soil water characteristic curve is strongly dependent on soil texture and structure. Soils with primarily large pores, such as sands, lose nearly all their water at small (absolute value) soil water potentials. However, soils with a mixture of pore sizes, such as loamy soils, hold more water at saturation due to a larger porosity, and lose water more slowly as the absolute value of the soil water potential increases.

Terms relating to soil water content at different soil water potentials are illustrated in Figure 8. Gravitational water movement when a soil is at or near saturation may be important both in transport of waste constituents through a soil and in leaching of nutrients, which may result in decreased biological degradation of organic constituents. If water does not drain quickly from a soil, saturated conditions may have a harmful effect on microbial activity due to poor aeration. Saturation may also affect solubility of waste constituents due to a change in the oxidation-reduction potential of the soil.

The terms *field capacity* and *permanent wilting point* are qualitative descriptions of soil water content. Field capacity refers to the percentage of water remaining in a soil after having been saturated and after free gravitational drainage has ceased. Field capacity is not a unique value but represents a range of water contents. In sandy soils, soil water content at field capacity corresponds to matric potentials in the range of -0.10 to -0.15 bar, while in medium to fine-textured soils, potentials at field capacity range from -0.3 to -0.5 bar, with -0.3 bar most commonly used.

Drainage does not cease at field capacity but continues at a reduced rate due to movement of water through micropores by

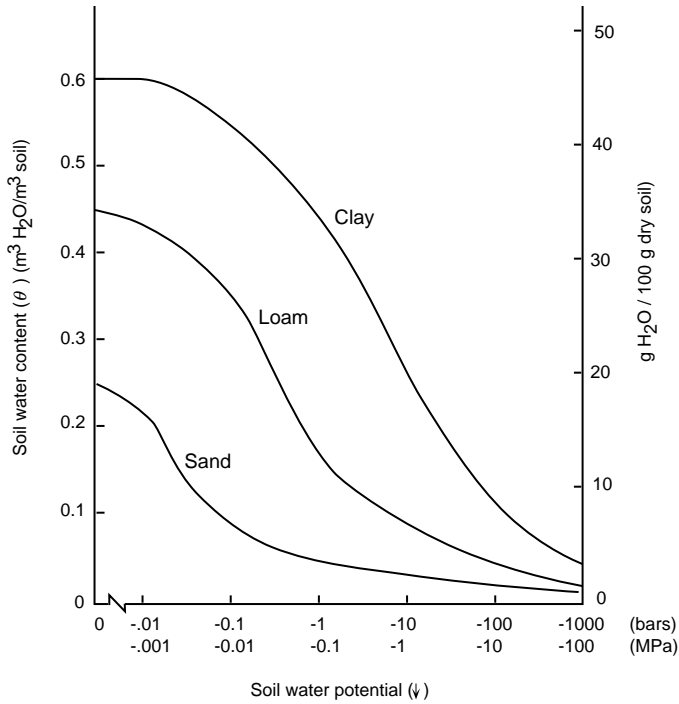


Figure 7. Soil water characteristic curves for three mineral soils. (Reprinted from *Nature and Properties of Soils*, 12/E, 1999, by N. C. Brady and R. R. Weil with permission of Prentice-Hall, Inc. New Jersey.)

capillarity. Adhesive attraction between water molecules and walls of micropores causes water to move through the pores, pulling along other water due to the cohesive attraction among water molecules. Capillary water can move in any direction in the soil, following micropore channels.

When moisture in a soil is no longer in adequate supply to meet the demands of plants growing in the soil, and plants wilt and remain wilted even when placed in a humid chamber, the water content is at the permanent wilting point. This water content occurs in most soils when the matric potential is in the range of -15 bars. The amount of water held in a soil between field capacity and the permanent wilting point is referred to as available water. This is the water available for plants and for soil microbial and chemical reactions. Information on optimal and marginal water potentials for growth, reproduction, and survival of individual species of microorganisms in soils is limited (Taylor et al. 1980). Bacterial activity is highest in wetter conditions, but usually noticeably decreases by about -3 bars (Clark 1967). Some fungi can grow and survive in soils under dry conditions. Hygroscopic water is water bound tightly by soil solids at potential values less than -31 bars. It is considered nonliquid and can only move in the vapor phase.

Though fine-textured soils have the maximum total water holding capacity, medium-textured soils have the maximum available water due to a range of pore sizes. Even at the permanent wilting point, soils contain a considerable amount of water, though unavailable for use.

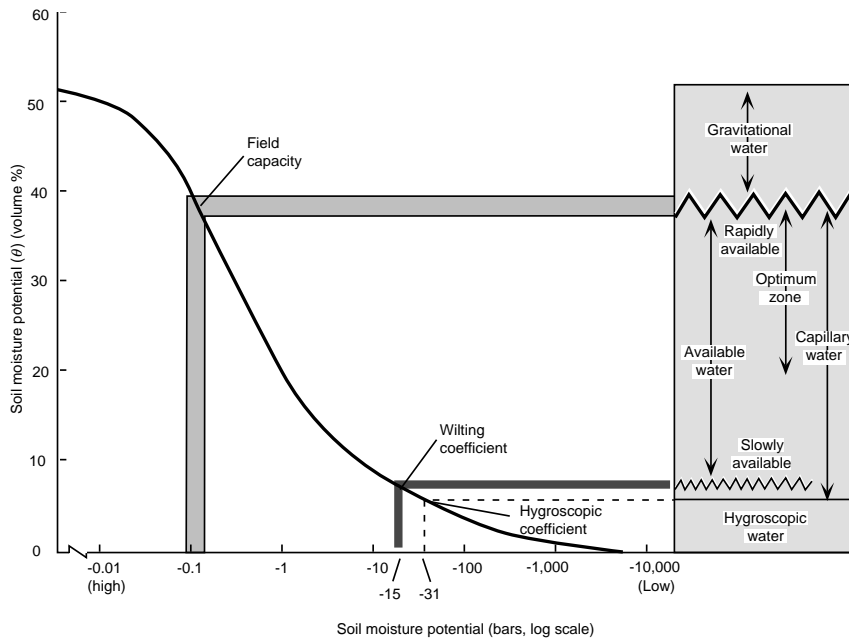


Figure 8. Soil water characteristic curve of a loam soil as related to terms used to describe soil water. (Reprinted from *Nature and Properties of Soils*, 12/E, 1999, by N. C. Brady and R. R. Weil with permission of Prentice-Hall, Inc. New Jersey.)

Soil Water Movement

Permeability

Permeability of a soil describes the ease with which liquids pass through the soil. Knowledge of permeability is required to predict the rate of movement of waste constituents through a soil.

Water moves through soils according to Darcy's Law:

$$q = K \, dH/dL$$

where:

- q = flux of water per unit cross sectional area (cm/h);
- K = permeability or hydraulic conductivity (cm/h); and
- dH/dL = total head (hydraulic gradient) (m/m).

The total head, H, is equal to the sum of the soil water pressure head (matric potential), h and the head due to gravity, z, or $H = h + z$. In most cases, the head due to osmotic effects is so low as to be negligible. However, at some contaminated sites where the presence of salts as part of contamination is significant, osmotic effects on water movement may be important.

The hydraulic conductivity, K, changes rapidly as a function of soil water content. Hydraulic conductivity decreases greatly as water content decreases below saturation. In sandy soils, though permeability is much higher at saturation than in loamy soils, permeability decreases more rapidly as the matric potential becomes more negative, eventually becoming lower than in medium-textured soils.

Even under conditions of constant water content, K may change due to swelling of clay particles or changes in the chemical nature of soil water. Due to their negatively charged nature, soil clay particles tend to repel each other and remain dispersed, resulting in low permeability. The presence of sodium in a soil often enhances dispersion and negatively affects permeability. Positively charged cations in soil water neutralize the negative charges and allow the soil particles to come close enough together so that flocculation can occur, which increases soil pore sizes and permeability. A soil low in salts but high in sodium may have low permeability.

Other chemicals, especially organic compounds, may also alter soil permeability (Sims et al. 1984). Increased permeability may result from: (1) dissolution of clay minerals by organic acids (Huang and Keller 1971); and (2) a change in the relative volume of a clay as a result of interactions with an organic solvent (Anderson et al. 1982). Potential for such changes should be investigated in order to predict and minimize leaching of the organic compound, if it is of environmental concern, or to determine if it would increase the leaching of associated waste constituents of concern.

Soil permeability is primarily determined by soil texture, with more coarse materials usually having higher conductivities. However, the development of strong soil structure may increase permeability in a finer-textured soil by increasing macropore space.

The Soil Conservation Service has developed guidelines for the classification of saturated soil permeability (Soil Survey Staff, 1962). For remediation of waste-contaminated soils, the most desirable soil would be a soil in which permeability was large enough to maximize soil attenuation processes (e.g., to maintain adequate aeration for aerobic microbial degradation)

but small enough to minimize leaching potential (assuming that lower permeabilities protect against leaching).

Drainability

Drainability is a term used to describe the relative rapidity and extent of removal of water from a soil. Drainability is dependent upon the permeability of the soil (i.e., K, the hydraulic conductivity) and ground-water relationships that are controlled by soil properties and the landscape position of the site (i.e., the hydraulic gradient, dH/dL). A well-drained soil (e.g., a loamy soil) is one in which water is removed readily but not rapidly; a poorly drained soil (e.g., a poorly structured, fine-textured soil) will remain saturated for extended periods of time, resulting in the formation of reducing conditions and depletion of oxygen, which may decrease biodegradation of organic waste constituents; an excessively drained soil (e.g., a sandy soil) is a soil in which water is removed so completely that droughty conditions may occur. Drainage classes for soils developed by the Soil Conservation Service are given in Table 4.

Another soil characteristic important in terms of potential transport of waste constituents is the depth to an impermeable layer, bedrock, or ground water, including seasonal variations. Soil depth affects drainability of a soil and the effective depth for waste constituent attenuation. Ryan and Loehr (1981) reported that with depths of less than 1.5 m, horizontal flow predominates, and saturated hydraulic conductivity can be assumed to be equal to the permeability of the saturated horizon with the highest permeability. The hydraulic gradient is assumed to be equal to the slope of the limiting layer and can be approximated by the slope of the soil surface. When depth to an impermeable layer, bedrock, or ground water is greater than 1.5 m, vertical flow is predominant. The saturated hydraulic conductivity of the soil can be assumed to be equal to the permeability of the most limiting horizon, and the hydraulic gradient is assumed to be one.

Table 4. Soil Conservation Service (SCS) Drainage Classes (Soil Survey Staff 1962)

| <i>Drainage Class</i> | <i>Observable Symptom</i> |
|------------------------------|--|
| Very poorly drained | Water remains at or on the surface most of the year |
| Poorly drained | Water remains at or near the surface much of the year |
| Somewhat poorly drained | Soils are wet for significant portions of the year |
| Moderately well drained | Soils are seasonally wet (e.g., high drained water table in spring) |
| Well drained | Water readily removed from the soil either by subsurface flow or percolation; optimum condition for plant growth |
| Somewhat excessively drained | Water is rapidly removed from the soil; characteristic of many uniform sands |
| Excessively drained | Very rapid removal of water with little or no retention |

Infiltration

Infiltration rate refers to the rate at which water enters the soil from the surface. When the soil is saturated, the infiltration rate is equal to the saturated hydraulic conductivity. However, when the soil initially is relatively dry, the infiltration rate is higher as water enters large pores and cracks. The infiltration rate is reduced rapidly to a near steady-state value as large pores fill and clay particles swell. Infiltration rates are affected by soil texture and structure, ionic composition of the applied liquid, condition of the soil surface, and the type of vegetation on the soil surface.

Since infiltration governs the amount of water that will enter a soil, engineering and agronomic practices that affect physical, chemical, and biological soil characteristics may be utilized to alter infiltration rates. Changes in bulk density, porosity, and percent of water-stable aggregates will affect the capacity of a soil for infiltration and the potential erodibility of a soil. Infiltration rates can be increased by lower bulk densities and higher porosity or by an increase in the number of macropores connecting to the soil surface.

Frozen soil often has a lower infiltration rate than unfrozen soil, especially if the soil was frozen when moist. Since frost usually penetrates deeper if soil is bare than if it is snow-covered, practices that prevent snow from blowing away may lessen frost penetration. However, the additional snow may increase surface runoff.

Potential for Off-site Migration

An assessment of the flooding frequency of a contaminated site should be made to determine potential for off-site migration of waste constituents in flood waters. Only slight hazards exist if the soil is usually not flooded any part of the year, moderate hazards if occasional flooding occurs (10-50 percent chance of flooding once every two years) and severe hazards if frequent flooding occurs (greater than 50 percent chance of flooding every two years) (Ryan and Loehr 1981).

Runoff is the portion of precipitation that appears in surface waters. Surface runoff is water that travels over the ground surface to reach a lake, stream, or river (overland flow). Surface flow may carry constituents in solution, in suspension, or adsorbed to suspended soil particles. Subsurface runoff and ground water carry primarily soluble constituents not strongly sorbed to soil particles.

Steenhuis and Walter (1979) described a method of categorizing pollutants with regard to potential losses in soil and water according to their relative concentrations in water and on soil particles, as indicated by adsorption/desorption isotherms. An adsorption partition coefficient, k_s , for a given solution concentration is calculated as the ratio of amount adsorbed to that in solution:

$$k_s = \frac{\text{concentration of substance adsorbed to particles (ppm, mg / kg)}}{\text{concentration of substance in solution (ppm, mg / l)}}$$

Group I pollutants are those with k_s values approximately equal to 1000. These include the strongly adsorbed and solid phase pollutants. The loss of these pollutants in baseflow and interflow is small. Their losses in overland flow may potentially be high and are related to the amount of sediment in the water and the amount of pollutant in the soil. Organic matter, which may be an important sorbent of waste constituents, is more easily eroded

than most mineral particles and tends to remain in suspension because of its low bulk density. Silt and clay are also more erodible than sand and are usually higher in organic matter content. Clays, because of the charge properties and surface area, are also important sorbents of waste constituents. Therefore, an "enriching process" occurs in overland runoff in which concentrations of waste constituents in eroded sediments may be much higher than in the original soil. Loss of Group I pollutants can be decreased by erosion control practices that minimize sediment detachment and transport.

Group II pollutants, with k_s values of about 5, include moderately sorbed pollutants (e.g., many pesticides). Their loss in overland flow is related to the amount of runoff water and not to the amount of soil loss. Erosion control practices that prevent sediment detachment and transport are not as effective as practices that reduce the total amount of runoff volume. Transport of sorbed substances by water passing through a soil is much slower than transport by surface flow. An equilibrium exists between substances dissolved in soil water and those sorbed to the soil. The greatest contamination of subsurface flow water is due to those waste constituents that are weakly adsorbed or those slow to degrade.

Group III pollutants have k_s of about 0 to 0.5 and non-sorbed or soluble pollutants. Their primary pathway of loss is through interflow and baseflow. Losses in surface runoff are small and therefore are not greatly affected by practices to control runoff. Reduced runoff may even increase subsurface flow and increase losses of Group III pollutants to interflow and ground water.

Moderately and weakly sorbed waste constituents usually migrate fairly rapidly after soil contamination with initial precipitation events. Strongly sorbed constituents, depending on their stability and recalcitrance, may pose hazards for years due to movement in overland flow.

Control of runoff can be accomplished by several means (Steenhuis and Walter 1979). Decreasing runoff velocity will reduce both surface runoff volume and sediment loss. More water remains on the soil for a longer period of time, thus permitting increased infiltration. Runoff velocity may be reduced in several ways: (1) by forcing water to move laterally rather than straight down slopes; (2) by reducing the slope of the land through land-forming; or (3) by increasing the roughness of the soil surface to dissipate the kinetic energy of the water.

An increase in surface storage will remove the stored water from the total surface runoff volume, resulting in decreased runoff velocity and a reduced sediment carrying capacity. Surface storage can be increased by various engineering and agricultural practices (e.g., creation of ridges of soil or vegetation) that allow water to pool. Moisture storage capacity in the soil itself can be increased by addition of organic matter or by draining or evaporating moisture already in the soil profile.

Runoff also can be controlled by reduction of the splash energy of falling rain. Raindrop impact on bare soil may break soil aggregates to component particles. These smaller particles may be carried by water into larger pores, thus forming a thin surface layer with low hydraulic conductivity. Dissipating raindrop energy by use of a plant canopy or mulch or by promotion of aggregate stability with organic matter addition may reduce this surface sealing effect.

Snowmelt occurring in the spring, often on frozen ground, can potentially carry a higher contaminant load than rainfall runoff

that has infiltrated the ground. Also, time frames in which rainfall runoff and snow melt runoff occur are different. Rainfall runoff occurs when the infiltration capacity of the soil is exceeded by the rate of precipitation. Infiltration capacity may be exceeded by the intensity of the rainfall event or its duration. However, spring snowmelt occurs over a period of time, usually interrupted periodically by subfreezing temperatures and continuing until all of the snow melts.

Hydrologic Budget

The preparation of a hydrologic budget or water balance for a contaminated site will aid in prediction of leaching potential of waste constituents and types and extent of attenuation processes (biodegradation, sorption, etc.) that will act upon the constituents. Inputs to the hydrologic budget include precipitation, run-on, and any additional water that may be required to accomplish the remediation technology. Factors that may limit the amount of additional water that may be added must also be considered, such as the total amount of precipitation relative to evaporation, seasonal distribution of precipitation, and changes in amount of precipitation from year to year. Losses from the site include evaporation, transpiration, percolation to ground water, and surface runoff.

Precipitation data may be based on measured rainfall events or on frequency analyses (e.g., 10-year/24-hour storm, 25-year/1-hour storm, etc.). Information should include the total rainfall a site receives as well as the intensity, duration, and frequency of single precipitation events.

Evaporation is the transfer of liquid water into the atmosphere. Factors affecting the rate of evaporation are the nature of the evaporating surface and vapor pressure differences as affected by temperature, wind, atmospheric pressure, ionic composition of water, and available energy (Schwab et al. 1981). In saturated soils, evaporation is expected to be the same as from open free water surfaces. However, in unsaturated soils with water content below field capacity, evaporation is low, as soil water movement is slow when the soil is relatively dry.

Transpiration is the process by which water vapor passes into the atmosphere through the tissues of living plants. Loss of soil moisture by transpiration is often a substantial portion of the total water available during a growing season. Transpiration is dependent on the moisture available, the kind and density of plant growth, climatic factors, and soil fertility and structure.

The measurement of evaporation and transpiration is usually combined and referred to as evapotranspiration. Evapotranspiration can either be measured directly or predicted using various models (Schwab et al. 1981). Methods to measure the movement of water out of the soil zone include tensiometric measurements and water flux meters (Hillel 1971).

SOIL AERATION

Soil aeration controls the levels of oxygen and carbon dioxide, which are gases involved in both respiration and photosynthesis (Brady and Weil 1999). In respiration, oxygen is utilized in the oxidation of organic compounds, with the production of carbon dioxide and water. In photosynthesis, the reaction is reversed, and carbon dioxide and water are combined to form simple organic compounds (i.e., sugars), and oxygen is released. For respiration to occur in a soil, oxygen must be replenished and carbon dioxide, which may reach toxic levels, removed. For most plants, the supply of oxygen in a soil should be kept above 10 percent.

Poor soil aeration occurs when the moisture content of a soil is too high so as to exclude gases in the pores, or when the exchange of gases with the atmosphere is too slow to maintain appropriate levels of soil gases (Brady and Weil 1999). Soil moisture may reach too high levels in areas with naturally poor drainage, in soils after excess amounts of water have been added through rainfall or irrigation, or in soils that have been compacted by plowing or machinery. Soil moisture content can often be controlled by artificial drainage with canals and tile drains.

Mass flow and diffusion control exchange of gases between the soil and the atmosphere. Mass flow, which is movement of air due to differences in pressure between the atmosphere and soil air, is enhanced by variations in soil water content (i.e., water added to a soil forces air out of the soil). When water is removed from soil by evapotranspiration, air is drawn into the soil.

Diffusion is primarily responsible for gaseous interchange in a soil. In diffusion, each soil gas moves in a direction determined by its own partial pressure. Therefore, gas movement can occur even when there is no overall pressure gradient for the total mixture of gases in a soil, for there is a concentration gradient for each individual gas, expressed as a partial pressure gradient. A higher concentration of oxygen in the atmosphere will result in movement of oxygen into a soil, even though the total soil air pressure and atmospheric pressure are equal. Carbon dioxide and water vapor generally move out of a soil to the atmosphere, since their concentrations are usually higher in soil than in the atmosphere.

The soil properties affecting the aeration of well-drained soils are those that determine the volume of the soil macropores (Brady and Weil 1999). Soil macropores affect the amount of total air space as well as the potential for gaseous exchange and biodegradation. These soil properties include: (1) soil texture; (2) bulk density; (3) aggregate stability; and (4) soil organic matter content.

POTENTIAL FOR WIND EROSION

Soil properties that affect off-site migration of waste constituents via air transmission are also important in site characterization. The degree of migration in air is an interaction between soil/site characteristics and waste constituent characteristics.

Soil properties that determine the extent and rate of volatility of waste constituents are those related to soil permeability and soil moisture. The total porosity of the soil, the distribution of macro- and micropores, and the tortuosity of soil pores should be characterized. The range of air-filled porosities exhibited by soils under moisture regimes encountered at a specific contaminated site should also be investigated, for wetter soils are less permeable to gases than dry soils. At lower soil water contents, there is also an increase in sorption of constituents.

The dispersion characteristics of an area are an important component of air migration potential. Greater dispersion associated with open lands is more favorable than areas with channel type dispersion, such as in valley and depressional areas. Determination of prevailing wind directions and wind velocities will give an indication of the extent and direction of migration.

SOIL MICROBIOLOGY

The upper layers of soil contain large numbers and a diversity of microorganisms. Biodegradation of organic waste

constituents is accomplished by enzymes produced by the microorganisms. Since many enzymes are not released by microbial cells, substances to be degraded must contact or be transported into the cells. Enzymes are generally specific in the substances they affect; therefore, many types may be required in order to complete degradation of organic constituents. The production of enzymes is genetically controlled, thus mutations and adaptations of the native soil microorganisms can improve the ability of the populations to degrade organic substances.

Microbial ecologists have identified ranges of critical soil environmental conditions that affect the activity of soil microorganisms (Table 5). Many of these conditions are controllable and can be managed to enhance biodegradation of organic constituents.

Water is necessary for microbial life, and the soil water matric potential against which microorganisms must extract water from the soil regulates their activity. (The soil matric potential is the energy required to extract water from soil pores to overcome adhesive and cohesive forces.) Soil water also serves as the transport medium through which many nutrients and organic constituents diffuse to the microbial cell, and through which metabolic waste products are removed, and influences soil aeration status. The nature and amount of soluble materials, soil water osmotic pressure, and pH of the soil solution are additional important aspects of the influence of soil water on microbial activity (Paul and Clark 1989).

Fungi appear to be more tolerant of low soil water potential than are bacteria (Gray 1978, Harris 1981). Microbial degradation of organic materials in drier soils is probably primarily due to fungi. When a soil becomes dry, many microorganisms form spores, cysts, or other resistant forms, while others are killed by desiccation.

Clay content of soil and presence of organic matter may affect oxygen content in soil. Clayey soils tend to retain a higher moisture content, which restricts oxygen diffusion (though development of soil structure may increase oxygen diffusion

potential), while the presence of organic matter may increase microbial activity and deplete available oxygen.

Loss of oxygen as a metabolic electron acceptor induces change in the activity and composition of the soil microbial population. Facultative anaerobic organisms, which can use oxygen when it is present or can switch to alternative electron acceptors such as nitrate (i.e., denitrifying bacteria) or sulfate (i.e., sulfate reducing bacteria) in the absence of oxygen, as well as obligate anaerobic organisms become the dominant populations. Generally, microbial metabolism shifts from oxidative to fermentative, becoming less efficient in terms of biosynthetic energy production.

Another soil parameter that describes the effect of the soil environment on metabolic processes is the redox potential of the soil (Paul and Clark 1989). Biological energy is obtained from the oxidation of reduced materials. Electrons are removed from organic and inorganic substrates to capture the energy that is available during the oxidative process. Electrons from reduced compounds are moved along respiratory or electron transport chains composed of a series of compounds. In an aerobic process, molecular oxygen (O₂) acts as the terminal electron acceptor. In some cases where O₂ is not available, nitrate (NO₃⁻), iron (Fe³⁺), manganese (Mn⁴⁺), and sulfate (SO₄²⁻) can act as electron acceptors if the organisms have appropriate enzyme systems. A measurement of the oxidation-reduction potential (redox potential) of a soil provides a measurement of the electron density of the system. As a system becomes reduced, O₂ is depleted, and other substances are used as terminal electron acceptors. There is a corresponding increase in electron density, resulting in a progressively increased negative potential. Redox potential is measured as Eh, expressed in millivolts, or as Pe, which is equal to -log [e⁻], where [e⁻] is the concentration of negatively charged electrons.

Oxygen levels in soil systems can be maintained by: (1) prevention of saturation with water; (2) presence of sandy and loamy soil materials (excessive clay contents are undesirable); (3) moderate tilling; (4) avoidance of compaction of soil; and (5) limited addition of supplementary carbonaceous materials.

Soil pH also affects the activity of soil microorganisms. Fungi are generally more tolerant of acidic soil conditions (below pH 5) than are bacteria. The solubility of phosphorus, an important nutrient in biological systems, is maximized at a pH value of 6.5. A specific contaminated soil system may require management of soil pH to achieve levels that maximize microbial activity. Control of pH to enhance microbial activity may also aid in immobilization of hazardous metals in soil systems. A pH level greater than 6 is recommended to minimize metal transport.

Microbial metabolism and growth are dependent upon adequate supplies of essential macro- and micronutrients. Required nutrients must be present and available to microorganisms in: (1) a usable form; (2) appropriate concentrations; and proper ratios (Dragun 1988). If the wastes present at a site are high in carbonaceous materials and low in nitrogen (N) and phosphorus (P), the soils may become depleted of available N and P required for biodegradation of organic waste constituents. Fertilization may be required at some contaminated sites as a management technique to enhance microbial degradation. A recommended ratio of carbon to nitrogen to phosphorus (C:N:P) to promote biodegradation of organic substances is approximately 120:10:1, the approximate ratio found in bacterial biomass (Alexander 1977, Kowalenko 1978).

Table 5. Critical Environmental Factors for Microbial Activity (Sims et al. 1984)

| Environmental Factor | Optimum Levels |
|----------------------|--|
| Available soil water | 25% - 85% of water holding capacity; -0.01 MPa |
| Oxygen | Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimum air-filled pore space of 10%; Anaerobic metabolism: O ₂ concentrations less than 1% |
| Redox potential | Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts |
| pH | 5.5 - 8.5 |
| Nutrients | Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth (Suggested C:N:P ratio of 120:10:1) |
| Temperature | 15° - 45°C (Mesophiles) |

Biodegradation of organic waste constituents declines with lowering of soil temperature, due to reduced microbial growth and metabolic activity. Biodegradation has been shown to essentially cease at a temperature of 0° C. Soils exhibit a variation in the temperature of surface layers, both diurnally and seasonally. Diurnal changes of temperature decrease with depth of the soil. Due to the high specific heat of water, wet soils are less subject to large diurnal changes than dry soils (Paul and Clark 1989). Factors that affect soil temperature include: (1) soil aspect (direction of slope); (2) steepness of slope; (3) degree of shading; (4) soil color; and (5) surface cover.

Soil mineralogy and organic matter are also important factors in soil microbial ecology. The high cation exchange capacity of certain clays (e.g., montmorillonite) and organic matter contributes to the buffering capacity of soils, reducing the impact of protons (i.e., hydrogen ions) released as a product of microbial metabolism. Sorption of organic and inorganic waste constituents by clays and organic matter affects the availability of substrates and nutrients to microorganisms. Sorption of waste constituents on soil materials strongly depends on soil solution pH. Critical pH values are defined by the pKa of the sorbate and the magnitude of charge on the soil material.

Soils contaminated by waste materials may contain elevated concentrations of salts. In addition, remedial technologies that utilize fertilizers or chemical agents may add salinity to the soil. Increased salinity increases the osmotic potential of soil solution, which may restrict the activity of soil microorganisms due to osmotic stress.

The environmental factors presented in Table 5, as well as soil and waste characteristics, interact to affect microbial activity at a specific contaminated site. Computer modeling techniques are useful to attempt to describe interactions and their effects on treatment of organic constituents in a specific situation.

FIELD SCALE FACTORS THAT AFFECT SOIL/WASTE CHARACTERIZATION AND MANAGEMENT

Climatic and Meteorological Information

Meteorological and climatological data are also required to assess the attenuation of waste constituents in soil systems as well as to assess public health and environmental impacts from the migration of waste constituents to receiving ground and surface waters and through air transmission.

Temperature of both the air and soil affects the rate of biological and chemical attenuation processes in the soil, volatilization of compounds, and the hydrologic budget. In general, soil temperature is difficult to control in a field situation, but may be affected by the use of natural mulches or artificial materials and soil water control.

Most soil microorganisms are mesophiles; i.e., they exhibit maximum growth and activity in the 20° to 35° C temperature range. Soils also contain microorganisms that grow best at temperatures below 20° C (psychrophiles) and others that exhibit maximum growth rates between 50° to 60° C (thermophiles). In general, organic matter decomposition increases with increasing temperature. The influence of temperature on microorganism activity may be used to estimate required times for utilization of biological remediation techniques at contaminated sites.

The availability of soil temperature data is much less than the availability of air temperature data. K.W. Brown and Associates,

(1980) discussed a method developed by Fluker (1958) for predicting annual soil temperature cycles. They also presented isotherm maps of soil temperature data at the 4-inch depth for the spring of 1979 in the United States.

Site Location and Topography

Potential for contaminant migration due to soil permeability, depth to ground water, erodibility, and flooding potential can sometimes be predicted by knowledge of the landform type on which a contaminated site is located. The landform type may also indicate possible site modifications required to minimize transport of waste constituents (Phung et al. 1978). For example, on upland crests and valley side landforms, surface water is limited to incident precipitation and controllable off-site runoff. These landforms may require diversion of surface waters to reduce the amount of water entering and infiltrating the site. Upland crests or valley sides may also pose a hazard to ground water since they are often in ground-water recharge areas.

Upland flat areas with fine-grained soils of low permeability pose less risk of high ground water and erosion and have greater attenuation potential than terrace landforms. Terrace landforms are often underlain by highly permeable coarse-grained soils, sometimes at shallow depths. Contamination from these sites may occur at nearby surface expressions of underlying ground water. The possibility of ground water intersecting a terrace site increases as the site position approaches either the valley wall or the level of the modern floodplain.

Warner (1976) describes four site conditions where pollution potential is especially high. They are as follows:

- (1) Sloping sites with relatively impermeable bedrock (e.g., shale, dense limestone, crystalline igneous rock) 0.6 m or less from the surface have a high potential for erosion, seepage, and overland flow of contaminated runoff.
- (2) Sites located in karst topography, with clayey soils overlying limestone or dolomite with fracture and solution porosity and permeability have a high potential for contamination of ground water, for although infiltration into soil is slow, liquids can rapidly enter bedrock where soil is absent, creating sinkholes and paths for direct flow into ground-water systems.
- (3) Sites with little topographic relief where the ground water is at or near the surface (e.g., old lake beds, floodplains) have a high pollution potential.
- (4) Sites with fractured bedrock and a shallow soil depth (e.g., in granitic areas) have high ground-water pollution potential.

Geological and Hydrogeological Factors

In addition to soil characteristics, geological information in the form of subsurface geological characteristics and hydrogeological factors are important in determining potential for off-site migration from contaminated soils and implementation of remedial techniques.

The geological framework of the site consists of the rocks or sediments in the formations beneath the site. Information is necessary on the composition, stratification, and thickness of the geological layers. For example, sedimentary layers (e.g., limestones, sandstones, and shales) tend to channel flows along bedding planes. Thus, flow directions may be determined by dips in the strata. In humid climates, solution channels may form in limestones, which may allow rapid transport of pollutants

over long distances with little attenuation. Fracture zones that occur in igneous and metamorphic bedrock (e.g., granites, diorite, marble, quartzite, slate, gneiss, and schist) may also permit rapid transport of polluted ground water (Blackman et al. 1980). The most favorable areas would be those covered by thick deposits of unconsolidated low permeability materials overlying shales or undisturbed fine-grained sedimentary bedrock formations that have no major structural variations or fractures affecting formation stability (Corbin 1980). Large thicknesses of unconsolidated materials allow opportunities for natural attenuation while providing a protective barrier to any usable aquifer system.

Hydrogeological factors relating to ground water are also required to assess potential for pollution from contaminated soils. For ground water in unconsolidated formations, less hazard exists if there is no connection with surficial or buried drift aquifers, especially if the contaminated site is overlain with low permeable materials to bedrock. For ground water in bedrock formations, more favorable conditions to minimize pollution potential from contaminated sites exist if the site is away from recharge areas to major freshwater aquifers or there is no direct connection to a usable bedrock aquifer (Corbin 1980). Confined ground water, which is isolated from the surface by a relatively impermeable bed consisting of clay, shale, or dense limestone, is not easily contaminated, nor is it affected much by local sources of recharge (Warner 1976).

Knowledge of the nature of ground-water flow patterns is also critical. Localized, rather than regional, ground-water flow patterns, preferably with known discharge points and a large distance to the water table are the most favorable conditions. Information required to assess hazards might include:

- (1) Elevations of water table and potentiometric surface (ground-water gradients);
- (2) Fluctuations in ground-water levels due to natural inputs and outputs of water;
- (3) Drawdowns of ground-water levels from wells (cones of depression caused by pumping can alter ground-water levels from that which would naturally exist);
- (4) Effects on ground-water flow patterns from changes in surface water flows or levels; and
- (5) Hydraulic characteristics of the aquifer, including transmissivity, specific yield, and specific retention.

Trafficability of Site for Site Characterization Activities and Implementation of Remedial Techniques

Site trafficability may be a determining factor in the performance of site characterization activities and the selection and implementation of remedial technologies at a contaminated site. Trafficability refers to the capability of a soil to permit movement of a vehicle over a land surface (Reeve and Fausey 1974). The trafficability of a soil under different climatological and soil moisture conditions should be assessed. There may be restrictions on the type of equipment that can be used and times when the equipment can be used. For example, the presence of boulders, steep slopes, or excessively wet conditions may cause difficulties in the use of equipment.

The primary concern at waste sites is for successfully performing given operations on the land without damaging the soil. Such damage might include: (1) decreased permeability to air and

water; (2) altered thermal relations; and (3) resistance to root penetration. Generally, trafficability means being able to perform required operations in such a way as to create a desired soil condition or to get an operation completed expediently. Operations that require manipulation (i.e., tillage) require a different interpretation of trafficability than do operations in which soil is used as a surface on which to operate (i.e., non-tillage).

The U.S. Army Corps of Engineers Waterways Experiment Station (1956) identified four soil characteristics that relate to trafficability of soils: (1) bearing capacity; (2) traction capacity; (3) slipperiness; and (4) stickiness. Any one or a combination of these may cause vehicle immobilization.

The trafficability of a soil is considered adequate for a vehicle if the soil has sufficient bearing capacity to support the vehicle and sufficient traction to develop the forward thrust necessary to overcome the rolling resistance. Bearing and traction capacities are related to soil strength or shear resistance. Soil strength can be determined by laboratory tests (e.g., direct shear, triaxial shear, and unconfined compression) or by a field test using a cone penetrometer.

Slipperiness is the condition of deficient traction capacity in a thin surface layer of soil that is otherwise trafficable. When soils adhere and build up on the running gears of a vehicle, increasing rolling resistance and making steering difficult, the condition is called sticky. Soil stickiness and slipperiness usually occur on soils high in clay. When the soil surface is cooler than the underlying soil, moisture migrates from the lower layers to the surface. If the evaporative demand is not large, the moisture accumulates at the surface and causes decreased traction. This condition is not a problem that can be alleviated by drainage but by water management. Decreased traction is especially a problem in seasons when the radiant energy input is low.

Damage to the soil by vehicular traffic usually results from compressing and puddling the soil. To avoid such damage, the soil should be manipulated or traversed only when the soil is below some critical moisture level, which is dependent on the type of soil. Wet soils are easily compacted by both tillage and nontillage operations. Clay soils are especially a problem, since they hold a large amount of water that must be removed by internal drainage or evaporation before tillage is possible.

Soil compaction can be reduced in several ways. Reducing the load intensity on a soil or reducing the number of trips over a soil can be accomplished by changing machinery configurations or tractor tire designs. Subsurface and surface drainage systems can also be used to reduce soil moisture content.

Other site conditions that may affect trafficability include slopes and the presence of coarse fragments, such as boulders. Reeve and Fausey (1974) presented a review of methods regarding determination of soil trafficability using predictive equations and empirical rating systems.

If the remedial technology requires certain site conditions, modifications must be made, if possible, to achieve that condition. An assessment must be made to determine if required modifications are feasible at that particular site. For example, the initial steps in biodegradation of a chlorinated organic compound may require anaerobic conditions followed by aerobic conditions. Thus, the site/soil infiltration, permeability, and drainability characteristics all determine whether anaerobic/aerobic conditions can be achieved.

SOIL CLASSIFICATION

In the United States, there are two systems under which soils are likely to be classified: (1) the Unified Soil Classification System (USCS); and (2) the U.S. Department of Agriculture (USDA) System (Fuller 1978).

The USCS was developed to describe engineering properties of soils (Fuller 1978). Classification of soil types into 15 categories are based on particle (grain) sizes and responses to physical manipulation at various water contents. An abbreviated description of the system (not including information on manipulation (i.e., liquid limit and plasticity index)) is given in Table 6.

The USDA System, developed for agricultural and other land management uses, is based on both chemical and physical properties of the soil. The first system (1938-1960) was based on soil genesis, i.e., how soils formed or were thought to have formed, while the present system is based on quantitatively measurable properties of soils as they exist in the field. The present system is constantly being refined but is in general use by U.S. soil scientists. The highest level of the present USDA System, the category referred to as soil order, is based on soil-forming processes as indicated by the presence or absence of major diagnostic horizons (Brady, 1990).

Fuller (1978) developed a comparison of the USDA System and USCS. The part of the USDA System that can be compared

Table 6. Major Divisions, Soil Type Symbols, and Type Descriptions for the Unified Soil Classification System (USCS) (Fuller 1978)

| <i>Major Divisions</i> | | <i>Symbol</i> | | <i>Description</i> | | |
|---|--|---|---|--|--|---|
| <u>Coarse-grained soils</u> More than half of material is larger than No. 200 sieve size | <u>Gravels</u> | <u>Clean gravel</u> (little or no fines) | G W | Well graded gravels, gravel-sand mixtures, little or no fines. | | |
| | More than half of coarse fraction is larger than No. 4 sieve size | | | GP | Poorly graded gravels or gravel-sand mixtures, little or no fines. | |
| | | | <u>Gravels w/fines</u> (appreciable fines) | GM | Silty gravels, gravel-sand-silt mixtures. | |
| | | | | GC | Clayey gravels, gravel-sand-clay mixtures. | |
| | | | <u>Sands</u> | S W | Well graded sands, gravelly sands, little or no fines. | |
| | More than half of coarse fraction is smaller than No.4 sieve size | | <u>Clean sands</u> (little or no fines) | | SP | Poorly graded sands or gravelly sands, little or no fines. |
| | | | | <u>Sands w/fines</u> (appreciable fines) | SM | Silty sands, sand-silt mixtures. |
| | | | | | SC | Clayey sands, sand-clay mixtures. |
| | | | | | ML | Inorganic silts and very fine sands, silty or clayey fine sands or clay silts with slight plasticity. |
| | <u>Fine-grained soils</u> More than half of material is smaller than No. 200 sieve size | <u>Silts and Clays</u> | | | CL | Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays. |
| Liquid limit is less than 50 | | | | | OL | Organic silts and organic silty clays of low plasticity. |
| | | | | | MH | Inorganic silts, micaceous or diatomaceous fine sandy or |
| Liquid limit is greater than 50 silty soils, elastic silts. | | | | | CH | Inorganic clays of high plasticity fat clays. |
| | | | | | OH | Organic clays of medium to high plasticity, organic silts. |
| Highly Organic Soils | | | | P | Peat and other highly organic soils. | |

Notes: ML includes rock flour. The No. 4 sieve opening is 4.76 mm (0.187 in); the No. 200 sieve opening is 0.074 mm (0.0029 in).

most directly in the USCS is soil texture and associated modifiers (e.g., gravelly, mucky). The size ranges for the USDA and USCS particle designations were shown in Table 1. The two systems are not directly comparable, since the soil texture designation in the USDA System is based only on amounts of sand-, silt-, and clay-sized particles (Figure 5), while in the USCS, soil type is determined both on amounts of certain sizes of soil particles as well as on the response of the soil to physical manipulation at varying water contents. Correlations of the USDA soil textures and USCS soil types are presented in Table 7.

Texture is a major criterion in the USCS but only a minor criterion in the USDA System. A soil of a given texture can be classified into only a limited number of the 15 USCS soil types. However, in the USDA System, soils of the same texture may be found in many of the 11 orders and 47 suborders of the system because of differences in the chemical properties or the climatic areas in which they are located.

The names of the classification units are combinations of syllables, most of which are derived from Latin or Greek. Since each part of a soil name conveys a concept of soil properties or genesis, the name reflects the properties of the soil being classified. Identification of the types of soils at a contaminated site in terms of the categories of the USDA System provides information that is relevant to identifying potential for attenuation and migration of waste constituents.

A complete description of the USDA System is presented in Soil Taxonomy (Soil Survey Staff 1975).

SOURCES OF INFORMATION

Soil Information for a Contaminated Site

Many waste sites may have been subjected to earlier acute emergency response cleanup actions or preliminary investigations to determine the degree and extent of contamination and the necessity for remedial action. Therefore,

there may be significant existing data on site and soil characteristics.

Examples of sources of existing information include the following:

- (1) Government investigative reports;
- (2) Engineering data from public and private agencies or firms (e.g., university soil science and geology departments, state water resource agencies, state geological surveys, city water departments);
- (3) Water well boring logs;
- (4) Geotechnical and soil reports from nearby facilities; and
- (5) Soil surveys.

Soil surveys are especially useful in providing information on soil characteristics and properties for specific soils at a contaminated site. A soil survey is a systematic examination, description, classification, and mapping of soils in an area. A soil survey report usually consists of two parts: (1) the soil map, which shows where specific soils are found; and (2) a description of the area shown on the map, which also provides information on the suitability of the soils (quantified in terms of slight, moderate, or severe limitations) for various agricultural, engineering, wildlife, recreational, and environmental uses. Each particular soil mapped is described with respect to: (1) genesis and formation; (2) topographical location; (3) climatic conditions; (4) hydraulic properties, such as infiltration, permeability, runoff, erosion potential, and water holding capacity; (5) organic matter content; (6) use and management; (7) selected chemical properties, such as CEC and pH; and (8) soil classification. Soil surveys in the U. S. are being developed for county and regional areas through the Cooperative Soil Survey, a joint effort of the U. S. Department of Agriculture, the Agricultural Experiment Station, and other agencies in each state. These surveys are easily accessible through government agencies and federal depository libraries.

Following an initial site inspection of a contaminated site for which a detailed soil survey exists, additional field work may only involve spot verification of the survey using a hand-held soil auger (Crites 1984). If the survey is more general, or if more information is required on specific soil features, backhoe pits should be used. Backhoe pits are recommended over soil borings because they allow direct viewing of the soil profile, including such conditions as fractured, near-surface rock, hardpan or clay layers, and mottling or blue/gray color streaks (an indication of high water table) and also allow accurate sampling of the soil profile.

Existing data should be assessed to determine adequacy for meeting further information requirements and to design subsequent data collection activities. If additional data collection is needed, soil scientists, geotechnical engineers, geologists, and other persons trained in appropriate disciplines should be consulted to generate the required information.

Methods for the collection and analysis of soil samples should be conducted according to recognized standard methods. Documents with a compilation of soil analysis standard methods include:

- (1) Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. Third Edition, SW-846 (U. S. Environmental Protection Agency 1986); and
- (2) Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods. Second Edition (Klute 1986), and Methods of Soil

Table 7. Corresponding USDA and USCS Soil Classifications (Fuller 1978)

| <i>United States Department of Agriculture (USDA) Soil Textures</i> | <i>Corresponding Unified Soil Classification System (USCS) Soil Types</i> |
|--|---|
| 1. Gravel, very gravelly loamy sand | GP, GW, GM |
| 2. Sand, coarse sand, fine sand | SP, SW |
| 3. Loamy gravel, very gravelly sandy loam, very gravelly loam | GM |
| 4. Loamy sand, gravelly loamy sand, very fine sand | SM |
| 5. Gravelly loam, gravelly sandy clay loam | GM, GC |
| 6. Sandy loam, fine sandy loam, loamy very fine sand, gravelly sandy loam | SM |
| 7. Silt loam, very fine sandy clay loam | ML |
| 8. Loam, sandy clay loam | ML, SC |
| 9. Silty clay loam, clay loam | CL |
| 10. Sandy clay, gravelly clay loam, gravelly clay | SC, GC |
| 11. Very gravelly clay loam, very gravelly sandy clay loam, very gravelly silty clay loam, very gravelly silty clay and clay | GC |
| 12. Silty clay, clay | CH |
| 13. Muck and peat | PT |

Analysis, Part 2: Chemical and Microbiological Methods. Second Edition (Page et al. 1982).

Further Information on Fundamentals of Soil Science

Additional information on properties and uses of soils can be obtained from introductory soil textbooks; e.g., Brady and Weil (1999), Foth (1984), Hausenbuiller (1978), and Donahue et al. (1983). Specific information concerning soils and hazardous waste management can be obtained from references such as Sims (1990), Sims et al. (1990), Sawhney and Brown (1989), Dragun (1988), Loehr and Malina (1986), Sims et al. (1984), Overcash and Pal (1979), and Guenzi (1974).

NOTICE

The U.S. Environmental Protection Agency through its Office of Research and Development funded the research described here. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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