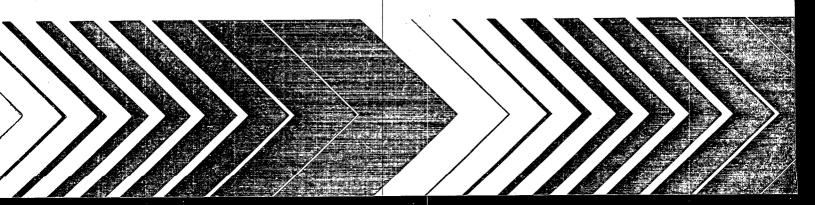


# **Bioremediation Using the Land Treatment Concept**



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## **Environmental Regulations** and Technology

Bioremediation Using the Land Treatment Concept

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August 1993

This report was developed by the Robert S. Kerr Environmental Research Laboratory U.S. EPA, ORD Ada, Oklahoma 74820



### **DISCLAIMER**

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### **FOREWORD**

EPA is charged by Congress to protect the nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

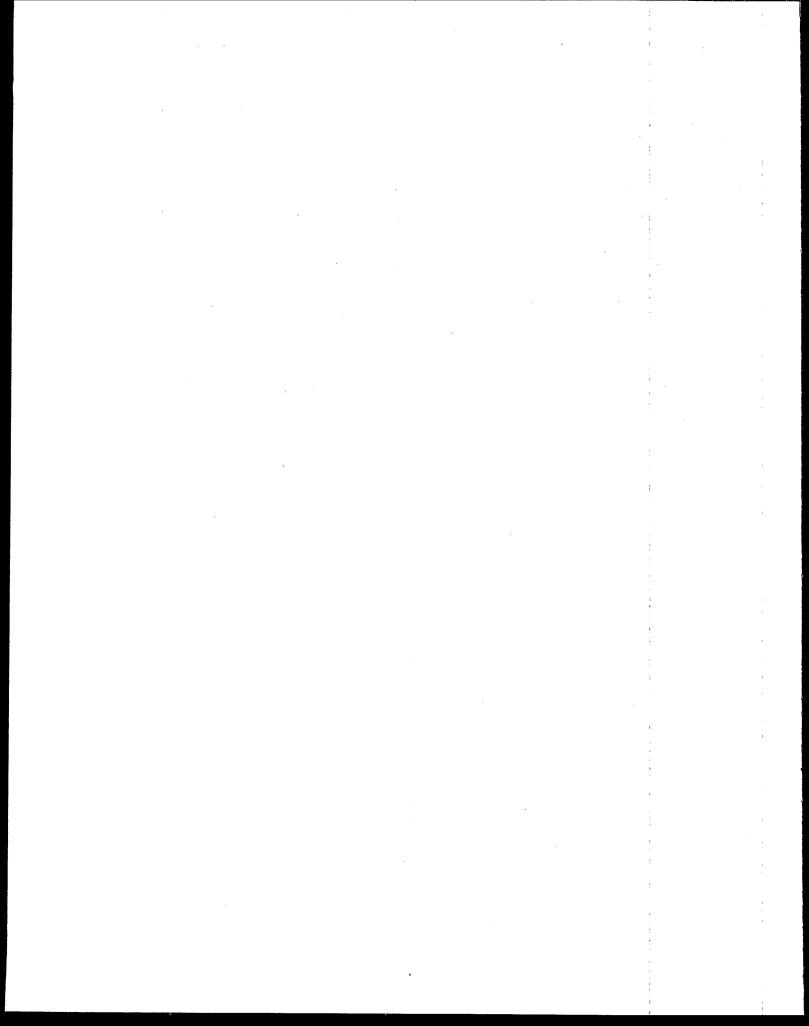
Bioremediation processes using the land treatment concept, whereby contaminated soil is treated in place or excavated and treated in prepared-bed treatment units, are common soil remediation technologies proposed for hazardous waste sites. However, RSKERL and other research and demonstration studies have identified complex biological, chemical and physical interactions within contaminated subsurface media which may impose limitations on the overall effectiveness of bioremediation processes utilizing the land treatment concept. This report was developed to summarize and discuss basic considerations necessary to implement and manage these types of bioremediation systems to improve their efficiency and effectiveness in reclaiming contaminated soils.

Clinton W. Hall

Director

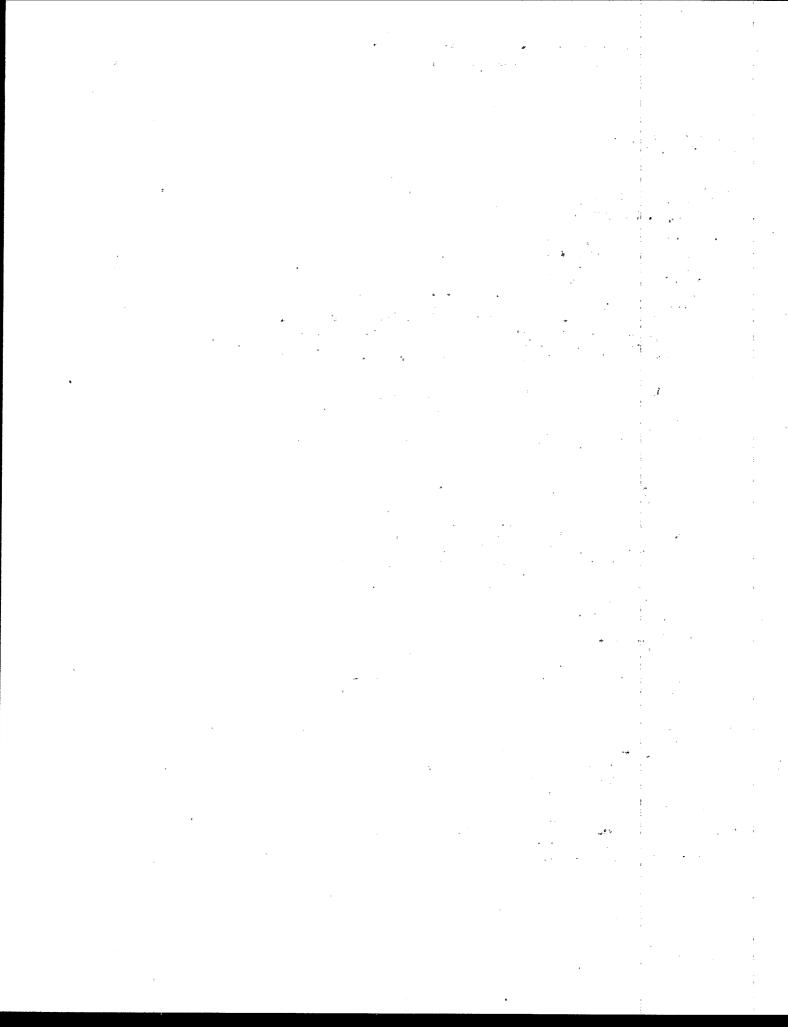
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### INTRODUCTION

This document is designed to be used by those who are involved with the use of land treatment technologies for the remediation of contaminated solid phase materials. In addition to a discussion of the basic processes which drive land treatment applications, the parameters involved in these processes are examined with respect to the efficiency as well as the failure of such systems. Design and operation criteria are suggested in areas ranging from pH control to tilling practices and moisture and nutrient requirements. Contaminants commonly related to the wood preserving and petroleum industries are addressed with respect to their applicability to land treatment in terms of treatability, loading rates, and cleanup levels. A bibliography containing references for further information is provided along with appendices covering soil properties important in land treatment and a discussion of monitoring procedures.

Bioremediation of contaminated soils using the land treatment concept is currently under consideration for implementation at a large number of Superfund, UST, and RCRA sites. The ultimate success of these remediations will depend on systematic design and operation of each specific land treatment unit. This document is designed to be used by those who have responsibility for design and day-to-day operation of a land treatment facility, or who are responsible for overseeing design and operation of the facility. The document provides a short discussion of fundamental processes involved in land treatment, design and operation of the land treatment unit (LTU), and a bibliography containing references for further study. Also included are appendices covering soil properties important in land treatment and a short discussion of monitoring procedures.

### **Definition of Land Treatment**

Land treatment involves use of natural biological, chemical and physical processes in the soil to transform organic contaminants of concern. Biological activity apparently accounts for most of the transformation of organic contaminants in soil, although physical and chemical mechanisms may provide significant loss pathways for some compounds under some conditions. Degradation by ultraviolet light may serve as a loss pathway for certain hydrophobic compounds at the soil surface. Volatilization of low molecular weight compounds also takes place at the soil surface and provides a significant loss pathway for such compounds. Certain chemical reactions such as hydrolysis can play an important role in transformation of some compounds. Humification, the addition of compounds to the humic materials in soil, can be important routes of transformation for some polycyclic aromatic compounds. The relative importance of these processes varies widely for different compounds under different circumstances. The

land treatment concept serves as the basis for design and operation of soil bioremediation technologies at a large number of waste sites requiring cleanup.

### Microorganisms and Bioremediation

Bioremediation is carried out by microorganisms. Both bacteria and fungi have been shown to be important in bioremediation processes. Most research in bioremediation has centered on bacteria, but some investigators have found that fungi can play an important role in bioremediation processes, especially with halogenated compounds (e.g., pentachlorophenol, a wood preservative). It is important to realize, however, that in almost all cases bioremediation relies on communities of microorganism species, rather than one or a few species.

Bioremediation consists of utilizing techniques for enhancing development of large populations of microorganisms that can transform the pollutants of interest, and bringing these microorganisms into intimate contact with the pollutants. In order to do this efficiently, necessary provisions for microbial growth and reproduction must be maintained.

Life processes for all known living creatures are carried out in water. Some organisms, such as human beings, can maintain an internal water environment while moving about in a relatively dry outer environment. Many microorganisms, however, cannot maintain an appropriate inner environment without being in a relatively wet outer environment. Most microorganisms that are active in bioremediation must live in water. This water may be in tank reactors or an aquifer, or it may be a thin film of water on a soil particle or oil droplet.

Microorganisms are sensitive to the osmotic potential of the solution in which they function. The osmotic potential affects the ability of the microorganism to maintain itself with a desirable amount of water internally. If the environment is too dry, or if the water in the microorganism's environment contains excessive concentrations of solutes, the microorganism cannot maintain the proper amount of water internally. This factor can be a problem for bioremediation schemes where, for example, process waters or contaminated soils have high levels of dissolved salts. Sudden changes in osmotic potential can inhibit microbial activity, often resulting in lysis (disintegration of cell walls). Microorganisms can adapt to environmental changes within limits if such changes are not induced rapidly.

Specific microorganisms are active within a relatively narrow range of temperatures. Most bacteria that carry out bioremediation processes are mesophiles ("middle lovers") and are most active from about 18 to 30 degrees centigrade. Significantly higher or lower temperatures will limit their activity. Within this range, activity will usually be greater at the higher temperatures. Activity decreases as the temperature moves further outside these limits. At lower temperatures, activity does not usually stop completely until the freezing point is reached.

Most microorganisms active in bioremediation processes are aerobic, that is, they require free (uncombined) oxygen. Some treatment processes make use of anaerobic microorganisms that do not require free oxygen; however, these processes are not yet widely used in environmental cleanups. Microorganisms living in aqueous reactors, aquifers, or in the subsoil may be supplied with oxygen by pumping air or oxygen-supplying compounds (e.g., hydrogen peroxide) into the environmental system. Microorganisms growing in surface soil are usually supplied with oxygen by tilling the soil to facilitate air entry. In many remediation situations the essential problem is the balance between water and oxygen: the more water, the less oxygen, and vice versa. In the soil environment, the oxygen supply and the water supply to microorganisms are essentially inversely related, since the pore space in soil is occupied by either air or water.

Microorganisms are active within a relatively broad pH range. The pH is a measure of the acidity or basicity of the environment. However, many microorganisms are inhibited below pH 5 or above pH 9. Although many microorganisms can adapt to pH levels within that range, it is thought that fungal species tend to be the more active members of the microorganism community below pH 6, and bacteria tend to dominate above pH 7.

The pH range within which bioremediation processes are considered to operate most efficiently is 6 to 8. The optimum pH range for a particular situation, however, is influenced by a complex relationship between the microorganisms, pollutant chemistry and external environment, and thus is site-specific. The pH can be adjusted to the desired range by the addition of acidic or basic substances (i.e., sulphur or lime).

Microorganisms are sensitive to the presence of a wide variety of compounds and elements. High concentrations of heavy metals, certain highly halogenated organics, some pesticides and other exogenous materials can inhibit bioremediation. Effects of these inhibitors vary with concentration, environmental factors, rapidity of contact with the inhibitors, and time of contact such that it is difficult to set any definite concentration limits above which bioremediation is precluded. Laboratory treatability studies often can be used to provide data necessary for management decisions regarding the impact of a given inhibitor at field scale.

Metals often are present in soils contaminated with organic wastes. These metals will not be treated (transformed or degraded) in the same sense as the organic materials. However, valence states may be changed and chemical bonds may be broken so as to change the toxicity or mobility of the metals. Addition of manures and other complex organic materials often used in land treatment may reduce the mobility of many metals by increasing the ion exchange capacity or adsorption capacity of the soil.

Microorganisms must have carbon sources and mineral nutrients (nitrogen and phosphorus, for example) in order to live and reproduce. In many cases, the pollutants themselves will supply the carbon source and some nutrients; however, mineral nutrients and a supplemental carbon source may be supplied if needed. Mineral nutrients are usually supplied as soluble salts (fertilizers). If necessary, carbon may be supplied as animal manures (which will also supply many mineral nutrients), molasses, glucose, wood chips, corn cobs or a variety of other carbon containing materials.

There must be a balance between the various mineral nutrients and the carbon source or the microorganisms will not be able to make optimum use of the carbon source. For most bioremediation situations, it is supposed that biodegradation is optimal at carbon/nitrogen ratios in the range of 10-30 to 1; and nitrogen/phosphorus ratios of about 10 to 1 by weight. Research and field experience indicates that these ratios may vary widely depending on the type of carbonaceous materials present.

There are 15 or more other mineral nutrients that must be available in appropriate amounts. With the exception of some process waters and ground waters, these minor nutrients are usually present in the environment in sufficient amounts. The amounts of foods and nutrients to be added should be based on results from laboratory and site treatability studies.

The availability of nutrients to microorganisms is strongly influenced by pH since soil pH generally is maintained or adjusted to the 6-8 pH range in a land treatment scenario. Limited availability of nutrients caused by pH is rarely a problem.

Since microorganisms are responsible for transformation of pollutants during bioremediation, it would seem reasonable to assume that the greater the number of microorganisms present, the faster the transformation would occur. However, results of population counts and analyses for parent compound disappearance or transformation are often not closely correlated. Instead, the rate of transformation is more closely correlated to the rate at which oxygen and electron acceptor can be transported to the system.

Several techniques have been devised to determine the microorganism population. One commonly used method is standard plate counting. Samples of soil, water, or other matrices in which microorganisms are growing are applied to Petri plates containing a nutrient media. The plates are incubated for several days to allow microorganisms to grow, after which the number of microorganism colonies growing on the plates are counted. These counts can then be related to the numbers of microorganisms present in the original matrix; however, the relationship between population counts and pollutant transformation rates is not well defined. Often, there are many types of microorganisms in the bioremediation environment that will be counted in plate counts, but only a few of these types may actually be involved in transformation of the contaminants of concern. The nutrient media may be spiked with waste compounds of interest; microorganisms that grow on such media are considered to be tolerant to the spiked compounds. The use of spiked media yields an indication of population levels of tolerant microorganisms in the soil tested. Note that this procedure does not give an indication of the microorganisms present that can degrade

the spiked compound, only those that can survive and grow in the presence of the spiked levels of the compounds.

There are several physical constraints on the use of microorganisms in remediation of soil contaminants. These are generally related to the problem of getting contaminants and microorganisms in close contact under environmental conditions conducive to microbial activity. Generally, a contaminant must be able to move through the waste/soil matrix and pass through the microorganism's cell membrane in order for transformation to occur. In some cases contaminants can be transformed by extracellular enzymes (cooxidation or cometabolism) without entering into the microorganisms.

Waste compounds that have low solubilities in water (for example, 4, 5, and 6 ring polycyclic aromatic hydrocarbons [PAHs]) move slowly from soil adsorption sites or free phase droplets into the soil water and from there into the microorganism. Wastes in solid matrices (soil) will have less solvent (water) in which to be dissolved, will be more likely to have highly variable concentrations throughout the matrix, will be harder to mix thoroughly for even distribution throughout the matrix, and often will have a relatively high tendency to be adsorbed onto matrix solids.

All of these factors tend to limit accessibility of contaminant compounds to the microorganisms; therefore it is often easier to achieve biodegradation of a given contaminant in water than in soil. Also, soil treatment processes where soil is suspended in water and constantly mixed (soil slurry bioremediation) will usually have faster biotransformation rates than simple solid phase soil bioremediation processes.

### LAND TREATMENT TECHNOLOGY

### In-Situ and Ex-Situ Land Treatment

Land treatment techniques for bioremediation purposes most often are used for treatment of contaminated soil, but certain petroleum waste sludges have long been applied to soil for treatment. Ideally, the contaminated soil can be treated in place (in-situ). Often, however, the soil must be excavated and moved to a location better suited to control of the land treatment process (ex-situ).

In-situ land treatment is limited by the depth of soil that can be effectively treated. In most soils, effective oxygen diffusion sufficient for desirable rates of bioremediation extends to a range of only a few inches to about 12 inches into the soil. Usually when it is desired to treat soil in-situ to depths greater than 12 inches, the surface layer of soil is first

treated to the desired contaminant levels, and then removed, or tilled so that lower layers are moved to the surface for treatment. Most tractor mounted tilling devices can till only to a depth of about 12 inches. Large tractors with specialized equipment that can till to depths of 3 feet or more have been used for in-situ land treatment. Large augers are now available that can move soil from 50-100 feet depths to the surface, but the practicality of this technique for in-situ land treatment has not been demonstrated.

Ex-situ treatment generally involves applications of lifts of contaminated soil to a prepared bed reactor. This reactor is usually lined with clay and/or plastic liners, provided with irrigation, drainage and soil water monitoring systems, and surrounded with a berm. The lifts of contaminated soil are usually placed on a bed of relatively porous non-contaminated soil.

Whether practiced in-situ or ex-situ, effective land treatment is generally limited to the top 6 to 24 inches of soil, with 12 inches or less being the preferred working depth. At depths below 12 inches, the oxygen supply is generally inadequate for useful rates of bioremediation using standard land treatment practices. Tilling is used to mix the soil and increase the oxygen levels, but is usually limited to 12 inches or less unless specialized equipment is available.

The land treatment process may be severely limited in clayey soils, especially in areas of high rainfall. This limitation is primarily related to oxygen transfer limitations and substrate availability to the microorganisms. Clayey soils should be applied in shallower lifts than sandy soils, preferably no more than 9 inches in depth. Tilth ("workability" of the soil) can often be improved by adding organic matter or other bulking agents to the soil. If high sodium content causes the soil to have poor tilth, gypsum (calcium sulfate) can be added.

The soil should be screened before application to remove any debris greater than one inch in diameter, especially if significant amounts of debris or rocks are present. Any large debris that may adsorb the waste compounds (i.e., wood), should be removed if possible and treated separately. Small rocks and other relatively nonadsorptive wastes can be treated if they do not interfere with tillage operations.

### Lift Application and Tilling

After application to the land treatment unit, each lift should be tilled at intervals to enhance oxygen infiltration and contaminant mixing with the microorganisms. The soil should be near the lower end of the recommended soil moisture percentage range before tilling. Tilling very wet or saturated soil tends to destroy the soil structure, reduce oxygen and water intake, and cause reduced microbial activity. Tilling should not begin until at least 24 hours after irrigation or a significant rainfall event. Tilling more than is necessary for enhanced oxygen infiltration and

contaminant mixing may be counter-productive since it tends to destroy the soil structure and compact soil below the tilling zone. Tillers tend to mix soil only along the tractor's line of travel, so tillage should be carried out in varying directions, i.e., lengthwise of the LTU, crosswise, and on the diagonal.

A tractor mounted rotary tiller is recommended. Occasionally a subsoil plow or chisel plow should be used to break up any hardpan or zone of compaction created by passage of equipment across the LTU. If the tiller does not operate deeply enough to mix soil from the last lift into the top few inches of soil from the preceding lift, a turning plow may be used to achieve desired mixing of the two lifts. Use of the turning plow should be followed immediately by tilling to complete the mixing action.

Each subsequent lift, usually 6-12 inches in depth, should be tilled into the top two or three inches of the previous lift. This will mix populations of well acclimated microorganisms from the treated lift into the newly applied lift, and help reduce the length of time for high populations of active degraders to be built up in the new lift.

Timing of application of succeeding lifts should be based on reduction to defined levels of particular compounds or categories of compounds in the preceding lift. For instance, the goal might be to reduce total petroleum hydrocarbons (TPH) to less than a regulatory or risk calculated limit in the current lift before application of a new lift.

Once desired target levels of compounds of interest are established, data obtained from the LTU monitoring activities can be statistically analyzed to determine if and when desired levels are reached and the LTU is ready for application of another lift.

### Nutrients, Carbon Sources, and Other Additives

Microorganisms in land treatment units require carbon sources and nutrients. Fertilizers can be used to supply the nutrients, while wood chips, sawdust or straw can supply carbon. Various animal manures are often used to supply both carbon sources and nutrients. High organic levels in manures, wood chips and the other organic amendments increase sorptive properties of soil, thereby decreasing mobility of organic contaminants.

Organic amendments will also increase the water holding capacity of soil, which can be desirable in sandy soils, but can cause difficulty when land treatment is conducted in areas of high rainfall and poor drainage. In an excessively wet soil the oxygen supply is reduced, which may essentially stop or severely limit transformation of waste constituents. Drainage must be carefully designed and managed in these situations.

Animal manures can provide desirable organic supplements. Manure should be applied to each lift at the rate of about 3% - 4% by weight of soil. The manure should be analyzed for nitrogen and phosphorus to determine if any additional amounts of these nutrients need be applied. The manure should be in small particles and should be thoroughly tilled into the soil lift. Initial contaminant levels should be measured after incorporation of organic supplements to avoid incorporating dilution effects into calculation of waste transformation.

Manures are often mixed with sawdust or straw since these materials are used as bedding in stock facilities. This is acceptable and even desirable since they act as bulking agents in soil. However, the high percentage of cellulosic material will usually exert a high nitrogen demand, thereby reducing the amount of nitrogen available to microorganisms for transforming contaminants of concern. If necessary, available nitrogen can be increased with addition of appropriate inorganic fertilizers, including fertilizer grade ammonium nitrate (for nitrogen), triple superphosphate (for phosphorus), or diammonium phosphate (for both nitrogen and phosphorus). Nitrogen fertilizers can cause soil pH to be lowered due to formation and leaching of the nitrate ion coupled with soil cations.

Agricultural fertilizer is usually supplied in prilled or pelleted form (the fertilizer compounds formed into pellets with a clay binder) suitable for easy application over large areas. Technical grade, unformulated fertilizer compounds (for instance, ammonium chloride crystals) are difficult to spread evenly over the land surface. The pelleted fertilizers may be applied with a hand-operated or tractor-operated cyclone spreader. Completely water-soluble fertilizers can be applied through irrigation systems, allowing application rates to be closely controlled, applications to be made as often as irrigation water is applied, and immediate availability to the microorganisms. Equipment is available to meter concentrated nutrient solutions into the irrigation system on a demand basis.

Nutrient requirements for biodegradation in the field have not been thoroughly studied, and detailed information is not available to indicate the optimal levels of particular nutrients. The amount of nitrogen and phosphorus needed may be estimated by having representative soil samples analyzed by the state agriculture department or university laboratory, or by a private agricultural soil testing laboratory. General fertilizer recommendations for vegetable gardens should be followed. The analytical laboratory should be made aware that the soil contains hazardous materials.

Sometimes inorganic micronutrients, microbial carbon sources, or complex growth factors may be needed to enhance microbial activity. Animal manures generally will supply these factors. Proprietary mixtures of these ingredients are sometimes offered for sale to enhance microbial activity. Proof of the efficacy/cost effectiveness of these mixtures is lacking in most cases.

### **Bioaugmentation**

Microorganism cultures are often proposed for addition to bioremediation units. Two factors limit use of these added microbial cultures in LTUs: (1) nonindigenous microorganisms rarely compete well enough with indigenous populations to develop and sustain useful population levels, and (2) most soils with long-term exposure to biodegradable wastes have indigenous microorganisms that are effective degraders if the LTU is managed properly. If the use of proprietary additives is proposed, results of well-designed treatability studies with appropriate controls should be provided by the vendor to support such use.

Certain soil factors may interfere with microbiological activity in the LTU soil. High salt levels, indicated by high electrical conductivity (EC) readings, may reduce or stop useful microbiological activity. If levels are too high, it may be necessary to leach the soil with water to remove excess salts before biodegradation can occur. High levels of sodium may be detrimental to soil structure. Sodium levels may be reduced by applying calcium supplements (usually gypsum, CaSO<sub>4</sub>) and leaching. Leaching of contaminants may also occur at the same time.

### **Soil Moisture Control**

Historically, it has been recommended that soil moisture be maintained in the range of 40% - 70% of field capacity; however, recent experience indicates that 70% - 80% of field capacity may be optimum. A soil is at field capacity when soil micropores are filled with water and soil macropores are filled with air. This condition allows soil microorganisms to get air and water, both of which are necessary for aerobic biodegradation to occur. Maintaining soil at somewhat less than 100% of field capacity allows more rapid movement of air into the soil, thus facilitating aerobic metabolism without seriously reducing the supply of water to microorganisms. If soils are allowed to dry excessively, microbial activity can be inhibited or stopped; if the wilting point is reached, cells may lyse or rupture.

Field capacity of a soil may be determined by saturating a soil sample with water and allowing it to drain freely for 24 hours. The soil is weighed, oven-dried at 105° C to constant weight, then weighed again. The difference between the weight of drained soil and the oven-dried soil gives the weight of water in that amount of soil at field capacity. The weight of water divided by the dry weight of the soil gives the percentage of water in the soil at field capacity. A sandy soil might hold as little as 5% of its dry weight in water at field capacity as compared to 30% for a clay soil.

Continuous maintenance of soil moisture at adequate levels is of utmost importance. Either too little or too much soil moisture is deleterious to microbial activity. Monitoring soil moisture and scheduling irrigation is important, requires constant attention, and is perhaps one of the most neglected areas of LTU operations.

Moisture enhancement can be accomplished by using traveling gun or similar irrigation systems that can be removed to allow easy application of lifts. Hand-moved sprinkler irrigation systems are more often used, although they are usually more expensive. Sprinkler systems can be designed with quick detach couplings to facilitate movement when placing lifts of contaminated soil. Permanently installed sprinkler systems with buried laterals and mains may be used, but the sprinkler uprights must be avoided when placing soil lifts and during other LTU operations. The uprights may need to be lengthened if many lifts are placed during the operating life of the LTU.

If a permanently installed, buried line system is used, the uprights should be connected to the buried lateral lines with a short piece of plastic pipe. Some of the uprights will be hit by field equipment during operations, and the plastic pipe will break before the lateral line or other parts of the piping system. The plastic pipe can be easily repaired, while a bent or broken lateral line or upright can be difficult to repair.

The operating pressure for most sprinklers ranges from 30 to 50 lb/in². Sprinklers may have two nozzles, one to apply water at a distance from the sprinkler (range nozzle) and one to cover the area near the sprinkler (spreader nozzle). Sprinklers may be static or rotating, with a hammer or other device to cause the sprinkler to rotate. Since one sprinkler will not apply water uniformly over an area, sprinkler patterns should be overlapped to provide more uniform coverage. The usual overlap is around 50%; that is, the area covered by one sprinkler reaches to the next sprinkler. Highly uniform coverage is difficult to achieve in the field, especially in areas where winds of more than 5 mph are common.

Small LTUs can be covered with sprinklers set only on the sides of the LTU. Sprinklers can cover full, half or quarter circles so that sprinklers on the sides or in the corners of the LTU will cover only the LTU and not the berm or areas outside the LTU.

The irrigation system should be sized to allow application of at least one inch of water in 10-12 hours. The rate of water application should never be more than the soil can absorb with little or no runoff since LTUs consist of bare soil and excessive runoff can rapidly cause significant erosion. Generally, coarser (sandy or loamy) soils can take up water at a faster rate than finer textured clay or clay loam soils. Usually, application rates of more than 0.5 inches of water per hour are not recommended; clayey soils with slopes greater than 0.2% - 0.3% will require lower rates of water application. A water meter to measure the volume of water applied is helpful in controlling application.

Surface drainage of the LTU can be critical in high rainfall areas. If soil is saturated more than an hour or two, aerobic microbial action is reduced. The LTU surface should be sloped no more than 0.5% - 1.0%, as greater slopes will allow large amounts of soil to be washed into the drainage system during heavy rains. Even a slope of 0.5% - 1.0% will allow soil to be eroded; therefore the drainage system should be designed to allow collection and return of eroded soil to the treatment unit.

Underdrainage is generally provided by a sand layer or a geotextile/drainage net layer under the LTU. The system should be designed so that excess water in soil pores over field capacity will be quickly drained away so microbial activity will not be inhibited. The lifts of contaminated soil are usually placed on a bed of sand or other porous soil, which results in a "perched" water table. In this event the contaminated soil lift will take up water from irrigation or rain until the soil nears saturation, at which point excess water will be discharged into the treatment unit drainage system. The interface between the lift and the coarse layer underneath should be composed of well graded materials so that the transition from the (usually) relatively fine soil texture of the lift to the coarse texture of the drainage layer is gradual rather than sudden. Grading of the materials reduces the tendency for the soil lift to become saturated before drainage occurs, which inhibits aerobic biological activity. The change in texture at the interface can be made more gradual by tilling the lift into the top few inches of the drainage layer.

Some storage capacity should be provided so that runoff and leachate water can be recycled onto the LTU. A one-inch rain might give a combined runoff and leachate of 10,000 to 27,000 gallons per acre if the LTU is being maintained at the proper (relatively high) moisture content. Therefore, it may not be practical to provide storage capacity for large rainfall/runoff events.

In many cases leachate/runoff water cannot be discharged without treatment. Biological reactors are commonly used to treat this water prior to discharge. Alternatively, effluent from the biological treatment unit may be applied to the LTU through the irrigation system. Nutrients and microorganisms from the biological treatment system may enhance the microbial activity within the LTU.

### Types and Concentrations of Contaminants Remediable by Land Treatment

The types of contaminants most commonly treated in land treatment units are petroleum compounds and organic wood preservatives. Historically, petroleum refineries have used land treatment to dispose of waste sludges. Although waste petroleum sludges currently are not often applied to soil for treatment, the technology has been applied to remediation of soil contaminated with many types of petroleum products, including fuel, lubricating oil and used petroleum products. Land treatment has historically been used to remediate contaminated process waters from wood preserving operations. This technology currently is not used for this purpose, but is currently used to remediate soil contaminated with wood preserving wastes.

Other applications for land treatment technology include remediation of soil contaminated with coal tar wastes, pesticides and explosives. Since coal tar wastes are similar

to creosote wastes (wood preserving creosote is made from coal tar), such wastes are considered amenable to land treatment. Land treatment appears to be potentially useful for certain pesticides, but the evidence for applicability of this technology to explosives contaminated soil is inconclusive.

#### **Petroleum Derived Contaminants**

Crude oil is refined into petroleum products including the following general groups: gasolines, middle distillates (diesel fuel, kerosene, jet fuel, lighter petroleum oils), heavier fuel oils and lubricating oils, and asphalts and tars. Certain individual compounds may also be produced from crude oil, including benzene, toluene, hexane, and many others.

Gasoline, a mixture of C4 to C12 hydrocarbons, includes paraffins (C<sub>N</sub>H<sub>2N+2</sub>), olefins (alkenes), naphthenes (5 and 6 carbon cycloparaffins and their alkyl derivatives, sometimes including polycyclic members), and aromatics (12% to 20% by weight of gasoline). Jet fuel includes avgas (for propeller-driven aircraft — similar to gasoline), Jet A & A1 fuel (commercial aircraft fuel, with a heavy kerosene base), JP4 (Air Force jet fuel, naphtha based), and JP5 (Army jet fuel-kerosene base). Diesel and kerosene are similar in composition, being largely composed of chains of 9-17 carbons in length. Heating oil and bunker C are heavy fuel oils. Lubricating oils contain long chain hydrocarbons (20+ C chain length). Tars and asphalts are mixtures of long chain, high molecular weight hydrocarbons including bitumens, waxes, resins and pitch.

Specific compounds found in petroleum products and refinery wastes include: aliphatics, olefins, naphthenes, and asphaltenes; single ring aromatics benzene, toluene, ethyl benzene and o,m,p-xylene; multiple ring aromatics (polycyclic aromatic hydrocarbons—PAHs), phenols and cresols; bitumens, waxes, resins and pitch; and metals including lead, chromium and cadmium. Caustics (alkali metal hydroxides) may also be found.

Refinery waste sources include production wastes (refinery effluents, slop oil-emulsion solids, leaded tank bottoms, heat exchanger bundle cleaning sludge); incidental wastes (runoff, equipment washdown, spills, ballast tank water); and treatment wastes (API separator sludge, float from air flotation units, sludge from biotreatment).

Since the majority of gasoline components have significant volatility, land treatment is not usually considered for treatment of gasoline contaminated soil due to the high losses of volatiles expected with routine land treatment operations. Diesel and kerosene type fuels have a significant portion of volatile components, but "weathered" wastes that have lost most of the volatile components usually are suitable candidates for land treatment. Most of the heavier petroleum products (fuel oils, lubricating oils, waste sludges and oils) are susceptible to land treatment. However, the long chain hydrocarbons (20+ carbons) and 5-6 ring PAHs that may be found in these materials

biodegrade slowly if at all. Petroleum products that consist mostly of long chain hydrocarbons and other high molecular weight compounds (asphalts, tars) are not suitable candidates for land treatment because of the resistance of such compounds to biodegradation and the physical difficulty of mixing these products with the soil.

### **Wood Preserving Contaminants**

The major portion of the wood preserving industry in the United States treats wood under pressure in cylinders with one of four types of preservatives:

- pentachlorophenol (penta, PCP) in petroleum, or other solvents;
- 2) creosote;
- water solutions of copper, chromium, and arsenic (CCA); ammoniacal solutions of copper and arsenic (ACA); ammoniacal solutions of copper, zinc and arsenic (ACZA); and
- 4) fire retardants, which include various combinations of phosphates, borates or boric acid, and zinc compounds. A relatively minor portion of the wood treating industry uses nonpressure treatment of wood with similar preservatives applied in a variety of ways.

Technical grade pentachlorophenol used for treating wood contains 85% to 90% pentachlorophenol, remaining materials being 2,3,4,6-tetrachlorophenol (4% to 8%), "higher chlorophenols" (2% to 6%), and dioxins and furans (0.1%). The principal chlorodibenzodioxin and chlorodibenzofuran contaminants are those containing six to eight chlorines. Pentachlorophenol is mixed with a carrier (usually a fuel oil similar to kerosene or diesel fuel) at 4% - 5% pentachlorophenol by weight in the carrier, in order to produce the solution used for treating wood.

The other major organic wood preservative used in the United States is coal tar creosote. Creosote is used either full strength or diluted with petroleum oil or coal tar. Wood preserving creosote contains approximately 85% polynuclear aromatic hydrocarbons (PAHs), 10% phenolic compounds, and 5% nitrogen, sulfur or oxygen containing heterocycles.

The carrier oils for pentachlorophenol and creosote are similar in biodegradability to the petroleum diesel fuel and kerosene products. Pentachlorophenol and the associated phenolics in pentachlorophenol and creosote treating solutions are biodegradable, though levels of pentachlorophenol in soil of about 1000 mg/kg are difficult to bioremediate. Higher pentachlorophenol levels are usually lowered by mixing with less contaminated soil before land treatment. The compounds of most interest in creosote are the PAHs, which vary in susceptibility to bioremediation according to the number of rings. The two-ring PAHs are readily biodegradable, the three-ring PAHs are more difficult, and biodegradation becomes increasingly more difficult for the four- and five-ring PAHs.

The inorganic wood preservatives will be discussed briefly since they are not usually remediated by biological means. Their main impact on bioremediation comes from the possible toxicity of the inorganic preservatives to microorganisms, and the necessity for providing means other than land treatment for remediation of inorganic contaminated soil. Generally, if soil is contaminated with organic and inorganic wood preservatives, it is first bioremediated to treat the organic contaminants, and then solidified/stabilized to treat the inorganics. There has been little research on concentrations of the inorganic wood preservatives that would be problematic in soil bioremediation.

### Levels of Contamination Susceptible to Land Treatment

The levels of petroleum product contamination amenable to land treatment vary by waste type and site conditions. In many cases, soils with higher levels of contaminants than are recommended for land treatment can be mixed with less contaminated soil to bring contamination levels down to recommended starting levels for treatment. Levels of petroleum product contamination as high as 25% by weight of soil have been reported as treatable, although experience indicates that levels 5% to 8% by weight or less are more readily treated. Long chain hydrocarbons (20 or more carbons in the chain) are more resistant to biological treatment, so petroleum products containing excessively high percentages of these compounds (bunker C, asphalt, tars, etc.) are not good candidates for land treatment under most commonly established cleanup standards for soil.

Soil contaminated with 15,000 to 20,000 mg/kg dry weight creosote wastes have been treated in soil systems, although more usual starting levels are in the 5,000 to 10,000 mg/kg range. Pentachlorophenol wastes are rarely treated at more than 1000 mg/kg starting levels since pentachlorophenol is quite toxic to microorganisms at the higher levels.

The final levels attainable also vary by waste and site conditions. Generally, once total contaminant levels are below 50-200 mg/kg PAH, remediation by land treatment is slow, and further treatment by conventional land treatment techniques may be ineffective. For instance, land treatment of creosote wastes is generally considered successful if total carcinogenic polynuclear aromatic hydrocarbons are reduced to below 50-100 mg/kg, and specific components are reduced to their "land ban" levels (for instance, pyrene to 7 mg/kg). Laboratory treatability studies may be used to assess the "best case" potential for final contaminant levels, with the assumption that actual final levels in the field would rarely be lower than those found in the laboratory study.

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## APPENDIX A SOIL PROPERTIES

Soils are composed of organic matter, inorganic solids (sand, silt, clay, and larger fragments), air, and water. Organic matter may range from less than one percent in many soils, especially those in hot or cold desert climates, to 50% or more in the peat soils found in peat bogs. Soils are generally classified according to their sand, silt and clay content; the ratios of these components may vary in almost any proportion. Air and water occupy the pore spaces among the sand, silt and clay particles. Pore space occupies about 20% - 60% of most uncompacted soils.

Soil parameters important in land treatment include: soil horizons, depth, texture (grain size distribution—sand, silt, clay proportions), bulk density, porosity (effective, total), hydraulic conductivity, permeability, tilth, cation and anion exchange capacity, organic matter content, pH, water content and water holding capacity, nutrient content, salinity, redox potential, color, and biological activity.

### **Soil Horizons**

Soil horizons are the various layers present in most soil columns. Physical and chemical differences between soils in the layers affect movement of contaminants through the soil profile. Organic matter from dead plants and animals accumulates in the upper, "A" horizons. A top layer of

almost pure organic matter is called the "O" horizon. As soils mature, clay particles are moved downward along with water. The clay tends to accumulate in lower soil layers. The zone of clay accumulation is called the B horizon. The C horizons comprise the relatively undifferentiated material, often distinguished from the parent rock only by the lack of consolidation.

### Depth

Soil depth to bedrock or ground water affects the volume of soil that may be contaminated, potential directions of contaminant movement, and the difficulty of access to the contaminated volumes of soil. Land treatment uses the concept of a "treatment zone," meaning a zone in which migrating contaminants are adsorbed and degraded. The depth and activity of this zone affects the potential for migration of contaminants to ground water.

#### **Texture**

Soil texture (as defined by the proportions of sand, silt, clay) influences porosity, hydraulic conductivity, permeability, tilth, cation exchange capacity (CEC), and sorption capacity for contaminants. Finer textured soils have greater surface areas per unit volume. The differences between the chemical and physical properties of the various sands and silts is largely due to the different particle sizes. Clays are not only much smaller than sands and silts but also are quite different in chemical composition. Clay particles have negatively charged surfaces that attract and hold cations (Ca++, Na+, NH<sub>4</sub>+, H+, etc.) or other materials with a positively charged portion, giving rise to a cation exchange capacity. The edges of the clay particles may also have a positive charge, giving rise to an anion exchange capacity. Clay particles are flat, platelike structures, with a very high surface area. Clay particles have interior layers that can separate enough to allow water and many ions to enter and be held. "Shrink-swell" clays allow much water to enter these interior areas, causing the clay particles to change greatly in volume as the moisture content changes.

### **Bulk Density**

The soil bulk density is the mass of dry soil per unit bulk volume. The bulk volume is determined before drying the soil to obtain the mass. Bulk density is used in most soil transport and fate models.

### Porosity, Hydraulic Conductivity, and Permeability

Porosity, hydraulic conductivity, and permeability are three parameters that are closely related and commonly confused. The terms describe the soil characteristics and rate of water movement through the soil.

Porosity is the ratio of the volume of void spaces in a soil to the total volume of the soil. The void spaces may be occupied by air, water, or other fluids, such as contaminants. The effective porosity represents the interconnection between the void spaces and is defined as the volume of void spaces through which water or other fluids can travel, divided by the total volume of the soil.

Primary porosity is a characteristic of the original soil or rock matrix; secondary porosity is caused by weathering or fracturing processes occurring after the soil or rock was emplaced. Secondary porosity can greatly enhance the effective porosity of the soil or rock.

Typically, more rounded particles such as gravel, sand, and silt have lower porosities than soils rich in the platy clay minerals. Soils containing a mixture of grain sizes will also exhibit lower porosities. The smaller particles tend to fill in void spaces between the larger ones.

Porosity can be an important controlling influence on hydraulic conductivity, which is a proportionality constant describing the rate at which water can move through the soil. Hydraulic conductivity is a function of the properties of both the porous medium and the fluid passing through it. Typically, the hydraulic conductivity has higher values for gravel and sand and lower values for clay. Thus, even though clay-rich soils usually have higher porosities than sandy or gravelly soils, they usually have lower hydraulic conductivities, because the pores in clay-rich soil are much smaller.

The hydraulic conductivity can vary over 13 orders of magnitude, depending on the type of material and whether the measurement was made in the field or in the laboratory. The methods of measurement differ significantly, and interpretations placed on the values may be dependent on the type of measurement. In practical terms, this implies that an order-of-magnitude knowledge of hydraulic conductivity may be all that is attainable, and that decimal places beyond the second probably have little significance.

Pore spaces may be classified according to size as micropores and macropores. Porosity of sandy soils largely consists of macropores, while porosity of clay soils is largely micropores. The ratio of micropores to macropores influences the movement of soil gases and water in the soil and is of particular importance for bioremediation, since the ratios and interactions of soil gas and water greatly influence microbial activity.

Permeability describes the conductive properties of a porous medium independently of the fluid flowing through it. It includes the influence of media properties that affect flow, including the grain size, distribution and roundness, and the nature of their arrangement. Permeability is widely used in situations where multiphase flow systems (vapor, water, and nonaqueous phase liquids) are present.

These conductive properties determine the feasibility of adding or removing materials such as water, air, and

nutrients to the soil. Soil hydraulic conductivities of about 1.0 X 10<sup>-4</sup> to 1.0 X 10<sup>-6</sup> cm/sec are favorable for adding or removing materials. Soils with conductivities above this range may require careful management to prevent excessive drainage or contaminant mobility for some remediation technologies: in soils with conductivities below this range it may be difficult to add or remove materials for remediation.

The hydraulic conductivity of saturated soils is a function of the grain size and sorting of the particulate materials, and therefore, is somewhat stable over time. Hydraulic conductivity in unsaturated soil is not only influenced by grain size and sorting but also is strongly influenced by water content of the soil. At low soil water content, soil water moves largely in response to adhesive and cohesive forces in the soil, which are measured as matric potential. Soluble contaminants in unsaturated soil move in the thin films of water surrounding the soil particles. The thicker the film of water (e.g., the wetter the soil), the larger the conduit for contaminant movement, and more of the contaminant that can move in a given period of time.

Movement of contaminants in the vadose zone is usually in the soil gas, pore water or as nonaqueous phase liquids (NAPLs). Soil gases may move into the atmosphere, ground water, soil pore water, be adsorbed on soil particles or undergo chemical/biological transformation. Dissolved contaminants in soil water undergo similar changes. NAPLs move in response to gravity and changes in soil permeability.

### **Soil Moisture and Water Holding Capacity**

Soil moisture holding capacity is determined by the proportion of clay and organic matter in the soil. Clays and organic matter tend to hold larger amounts of water relative to their volume than do the coarser grained silts and sands. When a soil is saturated with water, then allowed to drain freely for 24 hours, the soil is said to be at field capacity. Essentially this means that the soil micropores are filled with water, and the macropores are filled with air.

The ratio of air and water in the soil strongly influences many important processes in the soil. Aerobic microbial activity is usually optimum when soil moisture is about 70% - 80% of field capacity; the higher end of the range is more desirable for coarser soils. Relatively dry soils tend to adsorb many contaminants more strongly than wetter soils, since water competes with the contaminants for adsorption sites. When the soil is not saturated, water and water-soluble compounds may move in any direction in the soil in response to matric potential, whereas water in saturated soils moves largely in response to gravity. Water and water-soluble compounds move faster through wetter soils than drier soils. Very dry soils, especially soils with high organic matter content, may be very difficult to wet since dry organic matter tends to be hydrophobic. NAPLs may move through moderately wet soils faster than either dry or very wet soils, since dry soils tend to adsorb much of the NAPL and the pores full of water in wet soils inhibit NAPL movement.

### Tilth

Tilth refers to ability of the soil to undergo manipulation (plowing, tilling) and retain a desirable loose, friable structure that promotes ready movement of water and air. Structure refers to the tendency of soil to agglomerate into units called peds, granules or aggregates. In surface soils, this agglomeration is influenced by the microbial secretion of polymeric materials that cement soil materials together into small particles. High levels of sodium in the soil (measured as exchangeable sodium percentage (ESP) or sodium absorption ratio (SAR)) may disperse the soil particles causing a loss of structure. Sodium absorption ratios higher than 15 may indicate a problem, as do ESP values greater than 10% of the cation exchange capacity (CEC) in fine textured soils and greater than 20% of the CEC in coarse textured soils.

### **Sorptive and Exchange Capacity**

Clay materials in soils generally have a high adsorptive capacity for many organic and inorganic materials. Coarse, sandy soils may allow rapid movement of relatively small amounts of contaminants into lower soil layers and aquifers. while soils high in clay may significantly retard movement of many contaminants. Inorganics and some organics may be influenced by the CEC, which denotes the capacity of the clay particle for adsorption of positively charged materials on the negatively charged surfaces of the clay. Mobility of metals in the soil may be greatly affected by the CEC. Clays may have an anion exchange capacity due to the positive charge on the edges of some clay particles. The anion exchange capacity is usually less than the cation exchange capacity. Clays also will adsorb uncharged molecules due to Van der Waals interactions of the uncharged materials with clay particles.

### **Organic Matter**

Soil organic matter is generally composed of 25% - 35% polysaccharides and protein-like compounds which are readily decomposed by microorganisms and therefore have a short halflife in soils. About 65% - 75% of the soil organic matter is composed of humic materials, which are complex mixtures of high molecular weight organics and are resistant to degradation. These percentages do not include those organic compounds that may be present as contaminants; i.e., oil and grease, volatile organics, etc. Soils high in organic matter will adsorb significant quantities of organic contaminants, since organic compounds have a strong tendency to adsorb onto soil organic matter, thereby slowing movement. Soil organic matter usually has a relatively high CEC and may have a significant anion exchange capacity, although anion exchange capacity is usually much less than the CEC. Increased soil organic levels are generally favorable to microbial activity, due to increased CEC, tilth, water holding capacity, and available carbon. Soil organic matter levels tend to be lower in warm, moist climates, since these conditions allow rapid microbial oxidation of the organic matter. Soil organic matter may be increased by addition of straw, hay, sawdust or wood chips, manures, and many other organic materials. Addition of easily transformed organic materials may cause shortages of nutrients (particularly nitrogen and phosphorus) due to the increased microbial population feeding on the added organic matter.

#### pН

The pH of the soil affects microbial activity, availability of nutrients, plant growth, immobilization of metals, rates of abiotic transformation of organic waste constituents, and soil structure. A pH range of 6-8 is considered optimum for bioremediation in most cases. Most metals tend to be less mobile in high pH soils (arsenic is an exception), but acidic organics such as pentachlorophenol are more mobile. Soils with high sodium levels and high pH (most often found in dry climates) tend to deflocculate and crust, limiting oxygen diffusion and water uptake. Soil pH may be lowered by addition of ferrous or aluminum sulfate, elemental sulfur or sulfuric acid; soil pH may be raised by addition of agricultural lime.

### **Nutrients**

Nutrient content relates to the concentration of nutrients available for use by microorganisms. Nitrogen and phosphorus often limit microbial activity in soils. An organic carbon:nitrogen:phosphorus ratio of 100-300:10:1 is recommended to stimulate microbial activity, with the lower C:N ratios recommended when most of the carbon is in a readily degradable form. The percent base saturation, a general indicator of soil fertility, is defined as the total of the four principal exchangeable bases (calcium, magnesium, sodium, potassium) divided by the total exchange capacity of the soil. A base saturation of about 80% is desirable, with calcium comprising about 60% - 70% of the CEC and potassium about 5% - 10% of the CEC.

Most soils have low levels of nitrogen, although soils with high levels of organic matter may have significant amounts of nitrogen as part of the organic matter; this nitrogen is usually released slowly as the organic matter decomposes. Inorganic nitrogen in the soil is usually quite water soluble and therefore readily lost to leaching, which may cause ground water pollution problems. Since microorganisms benefit from a steady supply of nitrogen, it is advantageous to supply nitrogen either in small amounts frequently or in a form (e.g., as organic fertilizers or "slow-release" inorganic fertilizers) that supplies nitrogen to the microorganisms slowly.

Many soils contain significant quantities of phosphorus, but the phosphorus may be strongly bound in the soil, and little may be readily available to the microorganisms. Usually bound phosphorus is in equilibrium with phosphorus dissolved in the soil water; the equilibrium is heavily weighted toward the bound form. For this reason, phosphorous fertilizers are often applied to raise the amount of phosphorus in the soil water.

### **Salinity**

The electrical conductivity (EC) of a soil reflects the soluble salt content (salinity). An EC of 2 or less indicates that salinity is not a problem in most instances. An EC of 2-4 may inhibit activity of very salt-sensitive microorganisms, while an EC of 4-8 may restrict activity of many microorganisms. An EC greater than 8 will restrict activity of most microorganisms.

### **Redox Potential**

The redox potential of the soil (oxidation-reduction potential, reported as Eh) is controlled by the concentration of O<sub>2</sub> in the gas and liquid phases. The O<sub>2</sub> concentration is a function of the rate of gas exchange with the atmosphere and the rate of respiration in the soil. Respiration in the soil may deplete O<sub>2</sub>, lowering the redox potential and creating anaerobic (reducing) conditions. These conditions are unfavorable to aerobic biotransformation, but may promote anaerobic processes such as reductive dehalogenation. Many reduced forms of polyvalent metal cations are more soluble (and mobile) than their oxidized forms. Well aerated soils have an Eh of about 0.8 to 0.4 volts; moderately reduced soils are about 0.4 to 0.1 V; reduced soils are about 0.1 to -0.1 V; and highly reduced soils are about -0.1 to -0.3 V. Redox potentials are difficult to measure and are not widely used in the field.

#### Color

The color of soils is largely due to chemical changes and organic matter content. Dark colors in soil are caused by highly decayed organic matter. Reds and yellows are caused by oxidized and hydrated iron in soil minerals. Uniform reds, yellows, and browns indicate that a soil is well drained. Mottled grays or blues may indicate poor drainage. The location of any mottled layers may indicate the level of the seasonal high water table.

### **Biological Activity**

Biological activity in the soil is affected by all of the soil characteristics discussed in this Appendix. Biological activity apparently accounts for most of the transformation of organic contaminants in soil.

Both bacteria and fungi have been shown to be important in bioremediation processes. Most research in bioremediation has centered on bacteria, but some investigators have found that fungi can play an important role in bioremediation processes, especially with halogenated compounds (e.g.,

pentachlorophenol). In most cases bioremediation relies on communities of microorganism species, rather than one or a few species. Bioremediation consists of utilizing techniques for enhancing development of large populations of microorganisms that can transform pollutants of interest, and bringing these microorganisms into intimate contact with the pollutants. In order to do this efficiently, necessary conditions for the growth and activity of the microorganisms must be maintained.

Microbial activity in the soil can be estimated by using plate counts, most probable number (MPN) counts, direct microscopic counts, respiration measurements, ATP activity measurements, and others. Unfortunately, the relationship of these measurements to practical use of bioremediation techniques is unclear, at best. Generally use of these measurements is limited to determining if soil conditions or waste characteristics are suitable for microbial activity, and whether particular management techniques have enhanced microbial activity.

By culturing soil microorganisms on special media, counts of "specific degraders" can be determined. For instance, if PAHs are added to a media with no other carbon sources present, any microorganisms that grow can be assumed to have the capability of using PAHs as a sole source of carbon. Again, the relationship of these counts to actual biodegradation in the field is unclear.

If biodegradable contaminants have been present in the soil for more than a few months or years, and microorganisms are able to grow and reproduce in the contaminated soil, microorganisms that can transform the wastes are likely to be present. Treatability studies can be used to determine techniques that might be appropriate to optimize their transforming activity, as well as determine if the microorganisms are capable of transforming the wastes to acceptable levels of acceptable end products in an acceptable time frame.

Bioaugmentation commonly takes two forms." Microorganisms may be isolated from the site in question, cultured in quantity and added to the site soil, or microorganisms isolated from other sites may be cultured and added to the site soil. It is very difficult to show that added microorganisms survive and grow in the soil, and even more difficult to show that the added microorganisms have any significant affect on transformation.

### **Metals in Soils**

The mean concentrations of metals commonly found in uncontaminated soils are shown in Table A-2. The actual "background" concentrations at a given site may vary widely from these numbers. High concentrations of certain metals (particularly the "heavy" metals lead, mercury, cadmium, chromium and others) are known to inhibit microorganism activity in laboratory studies, but the particular levels of metals that would be of significance in field bioremediation are not known with certainty. The influence of metals

concentration on bioremediation appears to be site, contaminant, and microorganism dependent. In cases where high concentrations of metals appear to be of concern, treatability studies should be conducted to determine the influence of metals concentrations on bioremediation.

TABLE A-2. MEAN CONCENTRATION (MG/KG) OF METALS IN THE EARTH'S CRUST AND SOILS a

	AI	Fe	Mn	Be	Cu	Cr	Cd	Zn	As	Se	Ва	Ni	Ag	Pb	Hg
Soils	72000	26000	550	0.92	25	54	0.35	60	7.2	0.39	580	19	0.05	19	0.09
Crust	82000	41000	350	2.6	50	100	0.11	75	1.5	0.05	500	80	0.07	14	0.05

<sup>&</sup>lt;sup>a</sup> McLean and Bledsoe, 1992

### APPENDIX B

### **MONITORING**

The land treatment unit should be monitored to determine the fate of the contaminants in the unit. Generally, success in land treatment has been determined by measuring the disappearance of the waste components. Since waste components may "disappear" from analytical view without actually being remediated, a mass balance approach should be taken, monitoring each soil phase (soil solids, gas, water and nonaqueous phase liquid) to determine how much of each waste component is in each phase. By this method, it can be determined whether remediation is actually taking place or whether the waste components are merely being moved to different phases. In addition, the toxicity of the various phases may be monitored to ensure that the transformation of waste components does not produce more toxic components, thereby creating a worse problem.

### **Waste Transformation**

### **Parent Compound Loss**

In most cases contaminant monitoring at soil bioremediation sites is confined to analysis for parent compound loss. This loss may be due to degradation, fixation, or any other process that transforms the parent compound or removes it

from the detection ability of the extraction and analytical method. The power of the extracting solution to remove the contaminant from the soil matrix is of considerable importance, since alternating temperature or moisture cycles can cause waste components to bind so strongly to the soil that removal is difficult. Parent compound loss is usually followed even if other monitoring schemes are also used.

#### **Breakdown Products**

At some sites analysis for breakdown products may be conducted, especially if such products are known to have significant toxicity. Often, the specific breakdown products are not known; it can be costly to determine the identity of these products. Usually, breakdown products must be identified using radiolabeled compounds and gas chromatography/mass spectrometry (GC/MS) analysis.

#### **Toxicity Reduction**

Measures of toxicity may be required to determine if toxicity of contaminants is actually reduced or if toxic contaminants are merely transformed to other toxic materials. One assay commonly used is the Microtox microbial bioassay. Cultures of phosphorescent (light-emitting) marine bacteria are exposed to soil extracts, and the decline in light output over time is measured. The Microtox assay measures general metabolic inhibition. The major advantages of the assay are that it is quick, easy, repeatable, inexpensive, and there is a large amount of published literature about its uses and results. Its major disadvantage (as for most acute bioassays) is that results of the assay have no direct relationship to toxicity of the contaminants of concern to humans.

The Ames test, a measure of the mutagenic potential of a sample, has been used widely in research, though somewhat less in field applications. There is a high correlation between mutagenicity (as measured in the Ames test) and carcinogenicity. The Ames test takes several days to complete and is more expensive than the Microtox assay.

Bioassays using many other species have been used for assessing toxicity of environmental samples. Most of these tests are time consuming and expensive.

### Microorganisms

Microbial activity in the soil can be estimated with several methods, including plate counts, most probable number (MPN) counts, direct microscopic counts, respiration measurements, ATP activity measurements, and others. Unfortunately, the relationship of these measurements to practical use of bioremediation techniques is not clear. Generally, use of these measurements is limited to determining if soil conditions or waste characteristics are suitable for microbial activity, and whether particular management techniques have enhanced microbial activity.

Oxygen and carbon dioxide levels can be useful as a general index of microbial activity. Monitoring oxygen or carbon dioxide alone can be deceiving since many soil components can take up or release oxygen or carbon dioxide by abiotic processes. Monitoring both yields a more reliable indication of microbial respiration. Soil gas concentrations of  $\mathrm{CO}_2$  and  $\mathrm{O}_2$  often fluctuate daily due to microbial activity; therefore, it is desirable to measure  $\mathrm{CO}_2$  and  $\mathrm{O}_2$  at the same time of day for each sampling event. Since the respiration estimated may not result only from transformation of the compounds of interest, respiration cannot be used as a direct measure of transformation of these compounds.

Soil microorganisms can be cultured on specific media to determine counts of "specific degraders." If PAHs are added to a media with no other carbon sources present, any microorganisms that grow in the media can be assumed to have the capability of using PAHs as a sole source of carbon. Again, the relationship of these counts to actual biodegradation in the field is unclear.

#### **Soil Moisture**

Monitoring methods for soil moisture range from "eyeballing" the soil, to the use of neutron probes. Since soil moisture appears to be one of the most important determinants of microbial activity, accurate and reproducible methods of determining soil moisture are of considerable interest. Gravimetric methods are very accurate, but somewhat time consuming, and rarely used in the field. Gypsum block monitors are often used in research, but are not suited to LTUs since the blocks require individual calibration, are permanently installed and would be disturbed by tilling.

Neutron probes are accurate but expensive. The moisture probes sold in garden supply stores, while inexpensive, are usually very inaccurate. The moisture monitoring devices most likely to be useful are those based on the porous cup tensiometer or soil capacitance. The capacitance based types are somewhat new, but the porous cup tensiometer types have been widely used in agriculture, are relatively simple in concept and use, and are inexpensive.

### **Nutrients**

Soil nutrients are usually determined by a number of standard tests used in agricultural laboratories. Many land grant universities have laboratories that analyze soil samples for farmers, and there are also commercial laboratories available. In most cases for LTUs, nutrient levels are based on the ratio of soil carbon to other nutrients. Generally, carbon to nitrogen to phosphorus (C:N:P) ratios of 100-300:10:1 in the soil have been used, although some investigators have found that C:N ratios of 100-120:10 may be more appropriate where most of the carbon is in a readily degradable form. Little research has been conducted on the specific concentrations of nutrients that would be optimal for LTUs; however, nutrient concentrations for optimal microbial activity may be similar to that for optimal growth of crop plants. There is a large variety of material available concerning nutrient levels versus growth and yield of crop plants.

### **SAMPLING STRATEGIES**

Sampling program goals must be delineated in order to decide how many samples are needed for a monitoring program. These goals may be formulated as a statement that "It is necessary to know the average concentration of this constituent in the LTU soil to +/- 5 ppm." If the variability of the concentration of this contaminant in the soil is known (or can be estimated), then statistical formulas can be used to calculate the number of samples likely to be necessary to estimate the concentration of that compound to the required precision. Other goals may also be of interest. For example, it might be necessary to know the highest concentration likely to be found, rather than the average. It also might be desirable to know that the concentration of a given contaminant does not exceed some given level. The accuracy needed for monitoring to determine operation and maintenance practices is usually somewhat less than the accuracy needed for regulatory monitoring to decide if target final levels have been achieved. In general, the LTU monitoring program design is based on the identified data needs:

What are the desired confidence limits for the data? (Is
it sufficient to know the concentration of the contaminant
is some value +/- 10 ppm, or must the concentration be
known to +/- 5 ppm?)

Is knowledge of the average concentration sufficient, or must it be known if the concentration is less than some value? (Is it sufficient to know that the average concentration over the LTU is less than some given value, or is there a need to be confident that there is no location in the LTU where the maximum value exceeds some given value?)

For monitoring purposes LTUs larger than about one acre should be divided into sections approximately equal in size. In most cases, sections should be no larger than one acre. If it is known that certain locations in the LTU have characteristic high or low concentrations ("hot spots" or "cold spots"), these locations should be segregated into separate sections when deciding on the size and coverage of the sampling sections. This procedure, sometimes known as "stratified random sampling," yields smaller confidence limits for the concentrations in the sections. Random locations for sampling should be determined in each section for each sampling event.

Locations for collecting samples may be determined by laying out a grid on the section and either choosing sample locations from the grid points randomly or in some regular pattern. If variability within the section is low or unknown, a regular sampling pattern is probably the best choice. In this case, the first sampling location would be chosen randomly. All of the following sampling locations would be chosen according to a pattern starting from the first randomly chosen location. If variability within the section is known to be high, and the approximate locations of high and low spots are known, the section can be subdivided into similar areas and each area sampled randomly. There are a number of methods for choosing sample locations under different scenarios of contaminant distribution: the references in the Bibliography section of this document cover the more commonly used methods.

Concentrations of contaminants in most LTUs are so variable that many more samples must be taken to achieve reasonable confidence limits for deciding if regulatory limits have been achieved. Obviously, the more samples one analyzes from a given section, the more one knows about the range of concentrations of the compounds of interest in that section. However, since analytical costs are usually a major portion of project costs, the number of samples one can afford to analyze is limited. Formulas are available to determine how many samples are necessary to give any required degree of precision in estimating the mean concentration or variability of concentration in the plot. Since the statistical basis for calculating the number of samples to be taken is moderately complex and beyond the scope of this brief review, references are provided in the Bibliography.

Compositing of samples eliminates high and low values, tending to compress all data toward the mean value for the LTU soil. Compositing decreases apparent variability of the data by a factor of the square root of (N-1), where N is equal to the number of subsamples composited to form the sample for analysis. If the data are used to determine compliance with maximum contaminant levels, data from composited

samples may indicate compliance has been achieved when such may not be the case for significant portions of the LTU. It is commonly supposed that compositing of samples, by reducing the apparent variability of the data, allows more accurate statistical analysis. However, data from sample analyses are used to estimate concentrations and variability of contaminants in the LTU; no manipulation of samples or data can actually change the concentrations and variability of the soil contaminants in the LTU. Since sample compositing eliminates high and low values from the data, data from composited samples should be used only to estimate the mean concentrations of LTU contaminants and not the range or variability of contaminant concentrations in the LTU. If it is desirable to know the range and variability of contaminant concentrations in the LTU, discrete soil samples should be taken and analyzed.

The amount of sample to be taken (the sample support) is largely determined by the requirements of the analytical procedure and any sample archiving required. The larger the sample, the more likely it is to be representative of the mean values in the whole section. Usually only a few grams are needed for analysis, so an aliquot must be taken for analysis from samples larger than this amount. This usually involves a mixing procedure in the field or lab, which may result in the loss of volatile contaminants. Sometimes subsamples are taken from a number of locations within the section and composited to make one or more samples for analysis. The object is to increase the sample support, making the sample more representative of the section while minimizing analytical costs. The caveats on compositing mentioned above also apply here.

The sampling schedule should be based on timing of lift applications. A lift should be sampled immediately before application of a new lift. The latest lift applied should be sampled immediately after application and tilling. Sampling should be continued on the latest lift at specified intervals after application until target levels of contaminants are reached and sustained; then another lift can be applied.

### **Measuring Transformation Rates**

Contaminant transformation rates may be determined to estimate the time required for treating a number of lifts of contaminated soil. At least five time-sequence points are needed to calculate transformation rates for compounds that degrade in a nonlinear fashion. This category includes most compounds of regulatory interest. Sampling time points should be evenly distributed throughout the time frame for which rate estimates are desired, although it may be desirable to have more replicate points for the beginning and ending time points if starting and ending concentrations are of particular interest. If the number of samples that can be taken or analyzed is limited, and the time endpoint of the experiment is not known at the beginning, time spacing between samples can be increased as the experiment proceeds. This is common in situations where it is desirable to reach a given final concentration of a waste component.

Rates should not be extrapolated beyond the time frame of the data from which the rates were calculated. For instance, in many treatability studies, data from laboratory experiments that last six months are used to calculate estimated results for months seven, eight, nine etc. Also, estimation of the time required for achieving certain contaminant concentrations is often extrapolated from experimental data taken from experiments that never reached the levels desired. Both procedures often result in estimates that are not verifiable in the field.

Runoff water from the LTU should be sampled after each major rainfall event if the runoff water is disposed. If the runoff water is recycled onto the LTU, it can be sampled as noted for recycled leachate.

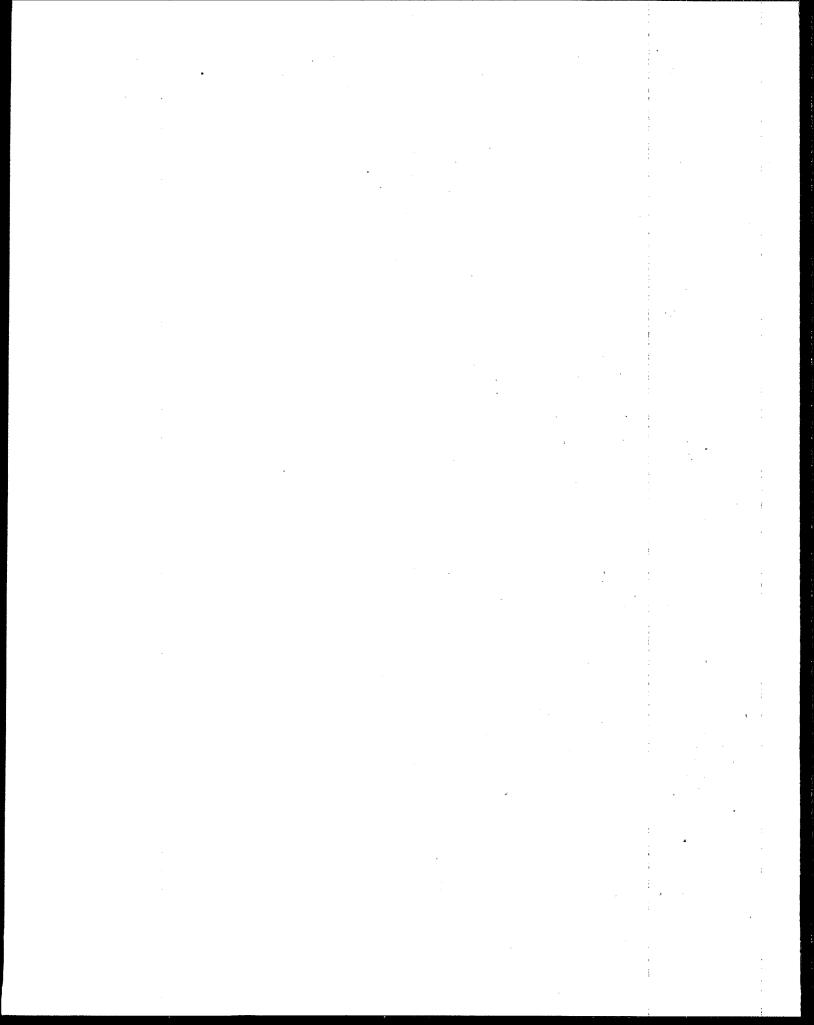
### Volatilization, Leachate and Runoff

When monitoring the transformation of waste compounds of interest in the LTU soil, it is important to try to achieve as complete a mass balance as possible. Routes of loss other than transformation must also be monitored. Leaching, volatilization and runoff are usually the most important alternate routes of loss to be considered in the LTU. Methods and equipment for monitoring these routes of loss are discussed below. The location and frequency of sampling for these routes of loss are subject to the same considerations as soil sampling as discussed above.

Volatilization is usually measured by collecting volatiles released from the soil surface. A canopy is placed over a defined area of contaminated soil and vapors collecting under the canopy are swept into an adsorbent for later extraction and analysis. In some cases the vapors may be measured directly with various kinds of detectors such as photoionization detectors (PID). Unless the canopy covers the entire LTU surface without interruption in time or space, the measurement must be considered as an approximation of the overall rate of vapor loss. Volatilization is often much greater immediately after application of a new lift of contaminated soil or after tilling.

Leaching from in-situ LTUs can be monitored with lysimeters. Porous cup and pan lysimeters are commonly used. Porous cup lysimeters have the advantage that they can be used to take samples of the soil pore water even when the soil is relatively dry. On the other hand, pan lysimeters collect only water that is actively moving down through the soil. Leachate monitoring for ex-situ LTUs is relatively straightforward since most ex-situ units have liners and leachate collection systems to collect leachate that may be generated. The collected leachate can be sampled periodically if it is treated separately or disposed. If the leachate is recycled as irrigation water for the LTU, it should be sampled at the end of the treatment cycle for each lift to establish the mass balance for that lift of contaminated soil.

In most cases, installation of monitoring wells downgradient of the LTU will be required in addition to lysimeters. Usually at least one monitoring well is placed upgradient of the LTU to determine if any contaminant detected in a downgradient well is coming from the LTU or another source of contamination.



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