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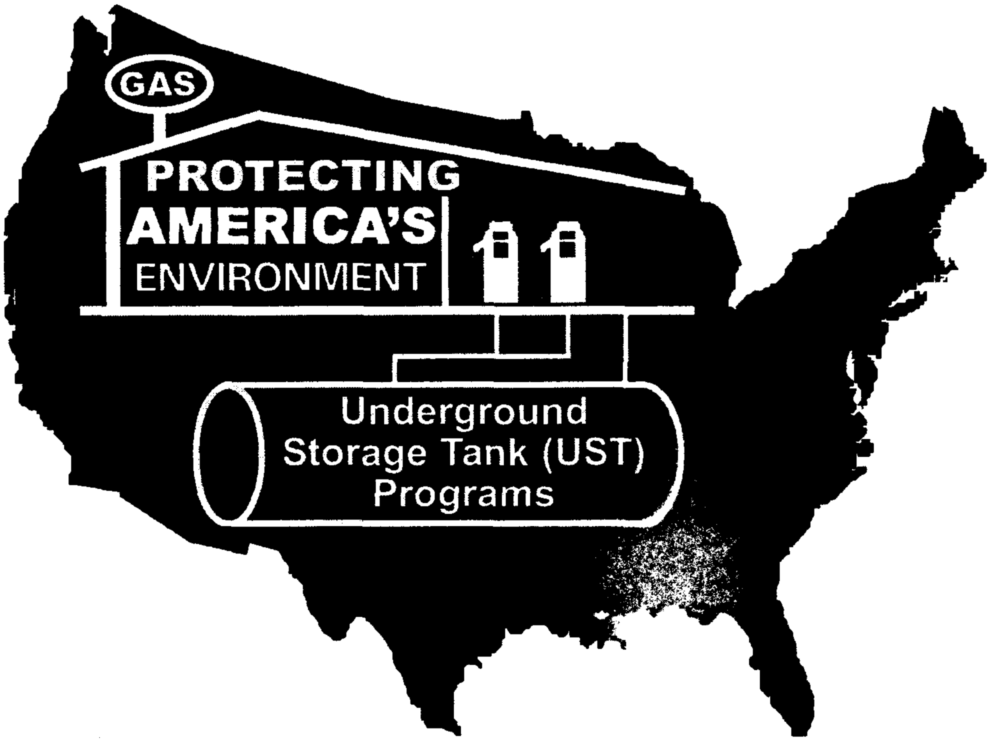
How To Evaluate Alternative Cleanup Technologies For Underground Storage Tank Sites

A Guide For Corrective Action Plan Reviewers



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How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites

A Guide for Corrective Action Plan Reviewers

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Introduction

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Background

As of September 30, 2003, more than 439,000 releases from leaking underground storage tanks (LUSTs) have been reported nationwide. Cleanups have been initiated at more than 403,000 of these sites, and more than 303,000 sites have been cleaned up. The backlog of sites still to be cleaned up is more than 136,000. In many cases, the workload for state regulators (who must oversee 50 to 400 cleanups at a time) is burdensome.

To compound the problem, cleanups are expensive. The costs of remediating sites with soil contamination vary between $10,000 and $125,000. Costs for remediating sites with groundwater contamination can range from $100,000 to over $1 million depending on the extent of contamination.

A primary factor in the high cost cleanups is the use of cleanup methods that are either inappropriately selected or not optimally designed and operated given the specific conditions of the site. Pump-and-treat, the most commonly used method for remediating groundwater, is often unsuccessful because either the source of contamination is not adequately addressed, or the systems are not optimized. Even when properly operated, pump-and-treat systems have inherent limitations[1]: they may not work well in complex geologic settings or heterogeneous aquifers; they often stop reducing contamination long before reaching intended cleanup levels; and in some situations they can make sites more difficult to remediate by smearing contamination across the subsurface. Landfilling, the most frequently used method for addressing contaminated soils, does not remediate soils; this method simply movess the problem from one location to another. In addition to being costly, transporting contaminated soil off-site increases the risk of harming human health and the environment.

With so many sites requiring remediation at such an enormous cost, the Environmental Protection Agency (EPA) actively promotes faster, more effective, and less costly alternatives to traditional cleanup methods. EPA's Office of Underground Storage Tanks (OUST) continues to work with

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[1] In spite of its limitations, there may be some situations where pump-and-treat is the most appropriate remediation alternative available (*e.g.*, to remediate a small, dissolved phase plume or to contain the plume in order to prevent migration into uncontaminated areas).

state and local governments to encourage the use of the most appropriate cleanup technology for each and every site. When this manual was first published in 1994, it covered the first eight technologies listed in the table of contents (Chapters II through IX). The manual was updated in 1995 to add two additional technologies (Chapters X and XI). Back then, these ten technologies were referred to as "alternative technologies" because although they had the ability to make cleanups faster, more effective, and less costly than traditional options, they were not widely used (although they certainly are today). The current update (May 2004) adds two new technologies (chemical oxidation-Chapter XI, and enhanced aerobic bioremediation-Chapter XII) to the suite of "alternative technologies".

Purpose Of This Manual

The purpose of this manual is to provide you—state and local regulators—with guidance that will help you review corrective action plans (CAPs) that propose alternative cleanup technologies. The manual does not advocate the use of one technology over another; rather it focuses on appropriate technology use, taking into consideration sitespecific conditions and the nature and extent of contamination. While the manual focuses on the remediation of leaking underground storage tank sites, some of its basic concepts can be applied at hazardous substance and hazardous waste sites as well. .

The manual is designed to enable you to answer two basic questions when reviewing a CAP:

- Has an appropriate cleanup technology been proposed?
- Does the CAP provide a technically sound approach to the cleanup?

Scope And Limitations

This manual is intended to provide technical guidance to state regulators who oversee cleanups and evaluate CAPs. The document does not represent the issuance of formal policy or in any way affect the interpretation of the regulations.

The text focuses on engineering-related considerations for evaluating each technology. It does not provide instruction on the design and construction of remedial systems and should not be used for designing

CAPs. Nor should it be used to provide guidance on regulatory issues such as securing permits and establishing cleanup standards, health and safety issues, state-specific requirements, or cleanup costs.

This document is not intended to be used as the sole reference for CAP review. Rather, it is intended to be used along with published references, guidance from others more experienced with alternative technologies, information from training courses, and current journals. The material presented is based on available technical data and information and the knowledge and experience of the authors and the peer reviewers.

How To Use This Manual

We encourage you to use this manual at your desk as you review CAPs. We have designed the manual so that you can tailor it to meet your state's or your own needs. The three-ring binder allows you to insert additional material and remove certain tools (*e.g.*, flow charts, checklists) for photocopying. Also, you can add your own notes in the margins provided.

The manual contains discussions of eight different alternative cleanup technologies. Tabs signal the beginning of each chapter (including the Introduction and Abbreviations And Definitions) so you can flip quickly to the appropriate section. We have included a table of contents in each chapter to help you locate the information you need.

Each technology chapter contains the following tools which can help expedite and/or improve the review process:

- An evaluation process flow chart, generally the third exhibit in each chapter, can help you understand the overall review process for each technology. This flow chart serves as a "road map" for the chapter and for the decisions you will make during the evaluation process.

- A checklist(s), located at the end of each chapter, can help you determine whether or not the CAP contains all of the necessary information. The checklist lists the most important factors to evaluate for the successful implementation of each technology.

- A list of current references, located near the end of each chapter, provides sources of additional information.

- Advantages and disadvantages of each technology, initial screening criteria, and other data specific to each technology.

How to Obtain Additional Copies of the Manual

A limited number of single copies are available directly from OUST. Contact OUST by telephone at 703-603-9900 and ask for "publications outreach". The entire document is also available in electronic format (PDF) from the "Publications" section of OUST's web site at *http://www.cpa.gov/oust/pubs/tums.htm.*

Chapter IX

Monitored Natural Attenuation

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Chapter IX
Monitored Natural Attenuation

Overview

The term "monitored natural attenuation" (MNA) refers to the reliance on natural attenuation processes (within the context of a carefully controlled and *monitored* site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods (EPA, 1999). Long-term performance monitoring is a fundamental component of a MNA remedy, hence the emphasis on "monitoring" in the term "monitored natural attenuation". Other terms associated with natural attenuation in the literature include "intrinsic remediation", "intrinsic bioremediation", "passive bioremediation", "natural recovery", and "natural assimilation". Note, however, that none of these are necessarily equivalent to MNA.

MNA is often dubbed "passive" remediation because natural attenuation processes occur without human intervention to a varying degree at all sites. It should be understood, however, that this does not imply that these processes necessarily will be effective at all sites in meeting remediation objectives within a reasonable time frame. This chapter describes the various chemical and environmental factors that influence the rate of natural attenuation processes. Because of complex interrelationships and the variability of cleanup standards from state-to-state and site-to-site, this chapter does not provide specific numerical thresholds to determine whether MNA will be effective.

The fact that some natural attenuation processes are occurring does not preclude the use of "active" remediation or the application of enhancers of biological activity (*e.g.*, electron acceptors, nutrients, and electron donors)[1]. In fact, MNA will typically be used in conjunction with, or as a follow-up to, active remediation measures, and typically only after source control measures have been implemented. For example, following source control measures[2], natural attenuation may be sufficiently effective to achieve remediation objectives without the aid of other (active) remedial measures, although this must be conclusively demonstrated by long-term performance monitoring. More typically, active remedial measures (*e.g.*, SVE, air-sparging) will be applied in areas with high concentrations of contaminants (*i.e.*, source areas) while MNA is employed

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[1] However, by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be "natural" attenuation.

[2] Note that MNA may be an appropriate remediation option only after separate phase product has been removed to the maximum extent practicable from the subsurface as required under 40 CFR 280.64.

for the dilute contaminant plume. In any case, MNA should be used very cautiously as the sole remedy at any given site since there is no immediate backup (although there should be contingency plans in place) should MNA fail to meet remediation objectives.

EPA does not consider MNA to be a "presumptive" or "default" remedy - it is merely one option that should be evaluated with other applicable remedies (EPA, 1999). EPA does not view MNA to be a "no action" or "walk away" approach, but rather considers it to be an alternative means of achieving remediation objectives that may be appropriate for specific, well-documented site circumstances where its use meets the applicable statutory and regulatory requirements (EPA, 1999). As there is often a variety of methods available for achieving remediation objectives at any given site, MNA may be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy. As with any other remedial alternative, MNA should be selected only where it meets all relevant remedy selection criteria, and where it will meet site remediation objectives within a time frame that is reasonable compared to that offered by other methods (EPA, 1999). Exhibit IX-1 provides a summary of the advantages and disadvantages of using monitored natural attenuation as a remedial option for petroleum-contaminated soils and groundwater.

Natural Attenuation Processes

Natural attenuation processes include a variety of physical, chemical, and biological processes that, under favorable conditions, reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in soil and/or groundwater. Processes that result only in reducing the concentration of a contaminant are termed "nondestructive" and include hydrodynamic dispersion, sorption and volatilization. Other processes, such as biodegradation and abiotic degradation (*e.g.*, hydrolysis), result in an actual reduction in the mass of contaminants and are termed "destructive" (Weidemeier, *et. al.*, 1999). For petroleum hydrocarbons, biodegradation is the most important (and preferred) attenuation mechanism since it is the only natural process that results in actual reduction in the mass of petroleum hydrocarbon contamination. Aerobic biodegradation consumes available oxygen resulting in anaerobic conditions in the core of the plume and a zone of oxygen depletion along the outer margins. As illustrated by Exhibit IX-2, the anaerobic zone is typically more extensive than the aerobic zone due to the rapid depletion of oxygen, the low rate of oxygen replacement, and the abundance of anaerobic electron acceptors[3] relative to dissolved oxygen (Weidemeier, *et. al.*, 1999). For this reason, anaerobic biodegradation is typically the dominant process . For both aerobic and anaerobic

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[3] Anaerobic electron acceptors include nitrate, sulfate, ferric iron, manganese, and carbon dioxide. For aerobic respiration the electron acceptor is oxygen.

processes, the rate of contaminant degradation is limited by the rate of supply of the electron acceptor not the rate of utilization of the electron acceptor by the microorganisms. As long as there is a sufficient supply of the electron acceptor, the rate of metabolism does not make any practical difference in the length of time required to achieve remediation objectives.

Corrective Action Plan (CAP)

The key components of a corrective action plan (CAP) that proposes MNA as a remediation alternative are:

- documentation of adequate source control,
- comprehensive site characterization (as reflected in a detailed conceptual site model),
- evaluation of time frame for meeting remediation objectives,
- long-term performance monitoring, and
- a contingency plan(s).

This chapter is intended to be an aide in evaluating a CAP that proposes MNA as a remedial option for petroleum-contaminated soil and groundwater. Note that a state may have specific requirements that are not addressed in this chapter. The evaluation process is presented in the four steps described below. A series of checklists have also been provided at the end of this chapter. They can be used as tools to evaluate the completeness of the CAP and to help focus attention on areas where additional information may be needed.

- **Step 1:** ***An initial screening of monitored natural attenuation applicability.*** This initial step is comprised of several relatively easily answered questions which should allow for a quick decision on whether or not MNA is even potentially applicable.

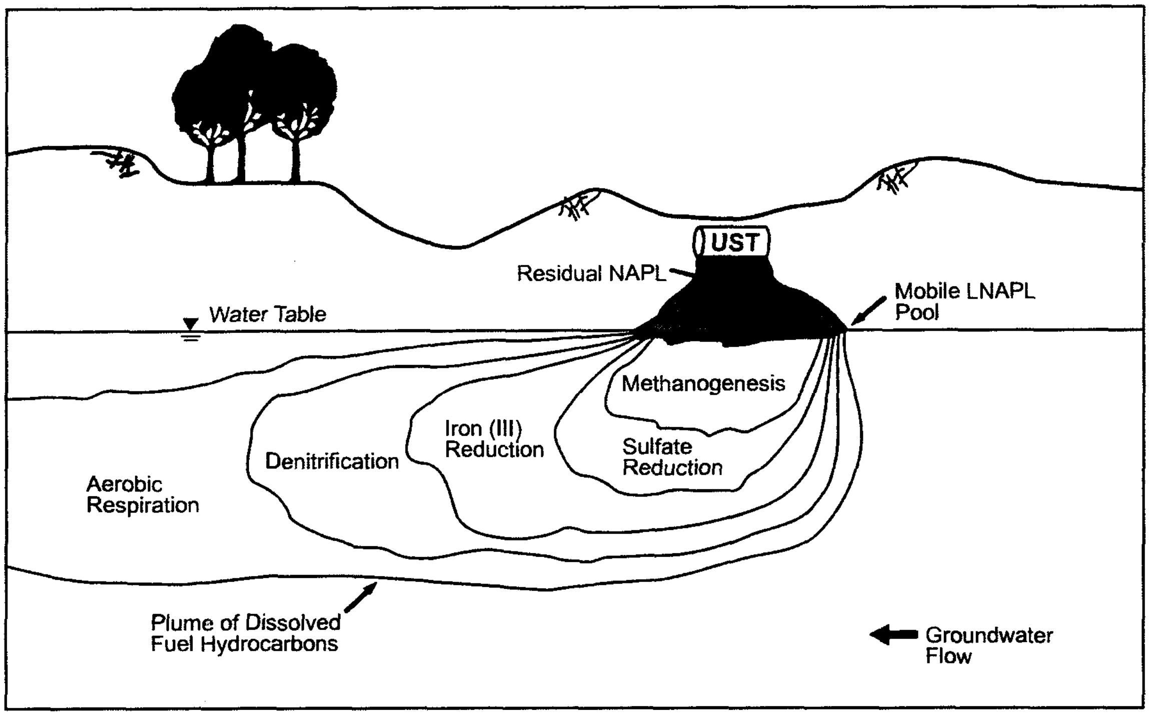
- **Step 2:** ***A detailed evaluation of monitored natural attenuation effectiveness.*** This step provides further criteria to confirm whether monitored natural attenuation is likely to be effective. To complete this evaluation, you will need to review monitoring data, chemical and physical parameters of the petroleum constituents, and site conditions. You will then need to determine whether site and constituent characteristics are such that monitored natural attenuation will likely result in adequate reductions of contaminant concentrations.

- **Step 3:** ***An evaluation of monitoring plan.*** Once it has been determined that MNA has the potential to be effective, the adequacy of the proposed long-term performance monitoring schedule must be evaluated.

Exhibit IX-1
Advantages And Disadvantages Of Monitored Natural Attenuation

Advantages	Disadvantages
■ Overall costs may be lower.	■ Much less effective where TPH concentrations in soil are high (> 20,000 to 25,000 mg/kg). Not suitable in the presence of free product.
■ Minimal disturbance to the site operations.	
■ Potential use below buildings and other areas that cannot be excavated.	■ Not suitable when contamination has impacted a receptor (*e.g.*, impacted ground water supply well, vapors in a building).
■ Does not generate remediation wastes. However, be aware of risks from methane produced during natural biodegradation of petroleum hydrocarbons.	■ Despite predictions that the contaminants are stationary, some migration of contaminants may occur. Not suitable if receptors might be affected.
■ Reduced potential for cross-media transfer of contaminants commonly associated with *ex-situ* treatment.	■ Longer periods of time may be required to mitigate contamination (especially true for heavier petroleum products).
■ Reduced risk of human exposure to contaminants near the source area.	■ May fail to achieve the desired cleanup levels within a reasonable length of time (and an engineered remedy should instead be selected).
■ Natural biodegradation may result in the complete destruction of contaminants *in-situ.*	■ Site characterization will necessarily be more detailed, and may include additional parameters. Site characterization will be more costly.
■ May be used in conjunction with, or as follow-up to, active remedial measures.	■ Institutional controls may be necessary to ensure long term protectiveness.
	■ Performance monitoring will generally require more monitoring locations. Monitoring will extend over a longer period of time.
	■ It may be necessary to implement contingency measures. If so, this may increase overall cost of remediation.
	■ May be accompanied by changes in groundwater geochemistry that can mobilize other contaminants.

Exhibit IX-2
Conceptualization of Electron Acceptor Zones In the Subsurface



(Adapted from Wiedemeier *et al.*, 1999. NOTE: Due to the presence of the mobile NAPL pool–"free product"–the site depicted in Exhibit IX-2 above would not be an appropriate candidate for MNA. After the free product has been removed from the subsurface to the maximum extent practicable, then the site may be evaluated as to whether or not it would be an appropriate candiate for MNA.)

- **Step 4:** ***An evaluation of the contingency plan.*** In the event that monitoring indicates that MNA does not appear to be effective in meeting remediation objectives in a reasonable time frame, a more aggressive remediation technology will need to be implemented. Several potential alternative technologies are presented in other chapters in this manual, and the applicable chapter should be consulted to evaluate the appropriateness of the contingency remedy.

Initial Screening Of Monitored Natural Attenuation Applicability

The policies and regulations of your state determine whether MNA will be allowed as a treatment option. As the first step in the screening process, determine if your state allows the use of MNA as a remedial option. For example, MNA may not be allowed if the contaminant mass is large enough that groundwater impacts are likely (or have already occurred), or if sampling indicates the presence of free product, or an existing contaminant plume isn't shrinking, or if there are potential receptors located nearby. Also be aware that it is possible that while allowing MNA as a remedial option, your state may have requirements that are more stringent than those described in this chapter.

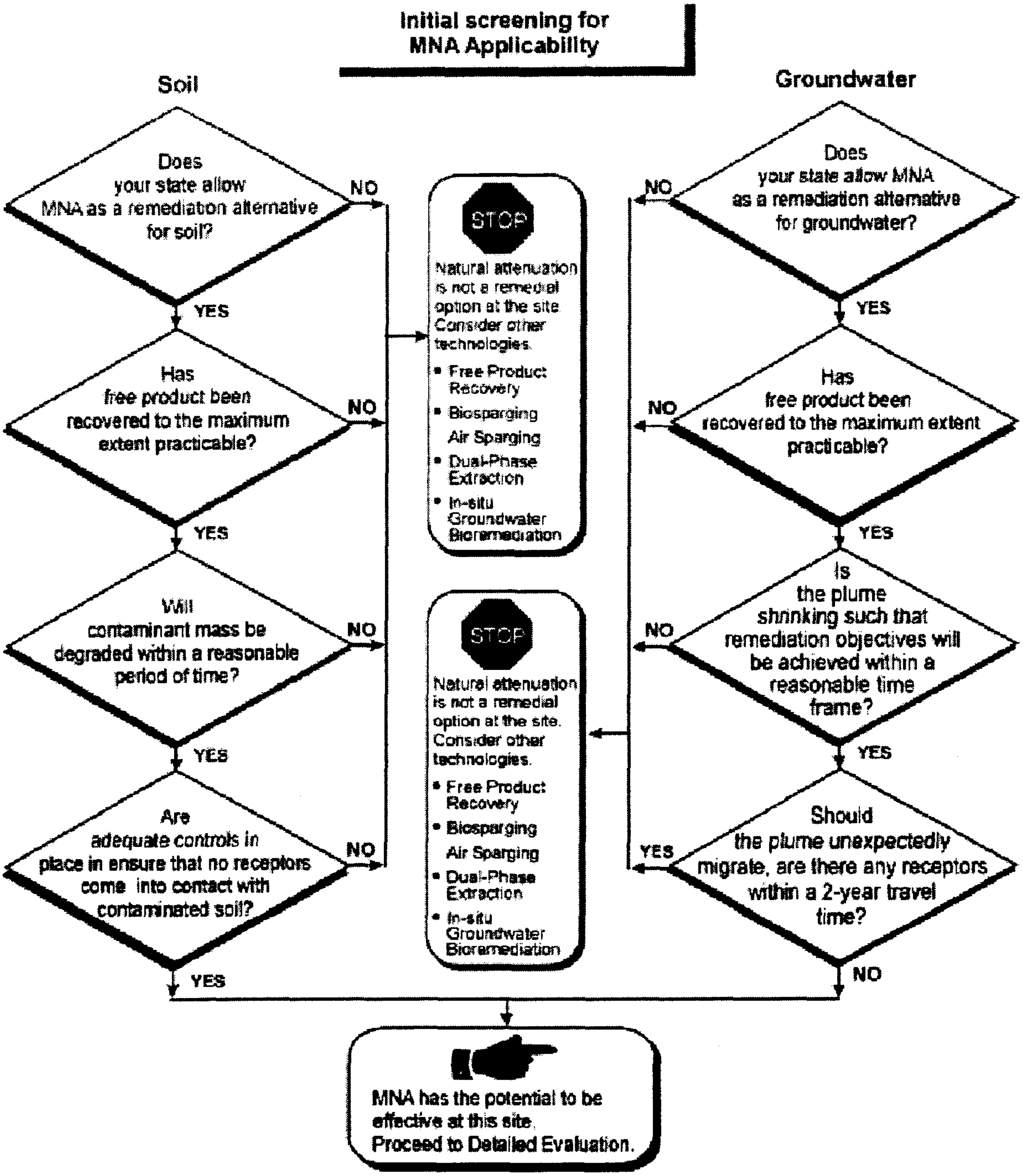
Although the specific screening criteria for both contaminated soil and groundwater might be expected to be very different due to the characteristics of the impacted media, they are actually quite similar. For both media the criteria focus on two elements: (1) source longevity and (2) potential receptor impacts. Source longevity influences not only the time to achieve remediation objectives but also the potential for groundwater contamination and plume migration. Receptors may be impacted through direct contact with source materials (such as residual soil contamination or free product), or through ingestion of dissolved-phase contaminants or inhalation of vapor-phase contaminants. The objective of the initial screening is to determine how long the source is likely to persist, and whether or not there are likely to be impacts to receptors during this time. The following section will provide guidance on how these criteria should be evaluated for either contaminated soil or contaminated groundwater. Exhibit IX-3 is a flow chart that can serve as a roadmap for the initial screening evaluation process. If results of the initial screening indicate that MNA is not likely to be effective, then other more aggressive measures (for example excavation of contaminated soil, or pump-and-treat for groundwater) should be employed.

Contaminant Transport and Fate

The most commonly encountered petroleum products from UST releases are gasoline, diesel fuel, kerosene, heating oils, and lubricating oils. Each of these petroleum products is a complex mixture often containing hundreds of compounds. Transport and fate characteristics of individual contaminants are a function of their chemical and physical properties.

Each fuel constituent will migrate via multiple pathways depending on its chemical and physical characteristics. Consequently, different chemicals will have different migration pathways. For example, a portion of the benzene in the fuel will partition out of the pure ("free product") phase and into the vapor phase, the sorbed phase, and the dissolved phase. Although the majority of the benzene mass will stay in the free product phase, a significant portion will either volatilize or dissolve into either soil moisture in the vadose zone or groundwater in the saturated zone.

Exhibit IX-3
Initial Screening of Monitored Natural Attenuation Applicability



Only a relatively small percentage will sorb onto soil particles. If the soil contains a higher percentage of organic carbon, a higher percentage of benzene will potentially be sorbed. In contrast to benzene's behavior, ethylbenzene will more likely sorb onto soil particles and would not be as soluble in water. Exhibit IX-4 is a schematic illustration of the interrelationships among the attenuation processes that govern the partitioning of free product into the soil, water and air in the subsurface environment.

Contaminated Soil

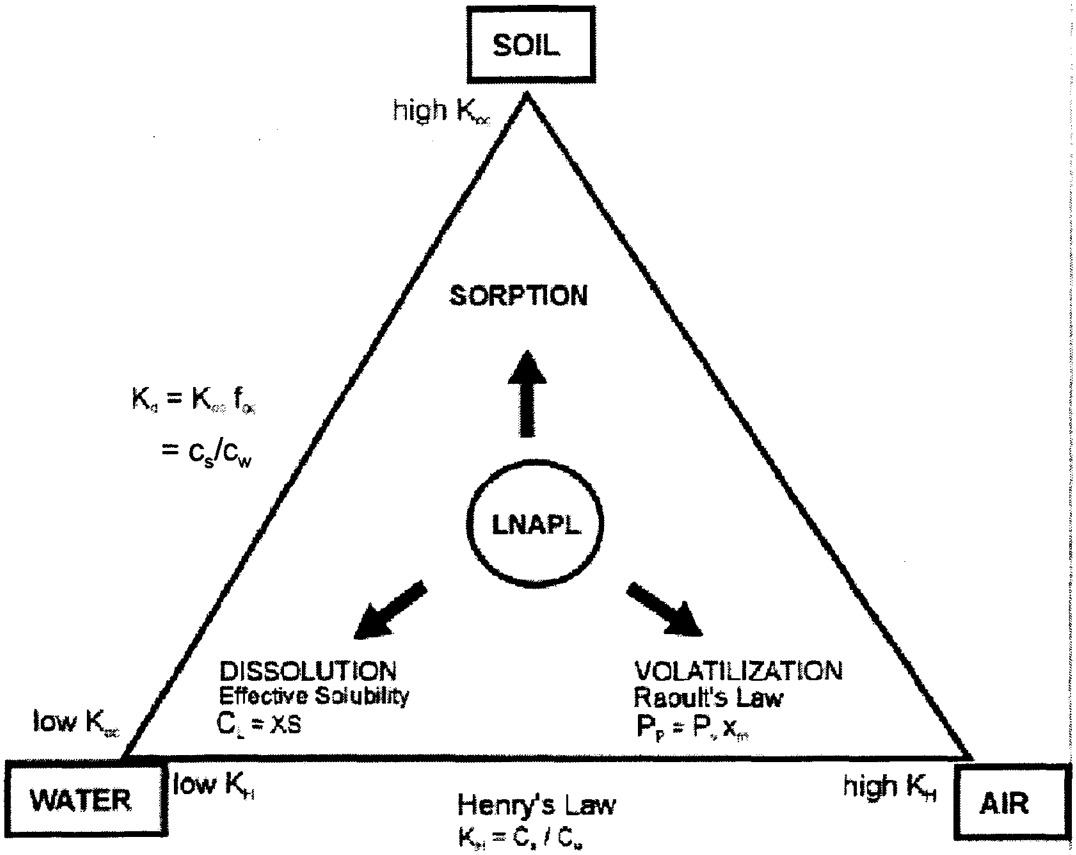
Often the primary concern associated with contaminated soil is that it can result in contamination of groundwater resources. Secondary concerns are direct exposure to the contaminated soil itself and vapors originating in the source area. However, given the particular conditions at a site, the relative order of these concerns may change. The potential for receptor impacts depends upon a number of site-specific conditions of which two of the most important are source mass and source longevity.

Despite the relatively low solubility of the hydrocarbons in petroleum fuels, they can be leached downward from the soil in the source area into the underlying groundwater. For the more soluble gasoline additives (for example MTBE and ethanol) this is especially true. Contaminated soil in the vadose zone can also be the source of vapors which migrate through the more permeable pathways in the soil and can accumulate in subsurface areas such as basements, parking garages, sewers and utility vaults. Where these vapors collect in sufficient quantity they can present an immediate safety threat from explosion, fire, or asphyxiation. Inhalation of lower concentrations of vapors over the long-term can lead to adverse health effects. All of these problems are magnified with increasing mass of contaminants and increasing amount of time that they are allowed to remain in the subsurface. The best way to reduce the likelihood of groundwater contamination and shorten the time required to achieve remediation objectives is to quickly and completely eliminate the mass of contamination in the subsurface. Contaminated soils may be remediated by a variety of *in situ* and *ex situ* technologies described in other chapters of this document. These include bioventing (Chapter III), soil vapor extraction (Chapter II), enhanced aerobic biodegradation (Chapter XII), chemical oxidation (Chapter XIII), low temperature thermal desorption (Chapter VI), biopiles (Chapter IV) and landfarming (Chapter V).

In several of the following sections on evaluation of MNA for soil-only sites (both in the initial and detailed evaluation sections) examples will be presented to illustrate the evaluation methodology. For consistency, three representative soils types are used with parameter values derived from the literature. Also, a hydrocarbon density of 730 kg/m^3 (typical of gasoline) was used and assumed to be representative of gasoline. Though it is possible that some of these examples may be representative of some actual sites, these exhibits are intended only to illustrate a methodology that could be used; in all cases site-specific data should be used to develop screening values.

Exhibit IX-4

Processes Governing the Partitioning of LNAPL Into the Soil, Water, and Air in the Subsurface Environment



where: K_d = the distribution coefficient
K_{oc} = organic carbon normalized soil/water partition coefficient
f_{oc} = fraction of organic carbon in soil
C_L = effective solubility of a given solute
X = mole fraction of a given solute in a mixture
S = pure phase solubility of a given solute
P_p = partial pressure of a given gas
P_v = vapor pressure of a given gas
X_m = mole fraction of a given gas in a mixture
K_H = Henry's law constant for a given solute
C_a = concentration of a given solute in vapor phase
C_w = concentration of a given solute in aqueous phase
C_s = concentration of a given solute in soil phase

If there is a possibility that groundwater will be impacted, or if protection of a particular groundwater resource is of vital importance, then a more detailed analysis (including the collection and analysis of groundwater samples) should be conducted and the appropriateness of MNA as a remedial alternative should be based on groundwater criteria instead of soil criteria.

Source Mass

Regardless of how biodegradable a contaminant may be, the larger the contaminant mass to be degraded, the longer it will take to do so. Obviously, the more biodegradable a contaminant is, the faster it will be degraded relative to a more recalcitrant (nondegradable) contaminant. The larger the source and the longer it resides in the subsurface, the greater the likelihood that groundwater contamination will occur. This is especially true when the depth to groundwater is relatively shallow, the amount of annual rainfall (and hence groundwater recharge) is high, and the soil is relatively permeable (and the soil surface is not covered with an impervious material such as asphalt or concrete).

Although an accurate estimate of the mass of the fuel release usually is not known, a legitimate attempt should be made to quantify the release volume. In the absence of reliable inventory data, the volume of fuel in the subsurface can be estimated by first determining the extent of contaminated soil and then integrating saturation data from soil samples over the volume of the contaminated soil mass. (For more information, see EPA, 1996b, Chapter IV.) The objective is to sufficiently characterize the extent and level of contamination with a minimum number of samples, although the accuracy of the volume estimate generally increases with an increasing number of samples. At a minimum, samples should be collected from locations where contamination is known to be greatest (*e.g.*, beneath the leaking UST or piping). Soil samples should be collected from the source area in the unsaturated zone and in the smear zone (if any) to define the three-dimensional extent of contamination.

These samples should be analyzed for the BTEX contaminants, TPH, and any other contaminants of concern at the site. If the primary contaminants of concern at the site are volatile organic chemicals (VOCs), monitoring of soil gas should supplement direct soil measurements at some locations. In addition, soil gas samples should be analyzed for oxygen, carbon dioxide, and methane (and sometimes hydrogen) to determine the microbial activity in the soils. As described above, reduced oxygen concentrations in the plume area (relative to background) and elevated carbon dioxide concentrations are a good indication that biodegradation is occurring.

Different soil types have different capacities for "holding" or "retaining" quantities of hydrocarbons released into the subsurface. The capacity for any particular soil type depends upon properties of both the soil and the type(s) of hydrocarbons released. In general, residual hydrocarbon saturation (s_r) increases with decreasing grain size. If it is assumed that a given volume of soil is initially hydrocarbon-free, the volume of hydrocarbon that the soil can retain is given by:

$$V_r = s_r \, n_e \, V_{soil}$$

where: V_r = volume of hydrocarbon retained [L^3]

s_r = residual hydrocarbon saturation [volume hydrocarbon/volume soil]
n_e = effective porosity [volume pore space/volume soil]
V_{soil} = volume of soil [L^3]

The above equation is simplistic and does not address factors such as spreading of the hydrocarbon, the rate at which the soil absorbs the liquid, or mass loss due to volatilization. However, it can be used as a screening criterion to determine whether a given UST release is likely to result in free product accumulation at the water table.

Exhibit IX-5 presents typical ranges for the concentration of hydrocarbons (*e.g.*, TPH) that each of three representative soil types could retain in the unsaturated zone. Values in the second column under "Concentration" are in terms of mass per square meter (kg/m^2). To obtain these values, first multiply the concentration in mg/kg by the bulk density of the soil (in kg/m^3) then divide by 1 million (to convert from mg to kg). Next, multiply the result by the thickness (in meters) of the contaminated soil. These concentrations can then be used to develop a rough "rule of thumb" to predict whether a spill will reach the water table. The volume of the material receiving the spill is estimated by multiplying the depth to ground water (in meters) by the "surface" area of the spill–this is the assumed thickness (in meters) of the contaminated soil. If no other information is available, assume the surface area is 1 m^2 (necessary to yield a volume). If the known (or suspected) volume of release (in gallons) divided by the volume (in cubic meters) to the water table exceeds the number of gallons per cubic meter (last column), then it is likely that free product will be present.

Exhibit IX-5
Maximum Hydrocarbon Concentrations For Soil-Only Contamination

Soil Type	Residual Hydrocarbon Saturation	Bulk Density[a] (kg/m^3)	Porosity[b]	Concentration		
				mg/kg	kg/m^2	gal/m^3
silty clay	0.05 to 0.25	1,350	0.36	10,000 to 49,000	13 to 66	5 to 24
sandy silt	0.03 to 0.20	1,650	0.41	5,000 to 36,000	9 to 60	3 to 22
coarse sand	0.01 to 0.10	1,850	0.43	2,000 to 17,000	3 to 31	1 to 11

Sources: [a] Boulding (1994), p.3-37. [b] Carsell and Parrish (1988)

Another use for the data in Exhibit IX-5 would be to compare measured hydrocarbon concentrations in soil samples with those in the table (second to last and next to last columns)—if measured concentrations are close to or exceed those in the table for a given soil type, then it could be expected that free product might accumulate at the water table. In situations where free product is present, monitored natural attenuation is not an appropriate remedial alternative because natural processes will not reduce concentrations to acceptable levels within a reasonable time period (*i.e.*, a few years). At all sites where investigations indicate that free product is present, Federal regulations (40 CFR 280.64) require that it be recovered to the maximum extent practicable. Free product recovery, and other engineered source control measures, are the most effective means of ensuring the timely attainment of remediation objectives. For more guidance on free product recovery, see U.S. EPA, 1996a.

From Exhibit IX-5 we see that one cubic meter of silty clay could potentially retain 5 to 24 gallons of gasoline assuming that it was spread evenly through the soil. For a LUST site where the depth to groundwater below the point of the release was, for example, 5 meters (15 feet), there is no information on the surface area of the spill, and the soil type is silty clay, then a release of up to 120 gallons (24 gallons per meter times five meters depth) might be retained within the unsaturated zone and free product would not be expected to accumulate on the water table. In contrast, a coarse sand might potentially retain a release of only 55 gallons. In either or both of these cases even if the release volume was small enough so that free product did not collect at the water table there could still be a groundwater impact through leaching of soluble hydrocarbons by infiltration of precipitation and groundwater recharge. In such an instance, release volumes much smaller than theoretically retained could result in significant and unacceptable groundwater impact.

Source Longevity

Once it has been determined that the entire release volume will remain trapped within the vadose zone and there is no likelihood of groundwater contamination, the next step is to estimate the lifetime of the residual contamination. The two primary factors that control source longevity are: (1) mass of contaminants present in the source area, and (2) availability of electron acceptors, of which oxygen is the most important.

As previously discussed, the larger the contaminant mass, the longer the period of time required for it to be completely degraded. Across a wide range of concentrations, the rate of biodegradation of petroleum hydrocarbons follows a hyperbolic rate law:

$$V = V_{\max}\left[C/(K + C)\right]$$

where:
V = the achieved rate of biodegradation (mg/liter in groundwater or mg/kg in soil)
V_{max} = the maximum possible rate of biodegradation at high concentrations of hydrocarbon
C = the concentration of hydrocarbon (mg/liter or mg/kg)
K = half-saturation constant (the concentration of hydrocarbon that produces one-half of the maximum possible rate of biodegradation; mg/liter in water or ppm [volume/volume in soil gas] or mg/kg in sediment)

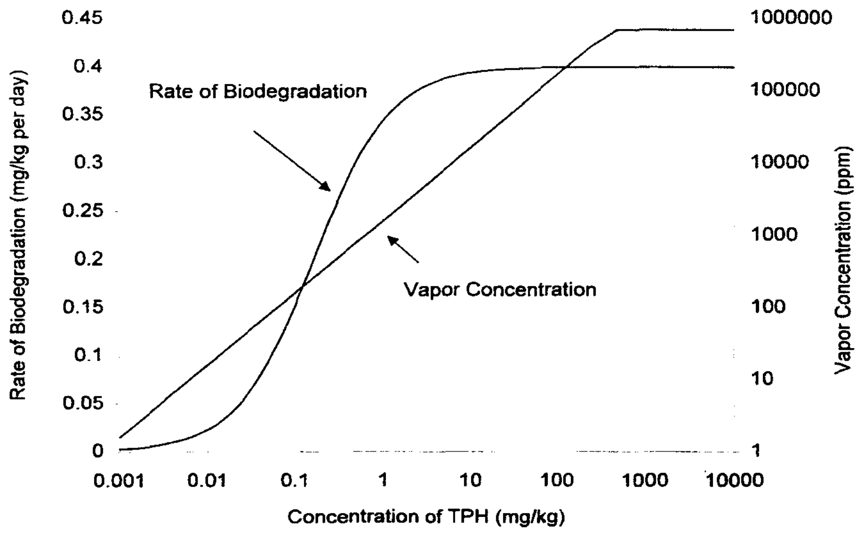
When hydrocarbon concentrations (C) are significantly lower than the half-saturation constant (K), the sum of (K+C) is approximately equivalent to K. Because $V_{\max}$ and K are constants, the rate of biodegradation (V) is proportional to the concentration of hydrocarbon (C). As the concentration of hydrocarbon decreases through biodegradation, the rate of biodegradation declines as well (*i.e.*, biodegradation follows a first-order rate law). When hydrocarbon concentrations are significantly higher than the half saturation constant, the sum of ($K+C$) is approximately equivalent to C and the value of $C/(K+C)$ approaches 1.0. Thus, the achieved rate of biodegradation (V) approaches the maximum rate (V_{max}). When C is more than ten times the value of K, the rate of biodegradation will be more than 90% of the maximum rate (V_{max}). These relationships are illustrated in Exhibit IX-6.

In Exhibit IX-6, V_{max} has been set at a value of 0.4 mg TPH per kg sediment per day. This corresponds to the V_{max} published for aerobic degradation of aviation gasoline vapors by Ostendorf and Kampbell (1991). The concentration of hydrocarbon vapors was calculated from the concentration of TPH, assuming that the air-filled porosity was 10%, the water-filled porosity was 10%, the sediment bulk density was 1.8 kg/liter, and the partition coefficient of dissolved hydrocarbon between water and air was 0.24. The rate of biodegradation was calculated from the concentration of hydrocarbons vapors, using a half saturation constant for aerobic biodegradation of aviation gasoline vapors of 260 ppm (Ostendorf and Kampbell, 1991).

The point of the preceding discussion is that at the high hydrocarbon concentrations typical of source areas in the unsaturated zone, the amount of hydrocarbons degraded per unit time is approximately constant, regardless of the actual concentration of hydrocarbons (*i.e.*, biodegradation follows a zero-order rate law). And, because the rate of degradation is constant with time, the time required for complete biodegradation is directly proportional to the initial concentration of hydrocarbons to be degraded. The difference between such an approximate rate (zero-order) and the true rate (first-order) is less than the usual statistical variation in the measurements.

The applicability of the above equation has been demonstrated in the field by Moyer *et al.* (1996). Thier work demonstrates that a zero-order rate law is the appropriate law to describe the biodegradation of hydrocarbons in the unsaturated zone. They found that the half saturation constant for biodegradation of hydrocarbon vapors in a sandy soil varied from 0.2 mg/kg to 1.6 mg/kg. As explained in the preceding paragraphs, when hydrocarbon concentrations are more than ten times the half saturation constant (*i.e.*, 2 mg/kg to 16 mg/kg for this example), the rate of biodegradation will approach the maximum rate. Note that these concentrations are already near or below cleanup (or action) levels for hydrocarbons in soil at many sites. Consequently, it can be assumed that biodegradation of hydrocarbons, at least in the relatively shallow unsaturated zone, should follow a zero-order rate law all the way down to cleanup levels. Be aware that this approximation applies only to petroleum hydrocarbons in the unsaturated zone: a first-order rate law must be used to determine the rate of biodegradation of hydrocarbons dissolved in groundwater.

Exhibit IX-6.
Graph of hyperbolic rate law for aerobic biodegradation of gasoline



Generally, petroleum hydrocarbons will be degraded most rapidly by microorganisms that require oxygen to sustain their metabolism. In situations where there is an abundance of oxygen and an excess of hydrocarbons for them to metabolize, aerobic microorganisms should degrade hydrocarbons at or near the theoretical maximum rate. But, this rarely occurs in the field for a variety of reasons. Oxygen is rapidly depleted in source areas in particular. Oxygen diffusion from the atmosphere through the soil in the soil gas to the smear zone containing hydrocarbons is a slow process, and when subsurface oxygen is depleted, it takes a relatively long time to replenish. As a consequence, the rate of aerobic biodegradation is limited by the rate that oxygen is supplied to the microorganisms by diffusion through the vadose zone.

Aerobic biodegradation is most effective in soils that are relatively permeable (with a hydraulic conductivity of about 1 ft/day or greater) to allow transfer of oxygen to subsurface soils where the microorganisms are degrading the petroleum constituents. Not surprisingly, the length of time required for oxygen to diffuse into the soil increases as the depth increases. The diffusion rate is also proportional to the air-filled porosity of the soil and the steepness of the diffusion gradient. Finer textured materials have more water-filled porosity and less air-filled porosity at field capacity. Soils with a low oxygen diffusion capacity can hinder aerobic biodegradation. Exhibit IX-7 presents calculations of the rate that hydrocarbons that could be mineralized if oxygen diffusion was the limiting factor.

Exhibit IX-7
Rate of Aerobic Biodegradation of Hydrocarbons (mg/kg/d)that can be Sustained by Diffusion of Oxygen through the Vadose Zone (Calculated for a Smear Zone that is One Meter Thick)

Depth to Top of Contaminated Soil (meters)	Silty Clay	Sandy Silt	Coarse Sand
1	5	12	22
2	2	6	11
3	2	4	7
4	1	3	6

Comparing Exhibit IX-5 and Exhibit IX-7, it is readily apparent that aerobic degradation of hydrocarbons under natural conditions won't expeditiously cleanup contamination, especially in tight soils. Using the biodegradation-capacity data in Exhibit IX-7 and applying it to the range of contamination levels in Exhibit IX-5 for each of the three representative soil types, projections can be made on the length of time (in years) that would be required for aerobic biodegradation to completely mineralize residual gasoline in the unsaturated zone. As a rough approximation, the time required to degrade hydrocarbons in the vadose zone can be estimated by dividing the highest concentration of hydrocarbon (TPH in mg/kg) by the rate of biodegradation of hydrocarbon (mg/kg per day). For example, a silty clay is able to retain 10,000 mg/kg to 49,000 mg/kg of hydrocarbon at residual saturation, but will support aerobic degradation of only 5 mg/kg/day at a depth of only 1 meter below land surface. Even for this relatively shallow contamination, it is projected that complete degradation would require from 6 to 28 years. With each meter of increased depth, the length of time increases by a multiple of approximately this same amount. Thus, for a depth of 3 meters, the projected length of time ranges from 17 to 84 years (approximately 3 times the range of 6 to 28 years).

These calculations of the rate of biodegradation allowed by diffusion of oxygen put an upper boundary on the rate of biodegradation, and a lower boundary on the time required to clean up a spill of gasoline. For comparison, results are also presented (last column of Exhibit IX-8) of the calculated time required for clean up when the maximum rate of biodegradation (V_{max}) is relatively slow. The time required was calculated using the V_{max} (0.41 mg/kg per day) reported by Ostendorf and Kampbell (1991) in the well-oxygenated unsaturated zone above the residually-saturated capillary fringe at an aviation gasoline release site in Michigan. The fertility of the sediment at this site is low, and as a consequence, the rate of biodegradation is slow compared to rates at other sites. When the rate of biodegradation is slow, the time required to clean up the gasoline may be longer than would be expected if the supply of oxygen supplied through diffusion was the limiting criteria.

Exhibit IX-8
Time Required (Years) To Consume Hydrocarbons Present At Residual Saturation

Soil Type	TPH at Residual Saturation (mg/kg)	Oxygen Diffusion-Limited Depth (meters) to top of contaminated soil in the vadose zone				Bio-degradation -Limited
		1	2	3	4	0.41 mg/kg per day
silty clay	10,000 to 49,000	6 to 28	11 to 56	17 to 84	23 to 113	67 to 326
sandy silt	5,000 to 36,000	1 to 9	2 to 17	4 to 26	5 to 34	33 to 240
coarse sand	2,000 to 17,000	<1 to 2	<1 to 4	1 to 6	1 to 8	13 to 113

These Exhibits (IX-5 through IX-8) demonstrate several important points. First, and most importantly, there is no substitute for field-measured rates of biodegradation. Estimates based on theory, microcosm studies, literature values, or modeling results should not be relied on as the sole basis for regulatory decision-making. Second, even for permeable material (*e.g.*, coarse sand) the concentration of hydrocarbon that can be biodegraded within a reasonable time frame (*e.g.*, 1 to 5 years) is relatively low. Third, although oxygen won't be the limiting criteria at many sites, the rate of aerobic biodegradation may still result in time frames measured in decades to achieve remediation objectives. And fourth, given the long projected times to achieve remediation objectives through reliance on natural processes alone, it will often be more effective and efficient to use an active remediation technology (e.g., bioventing, soil excavation, SVE) to mitigate the contaminant source even in the rare case where groundwater impacts are not anticipated.

Potential For Receptor Impacts

For contamination which remains in the soil in the vadose zone, the primary potential impacts to receptors are from direct contact with (or ingestion of) contaminated soil, safety threats due to fire and explosion hazards from accumulations of vapors, and health effects cause by inhalation of vapors. Each of these potential impacts should be fully evaluated. It is important to determine whether there are receptors that could come into contact with contaminated soil. Because soils associated with UST contamination are generally below the surface of the ground, there will usually be limited opportunity for receptors to come into contact with them. However, if the contaminated soils might be excavated (*e.g.*, for construction) before contaminant concentrations have been adequately reduced, receptor contact with contaminated subsurface soil could occur unless appropriate controls are implemented. If direct contact with contaminated soils is likely, controls to prevent such contact (or alternative remedial methods) should be implemented. The CAP should address these potential concerns and means of control.

Vapor generation and migration are generally of greater concern with the more volatile and flammable petroleum fuels (*e.g.*, gasoline). However, even with less volatile, combustible fuels (*e.g.*, heating oil) sufficient accumulations of vapors may occur. Like liquids, vapors move faster through the soil in zones of higher permeability than in zones of low permeability. Common vapor migration routes are in the coarse backfill around utility lines and conduits, in open conduits such as sewers, and through naturally permeable zones in the soil (*e.g.*, gravel stringers, fractures). Basements tend to draw in vapors in response to differential pressure gradients. In any of these situations, accumulations of vapors can present a safety threat from fire or explosion, as well as adverse long-term health effects. The potential for vapor generation and migration, and means to mitigate these hazards, should be addressed in the CAP.

Contaminated Groundwater

The two most common sources of groundwater contamination are from contaminated soil and free product. If left unaddressed, contaminated soil and/or free product can be a source of groundwater contamination that may persist for decades to centuries. Under certain conditions vapors, which are released directly into the soil, can also result in groundwater contamination. While some states may have in place resource nondegradation policies that could drive cleanup decisions, more often than not these decisions are made based on health-related impacts to human receptors followed by consideration of potential impacts to third parties. The two primary questions to consider when evaluating the potential impacts of contaminated groundwater are: “How long will the contaminant plume persist?” and “Will the contaminant plume migrate from the source area and reach current or future receptors?”

Plume Persistence

There are two key factors which control the persistence of a contaminant plume: (1) source mass, and (2) contaminant biodegradability. As one would expect, the larger the source mass the longer the persistence of the source and the greater the likelihood that a significant groundwater plume will form. If the volume of the release is sufficient such that free product is present on the water table, then MNA is not an appropriate remediation alternative. In fact, Federal regulations under 40 CFR 280.65 require that free product be recovered to the maximum extent practicable. For more information on free product recovery, see U.S. EPA, 1996a.

The longevity of the source is controlled by the rate of weathering of the residual fuel in the source area. If a portion the residual fuel is above the water table, volatilization also can remove contaminant mass. As groundwater flows past residual fuel, the water soluble constituents such as benzene, toluene, ethylbenzene, and three isomers of xylene (BTEX) plus oxygenates such as MTBE and ethanol will partition from the residual fuel mass into the groundwater and be transported downgradient. The concentration of any particular fuel constituent in groundwater is proportional to its mole fraction in the residual fuel. Over time, the mass of water soluble components remaining in the residual fuel is depleted and the groundwater concentrations of these components decrease. Conversely, as the mole fraction of less soluble components increases, their concentrations in the plume actually increase. Once the soluble components have dissolved into the groundwater, they can also be removed by biodegradation. The rate at which all these processes remove these components from residual fuel is roughly proportional to the fraction of the components that remain the residual fuel. As a consequence, the rate of overall weathering will typically follow a first order rate law with time.

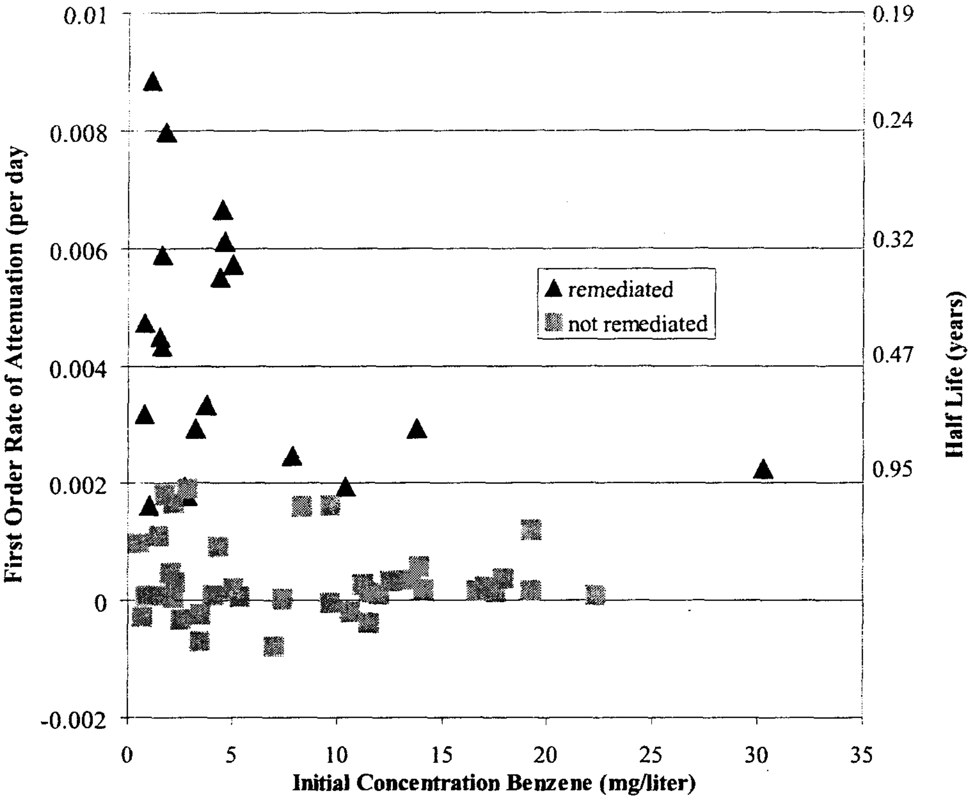
To estimate the achieved rate of attenuation of benzene and MTBE in groundwater in contact with residual gasoline, Peargin (2000) examined the long-term trends in the concentration of benzene and MTBE in monitoring wells that were screened in the LNAPL smear zone at 23 UST release sites. Source remediation had been completed at 8 of these sites; no remediation had been attempted at the remaining 15 sites. The first order rate of attenuation of benzene and MTBE was calculated from monitoring data from 79 wells for which statistically significant rates of attenuation could be derived. Exhibit IX-9 is a plot of the calculated attenuation rate versus initial benzene concentration for both remediated and non-remediated sites.

Although the rates of natural attenuation of benzene in the smear zone varied widely, there is a clear difference between rates at sites where active remediation had been completed, and sites with no active remediation. At sites with active remediation, the rate of attenuation of benzene in the source is near to or greater than 0.0022 per day, equivalent to a half-life of just under one year. At sites without remediation, the mean rate of attenuation of benzene is 0.00037 per day, equivalent to a half-life of more than five years. For benzene, the attenuation rate at remediated sites is about 6 times faster than that for the non-remediated sites. Peargin (2000) also presented data on the persistence of MTBE in wells in the smear zone. These data indicate the mean rate of attenuation at sites without remediation is 0.00011 per day, equivalent to a half life of seventeen years. For sites with active remediation the rate of attenuation of MTBE is 0.0035 per day, equivalent to a half-life of about 6 months. For MTBE, the attenuation rate at remediated sites is about 30 times faster than that for the non-remediated sites.

Note that for several of the non-remediated sites contaminant concentrations are increasing over time. It is also apparent that slower rates of attenuation of the source are associated with higher initial contaminant concentrations, thus, a longer period of time is required to achieve adequate reductions in concentration. For the case of both benzene and MTBE, significant reductions in the amount of time required to achieve cleanup goals can be realized if the source is adequately remediated. This is especially true with larger and more recent releases.

If the source contains sufficient mass of contaminants such that natural degradation will require longer than a decade (or other reasonable period of time), then MNA is generally not an appropriate remedial alternative. For a time frame of this duration, performance monitoring is going to be costly, and it is highly uncertain that the remedy will be protective. There is simply too much mass in the system and more aggressive measures should be implemented to reduce the mass in order for MNA to be able to achieve remediation objectives within a time frame that is reasonable.

Exhibit IX-9
Benzene Attenuation Rates Reported By Peargin (2000)



Plume Migration

Because monitored natural attenuation relies on natural processes to prevent contaminants from migrating, it is important to determine the status of the contaminant plume (that is whether it is "stable"[4], shrinking, or expanding) and

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[4] By definition, a "stable" plume is one that forms where there is a continuous (infinite) source of contaminants such that concentrations within the plume never change (*i.e.*, neither increase nor decrease and, thus, "stable"). Only when the flux of contaminants into the plume is exactly equal to the mass of contaminants that are degraded is the plume truly "stable". If the mass into the plume exceeds the mass that is biodegraded, then the plume expands; if the mass into the plume is less than the mass degraded, then the plume contracts. In practice, it may be difficult (or impossible) to determine whether the plume is expanding, contracting or stable. And unless there is a continuous release, a source isn't truly infinite. But, the source mass may be so large and the flux of contaminants into the plume so great that for practical purposes it behaves as an infinite source and the plume expands (though maybe very slowly) for a very long period of time. The implications of an expanding or stable plume is that remediation objectives can never be achieved in a "reasonable" time frame because infinity is not a reasonable length of time. Only after the contaminant source has been eliminated and the plume has been demonstrated to be contracting should MNA be evaluated as a potential remedial alternative.

Exhibit IX-10
Initial Dissolved Concentrations (µg/L) Of Benzene And MTBE That Can Be Biodegraded To Target Levels Within Various Time Periods

	BENZENE - target 5 µg/L at end of interval			
	1 year	2 years	5 years	10 years
Remediated Source (k= 0.0022/d)	11	25	280	15,000
Non-Remediated Source (k= 0.00037/d)	6	7	10	20
	MTBE - target 20 µg/L at end of interval			
	1 year	2 years	5 years	10 years
Remediated Source (k= 0.0035/d)	72	260	12,000	7,000,000
Non-Remediated Source (k= 0.00011/d)	21	22	24	30

whether receptors might be impacted by the release. These impacts could include ingestion of groundwater, direct contact with contaminated groundwater at discharge points (*e.g.*, streams or marshes), or inhalation of contaminant vapors, especially in a basement or other confined space. As a safety measure, sentinel wells may be installed between the leading downgradient edge of the dissolved plume and a receptor (*e.g.*, a drinking water supply well). A contaminated sentinel well provides an early warning that the plume is migrating. As such, sentinel well(s) should be located far enough up gradient of any receptor to allow enough time before the contamination arrives at the receptor to initiate other measures to prevent contamination from reaching the receptor, or in the case of a supply well, provide for an alternative water source. For those responsible for site remediation, this is a signal that MNA is not occurring at an acceptable rate, or that site conditions have changed (*i.e.*, transience) and the contingency remedy should be implemented. Sentinel wells should be monitored on a regular basis to ensure that the plume has not unexpectedly migrated.

Exhibit IX-10 compares maximum dissolved concentrations of benzene and MTBE that can be degraded over various time periods at sites where sources have been remediated and where sources have not been remediated. Note that for sites where the sources have not been remediated, the maximum concentrations of benzene or MTBE that can be biodegraded within a decade are not too much higher than the target concentrations.

The CAP should contain information regarding the location of potential receptors, the quality of groundwater, depth to groundwater, rate and direction of groundwater flow and its variability, groundwater discharge points, and use of groundwater in the vicinity of the site. If potential receptors are located near the site, the CAP should also contain monitoring results that demonstrate that receptors are not likely to be exposed to contaminants. Determination of whether a receptor is in close proximity to a site may be considered in terms of either contaminant travel time from the toe of the plume to the receptor or the distance separating the toe of the plume from the receptor. Both of these will vary from site to site depending upon site specific factors. The length of time necessary for contaminants to travel from the source to a downgradient receptor can be estimated only from site-specific data, which are the highest measured hydraulic conductivity, the hydraulic gradient, (effective) porosity, distance between the source and the nearest receptor, and the bulk density of the soil and its organic carbon content. The last two of these parameters, coupled with the contaminant's soil sorption constant (K_{oc}, which is discussed later), are necessary to determine if movement of the contaminant will be retarded by sorption to soil organic matter, or whether it will move at close to the velocity of the groundwater (i.e., not be retarded, hence "conservative"). It is important to realize that conservative contaminants (although initially at low concentrations) actually arrive at receptors *before* the time estimated based on average groundwater seepage velocity. The consequence is that estimated travel times based on average parameter values are longer than in actual fact, and receptors may be at risk sooner than anticipated. The subsurface migration of dissolved contaminants through porous media is as a dispersed plume rather than a concentrated, discrete slug. Whereas a slug that enters a well instantaneously raises the concentration of the extracted water to that of the slug, the leading edge of a contaminant plume is typically very dilute and concentrations in the well increase gradually with time. When contaminants first arrive at the well the concentration is very low, typically below even taste and odor thresholds. Continued exposure to such low, but gradually increasing, concentrations can cause receptors to become desensitized over time to the extent that they are unaware that their water is contaminated even though concentrations may be several hundreds of times greater than recognized taste and odor thresholds.

For biodegradable contaminants, a minimum travel time of 2 years or more should allow for an evaluation of the potential effectiveness of monitored natural attenuation and provide sufficient time to implement contingency measures should monitored natural attenuation prove to be ineffective in meeting remediation objectives. Therefore, if the maximum expected contaminant transport velocity (whether for a retard or conservative contaminant) at a site is 2 feet per day, it would require 2 years for such a contaminant to travel 1,500 feet (approximately ¼ mile). Therefore, at this site, all downgradient receptors within ¼ mile of the source should be identified and all wells be sampled and included in the regular monitoring program. It should be noted that the presence of layers of high permeability soil or rock, fractures or faults, karst, or utility conduits may accelerate the migration of contaminants. It is also possible that contaminants could be migrating along pathways that were undetected during characterization of the site. If less biodegradable and more mobile contaminants (such as MTBE) are of concern, then the travel time criteria should be reduced.

If the groundwater is potable and future land use is expected to be residential, potential future receptors should also be considered. If this information is not provided in the CAP, you will need to request the missing data. If contaminants are expected to reach receptors, an active remedial technology should be used instead of MNA.

Only under some rare circumstances might MNA be considered a remedial option even when there is potential for lingering groundwater contamination. For instance, active remediation to protect a groundwater resource may not be required if the affected groundwater is not potable (*e.g.*, because of high salinity or other chemical or biological contamination) nor will it be used as a potential source of drinking water within the time frame anticipated for natural attenuation processes to reduce contaminant concentrations to below established regulatory levels.

Exposure to petroleum contaminant vapors may also be a concern at some sites. Hazardous contaminants can volatilize from the dissolved-phase from a contaminated groundwater plume. Vapors tend to collect in underground vaults, basements, or other subsurface confined spaces, posing exposure risks from inhalation and creating the possibility of explosions. Inhalation and dermal exposure to volatile contaminants can also be significant if groundwater is used for bathing (even if it is not used for drinking), or even lawn irrigation and car washing. If vapor migration and associated health and safety risks are not addressed in the CAP, request additional information.

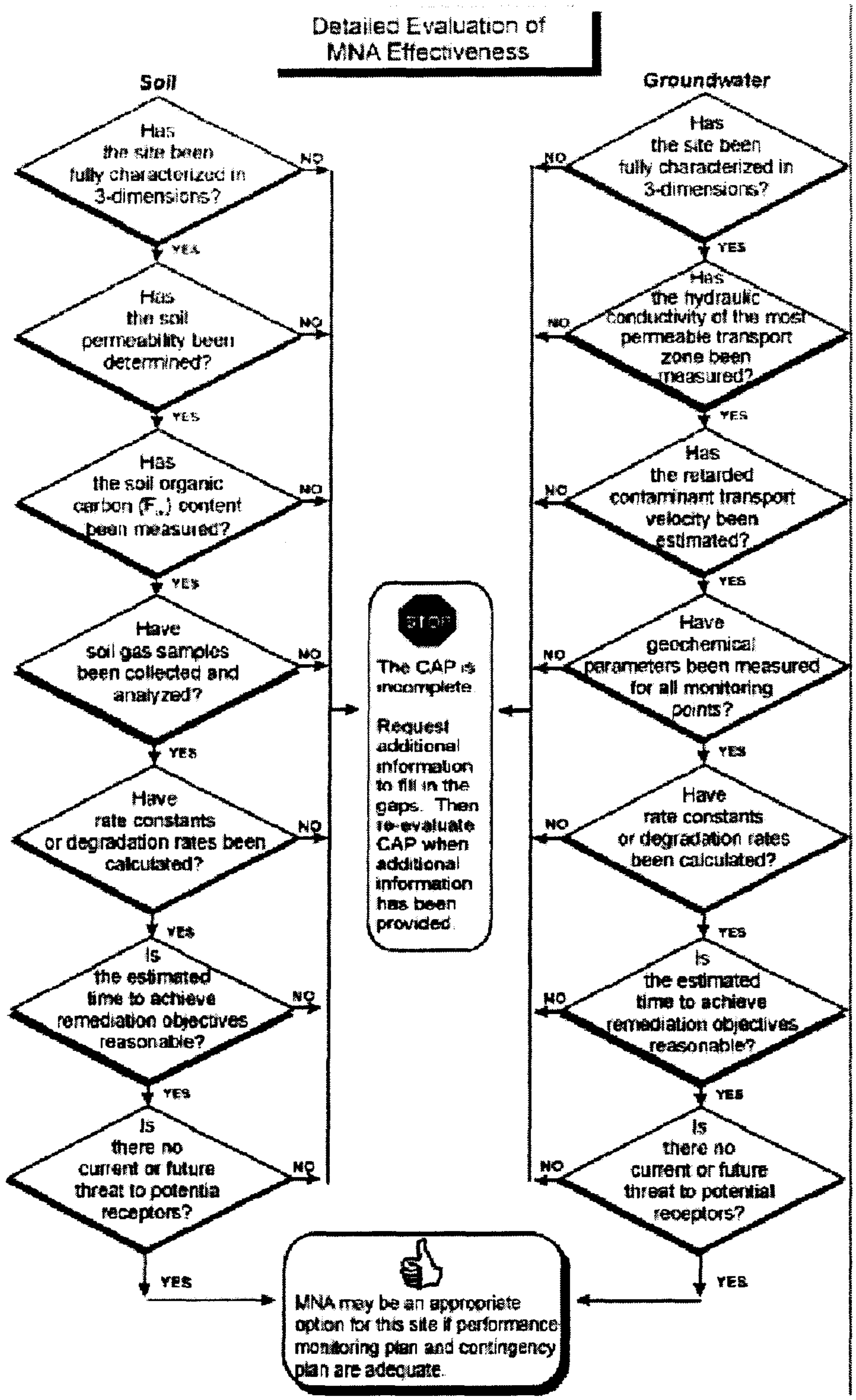
Detailed Evaluation Of Monitored Natural Attenuation Effectiveness

Once the initial screen has been completed, and is has been determined that monitored natural attenuation could potentially be effective at a site, it is necessary to conduct a more detailed evaluation of the CAP to determine whether or not MNA is likely to be effective. Exhibit IX-11 is a flow chart that can serve as a guide through the detailed evaluation process. A thorough understanding of natural attenuation processes coupled with knowledge of the site conditions and the contaminants present will be necessary to make this determination. This section begins with a general overview of natural attenuation mechanisms and site characterization and before getting into the specific parameters that should be evaluated for an MNA remedy for contaminated soil and contaminated groundwater.

Natural Attenuation Mechanisms

In order to assess site conditions to determine whether MNA is an acceptable alternative to active treatment, it is important to understand the mechanisms that degrade petroleum fuel components in soil and groundwater. Although it is not likely that all environmental conditions will be within optimal ranges under natural field conditions, natural attenuation processes will, to some degree, still be occurring. Mechanisms may be classified as either destructive (*i.e.*, result in a net decrease in contaminant mass) or non-destructive (*i.e.*, result in decrease in concentrations but no net decrease in mass). Mechanisms that result in destruction of petroleum hydrocarbons (and other fuel components) are primarily biological. The primary non-destructive mechanisms are abiotic, physical phenomena, although some abiotic processes are destructive. However, because most of these processes are relatively insignificant for hydrocarbon fuel components they will not be presented in the following discussion. The primary biological mechanisms of

Exhibit IX-11
Detailed Evaluation of Monitored Natural Attenuation Effectiveness



MNA are aerobic and anaerobic metabolism. The primary physical mechanisms are volatilization, sorption, and dispersion. Characteristics of these mechanisms are summarized in Exhibit IX-12.

Biological Processes

The driving force for the biodegradation of petroleum hydrocarbons is the transfer of electrons from an electron donor (petroleum hydrocarbon) to an electron acceptor. To derive energy for cell maintenance and production from petroleum hydrocarbons, the microorganisms must couple electron donor oxidation with the reduction of an electron acceptor. As each electron acceptor being utilized for biodegradation becomes depleted, the biodegradation process shifts to utilize the electron acceptor that provides the next greatest amount of energy. This is why aerobic respiration occurs first, followed by the characteristic sequence of anaerobic processes: nitrate reduction, manganese-reduction, iron-reduction, sulfate-reduction, and finally methanogenesis.

Aerobic biodegradation of petroleum fuel contaminants by naturally occurring microorganisms is more rapid than anaerobic biodegradation when there is an abundant supply of both electron acceptors and electron donors. Aerobic biodegradation occurs even at low concentrations of dissolved oxygen. Heterotrophic bacteria (i.e., those that derive carbon for production of cell mass from organic matter) are capable of carrying out aerobic metabolism at oxygen concentrations that are below the detection limit of most conventional methods for measuring oxygen content. The rate of oxygen depletion due to microbial metabolism typically exceeds the rate at which oxygen is naturally replenished to the subsurface. This results in the core region of the hydrocarbon plume being anaerobic (see Exhibit IX-2). Once the oxygen in the contaminated zone has been depleted (below about 0.5 mg/L), there is generally ample time for anaerobic reactions to proceed because the lifespan of contaminant sources and plumes is measured in years, even after most of the source material has been removed. In anaerobic biodegradation, an alternative electron acceptor (*e.g.*, NO_3^-, SO_4^{2-}, Fe^{3+}, Mn^{4+}, and CO_2) is used. Within only the past few years it has been realized that because there is a potentially much larger pool of anaerobic electron acceptors in groundwater systems, the vast majority of the contaminant mass removed from the subsurface is actually accomplished by anaerobes.

Physical Processes

Physical processes such as volatilization, dispersion, and sorption also contribute to natural attenuation. Volatilization removes contaminants from the groundwater or soil by transfer to the gaseous phase. In general, volatilization accounts for about 5 to 10 percent of the total mass loss of benzene at a typical site, with most of the remaining mass loss due to biodegradation (McAllister, 1994). For less volatile contaminants, the expected mass loss due to volatilization is even lower. Dispersion ("spreading out" of contaminants through the soil profile or groundwater unit) results in lower concentrations of contaminants, but no reduction in contaminant mass. In soil, hydrocarbons disperse due to the effects of gravity and capillary forces (suction). In groundwater, hydrocarbons disperse by advection and hydrodynamic dispersion. Advection is the movement of dissolved components in flowing groundwater. Hydrodynamic dispersion is the result of mechanical mixing and molecular diffusion. If groundwater velocities are relatively high, mechanical mixing is the dominant process and diffusion is insignificant. At low velocity, these effects are reversed. Sorption (the process by which particles

Exhibit IX-12
Primary Monitored Natural Attenuation Mechanisms

Mechanism	Description	Potential For BTEX Attenuation
Biological		
Aerobic Respiration	Microbes utilize oxygen as an electron acceptor to convert contaminants to CO_2, water, and biomass.	Most significant attenuation mechanism if sufficient oxygen is present. Soil air (O_2) $\geq$ 2 percent. Groundwater D.O. = measurable
Anaerobic Respiration ■ Denitrification ■ Sulfate reduction ■ Iron reduction ■ Manganese reduction ■ Methanogenesis	Alternative electron acceptors (*e.g.*, NO_3^-, SO_4^{2-}, Fe^{3+}, Mn^{4+}, CO_2) are utilized by microbes to degrade contaminants.	Rates are typically much slower than for aerobic biodegradation but represent the major biodegradation mechanisms
Physical		
Volatilization	Contaminants are removed from groundwater by volatilization to the vapor phase in the unsaturated zone.	Normally minor contribution relative to biodegradation. More significant for shallow or highly fluctuating water table. No net loss of mass.
Dispersion	Mechanical mixing and molecular diffusion processes reduce concentrations.	Decreases concentrations, but does not result in a net loss of mass.
Sorption	Contaminants partition between the aqueous phase and the soil matrix. Sorption is controlled by the organic carbon content of the soil, soil mineralogy and grain size.	Sorption retards plume migration, but does not permanently remove BTEX from soil or groundwater as desorption may occur. No net loss of mass.

Source: Adapted from McAllister and Chiang, 1994.

such as clay and organic matter "hold onto" liquids or solids) retards migration of some hydrocarbon constituents (thereby allowing more time for biodegradation before the contaminants reach a receptor).

Site Characterization

Site characterization (and monitoring) data are typically used for estimating attenuation rates, which are in turn used to estimate the length of time that will be required to achieve remediation objectives. Exhibit IX-13 lists the data that should be collected during site characterization activities and summarizes the relevance of these data. In general, the level of site characterization necessary to support a comprehensive evaluation of MNA is more detailed than that needed to support active remediation. This is not to say, however, that a "conventional" site characterization (typically consisting of 1 up gradient well and 2-3 wells downgradient with long screened intervals that intersect the water table) is adequate even for active remediation technologies. The primary reason why active remediation technologies often fail to meet remediation objectives is not so much that the technologies don't work, as it is that they are inappropriately designed and implemented based on information from inadequate site characterization. Many of these systems (especially pump-and-treat) are merely active containment measures, and while they often don't result in expeditious cleanup, they may at least serve to minimize the spread of contamination. Because an MNA remedy lacks an active backup system, it is even more important that site characterization be as accurate and comprehensive as possible.

Soil borings should be conducted such that continuous lithologic logs are generated that cover the interval from ground surface to significantly below the seasonal low water level. Care should be exercised to ensure that contaminants are not introduced into previously uncontaminated areas and that conduits for cross-contamination are not created—wells with long screened intervals that could interconnect different water-bearing strata should not be installed. Use of direct push technology is ideally suited for this purpose (see U.S. EPA, 1997, for more information). With increasing distance from the source area, delineation of preferential contaminant transport pathways is especially important because these pathways, which are often relatively small in scale, control contaminant migration. Monitoring wells should be "nested" and arrayed in transects that are perpendicular to the long axis of the plume. Several transects should be established to fully characterize both the subsurface stratigraphy and the contaminant plume in three-dimensions. In order to determine rates of biodegradation, several wells along the centerline of the plume are required. If an insufficient number of "cross-gradient" are installed, it will be impossible to determine where the centerline of the plume is located. Data from wells that are located off the centerline (in either the lateral or vertical direction) are erroneous, and lead to an overestimate of the rate of biodegradation. If the rate of biodegradation is overestimated, then the length of time required to reach remediation objectives will be underestimated. It is also especially important that all monitoring wells be sampled on a regular basis to ensure that seasonal variations in both water levels and contaminant concentrations are identified.

Data collected during site characterization should be incorporated into a conceptual site model. A conceptual site model is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual site model should not be static–it should be continually refined as additional data are acquired. In some cases, new data may require a complete overhaul of the conceptual site model. The conceptual model serves as an aide in; directing investigative activities, evaluating the applicability of potential remedial technologies, understanding potential risks to receptors, and developing an appropriate computer model of the site.

"Conceptual site model" is not synonymous with "computer model," although a calibrated computer model may be helpful for understanding and visualizing current site conditions or for predicting likely future conditions. However, computer modelers should be cautious and collect sufficient field data to test conceptual hypotheses and not "force-fit" site data into a pre-conceived, and possible inaccurate, conceptual representation. After the site conceptual model has been developed, it is possible to evaluate the applicability of using a computer model for simulating the site.

Computer models will not be applicable at all sites for a variety of reasons. All models are based on a set of simplifying assumptions. These assumptions reduce the enormous complexity of a real-world site to a manageable scale, but at the price of increased uncertainty. Model developers identify significant processes that form the theoretical basis of the model. Mathematical relationships are then derived for these processes and solved for contaminant concentrations, mass balances, fluxes, velocities, etc. Many different approaches have been used. The simplest models typically have the most restrictive assumptions: one-dimensional steady-state flow of water and transport of contaminants, homogeneous soil properties, well-defined source terms, infinite aquifer extent, among others. These formulations lead to analytical solutions that are easy to use and require only a few input parameters. Although outwardly simple, these models may not be adequate to represent contaminant transport at a certain site. Proper use, however, requires that the site conceptual model match the assumptions of the theoretical model. However, evaluation of whether or not the assumptions of the model are met requires that sufficient data have been collected in order to develop a site conceptual model, because it cannot be assumed *a priori* that a simplified model is adequate to represent complex site conditions. When model assumptions are not met then other approaches must be pursued.

Exhibit IX-13
Site Characterization Data Used To Evaluate Effectiveness Of Monitored Natural Attenuation In Groundwater

Site Characterization Data	Application
Direction and gradient of groundwater flow	Estimate expected rate of plume migration.
Hydraulic conductivity	Estimate expected rate of plume migration.
Definition of lithology	Understand preferential flow paths.
Aquifer thickness	Estimate volatilization rates and model groundwater flow.
Depth to groundwater	Estimate volatilization rates.
Range of water table fluctuations	Evaluate potential source smearing, influence of fluctuations on groundwater concentrations, and variation in flow direction.
Delineation of contaminant source and soluble plume	
Date of contaminant release	Compare expected extent without MNA to actual extent.
Historical concentrations along the primary flow path from the source to the leading edge	Estimate expected extent of plume migration.
Background electron acceptor levels up gradient of the source and plume	Evaluate status of plume (*i.e.*, steady state, decreasing, migrating).
Geochemical indicators of MNA: Alkalinity, hardness, pH, and soluble Fe and Mn, sulfate, nitrate, carbon dioxide, methane, (sometimes hydrogen) and redox potential both inside and outside the contaminant plume	Determine assimilative capacity of aquifer. Evaluate the mechanisms and effectiveness of MNA processes.
Locations of nearest groundwater recharge areas (*e.g.*, canals, retention ponds, catch basins, and ditches)	Identify areas of natural groundwater aeration.

Source: Adapted from McAllister and Chiang, 1994.

One type of model that might be used instead of an analytical solution is a numerical model. Numerical models allow for complex geology, variable boundary conditions, transient flow and transport conditions, among other features. The features of the site that commonly lead to selection of a numerical model are heterogeneous transport properties (*e.g.*, hydraulic conductivity, porosity, etc.), complex stratigraphy, and irregular flow boundaries. In general, as the complexity of the model increases, so does the amount and quality of data required as input. The complexity of some sites may preclude modeling because of the investment in data collection and analysis that would be required. Prime examples are karst and fractured rock sites where the cost of determining the location of preferential pathways that control contaminant migration is likely to be prohibitive. It cannot be assumed that site complexity and size are proportional—it may be just as prohibitively expensive to adequately model a small site as a large site.

Determining the values of input parameters to the model is a major concern (and usually a major expense). Subsurface properties may be difficult to measure and vary tremendously even over small distances. Some parameters required by the model may not be measured, but rather estimated from the scientific literature, rules-of-thumb, or "guesstimation". Some required parameters may be theoretically ill-founded (*e.g.*, dispersivity) or based upon assumptions that may be only imperfectly met (*i.e.*, degradation by first order rate processes). Model results are only as good as the data that goes into them, assuming that the model being used is appropriate under the given conditions at the site. Where the input parameter sets are constructed from such a set of estimates and imperfect measurements, a large amount of uncertainty will exist in the model results. Without comparison to measured concentrations, fluxes and/or other model outputs, the ability of the model to reproduce observed field conditions will be unknown.

"Calibration" has been developed as the process for minimizing the differences between model results and field observations. Through model calibration a parameter set is selected that results in model output that best fits the observed data. But, because of the number of parameters that must be identified, calibration is known to produce non-unique results. This is particularly the case in heterogeneous environments where every parameter of the model can vary from point-to-point. Confidence in the model, however, is increased by using the calibrated model to predict the response to some additional concentration or flux data (*i.e.*, that were not previously used in calibration). At each step in this process additional site investigation data improves knowledge of the behavior of the system. Projecting future contaminant levels from observed current levels requires proper use of a simulation model. This process is uncertain for many reasons. Some of the simple reasons are related to inability to predict future land and water use, future weather patterns, uncharacterized subsurface variability, and others. Where confidence in the data is uncertain, the most conservative (*i.e.*, protective) assumptions and parameters should be used. As such, prediction can best be thought of as an extrapolation from existing conditions. Often, with each new set of field data, model input parameters are adjusted so that model output matches this most recent data, but earlier field conditions would not be accurately simulated using these newer input values. What this means is that model simulations of future behavior may be as inaccurate as are earlier simulations of present conditions. **Under no circumstances should predictive modeling be used as the sole justification for selecting an MNA remedy, nor for terminating long-term performance monitoring.**

Contaminated Soil

A detailed analysis of whether MNA is likely to be effective in meeting remediation objectives is understandably more involved than the simple screening procedure outlined earlier. Exhibit IX-14 lists the factors which influence the effectiveness of MNA for contaminated soil. The CAP should be closely examined to ensure that each of these factors has been addressed. The significance of each of these factors is discussed in the following sections.

Exhibit IX-14
Factors Affecting MNA Effectiveness: Contaminated Soil

Factor	Effect On Monitored Natural Attenuation
Permeability	Coarse-grained soils provide the greatest drainage and aeration, but may also promote contaminant leaching and migration.
Soil Structure and Layering	Layered soils inhibit vertical migration and dispersion of contaminants, but may promote lateral spreading.
Sorption Potential	Higher organic carbon content and smaller grain size in soil results in greater sorption of contaminants and retarded migration.
Soil Gas Composition	Presence of oxygen necessary for aerobic biodegradation. Measurement of other parameters provides information on biodegradation processes.
Soil Moisture	Required for microbial activity. Optimal moisture is between 12 and 30% by weight (75-90% of field capacity).
pH	Generally not a limiting factor within a wide range (4-9). Biodegradation activity is greatest between soil pH values of 6 to 8.
Temperature	Generally not a limiting factor within a wide range (0-45°C).
Microbial Community	Generally present in almost all subsurface environments.

Permeability

Soil "permeability" controls the rate at which fluids (gases and liquids) move through the unsaturated zone. This directly influences the rate at which contaminants are leached from the source area to the water table, as well as the rate of vapor movement through the soil. While there are a number of ways to measure the permeability of soil, arguably the most familiar measure is hydraulic conductivity, which is a function of the properties of both the porous medium and the fluid. Another common measure of permeability is intrinsic permeability, which is a function of the properties of only the porous medium. Intrinsic permeability and hydraulic conductivity are related through this equation:

$$K = k\frac{\rho g}{\mu}$$

where: K = hydraulic conductivity
k = intrinsic permeability
ρ = density of the fluid (in this case, water)
g = acceleration due to gravity
μ = viscosity (dynamic) of the fluid

Fine-grained soils (*e.g.*, clays and silts), have lower hydraulic conductivity than coarse-grained soils (*e.g.*, sand and gravel). Thus, sandy soils (which have a hydraulic conductivity of about 2 ft/day or greater) promote drainage and aeration, which is favorable to both the dispersion and biodegradation of contaminants. However, high permeability also promotes faster migration of contaminants, which could result in more rapid and severe groundwater impacts. Clays and silts on the other hand, which due to their high sorptive capacities (owing to both small particle size and higher organic matter content), typically result in slower migration (*i.e.*, retardation) of contaminants and less degradation than that observed in more permeable soils. Thus, even though biodegradation may take longer, there may be little or no impact to underlying groundwater resources.

Soil Structure and Layering

Soil structure refers to the arrangement of soil particles into groups. Soil structure can enhance or inhibit contaminant migration. Layered soils tend to hinder the vertical migration of contaminants while enhancing lateral spreading. Soil macropores (naturally occurring fissures, cracks, root holes, or animal burrows), however, can facilitate the vertical interchange of contaminants from the ground surface through the soil to groundwater, as well as in the reverse direction. Low-permeability layers can also reduce aeration of the soils, slowing aerobic biodegradation. The soil types and structures may be identified by reviewing soil boring logs. Impervious soil covers (*e.g.*, concrete, asphalt) restrict the infiltration of water and air downward through the unsaturated zone, which can reduce the leaching rate of contaminants, in addition to the rate of oxygen replenishment. While both of these effects can lead to reduced rate of biodegradation, in some situations the benefit afforded by reduction in leaching of contaminants to the groundwater may offset the decrease in rate of biodegradation of contaminants.

Sorption Potential

Sorption is the general term for the interaction between contaminants and particulate surfaces. There are two types of sorptive processes: adsorption, where an excess of contaminant molecules accumulate on the surface of the particle, and absorption, where there is relatively uniform penetration by contaminant molecules into the surface of the particle. Because the nature of the contaminant-solid interaction is difficult to measure even under laboratory conditions, and thus it is essentially wholly unknown in the field, the generic term "sorption" is used to describe the phenomena without regard to the exact mechanism. The solid, or sorbing material, is referred to as the sorbent; a contaminant, which sorbs to the solid sorbent, is referred to as a sorbate. Partitioning is the term used to describe the process by which the contaminant (usually from the liquid, gas, or dissolved phase) is sorbed onto the particle surface.

Sorption potential is closely associated with soil type and soil organic matter content. Finer-grained soils typically have a higher organic carbon content than coarser-grained soils, and the higher the organic content, the greater the tendency to sorb organic compounds. The range of organic carbon typically found in soil is from 1 to 3%. The organic matter content in subsurface soils is typically an order of magnitude or more lower than in surface soils because most organic residues are incorporated or deposited on the surface. Fine-grained soils have more binding sites that can immobilize hydrocarbon compounds in the soil matrix, and soils with a high organic carbon content (*i.e.*, > 2 percent) also have greater capacities for holding fluids, which retards downward migration and facilitates biodegradation.

Sorption is important because it slows down (or retards) the rate of advance of the contamination front in the subsurface. Contaminants that sorb tightly to soil particles may be less subject to transport in the gaseous phase or in solution, whereas contaminants that are not tightly sorbed can be transported through soils, aquatic systems, and the atmosphere. Sorption is usually reversible for petroleum fuel constituents, but the rates of sorption and desorption may not be the same. With respect to the impact on MNA, the higher the sorption potential, the greater the retardation of contaminant migration. Increased sorption will increase the time required for contaminants to reach receptors, allowing greater time for biodegradation to occur. Conversely, sorbed contaminants may not be available to microorganisms as a food source. In this case, the contamination may linger undegraded for exceedingly long periods of time during which they can act as a slow, steady source of contamination. This can be particularly troublesome where groundwater resources are impacted. If this is (or is likely to be) the situation, then more aggressive source mitigation efforts should be undertaken prior to selecting MNA as a remediation alternative.

Partitioning between the contaminant phase and the solid (soil) phase is described by the distribution (or sorption) coefficient (K_d), which is a function of the organic matter in the soil (f_{oc}) and the organic carbon partition coefficient (K_{oc}):

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

where:
K_d = distribution coefficient
K_{oc} = organic carbon partition coefficient
f_{oc} = fraction of organic carbon in the soil

K_{oc} values can range from 10^0 to 10^7. Compounds that have higher K_{oc} and K_d values tend to remain sorbed on soil and not migrate and dissipate as readily as those with lower K_{oc} and K_d values. The K_{oc} values of BTEX contaminants are all low, indicating relatively weak sorption potential, as shown in Exhibit IX-15. None of the BTEX contaminants will remain strongly sorbed to soils; rather, other factors such as volatilization and solubility will be more important to their degradation because these factors increase the likelihood that contaminants will dissipate. Heavier petroleum constituents tend to have greater K_{oc} values and will thus sorb more strongly to soils, retarding contaminant migration. MTBE and ethanol have even lower K_{oc} values than the BTEX components; therefore MTBE and ethanol will sorb poorly onto organic matter in the soil.

Soil Saturation Limit

Two of the primary concerns associated with contaminated soil are the potential for (1) generation of volatile emissions and (2) leaching of contaminants into groundwater. Each of these potentials is compound-specific and must be determined for each contaminant of concern.

Exhibit IX-15
K_{oc} Values For Common Petroleum Fuel Constituents

Contaminant	Soil Sorption Constant K_{oc} (L/kg)
Benzene	49
Toluene	95
Ethylbenzene	250
m-Xylene	190
o-Xylene	129
p-Xylene	260
MTBE	11
Ethanol	16
Naphthalene	1,300

Source: Suggested values from *CHEMFATE Database*, Syracuse Research Corp., http://esc.syrres.com/efdb/chemfate.htm

The soil saturation concentration (C_{sat}) corresponds to the contaminant concentration in soil at which the sorptive limits of soil particles, the solubility limits of soil pore water, and saturation of soil pore gas have been reached. Above this concentration, the soil contaminant may be present in free phase (*i.e.*, nonaqueous phase liquids for common petroleum hydrocarbons and other fuel additives). C_{sat} is a function of the amount of contaminant in the vapor phase in the pore spaces of the soil in addition to the amount dissolved in the soil's pore water and the amount sorbed to soil particles. The equation for C_{sat} is:

$$C_{sat} = \frac{S}{\rho_b}\left(K_d \rho_b + \theta_w + K_H \theta_a\right)$$

where:
C_{sat} = soil saturation concentration (mg/kg)
S = solubility in water (mg/L)
ρ_b = dry soil bulk density (kg/L)
K_d = distribution coefficient
θ_w = water-filled soil porosity (vol/vol)
K_H = Henry's Law constant (dimensionless)
θ_a = air-filled soil porosity (vol/vol)

At C_{sat} for a given contaminant, the emission flux from soil to air reaches a plateau and emissions will not increase above this level no matter how much more chemical is added to the soil. Therefore, the inhalation route of exposure is not likely to be of concern for those contaminants with regulatory threshold concentrations (*e.g.*, site-specific screening levels, or SSLs) above C_{sat}. However, if the concentration of a contaminant is above C_{sat}, there is a potential for free phase liquid to be present and accumulations of NAPL may occur at the water table. In such cases further investigation of potential groundwater impacts is necessary.

The equation above may be modified so that it may be used to determine whether contaminant concentrations in soil are likely to result in groundwater impacts. The modified equation is:

$$C_t = C_w \left\{ (K_{oc} f_{oc}) + \frac{\theta_w + \theta_a K_H}{\rho_b} \right\}$$

where: C_t = screening level in soil (mg/kg)
C_w = target leachate concentration (mg/L)
K_{oc} = organic carbon partition coefficient
f_{oc} = fraction of organic carbon in the soil
θ_w = water-filled soil porosity (vol/vol)
θ_a = air-filled soil porosity (vol/vol)
K_H = Henry's Law constant (dimensionless)
ρ_b = dry soil bulk density (kg/L)

In the above equation, C_w is set at the regulatory concentration limit for a specific contaminant. After plugging in site-specific values for the remainder of the parameters, C_t yields the maximum allowable soil concentration for that contaminant. If this value is less than measured concentrations in the soil, then groundwater contamination is likely and MNA is not an acceptable remediation alternative on the basis of soil contamination. To determine if MNA may be appropriate for the site, a detailed evaluation of the potential groundwater impacts must be conducted. For more information on the Soil Saturation Limit, see U.S. EPA, 1996b.

Soil Gas Composition

It is important to measure the concentration of oxygen, carbon dioxide, methane, and volatile organics in soil gas in the source area. This will yield information on the progress of biodegradation of petroleum contaminants. The oxygen concentration will yield information on the effectiveness of oxygen replenishment, which is essential for aerobic biodegradation. Carbon dioxide is an indicator of aerobic respiration as well. Methane production is the result of anaerobic metabolism. The concentration of volatile organics will indicate whether or not vapor migration could be a potential problem at the site. The presence of volatile organics is also an indicator of the distribution of contamination in the subsurface.

The vapor pressure of a contaminant is a measure of its tendency to evaporate, or to move from the product phase to air. Contaminants with higher vapor pressures (*i.e.*, those contaminants that readily evaporate at room temperature) more readily disperse, as they have a greater tendency to partition into the vapor phase and are, therefore, more mobile in soil vapor. Alternatively, contaminants with relatively low vapor pressures are less likely to vaporize and become airborne.

Volatilization from soil or groundwater is highest for contaminants with higher vapor pressures.

Soil Moisture

Soil moisture is largely a function of precipitation in the region and the retention capacity of the soil. Infiltrating precipitation transports oxygen and nutrients as it percolates downward through the subsurface soils. In addition, water facilitates the movement of bacteria to other parts of the soil, where they can continue to degrade petroleum contaminants. However, especially in areas covered by pavement, replenishment of soil moisture is limited, and the amount of average annual rainfall may overestimate the amount of moisture replenishment that actually occurs. This is important because a moderate level of soil moisture is necessary to support the growth of microbial populations. Also, microbes can only utilize petroleum hydrocarbons when the hydrocarbons are in the dissolved phase. In the unsaturated zone, soil moisture content of 75 to 90 percent of field capacity, is considered optimal for aerobic microbial activity. High precipitation and highly permeable soils lead to increased leaching rates to groundwater.

pH

Soils that have a pH of 6 to 8 generally promote optimal bacterial growth. However, the range under which significant biodegradation has been observed to occur is from 4 to 9 (Wilson, 2001). The significance of this is that biodegradation is not all that sensitive to pH, and minor variances from the optimal range usually will have no significant detrimental effect.

Temperature

As with pH, the temperature range under which biodegradation occurs is quite broad; significant biological activity has been observed under near freezing conditions to almost boiling. This is not to say that the rate of biodegradation will be the same all year long. Especially in colder climates, biodegradation rates measured during the summer season should not be assumed to continue all year 'round. Temperature measurements are also important because certain parameters (*e.g.*, pH, concentration of dissolved gases) are temperature dependent.

Microbial Community

Microbes capable of degrading petroleum products are present in almost all subsurface environments. Therefore, the exercise of collecting soil samples and conducting laboratory microcosm studies is generally not necessary. However, in some situations, it may be important to analyze soil samples with the intent of confirming the presence of hydrocarbon degrading microorganisms, and the absence of toxic levels of contaminants (*e.g.*, heavy metals, corrosive materials, and pesticides) that could inhibit the effectiveness of the microbial community. If microcosm studies are conducted, the collection of soil material, the procedures used to set up, monitor, and analyze the study, and the interpretation of the results should be based on established procedures, such as those described in Section C.3.4, "Design, Implementation, and Interpretation of Microcosms Studies", in EPA's Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (U.S. EPA, 1998) and/or Section 2, "Laboratory Studies", in EPA's report on Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions (U.S. EPA, 2000b).

Rate Constants and Degradation Rates

The selection of MNA as an appropriate remedy for a given site should be based on a comparison of the rate of remediation that is expected using natural processes to the rate that is expected from active remediation. For most LUST sites, natural biodegradation will be the most important component of natural attenuation. Biodegradation reactions involving organic chemicals occur at rates which are a function of various site-specific environmental conditions. Projections of natural biodegradation should be extracted from site-specific data, and not from rates published in the literature for other sites. Degradation rate constants determined in the laboratory are generally higher than rates that occur under field conditions. This is particularly true when the rate in laboratory is limited by the activity of the microorganisms and the rate in the field is limited by the supply of oxygen. Wherever possible, field-determined rates should be used to estimate the time required to achieve remediation objectives. A site-specific rate may not be constant over time, in both the short-term (*i.e.,* seasonally) and the long-term. Under no circumstances should such estimates be used as justification to close a site. Site closure decisions should be based on monitoring data, not predictions.

Time To Achieve Remediation Objectives

As with any remediation method, one of the fundamental questions that arises is "How much time will be required before remediation objectives are achieved?" Suitable methodology has been presented in the earlier "Screening" section. This same methodology should be employed here, but with site-specific parameters instead of the generic parameters we used to illustrate the methodology.

After estimating a time to achieve remediation objectives, it is necessary to evaluate whether or not this time is "reasonable" for a given site. As this is a site-specific decision, no single generic number can be presented in this chapter. In general, a "reasonable" time frame is one that is comparable to that which could be achieved through active remediation (U.S. EPA, 1999). Since there are typically a variety of potential remediation options for a given site, there is likely to be more than one estimate of time necessary to achieve remediation options. Evaluation of the most appropriate time frame must be determined through an analysis of the various remedy alternatives. Some of the factors that should be considered in making a determination as to which time frame (and remediation alternative) is most appropriate include:

- Subsurface conditions which can change over an extended time frame required to achieve remediation objectives;

- Whether the contamination, either by itself or as an accumulation with other nearby sources (on-site or off-site), will exert a long-term detrimental impact on available water supplies or other environmental resources;

- Uncertainties regarding the mass of contaminants in the subsurface and predictive analyses (*e.g.*, remediation time frame, timing of future demand, and likelihood of receptors coming in contact with contaminants);

- Reliability of monitoring (and, if implemented, institutional controls) over the entire length of the time period required to achieve remediation objectives;

- Public acceptance of the time frame required to reach remediation objectives; and

- Provisions by the responsible party for adequate funding of monitoring, performance evaluation, and regulatory oversight over the time period required to achieve remediation objectives.

In general the time frame required for MNA remedies is often longer than that required for more active remedies. As a consequence, the uncertainty associated with the above factors increases significantly. Adequate performance monitoring and contingency remedies should be utilized because of this higher level of uncertainty. When determining reasonable time frames, the uncertainty in estimated time frames should be considered, as well as the ability to establish performance monitoring programs capable of verifying the performance expected from natural attenuation in a timely manner. Statistical confidence intervals should be estimated for calculated attenuation rate constants (including those based on methods such as historical trend data and microcosm studies). When predicting remedial time frames, sensitivity analyses should also be performed to indicate the dependence of the calculated remedial time frames on uncertainties in rate constants and other factors. A statistical evaluation of the rate constants estimated from site characterization studies of natural attenuation of groundwater contamination often reveals that the estimated rate constants contain considerable uncertainty. As an example, analysis of natural attenuation rates from many sites indicates that a measured decrease in contaminant concentrations of at least one order of magnitude is necessary to determine the appropriate rate law to describe the rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a 95% level of confidence (Wilson, 2001). Due to variability resulting from sampling and analysis, as well as plume variability over time, smaller apparent reductions are often insufficient to demonstrate (with 95% level of confidence) that attenuation has in fact occurred at all (U.S. EPA, 1999). When these conditions cannot be met using MNA, a remedial alternative that more likely would meet these expectations should be selected.

Contaminated Groundwater

A detailed analysis of whether MNA is likely to be effective in meeting remediation objectives is understandably more involved than the simple screening procedure outlined earlier. Exhibit IX-16 lists the factors which influence the effectiveness of MNA for contaminated groundwater. The CAP should be closely examined to ensure that these factors have been addressed. The significance of each of these factors is discussed in the following sections.

Effective Solubility

Solubility is the amount of a substance that will dissolve in a given amount of another substance (*e.g.*, water). Therefore, a contaminant's solubility provides insight to its fate and transport in the aqueous phase. Contaminants that are highly soluble (*e.g.* MTBE, ethanol) have a tendency to dissolve into the groundwater and are not likely to remain in the sorbed phase. They are also less likely to volatilize from groundwater into soil vapor. Conversely, chemicals that have low water solubilities tend to remain either in the sorbed phase or are likely to volatilize into soil vapor. In general, lower molecular weight contaminants tend to be more soluble and, therefore, migrate and disperse much more readily in groundwater or soil moisture than do heavier contaminants.

Exhibit IX-16
Factors Affecting MNA Effectiveness: Contaminated Groundwater

Factor	Effect On Monitored Natural Attenuation
Effective Solubility	The greater the contaminant's solubility, the greater the dispersion in groundwater. However, in a mixture, the solubility of each component is reduced–effective solubility is less than pure phase solubility.
Henry's Law Constant	A measure of a contaminant's tendency to partition between the aqueous phase and gaseous phase. The higher the Henry's law constant, the greater the tendency to volatilize from the dissolved phase
Groundwater Seepage Velocity	Higher velocity increases migration of dissolved contaminants, also promotes reoxygenation and replenishment of electron acceptors.
Sorption and Retardation	Higher organic carbon content and smaller grain size in soil results in greater sorption of contaminants and retarded migration.
Retarded Contaminant Transport Velocity	Due to effects of sorption, contaminant transport velocity is lower than groundwater seepage velocity.
Precipitation/Recharge	Primary benefit is in transport of dissolved oxygen into subsurface. Recharge can also cause plumes to dive and evade monitoring system.
Geochemical Parameters	Provide information on assimilative capacity of aquifer and the nature and effectiveness of biodegradation processes.

When contaminants are released into the environment from a mixture such as a petroleum hydrocarbon fuel, the water solubility of each individual compounds is typically lower than its pure phase solubility. This reduced solubility is referred to as effective solubility and is a function of the mole fraction (or proportion) of a given component in the whole mixture. The effective solubility equation can be written as:

$$C_L = X \cdot S$$

where:
C_L = effective solubility
X = mole fraction of component in mixture (*e.g.*, NAPL)
S = pure phase solubility in water

For complex mixtures it is necessary to estimate the weight percent and an average molecular weight of the unidentified fraction of the NAPL before the calculation can be completed. The effective solubility relationship indicates that for groundwater in contact with NAPL, the total concentration of the contaminant in the plume remains constant, even if the total concentration of the NAPL in the soil increases. Stated another way, aqueous-phase concentrations in leachate will increase together with soil concentrations only while the soil contaminants are sorbed (there is no NAPL present on the groundwater). Once the soil concentration reaches a point where NAPL is present, the concentration in the plume reaches a maximum concentration determined by the mole fraction of the contaminant in the NAPL and it's aqueous solubility. Exhibit IX-17 lists the solubility of the BTEX contaminants, MTBE, and ethanol. The higher the solubility, the more likely it is that the contaminant will be transported with flowing groundwater. Less soluble components may also be transported, although the aqueous concentration will be lower. More soluble gasoline additives (*e.g.*, MTBE, other ethers) are transported farther and faster than hydrocarbons. Often these additives can be detected in distant wells long before hydrocarbons would arrive (if they weren't first biodegraded to below detection limits).

Henry's Law Constant

Partitioning of a contaminant between the dissolved phase and the vapor phase is governed by Henry's law, and the Henry's law constant is a measure of a contaminant's tendency to volatilize from groundwater into soil gas. Henry's law states that the concentration of a contaminant in the gas phase is directly proportional to the compound's concentration in the dissolved phase.

The equation for Henry's law is:

$$C_g = K_H \, C_w$$

where:
C_g = contaminant concentration in gas phase (atm)
K_H = Henry's law constant (atm □m^3/mol)
C_w = contaminant concentration in dissolved phase (mol/m^3)

As shown in Exhibit IX-18, the Henry's law constants for the BTEX compounds are relatively low, and those for MTBE and ethanol are even lower. This means that there will be relatively little volatilization from the dissolved phase to the gas phase, and there is even less tendency for this to occur as the plume dives below the top of the water table. The consequence of this is that volatilization can be neglected entirely when using models to simulate biodegradation. However, volatilization may be of concern with regard to the accumulation of vapors at unsafe or unhealthy levels in basements, parking garages, utility conduits, sewers, etc.

Permeability

Aquifer "permeability" controls the rate at which liquids move through the saturated zone. This directly influences the rate at which contaminants are transported from source areas to receptors. While there are a number of ways to measure the permeability of aquifer media, arguably the most familiar measure is hydraulic conductivity, which is a function of the properties of both the porous medium and the fluid. Another common measure of permeability is intrinsic permeability, which is a function of the properties of only the porous medium. Intrinsic permeability (*k*) and hydraulic conductivity (*K*) are related through this equation:

$$K = k\frac{\rho g}{\mu}$$

Exhibit IX-17
Solubilities of Common Petroleum Fuel Constituents

Constituent	Typical Percentage in Gasoline^{a}	Pure Compound Solubility in Water^{b} (mg/L) (25°C)	Effective Solubility in Water^{c} (mg/L) (25°C)
Benzene	1 to 4	1,780	24 to 95
Toluene	2 to10	515	12 to 60
Ethylbenzene	5 to 20	152	8 to 33
m-Xylene	↑ 2 to 8 (all 3 isomers) ↓	160	3 to 13
o-Xylene		220	3 to 14
p-Xylene		215	4 to 16
MTBE	0 to 15	51,000^{c}	5,600 to 8,760
Ethanol	0 to 10	infinite^{c}	57,000^{d}

Sources:

[a] *A Guide to the Assessment and Remediation of Underground Petroleum Releases*, API Publication 162, 3rd Edition, 1996.

[b] *Selection of Representative TPH Fractions Based on Fate and Transport Considerations, Volume 3,* Total Petroleum Hydrocarbon Criteria Working Group Series, 1997. *http://www.aehs.com/publications/catalog/contents/Volume3.pdf*

[c] Recommended values from *CHEMFATE Database*, Syracuse Research Corp., *http://esc.syrres.com/efdb/chemfate.htm*

[d] "Achieving Clean Air and Clean Water: the Report of the Blue Ribbon Panel on Oxygenates in Gasoline", September, 1999, *http://www.epa.gov/otaq/consumer/fuels/oxypanel/r99021.pdf*

Exhibit IX-18
Henry's Law Constants For Petroleum Fuel Constituents

	Henry's Law Constant (@20-25° C)		
Contaminant	(atm • m^{3}/mol)	(conc/conc)	(atm)
Benzene	5.55E-03	0.227	308
Toluene	6.64E-03	0.272	369
Ethylbenzene	7.88E-03	0.322	438
m-Xylene	7.43E-03	0.304	413
o-Xylene	5.19E-03	0.212	288
p-Xylene	7.66E-03	0.313	426
MTBE	5.87E-04	0.024	32.6
Ethanol	5.20E-06	0.0002	0.29

Source: Recommended values from *CHEMFATE Database*, Syracuse Research Corp., http://esc.syrres.com/efdb/chemfate.htm

where:
K = hydraulic conductivity
k = intrinsic permeability
ρ = density of the fluid (in this case, water)
g = acceleration due to gravity
μ = viscosity (dynamic) of the fluid

Fine-grained media (*e.g.*, clays and silts), have lower hydraulic conductivity than coarse-grained soils (*e.g.*, sand and gravel). Thus, sandy media (which have a hydraulic conductivity of about 2 ft/day or greater) promotes groundwater reaeration, which is favorable to both the dispersion and biodegradation of contaminants. However, high permeability also promotes faster migration of contaminants, which could result in more rapid and severe groundwater impacts. Clays and silts on the other hand, which due to their high sorptive capacities (owing to both small particle size and higher organic matter content), typically result in slower migration (*i.e.*, retardation) of contaminants and less degradation than that observed in more permeable soils.

Groundwater Seepage Velocity

Dispersion and migration of contaminants increases with increasing groundwater flow rate. True groundwater velocity is referred to as the seepage velocity. Seepage velocity can be calculated from:

$$q_s = -\frac{K\,I}{n_e}$$

where:
q_s = seepage velocity [L/T]
K = hydraulic conductivity [L/T]
I = hydraulic gradient [unitless]
n_e = effective porosity [unitless]

For a given hydraulic gradient, the higher the hydraulic conductivity the higher the seepage velocity. Transport of dilute dissolved contaminants is a function of advection, dispersion, and chemical and physical reactions. Advection refers to the movement imparted by flowing groundwater, and the rate of transport is usually taken to be equal to the *average* linear groundwater velocity. Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical mixing and causes the dissolved contaminant plume to spread out with distance from the source. Molecular diffusion is generally only significant when groundwater movement is very slow. Mechanical mixing occurs as groundwater flows through the aquifer matrix twisting around individual grains and through interconnected pore spaces at differing velocities. The movement of some dissolved contaminants may also be affected by chemical and physical reactions, such as sorption and biodegradation, which act to reduce the transport velocity and decrease concentrations in the plume.

Classical tracer studies devised to study advection-dispersion phenomena typically employ a cylindrical column filled with a porous media. A continuous supply of tracer at a specified concentration is introduced at one end of the column under steady flow conditions and outflow concentrations are measured at various times after the tracer is injected. A graph of the outflow concentration with time is known as a breakthrough curve. Such a graph shows concentrations gradually increasing with time. The inflection point of this curve represents the arrival time of an undiluted slug of contaminant moving at the *average* linear groundwater velocity. There are two problems with the comparison of true contaminant transport and an undiluted slug. First, due to the presence of the porous media, slug (or plug) flow is impossible. Even at a relatively small scale (such as these cylindrical columns) the "plume" of tracer would be dispersed with distance in the column due to molecular diffusion and mechanical. Second, some of the tracer molecules are moving faster than the average linear groundwater velocity, and some are moving slower. This is also true for the water molecules although the velocity of individual water molecules is never measured. A common misconception is, thus, that due to dispersion, contaminants may move faster than groundwater. A correct statement is that some contaminants may move faster than the *average* linear velocity of the groundwater. This distinction is very important. It also leads to another important realization, which is that if some contaminant molecules are traveling faster than the average linear groundwater velocity, then the *maximum* linear groundwater velocity rather than the *average* linear groundwater velocity should be used to calculate how long (or short) a time it will take contaminants to first reach a receptor.

Sorption and Retardation

As previously discussed in the soil contamination section, the organic carbon partition coefficient (K_{oc}) is an approximation of the propensity of a compound to sorb to organic matter found in the soil. The sorption coefficient (K_d) value is an expression of the tendency of a contaminant to remain sorbed on soil and is the product of K_{oc} and the fraction organic carbon (f_{oc}) in the soil. Sorption tends to slow the transport velocity of contaminants dissolved in groundwater. When the average velocity of a dissolved contaminant is less than the average seepage velocity of the groundwater, the contaminant is said to be retarded. The coefficient of retardation, R, is used to "correct" the contaminant transport velocity. Under conditions where sorption is adequately described by K_d, (which is when the fraction of organic carbon is greater than 0.001), the retardation coefficient can be determined from:

$$R = 1 + \frac{\rho_b K_d}{n}$$

where: R = coefficient of retardation [dimensionless]
ρ_b = bulk density of soil in the aquifer [M/L^3]
K_d = distribution coefficient [L^3/M]
n = porosity [dimensionless]

Typical retardation coefficients for various organic compounds and different organic carbon content are given in Exhibit IX-19.

Exhibit IX-19
Retardation Coefficients For Different Organic Compounds And Different Organic Carbon Content

Contaminant	**log (K_{oc})**	**Fraction of Total Organic Carbon (f_{oc}) in Soil**			
		0.0001 (low for aquifers)	**0.001 (median for aquifers)**	**0.01 (high for aquifers)**	**0.1 (typical of soils)**
MTBE	1.08	1.0	1.1	1.6	7
Benzene	1.58	1.0	1.2	2.9	20
Ethylbenzene	1.98	1.0	1.5	5.7	48
Toluene	2.13	1.1	1.7	7.6	68
Xylene (mixed)	2.38	1.1	2.2	13	120

Source: Wiedeimeier, *et al.*, 1999, Table 3-4, p. 145.

Retarded Contaminant Transport Velocity

As mentioned in the preceding section, sorption tends to slow the velocity of contaminants in a plume, but not the seepage velocity of the groundwater itself. To "correct" for the effect of sorption, the coefficient of retardation is used to adjust the groundwater seepage velocity:

$$q_c = \frac{q_s}{R}$$

where:
q_c = contaminant velocity [L/T]
q_s = groundwater seepage velocity [L/T]
R = coefficient of retardation

From the retardation equation in the preceding section, when the distribution coefficient (K_d) is equal to zero (which means there is no sorption effect), then the coefficient of retardation is equal to unity and the contaminant velocity (q_c) is equal to the seepage velocity (q_s). As the value of K_d increases, R also increases, and the contaminant velocity becomes more retarded (*i.e.*, decreases).

Another method that is commonly used to determine retarded contaminant transport velocity is to divide the measured length of the contaminant plume by it's known age. The advantage to this method is that the transport velocity is based on actual field data, and is therefore, site-specific. The danger inherent in this method is underestimation of the true transport velocity which leads to overestimation of the rate of biodegradation. This can occur if the measured length of the plume is shorter than the actual length of the plume. Such an underestimation of plume length is a common consequence of relying on "conventional" monitoring wells (rather than nested wells arrayed in transects) for delineation of the leading edge (or "toe") of the plume.

Precipitation/Recharge

Recharge from precipitation can also cause contaminant plumes (even those comprised of contaminants that are less dense than water) to "dive" below the level of the water table. The plume migrates deeper and deeper with increasing distance from the source. As a consequence, the plume may migrate undetected below the screened intervals of shallow monitoring wells. Note that this phenomenon does not require a downward vertical gradient. It is a consequence of a layer of fresh water accumulating on top of the contaminant plume so gently that significant mixing does not occur (there will be some diffusion from the plume into the overlying clean water, but this is a very slow process). This is one of the primary reasons why nested, or multi-level, wells are absolutely required for an adequate site characterization. Even for typical less-dense than water contaminants such as BTEX, plume diving is a common phenomenon. In areas where much of the ground surface is covered with an impervious layer such as concrete or asphalt, actual recharge (especially in the source area) may be only a fraction of the total amount of annual rainfall. This may slow down the process of leaching contaminants from the source mass causing it to linger as slow, but relatively steady, source of groundwater contaminants for an extended period of time.

Geochemical Parameters

Biodegradation of organic compounds results in measurable changes in the chemistry of the groundwater in the affected area. By measuring the temporal and spatial distribution of these chemical changes, it is possible to document and evaluate the extent to which natural attenuation processes are occurring. Isopleth (or isoconcentration) maps should be prepared for all contaminants of concern as well as each of the geochemical parameters discussed in this section. These maps will aide in the qualitative interpretation of data on the distribution and relative transport and degradation rates of the contaminants of concern. There are three general groups of chemical changes: electron acceptors, metabolic byproducts, and daughter products.

Electron acceptors are elements or compounds that occur in relatively oxidized states and include dissolved oxygen, nitrate, ferric iron, manganic manganese, hydroxide, sulfate, and carbon dioxide. These compounds are reduced through coupled oxidation and reduction reactions during microbial respiration to yield energy to the microorganisms for growth and activity.

Dissolved oxygen is typically the first electron acceptor to be utilized during the biodegradation of many organic compounds, including constituents of petroleum hydrocarbon fuels. As a consequence, the concentration decreases and dissolved oxygen concentrations below background levels indicate aerobic biodegradation is occurring. After dissolved oxygen concentrations in the aquifer fall below about 0.5 mg/L, anaerobic processes (initially denitrification) will begin if sufficient anaerobic electron acceptors are present. It is extremely difficult to get an accurate measurement of dissolved oxygen concentration. Several factors influence the aqueous solubility of dissolved oxygen including temperature. Other factors that can influence a reading include the instrument itself (the design, calibration, maintenance, and operation) and the sample collection technique (it is very easy to oxygenate a sample, yielding a falsely high level of dissolved oxygen). In spite of these difficulties, it is extremely important to collect groundwater samples for dissolved oxygen measurements as the difference between background concentrations and concentrations within the contaminant plume can be used to estimate the mass of contaminants that are aerobically biodegraded.

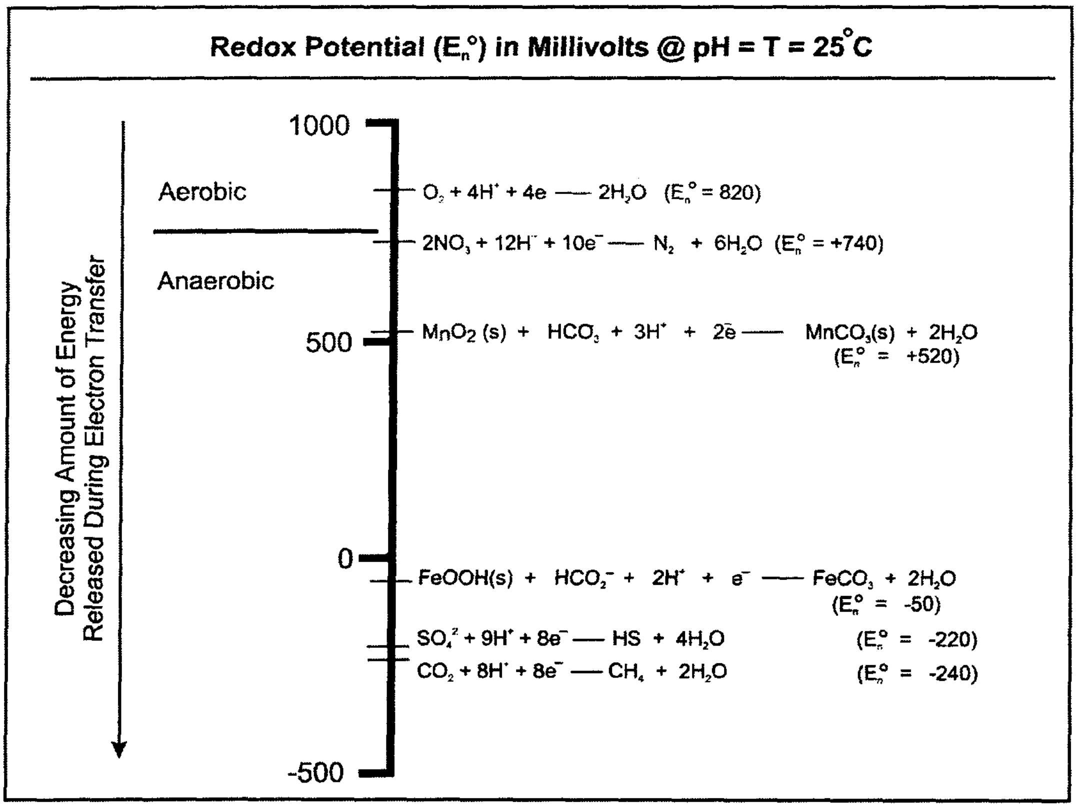
After dissolved oxygen has been depleted, biodegradation shifts from aerobic to anaerobic. The first anaerobic electron acceptor that may be utilized is nitrate by the process of denitrification. In the zone where denitrification is occurring, nitrate levels are lower than background. As with dissolved oxygen, the difference between levels within and outside the plume can be used to estimate the mass of contaminants being degraded by denitrification. The next electron acceptors to be oxidized under anaerobic conditions are manganic manganese, ferric iron, and sulfate. The final step in the anaerobic biodegradation series is methanogenesis, which utilizes carbon dioxide as the electron acceptor. As with nitrate (and dissolved oxygen before it), the difference between concentrations of these electron acceptors within and outside the plume can be used to estimate the mass of contaminants that are being degraded by each of these processes.

The sum of the estimated mass of degraded contaminants from all processes (both aerobic and anaerobic) can be used to provide an estimate of the biodegradative capacity of the subsurface system. Note that it is important to go through the exercise each time that samples are collected because natural processes are dynamic and even subtle changes can affect the rate and completeness of biodegradation. Such changes, if caught in time, will allow for contingency measures to be implemented should MNA prove not to be protective over the long period of time required to meet remediation objectives.

The second group of indicators of biodegradation are the metabolic byproducts. Each of the biodegradation processes mentioned above reduces an oxidized electron acceptor resulting in generation of measurable reduced species. The oxidation/reduction (redox) potential of groundwater is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Because redox reactions in groundwater are biologically mediated, the rates of biodegradation both influence and depend on redox potential. Many biological processes operate only within a prescribed range of redox conditions. The oxidation-reduction (redox) potential of the groundwater changes, with conditions becoming more reducing, through the sequence oxygen, nitrate, iron, manganese, sulfate, and carbonate. The redox potential of groundwater generally ranges from 800 millivolts to about -400 millivolts (Exhibit IX-20). The lower the redox potential, the more reducing and anaerobic the environment. Although the redox potential cannot be used for quantitative interpretation, the approximate location of the fuel hydrocarbon plume can be identified in the field through measurement of redox potential if background organic carbon concentrations are low. NOTE: field measurements will likely not be in the same units as indicated in Exhibit IX-20.

Each biodegradation process is also associated with a characteristic hydrogen concentration. By carefully measuring dissolved hydrogen concentrations, it is possible to distinguish among the various anaerobic zones. This level of detail is especially important at sites with chlorinated solvents, and less important for petroleum fuel hydrocarbon sites. Aerobic respiration, denitrification, iron and manganese reduction, and sulfate reduction result in generation of carbon dioxide. Though it is difficult to obtain an accurate measure of dissolved carbon dioxide because of carbonate in the groundwater, elevated levels of carbon dioxide relative

Exhibit IX-20
Redox Potentials For Various Electron Acceptors



Source: Modified from Norris et al., (1994)

to background may be observed and it is possible to estimate the degree of microbiological activity. Another consequence of carbon dioxide production is an increase in alkalinity. Alkalinity is important in the maintenance of groundwater pH because it buffers the groundwater system against acids produced during aerobic and anaerobic biodegradation. Measurement of dissolved inorganic carbon provides sufficient information to calculate alkalinity and CO_2. The reduction of oxidized forms of iron and manganese (Fe^{3+} and Mn^{4+}, respectively) results in the production of reduced species which are water soluble. Elevated levels of these reduced metals (Fe^{2+} and Mn^{2+}, respectively) in the plume relative to background is indicative of anaerobic biodegradation. Hydrogen sulfide is produced during sulfate reduction. Methane is produced by methanogenesis, which occurs only under strongly reducing conditions.

The third group of chemical indicators is daughter products. For most petroleum hydrocarbons daughter products are not significant. For MTBE, however, one of the intermediate degradation products is *tertiary*-butyl alcohol (TBA) which is more difficult to remediate than MTBE itself, and more toxic. However, TBA is also used as a fuel oxygenate in its own right, as well as an impurity in MTBE. Some conventional analytical techniques actually degrade MTBE and form TBA during sample analysis. When this occurs, obviously the analytical results are not representative of what's occurring in the subsurface. So, while the presence of TBA is of concern (and should be appropriately remediated) it does not necessarily indicate the biodegradation of MTBE and concentration data should not be used to establish biodegradation rates for MTBE–the estimated rate will likely be higher than what is actually occurring. Some of the daughter products of chlorinated solvents (particularly vinyl chloride) are of significant concern because of their toxicity.

Rate Constants and Degradation Rates

Rate constants for biodegradation or for the rate of bulk attenuation of contaminants in groundwater can be used to estimate how far a plume may extend. In some cases these rates can be incorporated into computer models, and the models can be compared to the existing distribution of contamination to determine if a plume is expanding or receding. However, they can not be used to estimate how long a plume will persist in the absence of source control. For most plumes, the rate of attenuation in ground water is faster than the rate of attenuation of the source. As a consequence, the persistence of the plume is controlled by the rate of attenuation of the source, and the rate of attenuation of the source must be understood to be able predict the time required to achieve remediation objectives.

A decision on whether or not MNA is an appropriate remedy for a given site is usually based on estimates of the rates of natural attenuation processes, and biodegradation rates in particular, for most LUST sites. Biodegradation reactions involving organic chemicals occur at rates which are a function of various site-specific environmental conditions. Quantifying the rate of biodegradation is important for biologically-mediated remediation alternatives, and especially MNA, since this rate is used to estimate the time required to achieve remediation objectives. It is important to note, however, that there are different types of rate calculations and it is imperative to use the constant that is appropriate for the given situation or the resultant "answer" will be incorrect. Biodegradation rate constants generally fall into three categories:

- *concentration vs. time attenuation rate constant:* the rate constant, in units of inverse time (*e.g.*, per day, time^{-1}), is equal to the slope of the line plotted as natural log of concentration vs. time measured at a selected monitoring location. This constant represents the change in source strength over time and can be used to estimate the time required to reach a remediation goal. Concentration vs. time constants provide information regarding potential source persistence at a single location only–they cannot be used to evaluate distribution of contaminant mass within the source area.

- *concentration vs. distance attenuation rate constant:* the rate constant, in units of inverse time (*e.g.*, per day, time^{-1}), is derived by plotting the natural log of concentration vs. distance, and (only if the data follow a first-order decay pattern) calculating the rate as the product of the slope of the line and the groundwater seepage velocity. Plots of concentration vs. distance serve to characterize the distribution of contaminant mass within space at a given point in time, but a single plot yields no information about the variation in concentration over time. These constants cannot be used to estimate the time required to meet a remediation goal. They indicate how quickly contaminants are *attenuated* (*e.g.*, accounting for sorption, dispersion, and biodegradation) once they leave the source area, but provide no information on how quickly a residual source zone is being attenuated. Because most LUST sites will, to some degree, have a lingering residual source (despite best efforts to completely recover free product), these constants are inappropriate for estimating plume longevity for most sites.

- *biodegradation rate constant:* the rate constant is denoted by the Greek lambda (□) and is in units of inverse time (*e.g.*, per day, time^{-1}). It can be derived in a variety of ways, including field tests and computer model simulations. The biodegradation rate constant is *NOT* the same as the concentration *vs.* distance attenuation rate constant since the latter reflects the combined effects of sorption, dispersion, and biodegradation. The biodegradation rate constant can be used to provide information on plume stability using models, but it *cannot* be used for estimating remediation time frames.

There are three commonly used models which describe the biodegradation of organic compounds in groundwater: (1) first-order decay, (2) Monod kinetics, and (3) "instantaneous reaction". Perhaps the most commonly used approach is to make the assumption that the biodegradation rate can be approximated using a first-order decay equation of the form:

$$C = C_0 \cdot e^{-kt}$$

where:

C = biodegraded contaminant concentration
C_0 = initial contaminant concentration
k = rate of decrease of contaminant (time^{-1})
t = time of interest

To estimate the time required to achieve a specific clean up goal, the above equation is rearranged to solve for t as follows:

$$t = \frac{\ln(C / C_0)}{-k}$$

In this configuration, C is the clean up goal concentration (or regulatory maximum allowable concentration), and C_0 is the most recent measured concentration. Note that if k is in units of "per day" (d^{-1}), then t will also be in days.

The first order decay model assumes that the solute degradation rate is proportional to the solute concentration. The higher the concentration, the higher the degradation rate. The primary advantage of this approach is that for many organic chemicals, k has been determined from laboratory experiments. The weaknesses of the model are that it does not account for site-specific information such as the availability of electron acceptors, and there is often considerable uncertainty in extrapolating laboratory constants to the field environment. In fact, there is substantial evidence that the first-order model may overestimate the amount of aerobic biodegradation of petroleum hydrocarbons. Under no circumstances laboratory-derived attenuation rates be used as the sole justification for selecting an MNA remedy, evaluating the length of time required to meet remedial objectives, or in deciding to terminate long-term performance monitoring.

One final advantage of using the first-order model is that first-order rate constants may easily be converted to half-lives ($t_{1/2}$) since they are inversely related to one another:

$$t_{1/2} = \frac{0.693}{k}$$

A more complex, and more accurate, model is the Monod kinetic model which is also referred to as the Michaelis-Menten kinetic model. This model is the hyperbolic saturation function and, for calculating the reduction in contaminant concentration, has the form:

$$\Delta C = M_t \mu_{\max} \frac{C}{K_c + C} \Delta t$$

where:
C = contaminant concentration
M_t = total microbial concentration
$\mu_{\max}$ = maximum contaminant utilization rate per unit mass microorganisms
K_c = half-saturation constant
Δt = time interval of interest

This model is actually quite complex; the graph of this rate equation has regions that are zero-order, first-order, and mixed-order. The rate constant accounts for both the activity of the degrading population and the dependence of the reaction on the substrate concentration. Although this model may be the most accurate of the three models, the difficulty in estimating $\mu_{\max}$ and K_c generally preclude its use under field conditions.

The "instantaneous reaction model" is also known as the electron-acceptor-limited model, and is used for simulating the aerobic biodegradation of petroleum hydrocarbons. The basis for this model is the observation that microbial biodegradation kinetics are fast in comparison with the transport of oxygen. The model assumes that the rate of utilization of the contaminant and oxygen by the microorganisms is very high, and that the time required to biodegrade the contaminant is very short (almost instantaneous) relative to the seepage velocity of the groundwater. The equation for the instantaneous reaction model using oxygen as the electron acceptor is:

$$\Delta C_R = -\frac{O}{F}$$

where:
ΔC_R = change in contaminant concentration due to biodegradation
O = concentration of oxygen in groundwater
F = utilization factor, the ratio of oxygen to contaminant consumed

The primary advantages of the instantaneous reaction model is that kinetic data are not required, because reactions are not limited by microbial kinetics. The model is, however, not applicable in all circumstances. Its applicability is limited to situations in which microbial biodegradation kinetics are fast relative to the rate of the groundwater flow that mixes electron acceptors with dissolved contaminants. There is increasing evidence that anaerobic biodegradation of petroleum hydrocarbons can be simulated using the assumption of instantaneous reactions (Wiedemeier, *et al.*, 1999).

Plume Migration

In determining whether a plume is shrinking, "stable" or migrating, the uncertainty associated with defining the limits of contaminant plumes should be considered. For example, a plume is typically delineated for each contaminant of concern as a 2- or 3-dimensional feature. Plumes are commonly drawn either by hand or computer contouring programs which estimate concentrations between actual data points. In reality, a plume boundary is defined by a zone rather than a line. Fluctuations within this zone are likely to occur due to a number of factors (*e.g.*, analytical, seasonal, spatial, etc.) which may or may not be indicative of a trend in plume migration. Therefore, site characterization activities and performance monitoring should focus on collection of data of sufficient quality and quantity to enable decisions to be made with a high degree of confidence. The only appropriate sites for a MNA remedy, therefore, are those where the plume can be statistically demonstrated to be shrinking. (See footnote #4, p.IX-19.)

Time Frame to Achieve Remediation Objectives

As with any remediation method, one of the fundamental questions that arises is "How much time will be required before remediation objectives are achieved?" At the current state of practice, the only practical approach available uses a statistical analysis of long term monitoring data from wells in the source area of the contaminant plume.

As an example of this approach, we'll use data presented by Kolhatkar *et al.* (2000). They collected long-term groundwater monitoring data from three wells at a gasoline release site in New Jersey. Their original data displayed extreme oscillations bouncing up and down from less than 1 µg/L to a high value and back over a single sampling interval. Although the scatter in the data set is typical of the variation seen at many other sites, the influence of these outliers on the statistical estimate of the rate of attenuation was removed by editing the data set to remove those points where the concentration of MTBE was less than 1 µg/L. These edited data are tabulated as Exhibit IX-21 and presented graphically as Exhibit IX-22.

The first order rate constant for attenuation was extracted from the data by taking the natural logarithm of the concentrations of MTBE in each well at each date and then, for each well, performing a linear regression of the natural logarithm of concentration on the time when the sample was collected. The slope of the regression for each well is the instantaneous rate of change of concentration of MTBE with time. The slope is the negative of the first order rate constant for attenuation. The rates calculated from the data in Exhibits IX-21 and XI-22 are presented in Exhibit IX-23. For purposes of illustration, the concentration at the last time of sampling and the rate constants were used to forecast the time required to reach a cleanup goal of 20 µg/liter.

Because there is natural scatter in the long-term monitoring data, there is uncertainty in the estimate of the rate of natural attenuation, in the projected time frame to achieve clean up. To account for this uncertainty, a confidence interval was calculated for each estimate of the rate of attenuation at a pre-determined level of confidence of 90% and 95% (Exhibit IX-23). The level of confidence is simply the probability that the true rate is contained within the calculated confidence

Exhibit IX-21
MTBE Concentration Measured In Monitoring Wells Over Time

MW-5		MW-6		MW-11	
Date	**Concentration (ppb)**	**Date**	**Concentration (ppb)**	**Date**	**Concentration (ppb)**
9/17/93	1,900	9/17/93	270	9/23/94	2200
9/23/94	1,800	9/23/94	200	5/17/96	880
5/17/96	1,300	5/17/96	120	11/7/96	660
8/10/96	980	8/10/96	120	12/8/97	339
11/7/96	620	11/7/96	66	3/27/98	426
12/8/97	500	3/27/98	71.2	7/23/98	419
3/27/98	635	9/18/98	44	12/16/98	144
7/23/98	470	3/1/99	42.2	3/1/99	123
9/18/98	1,210	9/7/99	43.2	6/21/99	464
12/16/98	379	3/20/00	36	9/7/99	195
3/1/99	700	6/22/00	51.2	9/7/99	155
6/21/99	574			12/30/99	220
9/7/99	792			3/20/00	173
9/7/99	1,050			6/22/00	146
12/30/99	525				
3/20/00	501				
6/22/00	420				

interval. Given the need to protect human health and the environment, and the absence of an active remediation system to serve as a fail-safe, a 90% confidence level is a reasonable level of confidence for many sites. At other sites a more stringent confidence level (*e.g.* 95%) may be more appropriate, depending the level of risk that is acceptable.

In most applications of regression the user wishes to calculate both an upper boundary and lower boundary on the confidence interval that will contain the true rate at the pre-determined level of confidence. This is termed a "two tailed" confidence interval because the possibility of error (the tail of the probability frequency distribution) is distributed between rates above the upper boundary and

Exhibit IX-22
MTBE Concentration Measured In Monitoring Wells Over Time

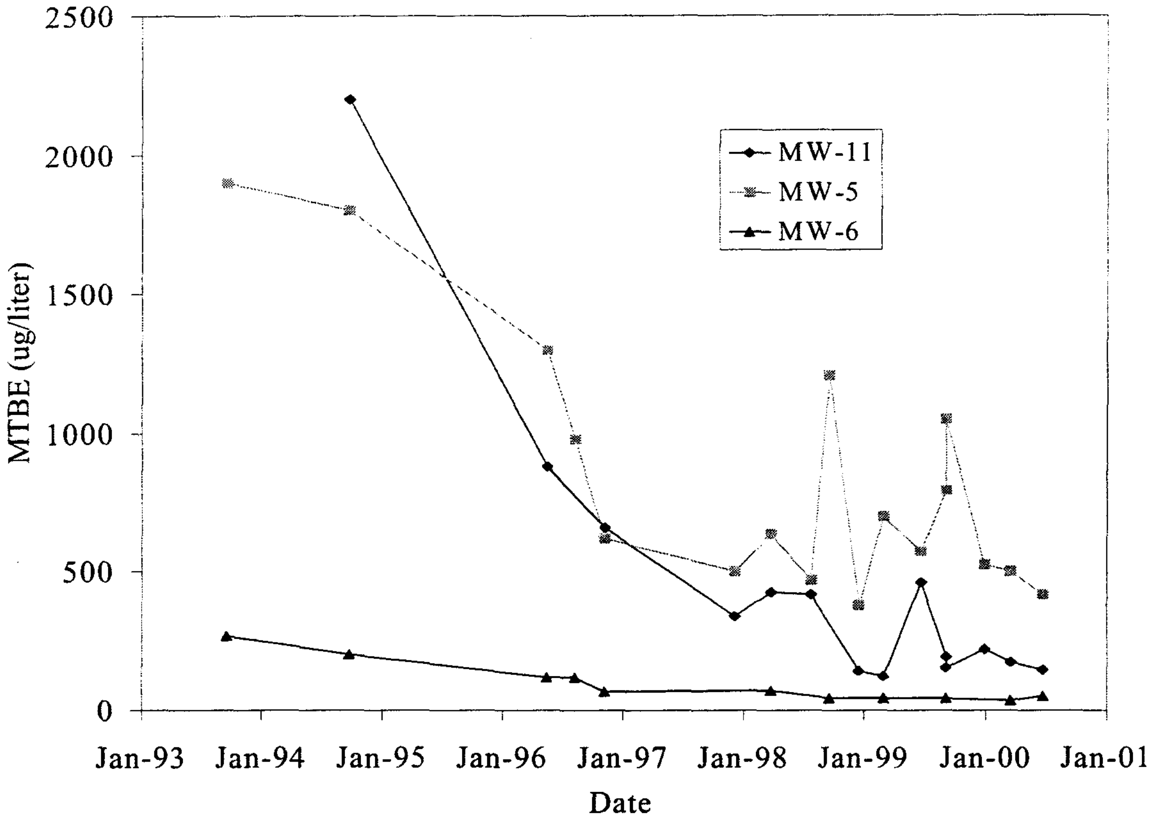


Exhibit IX-23
Rates Of attenuation Of MTBE In Monitoring Wells And The Projected Time Required To Reach A Clean Up Goal Of 20 µg/L As Calculated From The Data Presented In Exhibits IX-21 And IX-22

	MTBE (µg/L)		Estimated rate and time required		Rate and time significant at 90% confidence		Rate and time significant at 95% confidence	
Well	**First Sample 1993**	**Last Sample 2000**	**Rate (per year)**	**Time (years)**	**Rate (per year)**	**Time (years)**	**Rate (per year)**	**Time (years)**
MW-5	1900	420	0.188	16	0.127	24	0.109	28
MW-11	2200	146	0.453	4.4	0.365	5.4	0.337	5.9
MW-6	270	51.2	0.290	3.2	0.246	3.8	0.231	3.8

below the lower boundary of the confidence interval. As a consequence, tables of critical values in statistical reference books and computer applications provide a "two-tailed" confidence interval. At a 80% level of confidence, the estimate will be in error 20% of the time. The true rate will be contained within the calculated confidence interval 80% of the time, 10% of the time the true rate will be faster than the upper boundary of the confidence interval, and 10% of the time the true rate will be slower than the lower boundary of the confidence interval. Using the data in Exhibit IX-21 for MW-5, the slope of a regression of the natural logarithm of concentration of MTBE on time is -0.188 per year. The first order rate of change of concentration of MTBE on time is -0.188 per year, corresponding to a rate of attenuation of +0.188 per year. The boundaries of the "two tailed" confidence interval on the rate at 80% confidence are 0.248 per year and 0.127 per year. This means that 80% of the time the true rate will be between 0.248 and 0.127 per year, that 10% of the time the true rate is greater than 0.248 per year, and 10% of the time the true rate is less than 0.127 per year. The true rate will be greater than 0.127 per year 90% of the time.

Long-term monitoring data at many sites typically exhibits a great deal of variation. These variations are not necessarily errors in sampling and analysis of groundwater samples. In many cases they reflect real changes in the plume caused by seasonal variations in precipitation and groundwater elevations. These variations are a natural property of the plume. Where long-term monitoring data define a statistically significant trend of increasing contaminant concentrations, such sites are not appropriate candidates for MNA. Where the long-term monitoring data exhibit a statistically significant trend of decreasing concentrations, such sites may be appropriate for MNA. If no trend is discernible, then additional data should be collected over time. If the variation is large enough, one boundary of the "two tailed" confidence interval will be a positive number and the other boundary will be a negative number. When zero is included in the confidence interval on the rate, there is no evidence in the data that the true rate is different from zero. If this is the case it is possible that attenuation is occurring in that particular well over time, but the monitoring data do not present evidence that attenuation is occurring at the predetermined level of confidence. The variation in the monitoring data is too great to determine the trend over time one way or the other. Again, there is no appropriate role for MNA at these sites, because it is impossible to predict how long it will take to reach the clean-up goals.

There is little value in estimating the shortest possible time that would be required to reach the goals for clean up; remedial options are compared and evaluated based on the greatest time required to reach goals. At the selected level of confidence, all the possibility of error should be assigned to rates that are slower that the lower boundary of the confidence interval. This is a "one-tailed" confidence level; it includes all true rates that are faster than the lower boundary of the confidence interval. A "one tailed" confidence interval can be calculated as the slower of the two confidence intervals from a "two-tailed" test that has twice the uncertainty. In the example above, where "two tailed" confidence intervals were calculated for a confidence level of 80%, the true rate will be greater than a rate of 0.127 per year 90% of the time. The "one tailed" confidence intervals reported in Exhibit IX-23 were calculated in this fashion.

Note that for a given number of observations, as the level of confidence is increased, the interval that is expected to contain the real value for the rate constant increases as well. As the level of confidence increases, the lower boundary on the rate constant decreases, and the projected time required to meet the clean up goal increases. In the examples presented in Exhibit IX-23, the estimated rate of natural attenuation of MTBE in MW-5 is 0.188 per year, which requires 16 years to attain a concentration of 20 µg/L. At a 90% confidence level, the lower boundary of the confidence interval is 0.127 per year, which requires 24 years to meet the goal. At a 95% confidence level, the lower boundary is 0.109 per year, which requires 28 years to reach the goal. At the 95% confidence level the upper bound of the time expected to reach the clean up goal has increased by a factor of almost two (from 16 years to 28 years). This does not necessarily mean that the actual time to achieve cleanup will be 28 years; it simply means that the length of time that will actually be required is estimated to be no more than 28 years at a 95% level of confidence.

The ability to extract a rate of attenuation from long term monitoring data is related to the number of measurements, and the time interval over which they are collected. As an example, the rate of attenuation extracted from the last three years of monitoring data for well MW-5 (3/27/98 to 6/22/2000 in Exhibit IX-21 and IX-22) is 0.106 per year, but the "one tailed" 90% confidence interval is all rates greater than -0.125 per year. The confidence interval includes zero. If only these three years of data were available, there would be no evidence of natural attenuation of MTBE in well MW-5 at 90% confidence. The rate extracted from the last four years of data (5/17/1996 to 6/22/2000) is 0.130 per year. The 90% confidence interval on the rate (0.0302 per year) would reach the clean-up goal in 100 years. As presented in Exhibit IX-23, the rate extracted using all the seven years of monitoring data is 0.188 per year. The 90% confidence interval on the rate would reach cleanup in 24 years. A few extra years of monitoring data have a strong influence on the ability to extract useful rate constants.

Rate constants for natural attenuation can be used to project the time required to reach a clean-up goal once the source has been adequately addressed. However, there are a number of key points to keep in mind. First, an appreciable record of long term monitoring data must be available to make a statistically valid projection of the rate of natural attenuation. As a practical matter it is difficult to extract rate constants that are statistically significant with fewer than six sampling dates, or with a sampling interval of less than three years. Second, it is unrealistic to expect just a few years of monitoring data to accurately predict plume behavior several decades into the future. Third, it is important to realize that these estimates are merely estimates and that the true rate is likely to change over time. Fourth, under no circumstances should such estimates be used as justification to close a site. Site closure decisions should be based on actual long term monitoring data, not predictions. Fifth, monitoring should continue at any given site for a specified period of time (typically 1 to 2 years or more) after cleanup goals have been achieved to ensure that contaminant levels do not rebound and exceed the required cleanup level due to long-term fluctuations in groundwater table elevation or changes in flux from lingering vadose zone contamination.

After estimating a time to achieve remediation objectives, it is necessary to evaluate whether or not this time is "reasonable" for a given site. As this is a site-specific decision, no single generic number can be presented in this chapter. In general, a "reasonable" time frame is one that is comparable to that which could be achieved through active remediation (U.S. EPA, 1999). Since there are typically a variety of potential remediation options for a given site, there is likely to be more than one estimate of time necessary to achieve remediation options. Evaluation of the most appropriate time frame must be determined through an analysis of the various remedy alternatives. Some of the factors that should be considered in making a determination as to which time frame (and remediation alternative) is most appropriate include:

- Classification of the affected resource (*e.g.*, drinking water source, agricultural water source) and value of the resource;
- Relative time frame in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies);
- The stability of ground water flow in the aquifer. How might the plume change over the extended time frame necessary to achieve remediation objectives;
- Reliability of monitoring and of institutional controls over long time periods;
- Public acceptance of the time frame required to reach remediation objectives; and
- Provisions by the responsible party for adequate funding of monitoring and performance evaluation over the time period required to achieve remediation objectives.

Long-Term Performance Monitoring

The two fundamental objectives of performance monitoring are to verify that: (1) contaminant levels are decreasing, and (2) contamination is not spreading (*i.e.*, the plume is not migrating, but rather is shrinking). Due to the potentially longer remediation time frames, potential for ongoing contaminant migration, and other uncertainties associated with using MNA, performance monitoring is of even greater importance for MNA than for other types of remedies. The monitoring program developed for each site should specify the location, number, frequency, and type of samples and measurements necessary to evaluate whether the remedy is performing as expected and is capable of attaining remediation objectives. The objectives for all monitoring programs should include the following:

- Demonstrate that natural attenuation is occurring according to expectations;
- Detect changes in environmental conditions (*e.g.*, hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes;
- Identify any potentially toxic and/or mobile transformation products;
- Verify that the plume(s) is shrinking;
- Verify no unacceptable impact to downgradient receptors;
- Detect new releases of contaminants to the environment that could impact the effectiveness of the MNA remedy;
- Verify attainment of remediation objectives.

The frequency of monitoring should be adequate to detect, in a timely manner, the potential changes in site conditions listed above. At a minimum, the monitoring program should be sufficient to enable a determination of the rate(s) of attenuation and how that rate is changing with time. When determining attenuation rates, the uncertainty in these estimates and the associated implications should be evaluated (see McNab and Dooher, 1998). Flexibility for adjusting the monitoring frequency over the life of the remedy can be included in the monitoring plan. For example, it may be appropriate to decrease the monitoring frequency at some point in time, once it has been determined that natural attenuation is progressing as expected or very little change is observed from one sampling round to the next. In contrast, the monitoring frequency may need to be increased if unexpected conditions (*e.g.*, plume migration) are observed. Exhibit IX-24 is a flowchart that can serve as a roadmap to guide you in evaluating the long-term performance monitoring plan. A table summarizing the contaminants to monitor and the suggested monitoring frequency is presented as Exhibit IX-25, while more specific details are discussed in the sections that follow.

Performance monitoring should continue until remediation objectives have been achieved, and generally for a period of 1 to 2 years longer to ensure that contaminant levels remain below target levels. Under no circumstances should the results of predictive modeling (including statistical extrapolation) be used to justify a decision to terminate performance monitoring. This decision should be based only on adequate field data that convincingly demonstrates that contaminant levels have met remediation objectives. The institutional and financial mechanisms for maintaining the performance monitoring program should be clearly established in the remedy decision or other site documents, as appropriate.

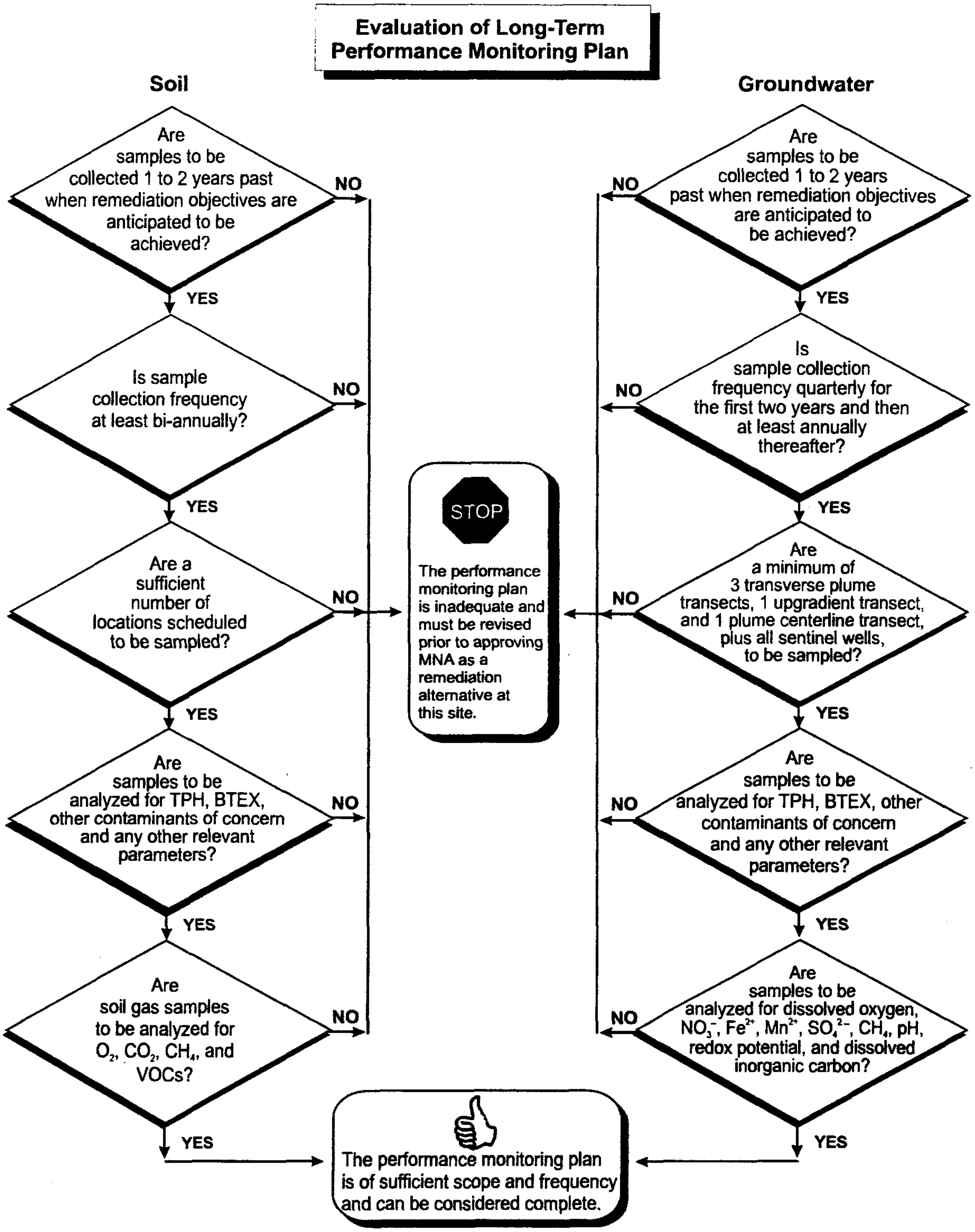
As with the active remediation technologies also described in this manual, if MNA does not appear to be effective in remediating the contamination at the site within a reasonable time frame, then an alternative active remedial technology (specified in the contingency plan section of the CAP) will be required.

Contaminated Soil

For a given volume of contaminated soil, the objective of sampling is to collect a minimum number of samples such that, with a satisfactory degree of confidence, the spatial distribution of contamination is accurately defined. Because this process will be repeated multiple times in the future, the methodology for selecting sampling locations and physically collecting the samples must be robust.

MNA is assumed to be effective if both the volume and the mass of contaminants are lower with each successive sampling event, and that after some reasonable period of time, contaminant levels fall below (and remain below) remediation objectives. One of the challenges of routine soil sampling is collecting sequential samples that can be compared with earlier samples in the series. Soil sampling is by its nature destructive, so once a discrete sample is collected, another one cannot be collected from exactly that same point in space. There is an implicit assumption that a future sample, collected in close proximity to a past sample, will be close enough so that the analytical results can be compared to determine if concentrations are decreasing at that location. At a minimum, samples should be collected from locations where contamination is known to be greatest (*i.e.*, source area) from previous sampling events. Generally, eight samples per sampling event should be sufficient to demonstrate whether or not concentrations are decreasing.

Exhibit IX-24



Evaluation of Long-Term Performance Monitoring Plan

Exhibit IX-25
Performance Monitoring Frequency, Analytes, And Sampling Locations

Medium	Monitoring Frequency	What To Monitor	Where/Number Of Samples To Monitor
Soil	at least bi-annually	BTEX; TPH; any other contaminants of concern; Soil gas O_2 ,CO_2, and CH_4.	a statistically significant number of continuous soil cores located throughout the area of contamination.
Groundwater	quarterly for the first two years, then at least annually thereafter.	BTEX; TPH; any other contaminants of concern; D.O., Fe^{2+}, SO_4^{2-},CH_4, NO_3^-,Mn^{2+} pH, and dissolved inorganic carbon.	a minimum of 3 perpendicular transects through the plume, 1 perpendicular transect up gradient of the plume, with multiple depth-discrete samples collected from each location, plus all sentinel wells (if any)

Sampling events should occur at least bi-annually (*i.e.*, every two years) to demonstrate reductions in contaminant concentrations.

Soil samples should be analyzed for the BTEX contaminants, TPH, and any other contaminants of concern at the site. If the primary contaminants of concern at the site are volatile organic chemicals (VOCs), monitoring of soil gas should supplement direct soil measurements at some locations. In addition, soil gas samples should be analyzed for oxygen, carbon dioxide, and methane (and sometimes hydrogen) to determine the microbial activity in the soils. As described above, reduced oxygen concentrations and elevated carbon dioxide concentrations (relative to background) in both the source area, and soils overlying the dissolved plume, are a good indication that biodegradation is occurring.

Contaminated Groundwater

Typically, groundwater monitoring wells are installed during site characterization activities (and often during active remediation), and, being permanent fixtures (relative to soil sampling locations) there is not as much uncertainty about the locations from which to collect groundwater samples (*i.e.*, wells) as there is about soil sample collection. The fundamental objectives, however, are the same: define the extent of contamination in three-dimensions, and identify trends in concentration levels.

Groundwater monitoring should be designed to ensure that the vertical and lateral extent of contaminants in groundwater is evaluated. Each distinct flow zone and geochemical regime should be monitored to assess remediation status. In general, for each distinct flow zone at the site, the following locations should be monitored: background, source area, main body of the plume, and the distal portions and boundaries.

Typical target zones for monitoring a contaminant plume include:

- *Source areas, and within and immediately downgradient of potential source areas.* The monitoring objective is to estimate a source mass which is critical for determining potential source longevity. These sampling points will also enable determination of future contaminant releases to the environment.

- *Flow zones with highest contaminant concentrations or hydraulic conductivity.* These are the zones where maintenance of a steady state or shrinking plume is a primary concern. A change in conditions in these zones may lead to a relatively rapid impact to a down-gradient receptor.

- *Distal or fringe portions of the plume.* These are areas where reductions of contaminants to levels required by remedial action objectives (*e.g.*, site-specific cleanup targets) may be attained most rapidly and where increases in concentrations that indicate impending plume expansion may be observed.

- *Plume boundaries.* Multi-level monitoring points should be placed at the side gradient, downgradient, and vertical plume boundaries, and between these boundaries and potential receptors. Results from these monitoring locations may directly demonstrate any unacceptable plume expansion.

- *Zones in which contaminant reduction appears to be recalcitrant.* These are the areas where attaining cleanup targets within reasonable time frames may be impeded due to site conditions (*e.g.*, presence of residual source materials, low flux of electron receptors). Such areas, if present, will be determined through data obtained throughout the performance monitoring period. These areas may require additional characterization and remedial actions to reduce contaminant concentrations to desired levels.

- *Background locations.* Background locations include monitoring points that are hydraulically up gradient and side gradient with respect to the plume. Multiple monitoring points should be used to determine the variability of background conditions. Data concerning the movement of electron receptors, donors, and any contaminants into the plume are required to interpret data from the plume. Background geochemical data is used to determine whether the observed differences in geochemical parameter concentrations within the plume are due to contaminant transformation processes rather than natural variations. Changes in geochemistry within the plume may not be directly related to attenuation of the contaminants, so geochemical changes outside the plume should be assessed and compared to geochemical changes taking place within the plume. If up gradient and lateral monitoring points show geochemical changes similar to changes in the plume, such changes may not be attributable solely to contaminant-related processes (*i.e.*, degradation), and therefore may not serve as supporting evidence for degradation processes.

Another type of well that should be monitored on a regular basis is a sentinel well. This is a well that is located between the leading downgradient edge of the dissolved plume and a receptor (*e.g.*, a drinking water supply well). A sentinel well(s) should be located far enough up gradient of any receptor to allow enough time before the contamination arrives at the receptor to initiate other measures to prevent contamination from reaching the receptor, or in the case of a supply well, provide for an alternative water source. A contaminated sentinel well provides an early warning that the plume is migrating. For those responsible for site remediation, this is a signal that MNA is not occurring at an acceptable rate and the contingency remedy should be implemented. For the downgradient well users, an alternate supply of water may be required.

In order to demonstrate that MNA is occurring, a sufficient number of monitoring wells that are appropriately located (both horizontally and vertically) are necessary. The density of sampling points will depend on site geology and hydrology, the overall size of the contaminant plume and the spatial scales at which contamination distribution varies horizontally, vertically, and temporally, and the desired level of confidence in the evaluation. Plumes vary significantly in concentration laterally and in vertical cross-section, making evaluation of contamination distribution and remedy performance difficult. Therefore, a dense network of multi-level monitoring points is required.

The recommended approach is to construct monitoring points that are positioned in transects both in the direction of groundwater flow as well as perpendicular to it (see Exhibit IX-26 for an optimal network design). The horizontal and vertical spacing of the monitoring clusters in each transect is determined by the scale of the hydrogeological heterogeneities that control contaminant transport and the dimension and spatial heterogeneity of the resulting contaminant distribution. The horizontal distance between transects is generally based on changes in contaminant concentration along the plume, and the location of the source and distal portions of the plume. The use of a transect-based approach to monitoring will greatly reduce the uncertainty in performance monitoring evaluations at sites by improving the definition of contaminant distribution and variability in three-dimensions. Transects also provide a better definition of contaminant distribution under conditions of changing hydraulic gradients. With reference to Exhibit IX-26, recommended transects would be as follows:

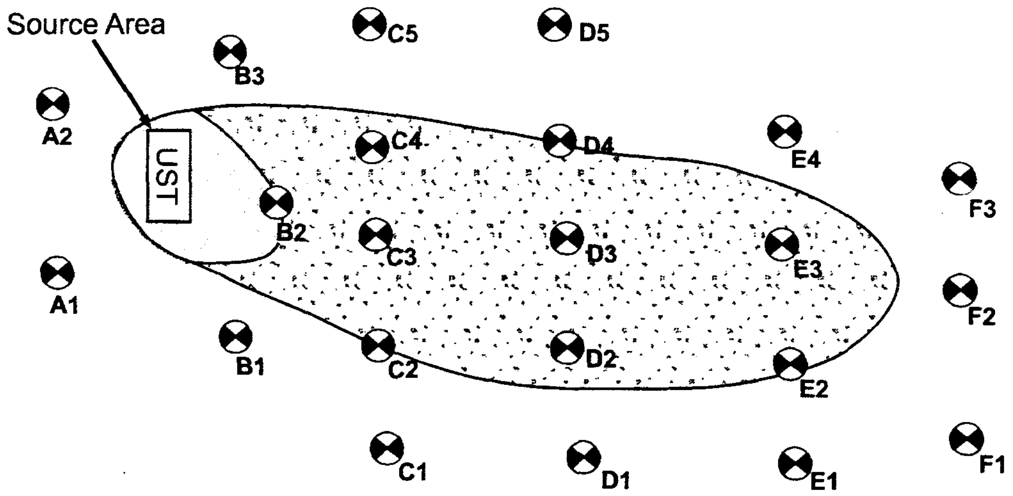
- source zone: B1 through B3
- mid-plume (transverse to flow): either C1 through C5, or D1 through D5
- plume toe: E1 through E4
- up gradient: A1 and A2
- plume centerline: B2-C3-D3-E3

Groundwater monitoring should be conducted no less than quarterly during the first two years to allow for determination of seasonal variation. Some sites may require quarterly (or more frequent) sampling for more than two years in order to establish a statistically significant trend. Thereafter, sampling frequency might then be reduced depending upon contaminant travel times and other site-specific factors (*e.g.*, travel time to nearest receptor). At a minimum, groundwater sampling should be conducted on an annual basis after the first two years.

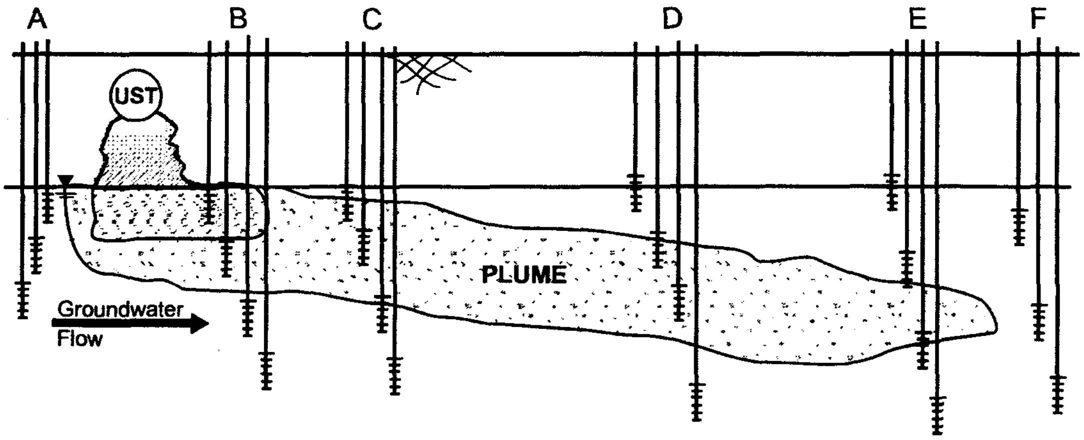
Groundwater samples should be analyzed for VOCs and other contaminants of concern, TPH (near the source area), dissolved oxygen, pH, temperature, redox potential, alkalinity, hardness, and other geochemical indicators as indicated in Exhibit IX-25. Isopleth (or isoconcentration) maps should be prepared for all contaminants of concern as well as each geochemical parameter. These maps will aide in the qualitative interpretation of data on the distribution and relative transport and degradation rates of the contaminants of concern.

Exhibit IX-26
Example of Optimal Groundwater Sampling Network Design for Performance Monitoring

Note: Figure not to scale.

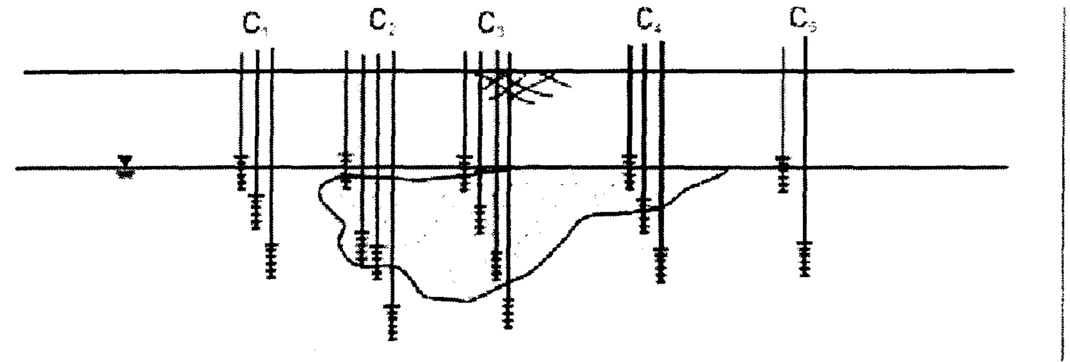


(A) Plan view of Optimal Groundwater Monitoring Network

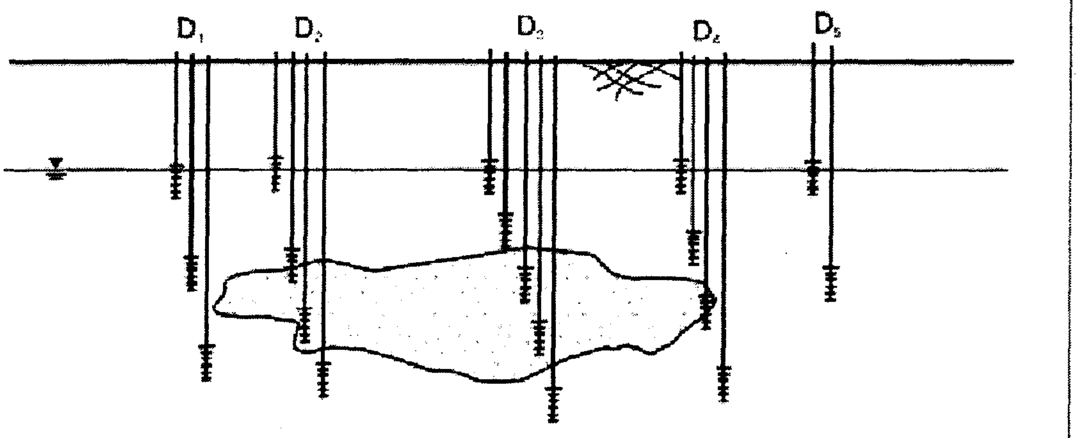


(B) Longitudinal Cross-Section of Optimal Groundwater Monitoring Network

Exhibit IX-26
(continued)



(C) Transverse Cross-section of Optimal Groundwater Monitoring Network at Transect "C"



(D) Transverse Cross-section of Optimal Groundwater Monitoring Network at Transect "D"

Note: Figure not to scale.

Contingency Plan

A contingency remedy is a cleanup technology or approach specified in the site remedy decision document that functions as a "backup" remedy in the event that the selected remedy (in this case MNA) fails to perform as anticipated. A contingency remedy may specify a technology (or technologies) that is (are) different from the selected remedy, or it may simply call for modification of the selected technology, if needed. Contingency remedies should generally be flexible—allowing for the incorporation of new information about site risks and technologies. It is also recommended that one or more criteria ("triggers") be established, as appropriate, in the remedy decision document that will signal unacceptable performance of the selected remedy and indicate when to implement contingency remedies. In establishing triggers or contingency remedies, however, care is needed to ensure that sampling variability or seasonal fluctuations do not unnecessarily trigger a contingency.

Contaminated Soil

Trigger criteria for contaminated soil should generally include, but not be limited to, the following:

- Contaminant concentrations in soil that are not decreasing as originally predicted during remedy selection;
- Migration of vapors into nearby structures (*e.g.*, sewers, basements);
- Near-source samples show large concentration increases indicative of a new or renewed release; and
- Changes in land use that might result in exposure.

Potential contingency remedies which are documented in other chapters of this guidance manual are: Thermal Desorption (Chapter VI), Land Farming (Chapter V), Biopiles (Chapter IV), SVE (Chapter II), Bioventing (Chapter III), Enhanced Aerobic Bioremediation (Chapter XII), and Chemical Oxidation (Chapter XIII).

Contaminated Groundwater

Trigger criteria for contaminated groundwater should generally include, but not be limited to, the following:

- Increasing contaminant concentrations in groundwater or the appearance of free product in monitoring wells;
- Near-source wells exhibit large concentration increases indicative of a new or renewed release;
- Contaminants are identified in monitoring wells located outside of the original plume boundary;
- Impacts to nearby receptors (especially wells) indicating that MNA is not protective;
- Contaminant concentrations are not decreasing at a sufficiently rapid rate to meet the remediation objectives;
- Concentrations of geochemical parameters are changing such that they indicate a declining capacity to support biodegradation of contaminants; and
- Changes in land and/or groundwater use will adversely affect the protectiveness of the MNA remedy.

Potential contingency remedies which are documented in other chapters of this guidance manual are: Air Sparging (Chapter VII), Biosparging (Chapter VIII), In-Situ Groundwater Bioremediation (Chapter X), Dual-Phase Extraction (Chapter

XI), Enhanced Aerobic Bioremediation (Chapter XII), and Chemical Oxidation (Chapter XIII).

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Checklists: Evaluating CAP Completeness andPotential Effectiveness of MNA

These checklists can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, complete the appropriate checklists which follow. They can be attached to the CAP for quick future reference. If the answer to any of the questions below is no, then the CAP is incomplete and you will need to request additional information to determine if MNA will achieve remediation objectives at the site.

Initial Screening–Soil Contamination ONLY

Site Name:

Date

Address1:

Initials

Address2:

Project/Case Number:

Recommendation:

Yes	No	
○	○	Has source mass been estimated?
○	○	Is the source mass likely to remain trapped within the soil?
○	○	Has source longevity been estimated?
○	○	Is the estimate of the length of time required to meet remediation objectives reasonable?
○	○	Is there no threat of potential receptors coming in contact with contaminated soil?
○	○	Is there no threat to potential receptors from vapor migration?

Initial Screening–Groundwater Contamination

Site Name:________________________________ **Date** ____________

Address1:________________________________ **Initials**__________

Address2:________________________________

Project/Case Number:________________________

Recommendation:____

____

____

____

____

Yes	No	
○	○	Has free product (if present initially) been recovered to the maximum extent practicable?______________________________
○	○	Has source mass been estimated? ___________________________
○	○	Has the plume lifespan been estimated? ______________________
○	○	Is the estimate of the length of time required to meet remediation objectives reasonable?______________________________ ____
○	○	Based on evaluation of field data, is the plume shrinking?______________ ______________________________
○	○	Are all potential receptors located at a distance represented by a minimum 2-year travel time?______________________________

Detailed Evaluation–Soil Contamination

Site Name:________________________________ **Date** ____________

Address1:________________________________ **Initials**__________

Address2:________________________________

Project/Case Number:____________________________

Recommendation:____

____

____

____

Yes	No	
○	○	Has comprehensive, 3-dimensional site characterization been completed?____________________________
○	○	Has soil permeability been measured?____________________
○	○	Is soil structure and layering conducive to natural attenuation processes?____________________________
○	○	Has soil organic carbon content (f_{oc}) been measured?____________________________
○	○	Have soil saturation limits been calculated for all contaminants of concern?____________________________
○	○	Are all soil saturation limits for all contaminants of concern below levels expected to cause unacceptable groundwater impacts? ____________ ____
○	○	Have soil gas samples been collected and analyzed?______________
○	○	Have soil geochemical parameters been measured and are they likely to support long-term biodegradation?______________________ ____
○	○	Have rate constants or biodegradation rates been calculated?____ ____
○	○	Is the estimated time to achieve remediation objectives reasonable?____________________________
○	○	Is there no current or future threat to potential receptors?__________ ____

Detailed Evaluation–Groundwater Contamination

Site Name:______________________ **Date** __________

Address1:______________________ **Initials**__________

Address2:______________________

Project/Case Number:______________________

Recommendation:______________________

____

____

____

____

Yes	No	
○	○	Has comprehensive, 3-dimensional site characterization been completed?____________
○	○	Has the hydraulic conductivity of the most permeable transport zone been measured?____________ ____________
○	○	Has the retarded contaminant transport velocity been estimated? ____________
○	○	Has the propensity for plume diving been determined?____________
○	○	Have contaminants of concern been measured for all monitoring points?____________
○	○	Have geochemical parameters been measured for all monitoring points?____________
○	○	Have isopleth maps been prepared for each parameter? ____________
○	○	Have rate constants or biodegradation rates been calculated?____________ ____________
○	○	Is the estimated time to achieve remediation objectives reasonable?____ ____________
○	○	Is there no current or future threat to potential receptors?____________ ____________

Long-Term Performance Monitoring–Soil Contamination

Site Name:______________________________ **Date** ___________

Address1:______________________________ **Initials**_________

Address2:________________________________

Project/Case Number:__________________________

Recommendation:____

____

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Yes	No	
○	○	Does the monitoring schedule extend for 1-2 years past when remediation objectives are expected to be achieved? _____________
○	○	Is sample collection frequency at least bi-annually?__________________________________
○	○	Are a sufficient number of locations to be sampled?_____________ _______________________________________
○	○	Are samples to be analyzed for BTEX, TPH, and other contaminants of concern (if any)?______________________________ _______________________________________
○	○	Are supplemental soil gas samples to be collected and analyzed?______ _______________________________________

Long-Term Performance Monitoring–Groundwater Contamination

Site Name:__________________________ **Date** __________

Address1:__________________________ **Initials**__________

Address2:__________________________

Project/Case Number:__________________________

Recommendation:____

____

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____

Yes	**No**	
○	○	Does the monitoring schedule extend for 1-2 years past when remediation objectives are expected to be achieved?____________ ____
○	○	Is sample collection frequency at least quarterly for the first two years?________________________________
○	○	Is sample collection frequency after the first two years at most annually? ____
○	○	Are a minimum of 3 transverse plume transects, 1 up gradient transect, and 1 plume centerline transect scheduled to be sampled every sampling event?________________________________
○	○	Are all sentinel wells (if any) scheduled to be sampled every sampling event? ____
○	○	Are samples to be analyzed for BTEX, TPH, and other contaminants of concern (if any)?____________________________ ____
○	○	Are samples to be analyzed for geochemical indicators and degradation products?________________________________ ____

Chapter XII

Enhanced Aerobic Bioremediation

Contents

List of Exhibits

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Chapter XII
Enhanced Aerobic Bioremediation

Overview

Enhanced aerobic bioremediation technologies are used to accelerate naturally occurring in-situ bioremediation of petroleum hydrocarbons, and some fuel oxygenates such as methyl tertiary-butyl ether (MTBE), by indigenous microorganisms in the subsurface. Enhanced aerobic bioremediation technologies include biosparging; bioventing[1]; use of oxygen releasing compounds; pure oxygen injection; hydrogen peroxide infiltration; and ozone injection[2]. These technologies work by providing a supplemental supply of oxygen to the subsurface, which becomes available to aerobic, hydrocarbon-degrading bacteria. The stoichiometric ratio of oxygen per hydrocarbon is 3 M O_2 per 1 mole of hydrocarbons. Oxygen is considered by many to be the primary growth-limiting factor for hydrocarbon-degrading bacteria, but it is normally depleted in zones that have been contaminated with hydrocarbons. By using these technologies, rates of biodegradation of petroleum hydrocarbons can be increased at least one, and sometimes several, orders of magnitude over naturally-occurring, non-stimulated rates.

Enhanced aerobic bioremediation technologies can be used to address contaminants in the unsaturated zone, the saturated zone, or both. Bioventing, for example, specifically targets petroleum hydrocarbon contaminants in the unsaturated zones and does not address contaminants in the capillary fringe or saturated zone. Most, but not all, enhanced aerobic bioremediation technologies primarily address petroleum hydrocarbons and some oxygenates that are dissolved in groundwater or are sorbed to soil particles in the saturated zone. The technologies are typically employed outside heavily contaminated source areas which will usually be addressed by more aggressive remedial approaches.

When used appropriately, enhanced aerobic bioremediation technologies are effective in reducing levels of petroleum contamination at leaking underground storage tank sites. Gasoline constituents dissolved in water are a likely target of enhanced aerobic bioremediations. Enhanced aerobic bioremediation technologies are most often used at sites with mid-weight petroleum products (e.g., diesel fuel,

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[1] For more information on Biosparging and Bioventing, see *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002), Chapter III ("Bioventing") and Chapter VIII ("Biosparging").

[2] Other enhanced aerobic bioremediation technologies, including surfactant enhanced microbubble injection and permeable polymeric tubing oxygen diffusion, are not discussed in this chapter because of their limited use and experimental status.

readily and can be removed more rapidly using other technologies (e.g., air sparging or soil vapor extraction). However, if these lighter products are present, enhanced aerobic bioremediation technologies can also effectively reduce contaminant concentrations. Heavier petroleum products such as lubricating oils generally take longer to biodegrade than the lighter products, but enhanced aerobic bioremediation technologies may still be effective at sites contaminated with these products.

It is generally not practical to use enhanced aerobic bioremediation technologies to address free mobile product or petroleum contamination in low permeability soil (e.g., clay). Because enhanced aerobic bioremediation is a relatively slow cleanup approach, it is not recommended to address current or imminent excessive human health or environmental risks.

Exhibit XII-1 summarizes the general advantages and disadvantages of enhanced aerobic bioremediation technologies. Discussions of bioventing and biosparging, two other enhanced aerobic bioremediation technologies, are provided in *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002, 2004), Chapter III ("Bioventing"), Chapter VIII ("Biosparging"), and Chapter X ("In-Situ Groundwater Bioremediation").

A brief description of several of the technologies is provided below.

Oxygen Releasing Compounds

Various enhanced aerobic bioremediation approaches rely on oxygen releasing compounds to remediate petroleum contamination. More commonly used oxygen releasing compounds include calcium and magnesium peroxides that are introduced to the saturated zone in solid or slurry phases. These peroxides release oxygen to the aquifer when hydrated by groundwater as the peroxides are ultimately converted to their respective hydroxides. Magnesium peroxide has been more commonly applied in field applications than calcium peroxide because of magnesium peroxide's lower solubility and, consequently, prolonged release of oxygen. Magnesium peroxide formulations placed in the saturated zone during a short-term injection event can release oxygen to groundwater over a four- to eight- month period. Significant quantities of magnesium peroxide are required based on stoichiometry and the fact that 90% of the weight of the compound is not oxygen. Oxygen amounting to approximately 10% of the weight of magnesium peroxide placed in the saturated zone is released to the aquifer over the active period.

Exhibit XII-1
Enhanced Aerobic Bioremediation
Primary Advantages and Disadvantages

Advantages

- Works with and enhances natural in-situ processes already at play (typically uses natural groundwater gradient, naturally occurring biodegradation)
- Destroys the petroleum contamination in place
- Produces no significant wastes (off-gases or fluid discharges)
- Can be a low-energy approach
- Is relatively inexpensive
- Complements more aggressive technologies (e.g., groundwater extraction) and less aggressive approaches (e.g., intrinsic remediation) that can be integrated into site remediation
- Causes minimal disturbance to site operations
- Has simple operation and monitoring requirements
- Is potentially more reliable than other, more active remedial technologies (e.g., groundwater extraction and treatment)
- Can be used in tandem with other remedial technologies that address small amounts of residual soil and groundwater contamination

Disadvantages

- May have longer remedial time frames than more aggressive approaches
- May not be able to reduce contaminants to background or very low concentrations
- Typically requires long-term monitoring of residual contamination in soil and groundwater
- May require permits for nutrient/oxygen injection
- May not be fully effective on all petroleum hydrocarbons and product additives (e.g., MTBE)
- Often must be accompanied by other technologies (e.g., product recovery) to address source areas
- May significantly alter aquifer geochemistry
- Can be misapplied to remediation at some sites if the conditions for use are not fully understood
- Oxygen supplied by enhanced aerobic bioremediation may be lost to chemical reactions in the subsurface which do not promote hydrocarbon contaminant oxidation and degradation.

Exhibit XII-2 compares the relative advantages and disadvantages of several different enhanced aerobic bioremediation technologies currently in use.

Exhibit XII-2
Enhanced Aerobic Bioremediation Technologies Comparative Matrix

	Oxygen Releasing Compounds	Hydrogen Peroxide Infiltration	Pure Oxygen Injection	Ozone Injection	Biosparging	Bioventing
Advantages						
No mechanical components required	X					
Minimal engineering design requirements	X					
Relatively low capital and operating costs	X					
Abiotic oxidation of contaminants contacting reagents		X		X		
Remediates contamination in unsaturated soils	X	X	X	X	X	X
Locally saturates groundwater with oxygen to further enhance biodegradation and oxygen distribution	X	X	X	X		
Can efficiently sustain widespread ambient (up to 8 mg/L) oxygen concentrations in groundwater					X	
Can efficiently sustain widespread ambient (up to ~21%) oxygen concentrations in unsaturated soils						X
Generally con[illegible]ed safe	X					X
Electricity/power source generally not required	X	X				

Exhibit XII-2
Enhanced Aerobic Bioremediation Technologies Comparative Matrix (continued)

	Oxygen Releasing Compounds	Hydrogen Peroxide Infiltration	Pure Oxygen Injection	Ozone Injection	Biosparging	Bioventing
Disadvantages						
Heavy reliance on groundwater advection, dispersion, and diffusion to distribute oxygen can limit treatment coverage and prolong remediation	X	X	X			
Increased risk of fugitive vapors entering building structures and utility conduits, particularly in absence of vapor recovery technology (e.g., soil vapor extraction)			X	X	X	
Does not target or treat saturated zone						X
On-site reactive chemical handling and storage required		X				
On-site gas production and delivery equipment (e.g., ozone generator) typically required			X	X		
Relatively few petroleum remediation projects completed using this technology		X	X	X		
May require reinjection permits	X	X			X	X
Radius of influence limited if using "socks"	X					
Zone of influence may be limited with compounds that are suspended in a well.	X					

Oxygen releasing compounds may be introduced into the saturated zone in several ways. The most common approaches include:

- Placing the compounds into drilled boreholes or other excavations (e.g., tank fields)
- Injecting a compound slurry into direct-push borings (e.g., Geoprobe)

- Mixing oxygen-releasing compounds directly with contaminated soil and then using the mixture as backfill or hauling it to a disposal site
- Suspending oxygen releasing compounds contained in "socks" in groundwater monitoring wells
- A combination of the above

Oxygen-releasing compounds may also be used to address source areas, entire plumes or plume tails (e.g., a treatment curtain aligned perpendicular to contaminant flow direction). Exhibit XII-3 provides a conceptual depiction of the deployment of oxygen releasing compounds to address a petroleum hydrocarbon plume. Many site-specific conditions must be considered before a remedial approach using this technology can be devised and implemented. One such site-specific concern is the proximity of drinking water supply wells to the treatment area and how the injected oxygen or other nutrients may affect these wells. Another concern is the limited zone of influence of oxygen releasing compounds when deployed in a well, which often provide increased oxygen levels only up to twice the diameter of the well. While the scope of this document does not allow a more in-depth discussion of this or other site-specific implementation, it is important to carefully consider site-specific issues (e.g., contaminant composition and behavior, site geology and hydrology) along with the conceptual information provided in this chapter.

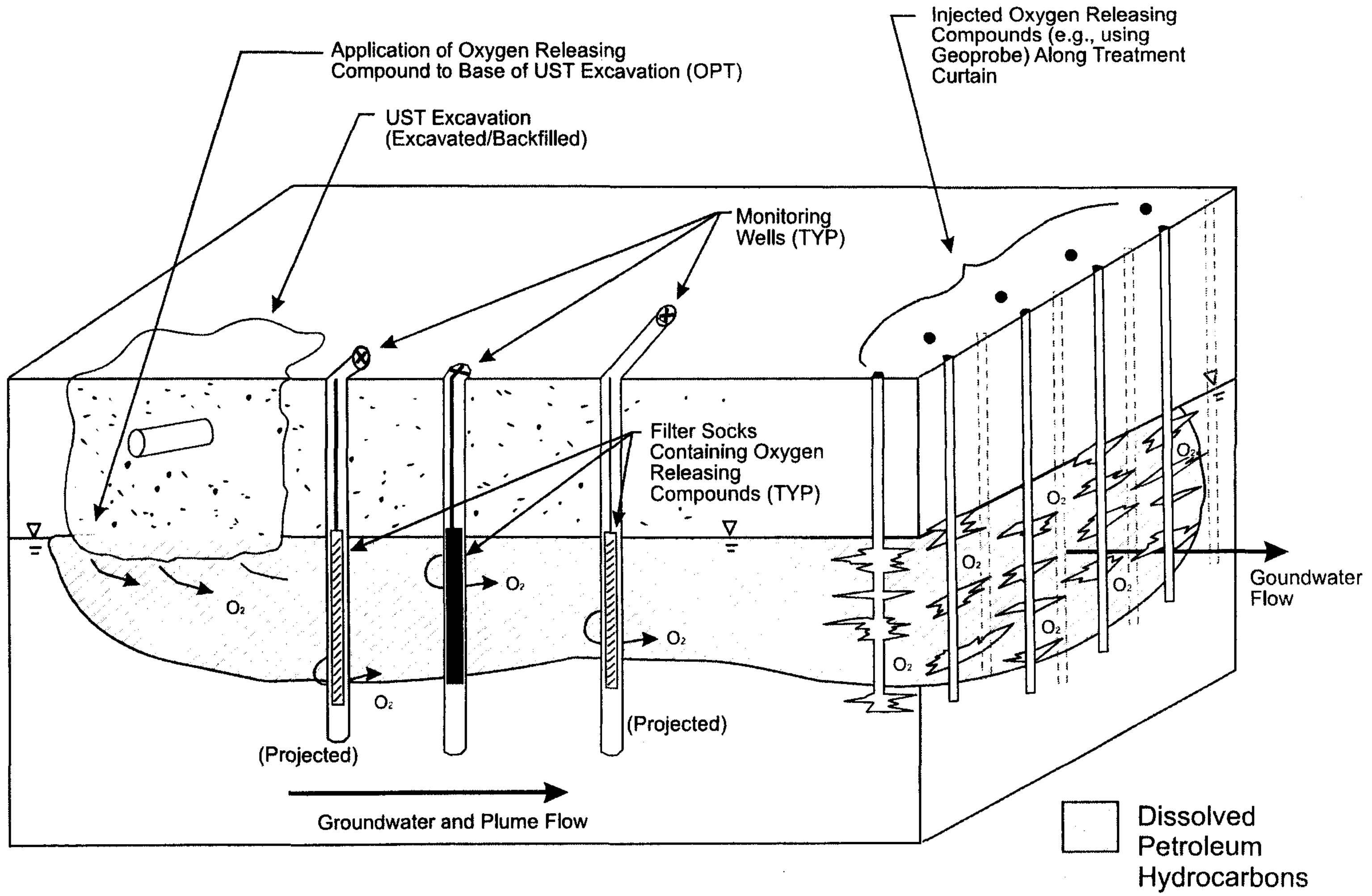
The following sections describe the use of pure oxygen injection, hydrogen peroxide infiltration, and ozone injection.

Pure Oxygen Injection

Injecting pure oxygen into groundwater can be a relatively efficient means of increasing dissolved oxygen levels in groundwater to promote aerobic biodegradation of petroleum hydrocarbons. In contrast to other enhanced aerobic bioremediation technologies, there is no carrier (e.g., amended groundwater) or delivery media (e.g., oxygen releasing compounds slurry) associated with pure oxygen injection. Approximately one gram of oxygen is delivered to the subsurface for every gram of oxygen directed to the subsurface. Oxygen is several times more soluble in groundwater when it is introduced in pure form than if the dissolved oxygen is derived by forcing groundwater to come into contact with atmospheric air, such as occurs with biosparging. Dissolved oxygen concentrations of up to 40-50 parts per million(ppm) can be achieved through pure oxygen injection, which contrasts to dissolved oxygen concentration limits of approximately 8-10 ppm when the saturated zone is aerated using atmospheric air, which contains approximately 21% oxygen.

Pure oxygen is most commonly introduced into the subsurface via vapor-phase injection. Vapor-phase oxygen (approximately 95% oxygen) is injected into the saturated zone near the base of the dissolved petroleum hydrocarbon contamination using a network of sparge wells. Oxygen sparge rates lower than

Exhibit XII-3
Typical Enhanced Aerobic Remediation Using Oxygen Releasing Compounds



air sparge flow rates are used in order to maximize contact time between the oxygen and contaminated groundwater before the injected oxygen rises through the contaminated zone to the water table. Trapping of sparged oxygen in the soil matrix (e.g., in soil pore spaces or semi-confining laminates) beneficially prolongs contact between the pure oxygen and the oxygen-depleted groundwater. Series of vertical oxygen injection wells are often alternately sparged in order to increase dissolved oxygen levels more efficiently over larger areas.

The spacing of injection wells is typically site-specific and based on the thickness of contaminated material, geology, hydrogeology, and other factors affecting the delivery and distribution of dissolved oxygen. Volatile organic vapor production and migration concerns are reduced with oxygen sparging relative to air sparging because of the significantly lower oxygen sparge air flow rates. However, vapor production and migration can be a concern and should be evaluated on a site-specific basis. A conceptual schematic of a pure oxygen injection system is depicted in Exhibit XII-4.

Hydrogen Peroxide Infiltration

Extracted and treated groundwater is amended and mixed with hydrogen peroxide prior to re-infiltration or re-injection. The hydrogen peroxide-amended groundwater is pumped into infiltration galleries or injection wells located in or near suspected source areas. Generally, the infiltration/injection and groundwater extraction scheme is designed to promote the circulation and distribution of hydrogen peroxide and dissolved oxygen through the treatment area.

Exhibit XII-5 provides a conceptual illustration of a hydrogen peroxide enhanced aerobic bioremediation system. The precipitation of chemical oxidants (e.g., iron oxides) can present potentially significant equipment fouling problems in this type of system, depending on the concentrations of naturally occurring levels of inorganic compounds, such as iron, in the subsurface.

Introducing hydrogen peroxide, which is a chemical oxidant, to the saturated zone can significantly augment existing oxygen levels because it naturally decomposes rapidly, generating oxygen. For each part (e.g., mole) of hydrogen peroxide introduced to groundwater, one-half part of oxygen can be produced. Hydrogen peroxide has the potential of providing some of the highest levels of available oxygen to contaminated groundwater relative to other enhanced aerobic bioremediation technologies because it is infinitely soluble in water. In theory, 10% hydrogen peroxide could provide 50,000 ppm of available oxygen.

However, when introduced to groundwater, hydrogen peroxide is unstable and can decompose to oxygen and water within four hours. This limits the extent to which the hydrogen peroxide may be distributed in the subsurface before it is transformed. Introducing concentrations of hydrogen peroxide as low as 100 ppm can cause oxygen concentrations in groundwater to exceed the solubility limit of

Exhibit XII-4
Typical Enhanced Aerobic Remediation Using Pure Oxygen Injection

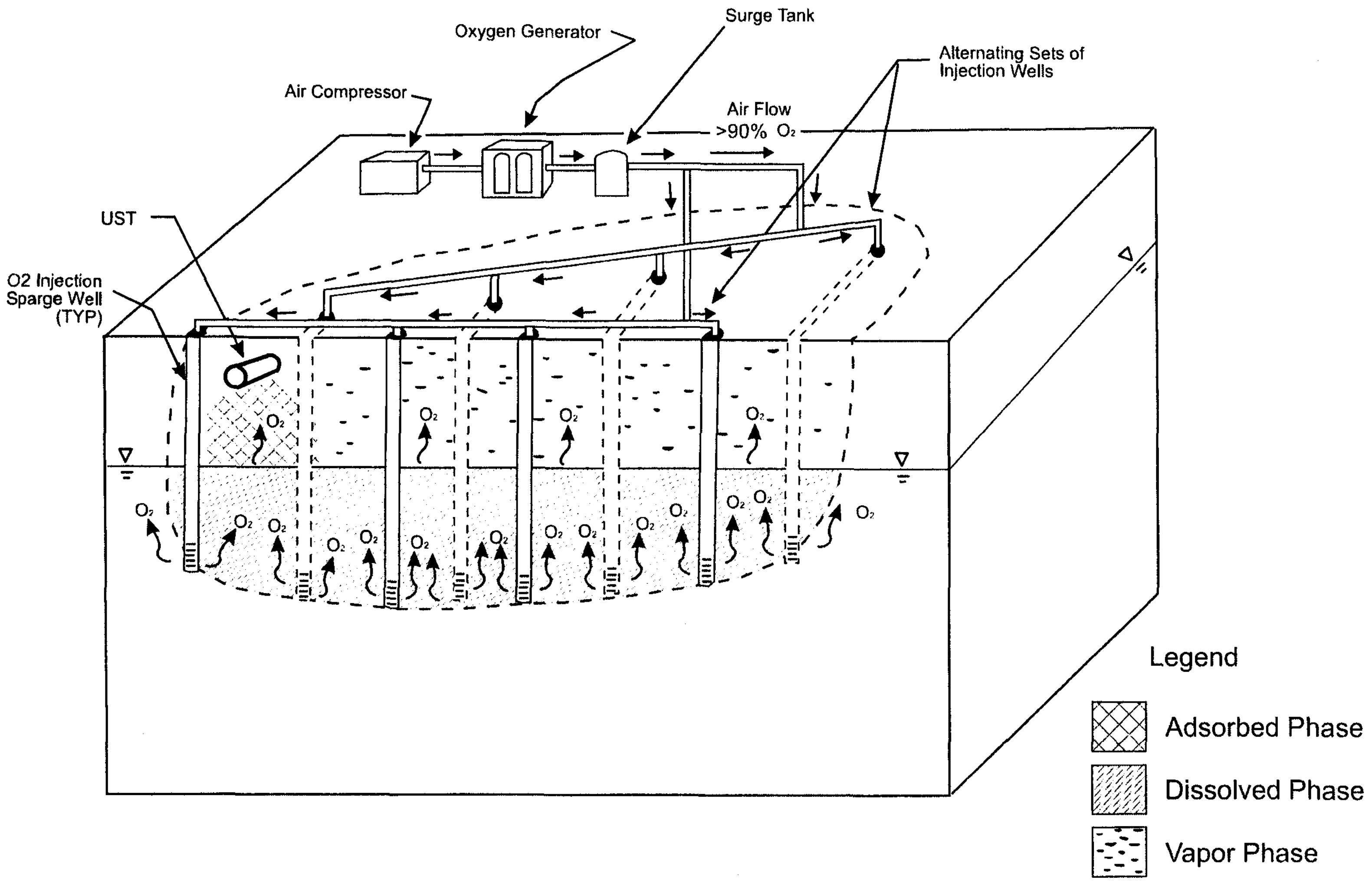
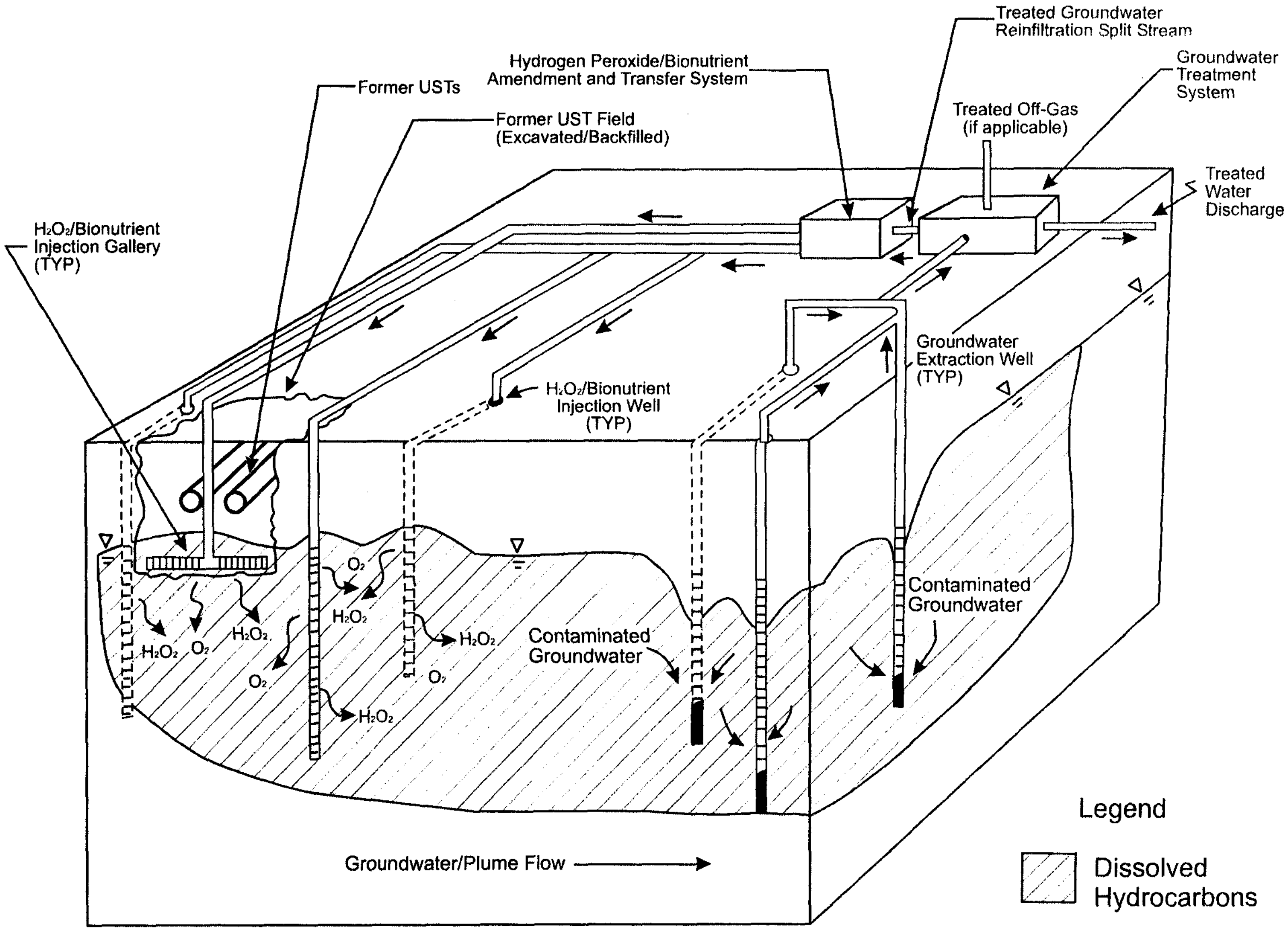


Exhibit XII-5
Typical Enhanced Aerobic Remediation Using Hydrogen Peroxide



oxygen in groundwater (40-50 ppm). When this occurs, oxygen gas is formed, which can be lost in the form of bubbles that rise through the saturated zone to the water table and into the unsaturated zone.

For enhanced aerobic bioremediation purposes, hydrogen peroxide is used at concentrations that maximize dissolved oxygen delivery to the petroleum-contaminated area while minimizing losses of oxygen through volatilization. Hydrogen peroxide is cytotoxic to microorganisms at concentrations greater than 100-200 ppm. This toxicity to aerobic petroleum degrading microbes can be amplified if carbon sources and nutrients are depleted in the contaminated media. Concentrations and application rates are typically determined on a site-specific basis, depending on site conditions, contaminant levels, and cleanup goals.

Hydrogen peroxide in a more concentrated form and in the presence of an iron catalyst can also be used to chemically oxidize site contaminants. This application of peroxide is not discussed in this chapter. When used in this manner, hydrogen peroxide's reaction with ferrous iron produces Fenton's reagent. Fenton's reagent chemical oxidation requires a comprehensive three-dimensional site characterization to locate preferential pathways for migration. It is important that any hydrogen peroxide remediation system contain an adequate number of soil vapor extraction wells to completely capture vapors. For more information on the use of hydrogen peroxide as an oxidant, see *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002), Chapter XIII, “Chemical Oxidation”.

The potential dangers of working with hydrogen peroxide should not be overlooked when considering the technology and determining how it should be applied. Hydrogen peroxide is an oxidant that can cause chemical burns. When introduced into a petroleum-contaminated area at high concentrations, hydrogen peroxide can produce heat and elevated oxygen levels that may lead to fire or explosions. Use of concentrated peroxide should be avoided to help reduce these hazards.

Ozone Injection

Ozone injection is both a chemical oxidation technology and an enhanced aerobic bioremediation technology. Oxidation of organic matter and contaminants occurs in the immediate ozone application and decomposition area. Outside the decomposition area, increased levels of dissolved oxygen can enhance aerobic bioremediation. Ozone is a strong oxidant with an oxidation potential greater than that of hydrogen peroxide. It is also effective in delivering oxygen to enhance subsurface bioremediation of petroleum-impacted areas. Ozone is 10 times more soluble in water than is pure oxygen.

Consequently, groundwater becomes increasingly saturated with dissolved oxygen as unstable ozone molecules decompose into oxygen molecules. About one-half of dissolved ozone introduced into the subsurface degrades to oxygen within approximately 20 minutes. The dissolved oxygen can then be used as a source of energy by indigenous aerobic hydrocarbon-degrading bacteria.

Because of its oxidization potential, injected ozone can also be toxic to indigenous aerobic bacteria and can actually suppress subsurface biological activity. However, this suppression is temporary, and a sufficient number of bacteria survive in-situ ozonation to resume biodegradation after ozone has been applied.

Ozone may be injected into the subsurface in a dissolved phase or in gaseous phases. Groundwater is often extracted and treated, then used to transport (through re-injection or re-infiltration) the dissolved phase ozone and oxygen into the subsurface contaminated area. More commonly, however, gaseous ozone is injected or sparged directly into the contaminated groundwater. Because of its instability, ozone is generated on-site and in relatively close proximity to the target contaminated area. Typically, air containing up to 5% ozone is injected into strategically placed sparge wells. Ozone then dissolves in the groundwater, reacts with subsurface organics, and decomposes to oxygen. Vapor control equipment (e.g., an soil vapor extraction and treatment system) may be warranted when ozone injection rates are high enough to emit excess ozone to the unsaturated zone, which may slow deployment timetables in some states. In many states, vapor control equipment requires a permit for off-gas treatment.

Special Considerations for MTBE. The gasoline additive methyl tertiary butyl ether (MTBE) is often found in the subsurface when gasoline has been released. In addition, MTBE is sometimes discovered at spill sites of middle distillate petroleum products like diesel, jet fuel, kerosene, and fuel oil. As such, whenever a petroleum hydrocarbon spill is investigated and remediated, the presence/absence of MTBE in the soil and ground water should be verified.

Several crucial characteristics of MTBE affect the movement and remediation of MTBE, including:

- MTBE is more soluble in water than most C6-C10 gasoline-range hydrocarbons. For example, MTBE is 28 times more soluble in water than is benzene.

- MTBE is less volatile from water (i.e., has a lower Henry's Constant) than most C6-C10 hydrocarbons. For example, MTBE is 11 times less volatile from water than is benzene.

- MTBE adheres less to soil organic matter than most C6-C10 hydrocarbons. This means that it has lower retardation and more rapid transport in groundwater than most gasoline-range compounds.

- At most sites, MTBE is less biodegradable in the subsurface than other gasoline compounds.

Because of these characteristics, some MTBE from a gasoline spill will be found with the BTEX compounds in the soil and groundwater near the site of petroleum release. But it is also quite common to find a dissolved-phase MTBE-only plume downgradient of the BTEX/TPH plume. Thus, when considering using enhanced aerobic bioremediation techniques for gasoline plumes that include MTBE, recognize that the MTBE may exist in two distinct regions:

- A near-source area where MTBE co-occurs with more readily biodegradable BTEX/TPH compounds
- A distal area where the only compound of concern is MTBE

Any petroleum impact remediation plan that addresses MTBE should account for the probable MTBE-only plume downgradient of the MTBE & hydrocarbon plume. The MTBE-only plume often has decreased levels of dissolved oxygen, due to its occurrence in the "oxygen shadow" region downgradient from the spilled petroleum source area where natural biodegradation is typically occurring (Davidson, 1995).

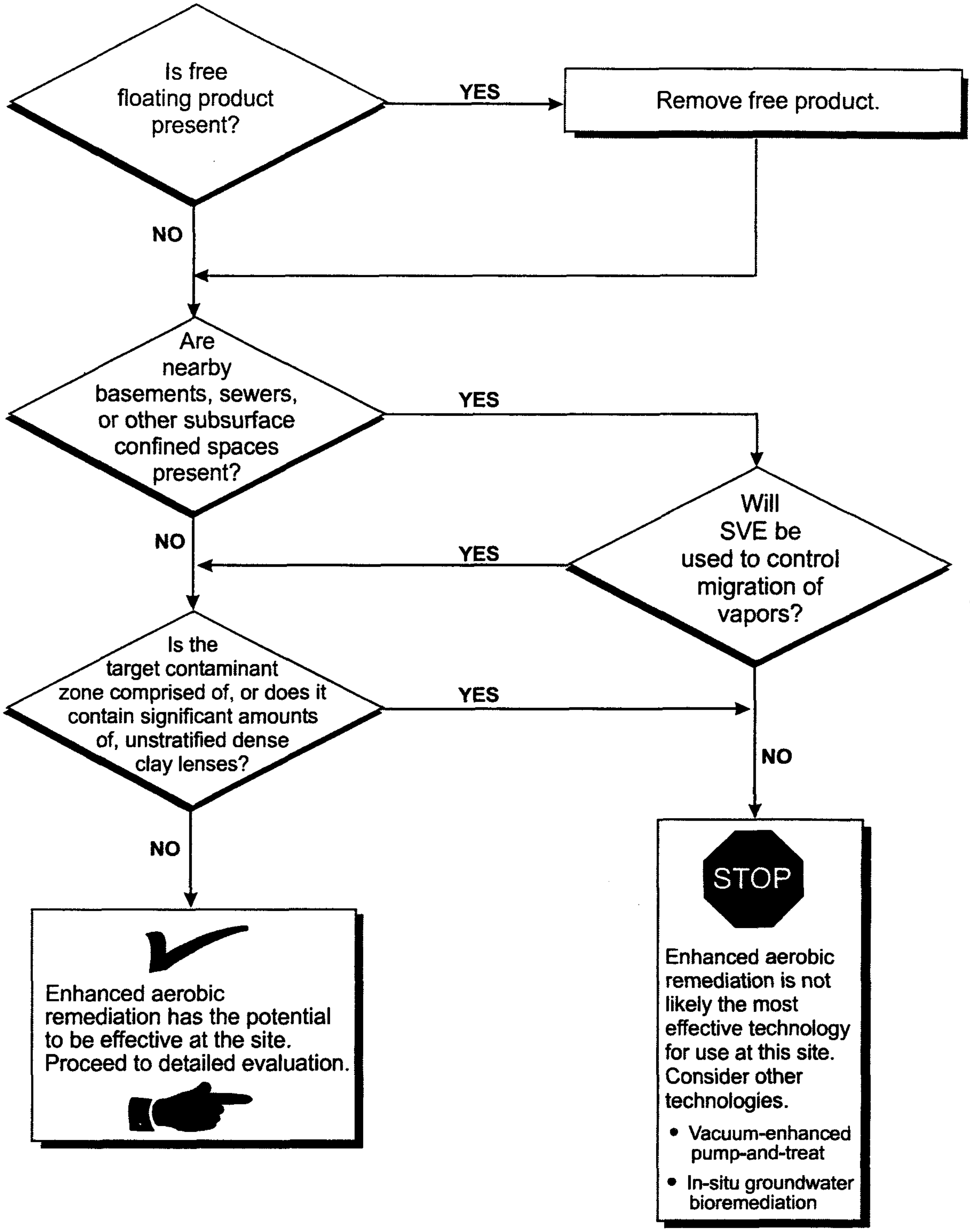
Enhanced Aerobic Bioremediation Technology Effectiveness Screening Approach

The descriptions of the various enhanced aerobic bioremediation technologies in the overview provide the basic information needed to evaluate a corrective action plan that proposes enhanced aerobic bioremediation. To assist with evaluation of the enhanced aerobic bioremediation corrective action plan, a step-by-step technology effectiveness screening approach is provided in a flow diagram in Exhibit XII–6. This exhibit summarizes this evaluation process and serves as a roadmap for the decisions to make during evaluation of the corrective action plan. A checklist has also been provided at the end of this chapter, which can be used to evaluate the completeness of the enhanced aerobic bioremediation corrective action plan and to focus attention on areas where additional information may be needed. The evaluation process can be divided into the four steps described below.

- **Step 1:** ***An initial screening of enhanced aerobic bioremediation effectiveness*** allows quick determination of whether enhanced aerobic bioremediation should be considered as a remedial approach for the site.

- **Step 2:** ***A detailed evaluation of enhanced aerobic bioremediation effectiveness*** provides further screening criteria to confirm whether enhanced aerobic bioremediation is likely to be effective. First, certain site-specific data on the nature/extent of contamination, potential risk to human health/the environment, subsurface geology and hydrogeology, and other relevant site

Exhibit XII-6
Initial Screening for Potential Effectiveness of Enhanced Aerobic Bioremediation



characteristics need to be evaluated. Next, the site-specific data must be compared to the criteria provided in the Exhibit to assess whether enhanced aerobic bioremediation is likely to be effective.

- **Step 3:** ***An evaluation of the enhanced aerobic bioremediation system design*** in the corrective action plan allows a reviewer to determine whether basic design information has been defined, necessary design components have been specified, the construction process flow designs are consistent with standard practice, and adequate feasibility testing has been performed.

- **Step 4:** ***An evaluation of the operation and monitoring plans*** allows a reviewer to determine whether baseline, start-up and long-term system operation and monitoring are of sufficient scope and frequency and whether remedial progress monitoring and contingency plans are appropriate.

Step 1 - Initial Screening of Enhanced Aerobic Bioremediation Effectiveness

This section reviews the initial screening tool to examine whether enhanced aerobic bioremediation is likely to be an effective approach to remediate the petroleum-impacted areas at a site. Before accepting enhanced aerobic bioremediation as the preferred remedial approach, determine whether the corrective action plan has taken into account key site-specific conditions. In addition, evaluate several "bright lines" that define the limits of enhanced aerobic bioremediation overall viability as a remedial technology. These bright lines will assist with evaluating the corrective action plan and determining whether enhanced aerobic bioremediation is appropriate as an appropriate solution. After establishing the overall viability of an enhanced aerobic bioremediation approach, look at basic site and petroleum contaminant information in order to further determine the expected effectiveness of enhanced aerobic bioremediation at the site.

Overall Viability

The following site conditions are considered to be the “bright lines” that define the general limits of enhanced aerobic bioremediation viability at a site. If review of the corrective action plan indicates that any of the following conditions exist, enhanced aerobic bioremediation is not likely to be a feasible or appropriate remedial solution for the site.

- *Free mobile product is present and the corrective action plan does not include plans for its recovery.* Enhanced aerobic bioremediation will not effectively address free product that will serve as an on-going source of dissolved phase contamination. Biodegradation of the petroleum hydrocarbons occurs predominantly in the dissolved-phase because the compounds must be able to be transported across the microbial cell boundary along with water, nutrients, and metabolic waste products. Therefore, in the presence of free product, rates of hydrocarbon mass destruction using enhanced aerobic bioremediation will be limited by the rate at which the free product is dissolved into groundwater. The relatively low solubilities of petroleum hydrocarbon constituents will likely extend remediation for several years, and could allow further expansion of the contaminated area if free product is not removed. Additionally, some enhanced aerobic bioremediation technologies could actually spread the free product. For free product recovery approaches see *How to Effectively Recover Free Product At Leaking Underground Storage Tank Sites: A Guide for State Regulators,* US EPA 510-R-96-001, September 1996.

- *Potentially excessive risks to human health or the environment have been identified and the corrective action plan does not include a supplemental mitigation plan.* While enhanced aerobic bioremediation can reduce petroleum hydrocarbon concentrations in the subsurface, site conditions may limit the level of such reductions and can significantly extend remedial timeframes. Close proximity of the petroleum contamination to basements, utilities, water supply wells, surface water bodies, or other potential receptorsthat could pose excessive risks should be mitigated using technologies that complement enhanced aerobic bioremediation (e.g., soil vapor extraction (SVE), hydraulic controls to protect water supply wells). Without the use of other remedial approaches, enhanced aerobic bioremediation may not be able to reduce concentrations of petroleum contaminants to sufficiently low concentrations to protect receptors in the predicted timeframes.

- *The target contaminant zone includes unstratified dense clay.* For remedial success, enhanced aerobic bioremediation technologies must effectively introduce and distribute oxygen to indigenous microorganisms present in the treatment zone, allowing microbial populations to expand and metabolize the petroleum contaminants. With the relatively low permeabilities inherent to clay or clay-rich soils, oxygen and oxygen carrier media (e.g., air) cannot be easily introduced or distributed. Any distribution of oxygen that could be delivered to such soils (e.g., placement of oxygen releasing compounds in borings or excavations) would largely be controlled by molecular diffusion, a very slow and ineffective process. Treatment zone oxygen levels, therefore, would not be uniformly increased, and biodegradation of the petroleum hydrocarbons could not be effectively enhanced.

While these bright lines offer general guidance on the applicability of enhanced aerobic bioremediation technologies, there may be site-specific application-specific exceptions to the rule. It may be appropriate, for example, for enhanced aerobic bioremediation technologies to be used to address contamination on the periphery of contamination while a different technology is employed to treat the source zone.

Step 2 - Detailed Evaluation of Enhanced Aerobic Bioremediation Effectiveness

Potential Effectiveness of Enhanced Aerobic Bioremediation

Before performing a more detailed evaluation of enhanced aerobic bioremediation's potential saturated zone remedial effectiveness and future success at a site, it is useful to review several key indicators. Two factors influence the effectiveness of enhanced aerobic bioremediation at a site: saturated zone permeability, and biodegradability of the petroleum constituents.

- **Saturated soil permeability**. Soil permeability can strongly affect the rate at which oxygen is supplied and uniformly distributed to the hydrocarbon-degrading bacteria in the subsurface. Enhanced aerobic bioremediation of groundwater contaminants in fine-grained soils, or in clays and silts with low permeabilities, is likely to be less effective than in coarse-grained soils (e.g., sand and gravels) because it is more difficult to effectively deliver oxygen in low-permeability materials. In coarse-grained soils, oxygen can be more easily delivered to bacteria, and beneficial populations of hydrocarbon-degrading bacteria may come into contact with more of the petroleum, which enhances biodegradation.

- **Biodegradability**. Biodegradability is a measure of a contaminant's propensity to be metabolized by hydrocarbon-degrading microorganisms. Petroleum products are generally biodegradable, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients. However, the rate and degree to which petroleum products can be degraded by the microorganisms present in the subsurface is largely determined by the relative biodegradability of the petroleum products. For example, heavy petroleum products (e.g., lubricating oils, fuel oils) generally contain a higher proportion of less soluble, higher molecular weight petroleum constituents that are biodegraded at a slower rate than more soluble, lighter fraction petroleum compounds (e.g., gasoline). As a general rule, these characteristics of petroleum compounds can limit biodegradation rates.

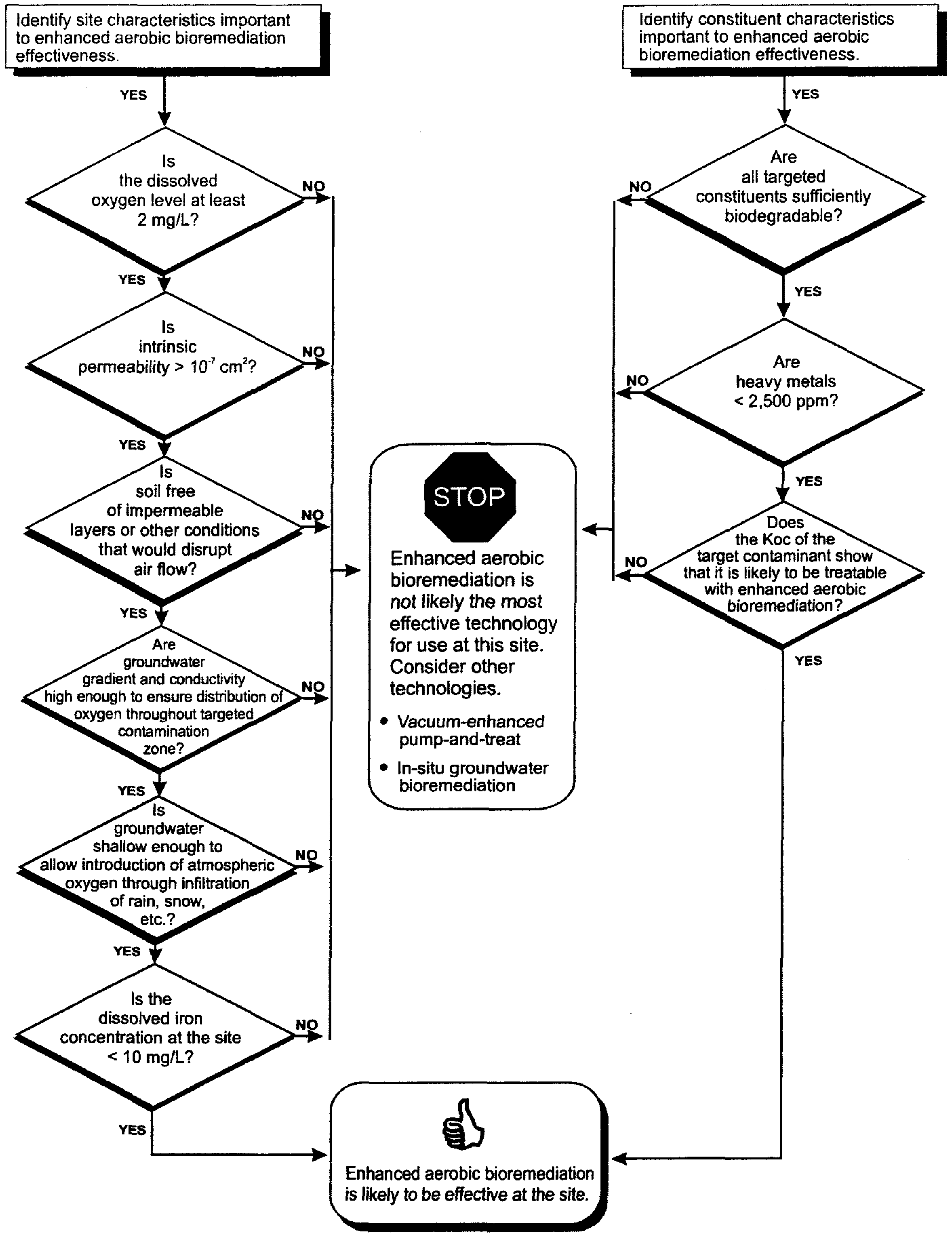
> Less soluble compounds are generally less available in the aqueous phase for microorganisms to metabolize. Larger petroleum molecules can slow or preclude the transport of some of these molecules into microbial cells for degradation, and larger or longer chain length structural properties may hinder the ability of the micro-organisms' enzyme systems to effectively attack the compounds. Therefore, even under identical site conditions, bioremediation of a lubricating oil spill will generally proceed more slowly than at a gasoline release. However, cleanup goals are frequently tied to specific petroleum compounds rather than the range of organic constituents that may comprise a petroleum product. Therefore, when considering enhanced aerobic bioremediation, the biodegradability of specific petroleum compounds common to the petroleum product and cleanup goals are of greatest relevance. Even though bioremediation of lubricating oil contamination may occur relatively slowly, cleanup of a lubricating oil spill site via bioremediation may be achieved more quickly than bioremediation of a gasoline spill site because fewer compounds in lubricating oil dissolve in groundwater, reducing the number of target species to clean up.

Some chemical species present in gasoline, such as methyl tertiary-butyl ether (MTBE), are more recalcitrant to bioremediation than are some of the heaviest and most chemically complex petroleum compounds. The detailed enhanced aerobic bioremediation effectiveness evaluation section of this chapter consider the biodegradability of specific petroleum hydrocarbon constituents, such as the benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, as well as that of fuel oxygenates, such as MTBE.

The following section provides information needed to make a more thorough evaluation of enhanced aerobic bioremediation effectiveness and help to identify areas that may require special design considerations. Exhibit XII-7 provides a stepwise process that reviewers should use to further evaluate whether enhanced aerobic bioremediation is an appropriate technology for a contaminated UST site. To use this tool, determine the type of soil present and the type of petroleum product released at the site.

To help with this more detailed evaluation, this section covers a number of important site-specific characteristics influencing the potential effectiveness of enhanced aerobic bioremediation that were not considered or fully explored in the initial screening of the remedial approach. Additionally, this section provides a more detailed discussion of key contaminant characteristics that influence the potential effectiveness of enhanced aerobic bioremediation. Key site and contaminant factors that should be explored in the detailed evaluation of enhanced aerobic bioremediation are listed in Exhibit XII-8. The remainder of this section details each of the parameters described in Exhibit XII-8. After reviewing and comparing the information provided in this section with the corresponding

Exhibit XII-7
Detailed Screening for Potential Effectiveness of Enhanced Aerobic Bioremediation



information in the corrective action plan, it should be possible to evaluate whether enhanced aerobic bioremediation is likely to be effective at the site.

Exhibit XII-8
Key Parameters Used to Evaluate Enhanced Aerobic Bioremediation Applicability

Site Characteristics	Constituent Characteristics
Oxygen Demand Factors ▪ Five-Day Biological Oxygen Demand (BOD_5) ▪ Contaminant theoretical oxygen demand ▪ Naturally occurring organic material (humic substances) – Microbial population density/activity – Nutrient concentrations – Temperature – pH	*Chemical Class and Susceptibility to Bioremediation* *Contaminant Phase Distribution* *Concentration and Toxicity*
Advective and Dispersive Transport Factors ▪ Intrinsic permeability ▪ Soil structure and stratification ▪ Hydraulic gradient ▪ Depth to groundwater ▪ Dissolved iron content	*Bioavailability Characteristics* ▪ Solubility ▪ Organic carbon partition coefficient (K_{oc})/sorption potential

Site Characteristics Affecting Enhanced Aerobic Bioremediation

The effectiveness of enhanced aerobic bioremediation depends largely on the ability to deliver oxygen to naturally occurring hydrocarbon-degrading microorganisms in the target treatment area. Oxygen can be introduced and removed from a contaminated groundwater zone in many different ways. Dissolved oxygen may enter the contaminated zone from any of the following sources:

- Flow of groundwater into the contaminated zone from background (upgradient) areas
- Precipitation infiltration
- Other enhanced aerobic bioremediation sources

Losses of oxygen from the contaminated zone may occur through:

- Biodegradation of organic contaminants
- Oxidation of naturally occurring organic and inorganic material in the soil
- Volatilization of dissolved oxygen
- Flow of groundwater containing depleted levels of dissolved oxygen leaving the contaminated zone

The success of enhanced aerobic bioremediation, therefore, hinges on the balance between oxygen sources, oxygen uptake, and the degree to which the transport of dissolved oxygen in groundwater is limited. To support aerobic biodegradation of petroleum contaminants, the most favorable dissolved oxygen (DO) level is 2 mg/L or higher. Anaerobic biodegradation processes in the anaerobic shadow become limited once dissolved oxygen levels approach or fall below 2 mg/L. Site characteristics affecting the delivery and distribution of oxygen in the subsurface and the effectiveness of enhanced aerobic bioremediation technology are discussed in the following sections.

Oxygen Demand Factors. Groundwater in petroleum spill source area and downgradient of the spill area is usually depleted of oxygen. This zone of oxygen-depleted groundwater, commonly referred to as the anaerobic shadow, results from the use of oxygen by naturally occurring microorganisms during aerobic metabolism of the spilled petroleum organic compounds. The oxygen is used in the microbiologically mediated oxidation of the petroleum contaminants. Aerobic biodegradation processes in the anaerobic shadow become limited once dissolved oxygen levels approach or fall below 2 mg/L. Enhanced aerobic bioremediation technologies can boost oxygen levels in the source area and in the anaerobic shadow to assist naturally occurring aerobic biodegradation processes but there are other oxygen demands that need to be considered before attempting to oxygenate the anaerobic shadow.

Each enhanced aerobic bioremediation technology has a particular way of delivering oxygen to the saturated zone. Once delivered to the saturated zone, dissolved oxygen can be further distributed in the treatment zone by groundwater advection and dispersion. However, from the point where it is introduced into the aquifer, dissolved oxygen concentration decreases along the groundwater flow path not only through mixing with the oxygen-depleted groundwater, but also because of biologically mediated and abiotic oxidation processes. The rate and degree to which oxygen concentrations decrease along the groundwater flow path and the degree to which the anaerobic shadow may be oxygenated depends, in part, on the degree to which oxygen is lost to microbiological and abiotic consumption in the saturated zone.

Demand for oxygen in the subsurface environment may stem from organic or inorganic sources. Microbial biodegradation of released petroleum hydrocarbons or naturally occurring organics (e.g., humic substances) as a carbon source by aerobic microorganisms will generate demand for oxygen.

Oxygen Demand From Biodegradation of Organic Compounds. Oxygen levels are generally depleted in the subsurface, but are particularly depleted at petroleum UST spill sites. This oxygen shortage results from the relative isolation of the subsurface from the oxygen-replenishing atmosphere, as well as the oxygen demands of naturally occurring organic and inorganic compounds and petroleum hydrocarbon releases. Because of these oxygen-depleted conditions, the most basic requirement for enhanced aerobic bioremediation is to deliver sufficient levels of oxygen to maintain an aerobic subsurface environment.

Exhibit XII-9 outlines the stoichiometric reactions for the complete oxidation or biodegradation of some common components of gasoline and other petroleum products. In theory, oxygen levels of at least 3 to 3.5 times the amount of subsurface petroleum mass that needs to be removed to meet cleanup goals must be delivered to the groundwater and distributed over the planned remedial period. Given typical oxygen solubility limits and the mass of contaminants that are often found at leaking underground storage tanks sites, delivering the required amount of oxygen can be a significant challenge. In practice, to convert one pound of hydrocarbon material into carbon dioxide and water requires between 3 and 5 pounds of available oxygen. This is valuable for evaluating the potential effectiveness of enhanced aerobic bioremediation.

Exhibit XII-9
Organic Compound Oxidation Stoichiometry

Petroleum Hydrocarbon	Oxidation Reaction	Oxygen Requirement (gram O_2 per gram Contaminant)
Benzene	$C_6H_6 + 7.5\ O_2 \rightarrow 6CO_2 + 3H_2O$	3.1
Toluene	$C_6H_5CH_3 + 9\ O_2 \rightarrow 7CO_2 + 4H_2O$	3.1
Ethylbenzene	$C_2H_5C_6H_5 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$	3.2
Xylenes	$C_6H_4(CH_3)_2 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$	3.2
Cumene	$C_6H_5C_3H_7 + 12O_2 \rightarrow 9O_2 + 6H_2O$	3.2
Naphthalene	$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$	3.0
Fluorene	$C_{13}H_{10} + 15.5O_2 \rightarrow 13CO_2 + 5H_2O$	3.0
Phenanthrene	$C_{14}H_{10} + 16.5O_2 \rightarrow 14CO_2 + 5H_2O$	3.0
Hexane	$C_6H_{14} + 9.5\ O_2 \rightarrow 6CO_2 + 7H_2O$	3.5

Because the solubility of O_2 by natural oxygen replenishment is limited and relatively low (9 mg/L at 25°C), only a small amount of organic or inorganic matter in the subsurface can consume all the naturally present dissolved O_2 in groundwater. For example, using the above stochiometric equation for the complete oxidation of benzene, oxidation of 2.9 mg/L of benzene would theoretically consume about 9 mg/L of O_2, leaving no residual oxygen in the water. It can be readily understood how external sources of oxygen enhanced aerobic bioremediation technologies can help aerobic bacteria by providing a source of energy so they may consume the petroleum as a source of carbon.

Microbial Population. Oxygen demand is also a function of the vitality of the microbial population. The larger and more active the population of aerobic microorganisms, the larger the biological oxygen demand. However, subsurface conditions may not be conducive to producing large numbers of microbial populations. Exhibit XII-10 shows the likely effectiveness of enhanced aerobic bioremediation as a function of the presence of heterotrophic bacteria in the subsurface.

Exhibit XII-10
Relationship Between Heterotrophic Bacterial Counts And Likely Enhanced Aerobic Bioremediation Effectiveness

Background Heterotrophic Bacteria Levels	Enhanced Aerobic Bioremediation Effectiveness
>1,000 CFU/gram dry soil	Generally effective
<1,000 CFU/gram dry soil	May be effective; further evaluation needed to determine if toxic conditions are present

Nutrients. The activity of the microbial population and the corresponding biological oxygen demand also depend on the availability of inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be initially available in sufficient quantities in the aquifer, but with time, they may need to be supplemented with additional nutrient loading to maintain adequate bacterial populations. Excessive amounts of certain nutrients (e.g., phosphate or sulfate) can repress bio-metabolism. The carbon:nitrogen:phosphorus ratios necessary to enhance biodegradation fall in the range of 100:10:1 to 100:1:0.5, depending on the constituents and bacteria involved in the biodegradation process.

However, to avoid over-application of nitrogen and phosphorus, which can unnecessarily incur added costs, plug wells, and even contaminate ground water with nitrate, it is important to understand how much carbon can be metabolized based on oxygen-limiting conditions. Nitrogen and phosphorus should be added to reach the proportions identified in the previous paragraph, based on the amount of carbon that can be metabolized at any given time compared to the total average concentration of carbon (i.e., petroleum contamination) in the subsurface. For example, if during full-scale operation a net 0.6 pound per hour of pure oxygen is introduced to the treatment area and is assumed to be completely consumed by aerobic microbial activity, approximately 0.17 pound per hour (4 pounds per day) of hydrocarbon is theoretically microbiologically oxidized (using a 3.5:1 oxygen:hydrocarbon stoichiometric ratio). Then, using the 100:10:1 to 100:1:0.5 C:N:P theoretically optimal ratio range for this example, between 0.4 and 0.04 pounds per day of nitrogen and 0.04 to 0.02 pounds per day of phosphorus may need to be added to the treatment area to keep up with the estimated carbon metabolism rate.

Alternatively, it would be reasonable for a practitioner to suggest monitoring oxygen demand during full-scale system operation before considering adding any nitrogen or phosphorus. If oxygen demand were to fall below about 10 mg/L in the petroleum contaminated area, the subsurface could be tested for nitrogen or phosphorus to determine whether insufficient concentrations of these micronutrients is limiting microbial activity. Only after this determination is made should nitrogen or phosphorus be added. Generally, nitrogen should not limit aerobic degradation processes unless concentrations fall significantly below 1 mg/L. This alternative may be particularly attractive at sites located near areas where aquifers already have nitrogen problems because it may be difficult to secure permits for the injection of these micronutrients. If nitrogen addition is necessary, slow-release sources should be used. Nitrogen addition can lower pH, depending on the amount and type of nitrogen added.

pH. Although the optimum pH for bacterial growth is approximately 7, enhanced aerobic bioremediation can be effective over a pH range of 5 to 9 pH units. Adjustment of pH conditions outside this range is generally not considered to be viable because it is difficult to overcome the natural soil buffering capacity, and because of the potential for rapid changes in pH to adversely affect bacterial populations. Oxygen releasing compounds may raise the pH even higher than the 5-9 range, which can be fatal to microbes.

Temperature. Oxygen uptake and bacterial growth rate are directly affected by temperature. From 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. Below 5°C, microbial activity becomes insignificant. In most areas of the United States, the average groundwater temperature is about 13°C. Groundwater temperatures may be somewhat lower or higher in the extreme northern and southern states. While individual microorganism growth rates decrease with temperature, a higher steady state biomass of active organisms (each one working more slowly, but more of them working) can result from lower temperatures. Because of this and the increased solubility of oxygen at lower temperatures, biodegradation can sometimes be as fast or faster at lower temperatures than at more moderate temperatures.

Inorganic Oxygen Demand. Oxygen demand arises from a depletion of subsurface oxygen from biological or inorganic processes coupled with poor oxygen replenishment. In contrast to surface water bodies, groundwater systems are typically isolated from the atmosphere, limiting the opportunity for natural oxygen to be replenished. This atmospheric isolation allows dissolved oxygen levels to become depleted and subsurface conditions to become geochemically reduced. Introducing and distributing oxygen under these reduced conditions are challenging for the application of enhanced aerobic bioremediation, because introduced oxygen may react with and become lost to organic or inorganic chemical constituents that would otherwise be relatively inconsequential to the environmental cleanup.

Exhibit XII-11 presents a sample of some common inorganic processes that consume oxygen in groundwater.[3] Corrective action plan data should be reviewed to identify what is already known about aquifer conditions in the area around the site to determine whether signficant reduced inorganic species exist in the subsurface that could remove oxygen from groundwater. If so, these species can limit the ability of biodegrading bacteria to effectively implement enhanced aerobic bioremediation. In such cases, soil core samples may need to be collected and analyzed for reduced iron, sulfide or other inorganic constituents. These samples can help to determine the potential loss of oxygen to the aquifer and to verify that enhanced aerobic bioremediation will be able to effectively deliver sufficient oxygen to overcome these limiting factors. This assessment cannot be made from analyses of groundwater samples, because the reduced inorganic complexes are primarily precipitated in the aquifer material.

Exhibit XII-11
Inorganic Oxidation Processes That Consume Dissolved Oxygen In Groundwater

Process	Reaction
Sulfide Oxidation	$O_2 + ½HS^- \rightarrow ½SO^{2-} + ½H^+$
Iron Oxidation	$¼O_2 + Fe^{+2} + H^+ \rightarrow Fe^{+3} + ½H_2O$
Nitrification	$O_2 + ½NH^{4+} \rightarrow ½NO^{3-} + H^+ + ½H_2O$
Manganese Oxidation	$O_2 + 2Mn^{2+} + 2H_2O \rightarrow 2MnO_2\ (s) + 4H^+$
Iron Sulfide Oxidation	$15/4O_2 + FeS_2\ (s) + 7/2H_2O \rightarrow Fe(OH)_3\ (s) + 2SO_4^{2-} + 4H^+$

Many inorganic oxygen-consuming reactions produce solid precipitates that can accumulate in soil pore spaces. As discussed below, these precipitates can restrict soil permeabilities and thus further affect the ability of enhanced aerobic bioremediation technologies to deliver and distribute oxygen to hydrocarbon-degrading microorganisms.

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[3] From Freeze R.A. and John A. Cherry, 1979. Groundwater. Prentice Hall.

Advective and Dispersive Transport Factors. The site conditions affecting advection and dispersion of dissolved oxygen are outlined below. These conditions are:

- Intrinsic permeability
- Soil structure and stratification
- Hydraulic gradient
- Depth to groundwater
- Iron and other reduced inorganic compounds dissolved in groundwater

Each of these factors is described in more detail below.

Intrinsic Permeability. Intrinsic permeability is a measure of the ability of soil to transmit fluids. Intrinsic permeability is the single most important soil characteristic in determining the effectiveness of enhanced aerobic bioremediation, because intrinsic permeability controls how well oxygen can be delivered and dispersed to subsurface microorganisms. Hydraulic conductivity is a measure of the resistance of aquifer material to groundwater flow. This unit of measure is particularly relevant to understanding the ability to move oxygen dissolved in groundwater through the saturated treatment zone. Hydraulic conductivity is related to intrinsic permeability by the following equation.

$$K = \frac{k\gamma}{\mu}$$

where:
K = hydraulic conductivity (L/T)
k = intrinsic permeability (L^2)
γ = weight density of water (F/L^3)
μ = dynamic viscosity of water ($F \bullet T/L^2$)
L = mean grain diameter
T = transmissivity
F = fluid density

Intrinsic permeability often decreases near injection wells or infiltration galleries. This also commonly results from precipitation of carbonates, or precipitates of other minerals derived from fertilizer solutions. In general, oxygen is more easily distributed in soils with higher soil permeabilities (e.g., coarse-grained soils such as sands) than in soils with lower permeabilities (e.g., fine-grained clayey or silty soils).

Calculation of intrinsic permeability can be derived from hydraulic conductivity measurements taken from on-site pump testing. Pump test or slug test-derived permeability ranges are typically representative of average hydraulic permeability conditions for heterogeneous conditions. Alternatively, intrinsic permeability can be estimated from soil boring logs.

Permeabilities derived from pump or slug test analyses or estimated from boring logs are only approximations of actual subsurface conditions and should be regarded as such in the evaluation of enhanced aerobic bioremediation potential effectiveness.

Intrinsic permeability can vary over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide range of earth materials. Exhibit XII-12 provides general guidelines on the range of intrinsic permeability values over which enhanced aerobic bioremediation is likely to be effective.

The intrinsic permeability of a soil is likely to decrease as enhanced aerobic bioremediation progresses. If the soil intrinsic permeability indicates borderline potential effectiveness (e.g., $10^{-6} \leq k \leq 10^{-7}$), the geochemistry should be further evaluated.

Exhibit XII-12

Intrinsic Permeability And Enhanced Aerobic Bioremediation Effectiveness

Hydraulic Conductivity (K) (in ft/s)	Intrinsic Permeability (k) (in ft^2)	Enhanced Aerobic Bioremediation Effectiveness
$K > 10^{-6}$	$k > 10^{-12}$	Effective to generally effective
$10^{-6} \leq K \leq 10^{-7}$	$10^{-12} \leq k \leq 10^{-13}$	Possibly effective; needs further evaluation
$K < 10^{-7}$	$k < 10^{-13}$	Marginally effective to ineffective

Soil Structure and Stratification. Often, soils in a target treatment area are not uniformly permeable (heterogeneous), but rather have large-scale or small-scale variations in permeability. Soil heterogeneity plays a very important role in enhanced aerobic bioremediation technologies because oxygen introduced to the subsurface is distributed preferentially along higher permeability layers in the saturated soil. For example, in a heterogeneous soil comprised of sand, silt and clay layers, oxygen may be effectively distributed through the sand layer to successfully reduce petroleum hydrocarbons there, but will be ineffectively delivered and distributed to the silt and clay layers. The relatively slow diffusion transport mechanism will become as important or more important than advection and dispersion in the distribution of oxygen to microorganisms in the silt and clay layers. If the silt and clay layers are thick relative to the sand horizon and contain significant petroleum hydrocarbon mass, enhanced aerobic bioremediation technologies may not be efficient or effective. In this case, the dissolved petroleum hydrocarbon mass will appear to shrink as the most permeable zone (i.e., the sand) will have undergone significant enhanced aerobic bioremediation treatment.

However, the petroleum mass in the silt and clay horizons will likely not biodegrade, and will also likely diffuse into the sand zone, causing a rebound in dissolved hydrocarbon concentrations at the site.

Unless site soils are homogeneous, average soil intrinsic permeability may not adequately determine the viability of enhanced aerobic bioremediation approaches because discrete low permeability soil horizons may exist, and these horizons might contain a large fraction of the subsurface petroleum mass. In most cases, it is prudent to evaluate petroleum mass distribution across all soil types to determine whether enhanced aerobic bioremediation is likely to be effective and will achieve cleanup objectives. If select soil horizons containing hydrocarbon mass are not expected to be effectively treated using enhanced aerobic bioremediation , enhanced aerobic bioremediation may not be viable for the site. For example, if 50% of the contaminant mass is contained and isolated in low permeability soil horizons and the site cleanup goals is a 95% reduction in petroleum contaminant concentrations, then it is reasonable to conclude that the goal cannot be achieved using enhanced aerobic bioremediation. However, in such circumstances, combining enhanced aerobic bioremediation with other technologies that enhance the permeability of low permeability horizons in the contaminated zone (e.g., soil fracturing) could be considered. Soil fracturing could allow dissolved oxygen and other microbial nutrients to be effectively delivered through the engineered fractures in low permeability soil. However caution should be observed when considering this option because the same fractures produced to enhance permeability for nutrient delivery could also be a potential preferential flow path for contaminant plume migration.

Hydraulic Gradient. Enhanced aerobic bioremediation technologies ultimately rely on groundwater advection and dispersion (i.e., flow) to distribute dissolved oxygen to the subsurface. Distribution of introduced dissolved oxygen is most effective under hydrogeologic conditions conducive to higher groundwater flow rates. These conditions exist when the combined values of hydraulic gradient and hydraulic conductivity are relatively high.

Note that state regulations may either require permits for nutrient injection or prohibit them entirely. Depending on the specific enhanced aerobic bioremediation technology and the state in which the site is located, permits that may be required include underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge. Several federal, state and local programs exist that either directly manage or regulate Class V aquifer remediation wells, and many of these require permits for underground injection of oxygen or bionutrients.

As the hydraulic gradient increases, the groundwater velocity increases proportionately. This same relationship exists between groundwater velocity and soil permeability. Groundwater velocity is inversely proportional to soil porosity. As porosity increases, groundwater velocity decreases. For purposes of evaluating the feasibility of using an enhanced aerobic bioremediation technology, keep in mind that the principal direction of groundwater flow and oxygen transport is along the line of maximum hydraulic gradient.

To maximize the distribution of dissolved oxygen through and biodegradation rates in the contaminated zone, enhanced aerobic bioremediation technologies often introduce dissolved oxygen at levels that exceed the solubility limit of oxygen in groundwater under atmospheric conditions. However, when the oxygen is not rapidly dissipated or used (e.g., as an electron acceptor during microbial respiration), the oxygen can partition out of the dissolved-phase and be lost to the unsaturated zone as a gas.

Depth to Groundwater. The depth to groundwater at a site can also affect the availability and transport of dissolved oxygen to the subsurface. Infiltrating precipitation, such as rainfall or snow, is a source of dissolved oxygen to the saturated zone. When groundwater is relatively deep or confined, less precipitation infiltrates, minimizing the amount of atmospheric dissolved oxygen that reaches the groundwater. Also, pavement prevents infiltration of rainfall or snowmelt At sites where the water table is close to the surface, more mixing of groundwater with air-saturated precipitation occurs, resulting in more opportunity for groundwater to be oxygenated. When this occurs, dissolved oxygen levels in groundwater can even approach those found in streams and other surface water bodies.

Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater. In addition to being a significant oxygen sink, the effective intrinsic permeability of the saturated zone can be significantly reduced if the enhanced aerobic bioremediation treatment zone contains naturally elevated levels of reduced iron (e.g., ferrous iron, or Fe^{+2}) or other mineral species. The net impact of elevated levels of reduced species can therefore be a loss of delivered oxygen and a decreased ability to distribute any excess oxygen to the aerobic microorganisms involved with the degradation of the petroleum hydrocarbons. Precipitation of oxidized inorganic complexes and biological mass can foul monitoring and injection well screens and potentially aquifer pore space where oxygen is delivered to the subsurface.

Exhibit XII-13 can be used as a guide to help determine whether the corrective action plan has considered site levels of dissolved iron and if dissolved iron levels at the site could have an adverse effect on the enhanced aerobic bioremediation approach.

In some situations, hydraulic gradients can be enhanced to help increase groundwater flow and oxygen delivery rates and flush dissolved oxygen through the contaminated zone. One common approach is to create an artificial gradient by removing groundwater downgradient of the source area, treating it, and re-introducing it in the upgradient source area. For example, hydrogen peroxide enhanced aerobic bioremediation applications often require extracting

Exhibit XII-13
Relationship Between Dissolved Iron And Enhanced Aerobic Bioremediation Effectiveness

Dissolved Iron Concentration (mg/L)	Potential Effectiveness of Enhanced Aerobic Bioremediation
$Fe^{+2} < 10$	Enhanced aerobic bioremediation will likely be effective.
$10 \geq Fe^{+2} \geq 20$	Enhanced aerobic bioremediation injection wells and delivery systems will require periodic testing and may need periodic replacement.
$Fe^{+2} > 2$	Enhanced aerobic bioremediation may not be cost effective due to loss of dissolved oxygen to the formation and equipment maintenance problems associated with inorganic precipitation. This would especially be the case where groundwater is extracted, treated, amended with oxygen (e.g., hydrogen peroxide) and reinjected.

contaminated groundwater from the downgradient portion of the dissolved hydrocarbon plume, treating the extracted groundwater for hydrocarbons, and re-injecting the treated groundwater amended with hydrogen peroxide into one or more upgradient locations.

This lowers the groundwater level in the downgradient extraction locations and raises it in upgradient injection locations, which provides an artificially increased gradient. This, in turn, increases the rate of groundwater and oxygen flow across the contaminated zone.

Even with preferential hydrogeologic conditions, distributing dissolved oxygen throughout the subsurface is difficult because of the inherent limits of groundwater flow and the number of oxygen "sinks," or uptakes, that can exist, particularly in areas contaminated with petroleum hydrocarbons. These limitations frequently require that the corrective action plan call for placement of a large number of oxygen delivery points in the treatment area to decrease enhanced aerobic bioremediation technology's reliance on groundwater flow as the principal source of distributed oxygen.

In addition to being a parameter considered in evaluating the potential effectiveness of enhanced aerobic bioremediation, hydraulic gradient is an engineering design issue. If the gradient is not steep enough to provide adequate flow and oxygen transport through the contaminated zone, then certain engineering provisions (e.g., spacing application points more closely, creating artificial hydraulic gradients) can be added to the design to enhance oxygen distribution. However, economic considerations limit the extent to which design changes can be made in an enhanced aerobic bioremediation delivery system to ensure adequate oxygen distribution.

Constituent Characteristic Affecting Enhanced Aerobic Bioremediation

It is important to evaluate the potential impacts of site contaminants on the performance of the proposed enhanced aerobic bioremediation approach. In particular, it is important to review how the chemical structure, chemical properties, concentrations and toxicities of the petroleum contaminants can influence remedial performance.

Chemical Class and Susceptibility to Bioremediation. Petroleum products are complex mixtures of hundreds or even thousands of hydrocarbon chemical constituents, other chemical constituents and additives. Each of these constituents has a different atomic structure that determines, in part, its relative biodegradability. Although nearly all constituents in petroleum products found at leaking underground storage tank sites are biodegradable to some extent, constituents with more complex molecular structures are generally less readily biodegraded than those with simpler structures. On the other hand, most low-molecular weight (nine carbon atoms or less) aliphatic and monoaromatic constituents are more easily biodegraded than higher molecular weight aliphatic or polyaromatic organic constituents.

Exhibit XII-14 lists the relative biodegradability of various petroleum products and constituents. The exhibit shows that hydrocarbon molecules containing a higher number of carbon atoms (e.g., lubricants with 26- to 38-carbon chains) degrade more slowly, and perhaps less completely, than those with shorter carbon chains (e.g., gasoline). However, cleanup goals are frequently tied to a small subset of chemical compound components of the various petroleum products in Exhibit XII-9 rather than a total petroleum hydrocarbon concentration. Often chemical compounds in petroleum products identified in Exhibit XII-14 as being less readily biodegradable are not present at contaminated sites at levels significantly above cleanup standards because of the low solubility characteristic that these compounds can have. Consequently, cleanup standards for contaminants in less readily biodegradable petroleum formulations may be reached through enhanced aerobic bioremediation more quickly than those for more soluble compounds in more biodegradable formulations.

Certain petroleum constituents are more recalcitrant than most other constituents. For example, MTBE, a gasoline additive, is frequently found at leaking UST sites because of its environmental persistence and its apparent resistance to bioremediation. Some researchers have estimated that the half-life of MTBE in the environment is at least two years, whereas the typical half-life for BTEX compounds in the environment is approximately two to three months.

Exhibit XII-14
Composition And Relative Biodegradability Of Petroleum Products

Product	Major Components	Relative Product Biodegradability
Natural Gas	Normal and branched-chain alkanes. One to five carbons in length. *Examples: ethane, propane.*	**Higher**
Gasoline	Normal and branched hydrocarbons between 6 and 10 carbons in length. *Examples: n-butane, n-pentane, n-octane, isopentane, methylpentanes, benzene, toluene, xylenes, ethylbenzene.*	
Kerosene, Diesel	Primarily 11 to 12 carbon hydrocarbons, although the range of carbons extends well above and below this range. Generally contains low to non-detectable levels of benzene and polyaromatic hydrocarbons. Jet fuel oils have a similar composition. *Examples: n-nonane, n-decane, n-dodecane, naphthalene, n-propylbenzene.*	
Light Gas Oils (e.g., No 2 Fuel Oil)	Twelve to 18 carbon hydrocarbons. Lower percentage of normal alkanes than kerosene. These products include diesel and furnace fuel oils (e.g., No. 2 fuel oil). *Examples: fluorene, naphthalene, phenanthrene, isopropylbenzene.*	
Heavy Gas Oils and Light Lubricating Oils	Hydrocarbons between 18 and 25 carbons long.	
Lubricants	Hydrocarbons between 26 and 38 carbons long.	
Asphalts	Heavy polycyclic compounds.	**Lower**

Therefore, one should carefully consider the biodegradability of the target contaminants when forecasting the potential effectiveness and usefulness of an enhanced aerobic bioremediation technology. The enhanced aerobic bioremediation design and implementation should focus on the most recalcitrant compounds within the released petroleum product, unless another remedial technology is being proposed to address those compounds.

It is not necessarily the most recalcitrant or most difficult compound to bioremediate that determines the duration of a remediation project. For example, the baseline concentration of the most recalcitrant site compound may be much closer to its respective cleanup goal or an acceptable risk-based concentration than a more readily biodegradable petroleum constituent at a baseline level much greater than its cleanup goal. In this case, the more biodegradable constituent may initially be the focus of the enhanced aerobic bioremediation design and cleanup. As remediation progresses, the mix of petroleum products remaining should periodically be compared to the site's proposed cleanup level to determine whether the remedial approach needs to be enhanced to address the remaining target compounds.

Researchers have estimated and published biodegradation rate constants for various petroleum hydrocarbons. These rate constants can indicate the relative biodegradability of petroleum hydrocarbon constituents under field conditions. However, actual degradation rates for target contaminants may depend on constituent-, site-, and enhanced aerobic bioremediation implementation-specific conditions. For example, the mixture and concentrations of the different petroleum constituents in the site soil and groundwater may play an important role in determining relative degradation rates. The amount of natural organic matter in the soil and the degree to which the petroleum constituents attach themselves to it will affect the relative rates of biodegradation. These issues, especially as they relate to contaminant characteristics that affect aerobic bioremediation, are discussed below.

Contaminant Phase Distribution. Spilled petroleum products may be partitioned into one or more phases and zones in the subsurface including:

- Unsaturated soils (sorbed phase)
- Saturated soil (sorbed phase)
- Dissolved in groundwater (aqueous phase)
- Unsaturated soil pore space (vapor phase)
- Free mobile product (liquid phase)
- Free residual product smeared onto soil above and below the water table

Understanding how the petroleum contaminant mass is distributed in the subsurface can be important to both evaluating the applicability of enhanced aerobic bioremediation and identifying a particular enhanced aerobic bioremediation technology that will be effective. Depending on site-specific cleanup goals and contaminant levels, a disproportionate amount of contaminant mass in one medium or another could preclude the use of enhanced aerobic bioremediation technologies. For example, if a relatively large portion of the mass of a site target compound (e.g., benzene) is held in residual free product that is vertically smeared above and below the water table, enhanced aerobic bioremediation may not be able to achieve the site cleanup goals within a reasonable period of time. However, in such a case, enhanced aerobic bioremediation could still potentially be used at the fringes of the contaminated area while a more aggressive technology is employed in the residual-free product zone.

Information on the distribution of target compounds in the subsurface can also be used to help identify the most appropriate enhanced aerobic bioremediation technology for a site. Depending on where most of the target contaminant mass is located, one or more of the enhanced aerobic bioremediation technologies may be viable. For example, a disproportionate amount of target contaminant mass in the unsaturated soil would logically lead to the selection of an unsaturated zone enhanced aerobic bioremediation approach (e.g., bioventing). On the other hand, if a disproportionate amount of target contaminant mass is in the saturated zone, one of the enhanced aerobic bioremediation technologies that introduces high concentrations of dissolved oxygen to the subsurface may be a reasonable approach.

Concentration and Toxicity. High concentrations of petroleum organics or heavy metals in site soils and groundwater have traditionally been thought to be potentially toxic to, or inhibit growth and reproduction of, biodegrading bacteria. Soil containing petroleum hydrocarbons in amounts greater than 50,000 ppm, or heavy metals in excess of 2,500 ppm, was thought to be inhibitory and/or toxic to many aerobic bacteria. However, it is becoming increasingly evident that many microorganisms are able to tolerate and adapt to petroleum concentrations well above 50,000 ppm. Some researchers have even reported being able to isolate living bacteria directly from gasoline product.

While it appears that bacteria may be more adaptable than initially believed, to the extent that these higher levels of petroleum hydrocarbons represent a large mass of contamination in unsaturated or saturated soil in contact with groundwater, the adapted populations of bacteria may not be able to address the contaminant mass in a reasonable timeframe. When considering the feasibility of enhanced aerobic bioremediation, it is important to evaluate the mass of the target contaminants of concern relative to potential biodegradation rates and the cleanup timeframe objective.

It is possible that the effects of elevated contaminant levels can include partial biodegradation of only a fraction of the hydrocarbons at reduced rates, or reduced bacterial reproduction rates or metabolism, resulting in minimal or no appreciable soil treatment. The guidance threshold values summarized in Exhibit XII-15 can be compared to average site concentrations provided in the corrective action plan as another way of forecasting the potential effectiveness of enhanced aerobic bioremediation. Again, it is important to recognize that the values shown in Exhibit XII-15 are guidance values only.

As outlined in Exhibit XII-15, the threshold petroleum concentrations above which biodegradation is inhibited could also indicate the presence of free or residual product in the subsurface. In the initial effectiveness screening of enhanced aerobic bioremediation (Step 1), one of the feasibility bright lines discussed was the absence of free mobile product. If threshold soil petroleum levels exist, then free or residual petroleum product most likely exists in the soil, and enhanced aerobic bioremediation will not be effective without first removing the product through other remedial measures.

Exhibit XII-15
Constituent Concentration and Enhanced Aerobic Bioremediation Effectiveness

Contaminant Levels (ppm)	Enhanced Aerobic Bioremediation Effectiveness
Petroleum constituents ≤ 50,000 Heavy metals ≤ 2,500	Possibly effective
Petroleum constituents > 50,000 or Heavy metals > 2,500	Not likely to be effective either due to toxic or inhibitory conditions to bacteria, or difficulty in reaching cleanup goal within reasonable period of time

Bioavailability Characteristics. The extent to which and the rate at which a particular petroleum hydrocarbon compound can be biodegraded by microorganisms depends not only on the compound's inherent biodegradability, but also on the availability of the compound to hydrocarbon-degrading bacteria ("bioavailability"). Several contaminant properties contribute to bioavailability in the subsurface. In particular, the compound-specific properties of solubility and the organic carbon partition coefficient (K_{oc}) help establish the relative bioavailability of contaminants. These properties can be used to help determine the susceptibility of the contaminant mass to enhanced microbial degradation and, ultimately, the potential effectiveness of enhanced aerobic bioremediation. Note that some compounds (e.g., MTBE) may be relatively bioavailable, but are difficult to biodegrade. Special considerations for MTBE are discussed beginning on page XII-39. This section continues with a discussion of the parameters of solubility and K_{oc} and their influence on enhanced aerobic bioremediation effectiveness.

Solubility. Solubility is the maximum concentration of a chemical that can be dissolved in water at a given temperature without forming a separate chemical phase on the water (i.e., free product). Most petroleum compounds have relatively low solubility values, thus limiting the concentrations of contamination that can be dissolved in groundwater and limiting their bioavailability in the aqueous phase. This is because less contaminant mass is able to reside in groundwater for biodegradation relative to contaminants with higher solubility limits. However, the solubility values for petroleum hydrocarbons range significantly – over four orders of magnitude – as shown in Exhibit XII-16. The solubility values in Exhibit XII-16 represent those of pure phase chemicals. For example, benzene dissolved in water by itself (with no other compounds present) can reach a maximum concentration in water of about 1.79 g/L before a separate phase develops. When multiple compounds are present such as at a petroleum release site, effective solubility values can be expected to be lower. While not representing effective solubility concentrations that may exist at particular petroleum release sites, the values present in Exhibit XII-16 provide a sense for the relative solubility concentrations for a range of fuel components. It is beyond the scope of this document to describe the chemistry involved and how effective solubility might be estimated.

Exhibit XII-16
Solubility Values And Organic Partition Coefficients For Select Petroleum Hydrocarbon Constituents

Compound	Molecular Weight (g/mol)	Solubility in Water (g/L)	Organic Carbon Coefficient (K_{oc} in mL/g)
MTBE	88.15	51	12
Benzene	78	1.79	58
Toluene	92.15	0.53	130
Ethylbenzene	106.17	0.21	220
Xylenes (total)	106	0.175	350
Cumene	120.19	50	2,800
Naphthalene	128	0.031	950
Acenaphthene	154	.0035	4,900

Compounds with higher solubility values are generally smaller, lower molecular weight molecules (e.g., benzene). When spilled, these compounds exist in groundwater at higher relative concentrations and move more quickly through the aquifer than do compounds of higher molecular weights. These compounds are generally more biodegradable because of both their relatively smaller size and bioavailability in the aqueous phase, because proportionately more contaminant mass is in the groundwater where it may be mineralized by aerobic bacteria.

Larger and higher molecular weight hydrocarbon molecules are generally less soluble in water; therefore, their dissolved concentrations in groundwater tend to be limited (e.g., acenaphthene). This property not only reduces the availability of these hydrocarbons to biodegradation, it also limits the mass of these contaminants that can migrate with groundwater over time. For bioremediation of higher molecular weight compounds at a particular site, these two factors may offset one another. In simpler terms, bioremediation of the larger hydrocarbons may take longer, but there is more time to complete the biodegradation because the contamination is not moving away from the treatment area as quickly. The most appropriate remediation for sites that are contaminated mostly with heavy petroleum constituents might be excavation and application of an off-site remedial technology, such as thermal desorption, or proper disposal of the contaminated soil.

Solubility is also an indicator of likely contaminant sorption onto soil. When contaminants are sorbed onto soil particles, they are less available for bioremediation. A compound with a relatively high solubility has a reduced tendency to sorb to soil contacting contaminated groundwater. Conversely, contaminants with relatively low solubility values will generally have an increased tendency to sorb to soil contacting contaminated groundwater. This concept is described in more detail below.

K_{oc} Factor. When groundwater is contaminated by a release from a petroleum underground storage tank, the proportion of hydrocarbon mass in the soil is often far greater than that dissolved in groundwater. This is due in part to the relatively low solubility thresholds for petroleum contaminants. However, another factor is the relatively strong tendency for most petroleum hydrocarbons to sorb to naturally occurring organic carbon material in the soils. This tendency, along with the sheer mass of soil relative to groundwater in a contaminated area, can lead to hydrocarbon mass distributions that are so lopsided they can make the mass in the dissolved-phase appear insignificant. However, because bioremediation occurs in the dissolved phase, that portion of a petroleum mass is always significant in a bioremediation project. It is important to also know how the target organic petroleum compounds are partitioned between the dissolved and unsaturated and saturated sorbed phases.

K_{oc} is a compound-specific property that helps define the equilibrium condition between organic carbon and the contaminant concentrations in an aqueous solution. Using site-specific soil organic carbon content data (i.e., fraction of organic content or foc), K_{oc} can be used to determine the equilibrium contaminant concentrations between groundwater and soil below the water table. The typical organic carbon content in surface soils ranges from 1 to 3.5 percent. In subsurface soils, organic carbon content is an order of magnitude lower because most organic residues are either incorporated or deposited on the surface.

The equation below shows how K_{oc} is defined and used with site-specific fraction of organic carbon (f_{oc}) data to determine the soil-to-groundwater concentration equilibrium ratio, K_d. Knowing the contaminant concentration in one media (e.g., groundwater), the contaminant concentration in the other media (e.g., soil) can be predicted using the site- and constituent-specific K_d sorption constant.

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

where:

K_d = grams contaminant sorbed/grams organic carbon
= grams contaminant/mL solution
K_{oc} = compound-specific sorption constant and
f_{oc} = fraction of organic carbon in site soil

Higher K_{oc} and K_d values indicate more contaminant mass is likely to be retained in soil and therefore less readily bioavailable. Conversely, lower K_{oc} and K_d values indicate lower contaminant concentrations will exist in equilibrium in soil for given concentrations in groundwater. Exhibit XII-16 provides petroleum constituent K_{oc} values for a list of common petroleum hydrocarbon. A comparison of the solubility and K_{oc} values for the sample group of petroleum hydrocarbons reveals the inverse relationship between the two parameters. For example, compounds with higher solubility values have lower K_{oc} constants.

The relative proportions of contaminants in the sorbed and dissolved phases is important to establish when evaluating the likely effectiveness of enhanced aerobic bioremediation. A disproportionate amount of target hydrocarbon contaminant mass sorbed to the soil, and therefore less bioavailable, may signal that enhanced aerobic bioremediation by itself may not be an effective method of reducing subsurface contaminant mass. In this case, it may be necessary to combine enhanced aerobic bioremediation with other technologies that can help bring more contaminant mass out of the sorbed phase and into the dissolved phase so it can be biodegraded. This highlights the importance of establishing a cleanup goal up front.

In the absence of site-specific data that reveal the distribution of contaminant mass, solubility and K_{oc} data can be used to obtain a general understanding of the likelihood that enhanced aerobic bioremediation is applicable at the site. Petroleum contaminants with generally high solubility limits and low K_{oc} values tend to be more bioavailable in groundwater, and the contaminant mass can often be destroyed by enhanced aerobic bioremediation technologies. When contaminant solubility constants are generally low and K_{oc} values are high, enhanced aerobic bioremediation will be limited in its effectiveness.

Special Considerations for MTBE. Not all sites have indigenous microbial suites capable of degrading MTBE. The MTBE chemical bonds are strong and not easily cleaved through chemical or biological means. As such, when enhanced aerobic bioremediation is to be utilized for addressing MTBE, it may be prudent to verify that native MTBE-degraders exist at a site, before implementing a costly and complex enhanced aerobic bioremediation plan. This can be done with standard microcosm tests. Such laboratory test can be also used to optimize the Enhanced aerobic bioremediation procedures for the site so as to insure enhanced biodegradation of both petroleum compounds and MTBE. If the microcosm tests indicate that insufficient MTBE-degrading microbes exist at a site, then it may be necessary to bioaugment the site by increasing the numbers of microbes. Caution is necessary when bioaugmenting with a cultured microbial suite as the technical effectiveness, cost-effectiveness, and longevity of microbes need to be well understood. Due to the vagaries of geochemistry and microbiology in the subsurface, site-specific microcosms and/or pilot tests may be advisable before full-scale implementation of a bioaugmentation system.

When MTBE biodegrades, it often produces an intermediary product called tertiary butyl alcohol (TBA). The subsurface creation of TBA has been noted at some enhanced aerobic bioremediation field sites that contain MTBE. Therefore, any enhanced aerobic bioremediation application at a site containing MTBE has the potential to create TBA. This constituent of concern has been noted to rapidly disappear from the subsurface at some biodegradation sites, while at other sites, the TBA seems to be recalcitrant. Field workers need to be aware of the possible subsurface creation of TBA, and seek to avoid creating a undesirable, recalcitrant TBA plume.

The presence of TBA in the subsurface at an MTBE-impacted site is not definitive proof of MTBE biodegradation. TBA is a gasoline additive that can be present in concentrations of up to 9.5% by volume, and it is often found in commercial-grade MTBE at 1-2% by volume. Therefore, it is possible to detect subsurface TBA at an MTBE site, even if no MTBE biodegradation is occurring. Careful study of TBA/MTBE ratios, as well as their plume patterns relative to each other and relative to the enhanced aerobic bioremediation activitie,s can help to determine if the TBA was in the original gasoline spill or if it is present due to biodegradation of TBA. It is also important to note that as an alcohol, TBA can be difficult to detect at low levels in water samples; detection limits from laboratory analyses can vary widely, and many analyses will not find TBA when it is present in low concentrations.

When considering enhanced aerobic bioremediation for a site that also contains the gasoline additive methyl tertiary butyl ether, the presence of MTBE mandates that several issues be considered. Exhibit XII-17 provides a list of the questions that should be asked before enhanced aerobic bioremediation is considered for treating MTBE at a petroleum UST site.

EXHIBIT XII-17
MTBE Considerations For Applying Enhanced Aerobic Bioremediation

- Does the presence of MTBE require treating a larger region of the aquifer?
- Does the presence of MTBE require treating a deeper portion of the aquifer, especially in the downgradient area of the plume where MTBE plumes sometimes "dive" ?
- Does either of these mandates require installing more oxygen application points?
- Are native MTBE-degrading microbes known to exist at that specific site? Are they sufficient in number to be effective? Are they located where the MTBE presently is? Are they located where the MTBE will be in the future?
- Is the addition of an MTBE-degrading microbial suite needed?
- Has the greater mobility of the MTBE been accounted for in the plan?
- Does the presence of more readily biodegradable compounds (example: BTEX) indicate a delay before MTBE is consumed by microbial populations? If so, what are the implications of this?
- Is the same remediation method being used for the hydrocarbons also sufficient to address the MTBE? Does the site contain a sufficient oxygen load and appropriate microbial suite (native or bioaugmented)?
- Has the corrective action plan accounted for the possible biological formation of the intermediary product tertial butyl alcohol (TBA), including the possibility of creating an undesirable TBA plume?

- Has the corrective action plan accounted for the possible biological formation of the intermediary product tertial butyl alcohol (TBA), including the possibility of creating an undesirable TBA plume?

The various technical issues raised in Exhibit XII-17 demonstrate that while enhanced aerobic bioremediation for MTBE and other similar oxygenates can be promising, a number of special factors should be considered before moving forward with application of an enhanced aerobic bioremediation project for MTBE. Although the addition of supplemental microbial suites (bioaugmentation) is beyond the scope of this chapter, it can be considered for such sites. For more information on the use of bioaugmentation, see *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002), Chapter X ("In-Situ Groundwater Bioremediation").

As discussed earlier, assessing the applicability of an enhanced aerobic bioremediation plan for MTBE is more complex than a similar assessment for other gasoline compounds. While typical gasoline compounds like BTEX have been found to be nearly ubiquitously biodegradable under a wide variety of subsurface conditions, the same cannot be said for MTBE. Studies of MTBE biodegradability have produced highly variable results.. Therefore, it is not yet possible to make universal statements about enhanced aerobic bioremediation effectiveness for MTBE. Instead, the reviewer is advised to carefully consider site-specific conditions before committing to enhanced aerobic bioremediation for MTBE. Exhibit XII-18 on the next page provides some guidance.

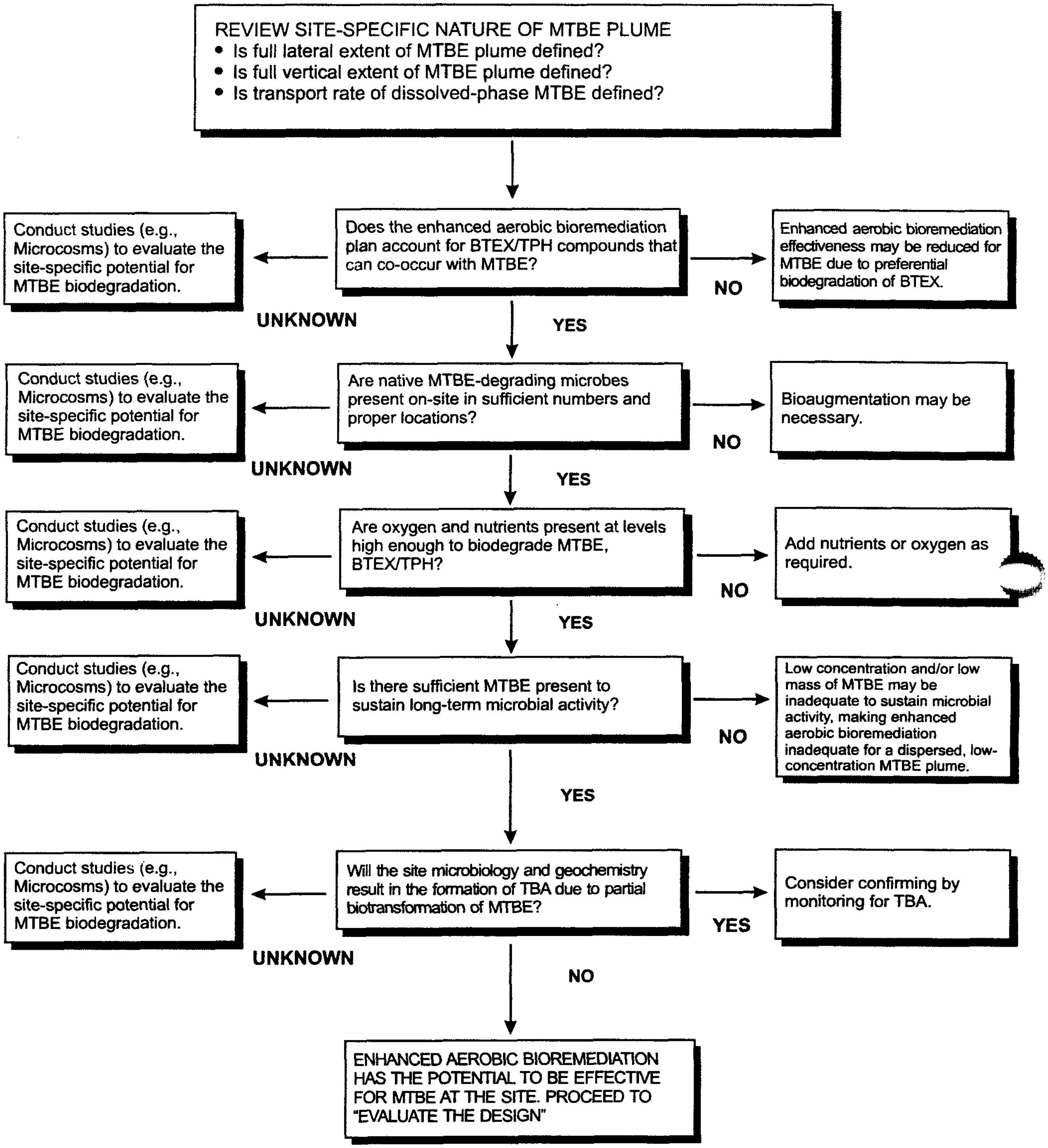
Because MTBE biodegradability still appears to be site-specific and because the state of knowledge is still developing, it may be advisable to conduct site-specific microcosm studies using the intended enhanced aerobic bioremediation method before committing to a full-scale remediation plan for MTBE. Such microcosm studies may investigate: MTBE biodegradation under varying conditions, the need for bioaugmentation, the production of TBA, etc.

Step 3 - Evaluation of Enhanced Aerobic Bioremediation Design

This section provides guidance on reviewing and evaluating the enhanced aerobic bioremediation design. It focuses on prompting reviewers to identify and review key elements of corrective action plans to help ensure they demonstrate a coherent understanding of the basis for the enhanced aerobic bioremediation system design. In addition, this section provides information on typical enhanced aerobic bioremediation technology components to help verify that the corrective action plan has included the basic equipment requirements for the remedial system.

It is assumed that the detailed technology screening process (described in Steps 1 and 2) has verified that enhanced aerobic bioremediation appears to be appropriate and is expected to be an effective cleanup approach, given site-specific conditions. If the enhanced aerobic bioremediation effectiveness evaluation has not been completed, it is strongly recommended that this be done before the design is evaluated.

Exhibit XII-18
Detailed Evaluation of Enhanced Aerobic Bioremediation Effectiveness for MTBE



Design Basis

Review of the corrective action plan should find consistency between site characterization work and information that is presented as the basis for the enhanced aerobic bioremediation design in the corrective action plan. To conduct the enhanced aerobic bioremediation effectiveness evaluation, the reviewer should have a solid understanding of the nature and extent of the site-specific petroleum constituents of concern, including an understanding of the contaminant phases present and the relevant site chemical, physical, and biological properties. When preparing and reviewing the corrective action plan design, the reviewer should also understand the site geology and hydrogeology, and the risks associated with the contamination. These data, which should have been developed and interpreted as part of the site characterization effort, serve as the foundation for the remedial system design.

While the site characterization data provide the core raw materials for the design, further refinement is often needed and useful. For example, while the site characterization work may identify potential human or ecological receptors that may be exposed to the contamination, specific cleanup goals may not have been established. In such cases, the specific remedial goals would need to be developed and identified in the corrective action plan through one or more established approaches, such as adopting state-published cleanup standards, developing site-specific risk-based standards acceptable to the state, or employing other state-specific and approved methods.

The corrective action plan may also include the results and interpretation of follow-up studies completed after the original site characterization. The need for such studies is often identified after a review of the site characterization shows that additional information is needed to complete the remedial system design. For example, the site characterization may suggest that one or more of the constituents of concern is believed to be marginally biodegradable, and the level of expected biodegradation is difficult to predict from the existing data.

Examples of typical information expected to be developed during the site characterization, or as a result of follow-up studies that are completed to support the basis for the technology selection and design of the corrective action plan, are summarized in Exhibit XII-19. Each of the items listed in Exhibit XII-19 is described in more detail below.

Cleanup Goals

The evaluation of alternative remedial approaches and the subsequent design of the selected approach are strongly influenced by the cleanup goals that the remediation program must achieve. Often, preliminary goals identified during the site characterization work evolve as a better understanding of site conditions and potential receptors is attained. However, owing to their importance for remediation planning and design, the cleanup goals should be fully evolved and solidified in the corrective action plan.

Exhibit XII-19
Enhanced Aerobic Bioremediation Design Basis Factors

Design Basis Factor	Source(s) of Design Information
Cleanup Goals ■ Target contaminant levels (soil and groundwater) ■ Remediation timeframe	Receptor survey, pre-design exposure or risk assessment analyses (potentially including numerical modeling), or state requirements
Geology ■ Uniformity ■ Stratigraphy ■ Geochemistry ■ Bedrock ■ Soil permeabilities	Site characterization soil borings, well installations, sampling/analysis, and site observations. Local geologic studies.
Hydrogeology ■ Depth to groundwater ■ Groundwater elevation and gradient ■ Aquifer/water bearing unit class (e.g, confined, unconfined, perched, bedrock) ■ Hydraulic parameters (e.g., conductivity, transmissivity, storativity, effective porosity) ■ Modeling results	Site characterization well gauging, aquifer pump testing, data analyses, and local hydrogeologic studies.
Petroleum Contamination ■ Target chemical constituents ■ Target contaminant and total hydrocarbon mass estimates (sorbed, dissolved, liquid and vapor phases) ■ Extent (vertical and lateral) ■ Bioavailability ■ Biodegradability ■ Fate and transport characteristics	Soil, groundwater and other media sampling/laboratory analysis, review of published data on contaminants and data interpolation and analysis.

Cleanup goals usually provide the end-point concentrations for petroleum constituents in soil and groundwater that are acceptable to state or other regulatory agencies. These cleanup thresholds could be goals that represent any of the following:

- Health-based numeric values for petroleum chemical constituents published by the respective regulatory agency
- Cleanup goals developed and proposed by the contractor specifically

for the contaminated site that are acceptable to the Implementing Agency
- Goals derived from site-specific risk assessment involving contaminant fate and transport modeling coupled with ecological and human-health risk assessment
- Generic state cleanup goals

Additional project goals that may or may not be regulatory requirements include hydraulic control of the contamination, a cleanup timeframe, or other performance goals established in the corrective action plan. Regardless of what the cleanup goals are and how they are established, the state-sanctioned goals should noted in the corrective action plan and recognized as a *fundamental* basis for the technology selection and design.

The cleanup goals presented in the corrective action plan answer important questions relevant to the viability of the selected remedial approach and the adequacy of the remedial design. These two critical questions are:

- Can the cleanup concentration goals be met by the designed enhanced aerobic bioremediation system?
- Can sufficient oxygen be delivered to the contaminated area to enable contaminants to be biodegraded to meet cleanup goals within a reasonable period of time?

Each of these questions is discussed in more detail in the paragraphs that follow.

- *Can the cleanup concentration goals be met by the designed enhanced aerobic bioremediation system?*

Below a certain "threshold" petroleum constituent concentration, bacteria may not be able to derive sufficient carbon from petroleum biodegradation to sustain vigorous levels of biological activity. As concentrations of petroleum contaminants fall below the threshold, further biodegradation of the petroleum hydrocarbons can become relatively insignificant. The level of diminishing returns is site-specific and representative of petroleum contamination that has been reduced in concentration to the technological limit of the specific enhanced aerobic bioremediation.

Although the threshold limit of enhanced aerobic bioremediation approaches can vary greatly, depending on bacteria-, petroleum constituent- and site-specific factors, it is generally observed that petroleum constituent soil concentrations cannot be reduced below 0.1 ppm without using supplemental technologies. In addition, reductions in total petroleum hydrocarbons (TPH) of greater than 95 percent can be very difficult to achieve because of petroleum products often contain "recalcitrant" or non-degradable petroleum hydrocarbons.

While further bioremediation of petroleum contaminant levels in the subsurface may become limited at some point due to the limited availability of a useable carbon source, it is quite possible that the target chemical constituents that may exist in soil and groundwater at that time may meet the cleanup standards. Even though total hydrocarbon levels may remain elevated in subsurface soil, the chemical constituents comprising the hydrocarbon mass may be those that are less soluble and of reduced environmental concern.

Exhibit XII-20
Cleanup Concentrations Potentially Achieved By Enhanced Aerobic Bioremediation

Cleanup Requirement	Feasibility of Meeting Cleanup Levels
Petroleum constituent concentration in soil >0.1 ppm (each contaminant with corresponding dissolved levels in groundwater) and TPH reduction < 95%	Feasible
Constituent concentration in soil ≤ 0.1 ppm (each contaminant with corresponding dissolved levels in groundwater) or TPH reduction ≥ 95%	Potentially infeasible to remediate in reasonable timeframe; laboratory or field trials may be needed to demonstrate petroleum concentration reduction potential

If comparing existing levels of site petroleum contamination to the cleanup goals indicates that either of these guidance criteria summarized in Exhibit XII-20 is exceeded, the proposed enhanced aerobic bioremediation. The system design may not achieve the expected remedial objectives in a reasonable time frame.

- *Can sufficient oxygen be delivered to the contaminated area to enable contaminants to be biodegraded to meet cleanup goals within a reasonable period of time?*

Cleanup goals establish the concentrations and allowable residual mass of petroleum constituents that can acceptably remain in the subsurface soil and groundwater subsequent to remediation. The difference between the current level of petroleum mass in the soil and groundwater and the allowable residual mass left in the subsurface is the mass that needs to be biodegraded using enhanced aerobic bioremediation. Using the theoretical 3 to 3.5 pounds of O_2 to degrade roughly 1 pound of petroleum hydrocarbon ratio discussed earlier, it is possible to estimate the minimum mass of O_2 needed to achieve the required petroleum mass biodegradation. This value assumes that there are no significant oxygen "sinks" in the subsurface (e.g., mineral species that oxidize such as iron) that would increase the total demand for oxygen.

For example, if the corrective action plan data indicate that approximately 5,000 pounds of petroleum hydrocarbons are in the site subsurface but the cleanup goals allow only 500 pounds to remain after remediation (based on allowable soil and groundwater constituent concentration limits), then 4,500 pounds of hydrocarbons require bioremediation. Assuming anaerobic biodegradation and abiotic degradation of site contamination are negligible, and that there are no other sources of oxygen or significant oxygen losses or sinks, and 3.5 pounds of O_2 are needed to aerobically biodegrade each pound of petroleum, then it can be estimated that a minimum of 15,750 pounds of oxygen would need to be provided by the enhanced aerobic bioremediation technology during remedial program implementation. During review of the corrective action plan, therefore, estimate the oxygen mass required to bioremediate the contamination and determine how the demand will be met by the proposed enhanced aerobic bioremediation system.

Furthermore, if pure oxygen injection is the proposed enhanced aerobic bioremediation technology, and the remediation timeframe is 3 years, the corrective action plan design should show how the pure oxygen injection system will be able to deliver and distribute a minimum of 15,750 pounds of oxygen over the 3-year period. In other words, the corrective action plan should demonstrate that an average of at least 0.6 pounds of pure oxygen per hour can be delivered over the 3-year period.

The example discussed above assumes that losses of oxygen to the aquifer are negligible. In reality, as discussed earlier in this chapter, significant losses of oxygen can occur from the application of the enhanced aerobic technology itself and from abiotic and microbiologically mediated reactions with the aquifer material. An attempt should be made to estimate what these potential oxygen losses could be in order to factor those losses into the oxygen delivery plan and cleanup schedule.

If the corrective action plan does not estimate the oxygen and bio-nutrient delivery requirements or does not demonstrate how the oxygen and bio-nutrient delivery requirements will be met by the enhanced aerobic bioremediation system, the corrective action plan may be incomplete. Under such circumstances, it may be prudent to request that this information be provided before approving the plan. Similarly, if site-specific cleanup goals have not been clearly established in the corrective action plan or previously, it may be appropriate to refrain from completing the review of the design until this critical information is provided.

Enhanced Aerobic Bioremediation Technology Selection

With the design basis established in the corrective action plan, the corrective action plan can be reviewed to confirm that enhanced aerobic bioremediation is a reasonable site-specific choice of remediation technology. Depending on project-specific circumstances, there can be only one or a few enhanced aerobic bioremediation technologies equally viable and appropriate for a site.

Alternatively, site-specific or project-specific circumstances may suggest that one of the enhanced aerobic bioremediation would address the on-site contamination better than any other technology.

Exhibit XII-2 presents the key advantages and disadvantages of each of the enhanced aerobic bioremediation technologies. Use these factors to evaluate the feasibility of using an enhanced aerobic bioremediation approach. Other differences between and among alternative enhanced aerobic bioremediation technologies can help to distinguish their most appropriate application(s). A key characteristic useful for evaluating the feasibility and appropriateness of a proposed enhanced aerobic bioremediation technology is oxygen delivery efficiency. More information on how this characteristic can be used is provided in the next paragraphs.

Oxygen Delivery Efficiency. All enhanced aerobic bioremediation technologies need to deliver oxygen to the subsurface to encourage aerobic biodegradation of petroleum contamination to occur. The effectiveness of each enhanced aerobic bioremediation technology is directly related to the amount of oxygen it can deliver and uniformly distribute in the contaminated area. Because of this commonality, it makes sense to explore the relative efficiency with which each technology is able to deliver oxygen to the treatment area as a distinguishing feature.

Oxygen produced from the decomposition of compounds used in enhanced aerobic bioremediation approaches follows the stoichiometric relationships shown in Exhibit XII-21. For instance, for every two parts of hydrogen peroxide injected, only one part of oxygen is produced. In contrast, one part ozone yields 1.5 parts of oxygen, a seemingly more efficient means of generating oxygen.

Exhibit XII-21
Basic Stoichiometry Oxygen Production From Chemical Decomposition

Enhanced Aerobic Bioremediation Technology	Basic Oxygen-Producing Stoichiometry
Oxygen-Producing Compounds	
Hydrogen Peroxide	$2H_2O_2 \rightarrow 2H_2O + O_2$
Ozone	$O_3 \rightarrow 1.5\ O_2$
Oxygen Releasing Compounds	
Magnesium Peroxide	$MgO_2 + H_2O \rightarrow Mg(OH)_2 + \frac{1}{2}O_2$
Sodium Peroxide	$Na_2O_2 + H_2O \rightarrow NaOH + H_2O_2$

A more practical way of measuring oxygen delivery efficiency is to determine the total amount of mass of carrier material (e.g., groundwater containing hydrogen peroxide) that needs to be delivered to the subsurface in order to deliver 1 gram of oxygen. In essence, this is a measure of the amount of effort, energy, and perhaps, time required to deliver oxygen using the different enhanced aerobic bioremediation technologies. Exhibit XII-22 compares seven alternative methods of delivering oxygen to the subsurface using this measure of delivery efficiency. It compares:

- Three approaches that use groundwater as the oxygen carrier
  - Re-injection of groundwater fully aerated with ambient air
  - Re-injection of groundwater fully aerated with pure oxygen
  - Re-injection of groundwater containing 100 ppm of hydrogen peroxide

- One method that delivers oxygen in the solid phase (oxygen releasing compounds)

- Three approaches that deliver oxygen in the vapor phase
  - Ozone injection
  - Biosparging/bioventing
  - Pure oxygen injection

While the re-infiltration of hydrogen peroxide-amended groundwater may be the least efficient method of oxygen delivery to the contaminated area, the hydraulic gradients induced by this activity may enhance the distribution of oxygen in the subsurface. For more information on factors affecting the distribution of oxygen in the subsurface, refer to discussions presented earlier as part of the detailed enhanced aerobic bioremediation effectiveness evaluation.
Each of the major headings in the table above is discussed in more detail below.

Design Components

Although the design elements of alternative enhanced aerobic bioremediation technologies can vary significantly, Exhibit XII-23 describes the most common design elements. Several of the more important elements are discussed below to assist with evaluation of the corrective action plan.

Oxygen and Bio-nutrient Delivery Design should be based primarily on petroleum mass reduction requirements, site characteristics and cleanup goals. Oxygen will generally need to be applied at a minimum 3:1 ratio relative to the petroleum hydrocarbon mass targeted for remediation. Bio-nutrient formulation and delivery rate (if needed) will be based on soil sampling. Common nutrient additions include nitrogen (in an aqueous solution containing ammonium ions) and phosphorus (in an aqueous solution containing phosphate ions). Note that state regulations may either require permits for nutrient and/or air injection or prohibit them entirely.

Exhibit XII-22
Relative Oxygen Delivery Efficiencies For Various Enhanced Aerobic Bioremediation Technologies

Oxygen Delivery Approach	Description	Oxygen Concentration in Delivery Material (mg/L)	Mass of Oxygen Carrier per Unit Mass of Oxygen Delivered (g/g)	Relative Oxygen Delivery Efficiency
Aqueous-Phase Oxygen Delivery				
Re-injection of Aerated/ treated Groundwater	Ambient Air Saturated	9	110,000	Lowest
Re-injection of Pure Oxygen-Amended Groundwater	Pure O_2 Saturated	45	22,000	
Re-injection of H_2O_2-Amended Groundwater	100 mg/L of H_2O_2	50	20,000	
Solid-Phase Oxygen Delivery				
Injection of Oxygen-Releasing Compounds	Mg-peroxide	N/A	10	
Vapor Phase Oxygen Delivery				
Injection of Ozone	5% Ozone (Converted to O_2)	98	12	
Biosparging with Air or Oxygen, or Bioventing	21% Oxygen (Ambient)	275	4	
Injection of Pure Oxygen	95% Oxygen	1,250	1	Highest

Exhibit XII-23
Common Enhanced Aeration Remediation Design Elements

- Oxygen and Bio-nutrient Delivery Design
  - Theoretical oxygen mass requirement
  - Bio-nutrient needs (e.g., N, P)
  - Application delivery rate
  - Number and depth of application points/position
  - Equipment

- Permit Requirements and Thresholds
  - Underground injection/well installation
  - Air injection into subsurface
  - Groundwater (wastewater) discharge
  - Air (soil vapor) discharge

- Performance Monitoring Plan
  - Ongoing distribution of oxygen and bio-nutrients
  - Expansion of microbial population
  - Reduction in contaminants (sorbed and dissolved phases)

- Contingency Plan
  - Inadequate oxygen distribution
  - Stagnation or die-off of microbial population
  - Lower-than-expected petroleum mass reduction rates
  - Excessive contaminant migration
  - Build-up of excessive recalcitrant petroleum constituents
  - Fugitive (soil vapor) emissions
  - Difficult-to-treat/fouling of treated wastewater discharge
  - Clogging of equipment or injection areas with iron oxide or biomass
  - Other contingencies

Permit Requirements and Thresholds should be identified in the design so that the system can be constructed to comply with permit requirements and constraints. Depending on the specific enhanced aerobic bioremediation technology and the state in which the site is located, permits that may be required include underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge.

Several federal, state, and local programs regulate Class V aquifer remediation wells, and many require permits for underground injection of oxygen or bio-nutrients. On the federal level, management and regulation of these wells fall primarily under the underground injection control program authorized by the Safe Drinking Water Act (SDWA). Some states and localities have used these authorities, as well as their own authorities, to extend the controls in their areas to address concerns associated with aquifer remediation wells. Aquifer remediation injection wells are potentially subject to at least three categories of regulation.

First, a state's underground injection control (UIC) program, operating with approval from the federal program, may have jurisdiction over such wells. Second, in some states without UIC programs, the state's program for groundwater protection or pollution elimination program requirements may apply to remediation wells. Third, remediation wells may be regulated by federal and state authorities, through Superfund programs, corrective action programs under RCRA (including the UST program), or other environmental remediation programs. In the case of remediation programs, the regulatory requirements typically address the selection of aquifer remediation as a cleanup alternative and establish the degree of required cleanup in soil and groundwater, while deferring regulation of the injection wells used in the remediation to other programs. In the case of voluntary cleanup programs, some concern exists because they may not be approved or completed according to standards typical of cleanups overseen by a state or federal agency.[4]

Performance Monitoring should be accounted for in the design in the form of a written plan that can be used to objectively evaluate enhanced aerobic bioremediation system performance. The plan should clearly describe the approaches and methods that will be used to evaluate enhanced aerobic bioremediation system effectiveness in each of the following:

- Delivering oxygen (and bio-nutrients) to the subsurface
- Distributing oxygen and bio-nutrients through the contaminated area
- Increasing microbial population density
- Reducing sorbed and dissolved phase petroleum concentrations
- Achieving other performance requirements consistent with site-specific cleanup goals

Contingency Plans should also be accounted for and prepared as part of the design. The design should anticipate low-likelihood problems and potentially changing environmental conditions, as well as outline specific response actions that may be taken. Examples include response actions to take if any performance monitoring data indicate the following:

- Inadequate oxygen distribution
- Stagnation or die-off of microbial populations
- Low petroleum mass reduction rates
- Excessive contaminant migration

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[4] US EPA, Office of Solid Waste memo dated 12/27/00 on the Applicability of RCRA Seciton 3020 to In-Situ Treatment of Ground Water.

- Recalcitrance of constituents
- Fugitive emissions
- Any other reasonably plausible scenario that can arise under site-specific conditions and project-specific circumstances.

Components of Enhanced Aerobic Bioremediation Systems

After review of factors that affect the selection and design of a particular enhanced aerobic bioremediation technology and the critical elements that should be included in the corrective action plan for enhanced aerobic bioremediation,, it is now appropriate to discuss major components of various enhanced aerobic bioremediation systems.

Exhibit XII-24 summarizes some of the major equipment components associated with each of the more common enhanced aerobic bioremediation technologies. Depending on which enhanced aerobic bioremediation technology has been selected in the corrective action plan, a subset of these major system components should be presented and discussed and schematically depicted (e.g., process flow diagram) in the corrective action plan. The design should relate capacities of these equipment components to design requirements (e.g., required oxygen production/delivery rates).

As shown in Exhibit XII-24, enhanced aerobic bioremediation systems employing oxygen-releasing compounds appear to require the least equipment in part because there is no need for any mechanical equipment once the oxygen-releasing compounds are deployed. By contrast, re-injection of hydrogen peroxide-amended groundwater requires the most equipment and a large number of mechanical components (e.g., pumps, blowers, etc.).

While the sets of major equipment components used by the enhanced aerobic bioremediation technologies differ significantly, the use of wells by each different approach warrants recognition and further discussion. In particular, the orientation, placement, number and construction of this common design element is worthy of a brief review.

Injection, Extraction and Re-infiltration Wells. Three important considerations for these wells are orientation, placement and number, and construction.

- **Well Orientation.** Both horizontal and vertical wells can be used to treat subsurface petroleum releases with any of the various enhanced aerobic bioremediation systems. Hydrogen peroxide-amended groundwater can be re-infiltrated using either vertical or horizontal wells. Although vertical wells are more common for ozone or pure oxygen injection, horizontal wells can be used.

Exhibit XII–24
Major Components of Enhanced Aerobic Bioremediation Systems

Component	Function
Oxygen Releasing Compound Systems	
Borings and Excavations	Used to inject or place a slurry of oxygen releasing compounds so that oxygen may be slowly imparted to the water bearing zone.
Application Wells	Often used to suspend a solid form of oxygen releasing compounds to provide oxygen to groundwater.
Monitoring Wells	Used to evaluate effectiveness of remedial approach. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination generally indicate how effectively oxygen is being delivered/dispersed and contaminants are being reduced.
Hydrogen Peroxide Injection Systems	
Extraction Wells	Often used to extract contaminated groundwater downgradient of the contaminated area for treatment and re-injection in the upgradient source area for plume containment and/or accelerated groundwater flow through the contaminated area.
Injection Wells or Infiltration Galleries	Injection wells, infiltration galleries or a combination of these are typically used to re-inject treated and hydrogen peroxide-amended groundwater so that dissolved oxygen may be flushed through the treatment zone.
Extraction, Injection, Transfer, and Metering Pumps and Tanks	Extraction, injection, transfer, and metering pumps are used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering hydrogen peroxide and bio-nutrients into the infiltration system to maintain design concentrations.
Groundwater Treatment Equipment	Extracted groundwater may be treated to remove petroleum hydrocarbons by various means such as: oil/water separation; air stripping; or granular activated carbon sorption or others.
Instrumentation and Controls	Used to integrate and activate/deactivate system components. Help maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges.

Exhibit XII–24
Major Components of Enhanced Aerobic Bioremediation Systems (continued)

Component	Function
Hydrogen Peroxide Injection Systems (continued)	
Monitoring Wells	Used to collect environmental samples analyzed in laboratories and field to evaluate on-going effectiveness of remediation. Groundwater well samples tested for dissolved oxygen and contamination to evaluate overall effectiveness of oxygen delivery/dispersal and the contaminant reductions over time.
Pure Oxygen Injection Systems	
Sparging Wells	Used as conduits to bubble pure oxygen into contaminated groundwater. The oxygen is delivered to the base of the soil and groundwater petroleum contamination so that it will rise through the contaminated material providing oxygen to the hydrocarbon degrading bacteria.
Air Compressing Equipment	Used to pressurize ambient air to: prepare it for subsequent treatment to increase Oxygen levels/purity; and to provide pressure needed to inject oxygen and ambient air beneath the water table.
Oxygen Generating Equipment	Used to generate nearly-pure oxygen gas (~ 95%) from ambient air. Synthetic zeolite sorbers are frequently employed to simply remove nitrogen from ambient air to produce high-purity oxygen.
Instrumentation and Controls	Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with design and to safeguard against inadequate treatment or inappropriate discharges.
Monitoring Wells	Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination generally indicate how effectively oxygen is being delivered or dispersed and contaminant reductions are occurring.

Exhibit XII–24
Major Components of Enhanced Aerobic Bioremediation Systems (continued)

Component	Function
Ozone Injection Systems	
Sparging Wells	Used as a conduit to inject ozone into contaminated groundwater. The ozone is sparged near the base of the soil and groundwater petroleum contamination so that it may contact the contaminants and provide oxygen to the hydrocarbon degrading bacteria.
Air Compressing Equipment	Used to pressurize ambient air needed to generate ozone and to provide the pressure needed to inject the ozone beneath the water table. Air compressor equipment must supply oil and contaminant free air to minimize in-line reactions with and premature decomposition of ozone.
Ozone Generating Equipment	Used to generate ozone gas on-site, typically at concentrations of about 5%.
Soil Vapor Extraction/ Treatment Equipment (Optional)	Used, if necessary, to control fugitive soil vapor ozone and volatilize organic compounds emissions in the unsaturated zone. May consist of low vacuum/flow blower to generate vacuum conditions in unsaturated zone and collect the vapors. Vapor treatment may consist of granular activated carbon or biofilters for low contaminant concentration air stream.
Instrumentation and Controls	Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges.
Monitoring Wells	Used to collect environmental samples tested in laboratories and the field to evaluate ongoing effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination generally indicate how effectively oxygen is being delivered or dispersed and contaminant reductions are occurring.

Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that require re-infiltration of amended groundwater into shallow groundwater at relatively high flow rates. They are also readily applicable if the affected area is located under a surface structure (e.g., a building), or if the thickness of the saturated zone is less than 10 feet.

- **Well Placement and Number of Wells**. The number and location of wells are determined during the design to accomplish the basic goals of: (1) optimizing reliable oxygen and bio-nutrient delivery to the contaminated area; and (2) providing conduits to measure enhanced aerobic bioremediation system performance. For hydrogen peroxide re-infiltration systems this typically means placing re-injection wells in the source area(s) while extracting groundwater from downgradient locations aimed at simultaneously providing enhanced hydraulic gradient and accelerated oxygen distribution across the impacted area. The number, location, and design of the extraction wells will largely be determined from site-specific hydrogeology, the depth(s) and thickness(es) of the contaminated area(s), and the results of field-scale pilot testing and hydraulic modeling.

Determining the number and spacing of the wells for ozone or pure oxygen injection may also be determined through field-scale pilot testing. However, the following general points should be considered.

- Closer well spacing is often appropriate in areas of high contaminant concentrations to enhance contaminant contact and oxygen delivery/distribution where the oxygen demand is the greatest.

- Direct delivery of oxygen into the contaminated material using closer well spacings can deliver and disperse more quickly than oxygen delivery through groundwater advection/dispersion and could significantly decrease the treatment timeframe.

- At sites with stratified soils, wells screened in strata with low permeabilities often require closer well spacing than wells screened in strata with higher permeabilities.

- **Well Construction.** Enhanced aerobic bioremediation system wells are generally constructed of one- to six-inch diameter PVC, galvanized steel, or stainless steel pipe. Oxygen or ozone injection sparge wells have screened intervals that are normally one to three feet in length and situated at or below the deepest extent of sorbed contaminants. Injection sparge points must be properly grouted to prevent the injected oxygen from moving directly up the well annulus to the unsaturated zone rather than being forced into the contaminated aquifer ("short circuiting" of the injected oxygen). When horizontal injection wells are used, they should be designed and installed carefully to ensure that the injected oxygen exits along the entire screen length.

Re-infiltration wells typically have screen lengths that extend from the base of the wells into the unsaturated zone. Groundwater extraction wells should ideally be screened in the saturated interval containing the greatest mass of hydrocarbons. Field-scale pilot studies and subsequent data analysis and hydraulic modeling can help to determine the configuration and construction design of groundwater extraction and injection wells.

Step 4 - An Evaluation of the Operation and Monitoring Plan

Remedial Progress Monitoring

Significant uncertainties associated with site conditions can remain even as remedial designs are completed and implemented. In the post-remedial startup period, these unknowns frequently can result in operations that vary from the design. These variances can be small or large and often require adjustments to account for unforeseen conditions and optimize system performance. Unfortunately, in many cases, the need for these adjustments can go unrecognized for a long time.

In some cases, the delay in recognizing that remedial system adjustments are necessary may be attributed to relatively slow responses in subsurface conditions to the applied technology (e.g., increases in microbial population and biodegradation of contaminants). Because these subsurface responses to the applied remedial technology can be delayed, there is often the tendency to give the remedial program more time to work (sometimes up to years) before making system modifications or adjustments. In other cases, the delay may stem from misuse or misinterpretation of site data leading to a belief that the remedial system is performing well when it is not. An example of this misuse is the practice of using groundwater analytical data from oxygen delivery wells as an indicator of remedial progress. In this case, an assessment is biased by the localized effects of bioremediation in the immediate vicinity of the oxygen delivery wells, but does not provide an objective measure of the enhanced aerobic bioremediation system's ability to distribute oxygen and promote biodegradation throughout the treatment area.

Wells that are used to carry out remedial actions should not be used as monitoring wells. Monitoring wells should be separate wells used only for that purpose. If remediation involves injection of gases, the monitoring wells should be tightly capped until used. If they are not capped, the monitoring wells can provide a path of least resistance for the injected air to return to the surface. Air can channel to a monitoring well, then bubble up through the standing water in the well preferentially removing contaminants from the area in and immediately around the well while the rest of the aquifer is short circuited.

However, at many sites remedial system operational efficiencies are not optimized simply because an adequate performance monitoring plan has either not been developed or has not been fully implemented. In such cases, the designed remedial system may be installed, started up, and allowed to run its course with insufficient numbers or types of samples collected to determine whether the remedial system is performing in accordance with design expectations. The result of such monitoring approaches can be the discovery of a sub-standard or failed remediation program years after its implementation.

The previous section discussed the importance of developing a comprehensive remedial progress monitoring plan. Because of its importance, this section covers the topics that should be addressed in such a plan to ensure objective gauging of remedial system performance and necessary optimization adjustments can be made early on and throughout the duration of enhanced aerobic bioremediation. In particular, a focused discussion on performance sampling and enhanced aerobic bioremediation system evaluation criteria is provided to assist with the corrective action plan review.

Evaluation Sampling

Evaluation sampling is performed to gauge the effectiveness of the enhanced aerobic bioremediation system relevant to design expectations. Based on a comparison of the actual field sampling data to design and operational expectations, timely modifications to the system or operating procedures (if any) can be made to optimize system performance early in the remediation program. Projects with regular performance reviews guided by the results of such sampling/monitoring programs have a greater chance of achieving the design remedial goals within desired time frames, potentially at lower cost.

Various environmental media are sampled to evaluate system performance. Groundwater, soil, and soil vapors from the treatment area and vicinity are commonly sampled to determine the degree to which the enhanced aerobic bioremediation system is meeting the basic objectives of the approach, including:

- Delivering oxygen to the saturated zone at required design rates
- Distributing dissolved oxygen across the target contaminated area to restore and maintain aerobic conditions
- Reducing concentrations of petroleum hydrocarbons in soil and groundwater at design rates through biodegradation of the petroleum compounds

Exhibit XII-25 identifies those parameters that are commonly measured in groundwater, soil, and soil vapor samples to help evaluate enhanced aerobic

Exhibit XII-25
Common Performance Monitoring Parameters and Sampling Frequencies

Analytical Parameter	Sampling Frequency			Purpose
	Startup Phase (7-10 days)	Remediation/Post-Application Long-Term Monitoring Phase (on-going)		
	Daily	*Weekly to Monthly*	*Quarterly to Annually*	
Groundwater				
Dissolved Oxygen	X	X		Determines system's effectiveness in distributing oxygen and ability to maintain aerobic conditions (i.e., dissolved oxygen > 2 ppm) in treatment area. Provides data to optimize system performance.
Redox Potential	X	X		Yields data on system's ability to increase the extent of aerobic subsurface environment.
pH	X	X		Confirms pH conditions are stable and suitable for microbial bioremediation or identifies trends of concern.
H_2O_2 or Ozone	X	X		Provides information on distances these oxygen-producing compounds can be transmitted by the remedial system before decomposing
Bio-nutrients			X	Determines if bio-nutrients injected into the groundwater are being consumed during bioremediation or accumulating and potentially degrading groundwater quality
Petroleum COCs			X	Indicates remedial progress

Exhibit XII-25
Common Performance Monitoring Parameters and Sampling Frequencies (continued)

Analytical Parameter	Sampling Frequency			Purpose
	Startup Phase (7-10 days)	Remediation/Post-Application Long-Term Monitoring Phase (on-going)		
	Daily	*Weekly to Monthly*	*Quarterly to Annually*	
Groundwater (continued)				
Degradation Daughter Constituents (e.g., TBA)			X	Offer direct evidence of contaminant bioremediation and enhanced aerobic bioremediation effectiveness
Water Table Elevations	X	X		Determines if hydraulic conditions (groundwater flow) are consistent with design intent or if enhanced aerobic bioremediation technology application has had an unanticipated affect on these conditions
Soil Vapor				
Carbon dioxide	X	X		Provides evidence of biodegradation
Oxygen	X	X		Indicates potential losses of introduced oxygen through the unsaturated zone
Volatile Petroleum COCs	X	X		Suggests residual sources in soil or fugitive emissions associated with the remedial effort
Fugitive Ozone or Hydrogen Peroxide	X	X		Determines losses of oxygen-yielding reagents delivered to the subsurface
Soil				
Petroleum COCs			X	Provide a measure of remedial progress and the extent to which biodegradation of sorbed contaminants is limited by

bioremediation progress and system performance. A brief description of the respective sampling frequencies and the relevance and significance of each parameter to the performance evaluation are also provided in the exhibit. A key element is the location(s) where performance evaluation sampling takes place relative to subsurface oxygen delivery points. As stated in the exhibit, performance evaluation samples should <u>not</u> normally be collected from oxygen delivery locations.

The performance of the enhanced aerobic bioremediation system should be determined by the chemistry and microbiology of soil and groundwater located between, around, and downgradient of oxygen delivery locations rather than inside or in the immediate vicinity of the oxygen delivery points. Conditions inside or in the immediate vicinity of oxygen injection locations have been preferentially altered by enhanced aerobic bioremediation to enhance biodegradation of the petroleum contaminants. Therefore, data from these locations are not representative of the subsurface conditions that exist beneath most of the site. To understand the effect the enhanced aerobic bioremediation system is having on the subsurface conditions as a measure of its performance, samples of soil, groundwater and soil gas should be collected from alternate locations.

In reviewing of the performance monitoring plan in the corrective action plan, a reviewer should verify that a sufficient number of sampling locations exist between oxygen application points to provide the necessary performance sampling data. A description of how these data may be used to evaluate the enhanced aerobic bioremediation system performance is provided below.

Particular attention should be taken with respect to sampling groundwater, soil vapor, and soil. In reviewing a sampling plan, pay attention to the proposed sampling frequencies and methods. Some factors to look for include:

Groundwater sampling. Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxygen delivery wells for evaluating system performance because they would only be representative of highly localized effects of the remediation program.

Soil vapor sampling. Samples should be collected from monitoring wells located in and around the treatment area that are screened in the unsaturated zone and from soil vapor extraction wells (if used). Samples should <u>not</u> be collected from oxygen delivery wells for evaluating system performance because they would only be representative of highly localized effects of the remediation program.

Soil sampling. Samples should be collected from borings or using Geoprobe sampling equipment in and around the treatment area. Soil samples should consistently be collected from same contaminated sections of stratigraphic interval for comparison to earlier samples from same locations and depths.

Evaluation Criteria

The evaluation sampling described above provides evidence needed to assess the enhanced aerobic bioremediation system performance. This evidence requires examination and interpretation to confirm enhanced aerobic bioremediation system effectiveness and whether system modifications may be warranted. A discussion of these data and how system performance can be interpreted is provided below. In particular, an evaluation of performance is examined from the following two broad enhanced aerobic bioremediation system requirements:

- Oxygen delivery and distribution
- Aerobic biodegradation

Each of these is described in more detail in the following paragraphs.

Oxygen Delivery and Distribution. Performance sampling may indicate that the enhanced aerobic bioremediation system is meeting design specifications for oxygen delivery and distribution if the data show the following:

- Vadose zone air sampling suggests that there are negligible losses of supplied oxygen to the atmosphere

- Oxygen is being delivered to the subsurface at the mass delivery rate required by the design

- Dissolved oxygen levels in groundwater samples collected across the target treatment area have been elevated to concentrations of 2 mg/L or more and reduction/oxidation conditions are uniformly in the aerobic range (greater than or equal to 750 mV)

If the performance monitoring data suggest that one or more of these conditions is not met, the system may not be meeting the requirements of the design and system adjustments or modifications may need to be made. As previously discussed, the remedial system design should include contingency planning that explores performance deficiency scenarios and identifies possible solutions.

Oxygen delivery deficiencies can normally be overcome by adjusting system flow rates or upgrading equipment capacities. However, occasionally, oxygen delivery rates may be limited by the capacity of the subsurface to absorb and/or transport the delivered oxygen mass. This may occur if an infiltration system component becomes hydraulically overloaded by the infiltration rates needed to meet the design oxygen delivery objectives. Also, groundwater could become over-saturated with dissolved oxygen at injection points requiring oxygen delivery rates to be reduced to avoid off-gassing losses of oxygen to the atmosphere. In both cases, additional infiltration or injection points could readily be added to the system to expand the oxygen delivery capacity to design-specified levels.

Loss of oxygen to the unsaturated zone and ultimately the atmosphere removes this supply of oxygen available to biodegrading microorganisms. One way to limit oxygen losses without decreasing application rates is to add application points with proportionally less oxygen delivered to each location. Another approach is to alternate the supply of oxygen to various locations in the contaminated zone, allowing existing levels of oxygen to dissipate before introducing oxygen again.

Perhaps the most challenging performance problem occurs when an enhanced aerobic bioremediation system is unable to restore and maintain aerobic conditions in a portion or multiple portions of a contaminated area. Oxygen distributed from delivery points can fail to reach target contaminated areas for many reasons:

- High biological oxygen demand in the delivery point vicinity
- Elevated soil organic content
- Low permeability heterogeneous soils
- Low hydraulic gradient and groundwater flow

Possible remedies to the performance problem include adding additional oxygen delivery points, increasing oxygen delivery rates, or enhancing hydraulic gradients and groundwater flow.

Aerobic Biodegradation. Successful oxygen delivery and distribution is probably the most important performance measure for an enhanced aerobic bioremediation system. However, this is only part of the performance. The second part requires confirmation that enhanced in-situ biodegradation of the petroleum contaminants is occurring as a result of, and at rates anticipated by, the enhanced aerobic bioremediation design. Performance monitoring that suggests that an enhanced aerobic bioremediation system is operating effectively includes the following.

- Decreasing dissolved and sorbed petroleum contaminant concentrations (i.e., gradual reduction of subsurface petroleum mass consistent with design expectations).

- Production of carbon dioxide in the subsurface, as evidenced by baseline and subsequent vadose zone sampling and field analyses. Carbon dioxide production in the saturated zone may also be evaluated by sampling groundwater and analyzing the groundwater for total inorganic carbon.

- Significantly increased microbial activity in the contaminated area as suggested by comparison of baseline and subsequent microbial population plate counts.

If only one or two of these conditions exist, there may not be enough evidence to conclude that bioremediation is a significant contributor to contaminant reduction or to conclude that the enhanced aerobic bioremediation system is effective. For example, apparent contaminant reductions in dissolved and sorbed phases could occur as a result of groundwater advection and dispersion or simply because of natural fluctuations in water levels. Or, if hydraulic manipulation (engineered hydraulic gradients) of the groundwater is part of the enhanced aerobic bioremediation system, apparent contaminant reductions could result from dilution or separation of the groundwater from the contaminated soil (e.g., if the water table is depressed below the contamination). In this case, contamination levels in groundwater could rebound to near preexisting concentrations if the hydraulic controls are turned off and groundwater re-contacts the contaminated soil.

The appearance of significant levels of carbon dioxide subsequent to enhanced aerobic bioremediation system activation is a good indicator of enhanced biological activity. However, if elevated carbon dioxide levels in the unsaturated zone are unable to be detected, this does not necessarily mean that microbial activity has not been enhanced. Carbon dioxide entering the vadose zone may be diluted by pore space air exchanges with the atmosphere, operation of vapor control systems, and other means, making it difficult to distinguish small differences in concentrations.

Possibly the most direct indication that enhanced aerobic bioremediation has increased the number of hydrocarbon degrading bacteria is observation of significantly increased populations of heterotrophic bacteria in the target treatment area. While larger populations of heterotrophic bacteria may not always translate to increased levels of petroleum hydrocarbon biodegradation, the increased number of bacteria over the baseline levels would serve as a strong indicator of biodegradation. If performance sample analyses detect intermediate degradation daughter products, this may be further evidence of contaminant biodegradation that has been enhanced.

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o	o	Is the density and configuration of oxygen delivery points adequate to uniformly disperse dissolved oxygen through the target treatment zone, given site geology and hydrologic conditions?

3. Written Performance Monitoring Plan

Yes	**No**	
o	o	Will a comprehensive set of baseline sampling be performed prior to enhanced aerobic bioremediation system start-up?
o	o	Does the plan specifically exclude sampling from oxygen delivery wells when collecting data to evaluate enhanced aerobic bioremediation system performance?
o	o	Are monitoring wells adequately distributed between oxygen delivery locations to collect groundwater and soil vapor samples to evaluate the performance of the enhanced aerobic bioremediation system?
o	o	Does the written plan include periodically collecting soil samples from the contaminated interval(s) at locations between oxygen delivery locations?
o	o	Will the soil, soil vapor and groundwater samples be analyzed for the majority of the recommended performance monitoring parameters?
o	o	Will frequencies of performance monitoring generally correspond to those identified in Exhibit XII – 25?

Chapter XIII

Chemical Oxidation

Contents

List of Exhibits

Chapter XIII
Chemical Oxidation

Overview

Petroleum contaminant decomposition and in-situ destruction may be accomplished using chemical oxidation technologies. In contrast to other remedial technologies, contaminant reduction can be seen in short time frames (e.g., weeks or months). As discussed in this chapter, a variety of chemical oxidants and application techniques can be used to bring oxidizing materials into contact with subsurface contaminants to remediate the contamination. With sufficient contact time with the organic contaminants, chemical oxidants may be capable of converting the petroleum hydrocarbon mass to carbon dioxide and water and ultimately irreversibly reduce concentrations of petroleum hydrocarbons in soil and groundwater. While many of the chemical oxidants have been used in wastewater treatment for decades, only recently have they been used to treat hydrocarbon-contaminated groundwater and soil *in-situ*.

Chemical oxidation technologies are predominantly used to address contaminants in the source area saturated zone and capillary fringe. Cost concerns can preclude the use of chemical oxidation technologies to address large and dilute petroleum contaminant plumes. More frequently, chemical oxidation technologies are employed to treat smaller source areas where the petroleum mass is more concentrated. However, where excessive petroleum contaminant mass exists in the source area and where there is a significant thickness of mobile non-aqueous phase liquids (NAPLs), other remedial technologies (e.g., free product recovery) may need to precede chemical oxidation for the remediation to be safe and cost-effective.

Concurrent treatment of source area saturated and unsaturated zones usually requires the integration of chemical oxidation with other remedial technologies that target unsaturated zone contamination (e.g., soil vapor extraction). Frequently, soil vapor extraction, which is used to treat the unsaturated zone, is included as a component of chemical oxidation remedial solutions even if there is no specific need to treat unsaturated soils in the source area. Use of soil vapor extraction in conjunction with chemical oxidation can help alleviate safety issues associated with controlling and recovering off-gas containing volatile organic carbons (VOCs), oxygen, oxidants and other reaction byproducts that can be generated by various chemical oxidants.

As discussed in greater detail below, each chemical oxidant and application technology has advantages and disadvantages. Some oxidants are stronger than others, yet some weaker oxidants may persist in the subsurface, allowing longer contact times with the contaminants. Careful evaluation of the contaminants of concern is needed before selecting a chemical oxidation technology. Certain contaminants (e.g., benzene) that are frequently remedial drivers at petroleum UST release sites are unable to be readily chemically oxidized *in-situ* using some chemical oxidants (e.g., permanganate).

Understanding the site hydrogeologic conditions is important when considering chemical oxidation technologies because these conditions often determine the extent to which the chemical oxidants may come into contact with the petroleum contaminants. Chemical oxidants may not be able to penetrate low permeability homogenous soils or horizons in heterogeneous soils that contain the bulk of petroleum contaminant mass.

Soil reactivity with chemical oxidants is also important when considering the costs of the use of chemical oxidation. Excessive loss of a chemical oxidant that is reacting with organics in soil, instead of reacting with the contaminants, may preclude the use of the technology as an economically viable approach to site remediation. Different chemical oxidation technologies are most appropriate for particular hydrogeologic conditions. For example, Fenton's Reagant may not be ideal for groundwater with high concentrations of carbonate. The carbonate ion preferentially scavenges the hydroxyl radicals created by Fenton's Reagant reactions before they have a chance to react with the petroleum contaminants. By contrast, the presence of carbonate minerals in the geologic matrix has generally positive effects on permanganate oxidation.

Remedial strategies for petroleum UST sites that include a combination of active source zone treatment with enhanced natural attenuation outside the contaminant plume core may consider chemical oxidation technologies. Many chemical oxidation techniques also provide residual dissolved oxygen that is used by aerobic microorganisms to biodegrade contaminants. In addition, these technologies may also oxidize reduced electron acceptors (e.g., nitrogen to nitrate, sulfides to sulfate), which are then used by anaerobic microorganisms to biodegrade contaminants. For more information on enhanced aerobic remediation technologies, see "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers" (EPA-510-B-95-007, 1995). For specific information on aerobic remediation technologies, see Chapter III, *Bioventing*, Chapter VIII, *Biosparging*, and Chapter X, *In-situ Groundwater Bioremediation*.

Exhibit XIII-1 summarizes the general advantages and disadvantages of chemical oxidation technologies.

Several chemical oxidants have been used to remediate petroleum contaminated UST sites. The most commonly used (and most effective) are Hydrogen Peroxide/Fenton's Reagent and Ozone. Sodium or Potassium Permanganate have been used, but experience with these compounds is more limited, although some recent bench-scale and field studies are showing promise.

EXHIBIT XIII-1
Chemical Oxidation
Primary Advantages and Disadvantages

Advantages

- Contaminant mass can be destroyed in-situ.
- Rapid destruction/degradation of contaminants (measurable reductions in weeks or months).
- Produces no significant wastes (VOC off-gas is minimal), except Fenton's.
- Some oxidants (not Fenton's) are capable of completely oxidizing MTBE (but production of degradation products may be problematic).
- Reduced operation and monitoring costs.
- Compatible with post treatment monitored natural attenuation and can even enhance aerobic and anaerobic biodegradation of residual hydrocarbons.
- Some oxidation technologies cause only minimal disturbance to site operations.

Disadvantages

- Potentially higher initial and overall costs relative to other source area solutions.
- Contamination in low permeability soils may not be readily contacted and destroyed by chemical oxidants.
- Fenton's Reagant can produce significant quantity of explosive off-gas. Special precautions (i.e., SVE system) are required for appropriate implementation of remedial action involving Fenton's Reagent/hydrogen peroxide.
- Dissolved contaminant concentrations may rebound weeks or months following chemical oxidation treatment.
- Dissolved contaminant plume configuration may be altered by chemical oxidation application.
- Significant health and safety concerns are associated with applying oxidants.
- May not be technically or economically able to reduce contaminants to background or very low concentrations.
- Significant losses of chemical oxidants may occur as they react with soil/bedrock material rather than contaminants.
- May significantly alter aquifer geochemistry; can cause clogging of aquifer through precipitation of minerals in pore spaces.

There has also been recent interest in and some field applications using sodium persulfate ($Na_2S_2O_8$) to oxidize organic contaminants or to reduce the oxidant demand of native soils before other oxidants are applied to the contamination. Some research has demonstrated that when mixed with ferrous iron as a catalyst, the sulfate free radical (SO_4^-) can be produced, which has an oxidation potential only slightly less than Fenton's Reagent. Field testing of this oxidant to date has primarily involved the destruction of chlorinated organics rather than petroleum hydrocarbons. Given the experimental status of this oxidant, it is not further described or discussed in this chapter.

A brief description of the three main petroleum hydrocarbon oxidants and associated application technologies is provided below. Exhibit XIII-2 compares the relative advantages and disadvantages of these chemical oxidation technologies.

Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide is a strong oxidant that can be injected into a contaminated zone to destroy petroleum contaminants. When injected to groundwater, hydrogen peroxide is unstable, and reacts with organic contaminants and subsurface materials. It decomposes to oxygen and water within hours of its introduction into groundwater generating heat in the process. Peroxide is typically shipped to a remediation site in liquid form at dose concentrations ranging from five percent to 50 percent by weight.

The reactivity of hydrogen peroxide can limit the extent to which it may be distributed in the subsurface before it decomposes. Injecting concentrations of hydrogen peroxide as low as 100 ppm (a small fraction of one percent) can cause oxygen concentrations in groundwater to exceed the solubility limit of oxygen in groundwater (typically 9-10 mg/L). When this occurs, oxygen gas is formed, and is lost in the form of bubbles that rise through the saturated zone to the water table and into the unsaturated zone.

Hydrogen peroxide is particularly effective when it reacts with ferrous iron (Fe^{2+}) to produce Fenton's Reagent. Ferrous iron may be naturally present in the subsurface soils and/or groundwater, or it can be added as a catalyst solution together with the hydrogen peroxide to produce this aggressive chemical reaction.

Hydrogen peroxide in the presence of ferrous iron (Fe^{2+}) reacts to form hydroxyl radicals ($OH\bullet$), ferric iron (Fe^{3+}), and hydroxyl ions (OH^-). The hydroxyl ions are very powerful oxidizers, and react particularly with organic compounds. The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as benzene, toluene, ethylbenzene, and xylene, as well as petroleum aromatic hydrocarbons (PAHs) and methyl tertiary butyl ether (MTBE), a common gasoline additive.

Fenton's Reagent requires soluble Fe^{2+} to form OH•. This optimal reaction occurs under relatively low pH conditions (e.g., pH of 2 to 4). pH adjustment in the treatment area is often necessary to enable the oxidation process to proceed efficiently. This can be accomplished by either acidifying the hydrogen peroxide or by adding a chelating acid. Using a ferrous sulfate solution `simultaneously adjusts aquifer pH and adds the iron catalyst needed for Fenton's Reagent. Because of the low pH requirement, Fenton's Reagent treatment may not be efficient or effective in limestone geology or sediments with elevated pH levels or with significant capacity to buffer these reactions. In addition, reaction between hydrogen peroxide and ferric iron can consume hydrogen peroxide, reducing the effectiveness of the oxidant dose. The same effect may also occur in soils with high ferric iron content.

Exhibit XIII-2
Chemical Oxidation Technologies Comparative Matrix

	Hydrogen Peroxide/ Fenton's Reagent	Permanganate	Ozone
Advantages			
Potential to complete remediation in shortest time	x		
Capacity to oxidize MTBE and benzene	x		x
No significant VOC off-gas produced by heat of reaction	x [1]	x	
Oxidizes over extended period, increasing possibility of contact with contaminants		x	
Increases dissolved oxygen levels for potentially enhanced aerobic bioremediation	x		x
Reduced health and safety concerns during application		x [2]	
Can be applied using automated system			x

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[1] If solid peroxide is injected below 10% strength, the heat of dilution is mitigated and VOC generation typically avoided.

[2] Note that sodium permanganate is often applied as a liquid at 40% strength, which poses a significant handling and explosion risk.

Exhibit XIII-2
Chemical Oxidation Technologies Comparative Matrix (continued)

	Hydrogen Peroxide/ Fenton's Reagent	Permanganate	Ozone
Disadvantages			
Inability to effectively oxidize benzene or MTBE		x	x
Increased risk of fugitive vapors entering building structures, utility conduits, particularly in absence of adequate vapor recovery technology (e.g., soil vapor extraction)	x		x
Increased risk of plume reconfiguration	x		x
Low permeability soil horizons less likely to be penetrated by oxidant over short injection period	x	x	x
On-site reactive chemical handling and storage required	x	x	x
On-site gas production and delivery equipment (e.g., ozone generator) required			x
Few petroleum remediation projects completed using this technology due to limited effectiveness		x	
Possible production of unwanted compounds or by-products in the subsurface[3]	x	x	x
Potential to precipitate solids and clog aquifer pores	x	x	

Fenton-like reactions produce the hydroxyl radical (OH•) which is one of the strongest oxidants, but the reaction proceeds so quickly that the radicals may not have sufficient time to come into contact with contaminant molecules so that they can be destroyed before the hydrogen peroxide decomposes. Also, some

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[3] Chemical oxidation may cause some may create some toxic or highly mobile secondary products. Ensure that analyses for potential secondary products are included in any corrective action plan that proposes the use of chemical oxidants.

contaminants may sorb so tightly to organic material in the soil that they are effectively protected from destruction.. This may be particularly true for sites with significant layers or lenses of low permeability that results from high clay content. In such cases, the oxidant may successfully address contaminants in more permeable layers or lenses of soil while leaving the bulk of the contamination that resides in the low permeability soils.

Difficulty in addressing contamination in low permeability soils may be alleviated to some degree by controlled pneumatic or hydraulic fracturing of the soil. However, engineered hydraulic fractures generally cannot be spaced more closely than about 5 feet, which means that chemical oxidants must still penetrate a substantial thickness of low permeability soil to come into contact with the contamination. Deep soil mixing with large diameter drill augers is the most effective method currently available to increase contact between adsorbed contaminants and the oxidants. In any case, long term post-injection monitoring of contaminant levels in groundwater is critical to evaluating the success of putting Fenton's Reagent into contact with adsorbed contaminants. If inadequate contact occurs, contaminant levels in groundwater samples will rebound as the adsorbed contaminant mass gradually (typically over months) bleeds back into groundwater.

Controlled oxidation is increasingly being practiced using solid peroxides, pH modifiers, and catalysts that promote the generation of free radicals. This new approach moderates the rate of dissolution and peroxide generation, which in turn controls that rate of reaction between peroxide and the petroleum contaminants. The use of slurried peroxides creates the opportunity to release oxidants and oxygen over a longer period, which can promote subsequent aerobic remediation.

“Modified” Fenton-type systems use pH-neutral and even higher pH conditions along with slurried solid peroxides and metallic or organo-metallic catalysts. The reaction of the oxidants with the catalysts generate hydroxyl radicals, which react with the organic contaminants within the subsurface. The advantage to this approach is the ability to use Fenton’s Reagant under neutral pH conditions, requiring no acidification of the aquifer. It leads to a mix of reducing and oxidizing reactions in the subsurface, which moderates the rate of dissolution and peroxide generation, which moderates the rate of reaction between the peroxide and the petroleum contaminants. This releases oxidants and oxygen over a longer period, and may promote subsequent aerobic remediation.

Fenton-like reactions are exothermic and can raise the temperature of groundwater, produce steam and generate significant pressures in the application area, particularly when the Fenton’s is added at strengths approaching 10-12%. Especially in deep vadose zones and in monitoring or injection wells where pressures may be elevated, Fenton’s-like reactions can lead to explosive conditions and present safety concerns that need to be promptly and effectively managed. In addition, migration of explosive vapors along preferential pathways may pose an explosion hazard.

Several incidents resulting in spontaneous explosions of subsurface vapors have occurred during Fenton's Reagent treatment of petroleum contaminated sites. Other incidences have involved VOC vapor migration and intrusion into buildings and contaminant plume expansion. To manage these risks, at a minimum, it is important before a chemical oxidation strategy is selected and implemented to:

- Locate pockets of high levels of petroleum contamination in the treatment area.
- Identify and evaluate preferential flow paths.
- Clear the area of subsurface utilities, basements or other enclosed spaces that could accumulate and transmit vapors.
- Ensure that no petroleum storage tanks or lines are in the treatment area.

During application of an oxidation technology, consider the following to manage risks:

- Use a field photo-ionization or flame ionization detector (PID/FID) and explosimeter to monitor for explosive conditions.

- Install and operate a soil vapor collection system during Fenton's Reagent treatment until such time it can be demonstrated that there is no significant threat.

- Use a heat probe to monitor subsurface temperatures. Hydrogen peroxide, for example, decomposes at temperatures above 65°C, so as reactions progress in the subsurface, it is important to control the temperature to ensure maximum efficacy of the oxidation process.

- Closely monitor hydrogen peroxide and catalyst injection into the treatment area and adjust levels based on field analyses of soil gas and groundwater samples.

- Consider hydraulically containing groundwater during the treatment process to minimize the possibility of the chemical reaction pressures expanding the contaminant plume. Note, however, that dissolved gases in groundwater often prevent this approach from being as effective as predicted.

Other safety concerns include those associated with storing and using concentrated hydrogen peroxide on site. Many applications of the technology have involved the storage and use of thousands of gallons of fifty-percent hydrogen peroxide. Skin burns and blindness can result from contact with this chemical at this concentration. Safety precautions include the use of skin protection and safety glasses during application of these chemicals. A shower and eye wash facility may need to be constructed for the duration of the application.

Hydrogen peroxide and catalyst solutions needed for Fenton's Reagent are usually added to the treatment area by pressure injection into one or more designated chemical oxidation injection wells, or gravity injection into one or more monitoring or other wells.

In pressure injection, compressed air is used to sparge the ferrous iron catalyst and relatively large volumes of peroxide solution (e.g., hundreds to thousands of gallons) into the contaminated soil and groundwater over a short period of time (e.g., days). The sparged air forces the chemical reactants down the injection well point(s) and out into the impacted saturated soil. This is an aggressive approach that poses inherent increased risks of VOC vapor production and migration as well as plume re-configuration. Plume re-configuration may occur because the zone of influence during injection is limited, and permeability decreases with application of the technology, which may create preferential flowpaths with continued injection. Operation of a soil vapor extraction system concurrently with oxidant injection is a sensible precaution.

In gravity injection, small volumes of reagents are gravity-fed into injection well(s) over a longer application period. The distribution and dissipation of the reagents in the saturated zone is largely controlled by the site hydrogeologic conditions. The gravity injection approach may reduce some of risks associated with chemical oxidation technologies. Additionally, given its prolonged application period, the oxidants may be able to penetrate into more of the lower permeability soils to address contaminants in these areas.

In both cases, multiple injection events, separated by extended periods of groundwater monitoring, may be required in order to approach cleanup objectives. Establishing which injection or application approach is likely to be most efficient or cost effective for a given site is challenging, given the recent emergence of this technology and the limited volume of scientifically defensible information that is currently available for the two basic application methods. Site-specific safety concerns may be a key determining factor of the most appropriate injection approach.

An additional benefit of hydrogen peroxide and Fenton's Reagent is the temporary increase of oxygen levels in and around the treatment area. The increased oxygen levels at the fringes of the treatment area can enhance naturally occurring aerobic biodegradation processes that reduce contaminant mass. While there may be concerns about oxidizing hydrocarbon-degrading bacteria in the chemical oxidation treatment area, many studies have shown that soil cannot be readily sterilized by Fenton's Reagent and that microbial populations rapidly rebound following chemical oxidation treatment. In addition to enhancing aerobic biodegradation, reduce nitrogen and sulfur are oxidized to nitrate and sulfate, which can be used by anaerobic microbes.

Permanganate

Permanganate is emerging as a chemical oxidant that can be used to destroy petroleum and other organic compounds in soil and groundwater, and has successfully treated MTBE in recent laboratory and bench-scale studies. This oxidant is weaker than hydrogen peroxide. Its inability to oxidize benzene can lead to the early elimination of permanganate as a candidate for oxidation technology at petroleum cleanup sites.

However, permanganate has several advantages over other oxidants. It:

- Oxidizes organics over a wider pH range.
- Reacts over a prolonged period in the subsurface allowing the oxidant to more effectively permeate soil and contact adsorbed contaminants.
- Does not normally produce heat, steam and vapors or associated health and safety concerns.

Permanganate may be applied to sites as either potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$). Where cost dominates over engineering factors at a site, potassium permanganate is the preferred chemical form because it is more widely available, less costly, and is available in solid form, which facilitates transport and handling. Where other factors are more important, the liquid form of sodium permangante is preferable.

When choosing potassium permanganate for application at a site, be aware of three properties that can cause concern to owner, operators or state regulators.

First, potassium permanganate is derived from mined potassium ores which, by their nature, typically contain salt and metal impurities (e.g., arsenic, chromium, lead). Depending on water quality criteria in the state in which the site occur and the quality and concentration of potassium permanganate used to oxidize the site contaminants, these impurities may generate concern. (This is also true of sodium permanganate, which is mined and processed in similar fashion.)

Second, potassium permanganate is used to produce pharmaceuticals and should be used and monitored carefully.

Third, potassium permanganate in flowable form contains silica, which can accumulate in wells and plug the screen.

As with other chemical oxidation technologies, the success of the use of permanganate relies heavily on its ability to come into contact with the site contaminants. The delivery mechanism must be capable of dispersing the oxidant throughout the treatment zone. To accomplish this, permanganate may be delivered in solid or liquid form in a continuous or cyclic application schedule using injection probes, soil fracturing, soil mixing, groundwater re-circulation or treatment fences.

Dissolved permanganate has been delivered to injection or re-circulation wells at concentrations ranging from 100 to 40,000 milligrams per liter (mg/L). Contaminated soils have been successfully oxidized through slurry injection, deep soil mixing or hydraulic fracturing using concentrated permanganate solutions ranging from 5,000 to 40,000 mg/L or up to 50 percent by weight solid permanganate.

In-situ permanganate reactions can yield low pH (e.g., pH 3) and high Eh conditions (e.g., +800 mV), which can temporarily mobilize naturally-occurring metals and metal contaminants that may also be present in the treatment area. The release of these metals from the aquifer formation, however, may be offset by sorption of the metals onto strongly sorbent MnO_2 solids that are precipitated as a byproduct of permanganate oxidation. In addition, high sodium permanganate concentrations can create sodium problems with clay permeability at the edges of the injection zone due to swelling clays and potential aquifer clogging. $Cr(OH)_3$ in soils may be oxidized to hexavalent chromium, which may persist for some time. This may generate concern if the aquifer is being used for drinking water. Questions remain about the mass of MnO_4 that is generated, and the effect, if any, the mass may have on subsurface permeability and remediation performance.

Ozone

Ozone (O_3) is a strong oxidant with an oxidation potential about 1.2 times greater than hydrogen peroxide. It can be used to destroy petroleum contamination in-situ. Ozone, a gas, is typically generated on-site using a membrane filtration system and typically delivered to the subsurface through sparge wells. Delivery concentrations and rates vary, however, because of the high reactivity of ozone and associated free radicals. Ozone needs to be generated in close proximity to the treatment area, and sparge wells generally need to be spaced closely in the target remedial zone.

Ozone can also be injected into the subsurface in a dissolved phase. The gas may be transferred to the dissolved phase on-site by sparging upgradient water with ozone. Groundwater that is extracted upgradient from the area to be treated may be amended with ozone, then re-injected or re-infiltrated into the subsurface, where it transports the dissolved phase ozone and oxygen into the contaminated area. (Check with appropriate state groundwater authorities to learn whether groundwater re-injection is allowed in the state.) More commonly, gaseous ozone is injected or sparged directly into contaminated groundwater.

Typically, air containing up to five percent ozone is injected into strategically placed sparge wells. Ozone then dissolves in the groundwater, reacts with subsurface organics, and ultimately decomposes to oxygen. Ozone can oxidize site contaminants directly or through formation of hydroxyl radicals (OH•), strong nonspecific oxidants with an oxidation potential that is about 1.4 times that of ozone. It is capable of oxidizing BTEX constituents, PAHs, and MTBE (with limited effectiveness).

Heat and VOC vapors may be generated as a result of ozone sparging and the oxidation reactions when ozone concentrations are high. As a result, vapor control equipment (e.g., a soil vapor extraction and treatment system) is often needed to operate in conjunction with the ozone sparging system to capture and prevent the vapors from migrating to, entering and impacting subsurface utilities or nearby structures.

Ozone is also effective in delivering oxygen to enhance subsurface bioremediation of petroleum-impacted areas. Ozone is 10 times more soluble in water than is pure oxygen. Consequently, groundwater becomes increasingly saturated with dissolved oxygen as the unstable ozone molecule decomposes into oxygen molecules. About one-half of dissolved ozone introduced into the subsurface degrades to oxygen within approximately 20 minutes. The dissolved oxygen can then be used by indigenous aerobic hydrocarbon-degrading bacteria.

The oxidizing properties of injected ozone can temporarily suppress subsurface biological activity in the immediate injection area. However, this suppression has been found to be temporary, and sufficient bacteria survive in-situ ozonation to resume biodegradation once ozone has been applied. Additionally, aerobic bacteria along the fringes of the treatment area may thrive under the oxygen rich conditions produced during ozone treatment. Biodegradation enhancement is a primary benefit of this oxidation technology.

Special Considerations for MTBE

As mentioned above, any of the three oxidation approaches may be applicable for remediating MTBE, either in the presence or absence of other gasoline hydrocarbons. Hydrogen peroxide and ozone addition have both been used on a number of MTBE-impacted field sites, with successes reported at many of them. The success of these techniques may be attributable to the combined effects of the oxidation, increased dissolved oxygen levels in the groundwater, and generated heat.

The available field data on these chemical oxidation projects for MTBE treatment is somewhat sparse. Some literature reports do not contain enough time-series sampling data on groundwater concentrations to ensure that the beneficial reductions of MTBE are not short-lived and that groundwater concentrations do not later rebound.

Very little published data exists on using permanganate on MTBE-impacted field sites, but recent laboratory batch testing looks promising. The method's ability to oxidize MTBE, but not benzene, may have application where an active remediation technology is desired for treating the MTBE, but the benzene is to be addressed by monitored natural attenuation. Further development and field confirmation of potassium permanganate's effectiveness for MTBE is needed.

With any oxidation method, the potential for creating unwanted intermediary products or other unwanted by-products always needs to be considered. In studies of aboveground oxidation of MTBE-impacted groundwater, the primary byproducts of concern were found to be acetone, tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF), and bromate (for ozone-based oxidation). The possible in-situ formation of these by-products, as well as their potential fate and possible impacts, should be considered as part of any plan to conduct subsurface chemical oxidation of MTBE. Several laboratory studies that addressed the oxidation of MTBE-impacted water have indicated that combining ultraviolet light with hydrogen peroxide may oxidize MTBE more effectively, with fewer byproducts. Although the UV light requirement may render this application infeasible for in-situ chemical oxidation projects, the effectiveness of ex-situ treatment technologies may be enhanced.

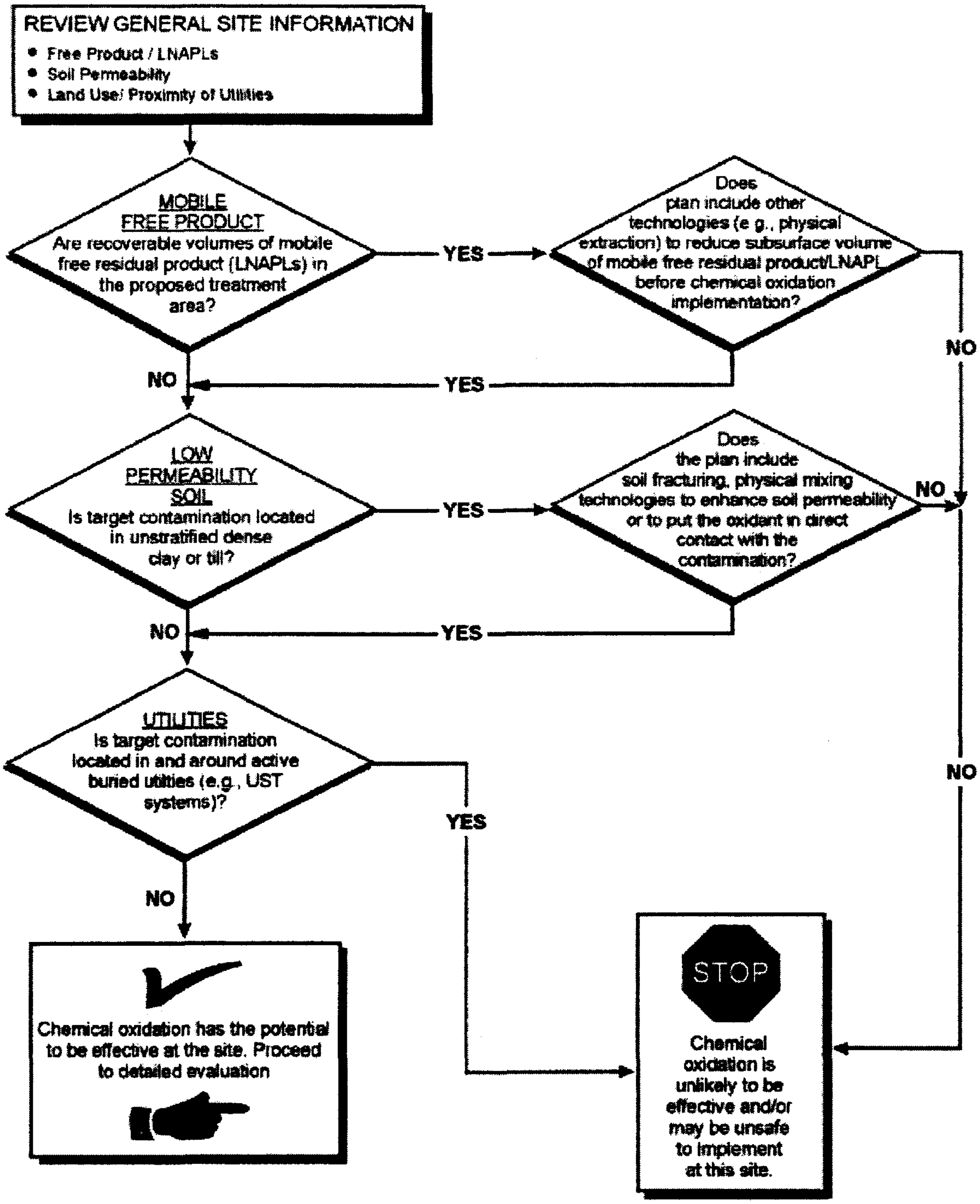
Another consideration for MTBE is whether chemical oxidation technologies can be cost effective for a highly soluble compound like MTBE and that is often found to exist in laterally extensive, mobile groundwater plumes. Chemical oxidation can be quite effective on the high hydrocarbon concentrations typically seen in groundwater and soils in source areas, but may not be applicable to the expansive, lower-concentration, dissolved-phase plumes often associated with MTBE-impacted sites.

Chemical Oxidation Technology Effectiveness Screening Approach

The descriptions of the various chemical oxidation technologies in the overview should provide the basic understanding needed to move forward with evaluation of a corrective action plan that proposes to use chemical oxidation. To assist with evaluation of the chemical oxidation corrective action plan, a step-by-step technology effectiveness screening approach is provided in a flow diagram in Exhibit XIII-3. This exhibit summarizes the evaluation process and serves as a roadmap for the decisions to be made during evaluation of a corrective action plan that proposes chemical oxidation technologies. A checklist has been provided at the end of this chapter for use as a tool to both evaluate the completeness of the chemical oxidation corrective action plan and to focus attention on areas where additional information may be needed.

Note that the first step in this screening includes information that can only be gleaned from a thorough assessment of the site, such as soil permeabilities and the nature of the aquifer geology, including heterogeneity, the presence of preferred pathways, and other characteristics. Before embarking on the selection of a chemical oxidation technology, be sure that a complete, and preferably three-dimensional, delineation of the subsurface and contaminant plume has been conducted.

Exhibit XIII-3
Initial Screening for Potential Effectiveness of Chemical Oxidation



The evaluation process can be divided into the four steps described below.

- **Step 1: An initial screening of chemical oxidation effectiveness** allows quick determination of whether chemical oxidation should be considered as a remedial approach for the site.

- **Step 2: A detailed evaluation of chemical oxidation effectiveness** provides further screening criteria to confirm whether chemical oxidation is likely to be effective. First, extract from the corrective action plan certain site-specific data on the nature/extent of contamination, potential risk to human health/the environment, subsurface geology and hydrogeology, and other relevant site characteristics. Then, compare the site-specific data to the criteria provided in the Exhibit to assess whether chemical oxidation is likely to be effective.

- **Step 3: An evaluation of the chemical oxidation system design in the corrective action plan** allows determination of whether basic design information has been defined, necessary design components have been specified, the construction process flow designs are consistent with standard practice, and adequate feasibility testing has been performed.

- **Step 4: *An evaluation of the operation and monitoring plans*** allows determination of whether baseline, start-up and long-term system operation and monitoring are of sufficient scope and frequency and whether remedial progress monitoring and contingency plans are appropriate.

Step 1: Initial Screening of Chemical Oxidation Effectiveness

This section allows you to perform an initial screening of whether chemical oxidation is likely to be an effective approach to remediate the petroleum-impacted areas at a site. Before selecting chemical oxidation as the preferred remedial approach, determine whether the corrective action plan has taken into account key site-specific conditions. In addition, evaluate several "bright lines" defining the limits of chemical oxidation overall viability as a remedial technology. These bright lines will assist in evaluating the corrective action plan and in determining the appropriateness of chemical oxidation as the site remedial solution. After establishing the overall viability of an chemical oxidation approach, basic site and petroleum contaminant information can be examined to further determine the expected effectiveness of chemical oxidation as the remedial choice.

Overall Viability

The following site conditions are considered to be the “bright lines” defining the general limits of chemical oxidation viability at a site. If review of the corrective action plan indicates that any of the following conditions exist, chemical oxidation is not likely to be a feasible or appropriate remedial solution for the site.

- **Free mobile product is present and the corrective action plan does not include other means for its recovery.** Chemical oxidation is not likely to cost-effectively address free product. Significant thickness and volumes of free product may need to be recovered using conventional approaches before oxidizing the residual hydrocarbons. For some chemical oxidation technologies, free product poses a safety issue, increasing chances of an explosion.

- **Utilities (active gas mains, petroleum USTs/piping, sewers, etc.) lie in the immediate vicinity of the treatment area.** Concerns associated with the heat, VOC vapors, elevated oxygen levels and potential corrosion that can occur from the induced chemical reactions during application of oxidants may preclude the use of this technology until the utilities can be removed or relocated. Potential risks associated with the use of chemical oxidation in the presence of buried utilities include explosion, combustion, and vapor intrusion into buildings.

- **The target contaminant zone is comprised of or includes unstratified dense clay.** With the low permeabilities inherent to clay or clay-rich soils, chemical oxidants cannot easily come into contact with the adsorbed contaminants. Without adequate contact, the petroleum contaminants will remain adsorbed to the low permeability soil, which often contains most of the contaminant mass, rendering remediation unsuccessful. Soil fracturing, use of slow reaction oxidants (e.g., permanganate) or multiple oxidant applications may be used to help bring the oxidants into contact with the contaminants, but technical and cost considerations may lead to consideration of other remedial approaches or technologies.

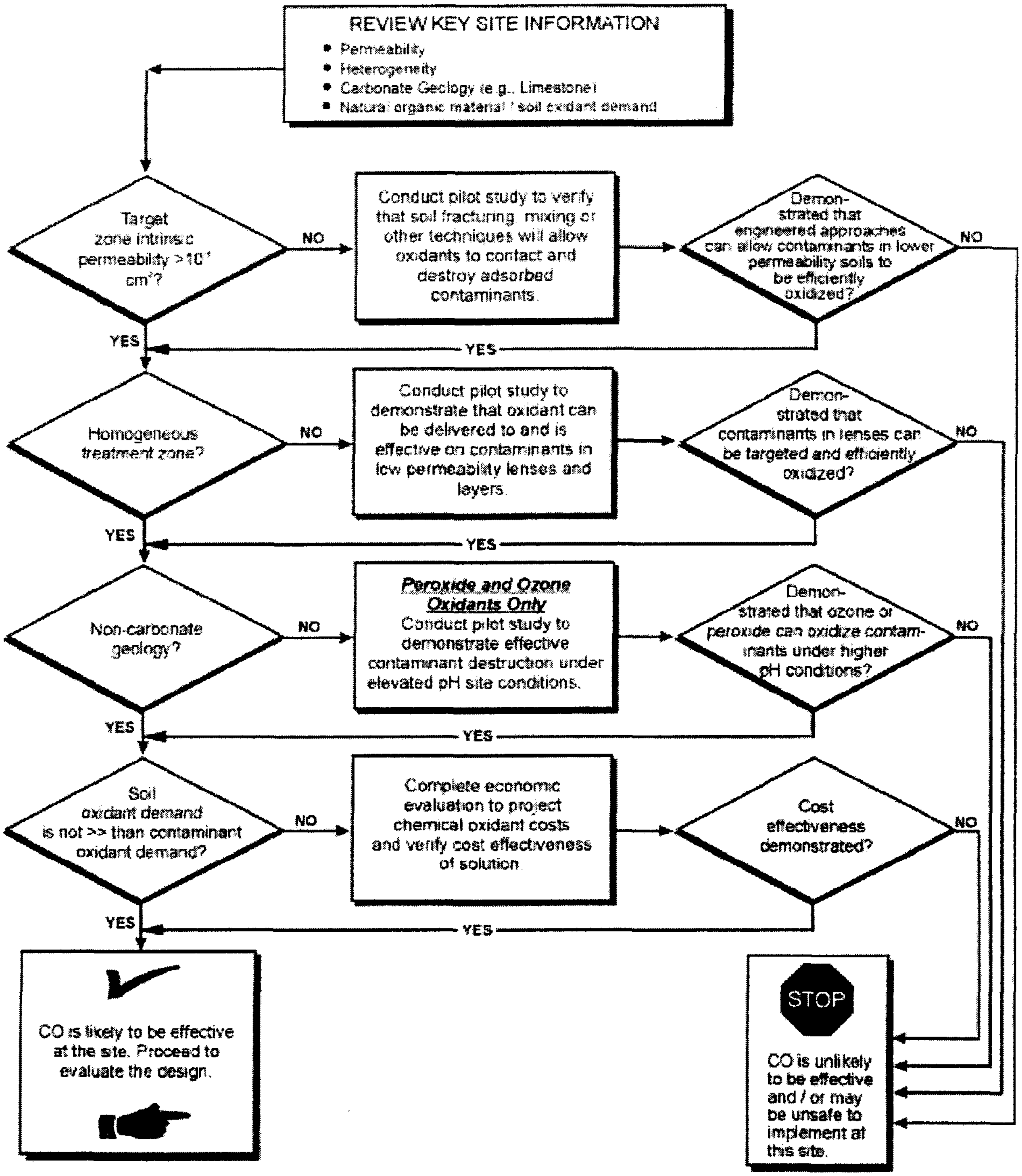
Potential Effectiveness of Chemical Oxidation

Before performing a more detailed evaluation of chemical oxidation's potential remedial effectiveness and future success at a site, it is useful to review several key indicators. One key factor that influences the effectiveness of chemical oxidation at a site is soil permeability.

Chemical oxidation of contaminants in fine-grained soils, or in clays and silts with low permeabilities, is likely to be less effective than chemical oxidation of contaminants in coarse-grained soils (e.g., sand and gravels) because it is more difficult to effectively contact chemical oxidants with organic contaminants in low-permeability materials.

It is also important to determine whether the chemical oxidant that may be used to address site contaminants is able to readily oxidize the chemical constituents of concern. For example, permanganate cannot readily oxidize benzene or MTBE, which may be target contaminants. The detailed chemical oxidation effectiveness evaluation section of this chapter considers the oxidizing strength of various oxidants and the resistance of specific petroleum hydrocarbon constituents to oxidation. The flowchart in Exhibit XIII-4 outlines the factors that

Exhibit XIII-4
Detailed Screening for Potential Effectiveness of Chemical Oxidation



should be evaluated in the detailed screening for the use of chemical oxidation technologies.

Step 2: Detailed Evaluation of Chemical Oxidation Effectiveness

If initial screening of the corrective action plan indicates that chemical oxidation may be feasible and potentially effective for the site, then a more detailed evaluation of the proposed chemical oxidation remedy should be performed to confirm this assessment. To help with this more detailed evaluation, this section covers a number of important site-specific characteristics influencing the potential effectiveness of chemical oxidation that were not considered or fully explored in your initial screening of the remedial approach. Additionally, this section provides a more detailed discussion of key contaminant characteristics influencing the potential effectiveness of chemical oxidation.

Key site and contaminant factors that should be explored in the detailed evaluation of chemical oxidation are listed in Exhibit XIII-5. The remainder of this section details each of the parameters described in Exhibit XIII-5. After reviewing and comparing the information provided in this section with the corresponding information in the corrective action plan, it should be possible able to evaluate whether chemical oxidation is likely to be effective at the site.

Exhibit XIII-5
Key Parameters Used to Evaluate Chemical Oxidation Applicability

Site Characteristics	Constituent Characteristics
▪ Oxidant Demand Factors ▪ Advective and Dispersive Transport Factors – Intrinsic Permeability – Soil Structure and Stratification – Hydraulic Gradient – Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater	▪ Chemical Class and Susceptibility to Chemical Oxidation ▪ Solubility Characteristics – Solubility – K_{oc} Factor

Site Characteristics That Affect Chemical Oxidation

This section addresses three factors at a site that can affect the ability of chemical oxidants to treat petroleum-contaminated groundwater at a site:

- Oxidant Demand Factors
- Advective and Dispersive Transport Factors
- Constituent Characteristics Factors

Each of these factors is described in detail below.

Oxidant Demand Factors. Once introduced into the saturated zone, chemical oxidants and catalysts may be distributed by advection and dispersion to address the target treatment zone. Ideally, the oxidant concentrations are sustained from the point of application until the oxidants contact the contaminants. However, the concentrations of oxidant more typically decrease by dilution through mixing with subsurface pore water and through consumption via chemical reactions that are not related to the degradation of the target constituents of concern. The loss of oxidant due to subsurface reactions unrelated to contamination oxidation, often referred to as the natural oxidant demand (NOD), is a significant consideration in determining the economic viability of chemical oxidation and in engineering the appropriate oxidation application dose and approach.

NOD stems from reaction with organic and inorganic chemical species naturally present in the subsurface. Oxidants that react with the natural organic material (NOM) are lost and are, therefore, subsequently unable to react with the target contaminants. In certain soil types (e.g., peat), the NOM and therefore the NOD can be extremely high. Inorganic oxidant demand may exist if naturally-occurring reduced mineral species (e.g., ferrous iron) are present in the groundwater or saturated soils. These reduced compounds can also react with the oxidants to remove oxygen available for reaction with the target contaminants. Exhibit XIII-6 presents a sample of some common inorganic processes that consume oxygen and oxidants in groundwater.

NOD almost always exceeds contaminant oxidant demand. If insufficient doses of oxidants are not provided to satisfy both demands, the target contaminants may not be degraded to the desired level. Bench testing should be used to determine the NOD for the saturated zone.

Exhibit XIII-6
Inorganic Oxidation Processes That Consume Dissolved Oxygen in Groundwater

Process	Reaction
Sulfide Oxidation	$O_2 + ½HS \rightarrow ½\ SO^{2-} + ½H^+$
Iron Oxidation	$¼O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + ½H_2O$
Nitrification	$O_2 + ½NH^{4+} \rightarrow ½NO^{3-} + H^+ + ½H_2O$
Manganese Oxidation	$O_2 + 2Mn^{2+} + 2H_2O \rightarrow 2MnO_2\ (s) + 4H^+$
Iron Sulfide Oxidation	$15/4O_2 + FeS_2\ (s) + 7/2H_2O \rightarrow Fe(OH)_3\ (s) + 2SO_4^{2-} + 4H^+$

Exhibit XIII-7 explores the theoretical oxygen demand of a number of petroleum hydrocarbon constituents common to petroleum UST cleanup sites. The exhibit outlines the stoichiometric reactions for the complete oxidation of the typical target hydrocarbons. In theory, oxygen levels of at least 3 to 3.5 times the amount of subsurface petroleum mass that needs to be removed to meet cleanup goals must be delivered to the groundwater and distributed over the planned remedial period.

Exhibit XIII-7
Organic Compound Oxidation Stoichiometry

Petroleum Hydrocarbon	Oxidation Reaction	Oxygen Requirement ($g\ O_2$ per g Contaminant)
MTBE	$C_5H_{12}O + 7.5\ O_2 \rightarrow 5CO_2 + 6H_2O$	2.7
Benzene	$C_6H_6 + 7.5\ O_2 \rightarrow CO_2 + 3H_2O$	3.1
Toluene	$C_6H_5CH_3 + 9\ O_2 \rightarrow 7CO_2 + 4H_2O$	3.1
Ethylbenzene	$C_2H_5C_6H_5 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$	3.2
Xylenes	$C_6H_4(CH_3)_2 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$	3.2
Cumene	$C_6H_5C_3H_7 + 12O_2 \rightarrow 9\ CO_2 + 6H_2O$	3.2
Naphthalene	$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$	3.0
Fluorene	$C_{13}H_{10} + 15.5O_2 \rightarrow 13CO_2 + 5H_2O$	3.0
Phenanthrene	$C_{14}H_{10} + 16.5O_2 \rightarrow 14CO_2 + 5H_2O$	3.0
Hexane	$C_6H_{14} + 9.5\ O_2 \rightarrow 6CO_2 + 7H_2O$	3.5

A number of experiments and field tests have determined that site NOD is highly variable and not easily predicted. For example, NOD associated with permanganate application has been found to vary from two to over 100 mg MnO_4^- per mg of total organic carbon (TOC) in the treatment area soil, and equal to or greater than the contaminant oxygen demand.

Oxidizing reactions associated with the NOD can produce solid precipitates that can accumulate in soil pore spaces. Particles may be produced by shearing off fragments of natural soil or by yielding reaction products (e.g., iron or manganese oxides). Permanganate oxidation results in the production of MnO_2 solids as a reaction product. These precipitates can potentially decrease soil permeability and remediation system function and performance; however, their effects in this regard have not been fully examined and are not well understood.

Advective and Dispersive Transport Factors. The site conditions affecting advection and dispersion of dissolved oxygen are:

- Intrinsic Permeability
- Soil Structure and Stratification
- Groundwater Velocity
- Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater

Each of these conditions is described in detail below.

Intrinsic Permeability. Intrinsic permeability is a measure of the ability of soil to transmit fluids. Intrinsic permeability often decreases near injection wells or infiltration galleries. This is also commonly a result of the precipitation of carbonate species, such as calcite. In general, oxygen is more easily distributed in soils with higher soil permeabilities (e.g., sands and gravels) than in soils with lower permeabilities (e.g., clays or silts). Intrinsic permeability can be calculated from hydraulic conductivity measurements taken from on-site pump testing. Pump test or slug test-derived permeability ranges are representative of average hydraulic permeability conditions for heterogeneous conditions. Alternatively, intrinsic permeability can be estimated from soil boring logs and laboratory tests. Intrinsic permeability values obtained through empirical means are less accurate and result in a wider range of permeability estimates. In any case, derived permeabilities are only approximations of actual subsurface conditions and should be regarded as such in the evaluation of chemical oxidation as a remediation technology. Intrinsic permeability can vary over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide range of earth materials. Exhibit XIII-8 provides general guidelines on the range of intrinsic permeability values over which chemical oxidation is likely to be effective.

Exhibit XIII-8
Intrinsic Permeability and Chemical Oxidation Effect

Hydraulic Conductivity (K) (in ft/sec)	Intrinsic Permeability (k) (in ft^2)	Chemical Oxidation Effectiveness
$K > 10^{-6}$	$k > 10^{-12}$	Effective to generally effective
$10^{-6} \leq K \leq 10^{-7}$	$10^{-12} \leq k \leq 10^{-13}$	Possibly effective; needs further evaluation
$K < 10^{-7}$	$k < 10^{-13}$	Marginally effective to ineffective

It is important to note that the intrinsic permeability of a soil can decrease as chemical oxidation progresses. The most likely cause of reduced intrinsic permeability while implementing chemical oxidation is the precipitation of inorganic complexes that form during oxidation of reduced, naturally occurring mineral species such as ferrous iron. If the soil intrinsic permeability indicates borderline potential effectiveness (i.e., 10-9 $\leq$ k $\leq$ 10-10), the geochemistry should be further evaluated. It may be necessary to determine the concentration of reduced inorganic species, primarily iron, in the soil to assess whether subsurface flow pathways could become constricted by precipitation of inorganic compounds, such as ferric oxides.

Soil Structure and Stratification. Soils in a target treatment area are not uniformly permeable (i.e., heterogeneous), but rather have large-scale and small-scale variations in permeability (i.e., heterogeneous). Heterogeneity controls movement of fluids in the subsurface. Soil heterogeneity plays a very important role in chemical oxidation technologies because oxidants and catalyst reagents introduced to the subsurface are distributed preferentially along higher permeability layers in the saturated soil. For example, in a heterogeneous soil comprised of sand, silt and clay layers, oxidants may be effectively distributed through the sand layer to successfully reduce petroleum hydrocarbons there, but will be ineffectively delivered and distributed to the silt and clay layers. If the silt and clay layers are thick relative to the sand horizon and contain significant petroleum hydrocarbon mass, chemical oxidation technologies may be inefficient or ineffective. In addition, the tendency for the development or enhancement of preferential flow paths may be increased by the addition of Fenton's reagant or the use of ozone sparging.

Unless site soils are homogeneous, average soil intrinsic permeability may not adequately determine the viability of chemical oxidation approaches because discrete low permeability soil horizons may exist, and these horizons might contain a large fraction of the subsurface petroleum mass. In most cases, it is prudent to evaluate petroleum mass distribution across all soil types to determine whether chemical oxidation is likely to be effective and will achieve cleanup objectives. If select soil horizons containing hydrocarbon mass are not expected to be effectively treated using chemical oxidation, chemical oxidation may not be viable for the site. For example, if 50 percent of the contaminant mass is contained and isolated in low permeability soil horizons, and the site cleanup goals is a 95 percent reduction in petroleum contaminant concentrations, then it is reasonable to conclude that the goal cannot be achieved using chemical oxidation. However, in such circumstances, combining chemical oxidation with other technologies that enhance the permeability of low permeability horizons in the contaminated zone (e.g., soil fracturing) could be considered. Or, alternatively, following source removal addition of peroxides could be employed to increase the rate of aerobic biodegradation to achieve remediation objectives. For more information about enhanced aerobic bioremediation, refer to Chapter XII in this manual.

Groundwater Velocity. Chemical oxidation technologies may rely on groundwater advection and dispersion to distribute oxidants and catalyst reagents in the subsurface. Distribution of oxidants and reagents can be most readily accomplished under hydrogeologic conditions conducive to higher groundwater flow rates. True groundwater velocity is referred to as the seepage velocity (q_s) and can be calculated from the equation at the top of the next page:

$$q_s = \frac{K(dh/dl)}{n_e}$$

where: dh/dl = aquifer hydraulic gradient (maximum difference in water table elevation or potentiometric surface (L)/distance between upgradient and downgradient measurement points (L)
K = hydraulic conductivity (L/T)
n_e = soil effective porosity (dimensionless)

As the hydraulic gradient increases, groundwater velocity increases proportionately. This same relationship exists between groundwater velocity and soil permeability. Groundwater velocity is inversely proportional to soil porosity. As porosity increases, groundwater velocity decreases. When a significant hydraulic gradient exists, targeted delivery of oxidant to the contaminant zones may require injection and extraction wells.

In addition, transport of dilute dissolved contaminants is a function of advection, dispersion, and chemical and physical reactions. Advection refers to the movement imparted by flowing groundwater, and the rate of transport is usually taken to be equal to the *average* linear groundwater velocity. Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical mixing and causes the dissolved contaminant plume to spread out with distance from the source. Molecular diffusion is generally only significant when groundwater movement is very slow. Mechanical mixing occurs as groundwater flows through the aquifer matrix twisting around individual grains and through interconnected pore spaces at differing velocities. The movement of some dissolved contaminants may also be affected by chemical and physical reactions, such as sorption and biodegradation, which act to reduce the transport velocity and decrease concentrations in the plume.

Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater. The effective intrinsic permeability of the saturated zone can be significantly reduced if the chemical oxidation treatment zone contains naturally elevated levels of reduced iron (e.g., ferrous iron, or Fe^{2+}) or other mineral species. For example, when dissolved iron is exposed to chemical oxidants, it may be oxidized to ferric iron (Fe^{3+}) oxide that can precipitate within the saturated zone and occlude soil pore space. On a large scale, this could reduce effective soil porosity, and oxidant delivery efficiency and availability. In such cases, decreases in soil porosity can be expected to occur closest to the oxidant delivery locations (i.e., near oxidant injection wells). Bench-scale tests may need to be performed to evaluate the inorganic NOD of the aquifer material and determine the feasibility of the remedial approach.

In addition to being considered in evaluating the potential effectiveness of chemical oxidation, hydraulic gradient can be an engineering design issue. If the gradient is not steep enough to provide adequate flow and oxidant transport through the contaminated zone, then certain engineering provisions (e.g., spacing application points more closely, creating artificial hydraulic gradients) can be added to the design to enhance oxidant distribution.

Constituent Characteristics That Affect Chemical Oxidation. It is important to evaluate the potential impacts of site contaminants on the performance of the proposed chemical oxidation approach. In particular, it is important to review how the chemical structure, chemical properties, concentrations and toxicities of the petroleum contaminants can influence remedial performance.

Petroleum products are complex mixtures of hundreds or even thousands of hydrocarbon chemical constituents, other chemical constituents and additives. Each of these constituents has a different atomic structure that determines, in part, how easily it may be chemically oxidized.

With the notable exception of benzene, most petroleum hydrocarbons have been demonstrated to be oxidized by all three primary chemical oxidants. Benzene is not readily oxidized by permanganate, and oxidation of MTBE has only been demonstrated to be oxidizable by permanganate at bench scale.

The two factors related to chemical classes, and their susceptibilities to chemical oxidation, are their solubility characteristics and their K_{oc} values. Each is discussed in more detail below.

Solubility Characteristics. Solubility is the maximum concentration of a chemical that can be dissolved in water at a given temperature without forming a separate chemical phase on the water (i.e., free product). Most petroleum compounds have low solubility values, thus limiting the concentrations of contamination that can be dissolved in groundwater. The solubility values for petroleum hydrocarbons range over four orders of magnitude, as shown in Exhibit XIII-9.

Compounds with higher solubility values are generally smaller, lower molecular weight molecules (e.g., benzene). When spilled, these compounds exist in groundwater at higher relative concentrations and move more quickly through the aquifer than do compounds of higher molecular weights. Larger and higher molecular weight hydrocarbon molecules are generally less soluble in water; therefore, their dissolved concentrations in groundwater tend to be limited (e.g., naphthalene). Long-chain hydrocarbons are often saponified by chemical oxidation, making them more soluble, particularly in the presence of any free product.

Exhibit XIII-9
Solubility Values and Organic Carbon Partition Coefficients For Select Petroleum Hydrocarbon Constituents

Compound	Molecular Weight (g/mol)	Solubility in Water (g/L)	Organic Carbon Coefficient (K_{oc} - ml/g)
MTBE	88	51	12
Benzene	78	1.79	58
Toluene	92	0.53	130
Ethylbenzene	106	0.21	220
Xylenes (total)	106	0.175	350
Cumene	120	50	454
Naphthalene	128	0.031	950
Acenaphthene	154	.0035	4,900

Solubility is also an indicator of likely contaminant sorption onto soil. There is an inverse relationship between a chemical compound's solubility and its organic carbon partition coefficient (K_{oc}). A compound with a high solubility has a reduced tendency to adsorb to soil that is in contact with contaminated groundwater and may be more readily contacted by chemical oxidants. Conversely, contaminants with low solubility values will likely have an increased tendency to adsorb to soil that is in contact with contaminated groundwater and may be less readily chemically oxidized. Note that some compounds are less predictable in this relationship, such as cumene. Cumene has a strong ability to sorb to soils, despite its very high solubility. If cumene is a key target contaminant, chemical oxidation may not be the most appropriate technology for removing it from groundwater. The relationship between solubility and K_{oc} is described in more detail below.

K_{oc} Factor. When groundwater is contaminated by a petroleum UST release, the proportion of hydrocarbon mass in the soil is often far greater than that dissolved in groundwater. This is due in part to the low solubility thresholds for petroleum contaminants. However, another factor is the strong tendency for most petroleum hydrocarbons to adsorb to naturally occurring organic carbon material in the soils. This tendency along with the sheer mass of soil relative to groundwater in a contaminated area can lead to hydrocarbon mass distributions that are so unevenly distributed that they can make the mass in the dissolved-phase appear insignificant. Because of the high proportionate amount of contaminant mass in the adsorbed phase, it is important to understand the ability of the chemical oxidant to come into contact with the soil contamination.

K_{oc} is a compound-specific property that helps define the equilibrium condition between organic carbon and the contaminant concentrations in an aqueous solution. Using site-specific soil organic carbon content data (i.e., fraction of organic content or foc), K_{oc} can be used to determine the equilibrium contaminant concentrations between groundwater and soil below the water table. The typical organic carbon content in surface soils ranges from 1 to 3.5 percent. In aquifer soils, organic carbon content is an order of magnitude lower – from 0.1 and 0.01 percent – because most organic residues are either incorporated into the soil matrix or deposited on the surface.

Higher K_{oc} and Kd values indicate that more contaminant mass is likely to be retained in soil, and therefore potentially less readily contacted by chemical oxidants. Conversely, lower K_{oc} and Kd values indicate that lower contaminant concentrations will exist in equilibrium in soil for given concentrations in groundwater. A comparison of the solubility and K_{oc} values for the sample group of petroleum hydrocarbons reveals the inverse relationship between the two parameters (i.e., compounds with higher solubility values have lower K_{oc} constants).

In the absence of site-specific data that reveal the distribution of contaminant mass, solubility and K_{oc} data can be used to obtain a general understanding of the likelihood that chemical oxidation is applicable at the site. Petroleum contaminants with high solubility limits and low K_{oc} values are more likely to come in contact with chemical oxidants and to be destroyed by chemical oxidation technologies. When contaminant solubility constants are low and K_{oc} values are high, chemical oxidants may not have adequate contact with the contaminants to effectively destroy contaminant mass, particularly in low permeability soils.

Step 3: Evaluation of Chemical Oxidation Design

This section provides guidance on reviewing and evaluating a chemical oxidation remediation system's design. This section focuses on identifying and reviewing key elements of corrective action plans to help ensure they demonstrate a coherent understanding of the basis for the chemical oxidation system design. This section provides information on typical chemical oxidation technology components to help verify that the corrective action plan has included the basic equipment requirements for the remedial system.

It is assumed that it has already been verified, through the detailed technology screening process described in Steps 1 and 2, that chemical oxidation appears appropriate and is expected to be an effective cleanup approach, given site-specific conditions. If chemical oxidation effectiveness evaluation has not been completed, it is strongly recommended that this be done prior to evaluating the design.

Two important factors that need to be considered in evaluating the design of chemical oxidation treatment are (1) the design basis and (2) the site cleanup goals. Each of these factors is discussed in more detail below.

Design Basis

A review of the corrective action plan should find consistency between site characterization work and information that is presented as the basis for the chemical oxidation design in the corrective action plan. It is important that during the chemical oxidation effectiveness evaluation a reviewer has a solid understanding of the nature and extent of the site-specific petroleum constituents of concern, including an understanding of the contaminant phases present and the relevant site chemical, physical, and biological properties. When preparing and reviewing the corrective action plan design, it is important to understand the site geology and hydrogeology, and the risks associated with the contamination. These data, which should have been developed and interpreted as part of the site characterization effort, serve as the foundation for the remedial system design.

While site characterization data provide the core raw materials for the design, further refinement is often needed and useful. For example, while the site characterization work may identify potential human or ecological receptors that may be exposed to contamination, specific cleanup goals may not have been established. In such cases, the specific remedial goals would need to be developed and identified in the corrective action plan through one or more established approaches. These approaches may include adopting state-published cleanup standards, developing site-specific risk-based standards acceptable to the state, or employing other state-specific and approved methods.

A corrective action plan may also include the results and interpretation of follow-up studies completed after the original site characterization. The need for such studies is often identified after a review of the site characterization shows that additional information is needed to complete the remedial system design. For example, the site characterization may suggest that one or more of the constituents of concern is believed to be marginally degradable, either chemically or biologically, and the level of expected degradation is difficult to predict from the existing data.

Examples of typical information expected to be developed during the site characterization, or as a result of follow-up studies that should be completed to support the basis for the technology selection and design of the corrective action plan, are summarized in Exhibit XIII-10.

Cleanup Goals

The evaluation of alternative remedial approaches and the subsequent design of the selected approach are strongly influenced by the cleanup goals that the remediation program must achieve. Often, preliminary goals identified during the site characterization evolve as a better understanding of site conditions and potential receptors is attained. However, owing to their importance to remediation planning and design, the cleanup goals should be fully evolved and solidified in the corrective action plan.

These goals usually provide the end-point concentrations for petroleum constituents in soil and groundwater that are acceptable to state or other regulatory agencies. These cleanup thresholds could be goals that represent any of the following:

- Health-based numeric values for petroleum chemical constituents published by the respective regulatory agency.
- Cleanup goals developed and proposed by the contractor specifically for the contaminated site.
- Goals derived from site-specific risk assessment involving contaminant fate and transport modeling coupled with ecological and human-health risk assessment.

Additional project goals that may be regulatory requirements include hydraulic control of the contamination, a cleanup time frame, or other performance goals established in the corrective action plan. Regardless of the cleanup goals and how they are established, the state-sanctioned goals should be noted in the corrective action plan and recognized as a fundamental basis for the technology selection and design.

The cleanup goals presented in the corrective action plan answer important questions about the viability of the selected remedial approach and the adequacy of the remedial design. The critical question is, Can the cleanup concentration goals be economically met by the designed chemical oxidation approach? It is important to understand how much oxidant will be consumed by NOD reaction, and how much will be lost attempting to permeate low permeability soils, in order to weigh the economics and technical feasibility of the approach. Multiple applications of the chemical oxidants may be required in order to accomplish the site objectives. Many logistical, political, risk-related, and cost issues are associated with successive attempts to oxidize the site contamination, and should be considered when such a proposal is put forth in a corrective action plan. Verification that the target petroleum constituents of concern can be chemically oxidized by the oxidant of choice should be completed.

Exhibit XIII-10
Chemical Oxidation Design Basis Factors

Design Basis Factor	Source(s) of Design Information
Cleanup Goals ▪ Target contaminant levels (soil and groundwater) ▪ Remediation timeframe ▪ Plume control ▪ Others	Receptor survey, pre-design exposure or risk assessment analyses (potentially including numerical modeling), or state requirements.
Geology ▪ Uniformity (homogeneity, heterogeneity) ▪ Stratigraphy (vertical profile of sand, silt, clay, etc.) ▪ Geochemistry (reduced mineral content, organic content, mineral demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.) ▪ Bedrock (description, depth, strike, dip, fracturing, etc.) ▪ Soil permeabilities	Site characterization, soil borings, well installations, sampling and analysis, and site observations. Local geologic studies.
Hydrogeology ▪ Depth to groundwater ▪ Groundwater elevation and gradient ▪ Aquifer/water bearing unit class (confined, unconfined, perched, bedrock, etc.) ▪ Hydraulic parameters (conductivity, transmissivity, storativity, effective porosity, etc.) ▪ Geochemistry (aqueous demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.) ▪ Modeling (simulation of groundwater flow and effects of manipulation of hydraulic head)	Site characterization, well gauging, aquifer pump testing, data analyses, and local hydrogeologic studies.
Petroleum Contamination ▪ Target chemical constituents ▪ Concentrations of other contaminants that can consume oxygen ▪ Mass estimates (adsorbed, dissolved, liquid and vapor phases) ▪ Extent (vertical and lateral) ▪ Fate and transport characteristics (solubility, partition coefficients) ▪ Vapor pressure and Henry's law constant for contaminants, especially if these contaminants are driven into the vapor phase by the remediation process ▪ Modeling (simulation of contaminant transport under various scenarios)	Soil, groundwater and other media sampling/laboratory analysis, review of published data on contaminants and data interpolation and analysis. Materials Safety Data Sheets can provide this information.

Chemical Oxidation Technology Selection

With the design basis established in the corrective action plan, it is now possible to review the corrective action plan to confirm that the proposed candidate chemical oxidation technology is a reasonable site-specific choice. Depending on project-specific circumstances, there may be a few chemical oxidation technologies equally viable and appropriate for a site. Alternatively, site-specific or project-specific circumstances may suggest that one of the chemical oxidation technologies would address the on-site contamination far better than any of the others.

Exhibit XIII-2 presented a comparative summary of each of the chemical oxidation technologies. These factors can be used to help evaluate the appropriateness and feasibility of the chemical oxidation approach outlined in the corrective action plan. Other differences among alternative chemical oxidation technologies can also help to distinguish their most appropriate application(s). Two characteristics that can be useful in evaluating the feasibility and appropriateness of a proposed chemical oxidation technology are (1) oxygen production for enhancement of aerobic biodegradation, and (2) chemical oxidation potential. Each of these is described in more detail below.

Oxygen Enhanced Biodegradation and Chemical Oxidation Potential. Another distinguishing characteristic of some chemical oxidation technologies is their ability to impart oxygen to the groundwater, which enhances aerobic biodegradation of contaminants while chemically oxidizing petroleum contaminants. In particular, both ozone and hydrogen peroxide are strong oxidizers. During their decomposition, these oxidizers may also generate the hydroxyl radical, an even more powerful chemical oxidizer of organic compounds. As these chemical oxidants react in the subsurface, oxygen is produced which may help enhance aerobic biodegradation processes occurring along the fringes of the treatment area. These chemical oxidation technologies not only chemically oxidize the contaminants in the treatment area but also provide oxygen to promote biodegradation of petroleum contamination. In addition, chemical oxidants can oxidized ferrous iron minerals to ferric iron, and transform other reduced forms to oxidized forms that anaerobic microbes can use.

Ozone and hydrogen peroxide can help to fully or partially chemically oxidize the recalcitrant subsurface petroleum contamination while providing oxygen for in-situ bioremediation of the contamination. Either of these technologies may be applied to sequentially treat the contamination via oxidation, followed by bioremediation, or configured for concurrent treatment relying on oxidation for core treatment with bioremediation as the treatment approach in the peripheral reaches of the plume.

Exhibit XIII-11
Relative Power of Chemical Oxidants[4]

Compound	Oxidation Potential (volts)	Relative Oxidizing Power (Cl_2 = 1.0)
Hydroxyl Radical	2.8	2.1
Sulfate Radical	2.6	1.9
Ozone	2.1	1.5
Hydrogen Peroxide	1.8	1.3
Permanganate	1.7	1.2
Chlorine Dioxide	1.5	1.1
Chlorine	1.4	1.0
Oxygen	1.2	0.90
Bromine	1.1	0.80
Iodine	0.76	0.54

However, both ozone and hydrogen peroxide are non-selective with respect to reaction with subsurface organic material. If naturally occurring organic materials (e.g., humic substances) are present in the site subsurface, injected ozone or infiltrated hydrogen peroxide may be lost through the oxidation of these organics, leaving fewer of the oxidants available to react with (and oxidize) the petroleum contaminants. The relative oxidizing power of the chemical oxidants may also be helpful in determining the most appropriate chemical oxidant for site conditions. Exhibit XIII-11 shows that the hydroxyl radical (Fenton's Reagent), ozone, hydrogen peroxide and permanganate, in order of decreasing oxidation strength, are among the strongest chemical oxidizers.

Design Components

Although the design elements of alternative chemical oxidation technologies can vary, Exhibit XIII-12 describes common ones. Several of the more important elements are discussed below to assist with evaluation of the corrective action plan. Each of the major headings in the exhibit above is discussed in more detail below.

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[4] Note that these compounds are provided for comparative purposes only. Many of these compounds are not typically used for in-situ chemical oxidation.

Exhibit XIII-12
Common Chemical Oxidation Remediation Design Elements

- Oxidant and Catalyst Delivery Design
    - Theoretical oxidant mass requirement
    - Natural oxidant demand estimates
    - Application delivery rate
    - Number and depth of application points/position
    - Equipment

- Permit Requirements and Thresholds
    - Underground injection/well installation
    - Groundwater (wastewater) discharge
    - Air (soil vapor) discharge

- Performance Monitoring Plan
    - On-going distribution of oxidants
    - Reduction in contaminants (adsorbed and dissolved phases)

- Contingency Plan
    - Inadequate oxidant distribution
    - Lower-than-expected petroleum mass reduction rates
    - Excessive contaminant migration
    - Build-up of excessive recalcitrant petroleum constituents
    - Fugitive (soil vapor) emissions
    - Difficult-to-treat/fouling of treated wastewater discharge
    - Aquifer clogging with precipitates or biomass

Oxidant Application Design should be based primarily on contaminant mass reduction requirements, site characteristics and cleanup goals. Oxidants need to be applied at concentrations and total mass levels that satisfies both the NOD and the oxidant demand of the petroleum hydrocarbons. Note that state regulations may either require permits for oxidant or catalyst injection or prohibit them entirely.

Permit Requirements and Thresholds should be identified in the design so that the system can be constructed to comply with permit requirements and constraints. Depending on the specific chemical oxidation technology and the state in which the site is located, permits may be required for underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge. Several federal, state and local programs either directly manage or regulate aquifer remediation wells (ARWs). Many of these programs require permits for underground injection of oxygen. On the federal level, management and regulation of these wells fall primarily under the underground injection control program authorized by the Safe Drinking Water Act (SDWA). Some states and localities have used these authorities, as well as their own, to extend the controls in their areas to address concerns associated with ARWs.

Aquifer remediation injection wells are potentially subject to at least three categories of regulation. First, a state's underground injection control program (or in direct implementation states, the federal UIC program) may have jurisdiction over such wells. Second, in some states without UIC programs, the state's program for groundwater protection or national pollution discharge elimination system (NPDES) requirements may apply to remediation wells. Third, remediation wells may be regulated by federal and state authorities through Superfund programs, corrective action programs under RCRA, the UST program, or other environmental remediation programs. In the case of remediation programs, the regulatory requirements typically address the selection of aquifer remediation as a cleanup alternative and establish the degree of required cleanup in soil and groundwater, while deferring regulation of the injection wells used in the remediation to other programs.

Performance Monitoring should be accounted for in the form of a written data quality objective plan that can be used to objectively evaluate chemical oxidation system performance. The monitoring plan should outline a data quality objective process that defined the criteria that the data collection should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner. It should describe the approaches and methods that will be used to evaluate chemical oxidation system effectiveness in each of the following:

- Delivering the oxidant and catalyst to the subsurface.
- Distributing the oxidant throughout the contaminated area.
- Reducing adsorbed and dissolved phase petroleum concentrations.
- Achieving other performance requirements consistent with site-specific cleanup goals.
- Confirming chemical oxidation effectiveness through long-term monitoring.

Contingency Plans should also be prepared as part of the remedial design. The design should anticipate low-likelihood problems and potentially changing environmental conditions, as well as outline specific response actions that may be taken. Examples include response actions to take if performance monitoring data indicate any of the following:

- Inadequate oxidant distribution
- Inadequate permeation of low permeability soil zones
- Low petroleum mass reduction rates
- Excessive contaminant migration
- Recalcitrance of constituents
- Production of excessive fugitive emissions
- Rebound in contaminant levels measured during long term post-application monitoring
- Evidence of oxidant moving in wrong direction

Components of Chemical Oxidation Systems

Having briefly covered factors that affect the selection and design of a particular chemical oxidation technology and the critical elements that should be included in the corrective action plan chemical oxidation design, it is now appropriate to discuss major components of various chemical oxidation systems. This discussion should help in the evaluation of the corrective action plan chemical oxidation design.

Exhibit XIII-13 summarizes some of the major equipment components associated with each of the more common chemical oxidation technologies. Note that this exhibit continues across three pages. Depending on which chemical oxidation technology has been selected in the corrective action plan, a subset of these major system components should be presented and discussed and schematically depicted (e.g., process flow diagram) in the corrective action plan. The design should relate capacities of these equipment components to design requirements (e.g., required oxidant production and delivery rates).

Exhibit XIII-13
Major Components of Chemical Oxidation Systems

Component	Function
Hydrogen Peroxide/Fenton's Reagent Injection Systems	
Extraction Wells	Wells may be used to capture soil vapor generated by the oxidation process that may be heated and contain elevated levels of VOCs and oxygen (i.e., soil vapor extraction). Can also be used to help control groundwater flow during oxidant and catalyst delivery (i.e., groundwater extraction).
Injection Wells or Infiltration Galleries	Injection wells, infiltration galleries or a combination of these may be used to inject hydrogen peroxide catalyst solution, and compressed air for reagent contact with the treatment zone contaminants. Diluted peroxide and peroxide slurries can be injected via lance points.
Extraction, Injection, Transfer, and Metering Pumps and Tanks	Extraction, injection, transfer, and metering pumps may be used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering hydrogen peroxide and catalyst into the infiltration system to maintain design concentrations. Note that pumps can be damaged by hydrogen peroxide and may need frequent replacement.
Blowers	Extraction blower(s) may be used to draw soil vapor from extraction wells to capture fugitive VOC vapors and oxygen.

Exhibit XIII-13
Major Components of Chemical Oxidation Systems (continued)

Component	Function
Hydrogen Peroxide/Fenton's Reagent Injection Systems (continued)	
Groundwater and Vapor Treatment Equipment	Extracted groundwater or soil vapor may be treated to remove petroleum hydrocarbons by various means such as: granular activated carbon adsorption, air stripping or others.
Instrumentation and Controls	Used to integrate and activate/deactivate system components. Help maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges.
Monitoring Wells	Used to collect environmental samples analyzed in laboratories and field to evaluate on-going effectiveness of remediation. Groundwater well samples tested for peroxide and contamination to evaluate overall effectiveness of oxidant delivery/dispersal and the contaminant reductions over time. Long term monitoring of contaminant concentrations is essential to evaluating the effectiveness of the technology.
Permanganate Injection Systems	
Extraction Wells	Wells may be used to enhance hydraulic gradient across the treatment area so that permanganate can be more rapidly delivered to and put in contact with site contaminants.
Injection Wells or Infiltration Galleries	Injection wells, infiltration galleries or a combination of these may be used to inject permanganate or permanganate amended groundwater into the treatment zone. Upgradient injections of amended groundwater with downgradient extraction of groundwater may enhance the hydraulic gradient across the treatment zone, thereby accelerating permanganate delivery to the contamination.
Extraction, Injection, Transfer, and Metering Pumps and Tanks	Extraction, injection, transfer, and metering pumps may be used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering permanganate into the infiltration system to maintain design concentrations.
Groundwater Treatment Equipment	Extracted groundwater may be treated to remove petroleum hydrocarbons by various means such as: granular activated carbon adsorption, chemical oxidation, air stripping or others.
Instrumentation and Controls	Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with design and to safeguard against inadequate treatment or inappropriate discharges.

Exhibit XIII-13
Major Components of Chemical Oxidation Systems (continued)

Component	Function
Permanganate Injection Systems (continued)	
Lance Injection Points	Permanganate in slurry form may be injected into the subsurface over a grid using push-point technologies.
Large Diameter Auger Deep Soil Mixing	Permanganate may be mixed deeply into the contaminated soil and groundwater using large diameter augers in patterned drilling over contaminated areas.
Monitoring Wells	Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination indicates how effectively oxygen is being delivered/dispersed and contaminant reductions are occurring.
Ozone Injection Systems	
Sparging Wells	Used as a conduit to inject ozone into contaminated groundwater. The ozone is sparged near the base of the soil and groundwater petroleum contamination so that it may contact the contaminants and provide oxygen to the hydrocarbon degrading bacteria.
Air Compressing Equipment	Used to pressurize ambient air needed to generate ozone and to provide the pressure needed to inject the ozone beneath the water table. Oil-less compressors are preferred, because air compressor equipment must supply oil- and contaminant-free air to minimize in-line reactions with and pre-mature decomposition of ozone.
Ozone Generating Equipment	Used to generate ozone gas on-site, typically at concentrations of about 5%.
Soil Vapor Extraction/ Treatment Equipment (optional)	Used, if necessary, to control fugitive soil vapor ozone and volatilize organic compounds emissions in the unsaturated zone. May consist of low vacuum/flow blower to generate vacuum conditions in unsaturated zone and collect the vapors. Off-gas treatment may be necessary and may be accomplished using granular activate carbon, biofilters or other technologies.
Instrumentation and Controls	Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges.
Monitoring Wells	Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination indicates how effectively oxygen is being delivered/dispersed and contaminant reductions are occurring.

While the sets of major equipment components used by the chemical oxidation technologies differ significantly, the use of wells by each different approach warrants recognition and further discussion. In particular, the orientation, placement, number and construction of this common design element is worthy of a brief review. wells or gravity-fed into vertical delivery wells. Additionally, hydrogen peroxide-amended groundwater can be re-infiltrated using either vertical or horizontal wells. Although vertical sparge wells are more common for ozone injection, horizontal sparge wells can be used. Permanganate amended groundwater can similarly be re-infiltrated using vertical wells, horizontal wells, infiltration trenches or combined approaches. Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that require re-infiltration of amended groundwater into shallow groundwater at high flow rates. They are also readily applicable if the affected area is located under a surface structure (e.g., a building), or if the thickness of the saturated zone is less than 10 feet.

Injection, Extraction and Re-infiltration Wells. Three important considerations are well orientation, well placement and number, and well construction.

- **Well Orientation.** Both horizontal and vertical wells can be used to treat subsurface petroleum releases with any of the various chemical oxidation systems. However, hydrogen peroxide and a catalyst (Fenton's Reagent) is most commonly injected into vertical sparge wells.
- **Well Placement and Number of Wells**. The number and location of wells are determined during the design to accomplish the basic goals of (1) optimizing reliable oxidant and catalyst delivery to the contaminated area, and (2) providing conduits to measure chemical oxidation system performance. For permanganate re-infiltration systems this typically means placing re-injection wells in the upgradient portion of the source area(s) while extracting groundwater from downgradient locations. This approach simultaneously provides an enhanced hydraulic gradient, which can accelerate oxidant distribution across the impacted area. The number, location and design of the extraction wells will largely be determined from site-specific hydrogeology, the depth(s) and thickness(es) of the contaminated area(s), and the results of field-scale pilot testing and hydraulic modeling. Note that well placement may need to be changed as remediation progresses, as wells often generate preferential flow paths over time.

Determining the number and spacing of the wells for ozone injection may also be determined through field-scale pilot testing. However, the following general points should be considered.

- Closer well spacing is often appropriate in areas of high contaminant concentrations to enhance contaminant contact and oxidant delivery/distribution where the oxidant demand is the greatest.

- Direct delivery of oxidant into the contaminated material using closer well spacings can deliver, disperse, and significantly decrease the treatment timeframe through groundwater advection/dispersion more quickly than oxidant delivery.

At sites with stratified soils, wells screened in strata with low permeabilities often require closer well spacing than wells screened in strata with higher permeabilities.

Well Construction. Chemical oxidation system wells are constructed of 1- to 6-inch diameter PVC, galvanized steel, or stainless steel pipe, although caution should be exercised in the use of stainless steel pipe in low-pH conditions. Ozone injection sparge wells have screened intervals that are normally 1-3 feet in length and situated within the contaminated zone. Injection sparge points must be properly grouted to prevent the oxidants from moving directly up the well annulus to the unsaturated zone rather than being forced into the contaminated aquifer ("short circuiting" of the injected oxygen) when horizontal injection oxidant exits along the entire screen length. Exhibit XIII-14 shows a cross-section typical ozone or hydrogen peroxide (Fenton's Reagent) sparge well.

Re-infiltration wells typically have screen lengths that extend from the base of the wells into the unsaturated zone. Groundwater extraction wells should ideally be screened in the saturated interval containing the greatest mass of hydrocarbons. Field-scale pilot studies and subsequent data analysis and hydraulic modeling can greatly assist one in determining the configuration and construction design of groundwater extraction and injection wells.

Step 4: An Evaluation of the Operation and Monitoring Plan

Remedial Progress Monitoring

Significant uncertainties associated with site conditions can remain even as remedial designs are completed and implemented. In the start-up period, these unknowns frequently can result in operations that vary from the original design. These variances often require adjustments to account for unforeseen conditions and to optimize system performance. Unfortunately, in many cases, the need for these adjustments can go unrecognized for a long time.

In some cases, the delay in recognizing that remedial system adjustments are necessary may be attributed to slow responses in subsurface conditions to the applied technology. Because these subsurface responses to the applied remedial technology can be delayed, there is often the tendency to give the remedial program more time to work (sometimes years) before making system modifications or adjustments. In other cases, the delay may stem from misuse or misinterpretation of site data, which can lead to the conclusion that the remedial system is performing well when it is, in fact, not. An example of this misuse is the practice of using groundwater analytical data from chemical oxidant delivery wells as an indicator of remedial progress. In this case, an assessment is biased by the localized effects of concentrated chemical oxidation in the immediate vicinity of the oxidant delivery wells, but does not provide an objective measure of the chemical oxidation system's ability to distribute the oxidant and contact the adsorbed contaminants throughout the treatment area.

However, at many sites remedial system or application operational efficiencies are not optimized simply because an adequate performance monitoring plan has either not been developed or has not been fully implemented. In such cases, the designed remedial system may be installed, implemented, and allowed to run its course with insufficient numbers or types of samples to determine whether the remedial system is performing in accordance with design expectations. The result of such monitoring approaches can be the discovery of a sub-standard or failed remediation program years after its implementation.

The previous section discussed the importance of developing a comprehensive remedial progress monitoring plan. This covers the topics that should be addressed in such a plan to ensure objective gauging of remedial system performance. Necessary optimization adjustments can be made early in the remediation program as well as throughout the duration of a chemical oxidation remedial program. The following section provides a focused discussion on evaluation sampling and chemical oxidation evaluation criteria that should be examined during review of a operations and monitoring plan that proposes to use chemical oxidation.

Evaluation Sampling

Evaluation sampling is performed to gauge the effectiveness of the chemical oxidation program relevant to design expectations. Based on a comparison of the actual field sampling data to design and operational expectations, timely modifications to the system or operating procedures can be made to optimize the application of chemical oxidants early in the remediation program. Projects with regular performance reviews guided by the results of such sampling and monitoring programs have a greater chance of achieving the design remedial goals within desired timeframes and, potentially, at a lower cost.

Various environmental media are sampled to evaluate system performance. Groundwater, soil, and soil vapors from the treatment area and vicinity are commonly sampled to determine the degree to which the chemical oxidation program is meeting the basic objectives of the approach, including:

- Delivering oxidants to the treatment zone at required design rates.

- Distributing the oxidants across the target contaminated area to contact the contaminants.

- Reducing concentrations of petroleum hydrocarbons in soil and groundwater at design rates through chemical oxidation of the petroleum compounds.

Exhibit XIII-14 identifies those parameters that are commonly measured in groundwater, soil and soil vapor samples to help evaluate chemical oxidation progress and system performance. A brief description of the respective sampling frequencies and the relevance and significance of each parameter to the performance evaluation are also provided in the exhibit. A key element is the location(s) where performance evaluation sampling takes place relative to subsurface oxidant delivery points. As stated in the exhibit, performance evaluation samples should not normally be collected from oxidant delivery locations.

Exhibit XIII-14
Common Performance Monitoring Parameters
and Sampling Frequencies

Analytical Parameter	**Sampling Frequency**			**Purpose**
	Start-up Phase (7-10 days)	**Remediation/ Post-Application Long-Term Monitoring Phase**		
	Daily	***Weekly to Monthly***	***Quarterly to Annually***	
GROUNDWATER *Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.*				
Dissolved Oxygen	X	X		Determines the effect of the oxidants on dissolved oxygen levels and potential to boost aerobic biodegradation as a secondary benefit.
Redox Potential	X	X		Yields data on system's ability to increase the extent of aerobic subsurface environment.

Exhibit XIII-14
Common Performance Monitoring Parameters and Sampling Frequencies (continued)

Analytical Parameter	Sampling Frequency: Start-up Phase (7-10 days)	Sampling Frequency: Remediation/ Post-Application Long-Term Monitoring Phase		Purpose
	Daily	*Weekly to Monthly*	*Quarterly to Annually*	
GROUNDWATER (continued) *Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.*				
pH	X	X		Confirms pH conditions are stable and suitable for Fenton's Reagent, or identifies trends of concern.
H_2O_2, Ozone, or Permanganate	X	X		Provides information on distances the oxidizing compounds are able to be transmitted by the remedial system before decomposing.
Petroleum COCs			X	Indicates remedial progress.
Degradation Daughter Constituents (e.g., TBA)			X	Could indicate incomplete oxidation process.
Water Table Elevations	X	X		Determines if hydraulic conditions (groundwater flow) are consistent with design intent or if chemical oxidation has had an unanticipated affect on these conditions.

Exhibit XIII-14
Common Performance Monitoring Parameters and Sampling Frequencies (continued)

Analytical Parameter	Sampling Frequency			Purpose
	Start-up Phase (7-10 days)	Remediation/ Post-Application Long-Term Monitoring Phase		
	Daily	*Weekly to Monthly*	*Quarterly to Annually*	
SOIL VAPOR *Samples should be collected from monitoring wells located in and around the treatment area that are screened in the unsaturated zone and from soil vapor extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.*				
Carbon Dioxide	X	X		Provides evidence of chemical oxidation.
Oxygen	X	X		Indicates potential losses of introduced oxygen through the unsaturated zone.
Volatile Petroleum Contaminants (Constituents) of Concern (COCs)	X	X		Suggests residual sources in soil or fugitive emissions associated with the remedial effort.
Fugitive Ozone or Hydrogen Peroxide	X	X		Determines losses of oxygen-yielding reagents delivered to the subsurface.
SOIL *Samples should be collected from borings or using push point or drill rig sampling equipment in and around the treatment area. Soil samples should consistently be collected from same contaminated sections of stratigraphic interval for comparison to earlier samples from same locations and depths.*				
Petroleum COCs			X	Provide a measure of remedial progress, contaminant mass reducions and the extent to which chemical oxidation of adsorbed contaminants is limited.

The performance of the chemical oxidation system should be determined by the chemistry of soil and groundwater located between, around and downgradient of oxidant delivery locations rather than inside or in the immediate vicinity of the oxidant delivery points. Conditions inside or in the immediate vicinity of oxidant injection locations have been preferentially altered by chemical oxidation to destroy the petroleum contaminants. Therefore, data from these locations are not representative of the subsurface conditions that exist beneath most of the site. To understand the effect the chemical oxidation system is having on the subsurface conditions as a measure of its performance, samples of soil, groundwater and soil gas should be collected from alternate locations. In review of the performance monitoring plan in the corrective action plan, it should be verified that a sufficient number of sampling locations exist between oxidant application points to provide the necessary performance sampling data. A description of how these data may be used to evaluate the chemical oxidation system performance is provided below.

Evaluation Criteria

The evaluation sampling described above provides the evidence needed to assess the chemical oxidation system performance. This evidence requires examination and interpretation to confirm chemical oxidation system effectiveness and whether system or application modifications may be warranted. A discussion of these data and how system performance can be interpreted is provided below. In particular, an evaluation of performance is examined from the following two broad chemical oxidation system requirements:

- Oxidant Delivery and Distribution
- Permanent Contaminant Mass Reduction and Attainment of Cleanup Goal

Each of these is discussed in more detail below.

Oxidant Delivery and Distribution. Performance sampling may indicate that the chemical oxidation system is meeting design specifications for oxidant delivery and distribution if the data show the following:

- Oxidant and catalyst are being delivered to the subsurface at the design mass delivery rate or design adjusted rate based on analysis of field monitoring data; and
- The oxidant and catalyst are detected in samples from the treatment area at the design concentrations.

If the performance monitoring data suggest that one or more of these conditions is not met, the system may not be meeting the requirements of the design, and system adjustments or modifications may need to be made. As previously discussed, the remedial system design should include contingency planning that explores performance deficiency scenarios and identifies possible solutions.

Oxidant delivery deficiencies may be overcome by simply adjusting system flow rates, upgrading equipment capacities or increasing oxidant dose concentrations. However, occasionally, oxidant delivery rates may be limited by the capacity of the subsurface to transport the delivered oxidant mass.

Perhaps the most challenging performance problem is when a chemical oxidation system or program is unable to deliver oxidants to a portion or multiple portions of a contaminated area. There are many ways that oxidants distributed from delivery points could fail to reach target contaminated area. These may include:

- Low permeability heterogeneous soils.
- Low hydraulic gradient and groundwater flow.

Possible remedies to the performance problem include adding additional oxidant delivery points; increasing oxidant delivery rates; increasing dose concentrations; or enhancing hydraulic gradients and groundwater flow.

Permanent Contaminant Mass Reduction And Attainment of Cleanup Goal. The effectiveness of a chemical oxidation program can only be determined after examining the reduction in contaminant mass, and after identifying whether the contaminant mass reduction is sufficient for the soil and groundwater to permanently meet cleanup standards.

It is not sufficient to simply review groundwater monitoring data collected during and weeks or even months after completing a chemical oxidation program. These data are often biased, reflecting the successful oxidation of the most readily contacted contaminants, predominantly contaminants in the most permeable soil zones. False positive evaluations of chemical oxidation program performance can result from reliance on short-term post-chemical oxidation application groundwater monitoring data. These false positive evaluations may become evident during long-term groundwater monitoring when contaminant levels rebound as untreated contaminant mass in the less permeable soil bleeds back out and re-contaminates the more permeable zones. Long term (e.g., months to years), post-chemical oxidation groundwater monitoring is needed to evaluate the effectiveness of a chemical oxidation program.

Program effectiveness may also be evaluated by estimating the mass of contaminants destroyed, which can be accomplished using sample analytical data. Provided that a sufficient number of soil samples are collected and analyzed for the treatment area, soil sampling using identical methods before and after implementation of a chemical oxidation program may indicate the volume of contaminant mass destroyed by the oxidants. Comparing the estimated actual mass destruction with the projected mass destruction (as predicted in the corrective action plan) will reveal the relative effectiveness the oxidant application program. If the contaminant mass destroyed is roughly the amount predicted during the design, the chemical oxidation program can be considered a success.

Should significantly more contaminant mass be destroyed than predicted, the program might be characterized as highly successful, but if significantly less contaminant mass is destroyed than predicted, it may be more accurately characterized as a failure. As the remediation program progresses, it may be necessary to review the project goals, particularly if the source has been effectively reduced (e.g., 70-90%), but significant contaminant mass remains in the associated plume. It may be necessary to perform a second phase of remediation (e.g., apply a different oxidant, move to monitored natural attenuation) to determine whether site cleanup has been achieved or is feasible.

The most direct measurement of the success of a chemical oxidation program is to determine whether the groundwater and soil remedial objectives have been met and can be sustained indefinitely following chemical oxidation treatment. Post-application monitoring should be conducted for a minimum of one year following chemical oxidation treatment to confirm that short-term reductions can be sustained, indicating that contaminant levels have been adequately reduced throughout the contaminated soil and groundwater.

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Checklist: Can Chemical Oxidation Be Used At This Site?

This checklist can help you to evaluate the completeness of the corrective action plan and to identify areas that require closer scrutiny. As you go through the corrective action plan, answer the following questions. If the answer to several questions is "no", you will most likely want to request additional information to determine if the proposed chemical oxidation technology and approach will accomplish the site cleanup goals.

1. Site Factors

Yes	No	
○	○	Is the soil intrinsic permeability greater than 10^{-9} cm^2?
○	○	Is the soil generally free of impermeable or low permeability layers that could retain significant petroleum contaminant mass and limit the bioavailability of this mass?
○	○	Is the soil profile determined from geologic boring logs generally free of natural organic material (e.g., layers of peat or humic material)?
○	○	Is the soil temperature expected to be 10°C or higher during remediation?
○	○	Is the pH of site groundwater between 5 and 9?
○	○	Is the dissolved iron concentration in the site groundwater < 10 mg/L?
○	○	Have imminent likely excessive risks to human health or the environment (if any, associated with the petroleum contamination) been eliminated?
○	○	Does the state have specific permitting requirements?

2. Chemical Oxidation Design

Yes	No	
○	○	Has the mass of petroleum hydrocarbons requiring biodegradation been estimated?
○	○	Has the mass of dissolved oxygen required to biodegrade the petroleum contaminants been estimated?
○	○	Can the proposed chemical oxidation approach deliver the necessary oxygen mass to the treatment area within the estimated cleanup time?
○	○	Is the capacity of the chemical oxidation treatment system sufficient to generate and deliver oxygen at the required design rate?
○	○	Is the density and configuration of oxygen delivery points adequate to uniformly disperse dissolved oxygen through the target treatment zone, given site geology and hydrologic conditions?

3. Permitting Issues

Yes	No	
○	○	Does the state have specific permitting requirements? If so, are they addressed in the plan?

4. Written Performance Monitoring Plan

Yes	No	
○	○	Will a comprehensive set of baseline sampling be performed prior to chemical oxidation system start-up?
○	○	Does the plan specifically exclude sampling from oxygen delivery wells when collecting data to evaluate chemical oxidation system performance?
○	○	Are monitoring wells adequately distributed between oxygen delivery locations to collect groundwater and soil vapor samples to evaluate the performance of the chemical oxidation system?
○	○	Does the written plan include periodically collecting soil samples from the contaminated interval(s) at locations between oxygen delivery locations?
○	○	Will the soil, soil vapor and groundwater samples be analyzed for the majority of the recommended performance monitoring parameters?
○	○	Will frequencies of performance monitoring correspond to those identified in Exhibit XIII–14?

APPENDIX

Abbreviations and Definitions

Appendix
Abbreviations and Definitions

Abbreviations

AS	Air Sparging
ASTM	American Society of Testing and Materials
atm	atmosphere (pressure)
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
Btu	British thermal unit
CAP	Corrective Action Plan
CFU	Colony Forming Units
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DPE	Dual-Phase Extraction
FID	Flame Ionization Detector
GAC	Granular Activated Carbon
GC	Gas Chromatograph
HDPE	High Density Polyethylene
Hg	Mercury, elemental
LEL	Lower Explosive Limit
LNAPL	Light Non-Aqueous Phase Liquid
LTTD	Low Temperature Thermal Desorption
LUST	Leaking Underground Storage Tank
MS	Mass Spectrometer
NAPL	Non-Aqueous Phase Liquid
NPDES	National Pollutant Discharge Elimination System
OUST	Office of Underground Storage Tanks (USEPA, Washington, DC)
PAH	Polyaromatic Hydrocarbon
PID	Photoionization Detector
PNA	Polynuclear Aromatic Hydrocarbon
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch (pressure)
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
ROI	Radius of Influence
SVE	Soil Vapor Extraction
TCLP	Toxicity Characteristic Leaching Procedure (EPA Method 1311)
TEA	Terminal Electron Acceptor
TPH	Total Petroleum Hydrocarbons
TRPH	Total Recoverable Petroleum Hydrocarbons (EPA Method 418.1)
UEL	Upper Explosive Limit
UST	Underground Storage Tank
VOC	Volatile Organic Compound

Definitions

abiotic: not biotic; not formed by biologic processes.

absorption: the penetration of atoms, ions, or molecules into the bulk mass of a substance.

Actinomycetes: any of numerous, generally filamentous, and often pathogenic, microorganisms resembling both bacteria and fungi.

adsorption: the retention of atoms, ions, or molecules onto the surface of another substance.

advection: the process of transfer of fluids (vapors or liquid) through a geologic formation in response to a pressure gradient that may be caused by changes in barometric pressure, water table levels, wind fluctuations, or infiltration.

aeration: the process of bringing air into contact with a liquid (typically water), usually by bubbling air through the liquid, spraying the liquid into the air, allowing the liquid to cascade down a waterfall, or by mechanical agitation. Aeration serves to (1) strip dissolved gases from solution, and/or (2) oxygenate the liquid. The rate at which a gas transfers into solution can be described by Fick's First Law.

aerobic: in the presence of oxygen.

afterburner: an off-gas posttreatment unit for control of organic compounds by thermal oxidation. A typical afterburner is a refractory-lined shell providing enough residence time at a sufficiently high temperature to destroy organic compounds in the off-gas stream.

aggregate: coarse mineral material (e.g., sand, gravel) that is mixed with either cement to form concrete or tarry hydrocarbons to form asphalt.

algae: chiefly aquatic, eucaryotic one-celled or multicellular plants without true stems, roots and leaves, that are typically autotrophic, photosynthetic, and contain chlorophyll. Algae are not typically found in groundwater.

aliphatic: of or pertaining to a broad category of carbon compounds distinguished by a straight, or branched, open chain arrangement of the constituent carbon atoms. The carbon-carbon bonds may be either saturated or unsaturated. Alkanes, alkenes, and alkynes are aliphatic hydrocarbons.

alkanes: the homologous group of linear saturated aliphatic hydrocarbons having the general formula C_nH_{2n+2}. Alkanes can be straight chains, branched chains, or ring structures. Also referred to as paraffins.

alkenes: the group of unsaturated hydrocarbons having the general formula C_nH_{2n} and characterized by being highly chemically reactive. Also referred to as olefins.

alkynes: the group of unsaturated hydrocarbons with a triple Carbon-Carbon bond having the general formula C_nH_{2n-2}.

ambient: surrounding.

anaerobic: in the absence of oxygen.

anisotropic: the condition in which hydraulic properties of an aquifer are not equal when measured in all directions.

aqueous solubility: the extent to which a compound will dissolve in water. The log of solubility is generally inversely related to molecular weight.

aquifer: a geologic formation capable of transmitting significant quantities of groundwater under normal hydraulic gradients.

aquitard: a geologic formation that may contain groundwater but is not capable of transmitting significant quantities of groundwater under normal hydraulic gradients. In some situations aquitards may function as confining beds.

aromatic: of or relating to organic compounds that resemble benzene in chemical behavior. These compounds are unsaturated and characterized by containing at least one 6-carbon benzene ring.

asymptote: a line that is considered to be the limit to a curve. As the curve approaches the asymptote, the distance separating the curve and the asymptote continues to decrease, but the curve never actually intersects the asymptote.

attenuation: the reduction or lessening in amount (e.g., a reduction in the amount of contaminants in a plume as it migrates away from the source).

Atterberg limits: the moisture contents which define a soil's liquid limit, plastic limit, and sticky limit.

auger: a tool for drilling/boring into unconsolidated earth materials (soil) consisting of a spiral blade wound around a central stem or shaft that is commonly hollow (hollow-stem auger). Augers commonly are available in flights (sections) that are connected together to advance the depth of the borehole.

autoignition temperature: the temperature at which a substance will spontaneously ignite. Autoignition temperature is an indicator of thermal stability for petroleum hydrocarbons.

autotrophic: designating or typical of organisms that derive carbon for the manufacture of cell mass from inorganic carbon (carbon dioxide).

bacteria: unicellular microorganisms that exist either as free-living organisms or as parasites and have a broad range of biochemical, and often pathogenic, properties. Bacteria can be grouped by form into five general categories: cocci (spherical), bacilli (rod-shaped), vibrio (curved rod-shaped), spirilla (spiral), and filamentous (thread-like).

baghouse: a dust-collection chamber containing numerous permeable fabric filters through which the exhaust gases pass. Finer particulates entrained in the exhaust gas stream are collected in the filters for subsequent treatment/disposal.

ball valve: a valve regulated by the position of a free-floating ball that moves in response to fluid or mechanical pressure.

Bentonite: a colloidal clay, largely made up of the mineral sodium montmorillonite, a hydrated aluminum silicate. Because of its expansive property, bentonite is commonly used to provide a tight seal around a well casing.

berm: a sloped wall or embankment (typically constructed of earth, hay bales, or timber framing) used to prevent inflow or outflow of material into/from an area.

bioassay: a method used to determine the toxicity of specific chemical contaminants. A number of individuals of a sensitive species are placed in water containing specific concentrations of the contaminant for a specified period of time.

biodegradability (or biodegradation potential): the relative ease with which petroleum hydrocarbons will degrade as the result of biological metabolism. Although virtually all petroleum hydrocarbons are biodegradable, biodegradability is highly variable and dependent somewhat on the type of hydrocarbon. In general, biodegradability increases with increasing solubility; solubility is inversely proportional to molecular weight.

biodegradation: a process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment.

biomass: the amount of living matter in a given area or volume.

boiling point: the temperature at which a component's vapor pressure equals atmospheric pressure. Boiling point is a relative indicator of volatility and generally increases with increasing molecular weight.

Btu: the quantity of heat required to raise the temperature of one pound of water one degree Fahrenheit at 39°F; used as the standard for the comparison of heating values of fuels.

bubble radius: the maximum radial distance away from a biosparging well where the effects of sparging are observable. Analogous to radius of influence of an air sparging well.

bulk density: the amount of mass of a soil per unit volume of soil; where mass is measured after all water has been extracted and total volume includes the volume of the soil itself and the volume of air space (voids) between the soil grains.

butterfly valve: a shut-off valve usually found in larger pipe sizes (4 inches or greater). This type of valve can be used for non-critical flow control.

capillary fringe: the zone of a porous medium above the water table within which the porous medium is saturated by water under pressure that is less than atmospheric pressure.

capillary suction: the process whereby water rises above the water table into the void spaces of a soil due to tension between the water and soil particles.

catalytic oxidizer: an off-gas posttreatment unit for control of organic compounds. Gas enters the unit and passes over a support material coated with a catalyst (commonly a noble metal such as platinum or rhodium) that promotes oxidation of the organics. Catalytic oxidizers can also be very effective in controlling odors. High moisture content and the presence of chlorine or sulfur compounds can adversely affect the performance of the catalytic oxidizer.

chemotrophs: organisms that obtain energy from oxidation or reduction of inorganic or organic matter.

coefficient of permeability: see hydraulic conductivity.

condensate: the liquid that separates from a vapor during condensation.

conductivity: a coefficient of proportionality describing the rate at which a fluid (e.g., water or gas) can move through a permeable medium. Conductivity is a function of both the intrinsic permeability of the porous medium and the kinematic viscosity of the fluid which flows through it.

cone of depression: the area around a discharging well where the hydraulic head (potentiometric surface) in the aquifer has been lowered by pumping. In an unconfined aquifer, the cone of depression is a cone-shaped depression in the water table where the media has actually been dewatered.

confined aquifer: a fully saturated aquifer overlain by a confining layer. The potentiometric surface (hydraulic head) of the water in a confined aquifer is at an elevation that is equal to or higher than the base of the overlying confining layer. Discharging wells in a confined aquifer lower the potentiometric surface which forms a cone of depression, but the saturated media is not dewatered.

confining layer: a geologic formation characterized by low permeability that inhibits the flow of water (see also aquitard).

conservative: (a) in the case of a contaminant, one that does not degrade and the movement of which is not retarded; is unreactive. (b) in the case of an assumption, one that leads to a worst-case scenario, one that is most protective of human health and the environment.

constituent: an essential part or component of a system or group (e.g., an ingredient of a chemical mixture). For instance, benzene is one constituent of gasoline.

cyclone: a type of separator for removal of larger particles from an exhaust gas stream. Gas laden with particulates enters the cyclone and is directed to flow in a spiral causing the entrained particulates to fall out and collect at the bottom. The gas exits near the top of the cyclone.

Darcy's Law: an empirical relationship between hydraulic gradient and the viscous flow of water in the saturated zone of a porous medium under conditions of laminar flow. The flux of vapors through the voids of the vadose zone can be related to a pressure gradient through the air permeability by Darcy's Law.

degradation potential: the degree to which a substance is likely to be reduced to a simpler form by bacterial activity.

denitrification: bacterial reduction of nitrite to gaseous nitrogen under anaerobic conditions.

density: the amount of mass per unit volume.

diffusion: the process by which molecules in a single phase equilibrate to a zero concentration gradient by random molecular motion (Brownian motion). The flux of molecules is from regions of high concentration to low concentration and is governed by Fick's Second Law.

dispersion: the process by which a substance or chemical spreads and dilutes in flowing groundwater or soil gas.

dissolution: dissolving of a substance in a liquid solvent (e.g., water).

downgradient: in the direction of decreasing static head (potential).

drawdown: lowering the water table due to withdrawal of groundwater as from a well.

dynamic viscosity: a measure of a fluid's resistance to tangential or shear stress.

effective porosity: the amount of interconnected pore space in a soil or rock through which fluids can pass, expressed as a percent of bulk volume. Some of the voids and pores in a rock or soil will be filled with static fluid or other material, so that effective porosity is always less than total porosity.

effluent: something that flows out, especially a liquid or gaseous waste stream.

empirical: relying upon or gained from experiment or observation.

entrained: particulates or vapor transported along with flowing gas or liquid.

enzyme: any of numerous proteins or conjugated proteins produced by living organisms and functioning as biochemical catalysts.

eucaryotes: an organism having one or more cells with well-defined nuclei.

evaporation: the process by which a liquid enters the vapor (gas) phase.

***ex situ*:** moved from its original place; excavated; removed or recovered from the subsurface.

facultative anaerobes: microorganisms that can grow in either the presence or the absence of molecular oxygen. In the absence of oxygen these microorganism can utilize another compound (e.g., sulfate or nitrate) as a terminal electron acceptor.

Fick's First Law: an equation describing the rate at which a gas transfers into solution. The change in concentration of gas in solution is proportional to the product of an overall mass transfer coefficient and the concentration gradient.

Fick's Second Law: an equation relating the change of concentration with time due to diffusion to the change in concentration gradient with distance from the source of concentration.

field capacity: the maximum amount of water that a soil can retain after excess water from saturated conditions has been drained by the force of gravity.

flow tube: a calibrated flow measuring device made for a specific range of flow velocities and fluids.

flux: the rate of movement of mass through a unit cross-sectional area per unit time in response to a concentration gradient or some advective force.

free product: a petroleum hydrocarbon in the liquid ("free" or non-aqueous) phase (see also non-aqueous phase liquid, NAPL).

friable: easily crumbled, not cohesive or sticky.

fungi: aerobic, multicellular, nonphotosynthetic, heterotrophic microorganisms. The fungi include mushrooms, yeast, molds, and smuts. Most fungi are saprophytes, obtaining their nourishment from dead organic matter. Along with bacteria, fungi are the principal organisms responsible for the decomposition of carbon in the biosphere. Fungi have two ecological advantages over bacteria: (1) they can grow in low moisture areas, and (2) they can grow in low pH environments.

gate valve: a valve regulated by the position of a circular plate.

globe valve: a type of stemmed valve that is used for flow control. The valve has a globe shaped plug that rises or falls vertically when the stem handwheel is rotated.

groundwater: the water contained in the pore spaces of saturated geologic media.

grout: a watery mixture of cement (and commonly bentonite) without aggregate that is used to seal the annular space around well casings to prevent infiltration of water or short-circuiting of vapor flow.

heat capacity: the quantity of energy that must be supplied to raise the temperature of a substance. For contaminated soils heat capacity is the quantity of energy that must be added to the soil to volatilize organic components. The typical range of heat capacity of soils is relatively narrow, therefore variations are not likely to have a major impact on application of a thermal desorption process.

Henry's law: the relationship between the partial pressure of a compound and the equilibrium concentration in the liquid through a proportionality constant known as the Henry's law constant.

Henry's law constant: the ratio of the concentration of a compound in air (or vapor) to the concentration of the compound in water under equilibrium conditions.

heterogeneous: varying in structure or composition at different locations in space.

heterotrophic: designating or typical of organisms that derive carbon for the manufacture of cell mass from organic matter.

homogeneous: uniform in structure or composition at all locations in space.

hose barb: a twist-type connector used for connecting a small diameter hose to a valve or faucet.

hydraulic conductivity: a coefficient of proportionality describing the rate at which water can move through a permeable medium. Hydraulic conductivity is a function of both the intrinsic permeability of the porous medium and the kinematic viscosity of the water which flows through it. Also referred to as the coefficient of permeability.

hydraulic gradient: the change in total potentiometric (or piezometric) head between two points divided by the horizontal distance separating the two points.

hydrocarbon: chemical compounds composed only of carbon and hydrogen.

hydrophilic: having an affinity for water, or capable of dissolving in water; soluble or miscible in water.

hydrophobic: tending not to combine with water, or incapable of dissolving in water; insoluble or immiscible in water. A property exhibited by non-polar organic compounds, including the petroleum hydrocarbons.

hypoxic: a condition of low oxygen concentration, below that considered aerobic.

in-line rotameter: a flow measurement device for liquids and gases that uses a flow tube and specialized float. The float device is supported by the flowing fluid in the clear glass or plastic flow tube. The vertical scaled flow tube is calibrated for the desired flow volumes/time.

***in situ*:** in its original place; unmoved; unexcavated; remaining in the subsurface.

indigenous: living or occurring naturally in a specific area or environment; native.

infiltration: the downward movement of water through a soil in response to gravity and capillary suction.

injection well: a well used to inject under pressure a fluid (liquid or gas) into the subsurface.

inlet well: a well through which a fluid (liquid or gas) is allowed to enter the subsurface under natural pressure.

inoculate: to implant microorganisms onto or into a culture medium.

intergranular: between the individual grains in a rock or sediment.

intrinsic permeability: a measure of the relative ease with which a permeable medium can transmit a fluid (liquid or gas). Intrinsic permeability is a property only of the medium and is independent of the nature of the fluid.

isotropic: the condition in which hydraulic properties of an aquifer are equal when measured in any direction.

kinematic viscosity: the ratio of dynamic viscosity to mass density. Kinematic viscosity is a measure of a fluid's resistance to gravity flow: the lower the kinematic viscosity, the easier and faster the fluid will flow.

liquid limit (LL): the lower limit for viscous flow of a soil.

liquidity index (LI): quantitative value used to assess whether a soil will behave as a brittle solid, semisolid, plastic, or liquid. LI is equal to the difference between the natural moisture content of the soil and the plastic limit (PL) divided by the plasticity index (PI).

lithology: the gross physical character of a rock or rock types in a stratigraphic section.

lower explosive limit (LEL): the concentration of a gas below which the concentration of vapors is insufficient to support an explosion. LELs for most organics are generally 1 to 5 percent by volume.

magnehelic gauge: a sensitive differential pressure or vacuum gauge manufactured by Dwyer Instrument Co. that uses a precision diaphragm to measure pressure differences. This gauge is manufactured in specific pressure or vacuum ranges such as 0 to 2 inches of water column. Magnehelic gauges are typically used to measure SVE system vacuums.

manifold: a pipe with several apertures for making multiple connections.

manometer: an instrument for measuring fluid pressure. Typically a U-shaped tube in which opposing fluid pressures reach an equilibrium. The pressure is equal to the differences in the levels of the fluid on either side of the tube.

methanogenic: referring to the formation of methane by certain anaerobic bacteria during the process of anaerobic fermentation.

microaerophilic: obligate aerobes that function best under conditions of low oxygen concentration.

microcosm: a diminutive, representative system analogous to a larger system in composition, development, or configuration. As used in biodegradation treatability studies, microcosms are typically constructed in glass bottles or jars.

microorganisms: microscopic organisms including bacteria, protozoans, yeast, fungi, mold, viruses, and algae.

moisture content: the amount of water lost from a soil upon drying to a constant weight, expressed as the weight per unit weight of dry soil or as the volume of water per unit bulk volume of the soil. For a fully saturated medium, moisture content equals the porosity.

molecular weight: the amount of mass in one mole of molecules of a substance as determined by summing the masses of the individual atoms which make up the molecule.

molecular diffusion: process whereby molecules of various gases tend to intermingle and eventually become uniformly dispersed.

monoaromatic: aromatic hydrocarbons containing a single benzene ring.

non-aqueous phase liquid (NAPL): contaminants that remain as the original bulk liquid in the subsurface (see also free product).

nutrients: major elements (e.g., nitrogen and phosphorus) and trace elements (including sulfur, potassium, calcium, and magnesium) that are essential for the growth of organisms.

obligate anaerobes: organisms for which the presence of molecular oxygen is toxic. These organisms derive the oxygen needed for cell synthesis from chemical compounds.

obligate aerobes: organisms that require the presence of molecular oxygen (O_2) for their metabolism.

occlude: to cause to become obstructed or closed and thus prevent passage either into or from.

octanol/water partition coefficient (K_{ow}): a coefficient representing the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher the K_{ow}, the more non-polar the compound. Log K_{ow} is generally used as a relative indicator of the tendency of an organic compound to adsorb to soil. Log K_{ow} values are generally inversely related to aqueous solubility and directly proportional to molecular weight.

off-gas treatment system: refers to the unit operations used to treat (i.e. condense, collect, or destroy) contaminants in the purge gas from the thermal desorber.

olefins: see alkenes.

orifice plate: a flow measurement device for liquids or gases that uses a restrictive orifice plate consisting of a machined hole that produces a jet effect. Typically the orifice meter consists of a thin plate with a square edged, concentric, and circular orifice. The pressure drop of the jet effect across the orifice is proportional to the flow rate. The pressure drop can be measured with a manometer or differential pressure gauge.

oxidation-reduction (redox): a chemical reaction consisting of an oxidation reaction in which a substance loses or donates electrons, and a reduction reaction in which a substance gains or accepts electrons. Redox reactions are always coupled because free electrons cannot exist in solution and electrons must be conserved.

paraffins: see alkanes.

partial pressure: the portion of total vapor pressure in a system due to one or more constituents in the vapor mixture.

permeability: a qualitative description of the relative ease with which rock, soil, or sediment will transmit a fluid (liquid or gas). Often used as a synonym for hydraulic conductivity or coefficient of permeability.

pH: a measure of the acidity of a solution. pH is equal to the negative logarithm of the concentration of hydrogen ions in a solution. A pH of 7 is neutral. Values less than 7 are acidic, and values greater than 7 are basic.

phototrophs: organisms that use light to generate energy (by photosynthesis) for cellular activity, growth, and reproduction.

pilot test: operation of a small-scale version of a larger system to gain information relating to the anticipated performance of the larger system. Pilot test results are typically used to design and optimize the larger system.

pitot tube: a device used to measure the total pressure of a fluid stream that is essentially a tube attached to a manometer at one end and pointed upstream at the other.

plastic limit (PL): the lower limit of the plastic state of a soil.

plastic soil: one that will deform without shearing (typically silts or clays). Plasticity characteristics are measured using a set of parameters known as Atterberg Limits.

plasticity index (PI): the range of water content in which soil is in a plastic state. PI is calculated as the difference between the percent liquid limit and percent plastic limit.

polyaromatic hydrocarbon: aromatic hydrocarbons containing more than one fused benzene ring. Polyaromatic hydrocarbons are commonly designated PAH.

polynuclear aromatic hydrocarbon: synonymous with polyaromatic hydrocarbon. Designated PNA.

pore volume: the total volume of pore space in a given volume of rock or sediment. Pore volume usually relates to the volume of air or water that must be moved through contaminated material in order to flush the contaminants.

porosity: the volume fraction of a rock or unconsolidated sediment not occupied by solid material but usually occupied by water and/or air.

pressure gradient: a pressure differential in a given medium (e.g., water or air) which tends to induce movement from areas of higher pressure to areas of lower pressure.

procaryotes: a cellular organism in which the nucleus has no limiting membrane.

protozoa: single-celled, eucaryotic microorganisms without cell walls. Most protozoa are free-living although many are parasitic. The majority of protozoa are aerobic or facultatively anaerobic heterotrophs.

psi (pounds per square inch): a unit of pressure or pressure drop across a flow resistance. One psi is equivalent to the pressure exerted by 2.31 feet of water column.

psig (pounds per square inch (gauge)): 0 psig = 14.696 psia (psi absolute) = 1.0 atmosphere.

pugmill: a chamber in which water and soil are mixed together. Typically mixing is aided by an internal mechanical stirring/kneading device.

radius of influence: the maximum distance away from an air injection or extraction source that is significantly affected by a change in pressure and induced movement of air.

recalcitrant: unreactive, nondegradable; refractory.

redox: short for oxidation-reduction.

refractory index: a measure of the ability of a substance to be biodegraded by bacterial activity. The lower the refractory index, the greater the biodegradability.

retardation: preferential retention of contaminant movement in the subsurface resulting from adsorptive processes or solubility differences.

saturated zone: the zone in which all the voids in the rock or soil are filled with water at greater than atmospheric pressure. The water table is the top of the saturated zone in an unconfined aquifer.

septa fitting: a special fitting used to seal vials (a liner for a threaded cap) or gas chromatographs (GCs) to provide closure. Septas can be manufactured in single, double, or triple layers of silicone rubber and other plastic materials. A syringe with a measured quantity of contaminant can be injected through a septa closure and into a GC column for separation analysis.

sentinel well: a groundwater monitoring well situated between a sensitive receptor downgradient and the source of a contaminant plume upgradient. Contamination should be first detected in the sentinel well which serves as a warning that contamination may be moving closer to the receptor. The sentinel well should be located far enough upgradient of the receptor to allow enough time before the contamination arrives at the receptor to initiate other measures to prevent contamination from reaching the receptor, or in the case of a supply well, provide for an alternative water source.

SESOIL: a one-dimensional model for estimating pollutant distribution in an unsaturated soil column. SESOIL results are commonly used to estimate the source term for groundwater transport modeling of the saturated zone.

short circuiting: as it applies to SVE and bioventing, the entry of ambient air into the extraction well without first passing through the contaminated zone. Short circuiting may occur through utility trenches, incoherent well or surface seals, or layers of high permeability geologic materials.

soil moisture: the water contained in the pore spaces in the unsaturated zone.

solubility: the amount of mass of a compound that will dissolve in a unit volume of solution.

sorbent canisters: gas-tight canisters typically filled with activated carbon (charcoal) for collection and transport of vapor samples. In the laboratory the vapors are desorbed and analyzed to identify the organic compounds and quantify their concentration.

sorbent tubes: glass tubes filled with a sorbent material that reacts chemically with specific organic compounds. Based on the nature of the sorbent and the extent of the chemical reaction, organic compounds can be identified and their concentration quantified.

sorption: a general term used to encompass the processes of absorption, adsorption, ion exchange, and chemisorption.

sparge: injection of air below the water table to strip dissolved volatile organic compounds and/or oxygenate the groundwater to facilitate aerobic biodegradation of organic compounds.

specific gravity: the dimensionless ratio of the density of a substance with respect to the density of water. The specific gravity of water is equal to 1.0 by definition. Most petroleum products have a specific gravity less than 1.0, generally between 0.6 and 0.9. As such, they will float on water--these are also referred to as LNAPLs, or light non-aqueous phase liquids. Substances with a specific gravity greater than 1.0 will sink through water--these are referred to as DNAPLs, or dense non-aqueous phase liquids.

sticky limit: the limit at which a soil loses its ability to adhere to a metal blade.

stratum: a horizontal layer of geologic material of similar composition, especially one of several parallel layers arranged one on top of another.

stratification: layering or bedding of geologic materials (e.g., rock or sediments).

sump: a pit or depression where liquids drain, collect, or are stored.

Tedlar bags: gas-tight bags constructed of non-reactive material (Tedlar) for the collection and transport of gas/vapor samples.

terminal electron acceptor (TEA): a compound or molecule that accepts an electron (is reduced) during metabolism (oxidation) of a carbon source. Under aerobic conditions molecular oxygen is the terminal electron acceptor. Under anaerobic conditions a variety of terminal electron acceptors may be used. In order of decreasing redox potential, these TEAs include nitrate, manganic manganese, ferric iron, sulfate, and carbon dioxide. Microorganisms preferentially utilize electron acceptors that provide the maximum free energy during respiration. Of the common terminal electron acceptors listed above, oxygen has the highest redox potential and provides the most free energy during electron transfer.

thermal desorption system: refers to a thermal desorber and associated systems for handling materials and treated soils and treating offgases and residuals.

thermal desorber: describes the primary treatment unit that heats petroleum-contaminated materials and desorbs the organic materials into a purge gas or off-gas.

total petroleum hydrocarbons (TPH): a measure of the concentration or mass of petroleum hydrocarbon constituents present in a given amount of air, soil, or water. The term total is a misnomer, in that few, if any, of the procedures for quantifying hydrocarbons are capable of measuring all fractions of petroleum hydrocarbons present in the sample. Volatile hydrocarbons are usually lost in the process and not quantified. Additionally, some non-petroleum hydrocarbons may be included in the analysis.

total recoverable petroleum hydrocarbons (TRPH): an EPA method (418.1) for measuring total petroleum hydrocarbons in samples of soil or water. Hydrocarbons are extracted from the sample using a chlorofluorocarbon solvent (typically Freon-113) and quantified by infrared spectrophotometry. The method specifies that the extract be passed through silica gel to remove the non-petroleum fraction of the hydrocarbons.

travel time: the time it takes a contaminant to travel from the source to a particular point downgradient.

turbine wheel: a rotor designed to convert fluid energy into rotational energy. Hydraulic turbines are used to extract energy from water as the water velocity increases due to a change in head or kinetic energy at the expense of the potential energy as the water flows from a higher elevation to a lower elevation. The fluid velocity tangential component contributes to the rotation of the rotor in a turbomachine.

unconfined aquifer: an aquifer in which there are no confining beds between the capillary fringe and land surface, and where the top of the saturated zone (the water table) is at atmospheric pressure.

unsaturated zone: the zone between land surface and the capillary fringe within which the moisture content is less than saturation and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is not included in the unsaturated zone.

unsaturated: the characteristic of a carbon atom in a hydrocarbon molecule that shares a double bond with another carbon atom.

upgradient: it the direction of increasing potentiometric (piezometric) head.

vadose zone: the zone between land surface and the water table within which the moisture content is less than saturation (except in the capillary fringe) and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is included in the vadose zone.

vapor density: the amount of mass of a vapor per unit volume of the vapor.

vapor pressure: the force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Vapor pressure is a measure of a substance's propensity to evaporate. Vapor pressure increases exponentially with an increase in temperature.

venturi: a short tube with a constricted throat for determining fluid pressures and velocities by measuring differential pressures generated at the throat as a fluid traverses the tube.

viscosity: a measure of the internal friction of a fluid that provides resistance to shear within the fluid. The greater the forces of internal friction (i.e. the greater the viscosity), the less easily the fluid will flow.

volatilization: the process of transfer of a chemical from the aqueous or liquid phase to the gas phase. Solubility, molecular weight, and vapor pressure of the liquid and the nature of the gas-liquid interface affect the rate of volatilization.

water table: the water surface in an unconfined aquifer at which the fluid pressure in the pore spaces is at atmospheric pressure.

weathering: the process during which a complex compound is reduced to its simpler component parts, transported via physical processes, or biodegraded over time.

wellhead: the area immediately surrounding the top of a well, or the top of the well casing.

windrow: a low, elongated row of material left uncovered to dry. Windrows are typically arranged in parallel.