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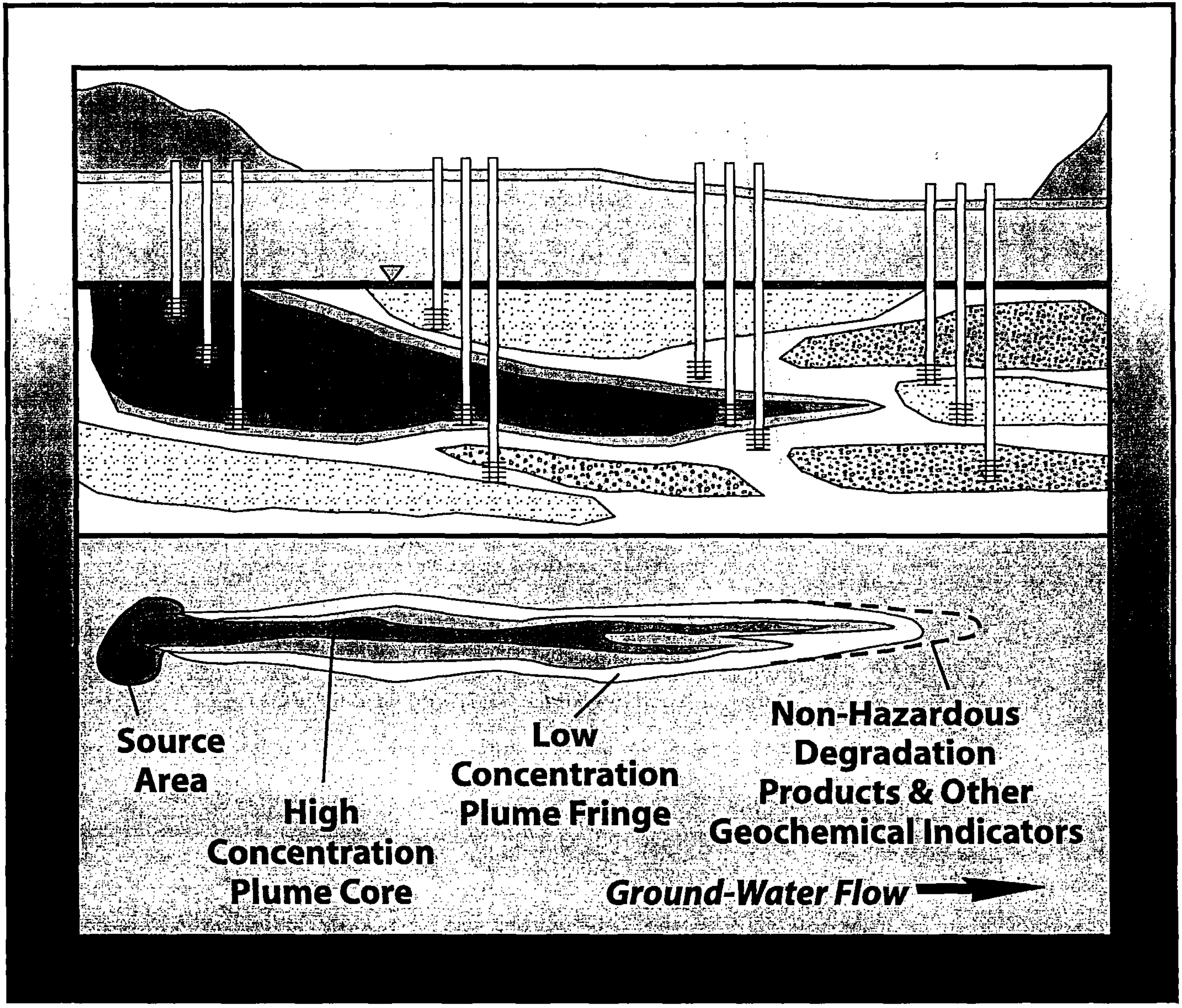
Performance Monitoring of MNA Remedies for VOCs in Ground Water



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Performance Monitoring of MNA Remedies for VOCs in Ground Water

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NOTICE

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All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Plan.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

Effective performance monitoring for remedies that rely on the natural attenuation of contaminants is a crucial element of remedial design and implementation. Effective monitoring system designs are formulated from an enhanced understanding of the migration and ultimate fate of the contaminants in the site-specific environment. This document provides technical recommendations regarding the types of monitoring parameters and analyses useful for evaluating the effectiveness of the natural attenuation component of ground-water remedial actions. The information will be helpful during the design of the performance monitoring plan as well as during its implementation.

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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.

- P 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.

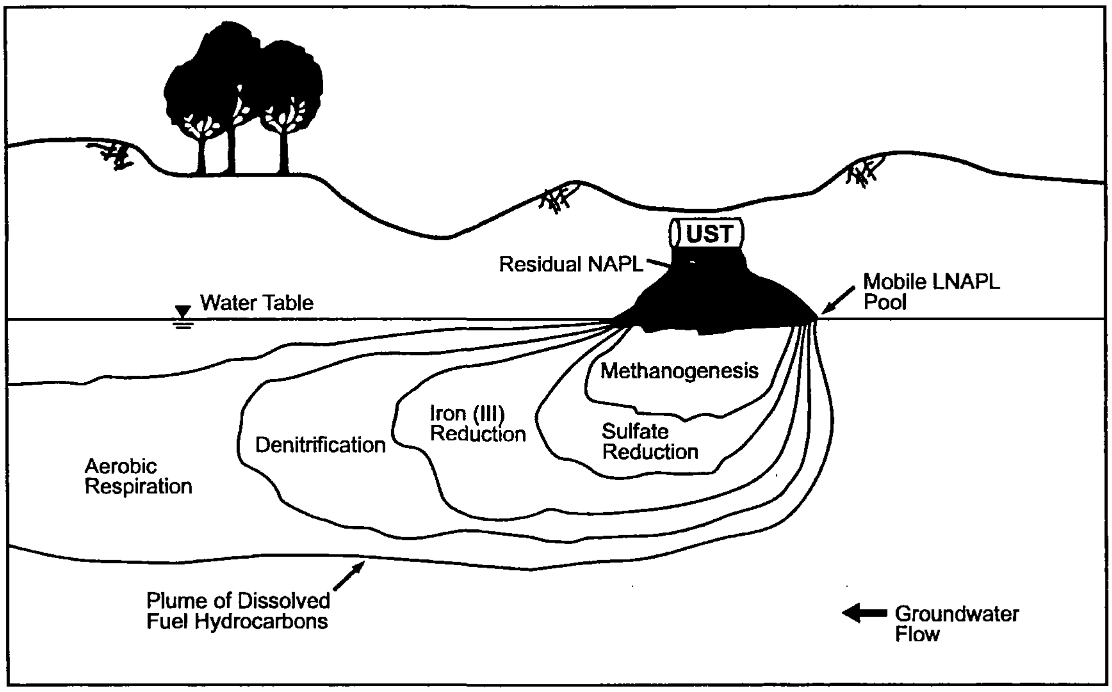
- P Step 2: ***A detailed evaluation of monitored natural attenuation effectiveness***. This step provides further criteria to confirm whether monitored natural attenuation is likely to be effective. To complete this evaluation, you will need to review monitoring data, chemical and physical parameters 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.

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

P 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.

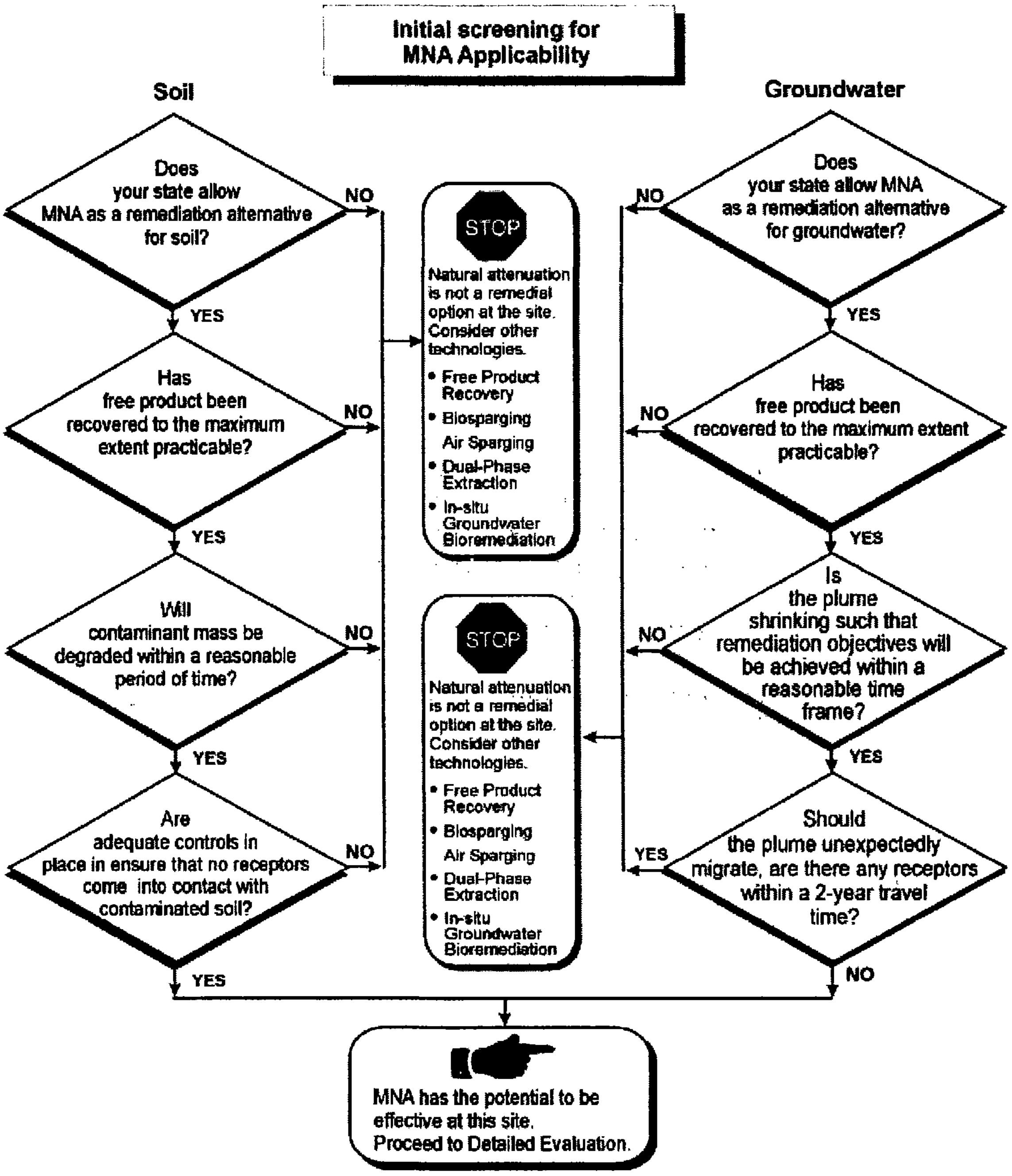
Although the specific screening criteria for both contaminated soil and groundwater might be expected to be very different due to the characteristics of the impacted media, they are actually quite similar. For both media the criteria focus on two elements: (1) source longevity and (2) potential receptor 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.

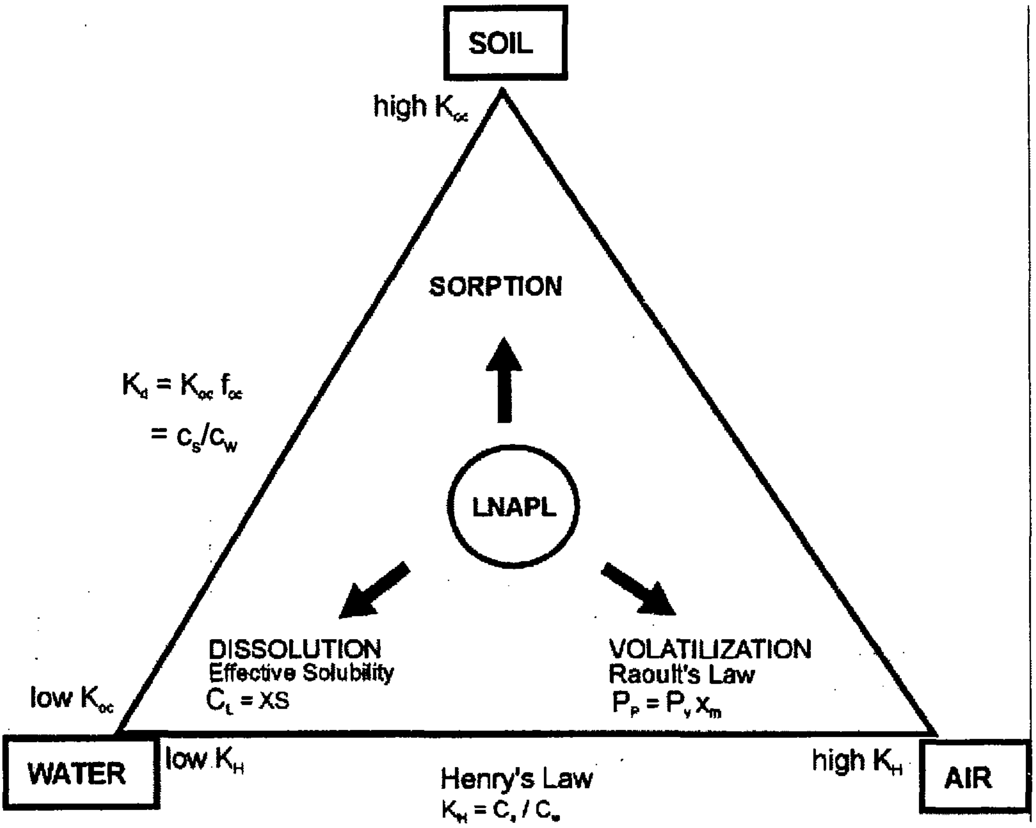
Contaminated Soil

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)

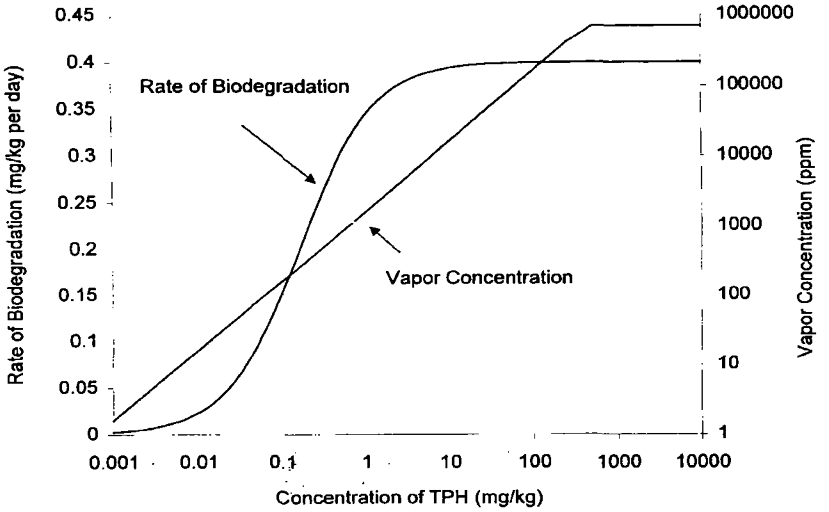
When hydrocarbon concentrations (C) are significantly lower than the half-saturation constant (K), the sum of (K+C) is approximately equivalent to K. Because $V_{\max}$ and K are constants, the rate of biodegradation (V) is proportional to the concentration of hydrocarbon (*C*). As the concentration 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 1	2	3	4	Bio-degradation -Limited 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.

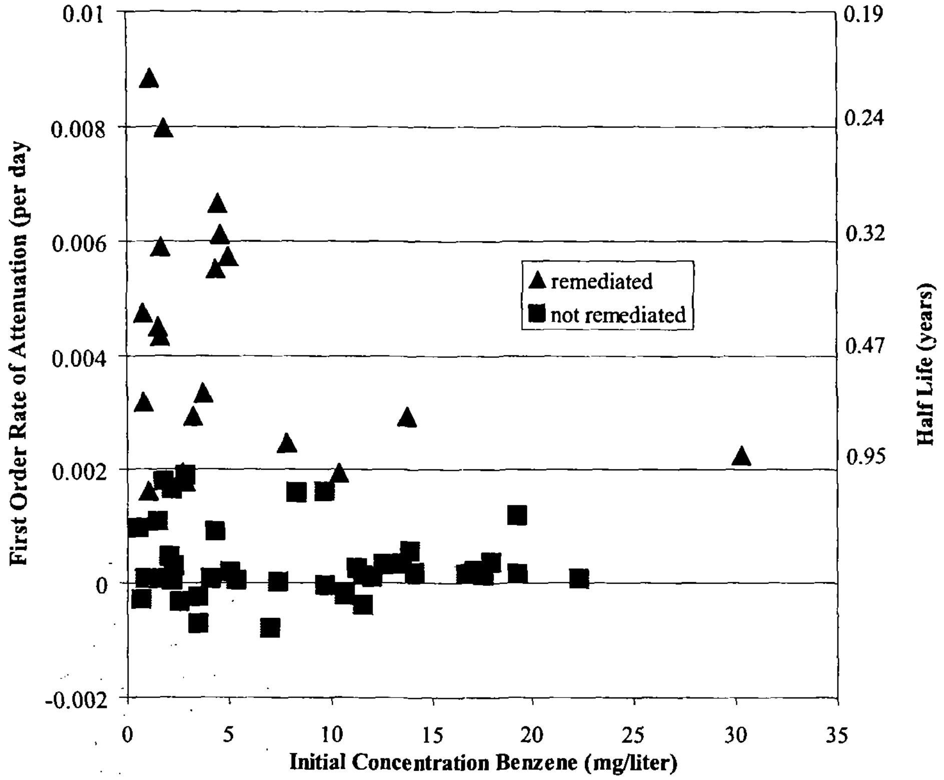
To estimate the achieved rate of attenuation of benzene and MTBE in groundwater in contact with residual gasoline, Peargin (2000) examined the long-term trends in the concentration of benzene and MTBE in monitoring wells that were screened in the LNAPL smear zone at 23 UST release sites. Source remediation 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.

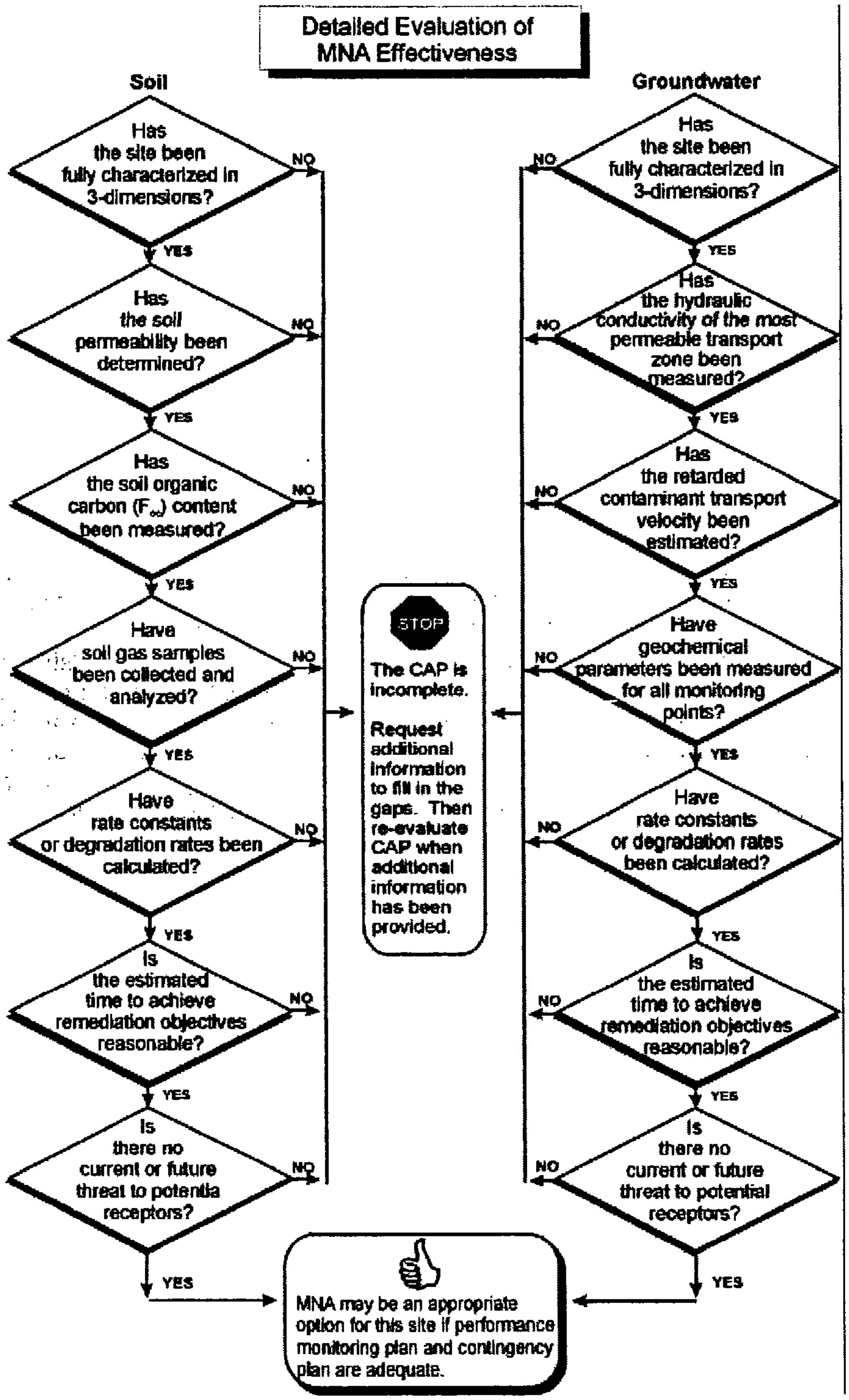
Detailed Evaluation Of Monitored Natural Attenuation Effectiveness

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 P Denitrification P Sulfate reduction P Iron reduction P Manganese reduction P 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.

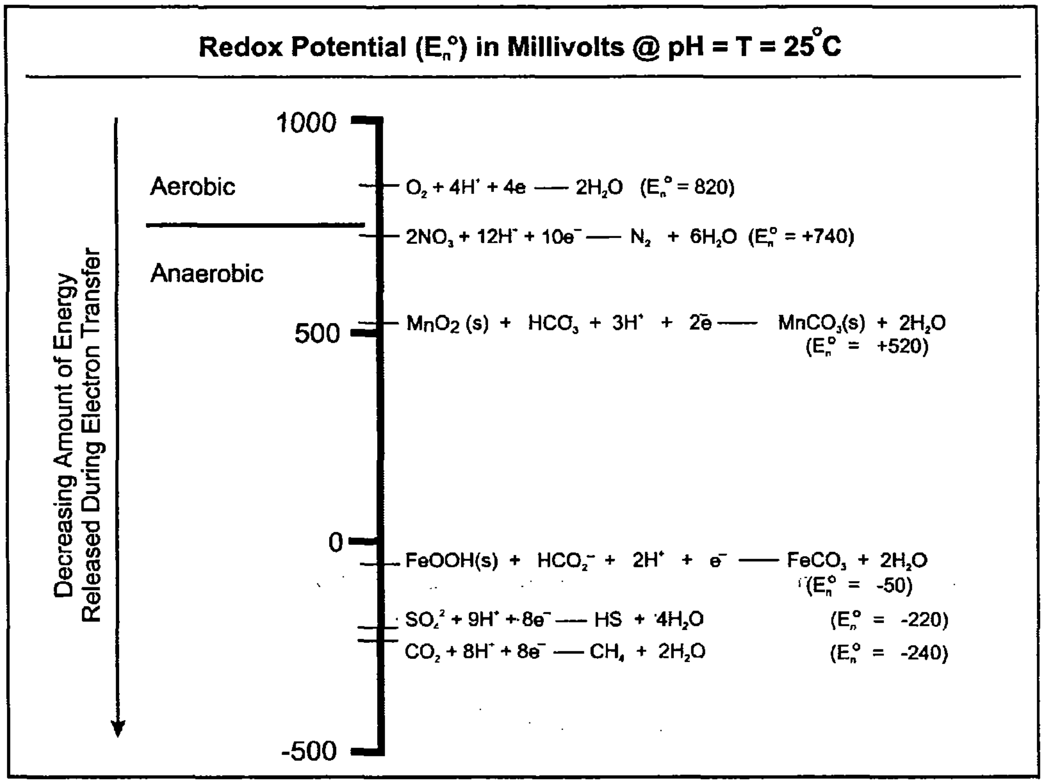
After dissolved oxygen has been depleted, biodegradation shifts from aerobic to anaerobic. The first anaerobic electron acceptor that may be utilized is nitrate by the process of denitrification. In the zone where denitrification is occurring, nitrate levels are lower than background. As with dissolved 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 (λ) 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 ($t_{½}$) 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

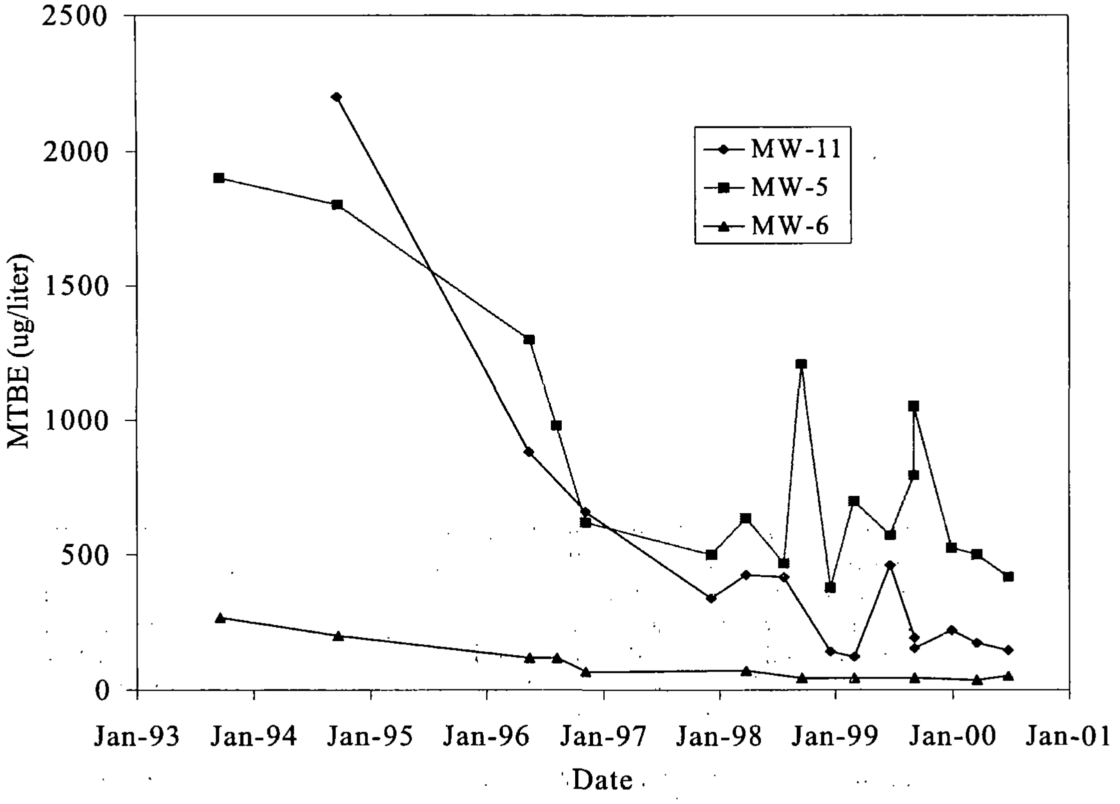


Exhibit IX-23
Rates Of attenuation Of MTBE In Monitoring Wells And The Projected Time Required To Reach A Clean Up Goal Of 20 µg/L As Calculated From The Data Presented In Exhibits IX-21 And IX-22

	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.

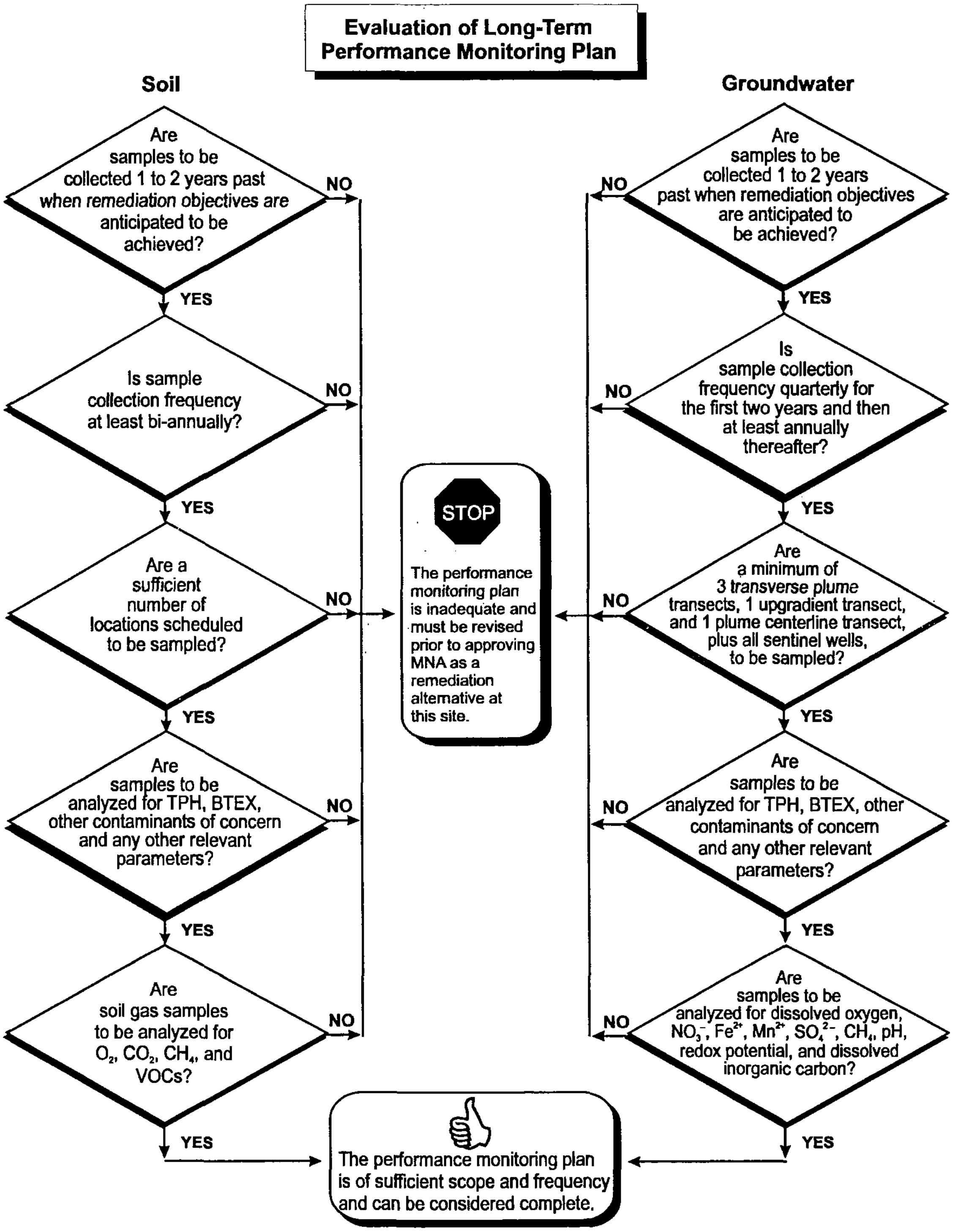
As with the active remediation technologies also described in this manual, if MNA does not appear to be effective in remediating the contamination at the site within a reasonable time frame, then an alternative active remedial technology (specified in the contingency plan section of the CAP) will be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

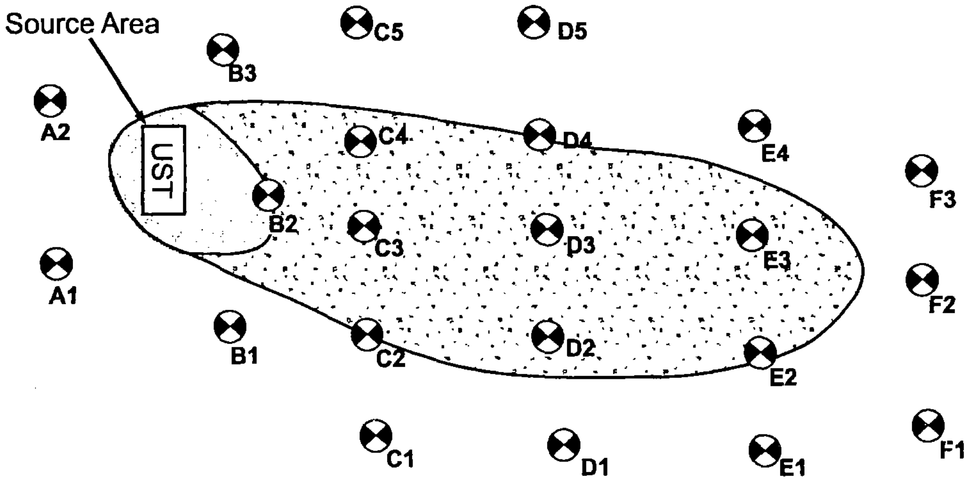
- source zone: B1 through B3
- mid-plume (transverse to flow): either C1 through C5, or D1 through D5
- plume toe: E1 through E4
- up gradient: A1 and A2
- plume centerline: B2-C3-D3-E3

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.

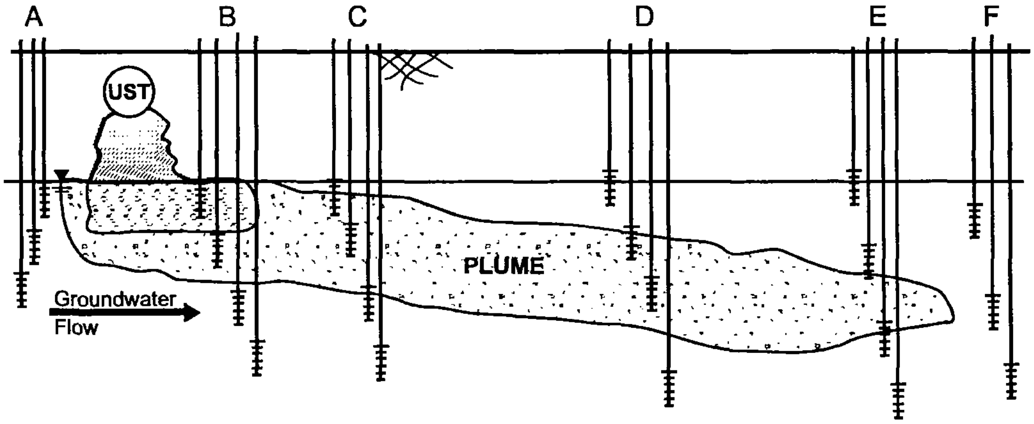
Groundwater samples should be analyzed for VOCs and other contaminants of concern, TPH (near the source area), dissolved oxygen, pH, temperature, redox potential, alkalinity, hardness, and other geochemical indicators as indicated in Exhibit IX-25. Isopleth (or isoconcentration) maps should be prepared 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.

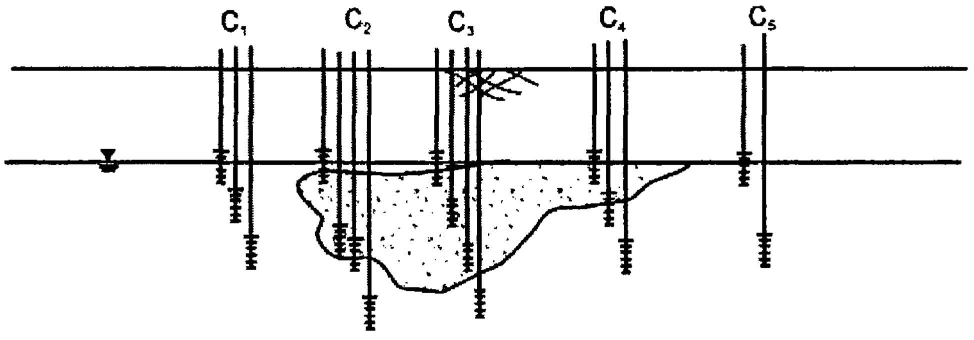


(A) Plan view of Optimal Groundwater Monitoring Network

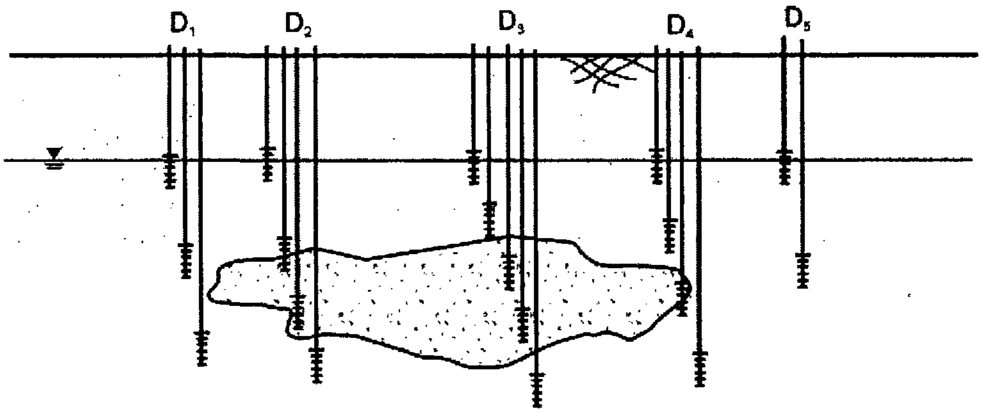


(B) Longitudinal Cross-Section of Optimal Groundwater Monitoring Network

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:____

____

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____

____

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?____________________

____