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INTRINSIC BIOREMEDIATION
OF PETROLEUM HYDROCARBONS

by

BATTELLE
Columbus, Ohio 43201-2693

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Intrinsic Bioremediation of Petroleum Hydrocarbons (TM-2185-ENV)
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page 6. Paragraph 1, 1st sentence	"...with U.S. EPA, sate..." should read "...with U.S. EPA, state..."
page 7. Paragraph 1, 3rd sentence	"...will require longer to remediation..." should read "...will require longer to remediate..."
page 37. Evidence for Intrinsic Bioremediation, 3rd bullet	"...within the anaerobic portion of the aquifer over..." should read "...within the anaerobic portion of the aquifer."
page 38. Site Conditions Influencing Intrinsic Bioremediation, 1st sentence	"The initial distribution of dissolved oxygen int he..." should read "The initial distribution of dissolved oxygen in the..."
page 38. Other Comments, 1st bullet	"Benzene was more persistent that ..." should read "Benzene was more persistent than ..."

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Prepared for

Naval Facilities Engineering Service Center
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Prepared by

BATTELLE
Environmental Restoration Department
505 King Avenue
Columbus, Ohio 43201

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EXECUTIVE SUMMARY

Intrinsic bioremediation is an innovative, cost-effective technology for remediating sites with petroleum-contaminated soil and groundwater. The technology works because common petroleum contaminants are readily biodegraded by microorganisms that occur naturally in the subsurface environment.

Intrinsic bioremediation, also known as natural attenuation, is a passive remediation method that can effectively reduce petroleum contamination in soil and groundwater to levels that do not pose a risk to human health or the environment. Intrinsic bioremediation results from the combined effects of several natural processes, including biodegradation, dilution, sorption, dispersion, and volatilization. For petroleum hydrocarbons, biodegradation is the most important process because it transforms contaminants to innocuous byproducts such as water and carbon dioxide and reduces the total mass of the contaminants in the subsurface. The other processes act to lower the concentration of the contaminants in the environment but not to reduce their mass.

Intrinsic bioremediation has several advantages over conventional remediation methods for petroleum contaminants:

- It is less costly than conventional engineered technologies such as pump and treat — costs for intrinsic bioremediation have been reported to range from $50,000 for typical gas station sites to around $200,000 for large fuel facilities, whereas, the cost of pump and treat can easily reach several million dollars.
- Minimal technical issues require resolution compared to conventional aboveground treatment requiring disposal of treated groundwater, compliance with stringent effluent guidelines, removal of nontoxic compounds from the groundwater that interfere with treatment, etc.
- It is nonintrusive, does not interfere with ongoing site operations, and can be used in inaccessible locations (e.g., below buildings).
- Remediation takes place in situ, reducing the potential for exposing site workers to contamination.
- With no operations and maintenance requirements, there are no limitations such as equipment failure.
- It can be used in conjunction with conventional remedial technologies such as pump and treat.
- Microorganisms ultimately reduce petroleum contaminants to harmless byproducts, whereas some technologies transfer contaminants to other locations or other phases in the environment.

The principal limitations of intrinsic bioremediation are that:

- Prevailing site conditions must be suitable to support sufficient microbial activity so that contaminant concentrations are reduced to acceptable levels before potential receptors are affected.
- It may not be an appropriate stand-alone remediation option when exposure pathways are already completed or receptors are already impacted.

- Site remediation to regulatory standards generally cannot be accomplished in very short time frames (i.e., it is not a quick fix).

Before intrinsic bioremediation can be implemented at a site, an evaluation is required to determine if it is a viable remediation method. Figure ES-1 illustrates the general decision process for determining if intrinsic bioremediation is feasible. Preliminary screening to determine if intrinsic bioremediation is applicable is followed by a detailed evaluation to determine if it will be effective at meeting remediation goals.

Regulatory approval typically is required to implement intrinsic bioremediation at a site. EPA generally finds intrinsic bioremediation an acceptable remediation option if the site conditions are appropriate for its use. The acceptance of intrinsic bioremediation by the states is changing rapidly with updates in rules, regulations, and policies to include more risk-based cleanup standards. Some states lack procedures to authorize intrinsic bioremediation; therefore, it is prudent to involve regulators early in the process to ensure that no barriers exist that might prevent its use at a site.

A detailed evaluation of intrinsic bioremediation should answer two questions. (1) Is biodegradation of the contaminants already occurring? (2) Is it occurring rapidly enough to be protective of potential receptors? The first objective requires a demonstration that links measurable losses of contaminants to microbial activity. Intrinsic bioremediation must prevent contaminants from migrating to potentially sensitive receptors to protect human health and the environment. Mathematical models that simulate the effects of biodegradation on the transport of contaminants in groundwater can be used to determine how far contaminants will migrate and if receptors will be affected.

A detailed evaluation of intrinsic bioremediation should also include a comparison with other remediation options. Key factors to consider are the ability to meet remediation goals, prevention of unacceptable exposure/risk, and cost effectiveness. Any potential risk to human or ecological receptors that could result from their exposure to contamination will be prevented if the contaminants are completely biodegraded before they migrate to receptor points. The principal costs associated with intrinsic bioremediation include costs to conduct the feasibility study and costs associated with long-term monitoring. In some cases, costs may also be incurred for source remediation and to implement institutional controls, such as land use restrictions, and contingency plans to prevent exposure to contaminants in the subsurface.

Implementation of intrinsic bioremediation involves monitoring over time to verify its ongoing effectiveness until site remediation goals are met. A monitoring strategy is required for intrinsic bioremediation that considers appropriate sample locations, parameters, and sampling frequency. Remediation of the source of contamination may also be a requirement to implement intrinsic bioremediation. The purpose of source remediation is to prevent the continued release of contaminants to the groundwater, to limit the growth of the plume, and to shorten remediation time. Common source remediation technologies for petroleum contamination include pumping methods, vapor extraction and air injection methods, engineered bioremediation, and excavation combined with aboveground treatment. Selection of a source remediation technology will depend on the amount of residual contamination present, whether free-phase contamination is present, the physical and chemical properties of the contaminant, and site-specific conditions.
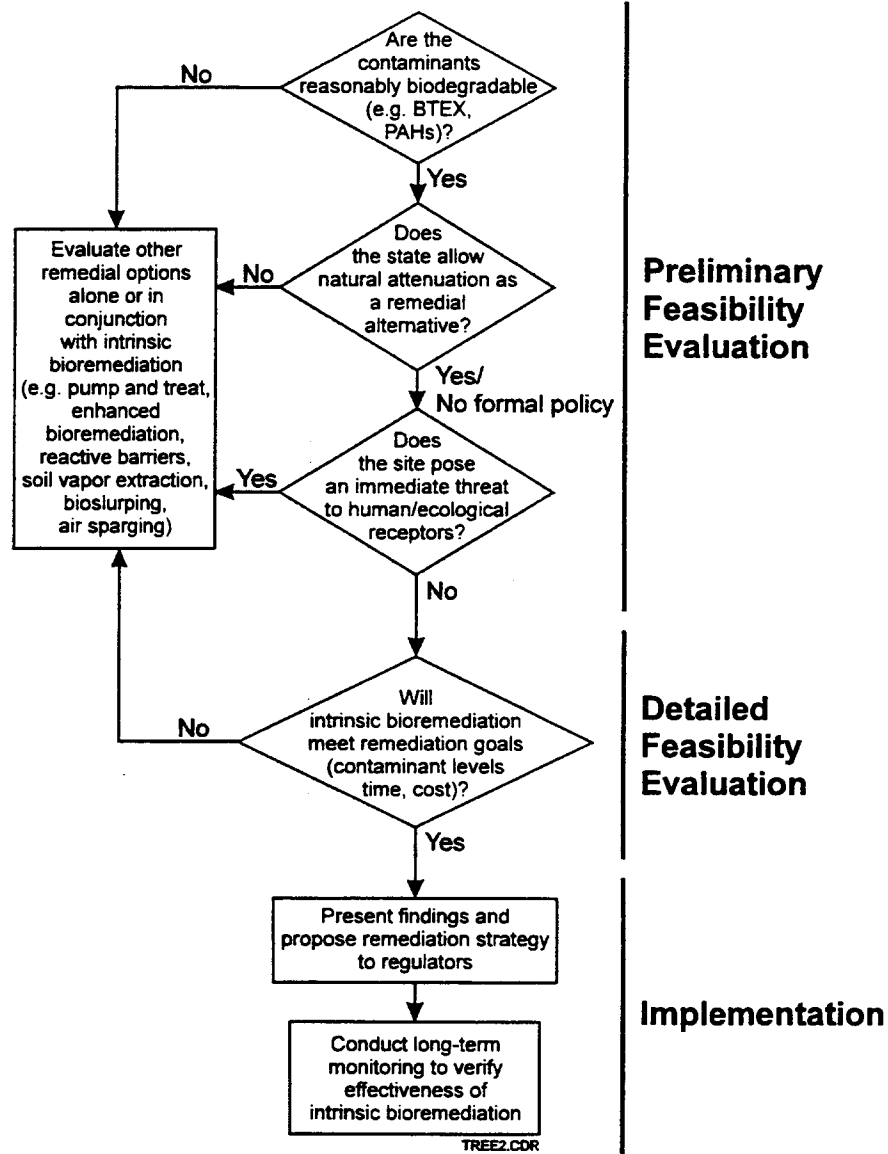
Figure ES-1. Generalized Decision Process for Intrinsic Bioremediation.

Section 1.0: INTRODUCTION

This document is organized into the following sections.

Section 1: defines terminology and provides background information about
the types of petroleum contaminants amenable to intrinsic
bioremediation.

Section 2: summarizes feedback received from federal and state regulatory
agencies about the acceptance of intrinsic bioremediation.

Section 3: discusses the theory behind the biological, physical, and chemical
processes involved in intrinsic bioremediation.

Section 4: presents an approach for evaluating the feasibility of intrinsic
bioremediation for petroleum-contaminated sites.

Section 5: discusses long-term monitoring and source remediation, which are
involved in implementing intrinsic bioremediation.

Section 6: presents case studies to illustrate the application of intrinsic
bioremediation.

Section 7: lists references pertaining to intrinsic bioremediation.

1.1   Background. Naturally occurring microorganisms in soil and groundwater can effec-
tively degrade a range of common petroleum contaminants. At many sites, ambient conditions will be
suitable for microorganisms to degrade contaminants without human intervention (i.e., stimulation).
In these cases, intrinsic bioremediation can provide an attractive remedial alternative to more costly
soil and groundwater cleanup methods.

Intrinsic bioremediation, also known as *natural attenuation*, results from the combined
effects of several natural processes, including biodegradation, dilution, sorption, dispersion, and
volatilization. For petroleum hydrocarbons, biodegradation is the most important process because it
transforms contaminants to innocuous byproducts such as water and carbon dioxide and reduces the
total mass of the contaminants in the subsurface. The other processes act to lower the concentration
of the contaminants in the environment but not to reduce their mass. Other terms that have been used
to describe intrinsic bioremediation include *intrinsic remediation* and *passive remediation*.

In intrinsic bioremediation, no actions are taken to enhance the biodegradation of contami-
nants beyond the existing capacity of the system. *Engineered bioremediation* refers to the acceleration
of microbial activities by engineered site modifications such as oxygen addition. Engineered
bioremediation is not discussed in this paper.

Intrinsic bioremediation is not a "no-action" alternative. It requires a detailed evaluation
to demonstrate that contaminant concentrations will be reduced to acceptable levels within a reason-
able amount of time and that the contaminants will not migrate to reach potentially sensitive receptors.

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Intrinsic bioremediation also differs from the no-action alternative in that it must be monitored over time to verify an ongoing reduction in contamination until remediation goals are met.

Intrinsic bioremediation has several advantages over contentional methods for remediating petroleum-contaminated sites, including:

- It is less costly than conventional engineered technologies such as pump and treat — the maximum cost for intrinsic bioremediation is expected to be around $200,000, whereas the cost of pump and treat can easily reach several million dollars.
- Minimal technical issues require resolution compared to conventional aboveground treatment requiring disposal of treated groundwater, compliance with stringent effluent guidelines, removal of nontoxic compounds from the groundwater that interfere with treatment, etc.
- It is nonintrusive, does not interfere with ongoing site operations, and can be used in inaccessible locations (e.g., below buildings).
- Remediation takes place in situ (i.e. in place), reducing the potential for exposing site workers to contamination.
- With no operations and maintenance requirements, there are no limitations such as equipment failure.
- It can be used in conjunction with conventional remediation technologies such as pump and treat.
- Microorganisms ultimately reduce petroleum contaminants to harmless byproducts such as carbon dioxide, water, and methane, whereas some technologies transfer contaminants to other locations or other phases in the environment.

The importance of cost is recognized more frequently today, especially for state-funded petroleum remediations (i.e., Underground Storage Tank (UST) programs). Traditional methods are often significantly more expensive than intrinsic bioremediation, yet they may be only marginally, if at all, more effective. Good examples are pump-and-treat for groundwater and dig-and-haul for soils, particularly after contaminants have been reduced to relatively low levels that still require cleanup. It is difficult to justify higher costs for alternative methods that do not achieve a proportional increase in effectiveness.

The principal limitations if intrinsic bioremediation are that:

- Prevailing site conditions must be suitable to support sufficient microbial activity so that contaminant concentrations are reduced to acceptable levels before potential receptors are affected.
- It may not be an appropriate stand-alone remediation option when exposure pathways are already completed or receptors are already impacted.
- Site remediation to regulatory standards generally cannot be accomplished in very short time frames (i.e., it is not a quick fix).

1.2 Petroleum Contaminants Amenable to Intrinsic Bioremediation. Petroleum products are complex mixtures of numerous compounds; however, the number of petroleum compounds that represent contaminants of concern are relatively few. Table 1-1 lists commonly selected contaminants

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of concern for petroleum fuel products based on their mobility, toxicity, and persistence in the environment.

Table 1-1. Commonly Selected Contaminants of Concern for Petroleum Products (from ASTM, 1995)

Contaminant	Unleaded Gasoline	Leaded Gasoline	Kerosene/ Jet Fuels	Diesel/ Light Fuel Oils	Heavy Fuel Oils
Benzene	x	x	x	—	—
Toluene	x	x	x	—	—
Ethylbenzene	x	x	x	—	—
Xylenes (m-, o-, p-xylene)	x	x	x	—	—
MTBE (methyl tert-butyl ether), ethanol, methanol, TBA (tert-butyl alcohol)	when suspected	when suspected	—	—	—
PAHs (polycyclic aromatic hydrocarbons)	—	—	x	x	x
Lead, EDC (ethylene dichloride), EDB (ethylene dibromide)	—	x	—	—	—

Most petroleum-derived hydrocarbons are sparingly soluble in water; only a few are commonly found in groundwater plumes resulting from releases of petroleum to the environment. Those compounds found most frequently in groundwater are the monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX). The BTEX compounds comprise a significant fraction of fuels compared to other individual compounds, are relatively water-soluble, and partition weakly to soils, making them some of the most mobile constituents in petroleum products. Several factors make BTEX compounds relatively easy to bioremediate: they can serve as the primary electron donor (primary energy source) for many bacteria that are widely distributed in the environment; they are rapidly degraded; the bacteria that degrade them grow readily in the presence of oxygen, and they are relatively soluble compared to other fuel components, making them available for biodegradation (NRC, 1993). These compounds also biodegrade anaerobically, but at a slower rate than when oxygen is present.

Other components of fuels detected in groundwater plumes, but to a much smaller extent than the monoaromatic hydrocarbons, are the polycyclic aromatic hydrocarbons (PAHs). Naphthalenes are the most mobile of the PAHs, due to their moderate water solubility and soil sorption potential relative to the other PAHs. Naphthalene biodegrades under both aerobic and anaerobic conditions (Chapelle et al., 1996). Intrinsic biodegradation of the other PAHs has not been widely studied.

Fuel oxygenates and octane boosters represent a third group of compounds found in reformulated gasoline but not in other fuel products. This group of compounds includes such constituents as MTBE, TBA, methanol, and ethanol, of which MTBE and ethanol are the most commonly used. Ethanol readily biodegrades in aerobic environments, whereas MTBE is recalcitrant under aerobic and anaerobic conditions (Suflita and Mormile, 1994; Mormile et al., 1994).

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Older gasoline spills may also include lead as well as EDB and EDC, commonly used as scavengers to reduce atmospheric emissions of lead, and tetraethyl lead, which was used as an octane booster.

Intrinsic bioremediation is primarily a groundwater remediation technology; therefore, it needs to be effective at treating the compounds most often found in groundwater at petroleum-contaminated sites.

Section 2.0: REGULATORY ACCEPTANCE OF INTRINSIC BIOREMEDIATION

Like any remedial technology, intrinsic bioremediation requires regulatory acceptance. Intrinsic bioremediation was once perceived as a "do nothing" or "no action" option that allows the responsible parties to avoid or delay remediation. However, intrinsic bioremediation is rapidly gaining acceptance as regulators become more familiar with it and the fact that it is an active process that can effectively destroy contaminants of concern.

The trend among the states to adopt regulations allowing risk-based corrective action (RBCA) has contributed to the growing acceptance of intrinsic bioremediation. RBCA is compatible with intrinsic bioremediation because it allows cleanup standards to be set at alternative compliance points (e.g., property boundary) rather than at the source. Thus, intrinsic bioremediation can occur within the portion of the contaminated groundwater or soil that is exempted from meeting the standards.

RBCA (pronounced "Rebecca") usually refers to the ASTM RBCA Standard E1739 (ASTM, 1995) which establishes a procedure for calculating cleanup goals for petroleum release sites through a tiered approach. More in-depth site-specific data are collected at each increasing tier. In Tier 1, corrective action is selected to achieve conservative (i.e., low), non-site-specific Risk-Based Screening Levels (RBSLs) that must be met at the contaminant source area. Tier 2 requires an expanded site assessment and allows negotiation of points of compliance located between the source and the receptors (e.g., at the property boundary) and calculation of site-specific target levels (SSTLs). Tier 3 requires additional site assessment and calculates SSTLs on the basis of more sophisticated statistical and fate and transport analyses using site-specific data. This tier also allows for compliance points away from the source. Tiers 2 and 3 are most applicable to intrinsic bioremediation because they provide for the establishment of compliance points between the source and the receptor and calculation of site-specific, risk-based target levels for cleanup.

U.S. EPA is encouraging adoption of ASTM's RBCA standard or other risk-based programs by the states and offers RBCA training in three modules to all interested states. Modules 1 and 2 provide a basic overview and training in the ASTM RBCA method. Module 3 provides more state-specific in-depth training. Figure 2-1 shows the training status of the states as of April 11, 1996 (McNeely, 1996). Almost all states either have risk-based criteria in place or are in the process of adopting them (Figure 2-2) (Barkan et al., 1996). EPA Region 5 has developed a RBCA guidance document based on the ASTM RBCA Standard (EPA Region 5, 1995) that outlines what must be demonstrated for approval of intrinsic bioremediation.

EPA generally finds intrinsic bioremediation an acceptable remediation option if the site-specific conditions show that it is appropriate for a particular site. EPA's Office of Solid Waste and Emergency Response (OSWER) is developing a policy on intrinsic bioremediation to include petroleum hydrocarbons as well as other types of contaminants. A general policy statement is expected in 1996. Although not final, key concepts likely to be included are that intrinsic bioremediation is not a "do nothing" alternative and should not be considered the default option applicable to most sites. Selection of intrinsic bioremediation should be a site-specific, risk-based decision based on site characterization and monitoring data. If free product is present, it needs to be removed. Monitoring is required and should demonstrate that the plume size and concentrations of contaminants of concern are being reduced" (Tulis, personal communication, 1996).
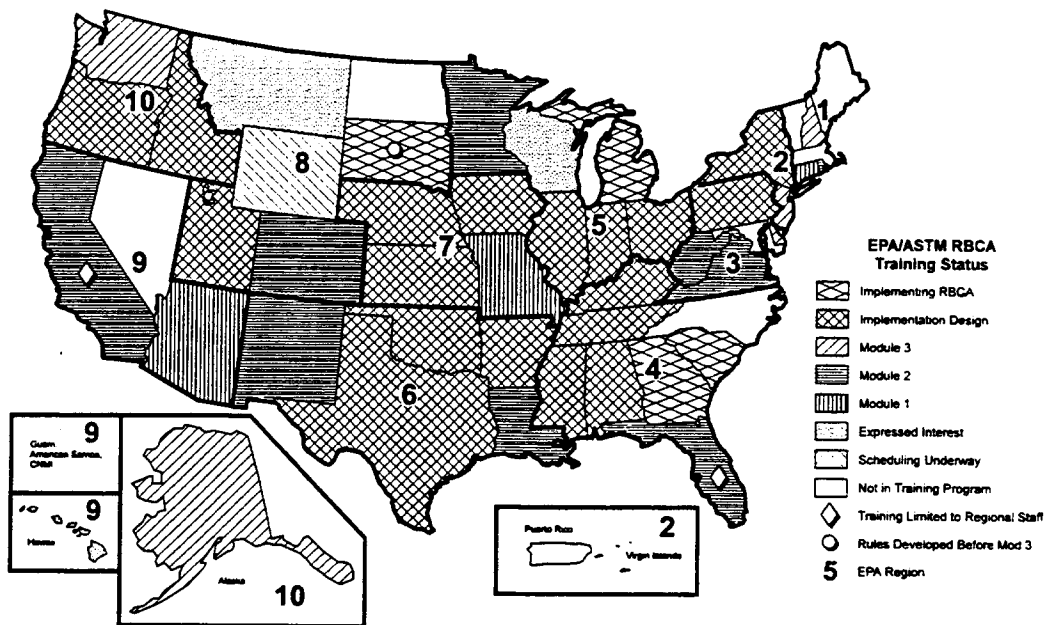
EPA/ASTM RBCA
Training Status

Implementing RBCA

Implementation Design

Module 3

Module 2

Module 1

Expressed Interest

Scheduling Underway

Not in Training Program

Training Limited to Regional Staff

Rules Developed Before Mod 3

5 EPA Region

Figure 2-1. Status of U.S. EPA's Risk-Based Corrective Action
Training Program as of April 11, 1996 (from McNeely, 1996)

Other evidence that there is growing recognition of intrinsic bioremediation as a viable remedial alternative is that ASTM, in cooperation with U.S. EPA, sate regulatory agencies, the petroleum industry, and the U.S. Air Force, is developing a standard guide on the use of intrinsic bioremediation at petroleum release sites. This standard is being developed in response to a recognized need by regulatory agencies and private industry for a consistent, practical approach to evaluating and utilizing intrinsic bioremediation as a remedial option in an effort to reduce costs associated with cleanup of petroleum releases.

The acceptance of intrinsic bioremediation by the states is changing rapidly with updates in rules, regulations, and policies to include more risk-based cleanup standards. An Air Force review in 1994 found that seven states and the District of Columbia allowed for intrinsic bioremediation in their regulations, but with differing terminology (U.S. Air Force, 1994). In general, they allowed for intrinsic bioremediation after action has been taken to eliminate sources of contamination (e.g., repair leaks), and free product has been removed to the extent practicable. This study found that North Carolina and Wisconsin had progressed further than other states in accepting intrinsic bioremediation. The other five states that had specific provisions for intrinsic bioremediation in their regulations as of 1994 are Delaware, Florida, Iowa, Michigan, and Ohio.
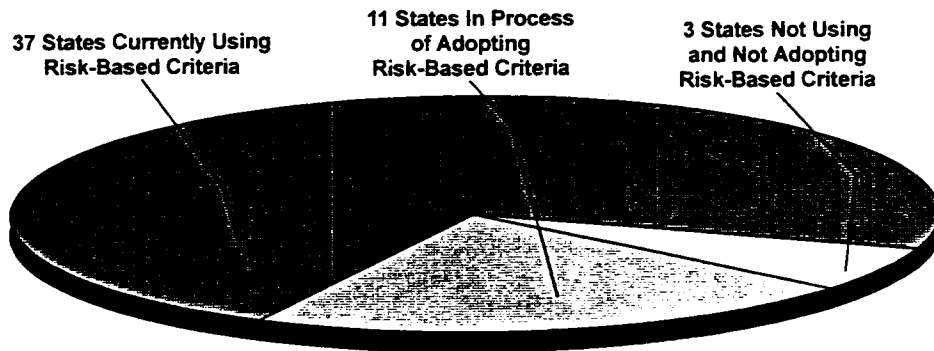
Figure 2-2. Status of States' Use of Risk-Based Corrective Action for Petroleum Release Sites (from Barkan et al., 1996)

In North Carolina, regulators have approved intrinsic bioremediation (natural attenuation) in the corrective action plans for approximately 140 sites. One North Carolina regulator indicated that for some sites on the coastal plain where soils are sandy and well-aerated and where the source has already been removed, contaminant concentrations were at background or very low by the time the corrective action plan was approved (Taber, 1996, personal communication). Other sites with clay-rich soil will require longer to remediation and North Carolina laws currently require that groundwater concentrations meet the state standards for four consecutive quarters. In general, North Carolina views intrinsic bioremediation as a cost-saving strategy, at least in the short term. A formal cost analysis has not been performed to determine potential long-term savings.

Wisconsin is another state where intrinsic bioremediation is being accepted and even encouraged. Wisconsin regulations require that at least three cleanup options be evaluated, one of which must be "passive bioremediation," and if passive bioremediation is feasible but not recommended, a rationale must be provided (U.S. Air Force, 1994). This technique is being used at approximately 80 sites in Wisconsin and the state has prepared a guidance document on the criteria and monitoring requirements for intrinsic bioremediation of hydrocarbons (Black, 1995). Also, Wisconsin regulators have teamed with U.S. EPA, Illinois regulators, and Amoco in a study to assess the feasibility of intrinsic remediation for cleanup of gasoline-contaminated sites in different types of conditions. Although the study is still in progress, monitoring results available as of August 1995 showed declining petroleum contamination and indicated that the contamination had not moved from any of the sites. An Amoco research engineer estimated that the cleanup costs at each service station will be approximately $50,000, compared to five times that much for conventional active approaches such as pump and treat (Black, 1995).

Suggested regulatory contacts on the topic of intrinsic bioremediation are Michael Barden of the Wisconsin Department of Natural Resources, Matthew Small of U.S. EPA Region 9 in San Francisco, California, and John Shauver of the Michigan Department of Environmental Quality. Barden and Small are co-chairmen of the ASTM Remediation by Natural Attenuation Task Group, which is preparing the ASTM Guide for Remediation by Natural Attenuation at Petroleum Release Sites. Shauver has prepared papers and presentations on the regulator's perspective on in situ bioremediation and natural attenuation.

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Michael Barden
Wisconsin Department of Natural Resources
P.O. Box 7921
Madison, WI 53707-7921
Phone: (608) 264-6007

Matthew Small
U.S. EPA, Region 9
75 Hawthorne Street, 10th Floor, H-2-1
San Francisco, CA 94105
Phone: (415) 744-2078

John Shauver
Michigan Department of Environmental Quality
P.O. Box 30028
Lansing, MI 48909
Phone: (517) 335-1178

California is an example of a state that is moving toward the acceptance of intrinsic bioremediation for petroleum-contaminated sites. A study performed for the California State Water Resources Control Board by the Lawrence Livermore National Laboratory (LLNL) (Rice et al., 1995a) reviewed the cleanup problems for leaking underground fuel tanks in California and made recommendations aimed at reducing the state's backlog of unremediated sites. Although this study has been criticized because its evaluation was based on a limited number of compounds, exposure pathways, geologic settings, and release scenarios, the study's first recommendation was "Utilize passive bioremediation as a remediation alternative whenever possible." EPA reviewed the LLNL study and prepared a fact sheet with their comments. EPA stressed the need to determine the appropriate technology for the site-specific conditions and the nature and the extent of the release. In general, these decisions need to be risk-based and site-specific with all exposure pathways and chemicals of concern evaluated and monitored. EPA also stated that intrinsic (passive) bioremediation should NOT be interpreted to mean "do nothing." It is an active remediation choice requiring site characterization, assessment of potential risk, evaluation of potential effectiveness, and documentation of remedial progress (monitoring). EPA's comments on the LLNL study are consistent with their (OSWER) proposed policy on intrinsic bioremediation.

Section 3.0: OVERVIEW AND THEORY OF INTRINSIC BIOREMEDIATION

Several processes affect the rate of migration and the concentration of contaminants in groundwater. For petroleum hydrocarbons, the most important processes are biodegradation, advection, hydrodynamic dispersion, sorption, and volatilization. These processes are categorized as destructive or nondestructive with respect to the contaminants of concern. The dominant driving mechanisms responsible for transporting contaminants in groundwater are advection and dispersion, which cause contaminants to spread and thus mix with uncontaminated groundwater to become diluted with increased travel distance. Although these processes lower the concentrations of the contaminants in groundwater, no contaminant mass is removed from the system. Sorption slows the migration of reactive contaminants relative to the rate of groundwater movement but it is also nondestructive. Volatilization, also nondestructive, results in the transfer of dissolved contaminants to the soil gas in the unsaturated zone above the aquifer, and in some cases to the atmosphere. Although generally not significant, volatilization can decrease concentrations of a contaminant in groundwater over time. Biodegradation is the most important destructive mechanism that can eliminate petroleum contaminants from groundwater and lead to site remediation. All of these processes contribute to the intrinsic bioremediation of a contaminant in groundwater, and each is governed by the physical, chemical, and geochemical properties of the contaminant and the aquifer.

3.1   Intrinsic Biodegradation. Intrinsic biodegradation refers to the degradation of contaminants by indigenous microorganisms under the prevailing site conditions. Intrinsic biodegradation destroys contaminants in the subsurface and is a necessary component of intrinsic bioremediation. Without making enhancements to facilitate microbial activity, in situ biodegradation can occur only if the following conditions are met: the contaminants of interest must be able to be biologically degraded or transformed; bacteria that can biodegrade or transform the contaminants must be present; organic and inorganic nutrients must be available to support biodegradation of the contaminants; and the physical and chemical conditions must be suitable for biodegradation.

A wide range of organic contaminants, including gasoline, diesel, and jet fuel components such as BTEX compounds and PAHs, can be biodegraded in the subsurface environment by naturally occurring microorganisms. Depending on the environmental conditions, these compounds can be completely mineralized into water, carbon dioxide, and/or methane. Bacteria use the contaminants for energy and cell production by catalyzing the transfer of electrons from an electron donor (i.e., the organic contaminant) to an electron acceptor (i.e., oxygen, nitrate, iron(III), sulfate, and carbon dioxide). Most fuel hydrocarbons are susceptible to biodegradation because they can be used as electron donors for energy and as a source of carbon for cell reproduction.

More than one electron acceptor can be involved in the overall remediation of fuels at a particular site. Microorganisms catalyze chemical reactions to derive energy for metabolic processes or to obtain carbon and materials for biosynthesis (Snoeyink and Jenkins, 1980). Those reactions are aerobic or anaerobic, based on whether oxygen is available and used as an electron acceptor (aerobic), or whether other electron acceptors are used (anaerobic). It is important to determine which electron acceptors and which biological mechanisms are most involved in the metabolism of contaminants, how those electron acceptors affect the rate of biodegradation, and whether biodegradation is limited by the bioavailability of the contaminants or by the availability of electron acceptors. Electron acceptors commonly used by microorganisms to degrade fuel hydrocarbons include oxygen, nitrate, iron(III), sulfate, and carbon dioxide.

The oxidation/reduction reactions that occur and the organisms that catalyze these reactions differ depending on which electron acceptors are available. This also controls the degradation rate. Some bacteria (facultative) can survive and grow under both aerobic and anaerobic conditions. In general, aerobic biodegradation rates for fuel hydrocarbons are much faster than anaerobic rates. Anaerobic microorganisms cannot get as much energy per mole of an organic substrate as aerobic organisms (Snoeyink and Jenkins, 1980) and thus do not grow as fast or use available substrates as rapidly as the aerobic bacteria. Aerobic respiration provides the most energy and results in the most rapid growth of microorganisms, followed by nitrate reduction, iron(III) reduction, sulfate reduction, and then methanogenesis (carbon dioxide reduction). Under each of those processes, the degradation rate of an organic contaminant would be expected to decrease as the environmental conditions evolve from aerobic to methanogenic.

Electron acceptors are used preferentially, beginning with oxygen and ending with carbon dioxide. If oxygen is available it is used before nitrate, which is used before iron, and so on until all electron acceptors have been exhausted except carbon dioxide. At that point, methanogenic bacteria proliferate, producing methane from carbon dioxide which serves as the electron acceptor in the process. Thus, the presence of methane often suggests the exhaustion of all other available electron acceptors. Throughout an actual plume, many of those biological processes can occur simultaneously. Figure 3-1 shows how different electron acceptors can be used within a plume. Typically, the outer edges of the plume are aerobic and the center of the plume is anaerobic. Nitrate reduction occurs immediately after oxygen is exhausted, followed by iron reduction, sulfate reduction, and methanogenesis, which occur at the center of the plume. Figure 3-1 also shows that the anaerobic portion of a plume can occupy a much larger volume than the aerobic fraction. Thus, although anaerobic rates are often orders of magnitude lower than aerobic rates, they can contribute to a significant fraction of the overall remediation, and they should be considered when assessing the capacity of an aquifer to remediate a petroleum hydrocarbon spill, and when estimating the duration of intrinsic bioremediation or any other remediation strategy.

Aerobic biodegradation of petroleum hydrocarbons, particularly BTEX compounds, has been well documented and demonstrated in the laboratory and in field demonstrations. Benzene typically biodegrades slower than the other BTEX hydrocarbons which degrade slightly faster. Individual hydrocarbon compounds also do not biodegrade at the same rate under aerobic and anaerobic conditions. Under anaerobic conditions, benzene and *o*-xylene often are recalcitrant to biodegradation. Acton and Barker (1992) showed evidence of anaerobic biodegradation of gasoline components and reported the following order of biodegradability:

toluene > *m*-xylene > ethylbenzene > 1,2,4-trimethylbenzene > *o*-xylene, benzene

3.2   Physical/Chemical Processes

Advection and Dispersion. Advection is the process by which solutes are transported by the bulk motion of flowing groundwater. Factors that influence advection include the hydraulic conductivity of the porous medium, which is a measure of the rate at which water can move through a permeable medium, the hydraulic gradient, which is the change in the total hydraulic head over the travel distance in any given direction, and porosity, which is the ratio of the volume of void spaces in
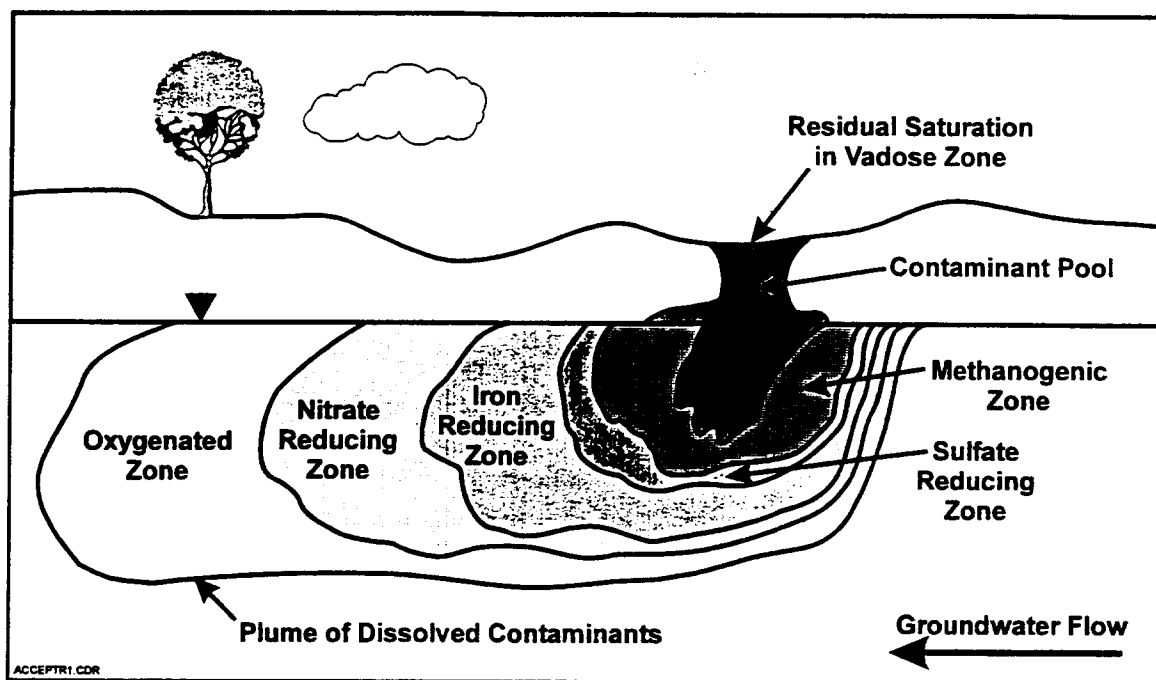
Figure 3-1. Groundwater Zones Resulting from Preferential Use of Electron Acceptors (from IGWMC, 1996)

a rock or sediment to the total volume of the rock or sediment. Groundwater velocity is directly proportional to hydraulic conductivity and hydraulic gradient, and inversely proportional to porosity.

Hydrodynamic dispersion is a mixing process that causes some solutes to move faster than the average groundwater flow velocity and others to move slower. Hydrodynamic dispersion is the result of the mechanical mixing of water as it travels through pore openings of different size and shape and through strata having different hydraulic properties. Dispersion is also a result of molecular diffusion, as compounds dissolved in water move from areas of higher concentration to areas of lower concentration. Usually, diffusion has a minor effect on the overall transport of contaminants in the subsurface compared to mechanical dispersion. Multidimensional expressions (2-D and 3-D models) of contaminant transport incorporate terms describing transverse as well as longitudinal dispersion. Dispersion causes spreading of the contaminant into a larger volume of water as it moves through the aquifer, thereby diluting the contaminant with travel distance. For nonreactive (i.e., nonsorbing, nondegrading) contaminants, the sum of the advection and dispersion processes determines the rate and extent of contaminant migration in groundwater.

Sorption. Sorption is the partitioning of contaminants between the aqueous and the solid phases of the soil matrix. A contaminant adsorbs onto the soil matrix when it partitions from the aqueous phase to the solid phase; it desorbs when it partitions from the solid phase to the aqueous phase. The effect of sorption on a contaminant in groundwater is to decrease its velocity relative to that of the groundwater. The retardation factor is a parameter that is used to describe how much faster the groundwater is moving relative to a contaminant that is sorbed. The movement of a

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contaminant that is strongly sorbed onto the solid phase of an aquifer is significantly retarded; a contaminant that is weakly sorbed migrates at a rate similar to the rate of groundwater flow.

Volatilization. Another physical mechanism that can cause a reduction in contaminant concentrations is volatilization, the process by which soluble contaminants partition from groundwater, through the capillary fringe, to the soil gas in the unsaturated (vadose) zone above the water table. Volatilization can result in the removal of contaminant mass from groundwater, but there is no net loss of contamination from the environment because contaminants are merely transferred to the unsaturated zone. Generally, volatilization is insignificant compared to biodegradation; it is more likely to result in the removal of contaminants with higher vapor pressures and for sites with shallow or highly fluctuating water table conditions. For contaminants that readily biodegrade aerobically, volatilization can enhance intrinsic bioremediation in the vadose zone if there is an active biological community and a relatively large supply of oxygen.

3.3   Process Interactions. Intrinsic bioremediation is achieved by the combined effects of physical, chemical, and biological processes. The effectiveness of intrinsic bioremediation depends on the type of contaminant, its rate of migration in groundwater, and its rate of biodegradation. Figure 3-2 illustrates the effects of biodegradation on a contaminant that is also subject to advection, dispersion, and sorption.

Figure 3-2(a) shows a contaminant slug moving in a horizontal direction (i.e., one-dimensional flow) over time. In the case of purely advective transport (A), a contaminant moves without spreading, and its concentration at any point in the groundwater flowpath equals the initial concentration at the source. The contaminant slug migrates at the average groundwater velocity. With dispersion (A+D), the slug spreads out and occupies more volume; thus, the concentration decreases with distance traveled as mixing continues to dilute the contaminant mass. Dispersion causes some of the dissolved contaminants to travel faster and slower than the average groundwater velocity. This is shown by the area under the A+D curve that is outside of the A curve. The spreading effect of dispersion in a planar (i.e., two-dimensional) flow field is shown in Figure 3-2(b) as the plume is spread over a larger area with time. When dispersion is the sole attenuating mechanism (i.e., for nonreactive contaminants), the center of mass at any distance coincides with the position of the advective contaminant slug.

Sorption (A+D+S) does not result in a reduction of total mass, but it does retard the rate of contaminant migration, as shown by the position of the (A+D+S) curve relative to the (A+D) curve on Figures 3-2(a) and 3-2(b). It takes longer for a reactive contaminant to migrate the same distance than it does for a nonreactive contaminant. Sorption also decreases the amount of spreading caused by dispersion, as indicated by the smaller area occupied by the contaminant under the A+D+S curve in Figures 3-2(a) compared to the contaminated area under the A+D curve. Another effect of sorption is to lower the peak concentration in groundwater because some of the contaminant mass is sorbed onto the aquifer matrix, as shown on Figure 3-2(a) by the lower peak concentration of the A+D+S curve compared to that of the A+D curve, and on Figure 3-2(b) by the diminished size of the A+D+S plume compared to the A+D plume.

Aside from volatilization, the only mechanism that can reduce the mass of the plume and ultimately prevent further migration of a contaminant is biodegradation. The advantageous effect of biodegradation is shown in Figure 3-2(a) by the lower peak concentration of the A+D+S+B curve compared to the peak concentration of the A+D+S curve. This is also shown in Figure 3-2(b) by

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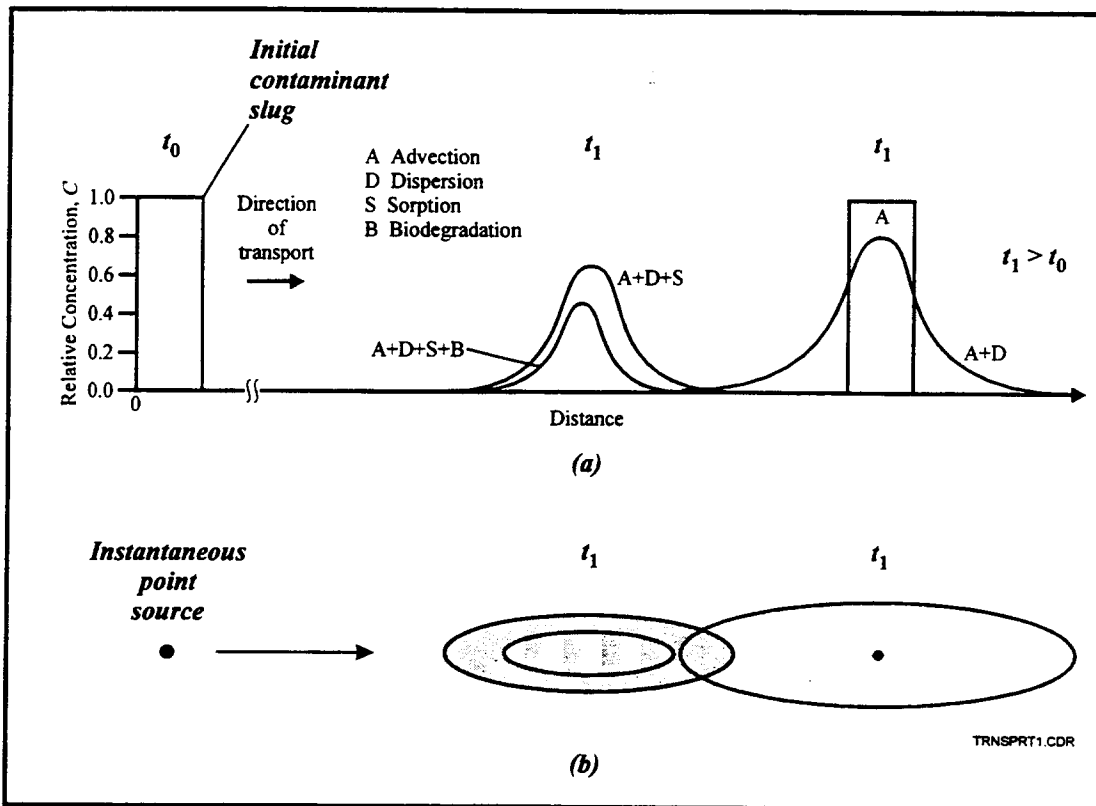
Figure 3-2. Influence of Natural Processes in a (a) One-Dimensional and (b) Two-Dimensional Constant Velocity Flow System (modified from Domenico and Schwartz, 1990 and Maidment, 1993)

the diminished size of the A+D+S+B plume relative to A+D+S plume. These two conditions can occur only if there is a reduction in contaminant mass in the plume.

Intrinsic bioremediation is effective if the rate of biodegradation, aided by sorption, is rapid enough to prevent significant plume migration by advection and dispersion, so that the plume does not reach sensitive receptors such as wells and surface water bodies. With this definition in mind, one can define the parameters necessary to evaluate the effectiveness of intrinsic bioremediation.

Section 4.0: EVALUATING THE FEASIBILITY OF INTRINSIC BIOREMEDIATION

Before intrinsic bioremediation can be implemented at a site, a detailed evaluation is required to determine that it is a viable remedial option. Because the effectiveness of intrinsic bioremediation depends largely on the prevailing conditions in the field, each site must be evaluated individually. This section discusses the factors to consider when deciding if intrinsic bioremediation is an appropriate remedial alternative for a site.

There are two primary objectives of an intrinsic bioremediation evaluation: (1) to determine if biodegradation of the contaminants is already occurring at the site, and (2) to determine if it is occurring rapidly enough to be protective of human health and the environment (i.e., to prevent unacceptable levels of contamination from migrating to a potential receptor). The first objective can be accomplished by demonstrating a loss of contamination in the field that is due to microbial activity. The second objective can be accomplished using a model that simulates the transport of contaminants in groundwater and accounts for the effects of biodegradation and other attenuating processes (i.e., dispersion, sorption) that may affect the fate of the contaminants. If there is a potential for contaminants to migrate away from the site before they are biodegraded to acceptable levels, an exposure pathway assessment is required to identify any potential receptors that might be affected.

If it can be demonstrated that unacceptable concentrations of the contaminants will not reach a potential receptor, intrinsic bioremediation augmented with a carefully designed monitoring plan may be an acceptable corrective action for a site. The use of intrinsic bioremediation is also dependent upon regulatory approval; therefore, early involvement of regulators is recommended to ensure that there are no barriers that may prevent its acceptance even if it is shown to be a technically feasible remedial alternative for a site.

A number of protocols for evaluating the effectiveness of intrinsic bioremediation at petroleum-contaminated sites have been developed (U.S. EPA, 1995; Wiedemeier et al., 1995c; McAllister and Chiang, 1994; Buscheck and O'Reilly, 1995; Mobil Oil Corporation, 1995; and Chapelle et al., 1996). The approach outlined in this section integrates the key points from these protocols that support the two primary objectives of an intrinsic bioremediation evaluation. Appendix A includes decision trees from selected protocols that identify additional factors to consider when evaluating intrinsic bioremediation at a site. Important types of data that are used to evaluate the feasibility of intrinsic bioremediation are summarized in Appendix B. The reader is referred to the individual protocols for more detailed information.

4.1 **Demonstrating Intrinsic Bioremediation.** The most direct indication of intrinsic bioremediation is a loss of contaminants over time that can be attributed to the activity of microorganisms. The NRC Committee on In Situ Bioremediation (1993) proposed a strategy for demonstrating the occurrence of intrinsic bioremediation based on multiple lines of evidence:

- Documented loss of contaminants from the site
- One or more pieces of evidence showing that the biodegradation reactions are actually occurring in the field
- Laboratory assays showing that microorganisms from site samples have the potential to transform the contaminants under the expected site conditions.

For most petroleum hydrocarbons, such as the BTEX compounds, laboratory microcosm studies will not be necessary because the conditions under which these compounds biodegrade are well known. Furthermore, the microbes capable of degrading these compounds are nearly ubiquitous in the environment, so it is not necessary to demonstrate their existence at every site. However, laboratory microcosm studies may be useful for compounds that are not easily degraded, such as some PAH compounds.

Demonstrating a Loss of Contaminants

Plume characterization provides one way to determine if there has been a loss of contaminants in the field. Petroleum hydrocarbons serve as a primary substrate (source of food or energy) for microorganisms; therefore, if biodegradation is contributing to intrinsic bioremediation of a contaminant dissolved in groundwater, its effects may be evident in the configuration and behavior of the contaminant plume over time. Sampling data delineating the extent and concentration distribution of the contaminants in groundwater over time are required to characterize the behavior of a plume. Three characteristic plume configurations are described that indicate the occurrence of intrinsic bioremediation: shrinking, steady state (stable), and slower than expected expanding. Other methods for detecting contaminant losses in the field include plotting plume centerline concentrations over time and monitoring the mass of dissolved contaminant over time.

Shrinking Plume. In a situation where bioremediation is occurring and the source of contamination (i.e., free or residual nonaqueous-phase liquid [NAPL]) has been removed or substantially removed, the plume will decrease in size over time. Shrinking plumes are recognized by declining concentrations in monitoring wells and a decrease in the areal extent of the contaminated area, evidence that the contaminant mass in the aquifer is decreasing. A shrinking plume is evidence that intrinsic bioremediation is occurring.

Steady-State (Stable) Plume. A stable plume develops when a source of contamination is still present and continues to contribute contaminants to the groundwater; however, the rate at which the contaminants are degrading is equal to the rate of contaminant input from the source. This situation results in a plume that is neither expanding nor receding. Stable plumes are characterized by dissolved contaminant concentrations that remain constant over time in monitoring wells. A steady-state plume is evidence of intrinsic bioremediation.

Slower Than Expected Expanding Plume. A third plume configuration develops when intrinsic bioremediation is occurring but at a rate that is too slow to prevent the spread of contaminants. Under these conditions, the plume will increase in size, but at a rate that is slower than would be expected if the contaminants were not biodegrading (i.e., based on the rate predicted by the average groundwater velocity and the retardation factor of the contaminant). A plume that is expanding at a slower than expected rate is demonstrated by comparing the measured plume size over time to the expected plume size due only to advection, dispersion, and sorption. An expanding plume is recognized by increasing contaminant concentrations in monitoring wells and an increase in the areal extent of the plume. This situation will continue until the plume stabilizes, therefore, predictive modeling may be required to determine how far the plume will migrate before it stabilizes.

Plotting Flowpath Concentrations. Plotting contaminant concentrations in wells aligned along a primary flowpath through the plume may provide evidence for intrinsic bioremediation. A decrease in concentration with distance from the source indicates some degree of natural attenuation

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(i.e., dispersion, biodegradation, sorption, etc.); however, it does not necessarily provide conclusive evidence that intrinsic bioremediation is occurring. Plotting flowpath concentrations over time will, however, reveal if the plume is shrinking, stable, or expanding.

Mass Balance Approach. The mass balance approach is another method for demonstrating contaminant loss in the field. This approach requires an extensive monitoring well network to define the vertical and horizontal distribution of contaminant concentrations in the aquifer. Sampling the monitoring network over time provides a means for determining changes in the total dissolved contaminant mass in the aquifer over time. A decrease in the total mass over time provides a direct indication of intrinsic bioremediation (Chiang et al., 1989). If conducted properly, this method can also be used to determine biodegradation rates (as discussed later in this section). The cost associated with the extensive monitoring network required for this method makes it impractical for most sites other than research sites.

If the mass remains constant over time, this could indicate that the inputs from sources are balanced by biodegradation and other attenuating mechanisms, or that there are no active sources and biodegradation is not occurring.

Linking Contaminant Loss to Microbial Activity

The second line of evidence for intrinsic bioremediation is a connection between the observed loss of contaminants and microbial activity. Biodegradation brings about predictable changes in the chemistry of the groundwater as a result of microbial metabolism. If these changes are measured, they can provide important information about the biodegradation processes that are active at a site. An observable loss of electron acceptors or accumulation of metabolic byproducts in the contaminated area of the aquifer provides compelling evidence that intrinsic bioremediation is occurring. Therefore, one goal of any intrinsic bioremediation assessment should be to determine if there is a spatial correlation between the contaminants and electron acceptors and/or metabolic byproducts of biodegradation. These correlations can be detected by mapping the concentration distribution of these compounds in groundwater.

There may be times when electron acceptor and metabolic byproduct data are lacking or inconclusive. In these cases, additional evidence of intrinsic bioremediation may be required. Other types of information for linking microbial activity to contaminant loss may include geochemical data and laboratory or field studies.

Loss of Electron Acceptors. As contaminants are consumed by the microorganisms, there is a corresponding consumption of the compounds that serve as electron acceptors in the process. During aerobic respiration, oxygen serves as the terminal electron acceptor; consequently, the concentration of dissolved oxygen in the contaminated area will decrease if microorganisms are degrading the contaminants. Under anaerobic conditions, nitrate, ferric (III) iron, sulfate, and carbon dioxide may be used as electron acceptors. A depletion of these compounds should be observable in the contaminated portion of the groundwater where these processes are active. The measurement of ferric (III) iron and carbon dioxide in groundwater systems is difficult; therefore, these compounds generally are not measured as evidence of intrinsic bioremediation.

Accumulation of Metabolic Byproducts. Bioremediation also causes an accumulation of metabolic byproducts. Therefore, increased concentrations of ferrous (II) iron in the contaminated

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portion of the aquifer indicate the occurrence of intrinsic bioremediation. Similarly, because methane is produced by microorganisms during methanogenesis, increased concentrations of methane provide an indication of anaerobic biodegradation under extremely anoxic conditions.

At most petroleum-contaminated sites, both aerobic and anaerobic biodegradation processes will be active in different portions of the contaminated area. However, not all of these processes may be active because of an insufficient supply of one or more electron acceptors in the groundwater. For example, investigators from the U.S. Geological Survey (Baedecker et al., 1993; Eganhouse et al., 1993; and Bennett et al., 1993) documented the occurrence of aerobic respiration, iron reduction, and methanogenesis as the primary mechanisms of biodegradation at the Bemidji, Minnesota crude oil spill. Nitrate reduction and sulfate reduction were not important anaerobic biodegradation mechanisms at this site due to low concentrations of these compounds in the native groundwater.

Geochemical Indicators. Geochemical parameters that can provide evidence of intrinsic bioremediation include oxidation-reduction (redox) potential, pH, carbonate hardness and alkalinity, and volatile fatty acids. The redox potential of groundwater can provide an indication of the contaminated area and the biological reactions that are operating at a site. Aerobic biodegradation of hydrocarbons will produce dissolved carbon dioxide and organic acids; consequently, a region of reduced pH should develop which coincides with the area of aerobic respiration. Associated with this region of reduced pH will be an increase in carbonate hardness and alkalinity. Volatile fatty acids are metabolic byproducts of the biodegradation of fuel hydrocarbons and can therefore provide direct evidence of intrinsic bioremediation.

Laboratory Microcosm Studies. Laboratory microcosm studies can be used to provide direct, qualitative evidence of intrinsic biodegradation. Typical microcosm studies involve taking aquifer samples from the candidate site to the laboratory where they are spiked with a known amount of the contaminant of interest and monitored over time for contaminant loss. Control microcosms provide a means for ensuring that contaminant loss was not the result of abiotic mechanisms (e.g., volatilization). Microorganisms responsible for biodegrading the contaminants generally are not identified during microcosm studies. Laboratory microcosm studies also can be used to estimate biodegradation rates, as discussed later in this section.

Microbial Counts. Microbial counts of total heterotrophic and hydrocarbon degraders can be used as an indicator of intrinsic bioremediation. The ratio of petroleum degraders to total heterotrophic bacteria should be higher in portions of the aquifer where intrinsic bioremediation of the hydrocarbons is occurring.

In Situ (Field) Experiments. Field dehydrogenase testing is a field method that can be used to determine if aerobic bacteria are present in the aquifer in quantities capable of biodegrading fuel hydrocarbons. Positive results indicate that a sufficient number of microbes capable of aerobic metabolism and/or denitrification are present in the aquifer. However, a negative test result gives no indication of the relative abundance of anaerobic microbes capable of utilizing sulfate, iron, or carbon dioxide during biodegradation.

Expected vs. Observed Plume Migration. Another line of evidence that can be used to demonstrate the occurrence of intrinsic bioremediation is a comparison of actual vs. expected plume

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migration. If intrinsic bioremediation is active at a site, the distance that the plume has migrated will be less than the distance it would have migrated without biodegradation. This calculation requires knowledge of the groundwater flow velocity, the retardation factor for the contaminants, and the date when the release occurred. Generally, this piece of evidence is significant only if it can be shown that there is a substantial difference between the actual distance the plume has migrated and the calculated distance. Models are useful tools in this capacity to help demonstrate intrinsic bioremediation.

4.2   Evaluating the Potential for Contaminant Migration. An evaluation of intrinsic bioremediation should consider the potential for future contaminant migration. The feasibility of intrinsic bioremediation as a remedial alternative for a site is based on its ability to degrade contaminants before they migrate to sensitive receptors at levels that will cause unacceptable risk. Often, this analysis will require the use of a model to predict the future migration and concentration of the contaminants of concern. Modeling can vary in complexity from the use of easily applied analytical equations to sophisticated numerical groundwater flow and transport computer codes. The choice of modeling tools depends on site-specific conditions (e.g., the variability of the aquifer hydraulic properties) and the amount of data available to support the modeling analysis.

Not all situations will require a modeling analysis. For example, if historical monitoring data clearly demonstrate that a plume has stabilized, and ample information has been gathered to indicate that intrinsic bioremediation is primarily responsible for the observed contaminant reduction, then a model is not needed to make predictions about future plume migration. Comparing data between two sampling events in 1992 and 1994, Doyle et al. (1995) demonstrated that a decrease in BTEX plume volume and mass had occurred. By demonstrating a strong correlation between the distribution of electron acceptors and the contaminated area, they were able to attribute the contaminant reduction to intrinsic bioremediation. These two pieces of information, which provided evidence of a shrinking plume caused by microbial activity, were sufficient to convince regulators that contaminants would not migrate away from the site.

Models are the best tool for predicting the extent of contaminant migration when field data indicate that the plume has not stabilized. If a modeling analysis is necessary, biodegradation rates at the site under consideration are required input data for the model and an exposure assessment should be conducted to identify any potential receptors that could be affected by a migrating plume of contaminated groundwater. The modeling analysis then should determine if the contaminant plume will reach the receptor locations before contaminants are degraded to levels that will not pose a risk to the receptors.

Determining Biodegradation Rates

Laboratory microcosms provide one method for estimating biodegradation rates; however, rates obtained under laboratory conditions may not be representative of field rates. Nevertheless, this method is most often used to estimate biodegradation rates. Approaches that are based on measurements of contaminant concentrations made at the site include the mass balance approach, the mass flux approach, statistical regression methods, and in situ microcosm studies. Models can also be used to estimate biodegradation rates.

Mass Balance Approach. As discussed previously, the mass balance approach requires an extensive monitoring well network to define the vertical and horizontal distribution of contaminant concentrations in the aquifer. A decrease in the total dissolved mass in the aquifer measured over

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time provides a quantitative method of demonstrating intrinsic bioremediation (Chiang et al., 1989; McAllister and Chiang, 1994). Examples of sites where a mass balance approach was used to calculate biodegradation rates are reported by Barker et al. (1987), Chiang et al. (1989), and Stauffer et al. (1994).

Mass Flux Approach. Another data intensive method that has been used to estimate biodegradation rates involves calculating the mass flux of a contaminant across transects oriented perpendicular to the groundwater flow direction. This technique is applicable for continuous sources at steady state (Rifai et al., 1995). Several transects are required at increasing distances from the source area in the direction of groundwater flow. By comparing the mass flux for several transects in the direction of groundwater flow, the reduction in contaminant mass can be observed. First-order biodegradation rate constants can be calculated from changes in contaminant mass between transects. This technique was demonstrated at the St. Joseph, Michigan site to determine the rate of TCE biodegradation (Weaver et al., 1995).

Regression Techniques. Buscheck and Alcantar (1995) present case studies demonstrating two regression techniques for estimating biodegradation rates based on field data. One method, the temporal analysis, involves constructing plots of contaminant concentration vs. time data for individual monitoring wells. The other method, spatial analysis, involves making plots of contaminant concentration vs. distance along a groundwater flow path through the plume. Both methods assume first-order decay and use readily available field data (contaminant concentration data measured in monitoring wells).

The *temporal analysis* requires one or more wells that exhibit decreasing concentrations over time. This is most commonly observed near the fringe of a hydrocarbon plume. In a temporal analysis, the slope of the line drawn through the concentration vs. time data is the decay rate (in units of % per day or day^{-1}). The temporal analysis is applicable only for a shrinking plume.

The *spatial analysis* can be applied if the plume is at steady state (i.e., concentrations vary with distance from the source but are neither increasing nor decreasing because the rate of degradation is equal to the rate of contaminant dissolution from the source). This method requires data from several wells aligned along a groundwater flowpath (preferably the plume centerline). A plot of the natural log of concentration vs. distance from the source should result in a straight line. In a spatial analysis, the slope of the line drawn through the concentration vs. distance data is equal to the biodegradation rate divided by the groundwater velocity (in units of L^{-1}). The biodegradation rate is obtained by multiplying the slope of the regression line by the groundwater velocity.

These methods do not correct for other attenuation mechanisms (i.e., dispersion, dilution, sorption); however, these effects are not likely to be significant for plumes that have stabilized (Chiang et al., 1989). The biodegradation rate can be corrected for these other processes by the use of a conservative tracer. Trimethylbenzene (TMB) isomers have been used by some investigators to correct for these effects (Wilson et al., 1995; Wiedemeier et al., 1995d). The three TMB isomers (1,2,3-TMB, 1,2,4-TMB, and 1,3,5-TMB) are generally present in fuel mixtures in sufficient quantities to be detected when dissolved in groundwater. These compounds have similar mobility properties (solubility, sorption, volatility) as the BTEX compounds; however, they degrade at a much slower rate under anaerobic conditions. Under aerobic conditions, the TMBs can be expected to biodegrade. The difference in the amount of attenuation observed for the TMBs compared to the individual BTEX compounds in the anaerobic portion of a plume can be attributed to intrinsic biodegradation.

Modeling Approach. Numerical or analytical models can be used to estimate biodegradation rates. This approach requires the presence of a conservative (nonbiodegradable) contaminant that was released at the same time as the biodegradable contaminants. The process involves first calibrating the model to reproduce the observed concentration distribution of the conservative compound in groundwater. Then, the calibrated model is used to simulate the observed distribution of the biodegradable contaminant by adjusting the biodegradation rate used in the model until there is a good fit between observed and simulated concentrations.

In Situ (Field) Microcosm Studies. Microcosm studies conducted in the field can sometimes provide more representative estimates of biodegradation rates than laboratory microcosm studies. Several investigators have demonstrated the utility of in situ microcosm devices for this purpose (Nielsen et al., 1996; Hunt et al., 1995; Acton and Barker, 1992; Gillham et al., 1990).

Modeling Contaminant Migration

Modeling contaminant fate and transport will be required if the plume is expanding. The objective of the modeling is to predict the future extent and concentrations of dissolved contaminants, considering the effects of advection, dispersion, sorption, and biodegradation. The analysis should answer two key questions (Rifai et al., 1995). 1. How far will the dissolved contaminants migrate before they are attenuated below an acceptable cleanup level? 2. How long will it take for intrinsic bioremediation to remediate the plume?

A detailed discussion of numerical modeling to simulate intrinsic bioremediation is beyond the scope of this paper; however, the process can be summarized as incorporating these steps (Rifai et al., 1995).

1. Construct and calibrate a model to the groundwater flow conditions at the site so that it correctly simulates the direction and rate of flow.
2. Calibrate the model to simulate existing contaminant conditions (distribution and concentration).
3. Use the calibrated model to predict the future contaminant distribution and concentration accounting for biodegradation.

A number of models that can be used to simulate contaminant transport with biodegradation are listed on Table 4-1. These models differ from standard contaminant transport models in that they incorporate mathematical expressions to simulate biodegradation kinetics (e.g., instantaneous, Monod, first-order). Other standard contaminant transport models that include a general first-order decay term in addition to terms for dispersion and retardation can be used to simulate transport with biodegradation. For example, Chapelle et al. (1996) used the SUTRA code (Voss, 1984) to model the fate of a hydrocarbon plume, substituting the biodegradation rates they determined in the laboratory and field into the model's decay term. If other attenuation mechanisms are active (e.g., volatilization), their effects must also be included in this lumped decay rate. A limitation of models that use a lumped decay term is that the electron acceptors consumed in the biodegradation process are not explicitly modeled; therefore, biodegradation is assumed to occur regardless of changes in the concentration of electron acceptors. This approach has the potential to overestimate the extent of biodegradation if electron acceptors are depleted in the field.

Table 4-1. Biodegradation Fate and Transport Models
(Sources: Rifai et al., 1995; Bedient et al., 1994)

Model	Model Description
BIO1D (Srinivasan and Mercer, 1988)	1-D, aerobic and anaerobic, Monod
BIOSCREEN (AFCEE, in preparation)	1-D, analytical spreadsheet model based on the Domenico (1987) analytical model; first-order decay or instantaneous; multiple electron acceptors (oxygen, nitrate, sulfate)
BIOPLUME (Borden and Bedient, 1986)	1-D, aerobic, Monod
BIOPLUS (Wheeler et al., 1987)	2-D model; aerobic, Monod
BIOPLUME II (Rifai et al., 1987)	2-D areal or vertical section model; aerobic as instantaneous (oxygen limited); anaerobic as constant first-order decay
BIOPLUME III (Rifai et al., in preparation)	2-D areal or vertical section model; aerobic and anaerobic; constant first-order, instantaneous, or Monod; multiple electron acceptors (oxygen, nitrate, sulfate)
BIOTRANS (ES&T, 1994)	2-D areal model; aerobic instantaneous (oxygen limited); anaerobic as constant first-order decay; multiple contaminant species
BIOF&T (Draper Aden, 1996)	2-D planar or radially symmetric vertical section, 3-D; aerobic instantaneous (oxygen limited) or Monod; anaerobic as first-order or modified Monod; saturated/unsaturated flow
BIOREM (Zei/Mi, 1996)	3-D model; aerobic instantaneous (oxygen limited) or Monod; anaerobic as Monod or first order decay; multiple electron acceptors (oxygen, nitrate, ferric iron, sulfate, carbon dioxide)

Identifying Potential Receptors and Exposure Pathways

If field monitoring and modeling show that a dissolved hydrocarbon plume is migrating, then an exposure assessment is necessary to identify any potential exposure points within the area between the current plume location and the downgradient point where the plume is expected to be completely attenuated. An adverse impact to human health or the environment is possible only if an individual or sensitive ecological receptor will be exposed to (i.e., contact) the contaminants in the plume. The modeling analysis should provide an estimate of how far the plume will migrate before the contaminants are completely destroyed and thereby provide an indication of whether or not the situation poses a potential threat to human health or the environment. Potential exposure points for petroleum contaminants in groundwater include:

- water supply wells (drinking, irrigation, etc.)
- surface water bodies (streams, wetlands) where contaminated groundwater may discharge

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- underground utilities (e.g., pipelines, etc.) that could intercept contaminated groundwater and expose workers during maintenance or repairs
- enclosed spaces such as basements where vapors may accumulate from a shallow groundwater plume
- outdoor activities (e.g., playgrounds) above the plume where vapors from a groundwater plume may diffuse to the atmosphere and expose individuals.

Consideration should be given to potential future changes in land use that could result in new exposure points during the expected lifetime of the plume. For example, if the area is likely to be developed in the near future for residential use, this could result in the construction of basements that approach the depth of a shallow aquifer.

If a plume will not encounter any exposure points before it is completely remediated, then there is no potential for risk to human or ecological receptors. This may be the case for many petroleum releases because dissolved BTEX plumes generally do not experience significant expansion due to intrinsic bioremediation. For example, in a study of 271 LUFT sites in California, Rice et al. (1995b) found that benzene plume lengths rarely exceeded 250 feet. This generalization may not be accurate for all geologic settings and all hydrocarbon contaminants in fuel; therefore, each site should be considered separately.

If modeling indicates that the plume is likely to reach an exposure point before it is completely degraded, there may be a potential risk to the human or ecological receptor(s) at the exposure point. In some situations, any amount of contamination reaching a potential exposure point would be considered unacceptable and an alternative remedial option that will prevent the contamination from reaching the exposure point(s) would need to be evaluated.

If the site is located in a state or region where there is an option for establishing risk-based remediation goals, then further analysis of the situation is possible. The modeling analysis can provide an estimate of the concentrations that are likely to reach the exposure point(s) over time. These estimates can then be used in a risk assessment to quantify the exposure (i.e., intake or dose) and risk for the likely scenario(s). If the resulting risk is within acceptable limits, then intrinsic bioremediation may be an acceptable remedial option. If the estimated risk is above acceptable limits, an alternative remedial option may have to be considered.

4.3   Comparing Intrinsic Bioremediation to Other Options. The key factors to consider when evaluating intrinsic bioremediation and other remedial options include:

- the ability of the technology to meet remedial goals
- prevention of exposure/risk, and
- cost effectiveness.

Remediation goals include numeric cleanup levels for contaminants of concern at specified locations. This could include locations at the source, inside the existing plume, and at downgradient compliance points. For sites that can be remediated under risk-based options, cleanup standards generally will not have to be met at the source unless there is a potential for exposure at the source. Given enough time, intrinsic bioremediation will be an effective site remediation process because it destroys the contaminants. Remediation goals could also include time frames by which the numeric

standards must be met. Because it is a natural process, intrinsic bioremediation may require more time than aggressive engineered remediation methods.

The ability of intrinsic bioremediation to achieve an acceptable level of risk or prevent exposure should be considered when comparing it to other remedial options. Intrinsic bioremediation will be a viable remediation method as long as contaminants are degraded to acceptable levels before they reach potential sensitive receptors. If there is a potential for direct exposure to contamination at the source, intrinsic bioremediation may not be a good choice for site remediation because of the time required to significantly reduce contaminant levels in the source area.

Intrinsic bioremediation should be analyzed to determine if it is a cost-effective method compared to other options. Costs associated with intrinsic bioremediation may include site characterization (monitoring well installation, chemical analyses); a detailed evaluation to determine its feasibility (e.g., data review, modeling, and reporting); regulatory negotiations; and long-term monitoring. Possible costs could be incurred for other activities such as source remediation or institutional controls (e.g., land use restrictions) that may be required to implement intrinsic bioremediation.

Intrinsic bioremediation can offer a substantial cost savings for groundwater remediation. According to U.S. EPA data, the average cost of cleaning up a leaking underground storage tank (LUST) site is $100,000, but for sites with groundwater contamination these costs typically range from $100,000 to over $1 million (U.S. EPA, 1994; U.S. EPA, 1993: NRC, 1994). Wiedemeier et al. (1995c) reported that it cost from $100,000 to $175,000 to fully implement the U.S. Air Force's natural attenuation protocol, depending on site-specific conditions. These figures are based on experience at approximately 40 sites and include costs for the following activities: monitor well installation and site characterization, chemical analyses, numerical modeling, report preparation, analysis of other remedial alternatives, and regulatory negotiations. Researchers from Amoco who are participating in a multisite evaluation of intrinsic bioremediation at gasoline-contaminated sites estimate that cleanup costs will be approximately $50,000 per site compared to five times that amount for more aggressive conventional approaches such as pump and treat (Black, 1995). Although these estimates for intrinsic bioremediation vary considerably, they are well below the maximum costs cited by the U.S. EPA for groundwater remediation at LUST sites. Cost savings can be even greater at sites that would require more extensive pump-and-treat systems than the average LUST site. For National Priorities List (NPL) sites, the average cost of groundwater remediation by pump and treat was found to be $7.1 million (Colglazier et al., 1991).

Section 5.0: IMPLEMENTING INTRINSIC BIOREMEDIATION

Intrinsic bioremediation can be implemented once it is demonstrated to be a viable remedial alternative for a site and regulatory approval has been obtained. Typically, implementation of intrinsic bioremediation will involve two activities, long-term monitoring and source remediation.

5.1   Long-Term Monitoring. Monitoring most likely will be a requirement at all sites where intrinsic bioremediation is implemented. The two objectives to monitoring intrinsic bioremediation are to: (1) ensure that the plume is not migrating to an extent that is greater than expected, and (2) evaluate the performance of intrinsic bioremediation in meeting the remedial goals (i.e., required concentrations at point of compliance within a specified time). Many of the details of a sampling program will be determined with regulatory agency input. Because it is not possible to provide a generic plan that will work for all sites, the following recommendations are provided.

A monitoring plan should be designed and implemented that considers appropriate sampling locations, frequency of sampling, and sampling parameters. A sufficient number of monitoring wells are required to determine changes in groundwater flow directions and velocities, trends in contaminant concentrations within the plume, and any further migration of the plume. If a modeling analysis was performed, the results should provide an estimate of how much migration can be expected. At a minimum, the monitoring well network should include the following wells:

- One monitoring well located upgradient of the plume to monitor background water quality
- One or more wells within the plume to monitor changes in contaminant concentrations (e.g., along the center flowpath through the plume)
- One well located immediately downgradient of the plume
- One or more sentinel wells located at a compliance point. If potential receptors have been identified, these wells should be located upgradient of them to provide early detection of contamination before the receptors are reached.

A monitoring well network for a hypothetical site is illustrated in Figure 5-1.

The frequency of sampling should be determined based on site-specific considerations. For example, if contaminant concentrations have been relatively stable during initial site monitoring, a long interval (e.g., several months to a year) between sampling events may be appropriate. However, a higher sampling frequency (e.g., monthly or quarterly) is required to resolve trends in the data when initial monitoring results fluctuate significantly. Wiedemeier et al. (1995c) recommend quarterly sampling initially, changing to annual sampling once the plume has stabilized and reached its maximum extent.

Which parameters to monitor is another site-specific decision. At a minimum, the following parameters should be measured:

- Concentrations of the contaminants of concern (e.g., BTEX)
- Water levels and thickness of NAPLs so that water table maps can be prepared to monitor flow direction and velocity.
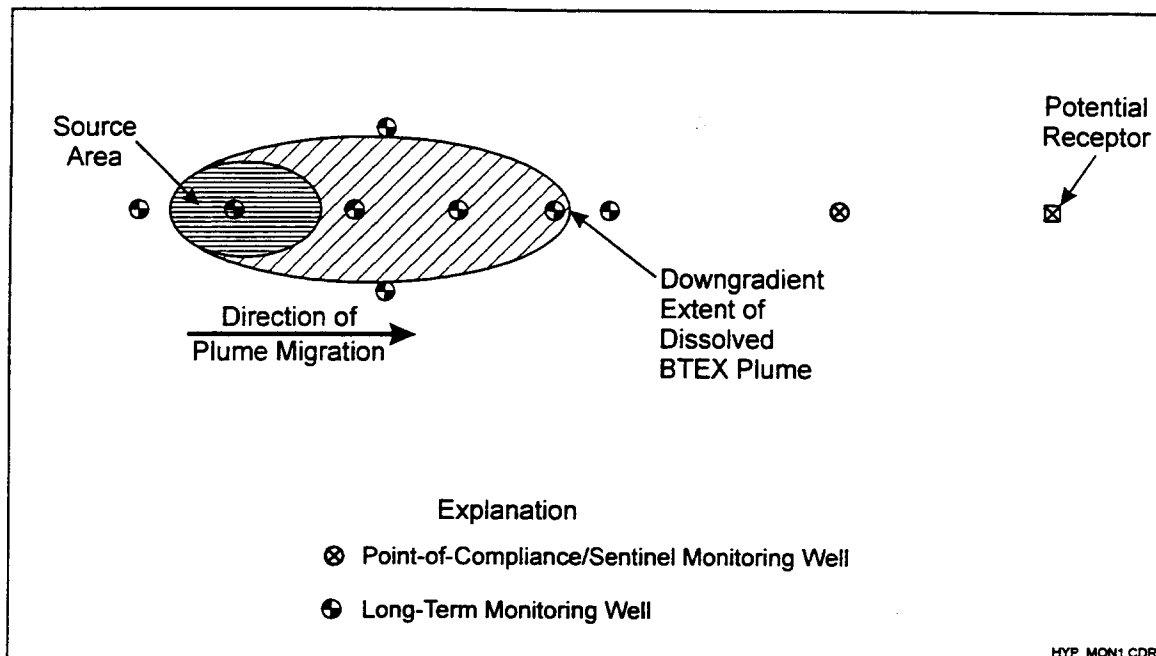
Figure 5-1. Well Network for Monitoring Intrinsic Bioremediation. (Adapted from McAllister and Chiang, 1994, and Wiedemeier et al., 1995c.)

Electron acceptors, metabolic byproducts, and general water quality parameters (e.g., temperature, pH, alkalinity, hardness, and redox potential) may also be measured to monitor changes in ambient water quality and provide further evidence of ongoing remediation.

A contingency plan should be included as part of the monitoring plan that identifies action that will be taken if the remediation goals are not achieved. The plan should explain in detail the activities that will be taken to ensure that there is no adverse impact to human health and the environment. At a minimum, the plan should identify an alternative remediation strategy to meet specified cleanup goals.

5.2   Source Remediation. Remediation of the source of contamination generally is required to implement intrinsic bioremediation. The Federal Underground Storage Tank Regulations given in 40 CFR 280.64 require that "owners and operators must remove free product to the maximum extent practicable as determined by the implementing agency." A survey of state regulations on intrinsic bioremediation found that the states allowing intrinsic bioremediation did so only after (1) action had been taken to eliminate sources of contamination (e.g., repair leaks) and (2) free product had been removed to the extent practicable (U.S. Air Force, 1994).

The objectives of source remediation are to prevent the continual release of contaminants to the groundwater, to shorten remediation time, and to restrict the growth of the contaminant plume. Source remediation should include the repair and/or removal of leaking tanks, fuel lines, and other associated equipment that could result in further unplanned releases to the environment. Source remediation should also involve removal of free product to the maximum extent possible, and it should

remediate residual contamination that is trapped in the unsaturated (vadose) zone or below the water table. One or more of these steps may be required depending on site conditions.

Source remediation technologies are summarized in Table 5-1. Selection of a source remediation technology will depend on the type of contaminants, the amount of residual contamination present, whether free product is present, and the site-specific conditions.

Table 5-1. Typical LNAPL Recovery/Remediation Technologies

Technology	Effectiveness		Implementability
	Free LNAPL	Vadose Zone Residual	
Skimming	Moderate	Low to none	Works best in uniform formations with moderate to high permeability and significant LNAPL thickness; recovered oil may contain a small amount of water possibly requiring decanting and disposal of water; uses simple, easily available equipment; commercial technology
Single-pump drawdown	High	Low to none	Works best in uniform formations with moderate to high permeability and significant LNAPL thickness; recovers an oil/water mixture requiring decanting and disposal of water; uses simple, easily available equipment; commercial technology
Dual-pump drawdown	High	Low to none	Works best in uniform formations with moderate to high permeability and significant LNAPL thickness; uses simple, easily available equipment; commercial technology
Bioslurping	High	High	Works best in uniform formations with moderate to high permeability; recovers an oil/water mixture requiring decanting and disposal of water; off-gas must be collected and treatment may be required; provides horizontal flow path which can reduce flow resistance in stratified geology; uses simple, easily available equipment; innovative technology
In-well air stripping	Low	Moderate	Works best in uniform formations with moderate to high permeability; mainly effective for treating plume dissolved in groundwater; air stream from the well must be collected and treatment may be required; uses moderately complex equipment; innovative technology
In situ air sparging	Low	Moderate	Works best in uniform formations with moderate to high permeability; air flow is sensitive to minute variation in permeability; uses moderately complex equipment; innovative technology
Soil vapor extraction	Low	High	Works best in uniform formations with moderate to high permeability; off-gas must be collected and treatment usually is required; uses simple, readily available equipment; commercial technology
Bioventing	Low to none	High	Works best in uniform formations with moderate to high permeability; uses simple, readily available equipment; commercial technology
In situ (engineered) bioremediation	Low to none	High	Works best in uniform formations with moderate to high permeability; effective delivery of oxygen- and nutrient-containing solution in situ can be difficult; uses simple, readily available equipment; innovative technology
Excavation and treatment	Moderate	High	Works best when contaminant concentration is high and the depth is shallow; commercial technology

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Section 6.0: CASE STUDIES

Eleven case studies well documented in the scientific literature were selected to (1) provide evidence that intrinsic bioremediation works in the field, (2) identify conditions under which intrinsic bioremediation has been shown to work for different fuel hydrocarbons, (3) identify the mechanisms responsible for biodegradation under the various conditions, and (4) present evidence that was used to demonstrate the occurrence of intrinsic bioremediation and to distinguish its effects from other attenuation processes such as dispersion, sorption, and volatilization. Wherever possible, information that demonstrated the effectiveness of intrinsic bioremediation at reducing contaminant concentrations in groundwater was presented.

Table 6-1 summarizes the case studies. All of the case studies were actual field applications. Most of the studies were carried out at sites that experienced unplanned releases of petroleum products to the environment. Some were conducted under controlled field conditions involving the planned injection of a known quantity of a contaminant and extensive monitoring to track the fate of the contaminants over time.

Table 6-1. Intrinsic Bioremediation Case Studies

Marine Corps Air Station, Beaufort, SC (Chapelle et al., 1996)	
Release Description	Groundwater impacted by a 10,600-gallon release of JP-5 from a below ground pipe in 1990
Biodegradation Mechanisms	Aerobic respiration, iron reduction, and sulfate reduction
Evidence for Intrinsic Bioremediation	• Dissolved oxygen is depleted and concentrations of reduced iron are elevated in the aquifer where hydrocarbons are present. • Measured hydrogen concentrations in anaerobic groundwater were in the range characteristic of iron reduction and sulfate reduction. • The extent of plume migration during the 4 years following the release was substantially less than expected without biodegradation. • Laboratory microcosm studies were performed to measure biodegradation rates and sorption characteristics of the hydrocarbon contaminants. • Numerical modeling predicted that dissolved hydrocarbon contaminants will be completely biodegraded before groundwater discharges to adjacent surface water bodies.
Biodegradation Rates	The following first-order rates were determined in laboratory studies: Toluene — 0.001%/d (anaerobic); 0.29%/d (aerobic) Naphthalene — 0.15%/d (aerobic)
Site Conditions Influencing Intrinsic Bioremediation	• Slow rate of groundwater movement (20 ft/yr) and high sorptive capacity of aquifer sediments minimized contaminant spreading. • Background concentrations of dissolved oxygen (3 to 4 mg/L) indicate that uncontaminated groundwater at the site is aerobic. • Sulfate concentrations were not well correlated with hydrocarbon contamination, perhaps because of anthropogenic contributions; however, the lowest concentrations were observed in the most contaminated well. • Background nitrate concentrations were too low for nitrate reduction to be a significant biodegradation mechanism at this site.
Other Comments	Biodegradation of naphthalene was evaluated in this study.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Seal Beach Naval Weapons Station, CA (Ball and Reinhard, 1996)	
Release Description	Groundwater contaminated with gasoline
Biodegradation Mechanisms	Nitrate reduction Sulfate reduction
Evidence for Intrinsic Bioremediation	• Toluene and o-xylene were mineralized in laboratory microcosms with sulfate as the electron acceptor. • Benzene was mineralized in laboratory microcosms under strict anaerobic conditions with sulfate as the presumed electron acceptor. • Ethylbenzene was anaerobically degraded only under nitrate-reducing conditions.

Biodegradation Rates	Under sulfate reducing conditions: 7.2 μg/L·hr (toluene)
	                                             4.1 μg/L·hr (m- and p-xylene)
	
	Under nitrate-reducing conditions: 4.2 μg/L·hr (ethylbenzene)
	                                        30.1 μg/L·hr (toluene)
	                                        5.4 μg/L·hr (m- and p-xylene)

Site Conditions Influencing Intrinsic Bioremediation	This study evaluated anaerobic biodegradation processes in laboratory microcosms.
Other Comments	Iron-reduction and methanogenesis were not important anaerobic biodegradation processes for the BTEX compounds in Seal Beach sediments.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

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Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

George Air Force Base (AFB), CA (Wilson et al., 1995 and Doyle et al., 1995)	
Release Description	Groundwater contaminated with JP-4 (BTEX, TMB).
Biodegradation Mechanisms	Aerobic respiration Nitrate reduction Sulfate reduction
Evidence for Intrinsic Bioremediation	• An observed decrease in contaminant mass and plume volume over a 2-year sampling period. • Spatial correlation between reduced concentrations of electron acceptors and the areas of contaminated groundwater. • An observed decrease in contaminant concentrations downgradient of the spill beyond what could be attributed to dilution alone. Trimethylbenzenes present in the fuel provided a conservative tracer to distinguish biodegradation from other attenuation mechanisms (i.e., dilution, sorption, volatilization).
Biodegradation Rates	Benzene — 0.053, 0.058%/day Toluene — >0.032%/day Ethylbenzene — 0.06%/day Xylene — 0.14 to >0.29%/day
Site Conditions Influencing Intrinsic Bioremediation	• Naturally occurring levels of electron acceptors (oxygen, nitrate, and sulfate) are adequate for intrinsic biodegradation. • Contaminant travel times to the nearest receptor are substantial (greater than 200 years). • A continuous aquitard underlies the contaminated aquifer. • Provisions were made to place deed restrictions on the property overlying the contaminated aquifer prior to land transfer.
Other Comments	• A 100-fold decrease in benzene concentrations was observed along a flowpath of 360 meters due to biodegradation. • Source removal was conducted concurrently with intrinsic bioremediation.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Hill AFB, UT (Wiedemeier et al., 1995c and Wiedemeier et al., 1995d)	
Release Description	Groundwater contaminated with JP-4.
Biodegradation Mechanisms	Aerobic respiration Nitrate reduction Iron reduction Sulfate reduction (dominant mechanism) Methanogenesis
Evidence for Intrinsic Bioremediation	• Areas at the site with BTEX contamination coincide with low redox potentials, low concentrations of electron acceptors (oxygen, nitrate, sulfate), and elevated levels of reduced (ferrous) iron and methane. • Observed BTEX concentrations along the groundwater flowpath were significantly reduced compared to predicted concentrations due to dilution, sorption, and volatilization, thus confirming intrinsic biodegradation. TMBs, comingled with the BTEX compounds in the groundwater, provided a conservative tracer to distinguish the effects of nonbiological attenuation.
Biodegradation Rates	Not reported
Site Conditions Influencing Intrinsic Bioremediation	• Naturally occurring levels of electron acceptors (oxygen, nitrate, and sulfate) are adequate for intrinsic biodegradation (background oxygen levels are 6 mg/L; nitrate 29 mg/L; sulfate 100 mg/L). The total assimilative capacity of the groundwater was determined to be sufficient to degrade dissolved BTEX before it migrates 500 m downgradient from the source area. • Ambient groundwater chemistry is conducive to intrinsic bioremediation. The pH ranges from 6.3 to 8.3. Alkalinity is high, ranging from 349 to 959 mg/L. Average temperature is 18°C.
Other Comments	• The U.S. Air Force has recommended intrinsic bioremediation with long-term monitoring (semiannual sampling for 13 years) to remediate groundwater containing dissolved BTEX for this site. Contaminant concentrations in the three downgradient POC wells must meet federal drinking water standards. • Bioventing and free-product recovery operations are being implemented concurrent with natural attenuation to address the source of contamination. • Land use restrictions are required to prevent potential use of shallow groundwater downgradient of the source area.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Patrick AFB, FL (Wiedemeier et al., 1995c and Wiedemeier et al., 1995d)	
Release Description	Groundwater impacted by a 700-gallon gasoline (unleaded) spill
Biodegradation Mechanisms	Aerobic respiration Iron reduction Methanogenesis (dominant mechanism)
Evidence for Intrinsic Bioremediation	• Decreases in the area of the BTEX plume and BTEX concentrations within the plume were observed over a 1-year sampling period. No downgradient migration of the plume was observed during this period. • Areas of the site with low redox potential correlate with areas of BTEX contamination, low electron acceptor concentrations (oxygen) compared to background, and elevated levels of ferrous iron and methane. • Observed BTEX concentrations along a groundwater flowpath were significantly lower than concentrations that were predicted if dilution, sorption, and volatilization were the only active attenuation mechanisms. TMBs present with the BTEX compounds in the groundwater provided a conservative tracer to distinguish the effects of nonbiological attenuation. • Positive detection of volatile fatty acids in groundwater contaminated with BTEX provided direct evidence for microbial degradation of BTEX.
Biodegradation Rates	Not reported
Site Conditions Influencing Intrinsic Bioremediation	• Ambient groundwater conditions are conducive to intrinsic bioremediation. The pH ranges from 6.7 to 7.6. Alkalinity ranges from 148 to 520 mg/L. Temperatures are high, ranging from 24.7 to 27.8°C. • The total assimilative capacity of the shallow groundwater was determined to be sufficient to degrade dissolved BTEX before the plume migrates 400 m from the source area. Predictive modeling using BIOPLUME II supported this conclusion. • High background concentrations of sulfate (up to 86 mg/L) exist. There was no correlation between sulfate concentrations and BTEX distribution, suggesting that sulfate reduction is not a significant biodegradation mechanism. • Background nitrate concentrations are low (0.05 to 0.29 mg/L), indicating nitrate reduction is not a significant biodegradation mechanism.
Other Comments	• The U.S. Air Force has proposed intrinsic bioremediation with long-term monitoring (semiannual sampling over 10 years) as a remedy for this site, to confirm modeling results, and to monitor migration and degradation of the dissolved BTEX plume. Contaminant concentrations in the three Point of Compliance (POC) wells must meet Florida regulatory standards. • Bioventing is being performed to remediate residual hydrocarbon above the saturated zone.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

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Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

McChord AFB, WA (Testa and Colligan, 1994)	
Release Description	Jet fuel and light diesel-range hydrocarbons in a smear zone within the saturated and unsaturated portions of the soil covering approximately 8 acres.
Biodegradation Mechanisms	Not reported
Evidence for Intrinsic Bioremediation	• Microcosm tests of soil samples from the smear zone revealed that petroleum degraders comprised 20% of total heterotrophs which numbered 10^5 to 10^6 CFU/gram of soil. In contrast, soil samples outside the smear zone contained only 0.1% petroleum degraders. • Significantly lower concentrations of total petroleum hydrocarbons were observed in the unsaturated portion of the smear zone (1,000 mg/kg) compared to the saturated portion (10,000 mg/kg) that was attributed to biodegradation.
Biodegradation Rates	Not reported.
Site Conditions Influencing Intrinsic Bioremediation	• Carbon to nitrogen ratio of 20:1 is favorable for biodegradation. • No regulated compounds such as BTEX were detected in the lower saturated smear zone.
Other Comments	• Attempts to recover residual product in the soil using trenches were unsuccessful. • The ROD for the site was revised to allow for natural attenuation with long-term monitoring instead of active remediation.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

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B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

U.S. Coast Guard Air Station, Traverse City, MI (Rifai et al., 1988; Wilson et al., 1986; Twenter et al., 1985)	
Release Description	Groundwater contaminated with aviation fuel (major contaminants are BTX) from a 10,000-gallon spill in 1969.
Biodegradation Mechanisms	Aerobic respiration Methanogenesis
Evidence for Intrinsic Bioremediation	• Dissolved oxygen concentrations are significantly reduced in wells with petroleum hydrocarbons. High concentrations of methane were detected to the anaerobic portion of the hydrocarbon plume. • A reduction in contaminant mass was observed based on sampling from 1985 through 1986 beyond what could be explained by volatilization and dispersion alone. Mass loss due to biodegradation was calculated quarterly by comparing the BTX mass in the system for successive quarters and subtracting the BTX mass captured by the groundwater extraction system. • Laboratory microcosm studies confirmed anaerobic degradation of BTX by methanogenesis.
Biodegradation Rates	Field rates were not reported. Rates from laboratory microcosms were as follows: Benzene 11%/wk Toluene 10%/wk m-Xylene 14%/wk o-Xylene 13%/wk
Site Conditions Influencing Intrinsic Bioremediation	• Background concentrations of dissolved oxygen (approximately 8 mg/L) are conducive to aerobic biodegradation. • Rapid groundwater flow rates (5 ft/d) resulted in contamination reaching Grand Traverse Bay before complete degradation occurred. • Rapid groundwater flow rates also minimized lateral spreading of the contaminants, creating a long, narrow plume. Most degradation occurred along the sides of the plume. Center of plume is anaerobic, with high concentrations of methane.
Other Comments	• Natural attenuation was effective in reducing contaminant concentrations between the source area and Grand Traverse Bay; however, because of rapid groundwater flow it was not adequate for preventing the plume from reaching the Bay. • A groundwater extraction system was installed to capture contaminated groundwater before it entered Grand Traverse Bay. • Biodegradation was determined to be more successful than pumping for removing BTX mass.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Rocky Point, NC (Borden et al., 1995)	
Release Description	Groundwater impacted by a gasoline spill
Biodegradation Mechanisms	Aerobic respiration Nitrate reduction Sulfate reduction Iron reduction Methanogenesis
Evidence for Intrinsic Bioremediation	• A depletion of electron acceptors (dissolved oxygen, nitrate, and sulfate) within the BTEX plume and increased concentrations of reduced iron (Fe^{2+}) and carbon dioxide were observed. • Certain BTEX compounds were shown to be preferentially removed. Toluene and o-xylene concentrations decrease most rapidly downgradient of the source followed by m-xylene, p-xylene, and benzene. Ethylbenzene degrades very slowly under anaerobic conditions present at the plume center.
Biodegradation Rates	Not reported
Site Conditions Influencing Intrinsic Bioremediation	• Background phosphorous concentrations are low (<0.2 mg/L) and could be limiting biodegradation. • The rate and extent of biodegradation were strongly influenced by type of electron acceptors present in the aquifer. In the upgradient part of plume, nitrate, ferric iron, and oxygen are used as terminal electron acceptors. In the downgradient part of the plume, sulfate and iron are the dominant electron acceptors.
Other Comments	Plume is at steady state.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Bemidjii, MN (Baedecker et al., 1993, Bennett et al., 1993; and Eganhouse et al., 1993)	
Release Description	Crude oil release from an underground pipeline into a shallow sand and gravel aquifer
Biodegradation Mechanisms	Aerobic respiration Iron/manganese reduction Methanogenesis
Evidence for Intrinsic Bioremediation	• Historical monitoring data over a 5-year period show that the plume has stabilized. • Decreased concentrations of electron acceptors (oxygen) and increased concentrations of methane, reduced iron (Fe^{2+}), and manganese (Mn^{2+}) relative to background concentrations coincide with areas where hydrocarbons are present in groundwater. • A significant decrease in contamination (measured as VDOC) was observed over a short distance (41% to 13.9% of TDOC over 41 m) within the anaerobic portion of the aquifer over. Also, further reduction in VDOC (13.9% to 3.1% of TDOC) was observed over a short (10 m) travel distance in the aerobic portion (front) of the plume. • Predictive modeling confirmed that dispersion and sorption could not account for the observed decrease in contamination over the 41-m flowpath.
Biodegradation Rates	Not reported
Site Conditions Influencing Intrinsic Bioremediation	Naturally occurring concentrations of nitrate and sulfate are low; therefore, nitrate reduction and sulfate reduction are not significant anaerobic degradation processes at this site.
Other Comments	The primary processes responsible for biodegradation of hydrocarbons in the anaerobic part of the plume are methanogenesis and iron and manganese reduction. Methanogenesis was a process that evolved after iron and manganese reduction.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Canadian Forces' Base Borden, Ontario (Barker et al., 1987)	
Release Description	Controlled natural-gradient BTX injection experiment into a sand aquifer
Biodegradation Mechanisms	Aerobic respiration
Evidence for Intrinsic Bioremediation	A dense network of multilevel sampling points provided evidence that BTX was essentially completely degraded in the aquifer within a period of 410 days and a travel distance of less than 15 m of the injection well. Initial concentrations were 2,360 μg/L (benzene); 1,750 μg/L (toluene); 1,080 μg/L (p-xylene); 1,090 μg/L (m-xylene); and 1,290 μg/L (o-xylene).
Biodegradation Rates	The following zero-order field rates were reported: Benzene 30 mg/d Toluene 37 mg/d o-xylene 33 mg/d m-xylene 47 mg/d p-xylene 55 mg/d
Site Conditions Influencing Intrinsic Bioremediation	The initial distribution of dissolved oxygen int eh Borden aquifer was adequate for aerobic biodegradation of the contaminant slug introduced into the aquifer (1,800 L).
Other Comments	• Benzene was more persistent that toluene and the xylenes. • BTX persisted longer in parts of the aquifer with less dissolved oxygen, indicating oxygen availability is a dominant control of hydrocarbon persistence. The rate of aerobic biodegradation was likely controlled by the rate of oxygen transport into BTX-containing water.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

Table 6-1. Intrinsic Bioremediation Case Studies (Continued)

Manufactured Gas Plant Site, Northern Michigan (Chiang et al., 1989)	
Release Description	(BTX) contamination in a shallow aquifer
Biodegradation Mechanisms	Aerobic respiration
Evidence for Intrinsic Bioremediation	• Data from 42 monitoring wells and 10 sampling events over a 3-year period document a significant reduction in total benzene mass in groundwater with time. • Spatial relationships between dissolved oxygen and total BTX were shown to be strongly correlated by statistical analyses and solute transport modeling.
Biodegradation Rates	A biodegradation rate of 0.95%/day was determined for benzene based on material balance and non-least squares analyses.
Site Conditions Influencing Intrinsic Bioremediation	• A dense monitoring well network allowed calculation of total dissolved mass in groundwater during each sampling period. • Volatilization was shown to be an insignificant attenuation process.
Other Comments	BTX were most rapidly degraded in laboratory microcosms when DO concentrations were >2 ppm. Rates slowed when DO concentrations fell below 2 ppm. Little or no biodegradation was observed at DO concentrations below 0.5 ppm.

B = benzene; T = toluene; E = ethylbenzene; X = xylenes (m-xylene, o-xylene, p-xylene); CFU = colony forming units; ROD = Record of Decision; TMB = trimethylbenzene; TDOC = total dissolved organic carbon = NVDOC + VDOC; NVDOC = nonvolatile dissolved organic carbon; and VDOC = volatile dissolved organic carbon.

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APPENDIX A

**DECISION TREES FOR EVALUATING THE FEASIBILITY
OF INTRINSIC BIOREMEDIATION**

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Figure A-1. Framework for Assessing the Efficiency of Intrinsic Bioremediation (from Chapelle et al., 1996).

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**INITIAL SCREENING OF
NATURAL ATTENUATION EFFECTIVENESS**

Does
the state allow
natural attenuation
as a remedial
alternative? — **NO**

YES

Are TPH
concentrations
lower than 25,000
ppm in soil? — **NO**

YES

Is there
current or projected
groundwater use within
a 2 year travel time
from the site? — **YES**

NO

Are
there nearby
receptors that the
contamination
could affect? — **YES**

NO

STOP

Natural attenuation
is not a remedial
option at the site.
Consider other
technologies.

- Bioventing
- Landfarming
- Biomounding
- Thermal
  Desorption

Natural attenuation has
the potential to be
effective at the site.
Proceed to next panel.

Figure A-2. Natural Attenuation Evaluation Process Flowchart (from EPA, 1995).

| DETAILED EVALUATION OF NATURAL ATTENUATION EFFECTIVENESS | EVALUATION OF REMEDIAL PROGRESS MONITORING |

Left column (Detailed Evaluation of Natural Attenuation Effectiveness):

Identify soil, groundwater, and environmental characteristics and product constituent properties important to natural attenuation effectiveness

↓

Soil:
- Is soil permeability > $10^{-8} cm^2$?
- Are soil oxygen levels ≥ 2%?
- Does soil have a pH of 6 - 8?
- Does soil have a moisture content of 40 - 85%?
- Does soil have a C:N:P ratio of approximately 100:1:0.5 to 100:10:1?

NO → / YES ↓

Groundwater:
- Is contaminant travel time to receptor at least 2 years?

NO → / YES ↓

Climate:
- Is precipitation 10 - 60 in./yr.?
- Is the average ambient temperature 5° - 45° C?

NO → / YES ↓

Product Constituents:
- Are constituents at most slightly soluble?
- Are constituents not highly volatile?
- Are Koc and Kd values high enough to adequately retard migration?
- Are constituents sufficiently biodegradable?

NO → Proceed with caution.

YES ↓

You may consider natural attenuation as a remedial alternative.

Right column (Evaluation of Remedial Progress Monitoring):

Is monitoring frequency annually for soils and quarterly for groundwater?

NO → / YES ↓

Does soil/groundwater monitoring include analysis for TPH, BTEX, and other constituents of concern?

NO → / YES ↓

Does soil gas analysis include analysis for oxygen? Does groundwater monitoring include analysis for oxygen, pH, alkalinity?

NO → STOP — The proposed natural attenuation monitoring plan is incomplete. Request additional information.

YES ↓

Are an adequate number of samples being collected in soil and around the boundary of contaminated areas?

NO → / YES ↓

Are an adequate number of groundwater samples being collected from appropriate locations?

NO → / YES ↓

The remedial progress monitoring plan is of sufficient scope and frequency and can be considered complete.
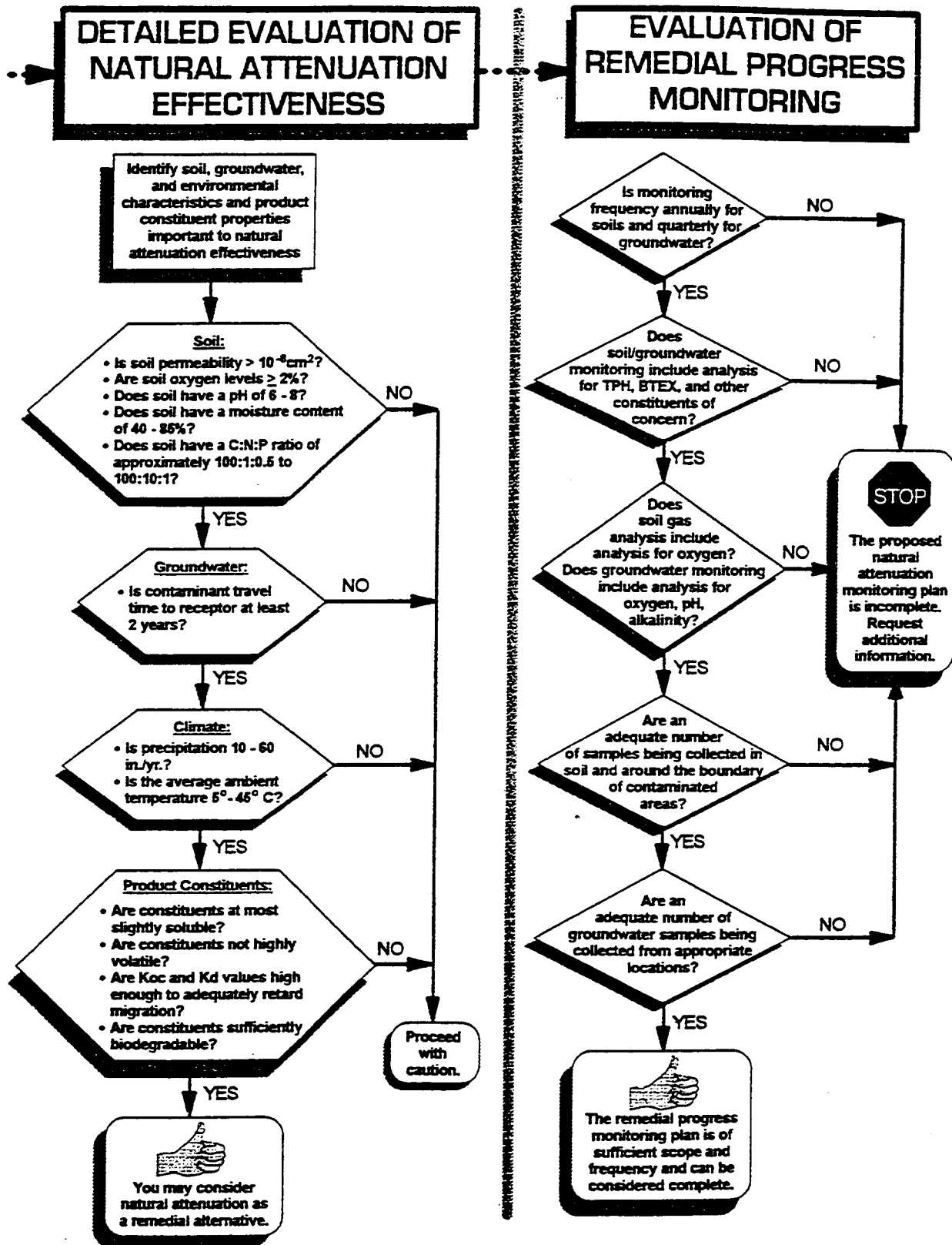
Figure A-2. Natural Attenuation Evaluation Process Flowchart (continued).

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APPENDIX B

**TYPES OF SITE ASSESSMENT DATA USED TO EVALUATE
INTRINSIC BIOREMEDIATION**

Table B-1. Site Assessment Data Useful for Evaluating Intrinsic Bioremediation (Modified from McAllister and Chiang, 1994)

Data Type	Application
Date of contaminant release	Understand the extent of plume migration since date of release
Delineation of contaminant source and soluble plume boundaries for contaminants of concern (BTEX, PAHs, etc.)	Use in preliminary model estimates of plume migration. Compare expected extent without natural attenuation to actual extent of contamination
Direction and gradient of groundwater flow, hydraulic conductivity, definition of lithology, aquifer thickness, depth to groundwater, and range of water table fluctuations	Estimate the expected direction and rate of groundwater flow
Organic carbon fraction, bulk density, porosity of aquifer, organic carbon partition coefficient of contaminants, dispersion coefficient, biodegradation rates	Estimate the extent of contaminant migration since date of release, model future contaminant movement
Historical contaminant concentrations in wells located throughout the plume and along the primary flowpath from the source to the leading edge	Evaluate status of plume (i.e., shrinking, steady state, or expanding) to identify loss of contaminants
Background dissolved oxygen concentrations upgradient of the source and plume	Determine if there is sufficient oxygen present for aerobic biodegradation (> 1 to 2 mg/L)
Dissolved oxygen (O_2) levels inside and outside the contaminant plume	Identify inverse correlation indicative of aerobic biodegradation
Dissolved nitrate (NO_3^-), iron (Fe^{2+}), manganese (Mn^{+2}), sulfate (SO_4^{-2}), sulfide (H_2S, HS^-), methane (CH_4)	Identify correlation between electron acceptors and metabolic byproducts indicative of anaerobic biodegradation
Alkalinity, hardness, pH, oxidation-reduction (redox) potential, volatile fatty acids inside and outside the contaminant plume	Geochemical indicators of intrinsic biodegradation
Chloride (Cl^-), conductivity, temperature	General water quality parameters used as markers to verify that site samples are obtained from the same groundwater system