Designation: E 1943 – 98 (Reapproved 2004)

Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites[1]

This standard is issued under the fixed designation E 1943; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This is a guide for determining the appropriateness of remediation by natural attenuation and implementing remediation by natural attenuation at a given petroleum release site, either as a stand alone remedial action or in combination with other remedial actions.

1.2 Natural attenuation is a potential remediation alternative for containment and reduction of the mass and concentration of petroleum hydrocarbons in the environment to protect human health and the environment. Remediation by natural attenuation depends upon natural processes such as biodegradation, dispersion, dilution, volatilization, hydrolysis, and sorption to attenuate petroleum constituents of concern to achieve remedial goals.

NOTE 1—Remedial goals must be established through another process as determined by the appropriate regulatory agency.

1.3 In general, remediation by natural attenuation should not be considered a presumptive remedy. A determination of whether remediation by natural attenuation is appropriate for an individual petroleum release site, relative to site-specific remedial goals, requires site characterization, assessment of potential risks, evaluation of the need for source area control, and evaluation of potential effectiveness similar to other remedial action technologies. Application and implementation of remediation by natural attenuation requires demonstration of remedial progress and attainment of remedial goals by use of converging lines of evidence obtained through monitoring and evaluation of resulting data. When properly applied to a site, remediation by natural attenuation is a process for risk management and achieving remedial goals. Monitoring should be conducted until it has been demonstrated that natural attenuation will continue and eventually meet remedial goals.

1.3.1 The primary line of evidence for remediation by natural attenuation is provided by observed reductions in plume geometry and observed reductions in concentrations of the constituents of concern at the site.

1.3.2 Secondary lines of evidence for remediation by natural attenuation are provided by geochemical indicators of naturally occurring degradation and estimates of attenuation rates.

1.3.3 Additional optional lines of evidence can be provided by microbiological information and further analysis of primary and secondary lines of evidence such as through solute transport modeling or estimates of assimilative capacity.

1.4 The emphasis in this guide is on the use of remediation by natural attenuation for petroleum hydrocarbon constituents where ground water is impacted. Though soil and ground water impacts are often linked, this guide does not address natural attenuation in soils separate from ground water or in situations where soils containing constituents of concern exist without an associated ground water impact. Even if natural attenuation is selected as the remedial action for ground water, additional remedial action may be necessary to address other completed exposure pathways at the site.

1.5 This guide does not address enhanced bioremediation or enhanced attenuation.

1.6 Also, while much of what is discussed is relevant to other organic chemicals or constituents of concern, these situations will involve additional considerations not addressed in this guide.

1.7 The guide is organized as follows:

1.7.1 Section 2 lists referenced documents.

1.7.2 Section 3 defines terminology used in this guide.

1.7.3 Section 4 describes the significance and use of this guide.

1.7.4 Section 5 provides an overview of the use of natural attenuation as a remedial action alternative, including;

1.7.4.1 Advantages of remediation by natural attenuation as a remedial alternative;

1.7.4.2 Limitations of remediation by natural attenuation as a remedial alternative; and

1.7.4.3 Using multiple lines of evidence to demonstrate the appropriateness of remediation by natural remediation.

1.7.5 Section 6 describes the decision process for appropriate application and implementation of remediation by natural attenuation including;

1.7.5.1 Initial response, site characterization, selection of chemicals of concern, and establishment of remedial goals;

---

[1] This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment and is the direct responsibility of Subcommittee E50.04 on Performance Standards Related to Environmental Regulatory Programs.

Current edition approved May 1, 2004. Published June 2004.Originally approved in 1998. Last previous edition approved in 1998 as E 1943-98.

1.7.5.2 Evaluation of plume status;

1.7.5.3 Collection and evaluation of additional data;

1.7.5.4 Comparing remediation by natural attenuation performance to remedial goals;

1.7.5.5 Comparing remediation by natural attenuation to other remedial options;

1.7.5.6 Implementation of a continued monitoring program;

1.7.5.7 Evaluation of progress of remediation by natural attenuation; and

1.7.5.8 No further action.

1.7.6 Section 7 lists keywords relevant to this guide.

1.7.7 Appendix X1 describes natural attenuation processes;

1.7.8 Appendix X2 describes site characterization requirements for evaluating remediation by natural attenuation;

1.7.9 Appendix X3 describes considerations for designing and implementing monitoring for remediation by natural attenuation;

1.7.10 Appendix X4 describes sampling considerations and analytical methods for determining indicator parameters for remediation by natural attenuation;

1.7.11 Appendix X5 describes the interpretation of different lines of evidence as indicators of natural attenuation;

1.7.12 Appendix X6 describes methods for evaluation and quantification of natural attenuation rates; and

1.7.13 Appendix X7 describes example problems illustrating the application and implementation of remediation by natural attenuation.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of any regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 888 Test Methods for Dissolved Oxygen in Water
D 1125 Test Methods for Electrical Conductivity and Resistivity of Water
D 1293 Test Methods for ph of Water
D 1452 Practice for Soil Investigation and Sampling by Auger Borings
D 1498 Practice for Oxidation-Reduction Potential of Water
D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils
D 4043 Guide for Selection of Aquifer-Test Method in Determining of Hydraulic Properties by Well Techniques
D 4044 Test Method (Field Procedure) for Instantaneous Change in Head (Slug) Tests for Determining Hydraulic Properties of Aquifer Systems
D 4050 Test Method (Field Procedure) for Withdrawal and Injection Well Tests for Determining Hydraulic Properties of Aquifer Systems
D 4104 Test Method (Analytical Procedure) for Determining Transmissivity of Nonleaky Confined Aquifers by Overdamped Well Response to Instantaneous Change in Head (Slug Tests)
D 4105 Test Method (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Modified Theis Nonequilibrium Method
D 4106 Test Method (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Theis Nonequilibrium Method
D 4372 Specification for Flame-Resistant Materials Used in Camping Tentage
D 4448 Guide for Sampling Groundwater Monitoring Wells
D 4658 Test Method for Sulfide Ion in Water
D 4700 Guide for Soil Sampling From the Vadose Zone
D 4750 Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well)
D 5092 Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers
D 5269 Test Method for Determining Transmissivity of Nonleaky Confined Aquifers by the Theis Recovery Method
D 5270 Test Method for Determining Transmissivity and Storage Coefficient of Bounded, Nonleaky, Confined Aquifers
D 5434 Guide for Field Logging of Subsurface Explorations of Soil and Rock
D 5473 Test Method for (Analytical Procedure For) Analyzing the Effects of Partial Penetration of Control Well and Determining the Horizontal and Vertical Hydraulic Conductivity in a Nonleaky Confined Aquifer
E 1599 Guide for Corrective Action for Petroleum Releases
E 1689 Guide for Developing Conceptual Site Models for Contaminated Sites
E 1739 Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites
E 1912 Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Releases

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *assimilative capacity*—a semi-quantitative estimate of the potential mass of hydrocarbons per unit volume of ground water that can be metabolized by aerobic and anaerobic biodegradation under existing site conditions.

3.1.2 *attenuation rate*—measured reduction in concentration or mass of a compound with time or distance expressed as an amount of reduction per unit time or per unit distance.

3.1.3 *conceptual site model*—a written or pictorial representation of an environmental system and the biological, physical, and chemical processes that determine the transport of constituents of concern from sources through environmental media to environmental receptors within the system.

3.1.4 *constituents of concern*—specific petroleum constituents that are identified as posing a potential risk to human health or the environment.

---

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.5 *corrective action*—actions taken to identify and clean up a release of petroleum. These activities include site assessment, interim remedial action, remedial action, operation and maintenance of equipment, monitoring of progress, and termination of the remedial action.

3.1.6 *electron acceptors*—elements or compounds that are reduced by receiving electrons produced by the oxidation of organic compounds through microbial metabolism or abiotic chemical oxidation processes.

3.1.7 *expanding plume*—configuration where the solute plume margin is continuing to move outward or down gradient from the source area.

3.1.8 *institutional controls*—the restriction on use or access (for example, fences, deed restrictions, restrictive zoning) to a site or facility to eliminate or minimize potential exposure to a constituent(s) of concern.

3.1.9 *monitoring points*—a monitoring well or other monitoring device placed in a selected location for observing parameters such as liquid levels or pressure changes, or for collecting liquid samples. The monitoring point may be cased or uncased, but if cased the casing should have openings to allow flow of borehole liquid into or out of the casing (modified from Test Method D 4750).

3.1.10 *natural attenuation*—reduction in mass or concentration of a compound in ground water over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes, such as; biodegradation, dispersion, dilution, sorption, and volatilization.

3.1.11 *optional lines of evidence*—solute transport modeling, estimates of assimilative capacity (to estimate the mass of BTEX and other constituents of concern degraded), and microbiological studies.

3.1.12 *plume*—volume of ground water where constituents of concern are present.

3.1.13 *point of compliance*—a location(s) selected between the source area(s) and potential point(s) of exposure where concentrations of constituents of concern must be at or below the determined ground water target levels.

3.1.14 *primary lines of evidence*—historical concentration data are the primary line of evidence for natural attenuation and are based on measured petroleum hydrocarbon constituent concentrations over time to define the plume as shrinking, stable, or expanding similar to the first line of evidence suggested by NRC (1993).[3]

3.1.15 *receptor*—persons, structures, utilities, ecological receptors, and water supply wells that are or may be adversely affected by a release.

3.1.16 *remedial goals*—remediation objectives established to protect human health and the environment. Remedial goals may be concentration-based target levels applied at specific points throughout the plume or performance-based criteria, such as demonstrated containment of the solute plume or demonstrated reduction in concentrations of constituents of concern over time within the plume or with distance from the source area.

3.1.17 *remediation/remedial action*—activities conducted to protect human health, safety, and the environment. These activities include evaluating risk, making no further action determinations, monitoring, and designing and operating cleanup equipment.

3.1.18 *remediation by natural attenuation*—a remedy where naturally occurring physical, chemical, and biological processes will achieve remedial goals. The use of natural attenuation processes as a remedial action also has been described by a variety of other terms, such as intrinsic remediation, intrinsic bioremediation, passive remediation, natural biodegradation, passive bioremediation, etc. Remediation by natural attenuation does not include remediation methods that require human intervention beyond monitoring.

3.1.19 *secondary lines of evidence*—geochemical indicators of naturally occurring biodegradation and estimates of natural attenuation rate.

3.1.20 *sentinel well*—monitoring points established at a location(s) between the leading edge of the solute plume and a sensitive receptor (for example, drinking water well) to ensure that there will be time for other remedial actions to be taken, if the plume does migrate beyond predicted boundaries.

3.1.21 *shrinking plume*—configuration where the solute plume margin is receding back toward the source area over time and the concentrations at points within the plume are decreasing over time.

3.1.22 *source area*—the location of free phase liquid hydrocarbons or the location of highest soil and ground water concentrations of constituents of concern.

3.1.23 *stable plume*—configuration where the solute plume margin is stationary over time and concentrations at points within the plume are relatively uniform over time or may decrease over time.

3.1.24 *user*—an individual or group involved in the corrective action process at petroleum release sites, which may include environmental consultants, industry, and state, local, and federal regulators.

4. Significance and Use

4.1 The approach presented in this guide is a practical and streamlined process for determining the appropriateness of remediation by natural attenuation and implementing remediation by natural attenuation at a given petroleum release site. This information can be used to evaluate remediation by natural attenuation along with other remedial options for each site.

4.2 In general, remediation by natural attenuation may be used in the following instances:

4.2.1 As the sole remedial action at sites where immediate threats to human health, safety and the environment do not exist or have been mitigated, and constituents of concern are unlikely to impact a receptor;

4.2.2 As a subsequent phase of remediation after another remedial action has sufficiently reduced concentrations/mass in the source area so that plume impacts on receptors are unlikely; or

---

[3] National Research Council (NRC), 1993, In Situ Bioremediation: When Does It Work? National Academy Press, Washington, DC.

4.2.3 As a part of a multi-component remediation plan.

4.3 This guide is intended to be used by environmental consultants, industry, and state and federal regulators involved in response actions at petroleum release sites. Activities described in this guide should be performed by a person appropriately trained to conduct the corrective action process.

4.4 The implementation of remediation by natural attenuation requires that the user exercise the same care and professional judgement as with any other remedial alternative by:

4.4.1 Ensuring that site characterization activities focus on collecting information required to evaluate and implement remediation by natural attenuation;

4.4.2 Evaluating information to understand natural attenuation processes present at the site;

4.4.3 Determining whether remediation by natural attenuation is the most appropriate and cost-effective remedial alternative with a reasonable probability of achieving remedial goals; and

4.4.4 Monitoring remedial progress.

4.5 Application and implementation of remediation by natural attenuation is intended to be compatible with Guide E 1739 or other risk-based corrective action programs.

4.6 This guide does not address specific technical details of remediation by natural attenuation implementation such as site characterization (see Guide E 1912), sampling, data interpretation, or quantifying rates. For additional discussion and guidance concerning these technical issues for remediation by natural attenuation see Appendix X1 through Appendix X7.

4.7 This guide does not specifically address considerations and concerns associated with natural attenuation of non-petroleum constituents, such as chlorinated solvents. Care must be taken to ensure that degradation by-products will not cause harm to human health or the environment. In addition, if constituents are present which do not readily attenuate, such as methyl-t-butyl ether (MTBE), remediation by natural attenuation may not be a suitable remedial alternative or may need to be supplemented with other remedial technologies.

4.8 This guide is intended to be consistent with Guide E 1599 and U.S. EPA guidance for implementation of remediation by natural attenuation (U.S. EPA, 1995, Chapter 9).[4]

5. Natural Attenuation as a Remediation Alternative

5.1 At petroleum release sites petroleum migrates outward from a source area through the environment creating a plume of petroleum constituents. The configuration of a solute plume is controlled by the source mass-loading rate relative to the removal rate of natural attenuation processes. Typically, the plume will expand until it reaches steady-state where the rate of petroleum constituents contributed from the source is balanced with the rate of natural attenuation. At steady-state the plume stabilizes. The time scale over which this steady-state condition is reached can vary depending on specific site conditions. When the source area is depleted to the point that the rate of natural attenuation exceeds the source input the result will be a shrinking plume over time.

5.2 Remediation by natural attenuation relies on natural attenuation mechanisms to degrade and reduce concentrations of constituents of concern in ground water. The natural processes involved are physical, chemical, and biological in nature such as dispersion, dilution, volatilization, sorption, and biodegradation. Biodegradation is the process which accounts for the majority of mass removal and associated concentration reduction for constituents of concern. Biodegradation actually reduces the mass of constituents through microbial metabolization of constituents of concern. The ultimate products of this reaction are carbon dioxide, water, and biomass. These mechanisms are described in Appendix X1.

5.3 The processes which contribute to remediation by natural attenuation occur to some extent at all sites. remediation by natural attenuation is effective when these naturally occurring attenuation mechanisms achieve remedial goals. Depending on site conditions, remediation by natural attenuation may be a long-term remedial option. Remediation by natural attenuation is a remedial action approach that is compatible with existing remedy selection processes. It is not exclusive of other options and should be evaluated in the same manner as other remedial action options for a site.

5.4 Remediation by natural attenuation should not be considered to be a presumptive remedy.

5.5 *Advantages of Remediation by Natural Attenuation as a Remediation Alternative*:

5.5.1 Petroleum hydrocarbon constituents of concern which undergo biodegradation can be ultimately transformed to innocuous products (for example, carbon dioxide and water), not just transferred to another phase or location within the environment.

5.5.2 Remediation by natural attenuation is less intrusive; it results in minimal disturbance to the site operations and allows continuing use of the site's infrastructure during remediation.

5.5.3 More conventional remedial technologies can pose greater risk to potential receptors than natural attenuation due to site disruption and/or an inability to properly control these engineered remedial processes (for example, risk to on-site workers, releases to atmosphere, fugitive vapors, induced migration, etc.).

5.5.4 Remediation by natural attenuation can be used in conjunction with conventional remedial technologies such as excavation, pump and treat, soil vapor extraction, bioventing, and dual-phase extraction. It can also be used at sites where other remedial technologies are not technically feasible to use to achieve required cleanup target levels.

5.5.5 Remediation by natural attenuation can be less costly than other currently available remedial technologies when implemented with an appropriate monitoring program.

5.5.6 Remediation by natural attenuation can be evaluated by collecting adequate and appropriate geologic and hydrogeologic data during the site characterization phase. Data can be collected using relatively inexpensive field and laboratory analytical methods (see Appendix X2 and Appendix X4). If it is shown that remediation by natural attenuation is not solely sufficient to provide adequate protection of potential receptors,

---

[4] U.S. EPA, 1995, Evaluating Alternative Cleanup Technologies for Underground Storage Tanks: A Guide for Corrective Action Plan Reviewers. U.S. Environmental Protection Agency, Office of Underground Storage Tanks, Washington, DC, EPA 510-B-95-007, May 1995.

the data collected for the remediation by natural attenuation study can be used to design supplemental remedial alternatives.

5.5.7 Use of remediation by natural attenuation can help to focus funds and efforts on sites which require active remediation.

5.5.8 Remediation by natural attenuation is not subject to the limitations imposed by the use of mechanized remediation equipment (that is, no equipment down-time) and can be employed for constituents of concern below buildings and other areas that are not accessible.

5.5.9 Constituents such as benzene, toluene, ethyl benzene, and xylenes (BTEX) that typically pose the greatest risk and are commonly the major constituents of regulatory concern at petroleum release sites are generally the most susceptible to biodegradation.

5.6 *Limitations of Remediation by Natural Attenuation as a Remediation Alternative*:

5.6.1 The ability of remediation by natural attenuation to achieve remedial goals can be sensitive to natural and human-induced changes in local hydrogeologic conditions and site operations. Potentially important effects include changes in ground water gradients/velocity, rainfall, temperature, pH, electron acceptor concentrations, exposures not previously anticipated, or potential future releases. Such changes could be brought about by alterations in land use, changes in the local pumping regime, removal of an asphalt cap, or third party impacts, or a change in the location of receptors.

5.6.2 Time frames for achieving remedial goals may be relatively long, particularly for heavier petroleum constituents, compounds which attenuate slowly, and sites with a large source mass. Remediation by natural attenuation may take longer to mitigate constituents of concern than for more aggressive remedial measures. Remediation by natural attenuation may not always achieve the desired cleanup levels within a manageable time-frame.

5.6.3 In the public perception, remediation by natural attenuation may be viewed as a “do-nothing” remedial alternative.

5.6.4 Long-term monitoring for remediation by natural attenuation can represent significant cost and a continued funding commitment.

5.6.5 Application of remediation by natural attenuation may require supplemental source area removal or more active remediation when exposure pathways are completed or receptors are potentially impacted.

5.6.6 Technical limitations may obstruct the implementation or progress of remediation by natural attenuation and require the consideration or use of other remediation alternatives. Such limitations can include constraints associated with inadequate data used to construct the site conceptual model, the inability to implement the monitoring program, insufficient data to perform predictive solute transport modeling, and changes in site conditions.

5.6.6.1 The implementation of remediation by natural attenuation fundamentally requires adequate definition of the solute plume and understanding of site hydrogeology. The lack of necessary site data or inability to obtain representative, or otherwise requisite samples, necessary to construct an acceptable site conceptual model (for example, aquifer parameters, ground water and soil chemistry, etc.) and design an adequate long-term monitoring plan can preclude appropriate implementation of remediation by natural attenuation.

5.6.6.2 Remediation by natural attenuation relies on empirical data generated by ground water monitoring. The inability to place monitoring points and collect ground water samples in appropriate locations due to surface obstructions or other impediments, changes in aquifer water levels rendering monitoring points unusable, and monitoring where the sampling and analytical protocols are not observed can preclude appropriate implementation of remediation by natural attenuation. Also, the inherent variability of the ground water monitoring data may preclude effective evaluation of plume behavior.

5.6.6.3 Remediation by natural attenuation requires that site conditions persist or do not change adversely. Actual or proposed land use changes may result in the site being reclassified to a higher risk level. A new source may introduce additional petroleum product to the system at the site or another up gradient plume may reduce available electron acceptors for biodegradation. Changes in aquifer conditions may alter the long-term ground water transport rates and direction or produce short-term changes that are unacceptable.

5.7 *Multiple Lines of Evidence to Demonstrate Appropriateness of Remediation by Natural Attenuation*:

5.7.1 The National Research Council (1993)[3] suggests a strategy to demonstrate in situ bioremediation which includes three types of evidence:

5.7.1.1 Documented loss of constituents of concern from the site;

5.7.1.2 Evidence showing bioremediation is actually realized in the field; and

5.7.1.3 Laboratory assays showing that microorganisms in site samples have the potential to transform constituents of concern.

5.7.2 This guide suggests the demonstration of remediation by natural attenuation may include primary, secondary, and optional lines of evidence. At a minimum, primary lines of evidence are required to demonstrate the effectiveness remediation by natural attenuation. The decision to collect secondary and optional lines of evidence should be based on the intended use of the data. The cost benefit of obtaining these lines of evidence should also be considered. The primary lines of evidence include constituent of concern data, used to define the plume as shrinking, stable, or expanding, similar to the first line of evidence suggested by NRC (1993).[3] For sites which have sufficient historical monitoring data, the primary lines of evidence will often be adequate to demonstrate remediation by natural attenuation.

5.7.3 Secondary lines of evidence include geochemical indicators of naturally occurring biodegradation and estimates of natural attenuation rate. If the primary lines of evidence are inconclusive, it may be necessary to obtain secondary lines of evidence. For those sites where assessment efforts have recently been initiated, it may be appropriate to supplement the primary lines of evidence by measuring indicators of naturally occurring biodegradation, consistent with the second line of evidence suggested by NRC (1993).[3] Estimates of attenuation rate are based on temporal and/or spatial trends for constituents of concern. Once this secondary line of evidence has been established, the user must continue to monitor and collect data to substantiate the primary line of evidence.

5.7.4 Optional lines of evidence may be used to more rigorously interpret data developed as secondary lines of evidence, particularly if the primary and secondary lines of evidence are inconclusive to demonstrate remediation by natural attenuation. Optional lines of evidence include solute transport modeling, estimates of assimilative capacity (to estimate the mass of BTEX and other constituents of concern degraded), and microbiological studies. Attenuation rates can be used in modeling transport of constituents of concern. Indicators of naturally occurring biodegradation can be used to estimate assimilative capacity. Microbiological studies, as suggested in the third line of evidence by NRC (1993),[3] confirm the presence of microorganisms in the subsurface. Once optional lines of evidence have been established, the user must continue to monitor and collect data to substantiate the primary line of evidence.

6. Decision Process for Appropriate Application and Implementation of Remediation by Natural Attenuation

6.1 The key components of the remediation by natural attenuation process are described in the following sections. The major decisions and actions required to determine the appropriateness of applying and implementing remediation by natural attenuation at a given site been are summarized in the flowchart shown in Fig. 1.

6.1.1 Site characterization and establishment of remedial goals;

6.1.2 Evaluation of plume status;

6.1.3 Comparing RNA performance to remedial goals;

6.1.4 Comparing RNA to other remedial options; and

6.1.5 Development and implementation of an appropriate monitoring program.

6.2 *Initial Response, Site Characterization, Determine Constituents of Concern, and Establish Remediation Goals*:

6.2.1 Initial response should be taken in accordance with implementing agency requirements to report any release of petroleum products; prevent any further release of, or exposure to hydrocarbons in vapor, dissolved, or liquid phase; and mitigate fire and safety hazards. Table 1 in Guide E 1739 provides example site classification and initial response actions.

6.2.2 The site characterization must provide the user with adequate information necessary to determine if remediation by natural attenuation is a viable remedial option for the site, either used by itself or in conjunction with other technologies. Site characterizations may be conducted in accordance with Section 7 of Guide E 1599, and Guide E 1912 taking into consideration evaluation of sources, pathways, and receptors as discussed in 6.2 of Guide E 1739. The types of site characterization information that may be necessary for remediation by natural attenuation are detailed in Appendix X2. Not all the data listed in Appendix X2 may be needed for each site and considerations for when and how this data can and should be used is explained in 6.3 and 6.4.

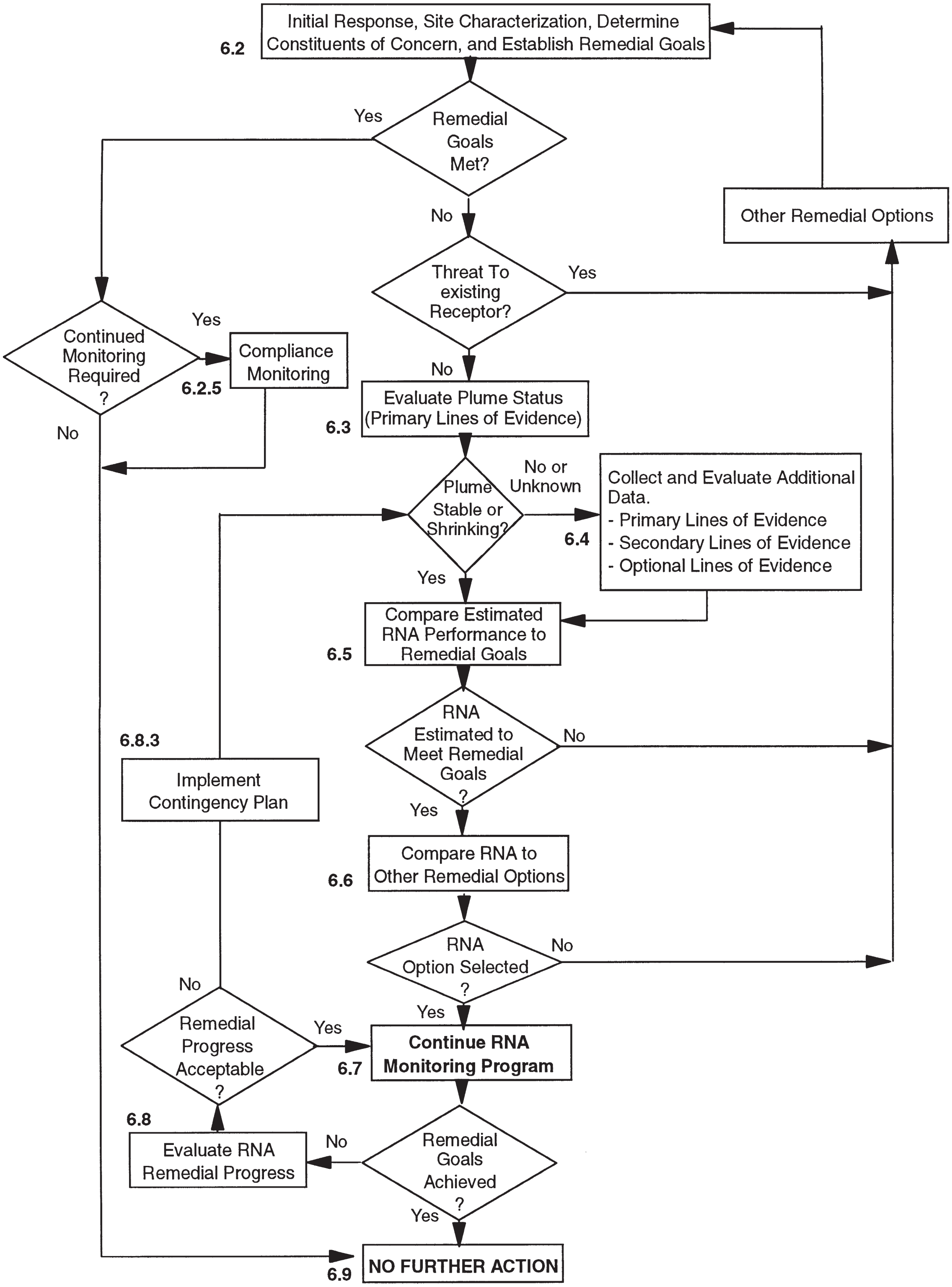
6.2.2.1 As part of the site characterization process an initial conceptual model should be developed before beginning any field work. The conceptual model should focus on specific features that are relevant to the assessment objectives. For example, the features of a conceptual model of a leaking underground storage tank site may include preliminary estimates of: (*1*) source areas; (*2*) three dimensional distribution of constituents of concern; (*3*) distribution of constituents of concern and impacts to ground water; (*4*) geologic units or structures that influence migration of constituents of concern; (*5*) ground water depth, flow direction and velocity; and (*6*) location of potential receptors and migration pathways. Hydrogeologic, and analytical data collected during the field investigation should be periodically interpreted and used to refine the conceptual model in an iterative process. The components of the conceptual model that are emphasized depends on the purpose of the assessment (See Guide E 1689, and Guide E 1912 5.4 and 5.7).

6.2.3 The determination of constituents of concern is based on the site specific consideration of exposure routes, concentrations, mobilities, toxicological properties, and aesthetic characteristics (taste, odor, etc.). In addition, regulatory requirements may dictate certain constituents of concern. Appendix X1 in Guide E 1739 contains additional discussion regarding determination of constituents of concern.

6.2.4 Remedial goals for the site should be determined by applying the risk-based corrective action process in Guide E 1739 or other accepted state-approved method. Remedial goals may take the form of concentration target levels or performance criteria, including demonstration of containment of the petroleum hydrocarbon plume. Remedial goals may also have some time frame associated with them. An evaluation of the need for source area control measures should be integrated into remedial decision-making at all sites where natural attenuation is under consideration. Source area control measures include physical removal, treatment, and stabilization.

6.2.4.1 Remedial goals may be concentration-based target levels applied at specific points throughout the plume or performance-based criteria, such as demonstrated containment of the solute plume or demonstrated reduction in concentrations of constituents of concern over time within the plume or with distance from the source area. Both must be protective of human health and the environment. In general, remediation by natural attenuation is more amenable to achieving performance-based remedial goals. Also, remediation by natural attenuation performance can provide verification of natural attenuation rates used to determine risk-based target cleanup levels developed through predictive solute transport modeling. When using remediation by natural attenuation as a containment option, institutional controls may be required to manage and prevent on- and off-site exposures.

6.2.5 Once remedial goals have been established, site conditions should be examined to see if these goals have already been met. If remedial goals have already been met at the site, the site may be deemed to require no further action. In some cases continued monitoring may be needed to confirm compliance with remedial goals prior to a determination of no further



NOTE 1—Numbers next to boxes in the flowchart refer to sections in the text.

FIG. 1 Remediation by Natural Attenuation Process Flowchart

action. If remedial goals have not been met at the site, then additional remedial action will be required.

6.2.6 The potential for impacts to human health and the environment must be determined by conducting surveys of primary and secondary sources, transport mechanisms, viable exposure pathways and potential receptors. Guide E 1739 provides a standardized approach to this type of analysis.

6.2.6.1 If the potential exists for immediate impacts to an identified receptor (for example, see Guide E 1739 Table 1), then other remedial actions or risk-management strategies may be required at the site. If risk-management strategies are not sufficient to prevent impacts to an identified receptor, then remediation by natural attenuation is inappropriate as a stand-alone option.

6.2.6.2 If the potential for a near-term impact to an existing receptor is determined to be low, then remediation by natural attenuation may be used as a stand-alone option for meeting remedial goals within the ground water.

6.3 *Evaluate Plume Status (Primary Lines of Evidence)*:

6.3.1 The dissolved petroleum constituent plume is categorized based on historical constituent of concern concentrations obtained from monitoring points. These historical data are the primary line of evidence for natural attenuation and are based on measured petroleum hydrocarbon concentrations over time to define the plume as shrinking, stable, or expanding. Evidence of reductions of constituents of concern is also the first line of evidence suggested by NRC (1993).[3] The implications of the three plume categories are as follows:

6.3.1.1 A shrinking plume is evidence of natural attenuation. The natural attenuation rate of a shrinking plume necessarily exceeds the mass loading rate of constituents of concern to ground water.

6.3.1.2 A stable plume is evidence of natural attenuation. The source of constituents of concern may persist in soils at the water table but the natural attenuation rate approximately equals the mass loading rate for constituents of concern to ground water.

6.3.1.3 In the case of an expanding plume the mass loading rate of constituents of concern to ground water exceeds the natural attenuation rate. An expanding plume will become stable when the mass loading rate of constituents of concern to ground water is balanced by the natural attenuation rate.

6.3.2 For sites which have sufficient historical monitoring data, the primary lines of evidence will often be adequate to demonstrate remediation by natural attenuation. For sites which have insufficient historical monitoring data, collection and evaluation of geochemical data may be appropriate to expedite the demonstration of remediation by natural attenuation. Paragraph 6.7 and Appendix X3 describe monitoring considerations.

6.3.3 The evaluation of plume status can be accomplished by either of the following methods, which are described in detail in Appendix X3.2.1 and Appendix X5. The effects of historical source removal and remediation efforts should be incorporated into the evaluation of plume status.

6.3.3.1 Monitoring points or other sampling devices should be located to allow the construction of contour maps for BTEX and other constituents of concern concentrations. Ideally, the map will include a non-detect or compliance level contour. Based on changes (or lack of changes) over time, the plume can be characterized as shrinking, stable, or expanding. The example problem in X7.1 illustrates this method.

6.3.3.2 Concentrations of BTEX and other constituents of concern can be determined over time at appropriately located monitoring points down gradient of the source and oriented along the direction of ground water flow (see 6.7 and Appendix X3 for important considerations regarding placement of monitoring points). The trend in BTEX and other constituents of concern concentrations at these points will determine whether the plume is shrinking, stable, or expanding (for example, if the plume is shrinking, concentrations will decrease over time or space; if the plume is stable, concentrations will remain relatively constant over time and space).

6.4 *Collect and Evaluate Additional Data*:

6.4.1 It may be necessary to obtain additional monitoring data before a plume can be defined as stable or shrinking. In the case of a newly discovered petroleum release site, the historical monitoring data necessary to evaluate plume status discussed in 6.3 will not be available. Therefore, one of the methods described in 6.3.3 may be used following additional monitoring events. For newly discovered sites, collection and evaluation of geochemical data may be appropriate to expedite the demonstration of remediation by natural attenuation.

6.4.2 Secondary lines of evidence may be required if the primary line of evidence, the evaluation of plume status, is inadequate or inconclusive to demonstrate remediation by natural attenuation. This may be the case for sites where only one or two monitoring events have been performed.

6.4.3 One secondary line of evidence is to estimate the natural attenuation rate. This estimate is based on the same data used in the evaluation of plume status (see 6.3). Another secondary line of evidence includes geochemical data which serve as indicators of naturally occurring biodegradation. Geochemical parameters are measured in ground water samples.

6.4.3.1 The estimate of attenuation rate can be performed by several methods. A mass balance approach is described in X6.1. The technique includes a calculation for the constituent of concern source rate (mass loading to ground water). This method yields an estimate for attenuation rate depending on whether the plume is shrinking, stable, or expanding.

6.4.3.2 Appendix X6.2 presents graphical and regression techniques to estimate the attenuation rate. These techniques include plots of (*1*) concentration versus time for individual monitoring points and (*2*) concentration versus distance for three or more monitoring points approximately oriented with ground water flow direction. Attenuation rates can be estimated by regression of concentration versus time or distance, or both. By plotting the log of concentration versus time or distance as a straight line (semi-log paper), the assumption of first-order decay can be demonstrated. The attenuation rate is graphically determined by the slope of the straight line. These calculations are described in X6.2. An example problem for concentration versus distance appears in X7.2.

6.4.3.3 Indicators of naturally occurring biodegradation are useful because biological transformation of petroleum hydrocarbons is the single most important process contributing to natural attenuation of petroleum constituents. Other attenuation processes (dispersion, sorption, dilution, volatilization) also contribute to reductions in concentrations of constituents of concern in ground water to a lesser extent. One line of evidence to demonstrate naturally occurring biodegradation, as suggested by the NRC (1993),[3] includes data which show that predicted biodegradation potential is actually realized in the field. To this end ground water monitoring points can be sampled for geochemical parameters to demonstrate naturally occurring biodegradation potential at field sites. These indicator parameters are summarized in Table 1.

NOTE 2—These are the most common parameters, other methods or parameters may also be useful in certain cases.

6.4.3.4 Temperature, pH, and conductivity are standard measurements for ground water sampling. Dissolved oxygen (DO) concentrations define aerobic versus anaerobic conditions. Oxidation reduction potential identifies oxidizing versus reducing conditions in ground water. Nitrate and sulfate may serve as electron acceptors after DO is consumed. Carbon dioxide, methane, ferrous iron, and manganese are the primary products of aerobic or anaerobic biodegradation of petroleum hydrocarbons. Paragraph X5.3.3 of Appendix X5 describes the significance of these indicator parameters. Sampling considerations and analytical methods for the indicator parameters are provided in Appendix X4.

6.4.4 Additional optional lines of evidence may be useful for the a small percentage of sites where the primary and secondary lines of evidence are inconclusive to demonstrate remediation by natural attenuation. These optional lines of evidence may include solute transport modeling, estimates of assimilative capacity, and microbiological studies.

6.4.4.1 Solute transport models may be used for several purposes. Transient analytical solutions can estimate the time required for a shrinking or expanding plume to reach a particular configuration. Steady-state solutions can be used to estimate the extent of a stable plume and aid in selection of locations of down gradient monitoring points. Appendix X6.3 describes the use of a steady-state solution which is coupled to the regression of concentration versus distance (see X6.2.2), for a stable plume.

6.4.4.2 One, two, and three-dimensional analytical solutions are presented in X6.4. The justification for two or three-dimensional analytical models should be based on the availability of data. Two of the more sensitive input parameters are the decay rate and source term. Site-specific attenuation or decay rates, as determined by one of the Appendix X6 methods, can be used in the analytical solution. A source of constituents of concern can be defined as a constant or decaying term.

TABLE 1 Indicator Parameters for Biodegradation

Dissolved oxygen	oxidation/reduction potential
pH	manganese
Temperature	alkalinity
Conductivity	methane
Nitrate	carbon dioxide
Sulfate	ferrous iron

6.4.4.3 Numerical models are appropriate where site characterization data are available to describe a complex hydrogeologic system. Numerical models require input parameters similar to those used for analytical models, but their spatial distributions must be known to warrant the use of these models **(1)**.[5]

6.4.4.4 The estimate of assimilative capacity uses the indicator parameters for naturally occurring biodegradation, presented 6.4.3.3 and described in X5.3. These indicator parameters can be used to estimate the potential mass of BTEX and other constituents of concern degraded per unit volume by aerobic and anaerobic respiration. The qualitative estimate determines the assimilative capacity of the measured electron acceptors to completely metabolize BTEX and other constituents of concern dissolved in ground water. This approach and its limitations are described in X5.3.2.

6.4.4.5 Microbiological studies are another line of evidence to demonstrate naturally occurring biodegradation. The NRC (1993) suggests the use of laboratory assays showing that microorganisms in site samples have the potential to transform the constituents of concern under the expected site conditions. There are at least two techniques to demonstrate the availability of microorganisms, microbial counts and microcosm studies, described in X5.3.5.2 and X5.3.5.3, respectively, of Appendix X5. Naturally occurring biodegradation of petroleum hydrocarbons is rarely limited by the availability of bacteria. For this reason, microbial counts and microcosm studies are not typically performed at petroleum release sites.

6.5 *Compare Estimated Remediation by Natural Attenuation Performance to Remedial Goals*:

6.5.1 Remediation by natural attenuation performance at a given site can be assessed by the following:

6.5.1.1 Plume behavior and containment due to remediation by natural attenuation;

6.5.1.2 Constituents of concern attenuation rates; and

6.5.1.3 Indicators of favorable biological conditions.

6.5.2 The performance of remediation by natural attenuation is generally acceptable if a plume is shrinking or stable (primary line of evidence) and there are no impacts to receptors. Risk reduction, containment, and performance goals are generally met if a plume is shrinking or stable. Secondary lines of evidence, such as estimates of natural attenuation rate and favorable biological conditions may also be used to demonstrate remediation by natural attenuation performance.

6.5.3 If a plume is expanding but at a rate lower than the ground water velocity, the risk reduction and performance goals may still be met depending on the presence and location of receptors. Further investigation and assessment may be necessary to more accurately predict the potential extent of plume migration and ensure protection of receptors.

6.5.4 A concentration-based goal may be achieved within a certain time frame if a plume is already shrinking. Remediation

---

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

by natural attenuation is a viable option for achieving concentration-based goals if the concentration is applied at an alternate point of compliance some distance from the source or the extent of natural attenuation between the source area and potential receptors is considered in setting concentration-based goals for source remediation. However, remediation by natural attenuation is unlikely to meet concentration-based remedial goals which require relatively low concentrations (for example, 5 ppb benzene) at or near the source of a petroleum release in short time frames. For a stable or expanding plume it is more difficult to estimate the time required to meet concentration-based goals at a given site with confidence. However, where a plume is stable and the primary source (for example, tank) is removed and no additional release adds to the source area, mass loading rate will eventually be reduced. An evaluation of the need for source area control measures should be integrated into remedial decision-making at all sites where natural attenuation is under consideration. Any source removal efforts undertaken should focus on those measures that effectively reduce mass loading rates to ground water.

NOTE 3—Source removal may be governed by technical feasibility as well as federal, state, and local guidelines.

6.6 *Compare Remediation by Natural Attenuation to Other Remedial Options*:

6.6.1 The purpose of this subsection is to describe the key considerations for comparing remediation by natural attenuation to other remedial options. The decision to implement remediation by natural attenuation over other alternatives should consider remedial goals, remedial time frame, risk reduction and exposure prevention, cost effectiveness, technical limitations, regulatory constraints, and land use. Each of these comparison criteria is discussed in more detail in the following paragraphs.

6.6.2 *Remedial Goals and Time Frame*—A major consideration when comparing remedial action alternatives is the probability that individual alternatives will meet the established remedial goals. As discussed in 6.5, if remediation by natural attenuation is likely to meet the remedial goals within the desired time frame, then it is a viable alternative. However, if the probability of remediation by natural attenuation meeting remedial goals within the desired time frame is low or uncertain, then supplementary or alternative remedial action measures may be appropriate (see 5.6.2). The time frame for achieving remedial goals is an important criterion for comparison of remediation by natural attenuation with other remedial options. Remediation by natural attenuation is generally a long-term option. However, care should be exercised in estimating remediation time frames for other remedial options so as to not bias the comparison with overly optimistic representations of cleanup time frames. If conflicts arise, time frame considerations are secondary to the goal of receptor protection.

6.6.3 *Risk Reduction and Exposure Prevention*—As part of a risk-based approach to corrective action, remedial options, including remediation by natural attenuation, should be compared to determine which alternative(s) are required to achieve an acceptable level of risk or exposure prevention. Remediation by natural attenuation should be considered a viable option if it provides the adequate level of risk reduction and exposure prevention. Another consideration may be the relative reduction in risk provided by remediation by natural attenuation versus other options and the expense required for the additional risk reduction provided by other remedial options. Additionally, the risks associated with other corrective action measures remedial technologies, such as direct exposure to impacted soils, releases to the atmosphere, and diversion of limited resources from high risk sites, should be considered.

6.6.4 *Cost Effectiveness*—In order to determine if remediation by natural attenuation is a cost effective remedial option, the costs of remediation by natural attenuation implementation need to be understood. Important costs associated with the implementation of remediation by natural attenuation include long-term monitoring and analytical expenses, costs to collect data and evaluate the lines of evidence supporting remediation by natural attenuation, and the potential costs of implementing institutional controls. In some cases, higher cost alternatives in the short term may be considered due to reduced long-term liability and monitoring costs.

6.6.5 *Regulatory Considerations*—The remediation by natural attenuation option, as with other remediation alternatives, is subject to approval by the regulatory agency which is responsible for the oversight of the cleanup of the petroleum release. Issues of regulatory concern may include requirements associated with the delineation of the plume; the degree to which free product needs be removed from the source area; whether performance-based (vis-a-vis concentration-based) remedial goals are acceptable; whether a time constraint is placed on achievement of the remedial goal; offsite migration; and length of time monitoring may be required.

6.6.5.1 Since each state has its own individual requirements regarding the application of remediation by natural attenuation, the user should consult with the appropriate regulatory agency to determine its current policy.

6.6.6 *Land Use*—Remediation by natural attenuation should be considered a viable option at locations where the reasonable potential land use is well defined and changes in land use which could cause exposure to constituents of concern are unlikely to occur without notice (for example, a retail service station to be operated for the foreseeable future in an area zoned commercial industrial). However, if the current land use is expected to change or is not restricted then reasonable potential future land uses should be considered prior to selecting remediation by natural attenuation as the preferred remedial option. In some areas, institutional controls such as restrictions on installation of water supply wells may need to be implemented to ensure that site uses which could create exposure to constituents of concern do not occur.

6.7 *Continue Monitoring Program for Remediation by Natural Attenuation*:

6.7.1 If the remediation by natural attenuation option is selected, it is necessary to develop and implement a monitoring program that both yields adequate information to evaluate the progress of remediation by natural attenuation in meeting remedial goals and is cost-effective. The cost associated with monitoring may well be the most expensive part of a natural attenuation remediation project. The objectives of the monitoring program are:

6.7.1.1 To evaluate performance and progress of remediation by natural attenuation toward meeting remedial goals; and

6.7.1.2 To ensure that the plume is not migrating to an extent greater than expected or in unexpected directions.

6.7.2 The monitoring program should include appropriate sampling locations, adequate sampling frequency, and meaningful sampling parameters. Monitoring considerations are discussed in Appendix X3. In some cases, the results of a solute transport model can be useful to aid in determining locations of monitoring points and appropriate sampling frequency.

6.7.3 *Sampling Locations*—The monitoring plan should include sufficient ground water monitoring points, both in number and location, to determine changes in ground water flow directions and velocities, trends in concentrations of constituents of concern within the plume (over time or distance, or both), and any further migration of the plume (Appendix X3).

6.7.3.1 For the evaluation of remediation by natural attenuation performance, monitoring point locations must include as a minimum, an up gradient monitoring point, two or more monitoring points within the plume, but outside any free product zone, and a down gradient monitoring point. An up gradient monitoring point will be required to establish the quality of ground water entering the site, both in terms of regulated constituents of concern and in terms of the secondary line of evidence if needed. A down gradient monitoring point, near the edge of the plume, will be necessary to establish the maximum extent of the plume in the direction of ground water flow. Consideration should be given to ground water flow rate and estimated solute transport velocities when selecting well spacing. In addition, monitoring points can be situated in a manner that will allow the gathering of data to determine plume behavior and remediation by natural attenuation progress, as discussed in 6.3, 6.4, 6.5, and Appendix X3.

NOTE 4—The previous discussion only addresses monitoring requirements directly related to evaluating the lines of evidence for natural attenuation. Other monitoring points and monitoring requirements may be necessary to fully evaluate ground water flow direction and seepage velocity.

6.7.3.2 Sentinel wells are monitoring points established at a location(s) between the leading edge of the solute plume and a sensitive receptor (for example, drinking water well) to ensure that there will be time for other remedial actions to be taken, if the plume does migrate beyond predicted boundaries. Sentinel wells always are required where a real use of ground water is threatened, or where entry into a surface water could occur. Sentinel wells may be appropriate but not required where a plume is suspected of expanding and neither of the two above conditions (existing use and potential entry into surface water) exist. Sentinel wells are optional to unnecessary for plumes where natural attenuation is apparent in the existing ground water monitoring network, where no real use of ground water is threatened, and where no entry into a surface water could occur. An adequate amount of site characterization must occur to document which, if any, of these conditions exists and to make the determination that a sentinel well is or is not appropriate.

6.7.4 *Monitoring Frequency*—Monitoring frequency is a site-specific consideration. The frequency with which long-term monitoring should be conducted based on plume status, water table fluctuations, ground water seepage velocity and the distance to receptors. For example, if the initial monitoring indicates that concentrations of constituents of concern fluctuate significantly over time, such as on a seasonal basis, a higher frequency of (shorter interval between) monitoring events will be necessary in order to establish (resolve) a significant trend. Alternatively, if concentrations of constituents of concern are relatively stable on a seasonal basis, a longer interval between monitoring events may be appropriate.

6.7.4.1 Monitoring frequency should be at least quarterly for a minimum of one year in order to define seasonal fluctuations in concentrations of constituents of concern, water table elevations, and hydraulic gradients. The lack of these data could make it very difficult or impossible to adequately resolve concentration trends in subsequent data sets. Subsequent monitoring should be conducted at a frequency appropriate to detect additional plume migration and changes in concentrations of constituents of concern. The length and frequency of monitoring will need to be determined on a site-specific basis and will depend on the present status of the plume, water-table fluctuations, ground water velocity, monitoring point spacing, and the distance from the plume to any sensitive receptor (see Appendix X3).

6.7.5 *Sampling Parameters*—Sampling parameters will include constituents of concern and may also include geochemical parameters as discussed in 6.5.

6.8 *Evaluate Remediation by Natural Attenuation Remedial Progress*:

6.8.1 Monitoring results should be evaluated to determine progress toward meeting remedial goals. As discussed in 6.5, remedial goals may be different depending on site specific conditions and regulatory requirements. If remedial goals are met, then no further action or a site closure plan may be implemented, as discussed in 6.9.

6.8.2 If remedial goals are not met, remediation by natural attenuation remedial progress needs to be evaluated. The evaluation is to determine the plume status and/or to demonstrate that natural attenuation is continuing to occur. This evaluation can be performed using the methodology described in 6.4 and 6.5. If historical data demonstrates that the solute plume has stabilized or is shrinking, then natural attenuation is occurring. If the solute plume is migrating at a rate significantly lower than expected based on the groundwater velocity, then remediation by natural attenuation is occurring to the extent that assumptions about the geology and groundwater conditions are correct."

6.8.3 If remedial progress matches estimates, remediation by natural attenuation monitoring program shall continue. If remedial progress does not match estimates, remediation by natural attenuation should be re-evaluated as to whether it is an appropriate remediation option for the site. If at any point during the long-term monitoring program, data indicates that natural attenuation is not adequate to achieve remedial goals, the contingency plan should be implemented. This plan could include considerations for changes in remedial approach including additional source removal, containment measures, more rigorous institutional controls, and augmenting remediation by natural attenuation with other remedial actions.

6.9 *No Further Action*:

6.9.1 When it can be demonstrated that target cleanup levels or performance-based criteria for the site have been achieved and further monitoring is no longer required to ensure that conditions persist, then no further action is necessary. Mechanisms or procedures must be implemented to ensure that institutional controls (if any) remain in place. Regulatory concurrence should be pursued on a determination of no further action.

6.9.1.1 If natural attenuation is demonstrated to be effective at a site and site conditions will not change, natural attenuation will continue to serve as an ongoing remedial action whether it is monitored or not.

6.9.2 *Key Criteria for No Further Action*—The key criteria for no further action at a site which has undergone remediation by natural attenuation are as follows:

6.9.2.1 There are no existing or potential receptor impacts (see, for example, Guide E 1739).

6.9.2.2 Remedial goals have been met, or it has been demonstrated that natural attenuation will continue and ultimately meet remedial goals (see 6.2.4).

6.9.2.3 The plume is stable or shrinking.

6.9.2.4 If needed, institutional controls are in place and maintained.

7. Keywords

7.1 attenuation; bioremediation; ground water; intrinsic remediation; natural attenuation; passive remediation; remediation; remedial action

APPENDIXES

(Nonmandatory Information)

X1. WHAT IS REMEDIATION BY NATURAL ATTENUATION?

X1.1 *Introduction*:

X1.1.1 Remediation by natural attenuation is the reduction in concentration, mass or mobility of chemical(s) of concern with distance and time due to naturally occurring processes in the environment. These processes can be classified as physical (such as dispersion, diffusion, dilution by recharge, and volatilization), chemical (sorption and chemical or abiotic reaction), and biological (biodegradation). The physical and chemical sorption processes result in the reduction of concentration and/or mobility of a chemical but not the total mass, and are referred to as "nondestructive" mechanisms. The chemical and biological reactions result in the reduction of the total contaminant mass in the system, and are referred to as "destructive" mechanisms. For petroleum hydrocarbons in the subsurface, biological degradation is often the most important process in the reduction of mass because the hydrocarbons are destroyed rather than phase partitioned.

X1.1.2 This appendix provides an overview of the processes of natural attenuation and their significance in the subsurface. It is divided into the following sections:

X1.1.2.1 Physical Processes,

X1.1.2.2 Chemical Processes, and

X1.1.2.3 Biological Processes.

X1.1.3 Much of the information presented is summarized from the references listed at the end of this appendix.

X1.2 *Physical Processes*—The physical processes of natural attenuation include hydrodynamic dispersion (diffusion and mechanical dispersion), dilution by recharge, and volatilization. These non-destructive mechanisms result in a reduction in the concentration of a chemical, but not the total mass in the system.

X1.2.1 Hydrodynamic dispersion, which includes molecular diffusion and mechanical dispersion, is the process whereby a contaminant plume spreads out in directions that are longitudinal and transverse to the direction of groundwater flow. It is generally the primary process causing dilution of dissolved constituents of concern.

X1.2.1.1 Mechanical dispersion describes the spreading of molecules due to interactions between advective movement of the chemical and the porous structure of the medium. It has two components, longitudinal dispersion which is the spreading of a solute in the direction of the ground water flow, and transverse dispersion which is the spreading in the direction perpendicular to the ground water flow. Longitudinal dispersion occurs because of variations in pore size, tortuosity (flow path length), and friction in the pore. Transverse dispersion is caused by the tortuosity of the porous medium which causes flow paths to branch out from the plume centerline **(2)**. Mechanical dispersion is the dominant mechanism causing hydrodynamic dispersion under normal advective flow systems.

X1.2.1.2 Molecular diffusion is the molecular movement of a chemical in response to concentration gradients, even in the absence of ground water flow. The molecular diffusion of a dissolved chemical in ground water is described by Fick's law. It is an attenuation mechanism that is negligible in normal advective flow systems because it is insignificant relative to mechanical dispersion, but is important in no-flow and very low ground water velocity situations **(3)**.

X1.2.1.3 The overall result of hydrodynamic dispersion is spreading and mixing of the contaminant plume with ground water. In addition to the dilution effect, which reduces the plume concentration, dispersion can facilitate biodegradation of organic compounds by spreading the plume into areas with more electron acceptors.

X1.2.2 Recharge due to precipitation, leakage from waterbodies or leakage from underlying aquifers introduces additional water into the solute plume. This results in dilution of the solute plume. An additional effect on natural attenuation is that supplemental dissolved oxygen can be furnished to the contaminant plume to increase the overall electron acceptor capacity for biodegradation of organic hydrocarbons. A similar phenomenon can be observed with the presence of trapped gas due to water level fluctuations caused by seasonal changes in aquifer recharge and discharge **(4)**.

X1.2.3 Volatilization causes a mass loss of volatile organic compounds from the subsurface to the atmosphere under the appropriate conditions. While not a destructive attenuation mechanism, it does remove contaminants from ground water. It is important for fresh spills of petroleum products, for older but highly volatile petroleum constituents (that is, jet fuel), and for free phase product and high levels of dissolved constituents of concern. As time passes after a discharge, this mechanism becomes less important.

X1.2.3.1 The volatilization process usually contains two steps: (*a*) the chemical from the impacted media (soil or ground water) volatilizes to the soil gas, that is, air in the soil pores, and (*b*) when ground water is shallow, the volatilized chemical in the gas phase moves into the atmosphere above the soil surface. The volatilization rate and the amount of mass loss depend on chemical-specific factors (Henry's law constant and diffusion coefficient) as well as media-specific conditions such as climate, depth to water, sorption, temperature, effective porosity, and soil type **(5, 6)**.

X1.2.3.2 Henry's law governs the tendency of a dissolved chemical to volatilize from ground water into the soil gas and is given by:

$$C_a = HC_l \tag{X1.1}$$

where:

H = Henry's law constant (dimensionless),
C_a = Concentration in air (g/cm^3-vapor), and
C_l = Concentration in water (g/cm^3-water).

The Henry's law constants of hydrocarbons range over several orders of magnitude **(7)**. Values of Henry's law constants for the BTEX compounds are given in Table X1.1. Volatilization can also affect NAPLs in the subsurface but this process is not described by Henry's law. In the study of Chiang et al. **(8)**, volatilization was calculated to account for no more than 5 % of the total mass loss of benzene. At sites where the water table is shallow or highly fluctuating, volatilization may contribute more to the total mass loss.

TABLE X1.1 Henry's Law Constants and Organic Carbon Partition Coefficients for Common Fuel Hydrocarbon Compounds[A]

Chemical	Henry's Constant, H (dimensionless)	Organic Carbon Partition Coefficient, log (K_{oc}), L/kg
Benzene	0.22	1.58
Toluene	0.26	2.13
Ethyl Benzene	0.32	1.98
Xylenes (mixed)	0.29	2.38

[A] Guide E 1739 (Standard for Risk-Based Corrective Action (RBCA) at Petroleum Release Sites).

X1.3 *Chemical Processes*—The chemical processes that cause natural attenuation include sorption and chemical (abiotic) reactions. Sorption is controlled by chemical forces and interactions in nature. It not only affects the chemical's mobility but also the rates of other transport and transformation reactions. Nonetheless, sorption can also be considered as a physical process because the mechanism itself does not result in irreversible changes of the compound. Abiotic chemical reactions refer to those reactions that do not involve metabolically active microorganisms or extracellular enzymes. While many organic chemicals in soil systems can be transformed through one or more chemical reactions, there is no evidence of abiotic chemical transformation of BTEX in the subsurface environment **(9)**.

X1.3.1 The term sorption is used to describe the interphase interaction of a chemical between the water and the soil. The sorption process retards the migration of mainly hydrophobic chemicals in the aquifer relative to the ground water flow velocity, and reduces the dissolved concentration in ground water, but usually results in higher concentrations in the soil phase. Thus, it is an attenuation mechanism that does not reduce the total mass, but affects the mobility and concentration of the chemical.

X1.3.1.1 Sorption is a complicated phenomenon caused by several chemical forces and interactions between chemicals and the aquifer matrix. For hydrocarbons of nonpolar molecular structure, sorption occurs mainly through the process of hydrophobic bonding **(10)**. Two components of the aquifer matrix have the most effect on sorption: organic matter and clay minerals. In most aquifers, sorption is controlled by organic matter. However, if the aquifer matrix has little organic matter, then sorption to the mineral surface may become important.

X1.3.1.2 The kinetics of sorption are also complicated as the result of the nonlinear and nonequilibrium behavior of specific compounds. A sorption isotherm describes the relationship between the concentration of chemical sorbed onto the soil and the concentration remaining in solution at equilibrium. The commonly used isotherms include the Langmuir isotherm, the Freundlich isotherm, and the linear isotherm (a special case of the Freundlich isotherm) **(11)**. The sorptive behavior of multi-compound systems are usually difficult to predict from those of individual compounds **(12)**.

X1.3.1.3 The most commonly used method of representing the distribution of an organic chemical between the soil and the ground water is the distribution coefficient (also called the partition coefficient), K_d:

$$K_d = C_a/C_l \tag{X1.2}$$

where:

K_d = distribution coefficient (cm^3/g),
C_a = sorbed concentration (g/g-soil), and
C_l = dissolved concentration (g/cm^3-solution).

The distribution coefficient is the slope of the sorption isotherm. The greater the distribution coefficient, the greater the sorption of the chemical. For systems described by a linear isotherm, the distribution coefficient is a constant. The distribution coefficient of an organic chemical also depends on the properties of the soil in the system. In general, the distribution coefficient increases as the fraction of organic carbon (f_{oc}) increases in the soil **(13)**. The linear relationship is likely to fail when the soil contains a low organic carbon fraction (less than 0.001) or large amounts of mineral clays, or when the organic compound is polar **(11)**.

X1.3.1.4 Two approaches are generally used to quantify the distribution coefficient for a given system **(11)**. The first method involves conducting batch or column sorption tests to determine K_d. The second method involves estimating K_d by using the organic carbon partition coefficient (K_{oc}) and the f_{oc} of the soil, where $K_d = (K_{oc})(f_{oc})$. A correlation has been developed to estimate K_{oc} based on readily available chemical properties such as water solubility or the octanol-water partition coefficient. Typical values of K_{oc} used for BTEX compounds are given in Table X1.1. Applicability of the second method has the same limitations as the linear relationship between K_d and f_{oc} discussed earlier. For systems where inorganic matter dominates the sorption, the surface area of the soil particles becomes important in determining K_d **(14)**.

X1.3.1.5 The retardation coefficient *R*, which is determined from the distribution coefficient, is often used to describe the attenuation of the plume due to sorption:

$$R = 1 + \rho_b K_d / n \qquad \text{(X1.3)}$$

where:

ρ_b = bulk density (g/cm^3), and

n = total porosity (cm^3/cm^3).

The retarded transport velocity of a sorbing chemical, v_c, is then given by:

$$v_c = v_x / R \qquad \text{(X1.4)}$$

where:

v_x = ground water seepage velocity, given by $v_x = ki/n_a$ (k = hydraulic conductivity, i = hydraulic gradient, and n_a = effective porosity).

X1.3.1.6 In addition to the retardation effect on natural attenuation of a chemical, sorption can also influence the relative importance of other attenuation processes. For example, the rates of volatilization, chemical reactions, and biodegradation of many organic chemicals are directly dependent upon the extent of adsorption **(7)**.

X1.3.2 The terms chemical and abiotic reactions in this text refer to non-biological transformation and degradation. Different from all the non-destructive attenuation mechanisms discussed above, they are classified as destructive. The results of an abiotic reaction may produce a compound of more or less environmental concern and of enhanced or decreased biological degradability. For petroleum hydrocarbons such as BTEX, the abiotic reactions are not important in the subsurface environment **(15)**.

X1.3.2.1 For organic compounds, the following chemical reactions are known to occur in the subsurface environment **(5,11)**: (*a*) hydrolysis/substitution occurs when an organic chemical reacts with either water or a hydroxide ion to produce an alcohol (hydrolysis) or with another anion as the nucleophilic agent (substitution); (*b*) elimination is the loss of two adjacent groups within a molecule and results in the formation of a double bond; (*c*) oxidation/reduction involves the transfer of electrons from one compound to another. However, in natural subsurface environments, biological systems tend to be predominant in these redox reactions **(16)**.

X1.4 *Biological Processes*—Like the abiotic chemical reactions, biodegradation is a destructive attenuation mechanism. Many studies have demonstrated that biodegradation by indigenous microbes can contribute significantly to the destruction of organic compounds (see Ref **(1)** for a list of references). For petroleum hydrocarbons, biodegradation is considered to be the primary mechanism by which the solute mass is removed. A brief description of the biological process is given here, Appendix X5 and Ref **(1)** provide further discussion of the metabolism of hydrocarbons involving the various electron acceptors.

X1.4.1 Biodegradation is an electron transfer process. The energy required for cell synthesis and maintenance is obtained through the oxidation of hydrocarbon compounds. Electrons are removed from organic substrates (electron donors) to capture the energy available through the oxidation process. Terminal electron acceptors are needed for the electrons moving through electron transfer or respiratory chains.

X1.4.2 Aerobic respiration is the most facile of the terminal electron accepting reactions used for biodegradation of petroleum hydrocarbons. This degradation process takes place in the presence of aerobic microbes. The ultimate products from the mineralization of organic compounds are carbon dioxide, water and cell mass. Facultative anaerobic organisms can use oxygen when it is present or can switch to alternative electron acceptors

X1.4.3 Other electron acceptors including nitrate, sulfate, ferric ion, manganese, and so forth, will be used when oxygen is not available. Obligate anaerobic organisms become dominant in the absence of oxygen. The rate of degradation may be relatively slow under anaerobic conditions. The metabolic products of anaerobic biodegradation include simple organic acids, CO_2, H_2O, CH_4, H_2, N_2, and cell mass.

X2. SITE CHARACTERIZATION FOR EVALUATION OF NATURAL ATTENUATION

X2.1 The purpose of this appendix is to discuss the site characterization data typically required to evaluate natural attenuation of constituents of concern in ground water. This appendix does not cover all site characterization information which may be required in a site assessment, but does include most of the site characterization data which are used directly in evaluating natural attenuation. Table X2.1 includes a brief description of each piece of site characterization information, the use of the data in evaluating natural attenuation, and a reference containing detailed methods for data collection.

TABLE X2.1 Site Characterization Data for Natural Attenuation at Petroleum Release Sites

NOTE 1—This table describes the typical site characterization information recommended to evaluate natural attenuation. Only the characterization information which is considered directly relevant to most evaluations of natural attenuation is discussed. Additional information may be necessary based on site specific considerations or some of the listed items may not be necessary.

Site Characterization Data	Application	Sources/Methods/Protocols[A,B]
Type of petroleum hydrocarbon released. gasoline, diesel, waste oil, etc.	The type of petroleum hydrocarbon released is needed to evaluate the amount of specific contaminants present, effective solubilities, and long term behavior of the source.	Directly from knowledge of type released. Analytical Methods. Gasoline, jet fuel, kerosene in soil or ground water - EPA 5030/8015. Diesel in soil - EPA 3550/8015. Diesel in ground water - EPA 3550/8015. It is recommended that results of these analyses be reported by carbon number range and chromatograms be examined to identify type of petroleum hydrocarbon. Waste Oil - EPA 418.1.
Date of release and date discovered.	Needed for calculation of expected plume travel distance and evaluation of time required to reach stability.	Inventory records. Release reports. Leak detection monitoring data.
Volume released.	Estimation of mass of each contaminant present and rate of decrease in source concentrations	Inventory records, size of tank. Estimates based on free product thickness in monitoring wells should be considered to have a high degree of uncertainty.
Regional Hydrogeology	Identify drinking water aquifers and regional confining units, and regional flow patterns.	State and Federal government agencies and technical publications.
Definition of site lithology and stratigraphy.	Assess preferential directions of ground water flow and contaminant transport. Guide proper location of monitoring points. Determine appropriate screened intervals for monitoring points. Identify hydrogeologic features which may prevent impact to potential receptors.	Guide D 5434 Field Logging of Subsurface Explorations of Soil and Rock
Survey of nearby water supply wells.	Identify locations of nearest potential ground water receptors.	Local health department and water agency records.
Locations of potential receptors	Identify potential exposure pathways of concern.	Guide E 1739 Risk Based Corrective Action Applied at Petroleum Release Sites
Identify high conductivity pathways. Natural or Anthropogenic.	Determine if natural geologic conditions or utility trenches, ditches, or subsurface utilities may impact groundwater flow direction and velocity. Determine if immediate action is necessary. Properly locate monitoring points.	As-built facility drawings from current or previous property owner. City or locality records on subsurface utilities.
Depth to ground water.	Evaluate impact of unsaturated soil contamination on ground water. Evaluate volatilization of contaminants from ground water.	Test Method D 4750 Determining Subsurface Liquid Levels in a Borehole or Monitoring Well(Observation Well)
Water Level Elevations	Determine direction of ground water flow. Determine horizontal and vertical hydraulic gradients to enable calculation of ground water flow velocities.	Test Method D 4750 Determining Subsurface Liquid Levels in a Borehole or Monitoring Well(Observation Well)
Direction of ground water flow.	Evaluate the predominant direction of flow and any seasonal variations. Proper placement of monitoring points. Identification of potential receptors.	

TABLE X2.1 *Continued*

Site Characterization Data	Application	Sources/Methods/Protocols[A,B]
Range of seasonal water level fluctuations.	Estimate source smear zone. Estimation of mixing zone for leaching. Variability of contaminant concentrations.	Periodic monitoring of water levels.
Hydraulic conductivity	Estimate ground water velocity and rate of transport of contaminants.	Pump tests or slug tests (D 4043-91, ASTM Test Methods D 5270-92, D 4105-91, D 5473-93, D 4104-91, D 4106-91, D 5269-92, D 4044-91, D 4050-91)
Delineation of dissolved phase contaminant plume.	Evaluate transport of contaminants and estimate attenuation rates.	ASTM D 4448 Guide for Sampling Ground water Monitoring Wells ASTM D 5092 Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers.
Potential for vertical migration	Vertical gradients and possible vertical contaminant migration should be assessed if regional hydrogeology or site specific information indicate a reasonable potential for vertical migration.	Multilevel piezometers and sampling points with relatively short screened intervals are recommended for evaluating vertical gradients and extent.
Porosity	Calculate ground water seepage velocity and retardation factors.	Typically determined from the literature based on soil type(s) or calculated based on bulk soil density measurements.
Aquifer thickness	Identify confining layers which prevent impact to deeper aquifers. Proper design of monitoring points.	Soil borings, cone penetrometer, regional hydrogeology.
Collect biological indicator data. Terminal electron acceptors. Degradation byproducts. Environmental conditions.	Described in detail in Appendix X4 and Appendix X5.	Described in detail in Appendix X4 and Appendix X5.
Extent of unsaturated soil impact. Vertical and lateral extent. Residual soil content.	Evaluate expected long term behavior of source.	ASTM D 1452 Practice for Soil Investigation and Sampling by Auger Borings. ASTM D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils. ASTM D 4700 Guide for Soil Sampling from the Vadose Zone.
Extent of residual separation phase and sorbed phase hydrocarbon. Soil Only. Soil and Ground Water. (includes both mobile and immobile hydrocarbon)	The extent of residual hydrocarbon impact is needed for evaluation of soluble plume attenuation. Wells at the downgradient edge of the source should be used to represent source concentrations, and distances to other wells should be determined from the downgradient edge of the source. The extent of the source area data on the presence of free product are necessary to evaluate free product transport.	ASTM D 1452 Practice for Soil Investigation and Sampling by Auger Borings. ASTM D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils. ASTM D 4700 Guide for Soil Sampling from the Vadose Zone.
Chemical analysis of separate phase hydrocarbon for BTEX.	Estimate source equilibrium concentrations. Evaluate long term leaching behavior of source.	For gasoline, jet fuel, kerosene or diesel use EPA 3580 for dilution/extraction and then analyze for BTEX by EPA 602, 8020, 8240, or 8260.
Locations of ground water recharge and discharge areas.	Identify areas where ground water aeration occurs or where water containing electron acceptors (particularly oxygen) enters the subsurface.	Visual observation of site.
Organic carbon content of saturated zone soils.	Determine retardation factor for components of soluble plume to estimate rates of transport.	Modified Mebius Procedure (heated rapid potassium dichromate oxidation) (Page 1982).

[A] EPA Methods - Test Methods for Evaluating Solid Waste, 1992. USEPA, Office of Solid Waste and Emergency Response, Washington D.C., SW-846.

[B] "Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, Second Edition," A.L. Page, editor, Agronomy, No. 9 (Part 2), American Society of Agronomy, Inc./Soil Science of America, Inc., 1982. (ISBN 0-89118-072-9 (pt. 2)) pp. 571-573.

X2.2 Table X2.1 lists the site characterization data which can be used as the primary lines or secondary lines of evidence. In characterizing a site for the primary lines of evidence, it is necessary to understand the site lithology, the direction and velocity of ground water flow, the type of hydrocarbons released, the extent of the soluble contaminant plume, and the locations of potential receptors. In the case of a newly discovered petroleum release site, the historical monitoring data necessary to evaluate plume status will not be available. For newly discovered sites, collection and evaluation of geochemical data in addition to the primary lines of evidence may be appropriate to expedite the demonstration of remediation by natural attenuation.

NOTE X2.1—This appendix is not intended to be an exhaustive list of methods and procedures. Other methods which provide equivalent data may be used as well.

X3. MONITORING CONSIDERATIONS

X3.1 *Introduction*:

X3.1.1 In any natural attenuation program, the placement of monitoring wells and the development of a monitoring protocol will be site specific.

NOTE X3.1—The following discussion only addresses monitoring requirements directly related to evaluating the lines of evidence for natural attenuation. Other wells and monitoring requirements may be necessary to fully evaluate groundwater flow direction and seepage velocity. In addition, other methods and requirements may be necessary in fractured rock systems.

X3.1.2 For the evaluation of remediation by natural attenuation performance, monitoring point locations must include as a minimum, an up gradient monitoring point, two or more monitoring points within the plume, but outside any free product zone, and a down gradient monitoring point. Other monitoring points and monitoring requirements may be necessary to fully evaluate ground water flow direction and seepage velocity.

X3.2 *Monitoring Well Placement*—An upgradient well will be required to establish the quality of groundwater entering the site, both in terms of regulated contaminants and in terms of the concentrations of terminal electron acceptors and their reduction products. A downgradient well, outside the plume, will be necessary to establish the maximum extent of the plume in the direction of groundwater flow. Consideration should be given to ground water flow rate and estimated solute transport velocities when selecting well spacing. In addition, monitoring wells should be situated in a manner that will allow the gathering of data to determine one or more of the following:

Plume type (stable, shrinking, expanding)
Natural attenuation rates
Warning of impact on sensitive receptor(s)

X3.2.1 *Characterization of Plume Type*—The primary line of evidence for natural attenuation is to define the plume as stable, shrinking or expanding. Wells must be positioned in a manner which will allow plume characterization. This can be accomplished in one of the two following ways: (*1*) wells should be positioned in a manner that will allow the drawing of BTEX contour maps. Ideally, the map will include a nondetect or compliance level (for example, drinking water criterion) contour. Based on changes (or lack of changes) in the contours over time, the plume can be characterized as expanding, shrinking or stable. (*2*) Alternatively, the BTEX concentration(s) in two or more wells located within the plume and downgradient of the source and oriented along the direction of groundwater flow can be monitored over time. The wells must contain measurable BTEX levels. The trend in BTEX concentrations will determine whether the plume is stable, shrinking or expanding (for example, if the plume is shrinking, concentrations will decrease over time or space; if the plume is stable, concentrations will remain relatively constant over time and space). The positioning of new wells may be based on data from previously installed wells, soil gas surveys, Geoprobe-type investigations or other approaches discussed in Appendix X2. Paragraph X3.2.4 covers other issues related to well placement and groundwater monitoring.

X3.2.1.1 Using secondary lines of evidence, terminal electron acceptors and their reduction products are monitored. This information may be presented by drawing terminal electron acceptor/reduction product contours alongside BTEX contours. As an alternative, electron acceptor/reduction product and BTEX concentrations versus distance from the source area may be plotted. Either approach will yield the information necessary to evaluate the relationship between BTEX and electron acceptor/reduction product concentrations.

X3.2.2 *Determining Natural Attenuation Rates*—Secondary lines of evidence includes evaluating natural attenuation rates. Several methods exist for measuring natural attenuation or biodegradation rates, or both, at a site, including the mass-balance (for any plume type), the concentration-versus-time (for a shrinking plume) and concentration-versus-distance (for a stable plume) approaches. These methods are discussed in detail in Appendix X6. Generally, the positioning of new wells may be based on data from previously installed wells, soil gas surveys, Geoprobe-type investigations or other approaches discussed in Appendix X2. Considerations specific to positioning wells for optimizing rate measurements are as follows:

X3.2.2.1 *Mass-balance Approach*—Well positioning is not a critical issue for the mass-balance approach. This approach will require: (*1*) a reasonable estimate of the source area perpendicular to groundwater flow, which can be determined through site investigation techniques discussed in Appendix X2 and (*2*) a reasonable estimate of site hydraulic conductivity and gradient.

X3.2.2.2 *Concentration-Versus-Time Approach*—If the plume is shrinking and a concentration-versus-time approach is to be used, one or more wells containing measurable BTEX levels will need to be positioned outside any free-product zone. It will be best to evaluate the change in BTEX concentration with time in more than one well.

X3.2.2.3 *Concentration-Versus-Distance Approach*—In a situation where the plume is stable and a concentration-versus-distance approach is used, it is appropriate to locate three wells (although two wells can be used) downgradient of the source and oriented along the direction of groundwater flow. Well placement will be satisfactory if at least two wells have measurable BTEX concentrations (the third, if used, can be nondetect) and each well differs in BTEX concentration by several fold from its upgradient neighbor.

X3.2.3 *Warning of Impact on Sensitive Receptor(s)*—One or more sentinel wells should be established at a compliance point(s) between the impacted groundwater and a sensitive receptor (for example, drinking water well). Such wells will call for longer-term monitoring and will ensure that there will be time for other remediation steps to be taken, if the plume does spread beyond predicted boundaries.

X3.2.4 *Other Considerations for Well Placement*—At any site, the need for additional wells can be evaluated based on a number of factors. Additional wells may be required to demonstrate that no "holes" exist in the monitoring network that would allow contamination to escape undetected. This issue is of particular concern in heterogeneous hydrogeological environments or fractured systems, where contaminants could migrate along discreet (but unmonitored) high-permeability pathways. No rules of thumb exist for the number of wells required; common sense and experience are the best guides. Additional wells may also be required to determine the depth (that is, thickness) of the plume, or the thickness, or both, of the upper-most water-bearing zone. At a particular site, the bottom of the upper-most water-bearing zone may not be defined by site data, and deeper portions of the zone may not be monitored. In this case, the three-dimensional extent of the plume is not characterized, and at least one deeper well may be required to demonstrate that the "bottom" of the plume is defined and/or geologically contained. Finally, it is important to note that care must be taken such that groundwater monitoring wells do not puncture an aquiclude (that is, confining layers between a contaminated and uncontaminated aquifer).

X3.3 *Monitoring Frequency*—The length and frequency of monitoring will need to be determined on a site-specific basis and will depend on the present status of the plume, water-table fluctuations, groundwater velocity, solute transport velocities and the distance from the plume to any sensitive receptor. As a general rule, though, enough information can be gathered in one year of quarterly monitoring to establish the relationship between BTEX and terminal electron acceptor (and their reduction products) concentrations. More than one year of monitoring may be necessary to establish whether the plume is stable, shrinking or expanding.

X3.4 *Monitoring Natural Attenuation at Pre-existing Sites*—It should be noted that at sites with historical contamination, large numbers of wells may have been already installed and several years of monitoring data may exist. In such cases, further installation of wells will not likely be necessary if the extent of the constituents of concern is defined. In addition, because of the already existing data base, monitoring frequency can often be substantially reduced compared to that required at a new site.

X3.5 *Well Installation Procedures*—Appropriate monitoring well installation procedures, as well as procedures for determining hydraulic conductivity and gradient, are covered in various ASTM documents and in the Air Force Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring For Natural Attenuation of Fuel Contamination Dissolved in Groundwater, as well as in State-specific guidelines.

X4. SAMPLING CONSIDERATIONS ND ANALYTICAL METHODS FOR NATURAL ATTENUATION INDICATORS

X4.1 Table X4.1 serves as a guide for selection of natural attenuation indicator parameters to be evaluated, the appropriate analytical methods, special sampling considerations, and the potential use of the data. This table is intended to provide guidance only, site specific considerations should be used when selecting the relevant natural attenuation indicator parameters.

NOTE X4.1—Not all of the parameters listed may be required.

TABLE X4.1 Sampling Parameters, Methods, and Special Considerations for Evaluating Remediation by Natural Attenuation in Groundwater for Petroleum Release Sites

Primary Lines of Evidence (Contaminant plume behavior):

The most reliable and direct demonstration of remediation by natural attenuation is based on the actual historical behavior of the contaminant plume. If historical data demonstrate that a plume has stabilized or is shrinking, then significant remediation by natural attenuation is occurring. If monitoring data indicate a plume is migrating or historical data are not available, then it is recommended that the secondary lines of evidence be evaluated in addition to the primary lines of evidence.

Parameter	Field or Laboratory Method	Analytical Method(s) (or equivalent method)	Comments	Use of Data
Benzene Toluene Ethylbenzene Xylenes Methyl Tertiary Butyl Ether (MTBE)	Laboratory	Purge and Trap GC Soil EPA 5030/8020 EPA 8240/8260 Ground water EPA 602 EPA 5030/8020 EPA 5030/8240 EPA 8260	Standard method - collect samples in 40 ml VOA vials, preserve on ice and acidify with HCl to pH = 2. Sampling frequency should be based on site specific conditions. During first one to two years of monitoring quarterly to semiannual sampling is recommended to understand seasonal variability. Frequency of long term monitoring should depend on plume stability and potential travel time to receptors.	For the primary lines of evidence, historical contaminant plume data is used directly to determine if a plume is expanding, stable, or shrinking. In some cases, historical data showing plume stability and no impact to potential receptors will be sufficient to support application of remediation by natural attenuation.
Conductivity	Field	EPA method 120.1 or SW-9050 direct-reading meter ASTM D 1125^A	Analyze in flow through cell or collect 100 to 250 mL of water and analyze immediately.	Conductivity can be used as an indicator that samples taken from separate sampling points are from the same hydrogeological zone.
Other potential parmaters/contaminants of interest.				

TABLE X4.1 *Continued*

Secondary Lines of Evidence (Contaminant plume behavior and indicators of biodegradation)

These parameters are collected as apparent indicators of biodegradation. In some cases, sufficient historical contaminant plume data may exist to evaluate remediation by natural attenuation and no further information is necessary. However in some cases it may be necessary or beneficial to better understand the potential for intrinsic biodegradation at a site. This may be the case for new releases with no historical plume data or sites with insufficient historical plume. These parameters may be used as indicators of potential aerobic and anaerobic biodegradation. It is recommended that sampling and analysis of these parameters be conducted in the initial site characterization and investigation. This entire list of parameters is not intended to be mandatory as knowledge of the geologic setting and site specific considerations may be used to select the parameters which are likely to provide important information. After the initial sampling event, only those parameters which may be significant should be included in future sampling events as needed. The cost and benefits of collecting secondary indicator data should be weighed when determining what parameters to collect in future monitoring events and in determining the frequency of sample collection.

Parameter	Field or Laboratory Method	Analytical Method(s)	Comments	Use of Data
pH	Field	EPA Method 150.1 or SW-9040 direct reading meter ASTM D 1293[A]	Can be analyzed in flow through cell or collect 100-250 mL of water in glass or plastic container and analyze immediately. Calibration should be conducted using manufacturers standard solutions.	Difference in pH between contaminated and uncontaminated groundwater may indicate biological activity is occurring.
Temperature	Field	EPA Method 170.1	Available from some DO, ORP, pH, or EC probes. Can be analyzed in flow through cell or from 100-250 mL of water collected and analyzed immediately.	Oxygen solubility is dependent on groundwater temperature. Biodegradation rates may depend on temperature. An increase in temperature may be seen within the solute plume.
Dissolved Oxygen (DO)	Field		With all DO methods extra care must be taken to avoid aeration during all steps of the analysis including well purging and sample collection.	An inverse correlation of DO to BTEX concentrations indicates aerobic biodegradation is occurring. This relationship may also be expressed as depressed or non-detectable levels of DO throughout the plume.
Parameter	Field or Laboratory Method	Analytical Method(s) (or equivalent method)	Comments	Use of Data
		Meter and Probe Flow through cell	Utilizes a flow thru cell with a dissolved oxygen electrode. Other parameters such as temperature, pH, oxidation reduction potential and conductivity can be measured simultaneously. If an oxygen consuming probe is used, then care must be taken to ensure sufficient and continuous flow from the well through the cell.	
		ASTM D 888[A] Winkler titration	Field kits for performing Winkler titrations can be used as the primary method of DO measurement or to confirm meter measurements. A combination of both methods can be used to ensure data quality.	
		Down hole probe	If an oxygen consuming probe is used down hole, then gentile agitation of the probe is required. Vigorous agitation should be avoided to prevent aeration. This technique is recommended only in low permeability conditions where continuous well purging is not possible.	
Ferrous Iron	Field	Colorimetric Std. Methods 18th[B] Edition. Method 3500-Fe D Hach[C] 25140-25	Collect 100 mL of water in glass container. Filter sample with 0.2 μ filter.	Increased concentrations of Fe(II) may indicate Fe(III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons. Also useful in assessing feasibility of other corrective action alternatives.
Total Dissolved Iron	Lab	Atomic adsorption SW-846 Method[D] 7380/7381 ICP SW-846 Method[D] 6010A	filter, 0.2 μ; acidity; refrigerate.	Increased dissolved Fe may indicate Fe(III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons. Also useful in assessing feasibility of other corrective action alternatives.
Oxidation Reduction Potential	Field	Ion Selective Electrode direct reading meter ASTM D 1498[A]	ORP probe can be inserted into flow thru cell and reading obtained simultaneously with DO, pH, T, and EC. Can be taken downhole if necessary.	Define regions of the plume under oxidizing and reducing conditions. Evaluate potential for biologically mediated redox reactions to occur. Helps validate DO measurements. Determine Eh values.

TABLE X4.1 *Continued*

Nitrate	Field	Colorimetric field kit	Collect 100 mL of water in a glass container.	Decreased nitrate concentrations in anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Lab	EPA method 353.2 SW9056 ASTM D 4327[A]	Collect 100 mL of water in a glass or plastic container, cool to 4°C and analyze within 48 hours.	
Sulfate	Field	Colorimetric field kit.	Collect 100 mL of water in a glass or plastic container, cool to 4°C, analyze immediately.	Decreased sulfate concentrations in anaerobic portion of the plume may indicate use of sulfate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Lab	EPA Method 375.4 or SW-9056 ASTM D 4327[A]	Collect 100 mL water in a glass or plastic container, cool to 4°C, analyze within 28 days.	
Manganese	Field	Colorimetric	Collect 100 mL of water in a glass container. Filter sample with 0.2 μ filter.	Increased Mn(II) may indicate Mn(IV) is being used during anaerobic biodegradation as a terminal electron acceptor.
	Lab	EPA Method 3010/200		
Alkalinity	Field	Field test kit	Collect 100 to 250 mL of water in a glass container.	Typically, total alkalinity is primarily due to carbonate alkalinity. Thus, alkalinity is a measure of dissolved carbonate and bicarbonate. A zone of increased alkalinity indicates biodegradation is either producing organic acids which lower the pH and solubilize carbonate from the soil or CO2 is being produced.
	Lab	EPA method 310.2 Colorimetric	Collect 100 mL of water in a glass container cool to 4°C	
Additional Parameters:	In some cases, it may be necessary to evaluate additional indicators of biodegradation if the primary indicators are insufficient, or if it is desired to further understand the potential mechanisms of biodegradation. These parameters may increase the complexity of interpretation and/or the analytical effort.			
Parameter	Field or Laboratory Method	Analytical Method	Comments	Use of Data
Methane	Field or Lab GC	Head Space; GC/FID. IJEAC[E]	Collect water samples in 40 mL VOA vials with butyl gray/Teflon-lined caps. Head space is analyzed by GC equipped with thermal conductivity and/or flame ionization detector.	Elevated concentrations may indicate anaerobic degradation using carbon dioxide as an electron acceptor.
Carbon Dioxide	Lab GC or Field Method	Head Space; GC/TCD. IJEAC[E] Field titration kit	Collect water samples in 40 mL VOA vials with butyl gray/Teflon-lined caps. Head space is analyzed by GC equipped with thermal conductivity and/or flame ionization detector.	Elevated carbon dioxide levels may indicate aerobic biodegradation or depleted levels may indicate methanogenesis is occurring. Carbon dioxide data must be collected and reviewed carefully due to complex geochemical interactions.
Dissolved sulfides	Field	Colorimetric ASTM D 4658[A]	Collect 100 mL of water in a glass container and analyze immediately.	Increased levels above background may indicate sulfate-based anaerobic respiration.

[A] ASTM - American Society for Testing of Materials, standard methods.

[B] Std. Methods - Standard Methods for the Examination of Water and Wastewater, 1992. American Public Health Assoc., American Water Works Assoc., Water Environment Assoc., 18th Edition.

[C] Hach - HACH Company, P.O. Box 389, Loveland, Colorado.

[D] EPA, SW-846 - Test Methods for Evaluating Solid Waste, 1992. USEPA, Office of Solid Waste and Emergency Response, Washington D.C., SW-846.

[E] IJEAC - Kampbell, D.H., J.T. Wilson, and S. A. Vandegrift, 1989. Dissolved oxygen and methane in water by a gas chromatography headspace equilibrium technique. International Journal of Environmental Analytical Chemistry, 36:249-257.

X4.2 Knowledge of regional hydrogeology and geochemistry may be used to define a more focused list appropriate for a specific geologic setting. The methods recommended here are generally recognized to meet data quality objectives, however this is not meant to be an all encompassing list of acceptable methods. Other methods, which can be demonstrated to meet data quality objectives may be used as well.

X5. INTERPRETATION OF NATURAL ATTENUATION INDICATORS

X5.1 *Introduction*—There are a number of parameters that can be used as indicators of the natural attenuation of petroleum hydrocarbons in ground water. The following sections summarize some of the direct indicators that demonstrate the occurrence of natural attenuation, including indicators of biodegradative processes. Biodegradative processes (often referred to as intrinsic bioremediation) are typically considered the primary mechanism for BTEX attenuation in ground water (**8,17-23**).

X5.2 *Primary Line of Evidence for Natural Attenuation - Plume Status*—The primary line of evidence for natural attenuation is to define the plume as stable, shrinking or expanding. Knowledge of the distribution and concentration of hydrocarbons of regulatory concern (for example, BTEX) over time is used to assess plume status. In general, a shrinking or stable plume is strong evidence that natural attenuation is effectively remediating a site. It should be noted that even in the case of an expanding plume, the influence of natural attenuation can be demonstrated in many cases.

X5.2.1 *Expanding Plume*—An expanding plume occurs when the margin of the solute plume continues to move outward and/or concentrations at points within the plume continue to increase over time. A total retardation factor can be used to estimate the influence of natural attenuation processes on an expanding plume. This factor is determined by dividing the distance that groundwater has migrated since the release (calculated from a knowledge of ground water velocity and the age of the release) by the distance from the source area to the actual plume edge (based on monitoring well data). If the retardation of plume expansion is due to sorptive processes only, then the natural attenuation factor for a BTEX plume should typically range from 1.5 to 3.0 (**24**). If the retardation factor is greater than this range, then other processes in addition to adsorption are likely. If a plume is expanding but at a rate lower than the ground water velocity, the risk reduction and performance goals may still be met depending on the presence and location of receptors. Further investigation and assessment may be necessary to more accurately predict the potential extent of plume migration and ensure protection of receptors.

X5.2.2 *Stable Plume*—A stable plume is a configuration where the margin of the solute plume is stable over time and/or the concentrations at points within the plume are relatively uniform over time. If a plume is stable, while ground water continues to move, then remediation through natural attenuation is evident. Simply, for the plume to be stable, the rate of natural attenuation of BTEX in the plume must be equal to the rate that BTEX mass is entering the plume from the source area. The rate of natural attenuation in a stable plume can be calculated through a mass balance approach or through a concentration versus distance approach. Both are discussed in detail in Appendix X6. In addition, the approach for estimating the influence of natural attenuation on an expanding plume given in X5.2.1 is applicable to a stable plume as well.

X5.2.3 *Shrinking Plume*—A shrinking plume is a configuration where the groundwater plume margin is shrinking over time and/or the concentrations at points within the plume are decreasing over time. If a plume is shrinking, while ground water continues to move, then remediation through natural attenuation is evident. Simply, for the plume to be shrinking, the rate of natural attenuation of BTEX in the plume must be greater than the rate that BTEX mass is entering the plume from the source area. The rate of natural attenuation in a shrinking plume can be calculated through a mass balance approach or through a concentration versus time approach. Both are discussed in detail in Appendix X6. In addition, the approach for estimating the influence of natural attenuation on an expanding plume given in X6.2.1 is applicable to a shrinking plume as well.

X5.3 *Secondary Line of Evidence - Indicators of Biodegradation*—Biodegradation is the process in which naturally-occurring subsurface microorganisms biodegrade contaminants, often completely degrading hydrocarbons to carbon dioxide and water. Evaluating indicators specific to the biodegradation process is of critical importance when presenting secondary lines of evidence for natural attenuation. The discussion presented below is confined to an assessment of the biodegradation of benzene, toluene, ethylbenzene and xylenes (BTEX). Because of their toxicity and especially their environmental mobility, these chemicals are typically the constituents of concern in groundwater at petroleum release sites. Other compounds (for example, oxygenated additives, naphthalene) may be of concern on a site specific basis depending on the age and nature of the petroleum release. A discussion of the bioremediation of such compounds is beyond the scope of the following presentation.

X5.3.1 *Introduction to Indicators of Biodegradation*—Microorganisms transform organic molecules, such as benzene, toluene, ethylbenzene and xylenes (BTEX), and obtain carbon and energy from these substrates for survival, growth and reproduction. Initially, the microbes "attack" these hydrocarbons through a series of enzyme-catalyzed oxidative-reduction reactions. The resulting metabolic intermediates are then either divered to biomass-producing pathways or completely oxidized to carbon dioxide and water. The oxidative reactions yield electrons which through a series of enzyme-catalyzed electron transport steps produce the energy the cell needs for maintenance and growth. In order for the electrons to pass through the energy generating steps, though, an electron sink is required. Typically, this electron acceptor (sink) is molecular oxygen (O_2) and the process is called aerobic respiration. In the absence or near absence of molecular oxygen (O_2) and in the order presented, nitrate (NO_3^-), manganese (Mn^{+4}), ferric iron (Fe^{+3}), sulfate (SO_4^{-2}) or carbon dioxide (CO_2) may serve, if available, as terminal electron-acceptors in a process called anaerobic respiration.

X5.3.1.1 The *aerobic* metabolism of benzene, toluene, ethylbenzene and xylenes has been widely documented. In subsurface soils and aquifer materials, both through *ex-situ* microcosm studies and through field studies **(8,17-18,21)**. It is likely that microorganisms capable of aerobically degrading BTEX constituents are nearly ubiquitous in subsurface environments.

X5.3.1.2 The *anaerobic* metabolism of toluene, ethylbenzene and xylenes has been widely demonstrated under nitrate-reducing **(19,25-28)**, sulfate-reducing **(27-30)**, iron- and manganese-reducing **(31-35)** and methanogenic **(36-38)** conditions. The anaerobic metabolism of benzene has not been well documented. Nevertheless, an increasing number of microcosm and field studies are demonstrating the metabolism of benzene under nitrate-, sulfate-, iron-reducing and methanogenic conditions **(32,34,36-42)**.

X5.3.1.3 The equations given in Fig. X5.1 show the reactants and products involved in the aerobic and anaerobic metabolism of BTEX. The reactions below are balanced based on toluene, but the reactions apply to all BTEX constituents.

X5.3.1.4 As shown in previous equations, under aerobic conditions, the metabolism of BTEX results in the consumption of oxygen and the production of carbon dioxide and water. Under anaerobic conditions, the metabolism of BTEX consumes the particular electron acceptor and yields the reduced electron acceptor, carbon dioxide and water (water is not produced in methanogenesis). Thus, coupled with BTEX attenuation, the disappearance in ground water of dissolved oxygen and/or anaerobic electron acceptors, or the appearance of electron-acceptor reduction products, (all relative to upgradient concentrations) is clear evidence of biodegradation.

X5.3.2 *A Quantitative Approach to Evaluating Indicators of Biodegradation*—Quantitatively, the balanced equations given in Fig. X5.1 allow a calculation of: (*1*) the mass of a terminal electron acceptor necessary to completely metabolize a given mass of BTEX; and (*2*) the yield of reduced electron acceptor per mg of BTEX metabolized. Based on the previous equations, 3.1, 4.6 and 4.8 mg/L of oxygen, sulfate and nitrate, respectively, are necessary to completely metabolize 1 mg/L BTEX, while 0.8, 11 and 22 mg/L of methane, Mn^{+2} and Fe^{+2}, respectively, are produced from the complete metabolism of 1 mg/L BTEX.

NOTE X5.1—These are values specific to toluene, but values for other BTEX constituents will vary only slightly.

AEROBIC RESPIRATION

$C_6H_5CH_3 + 9\ O_2 \rightarrow 7\ CO_2 + 4\ H_2O$

ANAEROBIC RESPIRATION

Nitrate Reduction
$5C_6H_5CH_3 + 36NO_3^- + 36H^+ \rightarrow 18N_2 + 35CO_2 + 38H_2O$

Manganese Reduction
$C_6H_5CH_3 + 18MnO_2 + 36H^+ \rightarrow 18Mn+2 + 7CO_2 + 22H_2O$

Iron Reduction
$C_6H_5CH_3 + 36Fe(OH)_3 + 72H^+ \rightarrow 36Fe^{+2} + 7CO_2 + 94H_2O$

Sulfate Reduction
$8C_6H_5CH_3 + 36SO_4^{-2} + 72H+ \rightarrow 36\ H_2S + 56CO_2 + 32H_2O$

Methanogenesis
$8C_6H_5CH_3 + 40H_2O \rightarrow 36CH_4 + 20CO_2$

NOTE 1—Equations are balanced using toluene and would slightly differ for other BTEX constituents. The equations balanced using benzene can be found in Wiedemeier et al. 1995 Ref. **(1)**.

FIG. X5.1 Aerobic and Anaerobic Pathways of BTEX Biodegradation

These are maximum values, since not all of the carbon will be completely oxidized (a significant portion of the carbon will be used for biomass). While a quantitative approach (for example, a decrease in BTEX concentration of 2 mg/L yielded a decrease in sulfate concentration of 10 mg/L) is valuable and has been utilized **(22,23)** the possible environmental sources and sinks for electron acceptors and metabolites can make quantification very difficult. Therefore, a qualitative approach is usually followed, with a direct or inverse correlation between electron acceptors/reduction products and BTEX concentrations providing clear evidence for biodegradation.

X5.3.2.1 Many of the electron acceptors and their reduction products given in Fig. X5.1 can be readily and accurately measured in ground water samples. These include O_2, Fe(II). Mn (II), NO_3, SO_4, CH_4 and CO_2. Measurement of these parameters is discussed in detail in Appendix X4. Thus, these parameters can be used to evaluate the influence of biodegradation on a solute plume. Other means of assessing biodegradation include measuring oxidation-reduction potentials, microcosm studies and microbial counts. Electron acceptors and their reduction products, as well as other methods for assessing biodegradation, are discussed in more detail below.

X5.3.3 *Electron Acceptors and Reduction Products (Secondary Lines of Evidence)*:

X5.3.3.1 *Oxygen*—In zones of high BTEX concentration, dissolved oxygen is depleted because the naturally-occurring microorganisms have utilized the available oxygen as they biodegrade BTEX and other constituents and any oxygen entering this zone is rapidly depleted (due to the high oxygen demand generated by the high BTEX concentrations and other constituents such as Fe(II), Mn(II), etc.). The inverse relationship of high hydrocarbon concentration and low dissolved oxygen concentration can be used as a key indicator of bioremediation.

X5.3.3.2 *Nitrate*—After dissolved oxygen has been depleted (typically considered <0.5 ppm) in a given ground water zone, nitrate, if available, may be used as an electron acceptor for anaerobic biodegradation. In anaerobic ground water zones with high BTEX concentrations, nitrate demand (by nitrate-reducing microorganisms capable of biodegrading BTEX) may be high and nitrate concentrations may be depleted relative to concentrations upgradient and outside the plume. Overall, an inverse relationship between BTEX concentrations and nitrate concentration should be expected.

X5.3.3.3 *Manganese*—The use of manganese (Mn^{+4}) as a terminal electron acceptor by microorganisms yields a reduced water-soluble manganese (Mn^{+2}). In anaerobic ground water zones where BTEX and a source of Mn^{+4} (MnO_2) are present, Mn^{+2} can be used as an indicator of biodegradation. Overall, a positive correlation between BTEX concentrations and Mn^{+2} concentration should be expected.

X5.3.3.4 *Iron*—The use of ferric (Fe^{+3}) iron as a terminal electron acceptor by microorganisms yields water-soluble ferrous (Fe^{+2}) iron. In anaerobic ground water zones where BTEX and a source of ferric iron are present, ferrous iron can be used as an indicator of biodegradation. Overall, a positive correlation between BTEX concentrations and ferrous iron concentration should be expected.

X5.3.3.5 *Sulfate*—Under strongly reducing conditions, after available oxygen, nitrate and ferric iron have been depleted, sulfate can be used as an electron acceptor for anaerobic biodegradation of BTEX. The process results in the production of sulfide, which may precipitate from solution as ferrous sulfide. Under sulfate-reducing conditions and in the presence of high BTEX concentrations, sulfate demand (by sulfate-reducing BTEX degraders) will be high and sulfate concentrations will be depleted relative to concentrations upgradient and outside the plume. Overall, in these sulfate-reducing zones, an inverse relationship between BTEX concentrations and sulfate concentration should be expected.

X5.3.3.6 *Methane*—Methane is produced only under strongly reducing conditions by a group of strict anaerobes. Methanogens either use CO_2 as a terminal electron acceptor, producing methane, or cleave acetate to CO_2 and methane. Because methane is not present in fuels, it can be used as an indicator of biodegradation. Under methanogenic conditions and in the presence of high BTEX concentrations, the rate of methane production can be significant, with the concentration of methane in this zone high relative to areas upgradient and outside the plume (where the methane concentration is typically nondetect). Overall, under methanogenic conditions, a positive correlation between BTEX concentrations and methane concentration should be expected.

X5.3.3.7 *Carbon dioxide*—Both aerobic and anaerobic biodegradative processes can yield large quantities of CO_2, as the BTEX constituents are completely oxidized. An accurate measurement of the CO_2 produced through biodegradation, though, is difficult because the carbonate-buffering system in ground water (measured as alkalinity) serves as both a sink and source of CO_2. Nevertheless, in many circumstances, a positive correlation between BTEX and CO_2 concentrations can be expected and can be used as a qualitative indicator of biodegradation.

X5.3.4 *Summary of the Relationship Between BTEX and Electron Acceptor/Reduction Product Concentrations*—The expected relationship between BTEX concentration and the concentration of a particular electron acceptor or its reduction product is summarized in Table X5.1.

X5.3.5 *Additional Indicators of Biodegradation*:

X5.3.5.1 *Oxidation-Reduction (Redox) Potential*—The oxidation-reduction potential of ground water is a measure of the relative tendency of a solution to accept or donate electrons. Importantly, redox reactions in ground water are usually mediated by microorganisms. Therefore, the redox potential can strongly depend on biodegradative processes and, in turn, the redox potential can strongly influence such processes. While the redox potential of ground water can range from –400 to 800 mv, certain biodegradative processes can only operate within a prescribed range of redox conditions (Fig. X5.2). By measuring upgradient redox values and values within the plume, zones where biodegradation (especially anaerobic processes) is lowering the redox potential can be identified.

TABLE X5.1 Expected Relationship Between BTEX and Electron Acceptor/Reduction Product Concentrations Within a Plume

BTEX	OXYGEN	NITRATE	Mn (II)	FE(II)	SULFATE	METHANE
HIGH	LOW	LOW	HIGH	HIGH	LOW	HIGH
LOW	HIGH	HIGH	LOW	LOW	HIGH	LOW

X5.3.5.2 *Microbial Counts*—Microbial counts, using both counts of total heterotrophic bacteria and hydrocarbon degraders, can be used as an indicator of biodegradation. The ratio of hydrocarbon degraders to total heterotrophic bacteria should increase in aquifer zones where biodegradation of BTEX is occurring. It should be noted, though, that microbial counts are often unreliable indicators of biodegradation **(21)**.

X5.3.5.3 *Microcosm Studies*—In microcosms studies, small quantities of ground water and aquifer solids are placed into serum bottles, shake flasks or into columns. The disappearance of a carbon substrate, sometimes along with the disappearance of a terminal electron acceptor or the appearance of the appropriate reduction product, is then measured over time. Microcosm studies are often used to clearly demonstrate the ability of native microorganism to biodegrade a given compound. As discussed, the biodegradation of BTEX constituents is well documented and, therefore, microcosm studies are not typically necessary. In addition, although microcosms studies can be used to estimate *in-situ* biodegradation rates, field methods detailed in Appendix X6 are preferred.

X5.4 *Measuring Nutrient Levels*—Measuring nutrient levels can provide an optional line of evidence. Measuring the concentration of electron acceptors or their reduction products should not be confused with measuring the level of microbial nutrients. Nutrients are incorporated into microbial biomass and are necessary for the formation of proteins, DNA, cell membranes and other components of microbial cells. Microbial nutrients are usually divided into two categories: macronutrients (for example, nitrogen and phosphorus), for which microorganisms require relatively large amounts, and micronutrients (for example, sulfur, manganese, magnesium and many others), for which only a trace amount is required. In contrast to nutrients, electron acceptors and their reduction products are not incorporated into microbial biomass, but the reduced compounds are "excreted" into the environment (for example, the microbes take in sulfate and release H_2S). Macronutrient (nitrogen and phosphorus) levels are often assessed in surface and subsurface environments by measuring ammonium (NH_4^+), nitrate (NO_3^-), organic (Kjeldahl) nitrogen, available phosphorus or phosphate (PO_4^{-3}) and total phosphorus (mostly organic phosphorus compounds + phosphate). Certain molecules, such as nitrate and sulfate, can serve either as nutrients or terminal electron acceptors. While the availability of electron acceptors in the subsurface is a critical factor in assessing the rate and extent of biodegradation **(24)**, as previously discussed, nutrient levels are rarely limiting microbial biodegradation activity in the subsurface, and, thus, measuring subsurface nutrient levels is unnecessary.

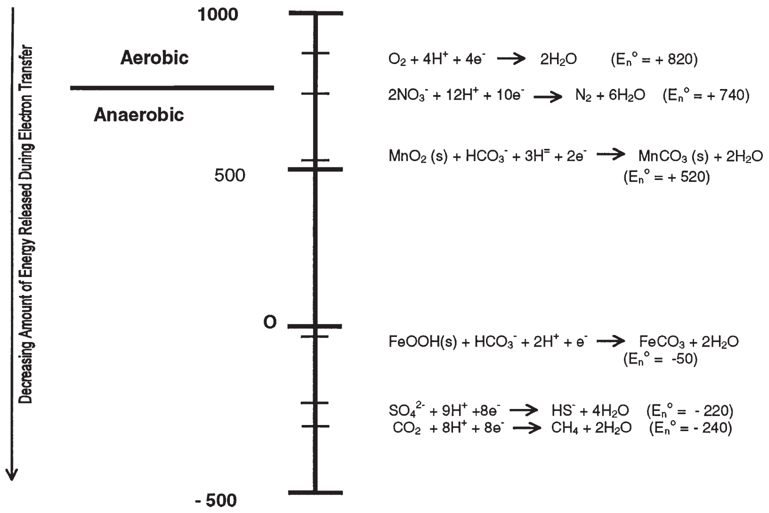


FIG. X5.2 Redox Potentials in Millivolts, pH 7, 25°C (from Wiedemeier et al. 1995)

X6. QUANTIFYING RNA RATES

INTRODUCTION

The primary line of evidence for natural attenuation is to define the plume as stable, shrinking, or expanding and efforts to quantify RNA rate are not necessary. In the secondary line of evidence, the natural attenuation rate may be estimated. The selection of a method to estimate RNA rate is based on the availability of contaminant data. Appendix X6 describes several methods to estimate RNA rate. The effort of calculating a natural attenuation rate achieves the following:

It strengthens the qualitative and semi-quantitative arguments for natural attenuation and;

It lends credence to the argument that natural attenuation can be an effective stand-alone remediation measure. As part of a demonstration of natural attenuation, it may be important to estimate a specific rate of destruction for dissolved BTEX.

This Appendix is divided into the following four sections:

X6.1 Mass Balance Approach,
X6.2 Graphical and Regression Techniques,
X6.3 One-Dimensional Analytical Solution for a Stable Plume, and
X6.4 One-, Two-, and Three-Dimensional Analytical Models.

Appendix X6.1 describes a mass balance approach which calculates the contaminant mass loading to the water table. Depending on the type of plume, the attenuation rate can be estimated based on the contaminant mass loading rate. The attenuation rate for a stable plume is approximately equal to the contaminant mass loading rate. The attenuation rate for a shrinking table plume exceeds the contaminant mass loading rate. In the case of an expanding plume, the attenuation rate is less than the contaminant mass loading rate.

Appendix X6.2 describes graphical and regression techniques useful to determine attenuation rates. Two of the conditions for which natural attenuation contributes to the configuration of a contaminant plume are a shrinking or stable plume. These techniques require data for contaminant concentration versus time and/or distance. Regression of contaminant concentration versus time for individual monitoring wells is an appropriate analysis technique for a shrinking plume. Regression of contaminant concentration versus distance is an appropriate method for either a shrinking or stable plume. Estimates of attenuation rate should be used with caution. The attenuation rate based on concentration versus time for a single monitoring well may not be representative of the entire dissolved plume. On the other hand, if multiple wells display exponential contaminant decay, estimates of attenuation rate may be appropriate to model the plume. Concentration versus distance techniques may yield attenuation rates more representative of the entire plume.

The graphical/regression techniques described in X6.2 yield an attenuation rate which does not distinguish between sorption, dispersion, and biodegradation. The objective of X6.3 is to evaluate the contribution of biodegradation to the overall attenuation rate for stable plumes. This is accomplished by using an analytical solution which includes advection, dispersion, sorption, and decay. For petroleum hydrocarbons, the decay term in the analytical solution is a measure of intrinsic bioremediation. The concentration versus distance regression for a stable plume is coupled with this analytical solution for one-dimensional, steady-state contaminant transport. This method is intended to distinguish those mechanisms which contribute to natural attenuation.

Appendix X6.4 presents one-, two-, and three-dimensional analytical models available in the literature. The attenuation and decay rates calculated in the earlier sections can be used in these models.

X6.1 Estimating Natural Attenuation Rate Using a Mass Balance Approach

X6.1.1 An estimated natural attenuation rate can be calculated by using a quantitative mass balance approach. The mass-balance approach is a tool for estimating mass loading from the source zone and concurrent mass attenuation within the plume. This method is most applicable to situations in which the plume is stable or shrinking. Procedures and an example are presented in this section.

X6.1.2 The additional step of calculating a natural attenuation rate has the following advantages:

X6.1.2.1 It strengthens the qualitative and semi-quantitative arguments given above and;

X6.1.2.2 Calculation of a natural attenuation rate lends credence to the argument that natural attenuation can be an effective stand-alone remediation measure. As part of a demonstration of natural attenuation, it may be important to quote a specific rate of destruction for dissolved BTEX.

X6.1.3 *Site Scenario*:

X6.1.3.1 As shown in Fig. X6.1, ground water flows onto a site, and is loaded with dissolved BTEX, through contact with the free product and smear zone. For a steady-state plume, this loading rate of dissolved BTEX is approximately equal to the natural attenuation rate.

X6.1.3.2 Therefore, the loading rate can be used as an estimate of the natural attenuation rate. The mass of dissolved BTEX which enters the ground water system per unit time (for example, daily) will be the product of the average BTEX concentration in and below the source area and the flow of contaminated ground water in and below the source area.

NOTE X6.1—This calculation is based on the steady state plume configuration. For an expanding plume, the actual natural attenuation rate would be somewhat less than that calculated for a steady state plume, and for a shrinking plume, it would be somewhat more.

X6.1.4 *Procedure and Example*:

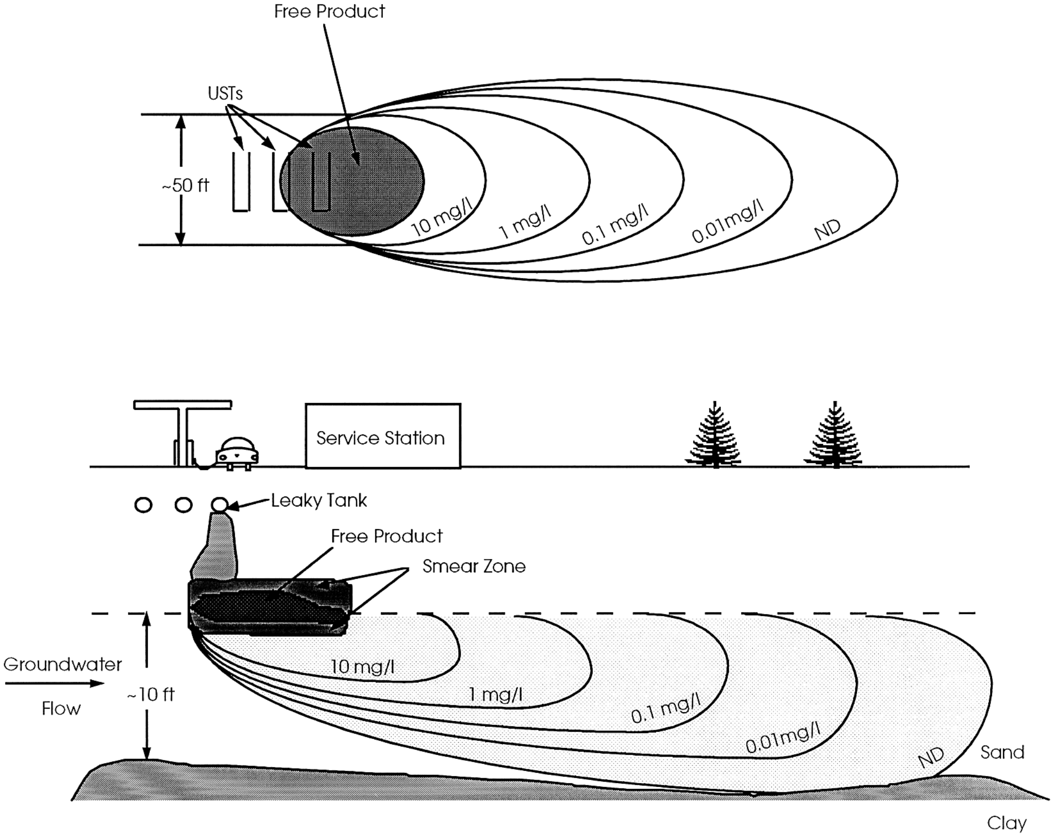


FIG. X6.1 Cross Section & Map View, Example Service Station, Hydraulic Gradient (i) = 0.005 Hydraulic Conductivity (K) = 100 ft/day

X6.1.4.1 The procedure to calculate the dissolved BTEX loading rate (and, therefore, the estimated natural attenuation rate) is presented in this section. An example is used and a dissolved BTEX loading rate calculated, based on the typical service station site presented in Fig. X6.1.

X6.1.4.2 The dissolved BTEX loading rate has two components: (*1*) the dissolved BTEX added to the ground water that flows horizontally through the smear zone below the water table, and (*2*) the dissolved BTEX added to the ground water beneath the smear zone, caused primarily by vertical dispersion and vertical advection.

X6.1.4.3 For both of these zones, an average concentration is estimated, and multiplied by the ground water flow rate through the zone. The calculation (using appropriate conversion factors, as discussed below) results in the mass of dissolved BTEX contributed for each zone.

X6.1.5 Calculation of BTEX mass added to ground water flowing through the smear zone involves the following steps.

X6.1.5.1 Estimate the cross-sectional area of the smear zone below the water table (A_{sz}), perpendicular to the direction of ground water flow. The average thickness of this zone will be equal to one-half the width of the zone of water table fluctuations. For the example site, historical records indicate maximum water table fluctuations equal to 6′. Therefore, the average thickness of the smear zone below the water table is 3′. The width of the smear zone is 50′ (see Fig. X6.1). Therefore:

$$A_{sz} = 3' \times 50' = 150 \text{ ft}^2.$$

X6.1.5.2 Estimate the hydraulic conductivity of the smear zone (K_{sz}). The value is less than the estimated hydraulic conductivity (K) based on slug tests and/or pumping tests conducted in waters containing no free product. This reduction in hydraulic conductivity is caused by the presence of product trapped in soil pores, and can be estimated using Table X6.1 (based on the data and equations of Parker *et al*. 1987 **(43)**: The hydraulic conductivity of the smear zone K_{sz} = the measured K value times the appropriate value from the table (or an interpolated value). For the example site (with a medium sand aquifer K = 100 ft/day), $K_{sz} = 100 \times 0.3 = 30$ ft/day.

X6.1.5.3 Calculate the ground water flow through the smear zone (Q_{sz}), as follows:

$$Q_{sz} = K_{sz} \times i \times A_{sz} \quad \text{(X6.1)}$$

Q_{sz}, K_{sz} an A_{sz} are as defined above, and
i is the hydraulic gradient.

For the example site, $Q_{sz} = 30 \times 0.005 \times 150 = 22.5 \text{ ft}^3$/day

X6.1.5.4 The mass flux of dissolved BTEX entering the ground water through the smear zone ($BTEX_{sz}$) is calculated using the following expression:

$$BTEX_{sz} = C_{sz} \times Q_{sz} \times CF \quad \text{(X6.2)}$$

$BTEX_{sz}$ and Q_{sz} are as defined above,
C_{sz} is equal to the theoretical solubility for BTEX in ground water in contact with gasoline components. This value is approximately 100 mg/L based on immiscible partitioning **(44)**. CF is a conversion factor to convert mg/L to lbs/ft^3, CF = 6.245×10^{-5} lbs-L/ft^3-mg.

For the example site, $BTEX_{sz} = 100 \times 22.5 \times 6.245 \times 10^{-5} = 0.14$ lbs/day

TABLE X6.1 Estimated Hydraulic Conductivities

Soil Type	Ratio of Smear Zone K to Measured K
Silty clay	0.8
Sandy silt/fine sand	0.5
Medium sand	0.3

X6.1.6 Calculation of BTEX mass added to ground water flowing below the smear zone involves an estimate of both the thickness of the dissolved plume below the smear zone and the average concentration of this plume.

X6.1.6.1 These parameters are not generally known. For most sites, water quality data in the source area involves measurements of concentration at a single depth, or perhaps no data is available at all (for example, if free product is present, water quality samples are typically not collected). In addition, while the thickness of the shallow water-bearing formation might be known, the vertical extent and distribution of contamination below the source area might not.

X6.1.6.2 However, observations have shown that the vertical extent of contamination below the smear zone is no more than 10 ft. This is based on field observations and theoretical considerations **(8,45-48)**. and personal communication, Gary Robbins, University of Connecticut, Storrs, 1995). The vertical spread of contaminants is dominated by dispersion, and the concentrations can be assumed to have a Guassian distribution (the theoretical distribution resulting from dispersion).

NOTE X6.2—The plume thicknesses discussed above are for relatively small smear zones, that is, measured in tens of feet in the direction of ground water flow. For larger smear zones, actual measurements of plume thicknesses at the downgradient edge of the smear zone are necessary, due to dispersion and/or vertical flow components as ground water travels the length of the smear zone.

X6.1.6.3 Of course, site physical conditions may dictate that the thickness of the plume below the smear zone is less than 10 ft; for example, a sand unit may be underlain by clay at a depth of less than 10 ft below the smear zone. In this case, the vertical concentration profile is the same as for 10 ft; however, the concentration profile is truncated at the lesser thickness, resulting in a higher average concentration.

X6.1.6.4 Assuming a Guassian concentration distribution from 100 mg/L at the smear zone to 0.001 mg/L at 10 ft below the smear zone, the Table X6.2 presents average BTEX concentrations for those cases where the thickness of the dissolved plume is physically constrained by a low permeability unit to less than 10 ft.

X6.1.6.5 The calculation of BTEX mass distributed to the ground water that flows below the smear zone involves the following steps:

(*1*) Estimate the cross sectional area of the dissolved plume below the smear zone (Ab_{sz}), perpendicular to the direction of

TABLE X6.2 BTEX Concentrations as a Function of Plume Thickness

Plume thickness below smear zone	Average BTEX concentration (mg/L)
2′	87
4′	62
6′	43
8′	33
10′[A]	26

[A] (use 10′ even if hydraulic zone > 10’) ground water flow. For the example site, the thickness of this zone is 10 ft, and the width of the smear zone is 50 ft (see Fig. X6.2). Therefore, $A_{bsz} = 10 \times 50 = 500\ ft^2$. Dissolved hydrocarbon plumes may decrease in size, as observed by declining contaminant concentrations in monitoring wells. The conditions of a shrinking plume suggest some form of source control or removal, either by engineered remediation or by natural source attenuation (flushing, biodegradation, etc.) A sufficiently deep water table may limit the contaminant mass loading to ground water. Given the conditions of a shrinking plume, the rate of natural attenuation must be greater than the rate of contaminant addition **(24)**. Salanitro **(21)** indicates a shrinking plume has significant reinfiltration of oxygenated water into the aquifer (precipitation). Wells on the periphery of these types of plumes have higher dissolved oxygen (DO) and lower BTEX concentrations, consistent with BTEX biodegradation. Analysis of shallow and deep monitoring wells show that the soluble plume "shrinks" in the longitudinal direction with little vertical dispersion **(8)**. In the three examples described by Salanitro **(21)**, mass balance analysis of the hydrocarbon in the aquifer show that natural biodegradation by soil biota must be responsible for most (80 to 100 %) of the apparent reduction and retardation of the BTEX plume. Exponential regression methods can be used to evaluate whether concentration versus time data fit a first-order decay observed for petroleum hydrocarbons under certain conditions. The solution to the first-order decay is given by the following equation:

$$C(t) = C_i\ e^{-(kt)} \tag{X6.3}$$

where:

$C(t)\ (M/L^3)$ = concentration as a function of time, t (T),

C_i = the concentration at t = 0, and

k = the first-order attenuation rate (T^{-1}).

The temporal regression technique is based on Eq X6.3, in which concentration is expressed as a function of time. Contaminant concentration versus time is plotted for a hypothetical monitor well in Fig. X6.2. Concentration is plotted on a log scale, consistent with the assumption of first-order degradation. If a first-order decay describes the apparent contaminant concentration decline, the data plot as a straight line. Exponential regression of log concentration versus time yields a value proportional to the slope of the regressed line (*k*), the y-intercept (C_i), and the goodness of fit (R^2 value). A more general form of Eq X6.3 may be appropriate to fit late-time data which are asymptotic. This equation is given as follows:

$$C(t) = (C_i - C_a)e^{-(kt)} + C_a \tag{X6.4}$$

where:

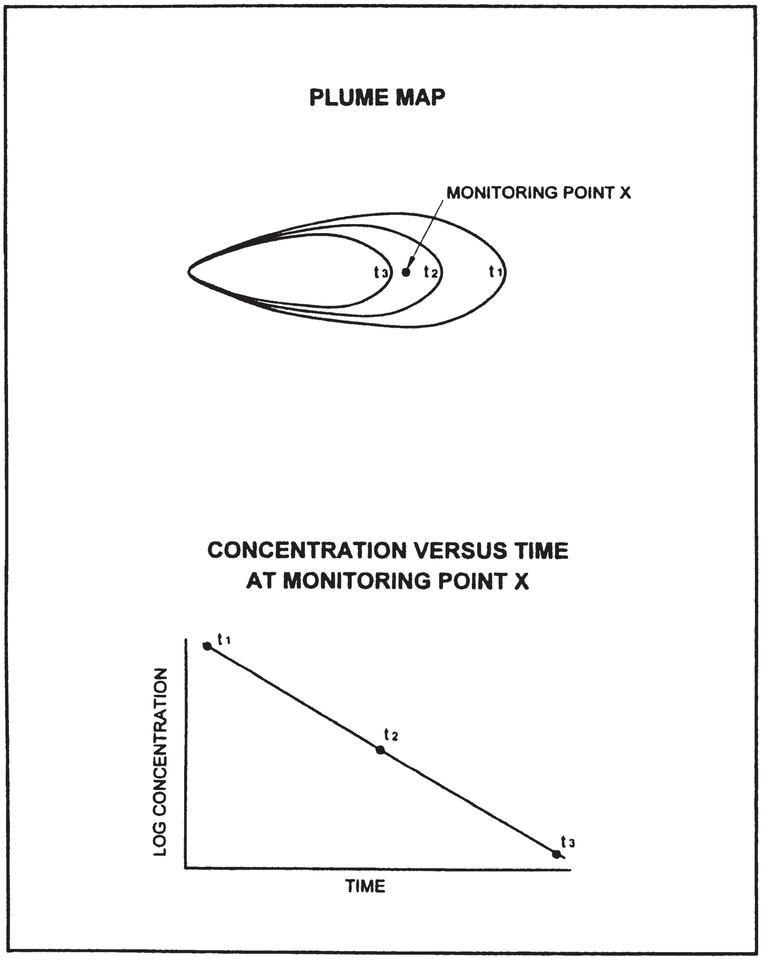


FIG. X6.2 Shrinking Plume

C_a = the asymptotic concentration.

As C_a approaches zero, Eq X6.4 reduces to Eq X6.3. Eq X6.4 is useful to fit data to an asymptotic concentration. It can also be used to confirm the long-term, asymptotic concentration **(8,49)**. The transport processes contributing to these first-order attenuation rates include volatilization, dispersion, sorption, dilution by recharge, and biological degradation. It is difficult to distinguish these mechanisms using the temporal method. However, as partitioning approaches equilibrium, sorption is less significant in reducing solute concentrations with time. Wilson et al **(50)** suggest the use of a recalcitrant, organic compound, having similar sorptive properties as the biodegradable compound of interest, to serve as a tracer.

NOTE X6.3—If the thickness of the hydrogeologic unit below the smear zone exceeds 10 ft, the thickness of this zone is assumed to be 10 ft.

(2) Calculate the ground water flow rate below the smear zone (Q_{bsz}) as follows:

$$Q_{bsz} = K \times i \times A_{bsz} \tag{X6.5}$$

where:

K = hydraulic conductivity estimated by slug or pumping tests,
i = hydraulic gradient, and
A_{bsz} = cross-sectional area below the smear zone.

For example site, $Q_{bsz} = 100 \times 0.005 \times 500 = 250$ ft^3/day.

(3) Estimate the average BTEX concentration (C_{bsz}) from the above table. For the example site, $C_{bsz} = 26$ mg/L.

(4) The mass flux of dissolved BTEX contributed to the ground water flowing below the smear zone ($BTEX_{bsz}$) is calculated using the following expression:

$$BTEX_{bsz} = C_{bsz} \times Q_{bsz} \times CF \tag{X6.6}$$

Q_{bsz} and C_{bsz} and CF are previously defined

For the example site, $BTEX_{bsz} = 26 \times 250 \times 6.245 \times 10^{-5} =$ 0.41 lbs/day.

The estimation of the total dissolved BTEX loading rate ($BTEX_{tot}$) and, therefore, the estimation of the overall natural attenuation rate, involves the addition of the mass flux of dissolved BTEX entering ground water flowing through the smear zone ($BTEX_{sz}$) to the mass flux of dissolved BTEX contributed to ground water below the smear zone ($BTEX_{bsz}$).

$$BTEX_{tot} = \text{Natural Attenuation Rate} = BTEX_{sz} + BTEX_{bsz} \tag{X6.7}$$

$BTEX_{tot}$, $BTEX_{sz}$ and $BTEX_{bsz}$ as previously

For the example site, $BTEX_{tot} = 0.14 + 0.41 = 0.55$ lbs/day = Natural Attenuation Rate

NOTE X6.4—To convert lbs to gallons of gasoline divide by 6.2.

This removal rate is comparable to what might be achieved by a successful pump and treat system. For example, a pump and treat system extracting 50 gpm containing 1 mg/L BTEX removes 0.5 lbs/day.

X6.2 Graphical and Regression Techniques

X6.2.1 *Concentration versus Time*—Shrinking Plume.

X6.2.2 *Concentration versus Distance*—Stable Plume.

X6.2.2.1 A stable plume is characterized by dissolved contaminant concentrations remaining constant over time in individual monitoring wells. Short-term variations in monitoring well concentrations due to water table fluctuation, variability in ground water flow direction, sampling variability, and analytical uncertainty should be distinguished from statistically significant concentration changes. In order for a plume to reach stable conditions, the rate of natural attenuation must be equal to the rate of contaminant addition to the aquifer from the source **(25)**. The contaminant source or influx rate is limited by the compound's effective solubility and the flow rate of water through the source area (infiltration, fluctuating water table, etc.).

X6.2.2.2 Time, t, can be described in terms of seepage velocity, v (L/T) and distance traveled, x (L).

$$t = \frac{x}{v} \tag{X6.8}$$

X6.2.2.3 The term "x/v" is the residence time for ground water to move some distance, x, from the source. Kemblowski *et al.* **(18)** substituted Eq X6.8 into Eq X6.3, and the first-order attenuation rate can be recast for concentration as a function of distance:

$$C(x) = C_o \, e^{-(k\frac{x}{v})} \tag{X6.9}$$

where:

C(x) = concentration as a function of distance, x (L).
C_o = concentration at x = 0, and
k = first-order attenuation rate (T^{-1}).

X6.2.2.4 The spatial regression technique is based on Eq X6.9. The regression of concentration versus distance is appropriate for the stable plume. It can also be used for a shrinking plume for individual monitoring events. The ground water flow direction is defined based on multiple monitoring events covering the hydrologic cycle. A minimum of three monitoring wells are selected along the ground water trajectory (see Fig. X6.3). Fig. X6.3 is a plot of compound concentration (log scale) versus distance. If data from multiple sampling events are available for a stable plume, the concentrations plotted should be the average concentration over time for each well. If concentrations decline with time, concentration versus distance can be plotted for individual monitoring events. From the exponent in Eq X6.9, the slope of the line in Fig. X6.3 is k/v (L^{-1}), the reciprocal of the attenuation distance. If this slope is multiplied by ground water velocity, v (L/T), we obtain the attenuation rate, k (T^{-1}). In the absence of a reliable estimate of ground water velocity, the k/v term is useful, particularly for selecting the downgradient monitoring well locations.

X6.2.3 *Expanding Plume*—The calculation of RNA rate is not as straightforward for an expanding plume as it is for a shrinking or stable plume. It is possible to compare the actual rate of migration to the expected rate of migration, assuming sorption only (contaminant velocity). Using the Mass Balance Approach described in X6.1, it is also possible to estimate the attenuation rate (lbs/day), as less than the contaminant mass loading to the water table. Transient analytical solutions can be used to predict the migration distance of an expanding plume or the time required to reach a particular configuration. These analytical models are presented in X6.4.

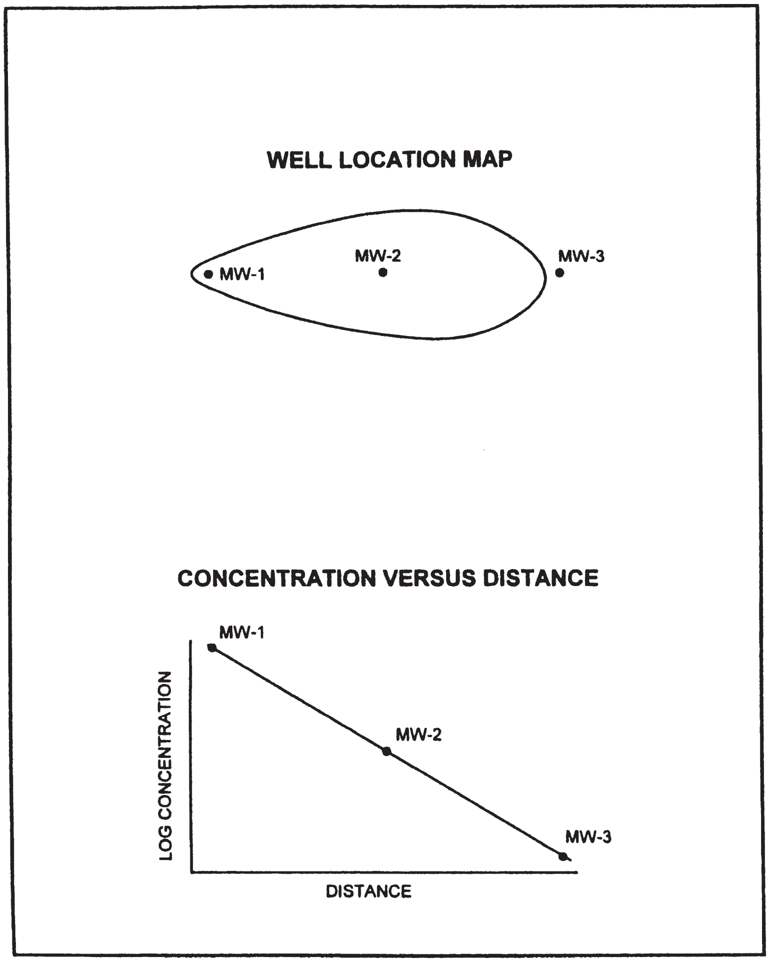


FIG. X6.3 Average Compound Concentration Versus Distance for a Known Stable Plume

X6.3 One-Dimensional Analytical Solution for a Stable Plume

X6.3.1 The graphical/regression techniques described in X6.2 yield an attenuation rate which does not distinguish between sorption, dispersion, and biodegradation. The objective of X6.3 is to evaluate the contribution of biodegradation to the overall attenuation rate. This is accomplished by using an analytical solution which includes advection, dispersion, sorption, and decay (biodegradation). The concentration versus distance regression for a stable plume is coupled with this analytical solution for one-dimensional, steady-state contaminant transport. This method, presented in Buscheck and Alcantar **(51)** is intended to distinguish those mechanisms which contribute to natural attenuation. Wiedemeier *et al.* **(52)** also demonstrate the use of this method.

X6.3.2 The general one-dimensional transport equation, with first-order decay of the contaminant, is given by the following equation:

$$\frac{\delta C}{\delta t} = \frac{1}{R}[D_x\frac{\delta^2 C}{\delta x^2} - v_x\frac{\delta C}{\delta x}] - \lambda C \qquad (X6.10)$$

Where D_x (L^2/T) is the dispersion of coefficient, v_x (L/T) the seepage velocity in the x direction, R (–) the retardation coefficient and λ (T^{-1}) is the total decay rate. The form of Eq X6.10 assumes D_x is constant and independent of distance, x. While the terms in brackets describe the mass transport by dispersion and advection, respectively, the retardation coefficient characterizes the contribution of sorption. The form of this equation assumes degradation occurs in the aqueous and sorbed phases at the same rate. If biological transformation of the contaminants occurs primarily in the aqueous phase, the term "λC" would also appear inside the brackets.

X6.3.3 Dispersion and linear ground water velocity are related by the longitudinal dispersivity, α_x (L), which has been described by empirical expressions:

$$D_x = \alpha_x v_x \qquad (X6.11)$$

X6.3.4 The retardation coefficient (R) accounts for partitioning between the solid and aqueous phases. R describes the relationship between the seepage velocity, v_x, and contaminant velocity, v_c (L/T):

$$R = \frac{v_x}{v_c} \qquad (X6.12)$$

X6.3.5 Chiang et al. **(8)** demonstrated that the contribution of volatilization to the dissolved contaminant attenuation was only 5 % at one site. Except in the case of very shallow ground water, volatilization is not expected to contribute significantly to the overall attenuation. Therefore, volatilization is neglected and the decay rate is assumed to be a measure of biodegradation of BTEX compounds.

X6.3.6 Bear **(53)** obtained the following solution for one-dimensional transport with a first-order decay:

$$C(x,t) = \left(\frac{C_o}{2}\right) \exp\left[\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{\frac{1}{2}}\right]\right] erfc\left[\frac{x - v_c t \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{\frac{1}{2}}}{(4\,\alpha_x t v_c)^{\frac{1}{2}}}\right] \qquad \text{(X6.13)}$$

This solution is based on the assumptions that the contaminant concentration is initially zero, a continuous dissolved hydrocarbon source exists at C_o, and the transport is contained within a semi-infinite medium. The respective initial and boundary conditions are as follows:

$$C(x,0) = 0$$
$$C(0,t) = C_o$$
$$C(\infty,t) = 0$$

Eq X6.11 reflects a steady-state when the complementary error function (erfc) argument approaches +2, such that the point of observation, *x*, is behind the advective front $vt(1+4\lambda\ \alpha_x/v_c)^{1/2}$ **(54)**. As such, the steady-state solution is:

$$C(x) = C_o \exp\left[\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{\frac{1}{2}}\right]\right] \qquad \text{(X6.14)}$$

For the case in which decay occurs only in the aqueous phase, the contaminant velocity, v_c, is replaced by the seepage velocity, v_x.

X6.3.7 As the decay rate, λ, increases with respect to the other transport mechanisms, the extent of the plume at steady-state will decrease. As decay rate increases relative to the other mechanisms, the concentration away from the source (x > 0), approaches zero since the material is decaying at a greater rate than it is being transported through the medium. Similarly, as the contaminant velocity increases, the decay becomes ineffective in reducing concentrations as a function of distance. Retarded contaminants therefore have a greater opportunity to decay because retarded velocities favor biodegradation kinetics over transport **(54)**.

X6.3.8 The regression of contaminant concentration versus distance was developed in X6.2.2. This equation yields the reciprocal of the attenuation distance, k/v_x (L^{-1}):

$$C(x) = C_o e^{-(k\frac{x}{v_x})} \qquad \text{(X6.15)}$$

Eq X6.14 and Eq X6.15 are of the same form:

$$C(x) = C_o \exp\,(mx) \qquad \text{(X6.16)}$$

The slope of the log-linear data is given by m. The one-dimensional, steady-state transport solution also describes the slope, m, of the log-linear data:

$$m = \left(\frac{l}{2\alpha_x}\right)[l - \left(l + \frac{4\lambda\alpha_x}{v_c}\right)\frac{1}{2}] \qquad \text{(X6.17)}$$

Therefore, the term k/v_x and Eq X6.17 both describe the slope of the log-linear data and can be equated to solve for the total decay rate, λ, a measure of intrinsic bioremediation of petroleum hydrocarbons. Dispersivity (α_x), contaminant velocity (v_c), and k/v_x are input to following equation to calculate the decay rate **(51)**.

$$\lambda = \left(\frac{v_c}{4\alpha_x}\right)\left(\left[l + 2\alpha_x\left(\frac{k}{v_x}\right)\right]^2 - l\right) \qquad \text{(X6.18)}$$

For the case in which decay occurs only in the aqueous phase, v_c is replaced by v_x in Eq X6.18.

X6.3.9 The Example Problem No. 2 in X7.2 presents a case study which couples the one-dimensional analytical solution to the regression of concentration versus distance for a steady-state or stable plume. This example problem illustrates the contribution of biodecay to the overall attenuation rate.

X6.4 One, Two, and Three-Dimensional Analytical Models

X6.4.1 Analytical models may be used for several purposes. Transient solutions can estimate the time required for an expanding or shrinking plume to reach a particular configuration. Steady-state solutions can be used to estimate the extent of a plume and select the locations of downgradient monitoring wells. The justification for a two or three-dimensional model should be based on the availability of data. Two of the more sensitive input parameters are the decay rate and the ground water seepage velocity. When using any of these models it is recommended that the model be calibrated to actual site data to confirm predicted results. While many of the models described in previous sections may yield similar first order rate constants, the rate constants are not necessarily interchangeable due to the differences in model assumptions and the lumped nature of the parameter. The analytical solutions which follow were derived in three dimensions, but can be easily simplified to the two or one dimensional cases.

X6.4.2 *Application of a Steady State Analytical Model*:

X6.4.2.1 The steady state analytical solution to the transport equation derived by Domenico **(55)** can be used to estimate the plume extent and to determine first order attenuation rate constants. Eq X6.19 represents the steady state, centerline solution of the transport equation assuming a finite sized, but constant source and unidirectional ground water flow. The solution accounts for ground water flow in the x direction, three-dimensional dispersion, and first order solute degradation.

$$\frac{C(x,0,0,\infty)}{C(0,0,0,0)} = \exp\left(\frac{x}{2\alpha_x}\left[1 - \left\{1 + \frac{4\lambda\alpha_x}{v_s}\right\}^{\frac{1}{2}}\right]\right) \mathrm{erf}\left(\frac{Y}{4[\alpha_y x]^{\frac{1}{2}}}\right) \mathrm{erf}\left(\frac{Z}{4[\alpha_z x]^{\frac{1}{2}}}\right) \qquad \text{(X6.19)}$$

Where, $C(x,0.0,\infty)$ is the contaminant concentration along the primary flow direction of the plume, C(0,0,0,0) is the steady state source concentration, and x is the coordinate in the direction of ground water flow. a_x, a_y, and a_z are longitudinal, transverse, and vertical dispersivities, respectively. 1 is the first order degradation rate constant, v_x is the ground water seepage velocity, Y is the width of the source zone in the transverse direction, and Z is the thickness of the source zone in the vertical direction.

X6.4.2.2 To facilitate the use of Eq X6.19 in site specific evaluations, a computer spreadsheet was used to generate solution curves for various parameter values. A nomograph was then generated for the parameters listed in Table X6.3.

TABLE X6.3 Typical Values for Parameters in Domenico Analytical Model[A]

Parameter	Value	Reference
Dispersivity longitudinal transverse vertical	α_x= 4 ft α_y= 0.33 α_x α_z= 0.035 α_x	Conservative values. Typical range for α_x is 4 to 20 ft. (Newell et al. (1996)).
Source Dimensions Transverse Vertical	Y = 20 ft Z = 5 ft	Typical width at UST site. Typical smear zone thickness. Site specific data can be used but these are not highly sensitive parameters.
First order degradation constant	λ = 0.001 to 0.01 day^{-1} Typical range for λ to be used as a check on realism of site specific value.	Salanitro (1993)
Ground water velocity	v_s= site specific value	

[A] Fig. X6.4 gives the steady state plume centerline concentration for values of l/v_s from 0.0001 to 1.0 with a longitudinal dispersivity value of 4 ft. As shown in Fig. X6.4, the centerline concentration is very sensitive to the ratio of l/v_s. This ratio provides a measure of the rate of contaminant degradation to the rate of ground water travel. Thus, as the value of l/v_s increases, the predicted extent of the plume decreases.

X6.4.2.3 An expanded view of Fig. X6.4 from 0 to 300 ft downgradient from the source is given in Fig. X6.5.

X6.4.3 *Estimation of Plume Extent*—Fig. X6.4 can be used to estimate the probable extent of a plume at steady state with two qualifications. First, a range of values for l/v_s should be considered and secondly, actual monitoring data should be collected to verify plume attenuation estimates. Here the plume extent is defined as the distance from the downgradient edge of the residual source along the plume centerline to the point at which the contaminant concentrations drop below a specified target concentration. To use Fig. 1 to estimate the extent of a plume at steady state, follow these steps:

X6.4.3.1 Select the appropriate range of values for l (the values in Table X6.2 are recommended for BTEX),

X6.4.3.2 Estimate the site specific ground water seepage velocity,

X6.4.3.3 Calculate the range of l/v_s values for the site,

X6.4.3.4 Determine the target concentration for the compound of concern and divide the target level by the source area concentration to get the normalized target concentration (for example, the source concentration is 10 000 ppb benzene and the downgradient target is 5 ppb then the normalized target concentration is 5×10^{-4}), and

X6.4.3.5 Read the range of estimated plume extent from Fig. X6.4 or Fig. X6.5 by determining the point at which the curves corresponding to the l/v_s values calculated in X6.4.3.2 cross the normalized target concentration calculated in X6.4.3.4.

X6.4.4 *Determination of First Order Decay Constant*—As mentioned above, estimates of plume extent should be followed by calibration of the model with site specific data to verify the assumptions and refine the estimates. To calibrate this modeling approach to site specific data and to determine first order rate constants, multiple monitoring points along the primary flowpath of the plume are necessary. The procedure for calibration with site specific data to determine l is outlined below:

X6.4.4.1 Normalize plume centerline concentrations by dividing by the source concentration,

X6.4.4.2 Determine the distance of each monitoring point from the downgradient edge of the source area,

X6.4.4.3 Plot the normalized centerline concentrations on Fig. X6.4 or Fig. X6.5,

X6.4.4.4 Read the value of l/v_s from the nomograph which corresponds to the curve which provides the best fit to the data, and

X6.4.4.5 Multiply the value of l/v_s by the site specific seepage velocity to determine l.

X6.4.5 The proper application of Fig. X6.4 can be demonstrated for an actual UST site (McAllister (**56**)). Historical monitoring data at this site indicate a stable plume and ground water seepage velocity of 0.03 ft/day. Centerline monitoring wells identified at the site and used in this example were MW-1 (source well), MW-4, and MW-8. The data on these wells is summarized in Table X6.4.

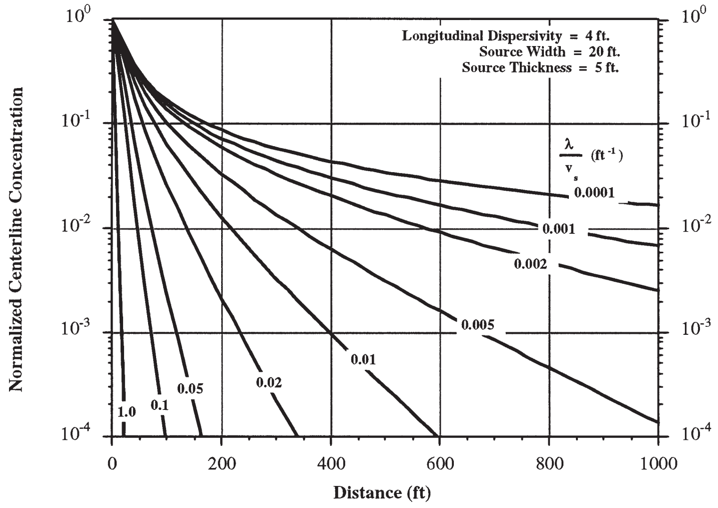


FIG. X6.4 Steady State Nomograph of Domenico (1987) Solution From 0 to 1000 ft Downgradient

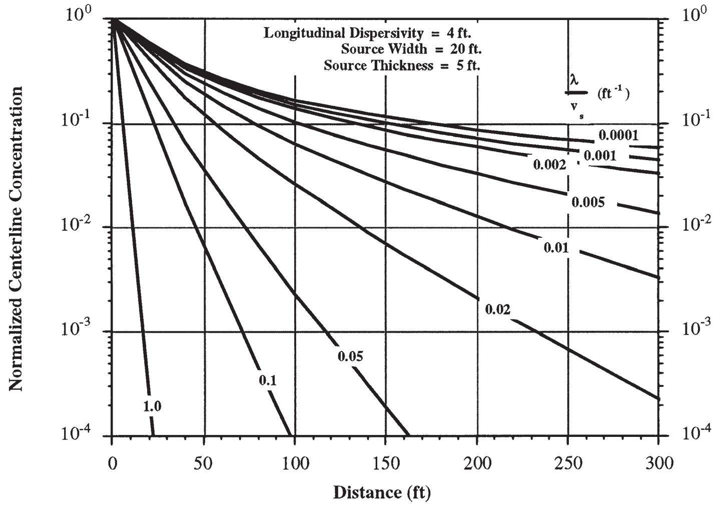


FIG. X6.5 Steady State Nomograph of Domenico (1987) Solution From 0 to 300 ft Downgradient

TABLE X6.4 Summary of UST Site Monitoring Well Data

Well ID	Distance from Source (ft)	Benzene Concentration (μg/L)	Normalized Benzene Concentration
MW-1	0	10 896	1.00
MW-4	23	1 207	0.11
MW-8	90	3	0.00028

X6.4.6 The normalized benzene concentrations in Table X6.4 were plotted versus distance from the source on Fig. X6.6 and the data clearly fall in the expected range of l/vs values, 0.033 to 0.33 ft^{-1}. The calibrated site specific value for l/vs was determined to be 0.1 ft^{-1}. Multiplying by the site ground water seepage velocity, the first order degradation rate constant was determined to be 0.003 day^{-1}.

X6.4.7 *Application of a Transient Analytical Model*:

X6.4.7.1 Consideration of transient plume behavior is important when establishing remedial goals, setting monitoring frequencies, evaluating the plume status, and determining when steady state models may be appropriately applied.

X6.4.7.2 To evaluate transient plume behavior, the transient, centerline analytical solution derived by Domenico **(55)** has been applied. Eq X6.20 represents the transient solution for the centerline concentration as a function of time.

$$\frac{C(x, 0, 0, t)}{C(0, 0, 0, 0)} = \frac{1}{2}\exp\left(\frac{x}{2\alpha_x}\left[1 - \left\{1 + \frac{4\lambda\alpha_x}{v_s}\right\}^{\frac{1}{2}}\right]\right)\mathrm{erfc}\left(\frac{x - v_s t\left[1 + \frac{4\lambda\alpha_x}{v_s}\right]^{\frac{1}{2}}}{2(\alpha_x x)^{\frac{1}{2}}}\right)\bullet \quad \text{(X6.20)}$$
$$\mathrm{erf}\left(\frac{Y}{4[\alpha_y x]^{\frac{1}{2}}}\right)\mathrm{erf}\left(\frac{Z}{4[\alpha_z x]^{\frac{1}{2}}}\right)$$

By comparison of Eq X6.19 and Eq X6.20 it can be seen that one-half of the steady state concentration is achieved when the erfc term in Eq X6.20 equals unity.

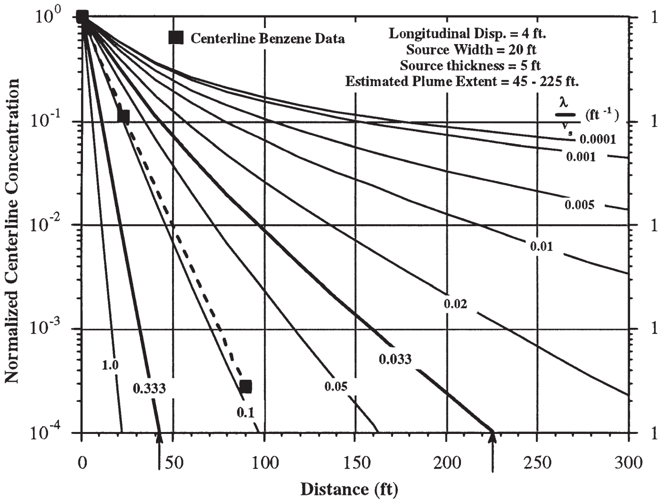


FIG. X6.6 Application of Domenico (1987) Steady State Solution to Estimate Plume Extent and First Order Degradation Rate Constant

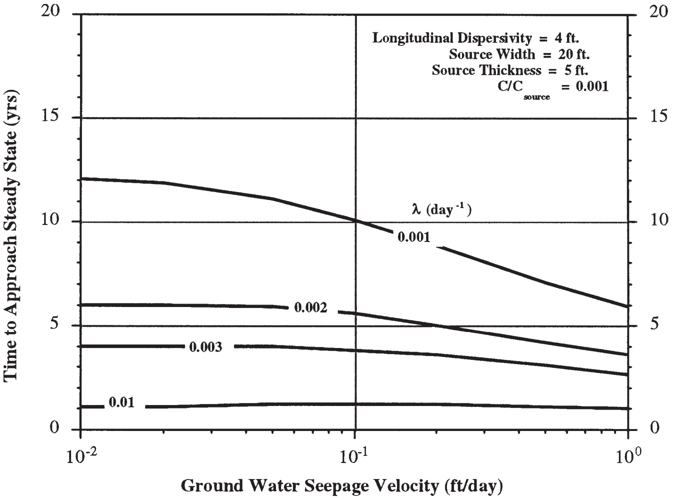


FIG. X6.7 Time to Approach Steady State Using the Domenico (1987) Transient Solution

$$\operatorname{erfc}\left(\frac{x - v_s t\left[1 + \frac{4\lambda\alpha_x}{v_s}\right]^{\frac{1}{2}}}{2(\alpha_x x)^{\frac{1}{2}}}\right) = 1 . \qquad (X6.21)$$

Solving Eq X6.21 for *t* gives the following expression for the time required to reach one-half the steady state concentration at any point along the primary flow path of the plume.

$$t_{ss} = \frac{x}{\left(1 + \frac{4\lambda\alpha_x}{v_s}\right)^{\frac{1}{2}} v_s} \qquad (X6.22)$$

Since one-half the steady state concentration is essentially the same as the steady state concentration given the typical variability in actual site data, the time t_{ss}, given in Eq X6.22 will be considered the time to approach steady state.

X6.4.7.3 Eq X6.22 was used to generate a nomograph by the following steps.

(*1*) Parameter values for l, v_s, and a_x were specified.

(*2*) Eq X6.20 and Fig. X6.4 were used to determine the steady state plume extent for a normalized target concentration of 10^{-3}.

(*3*) The value of t_{ss} was calculated from Eq X6.22.

(*4*) The procedure was repeated for various values of l and v_s.

X6.4.8 Shown in Fig. X6.7 are the time to approach steady state and the plume extent at steady state as a function of ground water seepage velocity for various values of l and a normalized target concentration of 10^{-3}(the normalized target concentration is the target concentration divided by the source concentration). The predicted behavior evident in these figures indicates that for high first order degradation rate constants ($\sim$0.01 day^{-1}), the time to steady state will become relatively independent of ground water seepage velocity and will be on the order of two years. As the value of l decreases, the predicted time to steady state increases and becomes more dependent on the seepage velocity.

X6.4.9 The use of Fig. X6.7, is demonstrated with data from the example site in X6.4.2. The site specific seepage velocity was 0.03 ft/day and the first order degradation rate constant was 0.003 day^{-1}. Thus, reading from Fig. X6.7 the time to approach steady state is approximately 4 years. The time to approach steady state for this site was consistent with the fact that the release was over six years old and monitoring data indicated the plume was stable.

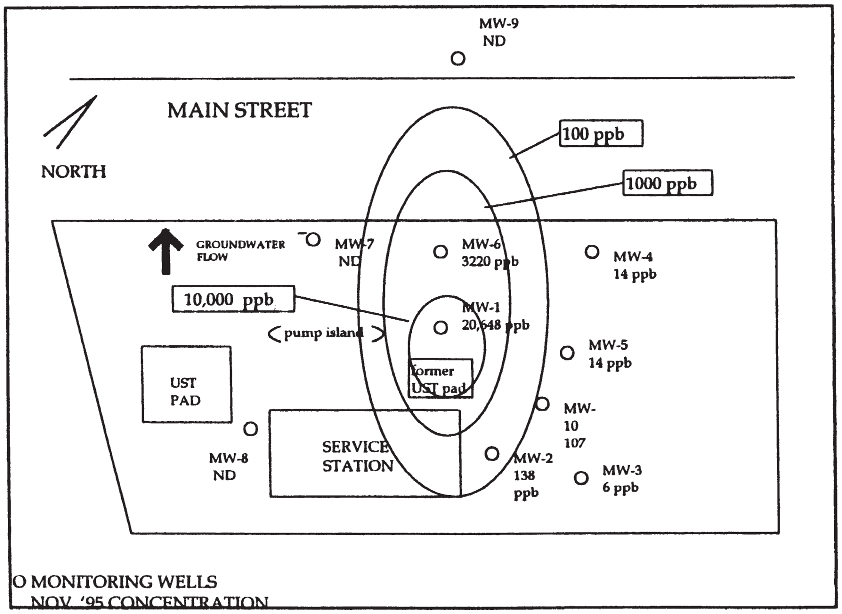
X7. EXAMPLE PROBLEMS

X7.1 Example Problem No. 1—Primary Lines of Evidence

X7.1.1 *Introduction*:

X7.1.1.1 The subject site is located on the east coast and is an active retail petroleum service station with nine monitoring wells on-site and one monitoring well offsite to the Northwest (Fig. X7.1). During a service station upgrade conducted in 1991, subsurface hydrocarbon impact was noted during UST removal activities. New USTs were installed along the western side of the property, with the former UST area located just south of MW-1 (Fig. X7.1). Depth to water is approximately 7 ft below grade and groundwater flow is to the northwest. Subsurface soils consist primarily of silts, with minor amounts of silty sands and clayey silts. No measurable free product has been found at the site. There are no private or public wells within a ½ mile radius of the site and city ordinances require hookup to the municipal water supply.

X7.1.1.2 A series of slug tests were conducted in monitoring wells MW-1, MW-4, MW-5, MW-8 and MW-9. The results of the analyses indicated that the site had an average hydraulic conductivity of 3.28 ft/day. With a site gradient of 0.01 ft/ft and



NOTE 1—Total BTEX concentrations and water table elevations in each monitoring well over nine consecutive quarters are given in Table X7.1. 1 in. = 40 ft.

FIG. X7.1 Service Station Site Map

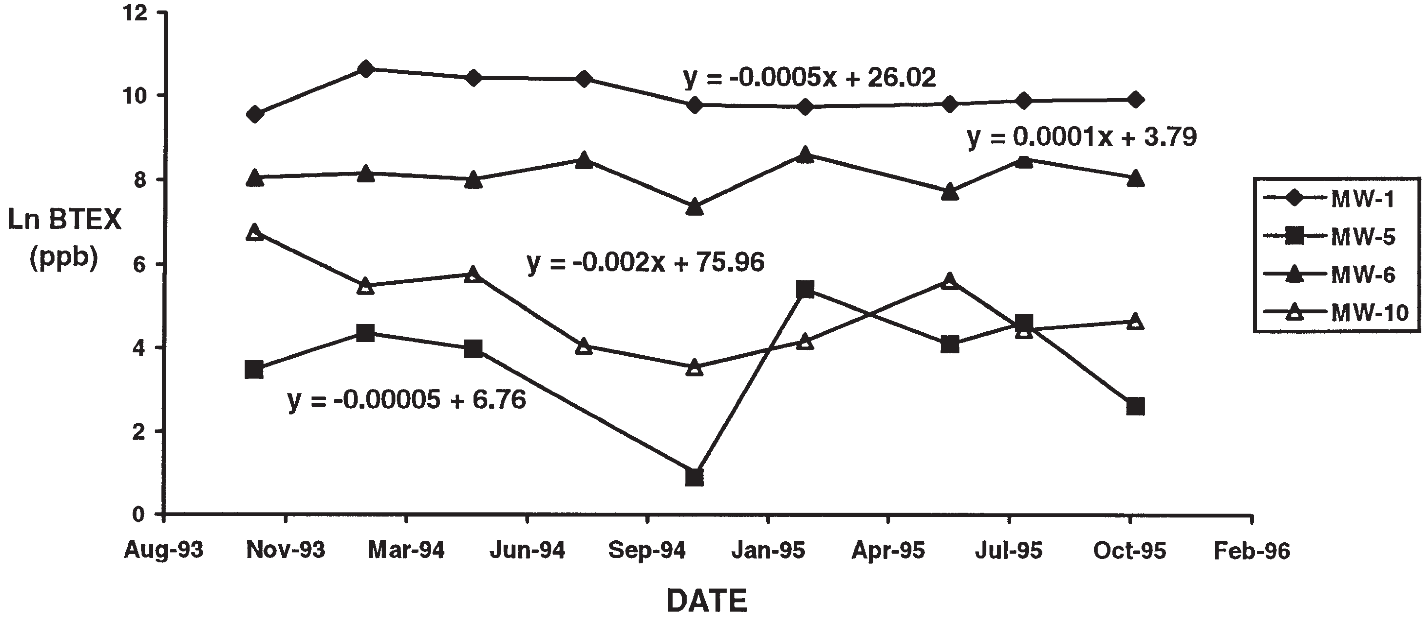
a soil porosity of 0.35 (default value based on aquifer texture), the resulting groundwater seepage velocity was 0.1 ft/day (37 ft/yr).

NOTE X7.1—This example does not address methods to properly evaluate groundwater flow direction or velocity. Such information can be found in other documents. For the purpose of this example, groundwater velocity and flow direction are assumed to be as stated.

X7.1.2 *Primary Lines of Evidence*:

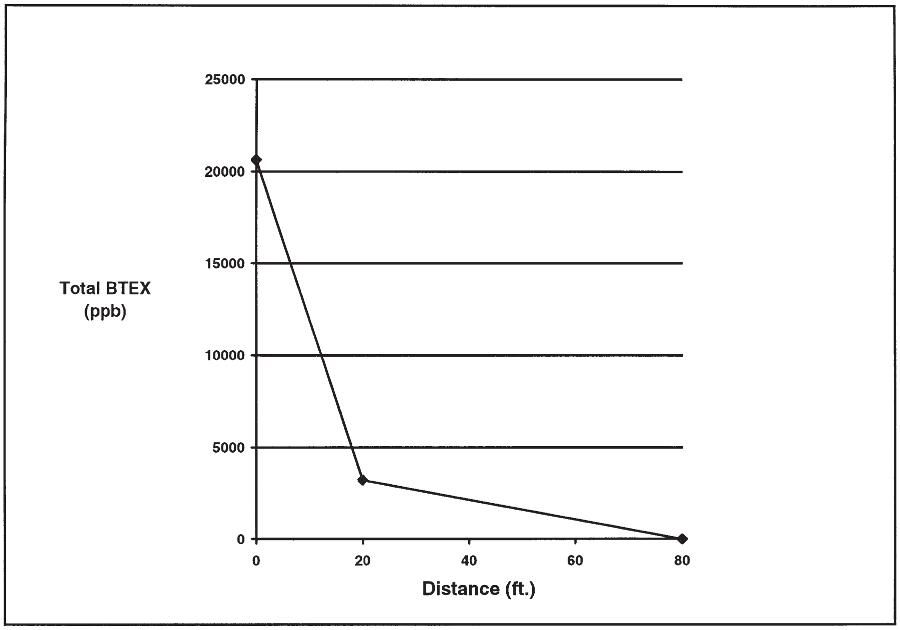
X7.1.2.1 The primary lines of evidence require a review of historical analytical data for dissolved BTEX in ground water (see Table X7.1). These data are used first to classify the plume as stable, shrinking or expanding.

X7.1.2.2 In this example, the natural log of BTEX concentrations versus time was plotted (Fig. X7.2) for four wells, in order to characterize the plume. The natural log of well concentrations was used in the evaluation so that increasing, stable or decreasing trends could be clearly differentiated from random concentration fluctuations. Linear regression analysis of the data was also used to determine the equation of the best fit line to the data for each of the four wells (Fig. X7.2). It is



NOTE 1—Equations associated with each data set represents equation of best fit line.

FIG. X7.2 Plot of Natural Log of BTEX Concentrations Versus Time in Four Site Wells



NOTE 1—Assuming MW-1 is in the source area (x = 0 ft.). MW-6 and MW-9 are 20 and 80 ft. from MW-1, respectively

FIG. X7.3 A Plot of Total BTEX Concentration Versus Distance, Using 3 Wells That Run Along the Plume Centerline (that is, MW-1, MW-6, MW-9)

clear from this analysis that concentrations in site wells have remained relatively stable for over two years, with the slope of the best fit line for each well approaching zero. In addition, the site map (Fig. X7.1) contains the 100, 1000, and 10 000 ppb total BTEX contours, based on the November 1995 data set **(57)**. Review of the data over the last nine sampling quarters illustrates that these contours have remained relatively stable. Thus, both the concentration versus time plots for site wells and an evaluation of concentration contours indicates that the plume is stable.

X7.1.2.3 As previously noted, the spill has existed since at least 1991. Based on a ground water velocity of 0.1 ft per day and a very conservative estimate of spill age of 5 years, site ground water has migrated over 185 ft. (0.1 ft/day × 365 days/year × 5 years). In contrast, in June 1995, site data indicated that the maximum extent of plume migration was less than 80 ft, with the downgradient well at 80 ft. remaining nondetect. In addition, an evaluation of total BTEX concentration versus distance (Fig. X7.3) in the three plume centerline wells, MW-1, MW-6 and MW-9 was conducted. As is typical, the placement of these three wells is not ideal, but the wells are the best available for the centerline analyses. The plot indicates order of magnitude decreases in BTEX concentration over short distances (tens of feet). Such rapid drops in concentration are clear evidence of the impact of intrinsic bioremediation on the plume. In contrast, concentration decreases over distances along the plume centerline due to dispersive effects would be small relative to the observed effects (see later examples).

X7.1.3 *Summary of Primary Lines of Evidence*:

X7.1.3.1 With the data base already in existence, it was possible to characterize the plume and evaluate the impact of natural attenuation without collecting additional data from the site. The plume is stable with no offsite impacts. A plume will only stabilize when the rate of BTEX mass removal through natural attenuation processes within the plume equals the mass of BTEX entering the plume from residually contaminated media. Thus, plume stability itself is strong evidence of the significance of ongoing natural attenuation processes within the plume. In addition, as previously noted, an evaluation of total BTEX concentration versus distance in the three plume centerline wells MW-1, MW-6 and MW-9, indicated order of magnitude decreases in BTEX concentration over short distances (tens of feet). Such rapid drops in concentration are clear evidence of the impacts of intrinsic bioremediations on the plume. In contrast, concentration decreases over distance in the plume due to dispersive effects would be small relative to the observed effects.

X7.1.3.2 The risk associated with contact with site groundwater is minimal to nonexistent. There are no public or private wells within ½ mile of the site. In addition, municipal ordinances require hookup to municipal water supplies. The closest downgradient residence is more than 200 ft. from the site, well beyond the maximum extent of the stable plume (<80 ft.). As noted, the site itself remains an active retail service station site and is paved, with no subsurface living spaces (no pathways for exposure to impacted groundwater).

X7.1.3.3 It is suggested that the number of wells monitored and monitoring frequency be reduced for this site. Only wells MW-1, MW-6 and MW-9 should continue to be monitored and on a reduced semi-annual basis for two years. If the plume remains stable or starts to shrink back, negotiations on closure can be further advanced with the regulating agency. A deed notice may be necessary for the site to restrict its use and protect against potential exposure pathways. If desired, the deed notice could be removed once natural attenuation mechanisms have reduced site concentrations to unrestricted-use and health-based limits.

TABLE X7.1 Total BTEX Concentrations and Water Table Elevations (WTE) in Site Monitoring Wells Over Nine Consecutive Quarters

WELL #	DATE	WTE	TOTAL BTEX (ppb)	WELL #	DATE	WTE	TOTAL BTEX (ppb)
MW-1	Nov 93	92.14	13,950	MW-6	Nov 93	91.75	3,180
	Feb 94	93.84	42,080		Feb 94	93.25	3,455
	May 94	94.17	33,899		May 94	93.84	3,022
	Aug 94	92.61	33,678		Aug 94	91.97	4,876
	Nov 94	91.85	18,051		Nov 94	91.55	1,635
	Feb 95	92.89	17,331		Feb 95	92.70	5,569
	Jun 95	92.00	18,474		Jun 95	91.84	2,329
	Aug 95	91.67	20,193		Aug 95	91.59	5,082
	Nov 95	93.16	20,648		Nov 95	92.99	3,220
MW-2	Nov 93	91.80	96	MW-7	Nov 93	91.62	18
	Feb 94	94.01	12		Feb 94	93.10	50
	May 94	94.16	<1		May 94	93.46	107
	Aug 94	92.45	16		Aug 94	92.10	<1
	Nov 94	91.36	8		Nov 94	91.32	<1
	Feb 95	93.27	10		Feb 95	92.67	9
	Jun 95	92.13	394		Jun 95	91.81	<1
	Aug 95	91.51	362		Aug 95	91.56	2
	Nov 95	93.28	138		Nov 95	93.06	3
MW-3	Nov 93	91.70	14	MW-8	Nov 93	92.05	<1
	Feb 94	94.05	<1		Feb 94	93.50	<1
	May 94	94.40	<1		May 94	93.88	<1
	Aug 94	92.40	<1		Aug 94	92.44	<1
	Nov 94	91.47	<1		Nov 94	90.54	<1
	Feb 95	93.27	<1		Feb 95	93.10	<1
	Jun 95	92.07	<1		Jun 95	92.24	<1
	Aug 95	91.42	20		Aug 95	91.77	<1
	Nov 95	93.43	6		Nov 95	93.50	<1
MW-4	Nov 93	90.78	14	MW-9	Nov 93	90.54	<1
	Feb 94	NS	NS		Feb 94	NS	NS
	May 94	93.76	10		May 94	93.19	<1
	Aug 94	92.16	<1		Aug 94	91.43	<1
	Nov 94	90.68	7		Nov 94	90.71	<1
	Feb 95	92.55	6		Feb 95	91.61	<1
	Jun 95	91.54	26		Jun 95	90.44	<1
	Aug 95	90.85	10		Aug 95	90.03	<1
	Nov 95	91.49	14		Nov 95	91.26	<1
MW-5	Nov 93	91.45	32	MW-10	Nov 93	91.17	874
	Feb 94	93.66	78		Feb 94	93.76	244
	May 94	94.11	54		May 94	94.21	321
	Aug 94	92.59	<1		Aug 94	92.48	58
	Nov 94	91.20	2		Nov 94	91.30	34
	Feb 95	92.76	229		Feb 95	92.94	65
	Jun 95	91.78	61		Jun 95	91.84	276
	Aug 95	91.28	102		Aug 95	91.36	86
	Nov 95	92.97	14		Nov 95	92.89	107

POTENTIOMETRIC SURFACE ELEVATIONS (ft)

	April, 1993	July, 1993	November, 1993	February 1994	June, 1994	September, 1994
MW-32	385.53	383.04	379.73	381.16	388.67	381.39
MW-17	379.16	378.25	376.14	377.19	378.44	377.26
MW-15	375.50	374.35	372.96	373.68	374.00	373.21
MW-2	373.37	372.36	371.26	371.87	371.74	371.35
MW-4	366.70	365.55	364.68	365.22	365.70	365.05
MW-37	351.62	349.36	351.76	349.09	349.52	348.02

BENZENE CONCENTRATIONS (mg/L)

	April, 1993	July, 1993	November, 1993	February, 1994	June, 1994	September, 1994
MW-32	2.2	3.1	2.3	2.4	1.9	2.9
MW-17	93	27	12	17	76	10
MW-15	4,700	2,400	1,500	2,100	2,000	1,500
MW-2	3,100	3,700	2,700	2,800	4,200	3,900
MW-4	79	120	210	74	140	310
MW-37	0.1	0.05	0.25	0.25	0.25	0.25

TOLUENE CONCENTRATIONS (mg/L)

TABLE X7.1 *Continued*

	April, 1993	July, 1993	November, 1993	February, 1994	June, 1994	September, 1994
MW-32	<0.5	7.5	<1	<1	<1	<1
MW-17	53	5.4	<1	<1	30	<1
MW-15	3,300	690	86	210	580	360
MW-2	460	700	200	160	390	170
MW-4	1.3	22	2.2	<1	1.6	2.9
MW-37	<0.5	<0.5	<1	<1	<1	<1

ETHYL-BENZENE CONCENTRATIONS (mg/L)

	April, 1993	July, 1993	November, 1993	February, 1994	June, 1994	September, 1994
MW-32	<0.8	1.5	<1	<1	<1	<1
MW-17	7.8	0.9	<1	<1	2.4	<1
MW-15	400	130	33	73	130	57
MW-2	220	250	180	130	240	160
MW-4	2.5	6.6	6.6	2.4	4.7	9.9
MW-37	<0.8	<0.8	<1	<1	<1	<1

XYLENE CONCENTRATIONS (mg/L)

	April, 1993	July, 1993	November, 1993	February, 1994	June, 1994	September, 1994
MW-32	<1.7	9.7	<2	<1	<2	<2
MW-17	43	6.2	<2	<2	70	<2
MW-15	2,600	940	610	650	960	480
MW-2	910	1,100	610	510	1,000	630
MW-4	26	54	42	18	37	59
MW-37	<1.7	<1.7	<2	<2	<2	<2

X7.2 Example Problem No. 2—Primary and Secondary Lines of Evidence

X7.2.1 *Introduction*—Example Problem No. 2 demonstrates the application of primary and secondary lines of evidence. Fig. X7.4 is a well location and ground water contour map for a terminal in Fairfax, VA. Ground water flow is to the northwest, as shown on the figure. Ground water elevation data for the past few years indicate flow conditions remain fairly

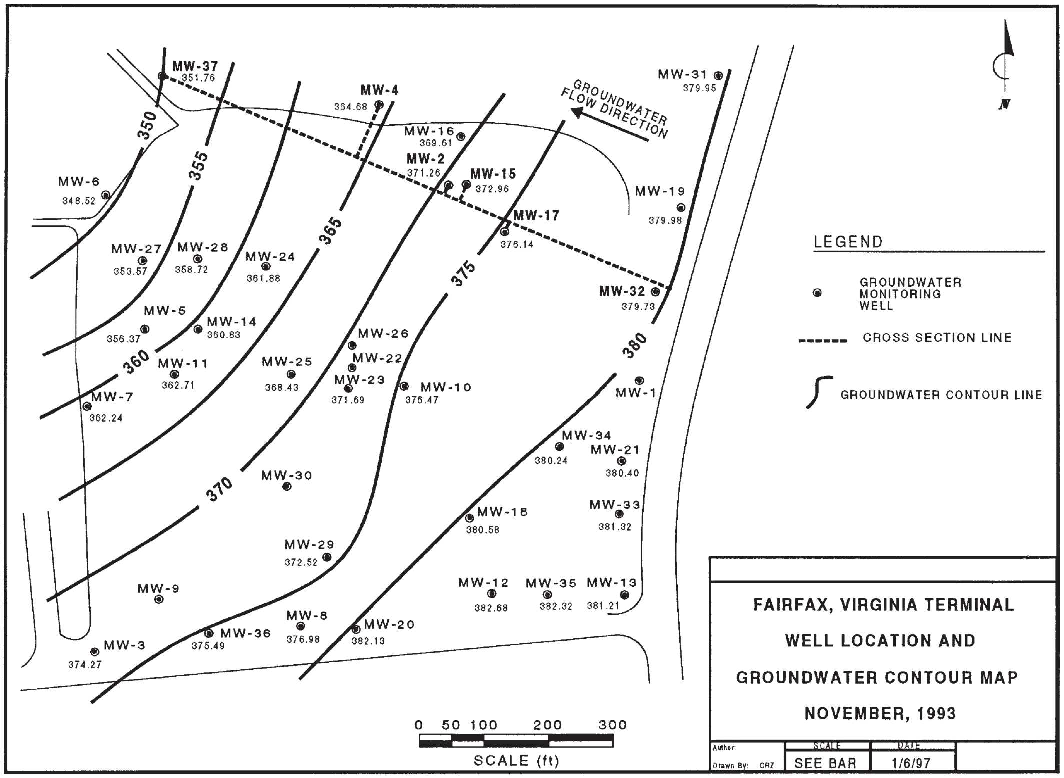


FIG. X7.4 Well Location and Groundwater Contour Map constant over time. Six monitoring wells are highlighted, oriented in the direction of ground water flow. BTEX concentrations suggest a contaminant source in the vicinity of MW-15.

X7.2.2 *Primary Lines of Evidence*—The primary lines of evidence entail a review of historical analytical data for dissolved BTEX in ground water. Table X7.1 summarizes six quarters (4/93-9/94) of ground water elevations and BTEX concentrations for the six monitoring wells oriented along the direction of ground water flow and shown in Fig. X7.4. The ground water flow direction and dissolved concentrations remain fairly constant over time. BTEX concentrations in the downgradient monitoring well, MW-37, are non-detectable for the period of record. These trends suggest a stable dissolved plume. Fig. X7.5 is a plot of concentration versus distance for four monitoring wells, MW-15, MW-2, MW-4, and MW-37. These are average concentrations for the six monitoring events. MW-15 is assumed to be in the vicinity of the contaminant source and is assigned to the origin. The distances separating the three downgradient wells from MW-15 are provided in Table X7.2. The plot in Fig. X7.5 illustrates the exponential decline in concentration versus distance. This relationship of concentration versus distance is further evaluated to obtain the secondary lines of evidence for natural attenuation.

X7.2.3 *Secondary Lines of Evidence*—The secondary lines of evidence include the following tasks: (*1*) regression of concentration versus distance to determine an attenuation rate and (*2*) evaluation of indicator parameters for intrinsic bioremediation.

X7.2.3.1 Log concentration versus distance for monitoring wells MW-15, MW-2, MW-4, and MW-37 is plotted in Fig. X7.6. The concentrations plotted in the figure are the average concentrations for each monitoring well for six quarters, as shown in Table X7.3. The data plot as a straight line, with a goodness of fit, $R^2 = 0.993$, suggesting first-order decay of concentration with distance. The slope of this line, k/v_x, is 0.02 ft^{-1} (attenuation rate divided by seepage velocity). With an estimate of seepage velocity, the attenuation rate can be determined. Pump test data indicate an average seepage velocity of 0.2 ft/day. Therefore, the attenuation rate is estimated as follows:

TABLE X7.2 Concentration Versus Distance

Monitor Well No.	Distance From MW-15 (ft)	Benzene Concentration (µg/L)[A]
MW-15	0	2367
MW-2	25	3400
MW-4	175	156
MW-37	505	0.2

[A] Average of data from 6 quarters (4/93 - 4/94).

$$k = (k/v_x)\ v_x \tag{X7.1}$$

$$k = (0.02\ ft^{-1})\ (0.2\ ft/day)$$

$$k = 0.004\ day^{-1}\ \text{or } 0.4\ \%/day$$

X7.2.3.2 The following intrinsic bioremediation indicator parameters were measured in ground water: dissolved oxygen (DO), oxidation-reduction potential, nitrate, sulfate, ferrous iron (Fe^{2+}), pH, biological oxygen demand (BOD), chemical oxygen demand (COD), and others. Fig. X7.7 illustrates plots for DO, oxidation-reduction potential, and ferrous iron versus distance from MW-15 (origin). Benzene concentrations are also shown on these plots. Dissolved oxygen (DO) concentrations are depleted in the middle of the dissolved plume, suggesting aerobic biodegradation is contributing to the configuration of the dissolved plume. The oxidation-reduction potential in the middle of the plume indicates reducing conditions where DO has been consumed. Ferrous iron is elevated in the middle of the plume, suggesting reduction of ferric iron (Fe^{3+}) as an alternative electron acceptor.

X7.2.4 *Optional Lines of Evidence*—An optional line of evidence applies a one-dimensional analytical solution for the stable plume. This solution is coupled with the concentration versus distance regression. The method calculates a decay rate which distinguishes between sorption, dispersion, and biodegradation.

X7.2.4.1 The slope of the line for concentration versus distance was determined by a secondary line of evidence (see

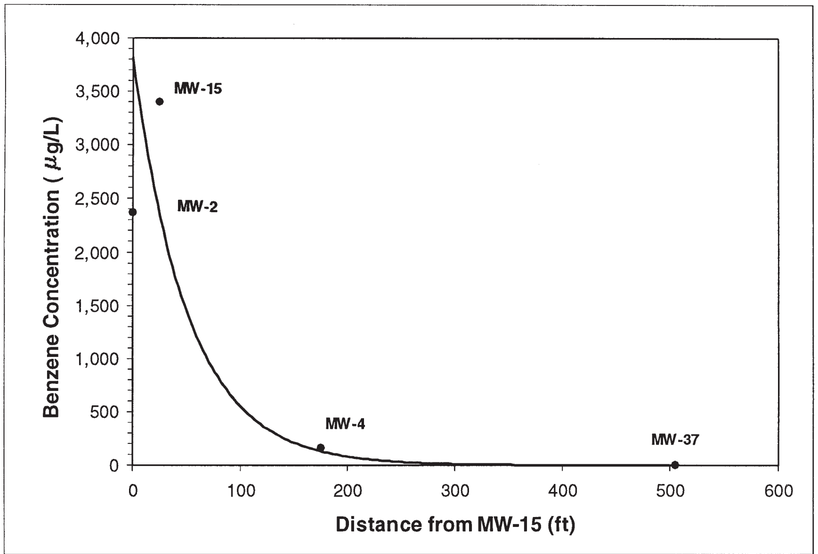


FIG. X7.5 Concentration Versus Distance

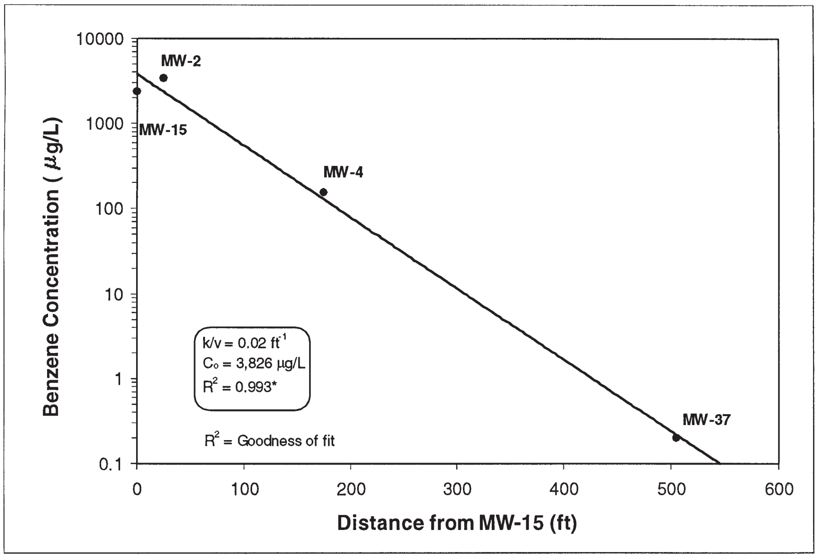


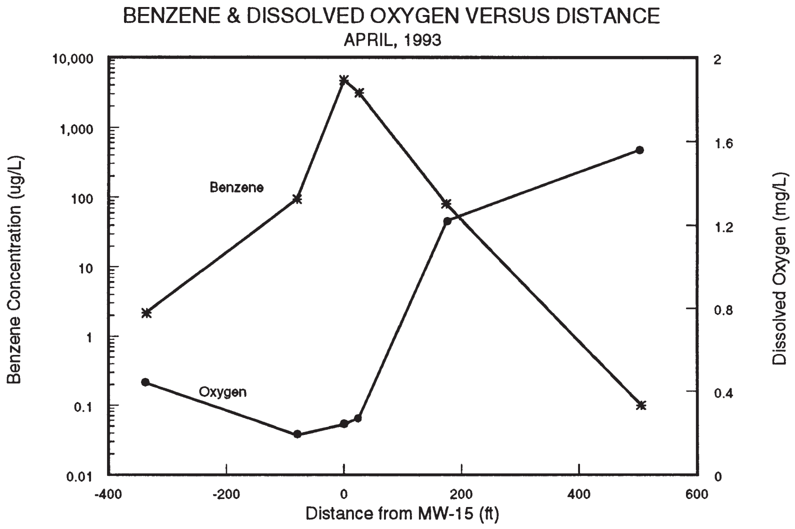
FIG. X7.6 Regression of Concentration Versus Distance

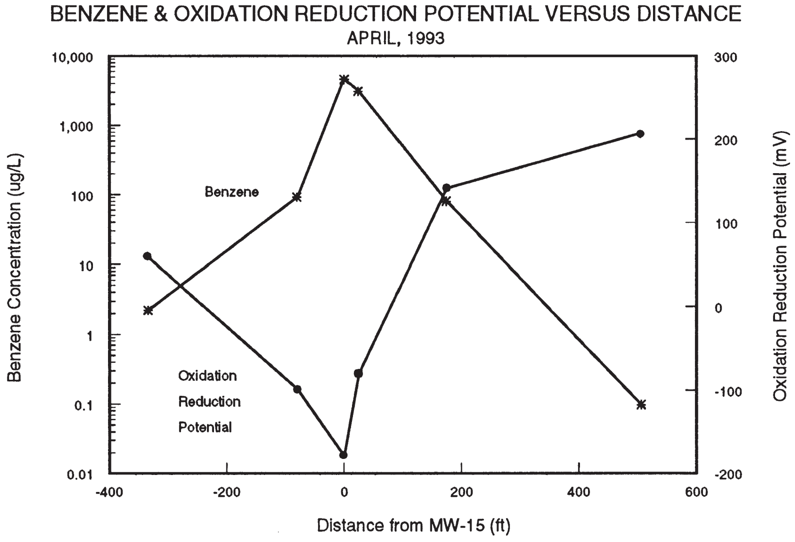
TABLE X7.3 Concentration Versus Distance

Monitor Well No.	Distance From MW-15 (ft)	Benzene Concentration (μg/L)^{A}
MW-15	0	2367
MW-2	25	3400
MW-4	175	156
MW-37	505	0.2

^{A}Average of data from 6 quarters (4/93 - 4/94).

X7.2.3.1). The slope, k/v_x =0.02 ft^{-1}, is used in the one-dimensional analytical solution to calculate a decay rate (Fig. X7.6). The results of equating the spatial regression with the steady-state analytical solution are presented in Table X7.4. The values for source concentration (C_o) and k/v_x were regressed using the data in Table X7.3. Table X7.4 includes k and the ratio, λ/k, the contribution of biodecay to the overall attenuation rate (expressed as %). In Case 1, seepage velocity is 0.2 ft/day based on aquifer pump tests. Retardation is estimated as 2 and dispersivity is estimated as 25 ft, approximately 5 % of the flow field (distance separating the two furthest wells). In Case 1, λ = 0.30 %/day (0.0030 days^{-1}); λ is 75 % of k for this case. The next three cases are performed to evaluate the sensitivity of changing various input parameters. In each of these cases C_o and k/v_x remain constant. In Case 2, seepage velocity is reduced by a factor of two (v_x = 0.10 ft/day), which reduces the decay rate by the same factor (λ = 0.15 %/day). In this case, only half the decay rate is required to maintain the Case 1 concentration decline with distance; as in Case 1, λ is 75 % of k in Case 2. In Case 3, the dispersivity is increased by a factor of two (α = 50 ft) and λ = 0.40 %/day. More decay is required with a larger dispersivity because more spreading of the contaminant occurs in the direction of ground water flow; λ is equivalent to k in Case 3. In Case 4, the retardation coefficient is 1, (v_c = v_x) and the dispersivity is reduced to 1 ft. In this case, biodecay is the only mechanism contributing to attenuation, therefore λ = k. These four cases demonstrate biodecay contributes significantly to the overall attenuation rate.


BENZENE & DISSOLVED OXYGEN VERSUS DISTANCE
APRIL, 1993


BENZENE & OXIDATION REDUCTION POTENTIAL VERSUS DISTANCE
APRIL, 1993

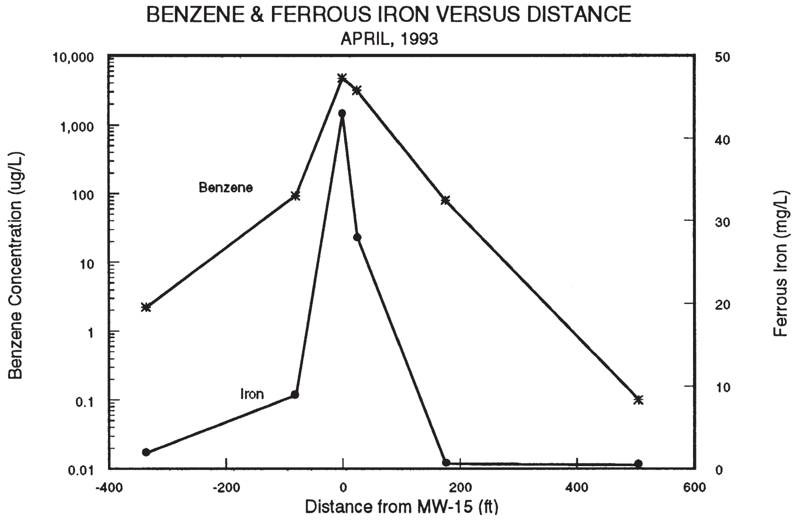

BENZENE & FERROUS IRON VERSUS DISTANCE
APRIL, 1993

FIG. X7.7 Indicator Parameters

TABLE X7.4 Decay Rates Based on Steady-State Analytical Solution, C_o = 3826 µg/L, k/v_x = 0.02 ft^{-1}. (Buscheck and Alcantar (1995)

	Seepage velocity, v_x (ft/day)	Retardation coefficient R	Contaminant velocity, v_c (ft/day)	Dispersity α (ft)	Attenuation rate, k (%/day)	Decay rate λ (%/day)	λ/k (%)
Case 1	0.20	2	0.10	25	0.40	0.30	75
Case 2	0.10	2	0.05	25	0.20	0.15	75
Case 3	0.20	2	0.10	50	0.40	0.40	100
Case 4	0.20	1	0.20	1.0	0.40	0.40	100

REFERENCES

(**1**) Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1995, Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Ground Water, *Air Force Center For Environmental Excellence*, Technology Transfer Division, Brooks Air Force Base, San Antonio, TX.

(**2**) Fetter, C.W., 1988. *Applied Hydrogeology:* MacMillan, New York, p 458.

(**3**) Freeze, R.A. and Cherry, J.A., 1979, Ground Water: Prentice-Hall, Inc., Englewood Cliffs, New Jersey, p 604.

(**4**) Fry, V.A., Istok, J.D., Semprini, L., O'Reilly, K.T. and Buscheck, T.E., 1995, Retardation of Dissolved Oxygen Due to a Trapped Gas Phase in Porous Media, Ground Water, 33, 391-398.

(**5**) Dragun, J., 1988, The Soil Chemistry of Hazardous Materials: Hazardous Materials Control Research Institute, Silver Spring, Maryland, p 458.

(**6**) Larson, R.A. and Weber, W.J., 1994, Reaction Mechanisms in Environmental Organic Chemistry: Lewis Publishers, Boca Raton, Florida, p 433.

(**7**) Lyman, W.J., Reidy, P.J. and Levy, B., 1992, Mobility and Degradation of Organic Contaminants in Subsurface Environments: C.K. Smoley, Inc., Chelsea, Michigan, p 395.

(**8**) Chiang, C. Y., Salanitro, J. P., Chai, E. Y., Colthart, J. D. and Klein, C. L., 1989, Aerobic Biodegradation of Benzene, Toluene, and Xylene in a Sandy Aquifer - Data Analysis and Computer Modeling, Ground Water, 27: 823-834.

(**9**) McAllister, P.M. and Chiang, C.Y., 1994, A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water, *Ground Water Monitoring Review*, Spring 1994, 161-173.

(**10**) Devinny, J.S., Everett, L.G., Lu, J.C.S. and Stollar, R.L., 1990, Subsurface Migration of Hazardous Wastes: Van Norstrand Reinhold, New York, p 387.

(**11**) USEPA, 1991 Site Characterization for Subsurface Remediation: EPA/625/4-91/026, p 259.

(**12**) Stuart, B.J., Bowlen, G.F. and Kosson, D.S., 1991, Competitive Sorption of Benzene, Toluene and the Xylenes onto Soil, *Environmental Progress*, 10(2), 104-109.

(**13**) Karickhoff, S.W., 1981, Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. Chemosphere, 10, 833-846.

(**14**) McCarty, P.L., Reinhard, M. and Rittmann, B.E., 1981, Trace Organics in Ground Water, *Environmental Science & Technology*, 15(1), 40-51.

(**15**) Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M. and Michalenko, E.M., 1991, *Handbook of Environmental Degradation Rates:* Lewis Publishers, Inc., Chelsea, Michigan, p 725.

(**16**) Chapelle, F.H., 1993, Ground Water Microbiology and Geochemistry: John Wiley & Sons, Inc., New York, p 424.

(**17**) Barker, J. F., Patrick, G. C. and Major, D., 1987, Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer, *Ground Water Monitoring Review*, 7: 64-71.

(**18**) Kemblowski, M. W., Salanitro, J. P., Deeley, G. M. and Stanley, C. C., 1987, Fate and Transport of Residual Hydrocarbon in Ground Water - A Case Study, In Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference: Prevention, Detection and Restoration Conference, *National Water Well Association and American Petroleum Institute*, Houston, TX., Nov., 17-22, pp. 207-231.

(**19**) Barbaro, J. R., Barker, J. F., Lemon, L. A. and Mayfield, C. I., 1992, Biotransformation of BTEX Under Anaerobic, Denitrifying Conditions: Field and Laboratory Observations, *J. Cont. Hydrology* 11: 245-272.

(**20**) Caldwell, K. R., Tarbox, D. L., Barr, K. D., Florenza, S., Dunlap, L. E. and Thomas, S. B., 1992, Assessment of Natural Bioremediation as an Alternative to Traditional Active Remediation at Selected Amoco Oil Company Sites, Florida, In Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, *National Ground Water Assoc./API*, Houston, Texas, Nov. 4-6, pp. 509-515.

(**21**) Salanitro, J. P., 1993, The Role of Bioattenuation in the Management of Aromatic Hydrocarbon Plumes in Aquifers, *Ground Water Monitoring and Remediation*, 13: 150-161.

(**22**) Wilson, J. T., Kampbell, D. H. and Armstrong, J., 1994a, Natural Bioreclamation of Alkylbenzenes (BTEX) from a Gasoline Spill in Methanogenic Ground Water, In Hinchee, R. E., Alleman, B. C., Hoeppel, R. E. and Miller, R. N. (eds) *Hydrocarbon Bioremediation*, Lewis Publishers, Ann Arbor, MI.

(**23**) Wilson, J. T., Pfeffer, F. M., Weaver, J. W., Kampbell, D. H., Wiedemeier, T. H., Hansen, J. E. and Miller, R. N., 1994b, Intrinsic Bioremediation of JP-4 Jet Fuel, *In Proceedings of the Symposium on Intrinsic Bioremediation of Ground Water*, Denver, CO. August 30 - September 1.

(**24**) McAllister, P. M. and Chiang, C. Y., 1994, A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water, *Ground Water Monitoring and Remediation*, 14: 161-173.

(**25**) Hutchins, S. R., 1992, Inhibition of Alkylbenzene Biodegradation Under Denitrifying Conditions by Using the Acetylene Block Technique, *Applied and Environmental Microbiology*, 58:3395-3398.

(**26**) Alvarez, P. J. J. and Vogel, T. M., 1994, Degradation of BTEX and Their Aerobic Metabolites by Indigenous Microorganisms Under Nitrate-Reducing Conditions, Abstracts of the 94th Annual Meeting, *American Society for Microbiology*, Q-339.

(**27**) Ball, H. A., Hopkins, G. D., Orwin, E. and Reinhard, M., 1994, Anaerobic Bioremediation of Aromatic Hydrocarbons in Seal Beach, CA: Laboratory and Field Investigations, Environmental Protection Agency Symposium on Intrinsic Bioremediation of Ground Water, August 30-September 1, 1994, Denver, Colorado.

(**28**) Ball, H. A. and Reinhard, M., 1995, Monoaromatic Hydrocarbon Degradation Under Anaerobic Conditions at Seal Beach, CA:Laboratory Studies, *Environmental Toxicology and Chemistry*, (in press).

(**29**) Beller, H. R., Grbic-Galic, D. and Reinhard, M., 1992, Microbial Degradation of Toluene Under Sulfate-Reducing Conditions and the Influence of Iron on the Process, *Applied Environmental Microbiology* 58: 789-793.

(**30**) Edwards, E. A. and Grbic-Galic, D., 1992, Complete Mineralization of Benzene by Aquifer Microorganisms Under Strictly Anaerobic

Conditions, *Applied Environmental Microbiology* 58: 2663-2666.

(**31**) Cozzarelli, I. M., Eganhouse, R. P. and Baedecker, M. J. 1990, Transformation of Monoaromatic Hydrocarbons to Organic Acids in Anoxic Ground Water Environment, *Environmental Geology and Water Science*, 16:135-141.

(**32**) Baedecker, M. J., Cozzarelli, I. M., Eganhouse, R. P., Siegel, D. I. and Bennett, P. E., 1993, Crude Oil in a Shallow Sand and Gravel Aquifer - III, Biogeochemical Reactions and Mass Balance Modeling in Anoxic Ground Water, *Applied Geochemistry*, 8:569-586.

(**33**) Cozzarelli, I. M., Baedecker, M. J., Eganhouse, M. J. and Goerlitz, D. F. 1994, The Geochemical Evolution of Low-Molecular-Weight Organic Acids Derived from the Degradation of Petroleum Contaminants in Ground Water, *Geochimica et Cosmochimica Acta*, 58(2), 883-877.

(**34**) Lovley, D. R., Woodward, J. C. and Chapelle, F. H. 1994, Stimulated Anaoxic Biodegradation of Aromatic Hydrocarbons Using Fe(III) Ligands, *Nature*, 370:128-131.

(**35**) Borden, R. C., Gomez, C. A. and Becker, M. T. 1994, Natural Bioremediation of a Gasoline Spill, In *Hydrocarbon Bioremediation*, ed. Hinchee, R. E., Alleman, B. C., Hoeppel, R. E. and Miller, R. N., pp. 290-295, Boca Raton, Lewis Publishers.

(**36**) Wilson, B. H., Smith, G. B. and Rees, J. F., 1986, Biotransformation of Selected Alkylbenzenes and Halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study, *Env. Science Technol*. 20: 997-1002.

(**37**) Wilson, B. H., Wilson, J. T., Kampbell, D. H., Bledsoe, B. E. and Armstrong, J. M. 1990, Biotransformation of Monoaromatic and Chlorinated Hydrocarbons at an Aviation Gasoline Spill Site, *Geomicrobiology Journal*, 8:235-240.

(**38**) Edwards, E. A. and Grbic-Galic, D. 1994, Anaerobic Degradation of Toluene and O-Xylene by a Methanogenic Consortium, *Applied and Environmental Microbiology*, 60:313-322.

(**39**) Major, D. W., Mayfield, C. J. and Barker, J. F. 1988, Biotransformation of Benzene by Denitrification in Aquifer Sand, Ground Water, 26: 8-14.

(**40**) Lovley, D. R., Coates, J. D., Woodward, J. C. and Phillips, E. J. P. 1995, Benzene Oxidation Coupled to Sulfate Reduction, *Applied and Environmental Microbiology*, 61:953-958.

(**41**) Caldwell, K. R. and Suffita, J. M. 1995, Anaerobic and Microaerophilic Degradation of Benzene in Aquifer Sediments, Abstracts of the Third International Symposium on In-situ and On Site Bioreclamation. San Diego, California, April 24-27, 1995, E(.6.

(**42**) Newell, C. J., McLeod, R. K., Gonzales, J. R. 1996, BIOSCREEN Intrinsic Remediation Decision Support System User's Manual Version 1.2.

(**43**) Parker, J. C., Lenhard, R. J. and Kuppusamy, T., 1987, A Parametric Model for Constitutive Properties Governing Multiphase Flow in Porous Media, *Water Resources Research*, 23: 618-624.

(**44**) Shiu, W. Y., Maijanen, A., Ng, A. L. Y. and Mackay, D., 1988, Preparation of Aqueous Solutions of Sparingly Soluble Organic Substances: II. Multicomponent Systems - Hydrocarbon Mixtures and Petroleum Products, *Environmental Toxicology Chemistry* 7:125-137.

(**45**) Martin-Hayden, J. M., Robbins, G. A. and Bristol, R. D., 1991, Mass Balance Evaluation of Monitoring Well Purging, Part II, Field Tests at a Gasoline Contamination Site, Journal of Contaminant Hydrology, 8:225-241.

(**46**) Robbins, G. A. and Martin-Hayden, J. M. 1991, Mass-Balance Evaluation of Monitoring Well Purging, Part I. *Journal of Contaminant Hydrology*, v. 8, 203-224.

(**47**) Garbedian, S. P., Leblanc, D. R., Hess, K. M. and Quadri, R. D. 1987, Natural-Gradient Tracer Test in Sand and Gravels: Result of Special Moments Analysis. In B. J. Franks, (ed.), U. S. Geol. Survey Open File Report, 87-109, U. S. Geological Survey Program on Toxic Waste - Ground Water Contamination: Proceedings of the Third Technical Meeting, Pensacola, FL. March 23-27, pp. B13-B16.

(**48**) Sudicky, E. A., Cherry, L. A., and Frind, E. O., 1983, Migration of Contaminants in Ground Water at a Landfill: A Case Study, *Journal of Hydrology*, 63: 81-108.

(**49**) American Petroleum Institute (API), 1991, Technological Limits of Groundwater Remediation: A Statistical Evaluation Method, API Publication No. 4510.

(**50**) Wilson, J. T., Kampbell, D. H. and Armstrong, J., 1993, Natural Bioreclamation of Alkyl Benzenes (BTEX) From a Gasoline Spill in Methanogenic Groundwater, *Proceedings of the Environmental Restoration Technology Transfer Symposium*, San Antonio, TX.

(**51**) Buscheck, T. E. and Alcantar, C. M., 1995, Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation, In Hinchee, R. E., Wilson, J. T. and Downey, D. C. (Eds.), Intrinsic Bioremediation, pp. 109-116.

(**52**) Wiedemeier, T. H., Swanson, M. A., Wilson, J. T., Kampbell, D. H., Miller, R. N. and Hansen, J. E., 1996, Approximation of Biodegradation Rate Constants for Monoaromatic Hydrocarbons (BTEX) in Ground Water, Ground Water Monitoring and Remediation 16(3): 186-194.

(**53**) Bear, J. 1979, Hydraulics of Groundwater, McGraw-Hill, New York, NY.

(**54**) Domenico, P. A. and Schwartz, F. W., 1990, Physical and Chemical Hydrogeology, John Wiley & Sons, New York, NY.

(**55**) Domenico, P. A., 1987, An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species, *Journal of Hydrology*, 91, 49-58.

(**56**) McAllister, P. M., 1996, Application of Screening Model Approaches for Evaluation of BTEX Natural Attenuation in Ground Water, Proceedings of Petroleum Hydrocarbons & Organic Chemicals in Groundwater: Prevention, Detection, and Remediation, Nov. 13-15, Houston, Texas.

(**57**) Buscheck, T. E. and Alcantar, C. M., 1995, Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation, In Hinchee, R. E., Wilson, J. T., and Downey, D. C. (Eds.), Intrinsic Biremediation, pp. 109-116.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).