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

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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.

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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;

1.7.5.2 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]

D888 Test Methods for Dissolved Oxygen in Water
D1125 Test Methods for Electrical Conductivity and Resistivity of Water
D1293 Test Methods for pH of Water
D1452 Practice for Soil Exploration and Sampling by Auger Borings
D1498 Test Method for Oxidation-Reduction Potential of Water
D1586 Test Method for Penetration Test (SPT) and Split-Barrel Sampling of Soils
D4043 Guide for Selection of Aquifer Test Method in Determining Hydraulic Properties by Well Techniques
D4044 Test Method for (Field Procedure) for Instantaneous Change in Head (Slug) Tests for Determining Hydraulic Properties of Aquifers
D4050 Test Method for (Field Procedure) for Withdrawal and Injection Well Testing for Determining Hydraulic Properties of Aquifer Systems
D4104 Test Method (Analytical Procedure) for Determining Transmissivity of Nonleaky Confined Aquifers by Overdamped Well Response to Instantaneous Change in Head (Slug Tests)
D4105 Test Method for (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Modified Theis Nonequilibrium Method
D4106 Test Method for (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Theis Nonequilibrium Method
D4372 Specification for Flame-Resistant Materials Used in Camping Tentage (Withdrawn 2002)[3]
D4448 Guide for Sampling Ground-Water Monitoring Wells
D4658 Test Method for Sulfide Ion in Water
D4700 Guide for Soil Sampling from the Vadose Zone
D4750 Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well) (Withdrawn 2010)[3]
D5092 Practice for Design and Installation of Groundwater Monitoring Wells
D5269 Test Method for Determining Transmissivity of Nonleaky Confined Aquifers by the Theis Recovery Method
D5270 Test Method for Determining Transmissivity and Storage Coefficient of Bounded, Nonleaky, Confined Aquifers
D5434 Guide for Field Logging of Subsurface Explorations of Soil and Rock
D5473 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
E1599 Guide for Corrective Action for Petroleum Releases (Withdrawn 2002)[3]
E1689 Guide for Developing Conceptual Site Models for Contaminated Sites
E1739 Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites
E1912 Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Releases (Withdrawn 2013)[3]

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.

[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] The last approved version of this historical standard is referenced on www.astm.org.

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.

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 D4750).

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).[4]

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

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

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

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 E1739 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 E1912), 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 E1599 and U.S. EPA guidance for implementation of remediation by natural attenuation (U.S. EPA, 1995, Chapter 9).[5]

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] 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.

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, 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)[4] 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).[4] 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).[4] 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),[4] 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:*

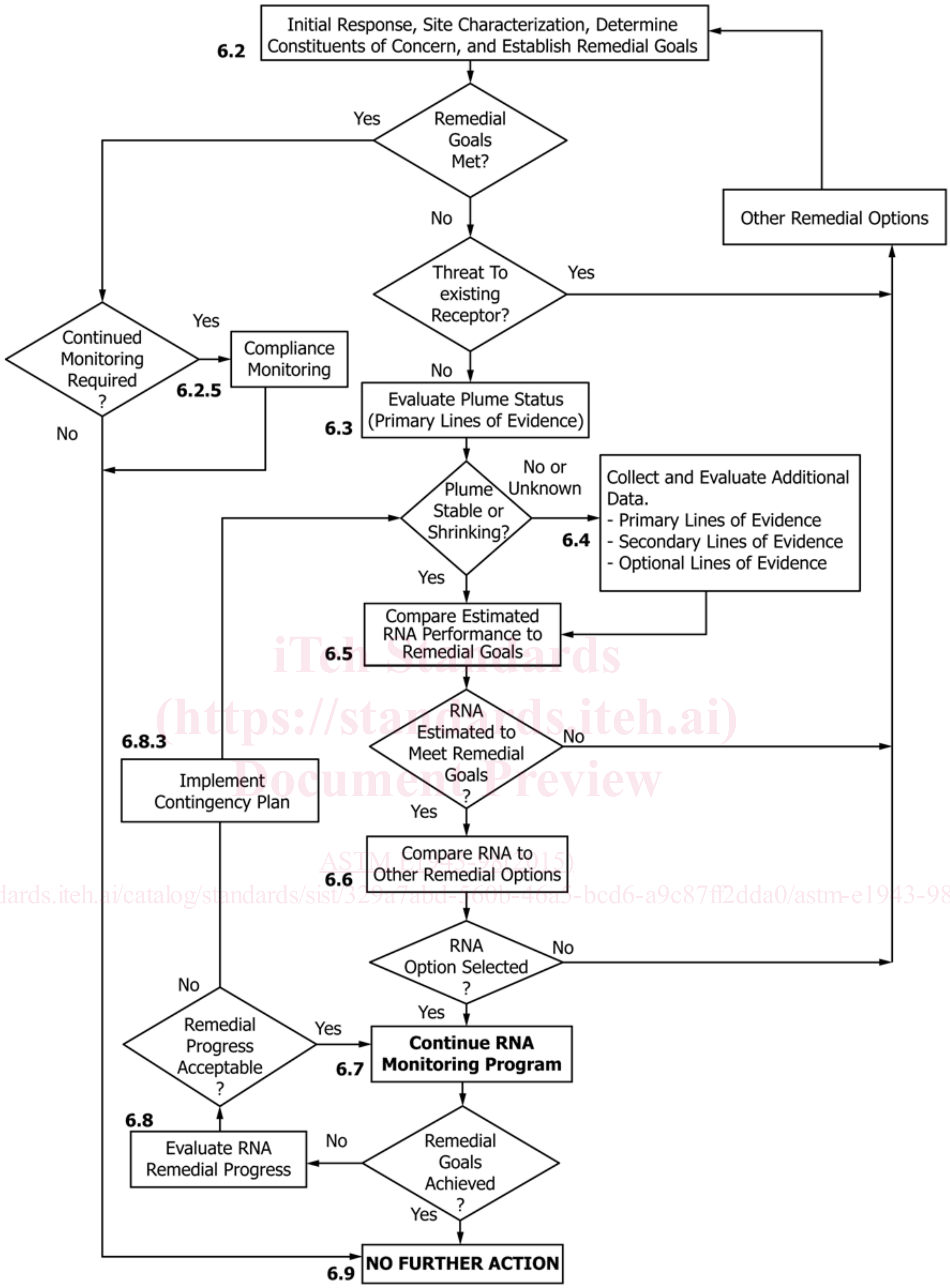
6.2.1 Initial response should be taken in accordance with implementing agency requirements to report any release of petroleum products; prevent any further release of, or exposure to hydrocarbons in vapor, dissolved, or liquid phase; and mitigate fire and safety hazards. Table 1 in Guide E1739 provides 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 E1599, and Guide E1912 taking into consideration evaluation of sources, pathways, and receptors as discussed in 6.2 of Guide E1739. 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 E1689, and Guide E1912 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 E1739 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 E1739 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



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

FIG. 1 Remediation by Natural Attenuation Process Flowchart

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 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 E1739 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 E1739 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).[4] 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),[4] 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.

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 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.

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**).[6]

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

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 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 E1739).

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