



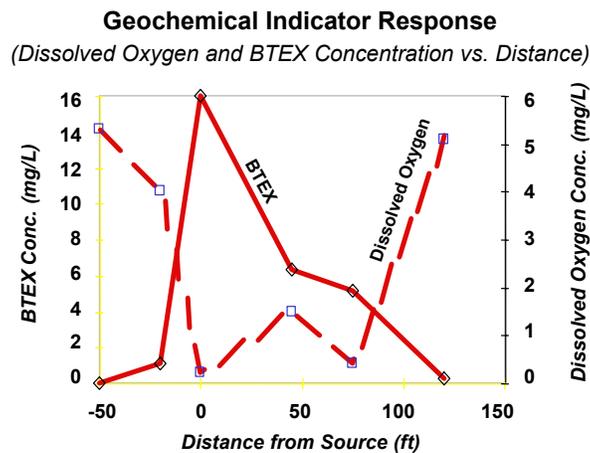
WASHINGTON STATE
DEPARTMENT OF
E C O L O G Y

Guidance on Remediation of Petroleum-Contaminated Ground Water By Natural Attenuation

Washington State Department of Ecology
Toxics Cleanup Program

July 2005

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Disclaimer: This document provides technical guidance on how to evaluate the feasibility and performance of cleanup action alternatives that use natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water under the Model Toxics Control Act (MTCA) Cleanup Regulation, chapter 173-340 WAC. It does not establish or modify regulatory requirements. This document is **not** intended, and **cannot** be relied on, to create rights, substantive or procedural, enforceable by any party in litigation with the State of Washington. The Washington State Department of Ecology (Ecology) reserves the right to act at variance with this guidance at any time. Any regulatory decisions made by Ecology in any matter addressed by this guidance will be made by applying the governing statutes and administrative rules to the relevant facts.

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Chapter 1 Introduction

1.1 Purpose of this Guidance

The purpose of this document is to provide technical guidance on how to evaluate the feasibility and performance of cleanup action alternatives that use natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water under the Model Toxics Control Act (MTCA) Cleanup Regulation, chapter 173-340 WAC.* This guidance does not establish or modify regulatory requirements. While this guidance provides several useful evaluation methods and tools to demonstrate compliance with regulatory requirements and makes recommendations regarding the appropriate use of those methods and tools, persons do **not** need to use those specific methods or tools and may use **alternative** methods or tools to demonstrate compliance.

This document is intended for Ecology site managers and anyone who is contemplating using natural attenuation to clean up ground water contaminated with petroleum hydrocarbons. Users of this guidance should be appropriately trained[†] in the performance of remedial actions, and should exercise the same care and professional judgment as when performing any other remedial action. This document is also intended to provide useful information to the public and other interested persons.

This document constitutes one part of the natural attenuation guidance package, which includes:

- ***Guidance on Remediation of Petroleum-Contaminated Ground Water by Natural Attenuation*, Washington State Department of Ecology, Pub. No. 05-09-091 (Guidance) ← THIS DOCUMENT**
- *User's Manual: Natural Attenuation Analysis Tool Package for Petroleum-Contaminated Ground Water*, Washington State Department of Ecology, Pub. No. 05-09-091A (User's Manual)
- *Workbooks: Data Analysis Tool Package*: (Two Microsoft Excel[®] Spreadsheets)

The technical guidance provided in this document is organized based on the steps in the cleanup process set forth in the MTCA Cleanup Regulation, chapter 173-340 WAC, and illustrated in Figure 1.1 of this document. This document provides specific guidance on the following:

- The advantages and limitations of using natural attenuation to clean up petroleum-contaminated ground water;

* For ease of reference, this document sometimes refers to natural attenuation simply as a cleanup action alternative, even though natural attenuation may actually constitute only one component of an alternative that includes other components, such as soil removal and ground water treatment.

[†] Most natural attenuation demonstration appears to fall within the scope of those activities that must be conducted by, or under the supervision of, a licensed professional engineer or geologist (Chapter 18.43 RCW and Chapter 18.220 RCW). Please consult with the appropriate licensing board for questions regarding these requirements.

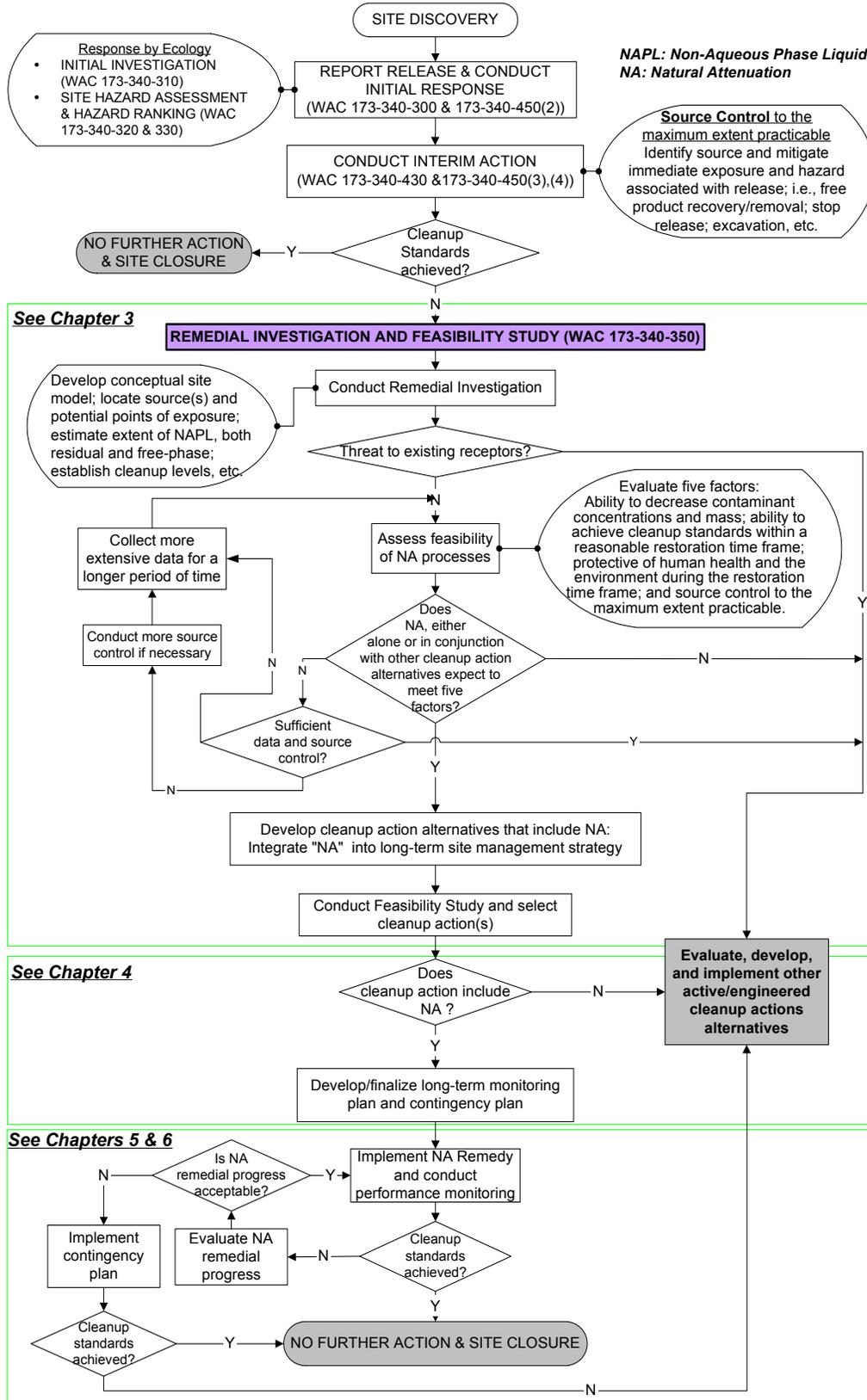
- What data should be collected as part of the remedial investigation to adequately evaluate the feasibility of natural attenuation as a cleanup action alternative;
- How to evaluate the feasibility of natural attenuation as a cleanup action alternative, including what evaluations should be conducted and what methods may be used to conduct those evaluations;
- How to assess a feasibility study of cleanup action alternatives;
- How to develop a performance monitoring plan for implementing natural attenuation as a component of the selected cleanup action, including what data should be collected to adequately evaluate the performance of natural attenuation;
- How to develop a contingency plan, including what site conditions may require conducting additional remedial actions and what remedial actions may be required; and
- How to implement natural attenuation as a component of the selected cleanup action.

This document does **not** provide comprehensive guidance on how to clean up petroleum-contaminated sites under the MTCA Cleanup Regulation, chapter 173-340 WAC. The guidance provided in this document is limited to technical guidance on how to evaluate the feasibility of natural attenuation as a cleanup action alternative and how to implement natural attenuation as a component of the selected cleanup action. For more comprehensive guidance on how to clean up petroleum-contaminated sites, including how to establish cleanup standards for petroleum, please refer to the forthcoming Ecology guidance document.

The technical guidance provided in these documents is based on numerous technical resource and guidance documents, which are listed in Appendix A of this document. The user should consult those references as appropriate to better understand the mechanisms of natural attenuation and how to evaluate those mechanisms. However, compliance with the guidance set forth in those references may not be sufficient to determine compliance with the MTCA Cleanup Regulation, chapter 173-340 WAC. The material contained in this guidance is based on the best available technical information at the time of its writing and the knowledge and experience of the authors and the reviewers.

*Note: The **Data Analysis Tool Package**, available separately, provides several different tools to assist in conducting each of the evaluations. Each tool is associated with a particular method specified in the guidance. The associated **User's Manual**, also available separately, provides detailed instructions on how to use the tools provided in the Tool Package. Although Ecology has provided these methods and tools to assist in conducting the evaluations, use of these specific methods and tools is **not required** to conduct the evaluations. For more information regarding the Data Analysis Tool Package, please refer to Section 3.3.1 of this guidance.*

Figure 1.1. Recommended Work Flow Path using Natural Attenuation as a Cleanup Action at Petroleum-Contaminated Ground Water Sites



1.2 Applicability of this Guidance

This guidance is intended to apply to the cleanup of **petroleum-contaminated ground water** at sites regulated under the Model Toxics Control Act (MTCA), chapter 70.105D RCW. This guidance is not intended for contaminants other than petroleum-related contaminants.

The applicability of this guidance to the cleanup of petroleum-contaminated ground water does not depend on the date the release was discovered, the degree or duration of prior ground water monitoring, or the degree of prior cleanup, including source control. However, the degree and nature of prior ground water monitoring will impact decisions regarding what additional data, if any, must still be collected to evaluate the feasibility of natural attenuation as a cleanup action alternative. Decisions to collect additional data should be based on identified data gaps. The degree of prior cleanup will impact the length of the restoration time frame and decisions regarding the feasibility of natural attenuation as a cleanup action alternative.

This guidance **may not** be applicable to the cleanup of ground water if any of the following conditions are present at a site:

- (1) The ground water is contaminated with **radionuclides** that pose a radiological hazard.

*The technical guidance provided in this document **cannot** be used to evaluate the natural attenuation of hazardous substances that pose a radiological hazard.*

- (2) The ground water is contaminated with hazardous substances other than petroleum (e.g., chlorinated solvents or metals) or mixtures of petroleum and other hazardous substances (e.g., petroleum and chlorinated solvents or metals).

While the basic concepts contained in this document pertaining to site investigations and monitoring **may be helpful** in evaluating the feasibility and performance of natural attenuation at these sites, this guidance may be insufficient to conduct these evaluations. For example, not all contaminants are as amenable to natural attenuation as petroleum hydrocarbons, and additional steps will likely be necessary to demonstrate chemical or biological degradation is occurring. Mixtures of contaminants behave differently than single substances so that simple models may not be sufficient to predict their behavior. Also, the degradation by-products of some compounds may be more toxic and mobile than the parent compound, and this may need to be considered in any analysis. For such sites, consult with the Ecology site manager to discuss the applicability of this guidance and what other factors need to be considered as part of the evaluation.

Additional technical information regarding the attenuation of non-petroleum ground water contaminants is available from a variety of other sources, including those listed in Appendix A of this document and the following:

- *US EPA, 1998, Technical Protocol for evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, EPA/600/R-98/128.*

- *Interstate Technology and Regulatory Cooperation, 1999, Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices.*

- (3) Where the contaminated ground water is strongly influenced by tides, rivers or stream fluctuations, or ground water extraction wells.

While the basic concepts contained in this document pertaining to site investigations and monitoring **may be helpful** in evaluating the feasibility and performance of natural attenuation at these sites, this guidance may be insufficient to conduct these evaluations. For example, because of the complexity of ground water flow in these situations, a more detailed hydrologic investigation will likely be required as well as more frequent sampling for site investigations and performance monitoring. More complex models may also be necessary. Surface water and sediment impacts will also need to be considered in detail. For such sites, consult with the Ecology site manager to discuss the applicability of this guidance and what other factors need to be considered as part of the evaluation.

This guidance is not applicable to the cleanup of the entire site, only the contaminated ground water associated with the site. More specifically, this guidance is not applicable to the cleanup of the following media:

- (1) The cleanup of contaminated soils.

This guidance is applicable only to the cleanup of the contaminated ground water at a site, not the soils above the water table. Note, however, that in most cases the soil contamination at a site has impacted the underlying ground water, and as such, the cleanup of the ground water is dependent on the cleanup of the contaminated soils.

This document does not provide guidance regarding the use of natural attenuation to clean up contaminated soils. Technical information regarding natural attenuation mechanisms for soil is available from a variety of sources, including those listed in Appendix A of this document and the following:

- US EPA, 1989, Bioremediation of Contaminated Surface Soils, EPA/600/9-89/073.
- US EPA, 1990, Assessing UST Corrective Action Technologies: Site Assessment and Selection of Unsaturated Zone Treatment Technologies, EPA/600/2-90/011.
- US EPA, 2004, How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers” (EPA 510-R-04-002), refer to pages IX-1 to IX-33 in Chapter IX ([Monitored Natural Attenuation](#)).
- Wisconsin Department of Natural Resources, August 1994, Naturally Occurring Biodegradation as a Remedial Action Option for Soil Contamination, Publ-SW-515-95.

- (2) The cleanup of contaminated surface water, sediments, or Non Aqueous Phase Liquid (NAPL).

1.3 Background on Natural Attenuation

The term “natural attenuation” as used in this guidance refers to a variety of physical, chemical, and/or biological processes that under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of hazardous substances in the environment. These *in situ* processes include: natural biodegradation; dispersion; dilution by recharge; sorption; volatilization; chemical or biological stabilization, transformation or destruction of hazardous substances (WAC 173-340-200). Several of these processes are defined in Section 1.7 of this guidance and further explained with sample calculations in Appendix D of the User’s Manual.

When applied as part of a cleanup action, natural attenuation is often referred to by US EPA as “monitored natural attenuation” to distinguish the action from “no action.” “Monitored natural attenuation,” as the term is used in US EPA, OSWER Directive 9200.4-17P (1999a), means the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by more active cleanup methods. It should be noted that this directive was conceptual and was intended to apply to natural attenuation of all contaminants in all media, which is more comprehensive than the scope addressed by this guidance.

The natural attenuation processes can be classified as either:

- Physical (dispersion, dilution by recharge, and volatilization);
- Chemical (sorption and chemical degradation); or
- Biological (biodegradation).

Natural attenuation processes that result in the reduction of concentration and/or mobility of a contaminant, but not the total mass, are referred to as “non-destructive” mechanisms. Those processes include the physical dispersion and dilution processes and the chemical sorption process (ASTM, 1998). Natural attenuation processes that result in the reduction of the total contaminant mass in the system are referred to as “destructive” mechanisms. Those processes include the chemical and biological degradation processes. For petroleum hydrocarbons in the subsurface, biological degradation is often the most important destructive mechanism because hydrocarbons can be destroyed (ASTM, 1998).

Although some natural attenuation typically occurs at most contaminated sites, the effectiveness of these processes varies depending on the types and concentrations of contaminants present at the site and the physical, chemical, and biological characteristics of the site. Consequently, use of natural attenuation as a cleanup action at a particular site often may be inappropriate. Natural attenuation should be evaluated as one potential remedial approach along with other cleanup action alternatives involving more active remedial technologies.

Evolution of the Concept of Natural Attenuation as a Remedy:

Both the early NRC (National Research Council) report (1993) and US EPA (1999a) recommended that natural attenuation be evaluated with three types of evidence:

- Observed (clear and meaningful) loss of contaminant;
- Evidence that biodegradation is feasible for the setting; and
- Evidence from the field that the biodegradation potential is actually realized.

This strategy has been further developed by others so that demonstration of natural attenuation may be completed by evaluating primary, secondary, and optional lines of evidence or a “weight of evidence approach.” Under this approach, primary and secondary lines of evidence are required to demonstrate that natural attenuation is occurring. The decision to collect optional lines of evidence should be based on site-specific factors.

The most common primary line of evidence is analytical data that define the plume as shrinking, stable, or expanding, similar to the first item suggested by NRC (1993). Sufficient historical monitoring data are needed to demonstrate this line of evidence.

Secondary lines of evidence include the evaluation of geochemical indicators for naturally occurring biodegradation and estimated rates of natural attenuation and biodegradation. The secondary lines of evidence are used to demonstrate that the main mechanism of natural attenuation is biodegradation. This line of evidence is consistent with the second item suggested by NRC (1993). Under this approach, even if the primary lines of evidence are conclusive, it may be necessary to obtain secondary lines of evidence.

Optional lines of evidence may also be used to more rigorously interpret data, particularly if the primary and secondary lines of evidence are inconclusive (ASTM, 1998). Optional lines of evidence may include solute transport modeling and microbiological studies NRC (1993). However, for petroleum hydrocarbons, if the primary and secondary lines of evidence are inconclusive, additional ground water data for a longer period of time may be the best approach rather than extensive modeling or microbiological studies.

Recently, US EPA (2001a) conducted a review of natural attenuation. US EPA concluded that when properly employed, natural attenuation is an “**effective knowledge-based remedy**” that can be protective of human health and the environment when a thorough engineering analysis provides for the understanding, monitoring, predicting, and quantitative documentation of the natural processes at a contaminated site.

Similar to the US EPA position, NRC (2000) refined this view by stating that natural attenuation should be selected only when a “**cause-and-effect relationship**” is established between the destruction and/or immobilization processes and the loss of contaminant. NRC (2000) prescribes a three-part strategy for implementing their approach for natural attenuation decision making:

- Develop a site conceptual model that identifies what destruction or immobilization processes are responsible for protecting human health and the environment;
- Obtain site-specific information that documents the cause-and-effect relationship between the destruction and/or immobilization processes and the contaminant loss; and
- Implement a long-term data acquisition and evaluation program that documents that these processes are sustained and are consistent with design objectives.

1.4 Requirements for Use of Natural Attenuation as a Cleanup Action

Under the MTCA Cleanup Regulation, the cleanup action selected for a site must meet each of the minimum requirements specified in WAC 173-340-360(2). To select the cleanup action, a Remedial Investigation and Feasibility Study (RI/FS) must be conducted in accordance with WAC 173-340-350.

For sites where the ground water is contaminated with petroleum hydrocarbons, one of the alternatives that could be considered during the RI/FS is an alternative that uses natural attenuation, either alone or in conjunction with other cleanup action components, to clean up the petroleum-contaminated ground water. In fact, several such alternatives could be evaluated, each of which relying to a varying degree on natural attenuation to clean up the ground water.

Natural attenuation is one of many cleanup action alternatives or components of an alternative that can be considered to address ground water contamination at a site. However, **natural attenuation is not a “model remedy,”** as defined in WAC 173-340-390, for addressing ground water contamination. Consequently, to select an alternative that uses natural attenuation, either alone or in conjunction with other cleanup action components, as the ground water cleanup action, the user must still conduct a feasibility study in accordance with WAC 173-340-350 and demonstrate that the alternative meets each of the minimum requirements specified in WAC 173-340-360(2).

*Note: This document does **not** provide comprehensive guidance on how to conduct a remedial investigation and feasibility study of cleanup action alternatives for a petroleum-contaminated site. For more comprehensive guidance on how to conduct a feasibility study for a petroleum-contaminated site, including the types of cleanup action alternatives that could be considered during such a study, please refer to other Ecology guidance.*

1.4.1 Remedial Investigation

Under the MTCA Cleanup Regulation, a remedial investigation must be conducted in accordance with the requirements set forth in WAC 173-340-350. As part of that investigation, sufficient information must be collected to conduct a feasibility study of cleanup action alternatives and then select a cleanup action.

This document provides technical guidance on how to conduct a remedial investigation for the purpose of evaluating cleanup action alternatives that use natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water. This document does not establish or modify regulatory requirements. The focus of the technical guidance provided in this document is limited to the following:

- What data should be collected as part of the remedial investigation to adequately evaluate the feasibility of natural attenuation as a cleanup action alternative;
- How to develop a remedial investigation work plan to collect the specified data; and
- How to develop a conceptual site model based on the data collected.

1.4.2 Feasibility Study

Under the MTCA Cleanup Regulation, a feasibility study must be conducted and a cleanup action selected in accordance with the requirements set forth in WAC 173-340-350. As part of that study, a range of cleanup action alternatives must be developed and evaluated based on the minimum requirements specified in WAC 173-340-360(2).

The cleanup action selected for a site must meet each of these **minimum requirements**. These requirements include, but are not limited to, the following:

- **Compliance with Cleanup Standards.** If a cleanup action alternative does not comply with cleanup standards, the alternative is an "interim action," not a "cleanup action." However, where an alternative involves containment of soils with hazardous substance concentrations exceeding cleanup levels at the point of compliance, the alternative may be determined to comply with cleanup standards provided it meets several specific requirements, including that the alternative is protective of human health and the environment.
- **Compliance with Applicable State and Federal Laws.** Cleanup levels and actions must comply with existing state or federal laws. For example, if the cleanup involves pumping and treating ground water and discharging the treated ground water to surface water, surface water discharge requirements in state and federal water quality laws must be met.
- **Protecting Human Health and the Environment.** The cleanup action selected must either reduce or remove (or destroy) the contamination, restoring the site to cleanup levels, or contain the contamination in such a way that will minimize future exposure of humans and ecological receptors. Cleanup action alternatives that achieve cleanup levels at the applicable points of compliance and comply with applicable state and federal laws are presumed to be protective of human health and the environment. Cleanup action alternatives that provide for the containment of soils must be demonstrated to be protective of human health and the environment through either quantitative or qualitative risk assessments.
- **Providing for Compliance Monitoring.** The cleanup action selected must provide for monitoring to verify that the cleanup action achieves cleanup or other performance standards and that the cleanup action remains effective over time.
- **Using Permanent Solutions to the Maximum Extent Practicable.** As required by the MTCA, the cleanup action selected must use permanent solutions to the maximum extent practicable. Permanent solutions (cleanup actions) are actions in which cleanup standards can be met without further action being required, such as monitoring or institutional controls. To select the most practicable permanent solution from among those cleanup action alternatives that are protective of human health and the environment requires conducting a disproportionate cost analysis. This analysis involves comparing the costs and benefits of alternatives and selecting the alternative whose incremental costs are not disproportionate to the incremental benefits. The comparison of benefits and costs may be quantitative, but will often be qualitative and require the use of best professional judgment.

- **Providing for a Reasonable Restoration Time Frame.** Some cleanup methods, such as natural attenuation, can take years or even decades to restore a site, depending on the contaminants. When evaluating alternative methods of cleanup, the period of time required to restore the site (to achieve cleanup and other performance standards) must be considered. The regulation specifies factors that must be considered when determining whether the restoration time frame is reasonable.
- **Considering Public Concerns.** Public notice and participation is an integral part of the remedy selection process. The public notice and participation requirements for cleanups conducted by Ecology or conducted by a potentially liable person under an order or decree are set forth in the rule. For example, the regulation requires that the draft cleanup action plan, which describes the proposed method of site cleanup, must be submitted for public review and comment. For cleanup plans where site-specific risk assessment is used to establish cleanup levels or to evaluate the protectiveness of a remedy or for cleanup plans that would restrict future site or resource use, public notices are required to specifically invite comment on these elements of the plan.

If the selected cleanup action relies primarily on **dilution and dispersion**, then it must also be demonstrated that the incremental cost of any active remedial measure over the cost of dilution and dispersion **grossly exceeds** the incremental benefit of the active remedial measure over the benefit of dilution and dispersion in accordance with WAC 173-340-360(2)(g). If the selected cleanup action uses natural attenuation and conforms to the expectations in WAC 173-340-370(7), then the cleanup action can be considered an active remedial measure. See definition of “natural attenuation” in WAC 173-340-200.

A cleanup action that uses natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water **conforms** to the **expectations** set forth in WAC 173-340-370(7) if:

- **Source control** (including removal and/or treatment of hazardous substances) has been conducted to the **maximum extent practicable**;
- There is evidence **that natural biodegradation or chemical degradation** is occurring and will continue to occur at a **reasonable rate** at the site;
- Leaving contaminants on-site during the restoration time frame does **not pose an unacceptable threat to human health or the environment**; and
- **Appropriate monitoring** is conducted to ensure that the natural attenuation process is taking place and that human health and the environment are protected.

This document provides technical guidance on how to develop and evaluate the feasibility of natural attenuation as a cleanup action alternative during the feasibility study. This document does not establish or modify regulatory requirements.

1.5 Expectations for Use of Natural Attenuation as a Cleanup Action

Although one of the cleanup action alternatives for a petroleum-contaminated site that can be considered during the remedial investigation and feasibility study is an alternative that uses natural attenuation, the use of natural attenuation may not always be appropriate at a petroleum-contaminated site.

1.5.1 Appropriate use of natural attenuation

Ecology expects that it may be **most appropriate** to rely **solely** on natural attenuation to achieve ground water cleanup standards at sites where all of the following have been met:

- Prior to relying solely on natural attenuation, **source control** actions (e.g., mitigation of the highly-contaminated plume areas and treatment [or removal] of free-product and contaminated soils) are conducted to the maximum extent practicable to prevent the further contamination of the ground water, and natural attenuation can achieve ground water cleanup standards without further source control or other engineered ground water remedial actions;
- Prior to relying solely on natural attenuation, the ground water plume is demonstrated to be **stable or shrinking**, thereby shortening the restoration time frame and ensuring that the plume will not continue to migrate and adversely impact ground water resources and other media (e.g., surface water, sediments, and air) or receptors (human or ecological);
- Natural chemical or biological degradation is a substantial mechanism of natural attenuation at the site;
- The destructive mechanisms of natural attenuation do not result in the exceedance of cleanup levels for by-products (i.e., daughter products);
- The estimated restoration time frame for natural attenuation is reasonable compared to that of other more active cleanup action alternatives, as determined by considering the factors set forth in WAC 173-340-360(4);
- There is no current or projected use of, or demand for, the affected ground water during the restoration time frame, or alternative water supplies are available;
- The use of natural attenuation will be protective of human health and the environment during the restoration time frame, as determined by conducting an appropriate quantitative or qualitative risk assessment and considering the threat posed by the ground water contamination to other media (e.g., surface water, sediments, and air) and receptors (human or ecological); and
- Adequate performance monitoring will be conducted throughout the restoration time frame to demonstrate that natural attenuation is both effective in reducing contaminants concentrations and protective of receptors.

1.5.2 Inappropriate use of natural attenuation

Ecology expects that it will **not** be appropriate to rely **solely** on natural attenuation to achieve ground water cleanup standards at sites where:

- **Free product** has not yet been removed to the maximum extent practicable, thereby promoting the expansion and the long-term persistence of the contaminant plume;

- The contaminant plume is still **expanding**, thereby threatening additional ground water resources and other media (e.g., surface water, sediments, air) and receptors (human or ecological); or
- **Receptors** (human or ecological) have been and continue to be contaminated by the ground water plume, even if the plume is not expanding. For guidance on identifying receptors, please refer to Section 3.1.2 and the definition in Section 1.7 of this document.

1.5.3 Discussion

The evaluation of natural attenuation as a cleanup action alternative may require an extensive remedial investigation, including a complete characterization of the nature and extent of contamination and the impact of that contamination on both human and ecological receptors. Also, natural attenuation requires documentation of the conditions for and progress of the different natural attenuation mechanisms throughout the plume, and a long-term monitoring plan that will continue to document the progress of those mechanisms to ensure that natural attenuation will continue to be both effective in reducing contaminant concentrations (and mass) and be protective of both human and ecological receptors during the restoration time frame.

Natural attenuation processes, particularly biological degradation, are currently best documented at petroleum fuel spill sites (US EPA, 1999a). Under appropriate field conditions, the regulated compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) may naturally degrade through microbial activity and ultimately produce non-toxic end products (e.g., carbon dioxide and water) (Morel and Hering, 1993; Cozzarelli et al., 1990; Wilson et al., 1990; Bouwer, 1992; ASTM, 1998; US EPA, 1999a, 1999b, 2004c; National Research Council, 2000). While BTEX contaminants tend to biodegrade with relative ease, other chemicals (e.g., methyl tertiary butyl ether [MTBE]) that are more resistant to biological or other degradation processes may also be present in petroleum fuels.

For most petroleum hydrocarbons, daughter products are not significant (US EPA, 2004c). For MTBE, however, one of the intermediate degradation products is tertiary-butyl alcohol (TBA) which is more difficult to remediate than MTBE itself, and more toxic. TBA is also used as a fuel oxygenate in its own right, as well as being an impurity in MTBE. Some conventional analytical techniques actually degrade MTBE and form TBA during sample analysis. When this occurs, the analytical results are not representative of what is occurring in the subsurface. Thus, the presence of TBA does not necessarily indicate the biodegradation of MTBE, and concentration data alone should not be used to establish the biodegradation rate for MTBE.

Where microbial activity is sufficiently rapid, the dissolved BTEX contaminant plume may stabilize (i.e., stop expanding), and contaminant concentrations in ground water may eventually decrease to levels below cleanup standards. Following degradation of a dissolved BTEX plume, a residue consisting of heavier petroleum hydrocarbons of relatively low solubility and volatility will typically be left behind in the original source (spill) area. Although this residual contamination may have relatively low potential for further migration, it still may pose a threat to human health or the environment, either from direct contact with soil in the source area or by continuing to slowly leach contaminants to ground water. In addition, the geochemistry of the ground water is usually permanently altered. For these reasons, natural attenuation alone

generally is not sufficient to remediate petroleum release sites. To achieve site cleanup goals within a reasonable restoration time, source control actions are almost always needed in conjunction with natural attenuation. In most cases, natural attenuation **serves as a polishing step** to manage the contamination remaining after engineered systems have removed the bulk of the contamination.

Ecology expects that natural attenuation is best used to address residual ground water contamination after other more active remedial actions have removed the vast majority of the contamination. Also, Ecology expects that natural attenuation will be most appropriate when used in conjunction (i.e., a treatment train) with other active cleanup action components (e.g., excavation of contaminated soil, pump and treat, soil vapor extraction, bioventing, and dual-phase extraction) or as a follow-up to active cleanup alternatives that have already been implemented.

*Note: **Hybrid Remedies:** an example of a situation where natural attenuation may be appropriate is a cleanup alternative that includes source control, a pump-and-treat system to mitigate the highly-contaminated plume areas, and natural attenuation in the lower concentration portions of the plume. In combination, these methods would maximize ground water restored to beneficial use in a timeframe consistent with future demand and would minimize cost. However, at such a site, if the plume was either expanding or threatening down-gradient wells or other environmental resources, then natural attenuation would not be an appropriate remedy.*

As with any cleanup action, if monitoring results indicate inadequate progress, then it will be necessary to reevaluate the cleanup action plan. Under these circumstances, implementation of a more active/engineered approach should be considered for all or part of the plume.

1.6 Technical Consultations under the Voluntary Cleanup Program

At sites where an independent cleanup action involving natural attenuation is being considered, Ecology strongly recommends consultation with Ecology under the Voluntary Cleanup Program (VCP) in the early stages of the cleanup process.

An independent remedial action is a remedial action that is conducted without Ecology oversight or approval and not under an order or decree. Although persons conducting independent remedial actions are not required to submit plans to Ecology for review and approval prior to performing the remedial actions set forth in those plans, the remedial actions conducted by the person must nonetheless meet the substantive requirements of chapter 173-340 WAC. See WAC 173-340-515(3). Also, any person who conducts an independent interim action or cleanup action must submit an independent remedial action report to Ecology upon completion of the action. The report must contain enough information for Ecology to determine if the action meets the substantive requirements of chapter 173-340 WAC. See WAC 173-340-515(4).

There are significant benefits to requesting technical consultations with Ecology under the VCP during the early phases of the cleanup process. Consulting with Ecology at an early stage can provide greater assurance that the proposed cleanup action involving natural attenuation meets the substantive requirements of chapter 173-340 WAC. Confirming the adequacy of the cleanup action plan based on the remedial investigation and feasibility study prior to enacting the plan,

may avoid the need to conduct additional investigations and implement contingency plans where natural attenuation fails to achieve cleanup goals.

Under the VCP, Ecology can provide technical assistance regarding:

- The development of a remedial investigation work plan, including what data should be collected to adequately characterize the site and evaluate the feasibility of natural attenuation as a remedial action;
- The evaluation of natural attenuation as a remedial action based on the data collected during the remedial investigation, including what evaluations should be conducted and what methods and tools may be used to conduct those evaluations; and
- The development of a performance monitoring plan to implement natural attenuation as a remedial action, including what data should be collected to adequately evaluate the performance of natural attenuation during the restoration time frame.

Under the Voluntary Cleanup Program, Ecology can also review a proposed cleanup action plan to determine whether the proposed plan meets the substantive requirements of the chapter 173-340 WAC. For general guidance regarding conducting independent remedial actions and obtaining technical consultations under the Voluntary Cleanup Program, please refer to the Ecology guidance document: “Independent Remedial Actions and Technical Consultations under the Voluntary Cleanup Program – Guidance” Ecology Publication No. 04-09-049.

For more specific guidance regarding what information should be submitted in the independent remedial action report for cleanup actions involving natural attenuation, please refer to Section 6.2 of this document.

1.7 Definitions

The definitions set forth in the MTCA Cleanup Regulation, chapter 173-340 WAC, shall control the meanings of the terms used in the Guidance and User’s Manual. Some of those definitions are included below for convenience. For terms not defined in the MTCA Cleanup Regulation, the definitions provided below are the intended meaning of the terms used in this Guidance and the associated User’s Manual.

“**Advection**” means the mass transport of a solute as it flows along with the ground water. Advection is the dominant transport process that drives solute migration in the ground water. The amount of solute that is being transported is a function of its concentration in the ground water and the quantity of ground water flow. The velocity at which a solute is transported through the ground water may not be the same as the velocity of the ground water due to other fate and transport processes. The velocity of water in the saturated zone is governed by three factors, each of which is characteristic of the specific ground water flow system: hydraulic gradient, hydraulic conductivity, and effective porosity. Advection is used to calculate dispersion and down-gradient plume migration. While not destroying or immobilizing contaminants, advection can affect the rate of reactions that contribute to natural attenuation.

“Assimilative capacity” means the potential capacity of ground water to biodegrade petroleum hydrocarbon contaminants into other compounds or elements. The potential capacity is determined by estimating the mass of petroleum hydrocarbon contaminants per unit volume of ground water that can be metabolized by aerobic and anaerobic biodegradation under existing site conditions (Weidemeier et al., 1999). In calculating assimilative capacity, the term *“Utilization Factor”* often is used which is the stoichiometric ratio of the mass of contaminants potentially biodegraded to the mass of electron acceptor utilized (or metabolically produced). Assimilative capacity is calculated by multiplying the background concentration of an electron acceptor by its utilization factor to provide an estimate of the ultimate assimilative capacity of the aquifer by that mode of biodegradation.

Whereas, **“Expressed assimilative capacity”** means the demonstrated capacity of the aquifer to degrade contaminants. Expressed assimilative capacity is calculated using the difference in concentration between a background well and a well in the area of contaminant plume.

“Biodegradation” means the biological attenuation process whereby hazardous substances are broken down through biotic reactions (e.g., aerobic and anaerobic respiration) into other contaminants or elements. The process is typically a multiple-step process that may result in organic contaminants being completely broken down or mineralized to carbon dioxide and water. The process may also result in the production of other contaminants that may be more or less toxic than the parent contaminant (WAC 173-340-200).

The biodegradation process involves the transfer of electrons. The energy required for cell synthesis and maintenance is obtained through the oxidation of hydrocarbon compounds. Electrons are removed from the organic substrates (electron donors) to capture the energy available through the oxidation process. Terminal electron acceptors are needed for electrons moving through electron transfer or respiratory chains (ASTM, 1998).

Biodegradation is a destructive attenuation mechanism that reduces not only the concentration, but also the total mass of the parent compound. For petroleum hydrocarbons, biodegradation is considered to be the primary destructive attenuation mechanism (ASTM, 1998). Biodegradation usually results in the complete transformation of petroleum hydrocarbon compounds into carbon dioxide and water (ASTM, 1998). However, the biodegradation process can result in some naturally occurring geochemical indicators more toxic and mobile than the original geochemical compounds.

“Biodegradation rate constant (λ)” means the rate at which biodegradation reduces contaminant concentrations over time for the overall plume. This rate constant is often expressed as a half-life.

“Bulk attenuation rate constant (k)” means the overall rate at which natural attenuation reduces contaminant concentrations over time. The bulk attenuation rate constant accounts for all natural attenuation mechanisms, both destructive (e.g., biodegradation) and non-destructive (e.g., dilution, adsorption). Although biodegradation is a significant attenuation mechanism, the biodegradation rate is not the same as the bulk attenuation rate. The biodegradation rate does not

account for other attenuation mechanisms (e.g., dilution and dispersion) and therefore, by definition, will always be less than the bulk attenuation rate.

“Chemical degradation” means the chemical attenuation process whereby hazardous substances are broken down through abiotic reactions into other compounds or elements. Chemical degradation may produce compounds that are more or less toxic and biodegradable than the parent compound. Chemical degradation is a destructive attenuation mechanism that reduces not only the concentration, but also the total mass of the parent compound. For petroleum hydrocarbons, though, chemical degradation is not considered a significant destructive attenuation mechanism (ASTM, 1998).

“Cleanup action” means any remedial action, except interim actions, taken at a site to eliminate, render less toxic, stabilize, contain, immobilize, isolate, treat, destroy, or remove a hazardous substance that meets cleanup standards and the other minimum requirements specified in WAC 173-340-360(2) and that is selected in accordance with the requirements and procedures in WAC 173-340-350 through 173-340-390. A cleanup action may consist of one or more cleanup action components (WAC 173-340-200).

“Cleanup action alternative” means one or more cleanup action components that individually or in combination, achieve a cleanup action at a site (WAC 173-340-300). Several cleanup action alternatives should be developed and evaluated as part of the feasibility study (see WAC 173-340-350(8)).

“Cleanup action component” means a treatment technology, containment action, removal action, engineered control, institutional control, or other type of remedial action that is used individually or in combination with other components, to achieve a cleanup action at a site (WAC 173-340-200).

“Cleanup level” means the concentration of a hazardous substance in a particular medium (e.g., ground water) that is determined to be protective of human health and the environment under specified exposure conditions (WAC 173-340-200). The cleanup level for each medium must be established in accordance with WAC 173-340-720 through 173-340-760, as applicable.

“Cleanup standard” means the standard for a hazardous substance in a particular medium (e.g., ground water) that must be achieved by the cleanup action. The cleanup standard consists of the following:

- The hazardous substance concentration that is protective of human health and the environment (“cleanup level”); and
- The location on the site where the cleanup level must be attained (“point of compliance”).

The cleanup standard for each medium must be established in accordance with WAC 173-340-720 through 173-340-760, as applicable. A cleanup standard may also include additional regulatory requirements that apply to a cleanup action because of the type of action and/or the location of the site. These requirements are specified in applicable state and federal laws and are

generally established in conjunction with the selection of a specific cleanup action (WAC 173-340-200).

“Conceptual site model” means a conceptual understanding of a site that identifies potential or suspected sources of hazardous substances, types and concentrations of hazardous substances, potentially contaminated media, and actual and potential exposure pathways and receptors. Typically this model is developed during the scoping of the remedial investigation and further refined as additional site information is collected. It is a tool used to assist in making decisions at a site (WAC 173-340-200).

“Contaminant” means any hazardous substance that does not occur naturally or occurs at greater than natural background levels (WAC 173-340-200).

“Degradation by-products” means the secondary product of biological or chemical processes that break down chemicals into other chemicals. These by-products may be more or less toxic than the parent compound (WAC 173-340-200).

“Dilution by recharge” means the simple dilution of a solute plume due to the introduction of additional water into the solute plume from precipitation, leakage from surface water bodies, or leakage from underlying aquifers.

“Dispersion” or **“hydrodynamic dispersion”** means the physical attenuation process whereby a solute plume expands in directions both longitudinal and transverse (perpendicular) to the direction of ground water flow as the solute plume moves through the ground water. Dispersion is a non-destructive attenuation mechanism that reduces the concentration but not the total mass, of contaminants. Dispersion is the primary process causing dilution of dissolved contaminants within the solute plume. Dispersion results in the expansion of the solute plume and the reduction in contaminant concentrations within the solute plume. The mechanisms leading to dispersion in the subsurface include mechanical dispersion and molecular diffusion.

- **“Mechanical dispersion (or, mixing)”** means the dispersion of a solute in response to different water velocities within individual pores, different water velocities within adjacent pores, and the tortuosity of the subsurface flow path. Mechanical dispersion is comprised of two components: longitudinal dispersion (which involves the spreading of a solute in the direction of the ground water flow); and, transverse dispersion (which involves the spreading of a solute in directions perpendicular to the ground water flow). Except at very low velocities, mechanical dispersion increases linearly with the average velocity of ground water. Mechanical dispersion is the primary mechanism causing dispersion under normal advective flow systems.
- **“Molecular diffusion”** means the dispersion of a solute in response to concentration gradients, even in the absence of ground water flow. The molecular diffusion of a solute is described by Fick’s law. Under normal advective flow systems, the dispersive effect of molecular diffusion is insignificant compared to mechanical dispersion. The dispersive effect of molecular diffusion is significant only at sites with extremely low ground water velocities.

“Ecological risk assessment” is a process for organizing and analyzing data, information, assumptions, and uncertainties to evaluate the likelihood that one or more stressors are causing or will cause adverse ecological effects.

“Ecology” means the Washington State Department of Ecology.

“Electron acceptors” means the elements or compounds that are reduced by receiving electrons produced by the oxidation of organic compounds through microbial metabolism or abiotic chemical oxidation processes (ASTM, 1998).

“Expanding plume” means a configuration where the solute plume margin is expanding over time, and/or concentrations of contaminants at points within the solute plume are increasing over time.

“Free product” means a non-aqueous phase liquid that is present in the soil, bedrock, ground water or surface water as a distinct separate layer. Under the right conditions, if sufficient free product is present, free product is capable of migrating independent of the direction of flow of the ground water or surface water (WAC 173-340-200).

“Ground water” means water in a saturated zone or stratum beneath the surface of land or below surface water (WAC 173-340-200).

“Ground water seepage velocity” means actual interstitial ground water velocity, that is, the rate at which the flux of ground water across the unit cross-sectional area of pore space occurs. Seepage velocity is Darcy velocity divided by effective porosity. Seepage velocity is often referred to as “average linear velocity.” Seepage velocity is a key parameter in natural attenuation studies because it can be used to estimate the time of travel of a contaminant front.

“Hazardous substance” means any dangerous or extremely hazardous waste as defined in RCW 70.105.010 (5) and (6), or any dangerous or extremely dangerous waste as designated by rule under chapter 70.105 RCW; any hazardous substance as defined in RCW 70.105.010(14) or any hazardous substance as defined by rule under chapter 70.105 RCW; any substance that is a hazardous substance under section 101(14) of the federal cleanup law, 42 U.S.C., Sec. 9601(14); petroleum or petroleum products; and any substance or category of substances, including solid waste decomposition products, determined by the director (of Ecology) or by rule to present a threat to human health or the environment if released into the environment.

The term hazardous substance does not include any of the following when contained in an underground storage tank from which there is not a release: crude oil or any fraction thereof or petroleum, if the tank is in compliance with all applicable federal, state, and local law (WAC 173-340-200).

“Independent remedial actions” means remedial actions conducted without Ecology oversight or approval and not under an order, agreed order, or consent decree (WAC 173-340-200).

“Institutional controls” means measures undertaken to limit or prohibit activities that may interfere with the integrity of an interim action or a cleanup action or result in exposure to hazardous substances at the site (WAC 173-340-200).

“Interim action” means a remedial action conducted under WAC 173-340-430 to partially address the cleanup of a site (WAC 173-340-200).

“Mass loading rate” means the rate at which the contaminant mass located within the source zone (source mass) enters the down-gradient portion of the ground water plume.

“Model Toxics Control Act” or **“MTCA”** means chapter 70.105D RCW, first passed by the voters in the November 1988 general election as Initiative 97 and as since amended by the legislature (WAC 173-340-200).

“MTCA Cleanup Regulation” means chapter 173-340 WAC.

“Natural attenuation” means a variety of physical, chemical or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of hazardous substances in the environment. These *in situ* processes include: natural biodegradation; dispersion; dilution by recharge; sorption; volatilization; and, chemical or biological stabilization, transformation, or destruction of hazardous substances. A cleanup action that includes natural attenuation and **conforms** to the **expectations** in WAC 173-340-370(7) can be considered an **active** remedial measure (WAC 173-340-200). In practice, natural attenuation also is referred to as “monitored natural attenuation” defined by US EPA (1999a). For ease of reference, this document sometimes refers to natural attenuation simply as a cleanup action alternative.

“Natural biodegradation” means biodegradation that occurs without human intervention. See definition of “biodegradation.”

“Non-Aqueous Phase Liquid” or **“NAPL”** means a hazardous substance that is present in the soil, bedrock, ground water, or surface water as a liquid not dissolved in water. The term includes both light non-aqueous phase liquid (LNAPL) and dense non-aqueous phase liquid (DNAPL) (WAC 173-340-200).

“Performance monitoring” means the monitoring used to confirm that the interim action or cleanup action has attained cleanup standards and, if appropriate, remediation levels or other performance standards (WAC 173-340-410(1)(b)). Performance monitoring is used to confirm both the progress of the cleanup action and the attainment of cleanup standards by the cleanup action.

“Petroleum” means crude oil or any fraction thereof that is liquid at standard conditions of temperature and pressure (60°F and 14.7 pounds per square inch absolute). The term includes petroleum-based substances comprised of a complex blend of hydrocarbons derived from crude oil through processes of separation, conversion, upgrading, and finishing, such as motor fuels, jet

fuels, distillate fuels, residual fuel oils, lubricants, petroleum-based solvents, and used oils (WAC 173-360-120).

“Plume” means the body of ground water where contaminants are present at greater-than-natural background levels.

“Point decay rate (1st-order) constant (k_{point})” means the rate at which natural attenuation reduces contaminant concentrations over time at a single monitoring point within the solute plume. The rate accounts for all natural attenuation mechanisms, both destructive (e.g., biodegradation) and non-destructive (e.g., dispersion and dilution). The rate is derived from the slope of the best-fit line of plot of the natural log of concentrations versus time for a single monitoring point.

“Points of compliance” means the point or points within a particular medium (e.g., ground water) where cleanup levels must be attained. This term includes both standard and conditional points of compliance (WAC 173-340-200). The points of compliance for each medium must be established in accordance with WAC 173-340-720 through 173-340-760, as applicable.

“Practicable” means capable of being designed, constructed, and implemented in a reliable and effective manner including consideration of cost. When considering cost under this analysis, an alternative shall not be considered practicable if the incremental costs of the alternative are disproportionate to the incremental degree of benefits provided by the alternative over other lower-cost alternatives (WAC 173-340-200).

“Receptor” means any potential human or ecological receptors including existing public and private potable wells, well head protection areas, well fields and ground water discharge areas, surface water body (e.g., stream and marshes), sediments, structures (basement and confined space for vapor intrusion) and utility trenches, ecosystems (e.g., wildlife and vegetations including sensitive and threatened or endangered species or habitats), or other environmental resources that may be adversely affected by the release.

“Release” means any intentional or unintentional entry of any hazardous substance into the environment, including but not limited to the abandonment or disposal of containers of hazardous substances (WAC 173-340-200).

“Remedial action” means any action or expenditure consistent with the purposes of chapter 70.105D RCW to identify, eliminate, or minimize any threat posed by hazardous substances to human health or the environment, including any investigative and monitoring activities with respect to any release or threatened release of a hazardous substance and any health assessments or health effects studies conducted in order to determine the risk or potential risk to human health (WAC 173-340-200).

“Remediation level” means a concentration (or other method of identification) of a hazardous substance in soil, water, air, or sediment above which a particular cleanup action component will be required as a part of a cleanup action at a site. Other methods of identification include physical appearance or location. See WAC 173-340-355 for a description of the purpose of

remediation levels and the requirements and procedures for developing a cleanup action alternative that includes remediation levels (WAC 173-340-200).

While a cleanup level defines the concentration of a hazardous substance above which a contaminated medium (e.g., ground water) must be cleaned up, a remediation level defines the range of hazardous substance concentrations over which a particular cleanup action component will be used (e.g., extraction and treatment of higher concentrations and natural attenuation of lower concentrations).

“Restoration time frame” means the period of time needed to achieve the cleanup levels at the point of compliance established for the site (WAC 173-340-200). In practice, for ground water, it starts from the date when monitoring of ground water concentrations started.

“Retardation” means the reduction in plume mobility due to sorption. The retardation coefficient (R) is based on the distribution coefficient (K_d) for sorption.

“Sentinel well” means a monitoring point established at a location between the leading edge of the solute plume and possible receptors (e.g., drinking water well, surface water body, sediment, public and private potable wells, well head protection areas, well fields and ground water discharge areas, surface water body, structures, and utility trenches that may be adversely affected by the release) to ensure that there will be time for other remedial actions to be taken if the plume migrates beyond predicted boundaries. Preferably a sentinel well needs to be a clean well.

“Shrinking plume” means a configuration where the solute plume margin is receding back toward the source area over time, and contaminant concentrations at points within the solute plume are decreasing over time.

“Site” means any building, structure, installation, equipment, pipe or pipeline (including any pipe into a sewer or publicly owned treatment works), well, pit, pond, lagoon, impoundment, ditch, landfill, storage container, motor vehicle, rolling stock, vessel, or aircraft, or any site or area where a hazardous substance other than a consumer product in consumer use, has been deposited, stored, disposed of, or placed, or otherwise come to be located (WAC 173-340-200).

“Solute” means a chemical dissolved in water.

“Sorption” means the chemical attenuation process whereby contaminant mass in the solute plume is transferred from the aqueous phase to the solid phase (i.e., from ground water to soil). Sorption results in the retardation of the solute plume and the reduction of contaminant concentrations within the solute plume, but may result in higher concentrations in the subsurface soils. Because contaminants sorbed remain in the subsurface soils, they can later be desorbed and re-contaminate the ground water. Sorption is thus a non-destructive attenuation mechanism that affects the mobility and concentration, but not the total mass, of contaminants.

Sorption is caused by interactions between contaminants and the aquifer matrix. The two components of the aquifer matrix that have the most effect on sorption are organic matter and

clay minerals (ASTM, 1998). In most aquifers, sorption is controlled by organic matter. Sorption due to organic matter is dependent upon the contaminant organic partition coefficient (K_{oc}) and the fraction of organic carbon (f_{oc}) in the soil. The relationship between the concentration of contaminant sorbed and the concentration remaining in solution at equilibrium is referred to as the sorption isotherm (Wiedemeier, 1999). For sites where there has been a release of petroleum hydrocarbons, the common practice is to use a linear isotherm.

“Source control” means any remedial action other than natural attenuation that reduces the source mass or the mass loading rate. Source control usually involves the removal and/or treatment of the source mass. Source control may also involve containment of source mass to reduce the mass loading rate.

“Source mass” means the contaminant mass located within the source zone.

“Source zone” means the portion of the site that contributes contaminant mass to the ground water plume. The source area is usually the location of the original release. The source zone may be defined as several distinct zones or layers. In practice, it includes the free product layer (for petroleum, the free product is commonly located at the ground water interface), contaminated soil in unsaturated and saturated zones, the smear zone, and the dissolved phase. For detailed methods for estimating contaminant mass in the source zone, please refer to Appendix D of this guidance.

- The **contaminated soil in the unsaturated zone** extends vertically from the ground surface to the seasonally high water table and laterally from the highest contamination to non-detectable levels.
- The **smear zone is where NAPL (either as free product or as isolated blobs) is present in the soil or ground water and** extends vertically from the highest water table to the lowest water table level. If the ground water has been pumped or otherwise significantly lowered, the lowest ground water level may define the lower bound on the vertical extent of the smear zone layer.
- The **dissolved phase zone** is that zone within the saturated zone where contamination is present in the ground water above detectable levels. It extends laterally where contamination has been detected and vertically from the seasonal high ground water table to the lowest elevation where contamination has been detected. Typically, the contaminant mass dissolved in the saturated zone is smaller compared to the contaminant mass located within the contaminated soil in unsaturated source zones.

“Stable plume” means a configuration where the plume margin is stationary over time, and contaminant concentrations at points within the solute plume are relatively uniform or decrease gradually over time.

“Surface water mass loading rate” means the mass loading rate in a vertical cross-section of a ground water plume that enters into the nearby surface water body.

“Technically possible” means capable of being designed, constructed, and implemented in a reliable and effective manner, regardless of cost (WAC 173-340-200).

“Total petroleum hydrocarbons” or **“TPH”** means any fraction of crude oil that is contained in plant condensate, crankcase motor oil, gasoline, aviation fuels, kerosene, diesel motor fuel, benzol, fuel oil, and other products derived from the refining of crude oil. For the purposes of chapter 173-340 WAC, TPH will generally mean those fractions of the above products that are the total of all hydrocarbons quantified by analytical methods NWTPH-Gx; NWTPH-Dx; volatile petroleum hydrocarbons (VPH) for volatile aliphatic and volatile aromatic petroleum fractions; and extractable petroleum hydrocarbons (EPH) for nonvolatile aliphatic and nonvolatile aromatic petroleum fractions, as appropriate, or other test methods approved by Ecology (WAC 173-340-200).

“Utilization factor” is the stoichiometric ratio of the mass of contaminants completely biodegraded to the mass of electron acceptor utilized (or metabolically produced) based on the balanced equations (ASTM, 1998). For a given background concentration of an individual electron acceptor, the potential contaminant mass removal depends on the utilization factor for that specific electron acceptor. Multiplying the background concentration of an electron acceptor by its utilization factor provides an estimate of the ultimate biodegradation capacity of the aquifer by that specific mode of biodegradation.

“Volatilization” means the physical attenuation process whereby contaminant mass in the solute plume is transferred from the aqueous phase to the vapor phase (i.e., from ground water to air). Volatilization results in the retardation of the solute plume and the reduction of contaminant concentrations within the solute plume. Volatilization, however, does not destroy or permanently immobilize contaminant mass. While the contaminant can biodegrade in the subsurface soils, it can also re-dissolve in infiltrating ground water or be transported to the surface, where humans may be exposed to the vapors. Volatilization is a non-destructive attenuation mechanism that removes contaminants from ground water.

Chapter 2 Advantages and Limitations of Natural Attenuation

During the feasibility study, the potential advantages and limitations of using natural attenuation to clean up contaminated ground water should be carefully considered in comparison to engineered (more active) remediation technologies. Some of those potential advantages and limitations, which have been adapted from US EPA (1999a) and ASTM (1998), are described below.

2.1 Potential Advantages

The potential advantages of using natural attenuation as part of a cleanup action include:

- Natural attenuation can be used at all or part of a site, including otherwise inaccessible areas;
- Natural attenuation can be used in conjunction with, or as a follow-up to, other (active) cleanup action components;
- Natural attenuation mechanisms (e.g., biodegradation) can destroy contaminants *in-situ*: for example, petroleum hydrocarbons can often degrade to less harmful products;
- Less intrusion, and therefore less disruption of site use and less disturbance of ecological receptors;
- Less remediation waste generation than *ex-situ* treatment and less short-term potential risk of human exposure to contaminants; and
- Lower overall cleanup action costs, even when considering the long-term costs associated with implementing the monitoring program.

Even if it is determined based on the feasibility study, that natural attenuation is not an appropriate cleanup action component, the data collected for that study can still be used to design other cleanup action alternatives.

2.2 Potential Limitations

The potential limitations of using natural attenuation as part of a cleanup action include:

- More extensive and complex remedial investigation required to evaluate the feasibility of natural attenuation;
- Longer restoration time frame;
- Potential for continued migration of contaminants and cross-media transfer of contaminants to surface water, sediments, and air;
- Biodegradation process may result in the production of contaminants that are more toxic and/or more mobile than the parent contaminant (e.g., transformation from MTBE to TBA);
- Additional source control or more active cleanup actions may be required if exposure pathways are complete or there is a potential for receptors to be impacted;
- Institutional controls may be required during the restoration time frame, even if exposure pathways are not complete, to ensure short-term protectiveness;
- Less reliable because effectiveness is more dependent on favorable site conditions (e.g., hydrologic and geochemical conditions), which should persist throughout the restoration time

frame, and is more sensitive to natural or human-induced changes in those conditions (e.g., ground water withdrawal altering direction of ground water flow);

- Less predictable because prediction of effectiveness is more dependent on site-specific conditions;
- More extensive and lengthy performance monitoring required to demonstrate the continued effectiveness and protectiveness of the cleanup action during the restoration time frame;
- Higher remedial investigation costs;
- Higher long-term monitoring costs;
- May fail to completely restore the impacted ground water resource; and
- Less public acceptance, requiring more education and outreach to address public concerns.

Some of these potential limitations are **not** unique to natural attenuation. Consequently, the user should be careful to consider in the feasibility study whether one or more of these limitations may also apply to the more aggressive cleanup actions.

2.3 Consideration of Metabolic By-Products

At most sites the geochemical conditions and processes that lead to biodegradation of petroleum hydrocarbons will chemically and biologically transform naturally occurring metals in the aquifer matrix such as arsenic, manganese, iron and nickel into more mobile and toxic forms. Concentrations of these metals in the ground water may exceed drinking water and surface water standards, and cause aesthetic problems (e.g., taste, odor, or staining). To fully restore the ground water, it may not be enough to reduce petroleum hydrocarbon concentrations to acceptable levels; the elevated concentrations of these metals should also be addressed. See WAC 173-340-720(4)(b)(iii)(C), chapter 246-290 WAC, and WAC 173-340-709.

2.4 Consideration of MTBE and Other Oxygenates to Fuels

Methyl tertiary-butyl ether (MTBE) is a low molecular weight oxygenated hydrocarbon that is often mixed with gasoline (at up to 15% by volume) to reduce auto emissions (US EPA, 1998b). MTBE has been added to gasoline sold in Washington State and has been found at leaking underground storage tank sites (Washington State Department of Ecology, 2000).

Unfortunately, unlike other petroleum hydrocarbons, MTBE has a stable and highly soluble molecular structure that does not easily biodegrade or readily adsorb to soils, resulting in much less mass reduction and retardation within the ground water plume. As a consequence, MTBE has often been found to migrate longer distances and threaten down-gradient water supplies at sites where the other petroleum hydrocarbons have either been stabilized or diminished due to natural attenuation.

When present in petroleum-contaminated site source zones and plumes, the high solubility and longer persistence of MTBE and other oxygenates introduce significant uncertainty about the effectiveness of natural attenuation at petroleum-contaminated sites. Therefore, the hazardous substances at a site and the fate and transport of those contaminants need to be determined and carefully considered when evaluating the appropriateness of natural attenuation as part of a cleanup action.

Refer to the list below for technical information regarding attenuation mechanisms of MTBE and other oxygenates contaminated ground water.

- API, 1998, Ten Frequently Asked Questions About MTBE in Water, API Soil and Groundwater Research Bulletins No. 3.
- API, 2000, Simulation of Transport of Methyl Tert-Butyl Ether (MTBE) to Groundwater from Small-Volume Releases of Gasoline in the Vadose Zone, API Soil and Groundwater Research Bulletins No. 10.
- API, 2000, Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE, API Soil and Groundwater Research Bulletins No. 11.
- API, 2000, Dissolution of MTBE from a Residually Trapped Gasoline source, API Soil and Groundwater Research Bulletins No. 13.
- API, 2000, Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE, API Publication 4699.
- API, MTBE Resource Center,
<http://apiep.api.org/printerformat.cfm?ContentID=9EC44CD5-E167-49C4-8EBE7B354E4B3CD9>.
- Landmeyer, J.E., Chapelle, F.H., Bradley, P.M., Pankow, J.F., Church, C.D., Tratnyek, P.G., 1998, Fate of MTBE Relative to Benzene in a Gasoline-contaminated Aquifer (1993-98), Fall GWMR, pp.93-102.
- US EPA, 1998, Remediation of MTBE Contaminated Soil and Groundwater, EPA 510-F-97-015, MTBE Fact Sheet #2.
- US EPA, 2000, Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions, EPA/600/R-00/006.
- US EPA, 2001, Summary of Workshop on Biodegradation of MTBE, EPA/625/R-01/001A.
- US EPA, 2005a, Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites, EPA/600/R-04/1790, January 2005.
- US EPA, MTBE (*methyl tertiary-butyl ether*) and Underground Storage Tanks,
<http://www.epa.gov/swrust1/mtbe/index.htm>.

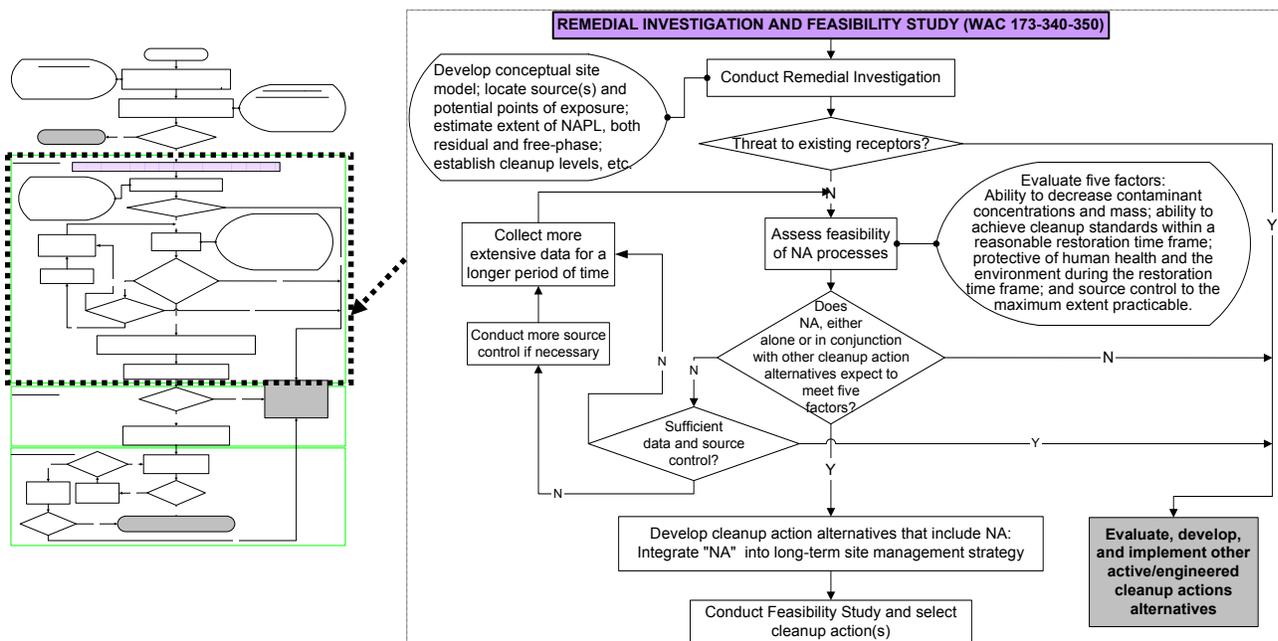
Chapter 3 Evaluating Natural Attenuation as a Cleanup Action Alternative

The purpose of this chapter is to provide technical guidance on how to conduct a remedial investigation and feasibility study for the purposes of evaluating cleanup action alternatives that use natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water. The focus of the technical guidance provided in this chapter is limited to the following:

- What data should be collected as part of the remedial investigation to adequately evaluate the feasibility of natural attenuation as a cleanup action alternative; and
- How to evaluate the feasibility of natural attenuation based on the data collected during the remedial investigation.

This chapter does not provide guidance on how to conduct a comprehensive remedial investigation and feasibility study. This step in the cleanup process is illustrated in Figure 3.1 below. Refer to Figure 1.1 for larger view.

Figure 3.1. Evaluating Natural Attenuation as a Cleanup Action Alternative



3.1 Conduct Remedial Investigation

The purpose of this section is to provide technical guidance on how to conduct a remedial investigation that will enable adequate evaluation of the feasibility of natural attenuation as a cleanup action alternative during the feasibility study. More specifically, this section provides technical guidance regarding the following:

- What data should be collected to evaluate the feasibility of natural attenuation as a cleanup action alternative;
- How to develop a remedial investigation work plan to collect the specified data; and
- How to develop a conceptual site model based on the data collected.

3.1.1 Develop a conceptual site model

The first step in understanding natural attenuation processes at a site involves creating a conceptual site model. Initially, it should be based on simplifying assumptions because data for a more detailed model generally are unavailable in the early stages of the remedial investigation. A conceptual site model serves to guide the investigation, remediation, and monitoring efforts used to deal with contamination. A preliminary conceptual site model is initially developed during the scoping of the remedial investigation and further refined as additional information is collected on the site. A conceptual site model:

- Describes all of the known or suspected sources of contamination (sources);
- Considers how, when, and where the contaminants are likely to move (pathways); and
- Identifies who and what are likely to be affected by contaminants (receptors).

Based on the data collected during the remedial investigation, the conceptual site model should be further refined to identify items such as the following:

- Suspected and confirmed source zones;
- Types and distribution of contaminants and impacts to ground water and other media;
- Geologic units that influence migration of contaminants;
- Ground water depth, flow direction, and velocity;
- Natural attenuation processes in ground water including biodegradation, chemical degradation, sorption, dispersion, dilution by recharge, and volatilization;
- Locations of potential human and ecological receptors;
- Actual and potential exposure pathways and risk assessment assumptions;
- Structures and utilities where vapors can accumulate; and
- Other potential contaminant transport pathways, exposure points, and potential receptors.

As the understanding of the site increases, a preliminary evaluation of natural attenuation processes can help to identify the dominant attenuation processes and additional data needs. The conceptual site model should be reexamined and refined as new data are gathered, especially at complex sites.

3.1.2 Determine scope of investigation

The scope of the investigation depends on the specific informational needs at the site. Since natural attenuation is a “knowledge-based” remedy, the remedial investigation is critical, and it is likely more information will need to be collected than otherwise would be required to make cleanup decisions. At a minimum, sufficient information should be collected to characterize the nature and distribution of hazardous substances at the site, the threat posed by those substances to human health and the environment, and sufficient information to evaluate the feasibility of natural attenuation as a cleanup action alternative. The nature and extent of information necessary to evaluate the feasibility of natural attenuation is dependent on many factors including:

- the extent of contamination;
- site complexity;
- proximity of sensitive receptors;
- uncertainty of the plume stability; and
- selected methods for evaluation.

For example, **more** information may be necessary for the evaluation of natural attenuation at a site with the following conditions:

- complex and multi-layered hydrogeology;
- free-product;
- receptors near the edge of contaminant plume; and
- hydrogeologic conditions that change over time.

Whereas, **less** information may be necessary for the evaluation of natural attenuation at a site with the following conditions:

- single-layer unconsolidated ground water-bearing units;
- no free-product;
- no receptors near the edge of contaminant plume; and
- hydrogeologic conditions that do not appear to change over time.

The information needs to be sufficient to enable the Ecology site manager to adequately evaluate the remedy. Although each of the recommended investigations set forth below may not always be required at a petroleum-contaminated site, collecting appropriate information during the investigation phase will likely reduce overall costs and result in faster and better decision-making.

As part of the scoping, consider what data have already been collected through prior investigations. Such data may be useful as part of the remedial investigation. However, that data alone may be insufficient. Consequently, determine the sufficiency of the previously collected data and what additional data still need to be collected.

To adequately characterize the site for evaluating the feasibility of natural attenuation, it is recommended that the following site-specific data be collected. This information is in addition to the information normally required to complete a remedial investigation and feasibility study as specified in WAC 173-340-350.

- Information on existing and potential human and ecological receptor and environmental resources, including:
 - Public wells or well fields and well capture zones within ½ mile of the site;
 - Private wells within 1,000 feet of the site;
 - Surface water bodies and wetlands within 1,000 feet of the site;
 - Discharge points to surface waters and wetlands;
 - Any nearby threatened or endangered species;
 - Current and projected land uses and zoning for the site and areas within 1,000 feet of the site;
 - Vapor migration potential -- basements and other subsurface enclosed building structure (with crawlspaces or slab-on-grade) on the site and within 100 feet of the site; and
 - Utility lines, roads, paved parking areas, buildings, and other structures on the site within 300 feet of the site.

- Information on source zone and extent of contamination, including:
 - History of the contaminant release and site activities;
 - A description of the source and approximate estimate of the mass of contamination by measuring depth, thickness, and areal extent of free-product (if present) on and in ground water; trapped residual product in the unsaturated, smear, and saturated zones; contaminated soils; and dissolved contaminants in ground water;
 - Any potential for a continuing source release from leaking product pipes, tanks, and residual; and
 - The extent of soil and ground water contamination and the characteristics of the soil and saturated material.

- Information on hydrogeology, including:
 - A description of the regional hydrogeologic setting including, geologic units, aquifers, confining units and regional recharge and discharge zones;
 - A description of the local hydrogeologic setting including;
 - geologic units,
 - recharge and discharge areas,
 - vertical and lateral extent of the soil and ground water contamination,
 - hydraulic conductivity of saturated geologic units,
 - preferential flow paths,
 - ground water elevation and seasonal fluctuations,
 - horizontal and vertical hydraulic gradients and flow direction within each geologic unit,
 - potentiometric (or, piezometric) surface maps quarterly for at least one (1) year,
 - A description and movement of contaminants and geochemical indicator distribution patterns over one year at a minimum (see Section 3.2 of this guidance for a detail).

There may also be a need to collect other data to evaluate natural attenuation. The type of data that is required is dependent on the selected evaluation method. For a more detailed description of what data may need to be collected to evaluate the feasibility of using natural attenuation as a cleanup action alternative, reasons for collecting those data, sampling methods, and analytical methods, please refer to Appendix G of this guidance and API (1998).

The following “rapid site characterization techniques” described in the below references may be helpful in rapidly and cost-effectively defining the characteristics of the contaminated site.

- ASTM:
 - E1912: Standards on Assessment and Remediation of Petroleum Release Sites.
 - D6235-04: Standard Practice for Expedited Site Characterization of Vadose Zone and Ground Water Contamination at Hazardous Waste Contaminated Sites.
<http://www.astm.org>
- Federal Remediation Technologies Roundtable: See technology screening tools for an explanation of field sampling and collection techniques (with information on maximum depth, production rate, waste volume, status, cost) and analysis (with information on selectivity, interference, detection limits, turn around time, quantitative data capability, and cost) matrix.
<http://www.frtr.gov/site/samplematrix.html>
- University of Connecticut: Expedited site assessment provides interactive technical guidance for investigating fuel releases at UST sites in a multimedia format. Direct push tools and methods, along with field screening, to evaluate site hydrogeologic conditions and contamination in three-dimension are explained.
<http://www.esacd.uconn.edu/info/overview/overview.html>
- US Department of Energy: Manual on expedited site characterization that explains innovative technology to provide information needed to quickly determine if a technology would apply to a particular environmental management problem.
<http://apps.em.doe.gov/ost/pubs/itsrs/itsr77.pdf>
- US EPA: Several sources provide information on systematic planning, dynamic work plans, and technologies that can be used in the field to characterize contaminated media and monitor the progress of remedial efforts to achieve more cost-effective site characterization and cleanup.
<http://www.epa.gov/tio/pubichar.htm>
<http://www.epa.gov/swerust1/pubs/sam.htm>
<http://www.epareachit.org/index3.html>
<http://www.brownfieldstsc.org>
<http://www.epa.gov/ordntrnt/ORD/WebPubs/projsum/600sr98020.pdf>
<http://fate.clu-in.org>
<http://clu-in.org/triad/>
<http://clu-in.org/download/char/dynwkpln.pdf>

<http://clu-in.com/goto.cfm?link=%2Fproducts%2Fmoreinfo%2Fdynwkpln%2Ehtm&id=73>
<http://www.clu-in.org/programs/scmt/Verarea.htm>

Quality Assurance and Sampling Protocols:

The DQO (Data Quality Objectives) process is a strategic planning approach based on the scientific method to prepare for a data collection activity. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner. For more detailed information, refer to US Department of Energy Data Quality Objectives Home Page (<http://www.hanford.gov/dqo/>) and US EPA Guidance (US EPA, 2000c).

More detailed technical information on how to sample ground water can be found in API (1998) and US EPA (2001b) documents. These documents provide a summary of current and recommended ground water sampling methodologies that will yield the most representative ground water samples.

3.1.3 Develop remedial investigation work plan and conduct investigation

Based on the identified data collection needs, a remedial investigation work plan should be developed and implemented. Data collected from the ground water monitoring network is then used to assess plume behavior, to extract the rate constants of attenuation, and to identify major attenuation mechanisms.

Monitoring Parameters:

The work plan should include a sampling and analysis plan that describes the sample collection, handling, and analysis procedures to be used. The plan should be developed in accordance with WAC 173-340-820. Hazardous substances for analytical analysis should include:

- BTEX (Benzene, Toluene, Ethylbenzene, Xylenes);
- Total Petroleum Hydrocarbons;
- MTBE (methyl tertiary-butyl ether) and other fuel additives if detected previously or suspected to be present; and
- n-hexane and other components if necessary as shown in Table 830-1 of WAC 173-340-900.

Geochemical indicators for analytical analysis should include:

- Dissolved Oxygen/Redox Potential/pH/Conductivity/Temperature; and
- Nitrate; Manganese (Soluble); Ferrous Iron (Soluble); Sulfate; Methane; and Alkalinity.

Monitoring Network and Frequency:

To collect the data necessary to directly evaluate the feasibility of natural attenuation, sufficient soil borings and wells need to be installed to fully characterize the extent of soil and ground water contamination. In addition, water level measurements and sampling data will need to be collected over time to establish seasonal variations in flow direction, gradient, and contaminant

concentrations. Monitoring plan recommendations for simple, well-defined sites are provided in Table 3.1.

The number of samples needed for evaluating natural attenuation depends on the pre-selected confidence level and the variance of the data. Sampling should be done with enough frequency and over a sufficiently long period of time to obtain a statistically meaningful correlation between the reduction of contaminant concentrations (or mass) and time. See US EPA (1999b).

Sampling frequency should be at least quarterly but at sites with fast ground water seepage velocity and a short distance to potential receptor exposure points, more frequent sampling may be necessary. A minimum of one year of data is recommended but longer time periods may be needed to determine the status of the plume (stable, shrinking, or expanding) and establish a relationship between contaminant concentrations and geochemical indicators.

Note that the monitoring wells used for the remedial investigation may or may not be sufficient for long-term performance monitoring. For additional guidance regarding the monitoring network design, please refer to Section 4.1 and Appendix H of this document.

Table 3.1. Recommended Monitoring Plan for Assessing Feasibility of Natural Attenuation

| Task | Duration and Frequency of Monitoring | Number and Location of Monitoring Wells |
|--|--|--|
| Hazardous Substances & Ground Water Table Elevation | At least four (4) sampling events spaced evenly over one (1) year to define seasonal fluctuations in the ground water elevation and flow direction and in the concentrations of contaminants | <ul style="list-style-type: none"> • One (1) well in up-gradient (not impacted) background area • One (1) well within source (most impacted) area • Two (2) wells near contaminated plume center line that are above cleanup levels • One (1) well in down-gradient “sentinel” area (not impacted) |
| Geochemical Indicators | At least four (4) sampling events spaced evenly over one (1) year to define seasonal fluctuations in concentrations of geochemical indicators | |

Note: The recommendations in this table apply to sites in simple hydrogeologic settings (e.g., uniform geology with one affected aquifer and no complicating factors such as nearby water supply wells or surface water) and where the sources of contamination and affected ground water have been well defined. Sites that have not been fully characterized or are in more complicated settings will likely require more monitoring wells and greater frequency and duration of monitoring.

Because natural attenuation evaluations can take a long time, before under taking such a study it should be verified that there are no immediate threats to existing receptors. Other more active and aggressive engineering remedies will need to be implemented if an immediate threat to a receptor is identified during the remedial investigation. If no threat is identified, natural attenuation can continue to be evaluated as outlined in this section.

3.1.4 Establish cleanup standards

Based on the collected data and the conceptual site model, next identify the indicator hazardous substances at the site (see WAC 173-340-703) and establish ground water cleanup standards,

including both cleanup levels and points of compliance, for those hazardous substances. The requirements and procedures for establishing ground water cleanup levels and points of compliance are set forth in WAC 173-340-720.

Unless it can be demonstrated otherwise, ground water cleanup levels must be met at the **standard point of compliance**, which is defined as throughout the site from the uppermost level of the saturated zone extending vertically to the lowest-most depth that could potentially be affected by the site. See WAC 173-340-720(8)(b).

Where it can be demonstrated that it is not practicable to meet the ground water cleanup levels at the standard point of compliance within a reasonable restoration time frame, Ecology may approve a **conditional point of compliance** as close as practicable to the source of the contamination, not to exceed the property boundary. In certain types of situations, Ecology may approve a **conditional point of compliance** beyond the property boundary, provided certain additional conditions are met. See WAC 173-340-720(8)(c) and (d).

For additional guidance regarding the establishment of ground water cleanup standards, please refer to the Ecology Focus Sheet: *Developing Ground Water Cleanup Standards under the Model Toxics Control Act*, Focus No. 01-09-049.

3.2 Conduct Feasibility Study

The purpose of this section is to provide technical guidance on how to develop and evaluate the feasibility of natural attenuation as a cleanup action alternative during the feasibility study. More specifically, this section provides technical guidance regarding the following:

- How to determine the feasibility of natural attenuation as a cleanup action alternative, including the methods and tools that may be used to make such a determination;
- How to develop natural attenuation as a cleanup action alternative, including the development of a performance monitoring plan and a contingency plan; and
- How to conduct a comparative analysis of cleanup action alternatives.

This section, however, does not provide comprehensive guidance on how to conduct a feasibility study of cleanup action alternatives for a petroleum-contaminated site. For example, although this document discusses the need for conducting quantitative or qualitative human health and ecological risk assessments to evaluate the protectiveness of a cleanup action alternative, this document does not provide specific technical guidance on how to conduct such risk assessments. This section also does not provide a list of potential cleanup action alternatives that could be considered as part of the feasibility study.

3.2.1 Determine feasibility of natural attenuation as a cleanup action alternative

The purpose of this subsection is to provide technical guidance on how to determine whether a cleanup action alternative that relies on natural attenuation to clean up petroleum-contaminated ground water, either alone or in conjunction with other cleanup action components, meets the minimum requirements for cleanup actions set forth in WAC 173-340-360(2).

To make such a determination, the following five factors should be **considered** and **evaluated**. These factors are based on the minimum requirements for cleanup actions set forth in WAC 173-340-360(2) and the expectations for cleanup actions involving natural attenuation set forth in WAC 173-340-370(7).

(1) What is the status of the ground water plume at the site?

Natural attenuation may be appropriate at sites where, prior to relying solely on natural attenuation to achieve cleanup standards, the **ground water plume is demonstrated to be stable or shrinking**, thereby shortening the restoration time frame and ensuring that the plume will not continue to migrate and potentially impact other media (surface water, sediments, or air) or receptors (human or ecological).

➔ See Section 3.2.1.1

(2) Is chemical or biological degradation a substantial mechanism of natural attenuation at the site?

Natural attenuation may be appropriate at sites where there is evidence that the **destructive mechanisms** of natural attenuation (i.e., chemical or biological degradation) that reduce the contaminant mass are **occurring and are substantial contributors to contaminant reductions observed at the site**. Natural attenuation may not be appropriate at sites where natural attenuation relies primarily on dilution and dispersion to reduce contaminant concentration.

➔ See Section 3.2.1.2

(3) What is the estimated restoration time frame?

Natural attenuation may be appropriate at sites where the **estimated restoration time frame is reasonable** compared to that of other more active cleanup action alternatives, as determined by considering the factors set forth in WAC 173-340-360(4).

➔ See Section 3.2.1.3

(4) Will the use of natural attenuation be protective of human health and the environment during the estimated restoration time frame?

Natural attenuation may be appropriate at sites where the use of natural attenuation will be **protective of human health and the environment** during the estimated restoration time frame, as determined by conducting appropriate quantitative or qualitative risk assessments and considering the threats posed to other media (surface water, sediments, or air) and receptors (human or ecological).

➔ See Section 3.2.1.4

(5) Has source control been conducted to the maximum extent practicable?

Natural attenuation may be appropriate at sites where, prior to relying solely on natural attenuation to achieve cleanup standards, **source control is conducted to the maximum extent practicable**, thereby shortening the restoration time frame and helping to ensure that the plume will not continue to migrate and potentially impact other media (surface water, sediments, or air) or receptors (human or ecological).

➔ See Section 3.2.1.5

This subsection provides specific technical guidance on how to evaluate each of these five factors. For each factor, the guidance provides several different methods to conduct the evaluation. The most appropriate method(s) for the site should be selected, considering the specific conditions of the site and the advantages and limitations of each method. A number of assessment tools and methods are recommended in this section. It is not necessary to use all of the assessment tools and methods discussed in this section at every site. The choice of which calculations (evaluations) and the required amount of data should be based on the **complexity of the site and the usefulness of the assessment methods** in understanding site hydrogeology, contaminant distribution and movement, and natural attenuation processes. At some sites it may be appropriate to use a combination of methods and a weight of the evidence approach to make the necessary demonstrations.

If based on the evaluation it is determined that a cleanup action alternative that uses natural attenuation, either alone or in conjunction with other cleanup action components, is feasible, then that alternative can be developed and included as part of the feasibility study. However, if it is determined that natural attenuation is not feasible, then that alternative should not be included in the feasibility study and more active cleanup action alternatives should be developed and evaluated. Those alternatives could still include natural attenuation as a component, but such alternatives would have to rely less on natural attenuation to clean up the petroleum-contaminated ground water.

Note: It is recommended that a preliminary geochemical indicators analysis be conducted to assess the effectiveness of a natural attenuation remedy prior to submitting the evaluation and reports to Ecology for formal evaluations.

3.2.1.1 Evaluate Plume Status

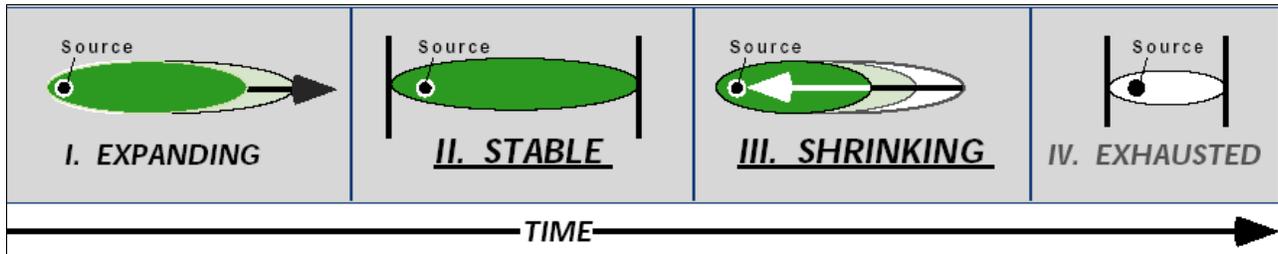
| | |
|-----------------|--|
| Question: | What is the status of the ground water plume at the site? |
| Evaluation: | Evaluate trends of contaminant concentrations within the plume and determine plume status. |
| Recommendation: | <ul style="list-style-type: none"> ✓ If plume is stable or shrinking, then CONTINUE to evaluate other factors ✓ If plume is expanding, then conduct MORE SOURCE CONTROL and/or EVALUATE OTHER CLEANUP ACTION ALTERNATIVES. |

To be considered a feasible cleanup action alternative, natural attenuation should be currently reducing contaminant concentrations over time under current site conditions. This ability to reduce contaminant concentrations is necessary for natural attenuation to achieve cleanup standards within a reasonable restoration time frame and prevent unacceptable threats to human health and the environment during that time frame.

Evaluation:

Generally, a contaminant plume will expand until it reaches steady-state. At steady-state, the mass loading rate of petroleum hydrocarbons contributed from the source is balanced with the natural attenuation rate. In other words, the plume becomes stable. When the source mass is depleted to the point that the rate of natural attenuation exceeds the source input, the plume begins to shrink over time. These concepts are illustrated in Figure 3.2.

Figure 3.2. Plume Lifecycle in Petroleum-contaminated Ground Water



Adapted from Newell and Connor (1997)

The mass loading rate depends on the amount of source mass and, hence, on the amount of source control previously conducted to reduce that mass, and the rate of dissolution (the process by which soluble contaminants partition from the NAPL into the aqueous phase) of contaminants from the source into the ground water plume. The ability of natural attenuation to reduce contaminant concentrations depends on whether the natural attenuation rate of the plume exceeds the mass loading rate from the source.

- If the mass loading rate $>$ natural attenuation rate, then contaminant concentrations will increase and the plume will expand.
- If the mass loading rate = natural attenuation rate, then contaminant concentrations will be unchanged and the plume will be stable.
- If the mass loading rate $<$ natural attenuation rate, then contaminant concentrations will decrease and the plume will shrink.

It should be demonstrated that the contaminated ground water plume is not expanding and that the concentrations of hazardous substances within that plume are not increasing. This demonstration should be made by evaluating ground water analytical data (measured concentration of ground water contaminants over time and distance from the source) collected during the remedial investigation to define the plume as shrinking, stable, or expanding.

Note: A plume may initially shrink or be stable when efficient electron acceptors (such as dissolved oxygen) are available to facilitate the oxidative degradation process. However, once the supply of favorable electron acceptors (i.e., dissolved oxygen) is exhausted, the plume may resume growing as reductive degradation ensues via slower reactions such as methanogenesis.

It is recommended that this evaluation be conducted using one or more of the methods described in Appendix D of this document. Those methods include log-linear regression analysis methods (including the visual or graphical analysis of contaminant concentrations or mass flux over time and distance), non-parametric statistical methods, and modeling approaches. The most appropriate method for the site should be selected based on the specific conditions of the site and the advantages and limitations of each method. Other methods may also be used to conduct the evaluation and demonstrate compliance, upon approval by Ecology. Below is a brief description of the methods in Appendix D and items to consider when using these methods:

- Assess plume stability with graphical and regression analysis:
Conduct graphical and/or regression analysis to assess plume stability. Assess whether there are temporal trends in site-specific contaminant concentration data and ground water elevation data by plotting these data vs. time on a graph to assess plume status for each well. Conduct linear regression analysis of log concentration vs. time, including level of significance on the slope as illustrated in Appendix D.2 of this document. Ecology recommends the use of 85% or higher level of confidence as a guide for evaluation of the feasibility of natural attenuation, where applicable. Also, visually inspect the data for trends. Examine simultaneous spatial/temporal trends in contaminant data to see overall plume status; if possible, spatial ground water analytical data (multiple sampling rounds) are to be plotted as concentration vs. monitoring distance on a graph and/or on a site plan as illustrated in Appendix D.2. Ground water elevation information should also be examined as part of this analysis to see if there is any systemic impact of changes in ground water elevation on the observed plume status.
- Assess plume stability with non-parametric statistical analysis:
Conduct non-parametric statistical analysis to assess plume stability. Assess whether contaminant concentrations are decreasing at each monitoring well. The Mann-Kendall or Mann-Whitney test is used for this analysis as illustrated in Appendix D.4. Non-parametric tests can be used to screen for shrinking and stable concentration trends for each well. Non-parametric statistics are distribution-free statistics. That is, there are no assumptions made about the parameters of the population from which the samples are taken so that the Mann-Kendall or Mann-Whitney test cannot be used to estimate time to clean up or determine any rate constants. If it cannot be concluded that there is a shrinking trend from a non-parametric test, then the monitoring data are unlikely to provide any useful information on rate constants and restoration time.
- Assess plume stability with plotting maps of plume iso-concentrations over time:
Examine maps of plume concentration contour over time to determine if the plume is expanding, is stable, or is shrinking. The visual assessment through plume iso-concentrations or graphs should clearly illustrate that the plume is either stable or shrinking, as illustrated in Appendix D.1. A database containing the data used to prepare the maps should be included. Minimum data required are well number, well location coordinates, well elevation, sampling dates, ground water elevation, concentration data for each contaminant of concern, laboratory qualifiers for that data, method detection limits, method reporting limits, and practical quantitation limits (PQL), etc.
- Assess plume stability with spatial mass flux calculation over time:
Assess the flux of contaminants (mass per unit time) flowing across specified cross-sectional areas of the plume as shown in Appendix D.5. Overall mass fluxes of contaminants should be clearly either declining or stable spatially along multiple down-gradient transects from the source over time.

When evaluating the plume status, the impact of factors other than natural attenuation should be carefully considered, including the impact of remedial actions and site hydrogeology.

- *Impact of changes in ground water elevation and infiltrating precipitation:*
Consider the impact of changes in ground water elevation on the observed status of the plume. Observed changes in contaminant concentrations may often result from changes in the ground water elevation. In fact, changes in water levels can often be more important in explaining an observed decrease in contaminants than biodegradation processes. Consequently, be careful to discriminate between changes due to water level and changes due to attenuation processes. The infiltrating precipitation into a subsurface system may also have a profound effect on contaminant concentrations. High rates of infiltration may lower the apparent ground water concentration of contaminants due to dilution. If contaminants are present in the vadose zone, however, high rates of infiltration may cause increases in concentrations due to leaching. Variation in ground water gradients or infiltration rates can cause the plume centerline to shift away from the established monitoring well network.
- *Impact of preferential flow pathways:*
Consider the impact of preferential flow pathways on the observed status of the plume. The status of the plume should be determined by observing trends within the entire plume, not just within the source. This is particularly important at sites where preferential flow pathways may control the movement of the plume. These pathways include, but are not limited to, inter-bedded permeable units, storm sewers, tile drains, gravel backfilled utility trenches below the water table, fractures in over-consolidated glacial tills, and building foundations materials.
- *Impact of historical source removal and remediation efforts:*
Consider the impact of other remedial actions including source removal, on the observed status of the plume. Be careful not to attribute such plume shrinkage due to other remedial actions to natural attenuation. Note that some remedial actions can cause a short-term increase in mass loading and hence cause a short-term expansion of a stable or shrinking plume. Significant changes in the source zone, pavement removal, and/or a rising water table may cause contaminant trends to reverse from a formerly stable condition, or cause a receding plume to advance. In the long term, such actions should eventually decrease mass loading and cause the plume to shrink more rapidly. Be attentive to collecting data over a longer period of time. Declining concentration trends in the source zone alone is not sufficient to establish that a plume is stable or shrinking. Note that a sentinel well can become contaminated even when decreasing concentrations are observed at monitoring wells within the source zone.

Recommendation:

It is not unusual that different concentration trends are exhibited between different wells located on the same site. Thus, be careful of drawing conclusions about a site using information obtained at a single monitoring location. To truly determine the status of the overall plume, evaluate historical monitoring data for all relevant hazardous substances from multiple monitoring points located at various points throughout the entire plume.

If the monitoring well concentrations are determined as **stable** or **shrinking** in 80% or more of the wells within the contaminated plume, then the site plume should be considered stable or

shrinking in most circumstances. Also, if the plume dimensions have not changed significantly over time, or are shrinking back to the source area, and variations in well concentrations cannot be attributed to random/systematic factors such as water table fluctuations, sampling variability, or analytical uncertainty, the plume can be considered stable or shrinking.

If the plume is **expanding** such that the concentrations of hazardous substances are consistently increasing and the dimensions of the plume are expanding (laterally or vertically), then it cannot be sufficiently demonstrated that the plume is stable or shrinking for the hazardous substances. For an expanding plume, this means that additional source control should be done to reduce the source mass and consequently the mass loading rate before relying on natural attenuation to achieve cleanup standards. If additional source control is not practicable, then other more aggressive cleanup action alternatives should be developed and implemented to minimize the spreading of contamination. If the plume status cannot be determined, additional monitoring wells may need to be installed and/or more sampling conducted for a longer period of time and the conceptual site model refined. The recommended number of monitoring wells and their locations are specified in Section 3.1.3 of this document. To interpret the plume status for each contaminant of concern, the guide shown in Table 3.2 is recommended.

Table 3.2. A Guide for Determining Overall Plume Status

| Plume Status | Location of Wells | | |
|---|--|--|--|
| | For monitoring wells within the contaminated plume, evaluate plume status: see note below. | For any clean sentinel well where contaminant was previously undetected, evaluate contaminant concentration: | For any water supply well where contaminant was previously undetected, if any, evaluate contaminant concentration: |
| Shrinking Plume , if ALL of the following occur | Plume status is defined as shrinking at more than 80% of all monitoring wells nearest the contaminated plume axis. | Contaminant Not Detected | Contaminant Not Detected |
| Stable Plume , if ALL of the following occur | Plume status is defined as shrinking or stable at more than 80% of all monitoring wells nearest the contaminated plume axis. | Contaminant Not Detected | Contaminant Not Detected |
| Expanding Plume , if ANY of the following occurs | Plume status is defined as expanding or undetermined at more than 20% of all monitoring wells nearest the contaminated plume axis. | Contaminant Detected over one or more consecutive rounds | Contaminant Detected |

Note: This table should be used in conjunction with the narrative discussion in this guidance.

- *Shrinking Plume: A plume is determined to be shrinking if selected monitoring wells within the contaminated plume that are above cleanup levels exhibit a trend of decreasing ground water contaminant levels in the source, or most impacted area, and in the down-gradient contaminant plume that is above cleanup levels.*

- *For a system with three wells within a contaminated plume, one well should be in the source, or most impacted area, and at least two wells should be in the down-gradient plume that is above cleanup standards. All three wells should individually show a trend of decreasing contaminant levels.*
 - *For a system with four wells within a contaminated plume, one well should be in the source, or most impacted area, and three wells should be in the down-gradient plume that is above cleanup levels. All four wells should individually show a trend of decreasing contaminant levels.*
 - *For a system with five or more wells within a contaminated plume, one well should be in the source, or most impacted area, and other wells should be in the down-gradient plume that is above cleanup levels. 80 % of the total number of wells in the plume above cleanup levels including the source well, should individually show a trend of decreasing contaminant levels.*
- *Stable Plume: A plume is determined to be stable if selected monitoring wells within the contaminated plume that are above cleanup levels exhibit a trend of decreasing or stable ground water contaminant levels in the source, or most impacted area, and in the down-gradient contaminant plume that is above cleanup levels.*
 - *For a system with three wells within a contaminated plume, one well should be in the source, or most impacted area, and at least two wells should be in the down-gradient plume that is above cleanup standards. All three wells should individually show a trend of decreasing or stable contaminant levels.*
 - *For a system with four wells within a contaminated plume, one well should be in the source, or most impacted area, and three wells should be in the down-gradient plume that is above cleanup levels. All four wells should individually show a trend of decreasing or stable contaminant levels.*
 - *For a system with five or more wells within a contaminated plume, one well should be in the source, or most impacted area, and other wells should be in the down-gradient plume that is above cleanup levels. 80 % of the total number of wells in the plume above cleanup levels including the source well, should individually show a trend of decreasing or stable contaminant levels.*

3.2.1.2 Evaluate mechanisms of natural attenuation

| | |
|-----------------|---|
| Question: | Is chemical or biological degradation a substantial mechanism of natural attenuation at the site? |
| Evaluation: | <ul style="list-style-type: none"> ✓ Evaluate geochemical indicators and expressed assimilative capacity. ✓ If necessary, estimate biodegradation rate constant or conduct other biological activity tests. |
| Recommendation: | <ul style="list-style-type: none"> ✓ If chemical or biological degradation is substantially occurring, then CONTINUE to evaluate other factors. ✓ If chemical or biological degradation is not substantially occurring, then conduct MORE SOURCE CONTROL and/or EVALUATE OTHER CLEANUP ACTION ALTERNATIVES. |

To be considered a feasible cleanup action alternative, chemical or biological degradation should be a substantial mechanism of natural attenuation at the site.

Evaluation:

Natural attenuation can decrease contaminant concentrations through both destructive mechanisms (e.g., natural biodegradation and/or chemical degradation) and non-destructive mechanisms (e.g., dispersion and dilution by recharge). While non-destructive mechanisms merely decrease contaminant concentrations spatially through redistribution of the contaminant mass, destructive mechanisms reduce contaminant concentrations through the destruction of the contaminant. Ecology expects that evidence of substantial chemical and/or biological degradation be demonstrated to retain natural attenuation as a component of a proposed cleanup action. Decreasing concentrations should not be solely the result of plume migration.

Natural biodegradation, which is the most effective destructive mechanism, involves the degradation of hydrocarbon compounds into other compounds or elements by indigenous microbes through biological processes, such as aerobic and/or anaerobic respiration. The driving force of biodegradation is the transfer of electrons from an electron donor (petroleum hydrocarbons) to an electron acceptor. The ability of natural biodegradation to destroy, and thereby decrease, contaminant mass depends on the biodegradation rate and the mass loading rate. The higher the biodegradation rate, the more effective natural biodegradation will be in decreasing the contaminant mass. The biodegradation rate is also dependent on the site-specific assimilative capacity of the saturated geologic strata.

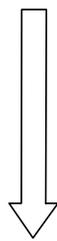
Changes in the geochemical indicators associated with the degradation process and the assimilative capacity of the ground water need to be evaluated and where there are no clear changes in the geochemical indicators, or, it may be possible to make a demonstration that substantial biodegradation is occurring by calculating a biodegradation rate constant. Other methods include microcosm studies, biochemical testing and, for MTBE, stable isotope testing. These methods are described in more detail below.

There are no performance standards for geochemical indicators that can be applied universally to all sites to indicate conclusively that substantial biodegradation is or is not occurring. Because of this, qualitative evaluation methods are generally used. Two commonly used qualitative methods are:

- Geochemical indicators are used to qualitatively assess geochemical changes within the ground water plume over time; and/or
- Geochemical indicators in wells located within and down gradient of the source are compared to up-gradient or background levels.

The primary biodegradation mechanisms and their associated geochemical indicators are summarized in Table 3.3. The transfer of electrons during the Redox reaction releases energy which is utilized for cell maintenance and growth. The biochemical energy associated with transformation of various compounds are noted in Table 3.3 and can be represented by the Redox potential where that transformation is expected to dominate. The more positive the Redox potential is, the more energetically favorable is the reaction utilizing that electron acceptor.

Table 3.3. Evaluation of Geochemical Indicators and Microbial Reactions

| Type of Microbial Respiration | Electron Acceptor | Metabolic By-Product | Geochemical Indicators Response | | Redox Potential E_H° <i>mV @ pH 7, 25°C</i> | |
|-------------------------------|--|----------------------------------|---------------------------------|-------------------|---|---|
| Aerobic (Oxidation) | Oxygen | CO ₂ | O ₂ ↓ | CO ₂ ↑ | + 820 | Most Preferred |
| Anaerobic (Reduction) | Nitrate (NO ₃ ⁻) | N ₂ | NO ₃ ⁻ ↓ | CO ₂ ↑ | + 740 |  |
| | Manganese (Mn ⁺⁴) | Mn ⁺² | Mn ⁺² ↑ | CO ₂ ↑ | + 520 | |
| | Ferric Iron (Fe ⁺³) | Ferrous Iron (Fe ⁺²) | Fe ⁺² ↑ | CO ₂ ↑ | - 50 | |
| | Sulfate (SO ₄ ⁻²) | H ₂ S | SO ₄ ⁻² ↓ | CO ₂ ↑ | - 220 | |
| | Carbon Dioxide (CO ₂) | Methane (CH ₄) | CH ₄ ↑ | CO ₂ ↑ | - 240 | |

Adapted from ASTM (1998) and Weidimeier (1999)

Note: The shaded arrows mean concentration is expected to go down.

Based on thermodynamic considerations, the most energetically preferred reaction should proceed in the plume until all of the required electron acceptor is depleted. At that point, the next most-preferred reaction should begin and continue until the electron acceptor is gone. In other words, when oxygen is present in the ground water aquifer, reactions utilizing oxygen as the electron acceptor will predominate and aerobic bacteria will dominate until the bacteria utilize all of the oxygen. Once depleted, the bacteria utilize alternative electron receptors with a sequential preference in order of decreasing Redox potential.

Geochemical indicators of naturally occurring biodegradation are useful for demonstrating that contaminant mass loss is due to biodegradation. The geochemical indicators associated with the biodegradation process consist of the electron acceptors (reactants) or metabolic by-products of the oxidation and/or reduction reactions that occur as part of the biodegradation process. Geochemical indicators of petroleum hydrocarbon biodegradation can include O₂, NO₃⁻, Mn⁺², Fe⁺², SO₄⁻², CH₄, Redox potential (E_H), and Alkalinity. Changes in these geochemical indicators (either decreases in reactants or increases in metabolic by-products) indicate that biodegradation is occurring. An evaluation of these indicators therefore requires an evaluation of whether and to what extent those indicators have changed since the release occurred. This requires the collection of ground water analytical data from different areas within the contaminated ground water plume and from uncontaminated areas up-gradient from the plume.

The Redox potential of ground water is a measure of electron activity and is an indicator of the relative tendency of a solute species to accept or transfer electrons. All Redox probes give results in millivolts (*mV*). Knowledge of the Redox potential of ground water is important because some biological processes operate only within a prescribed range of Redox conditions. Oxidation-reduction potential (E_H) and *pH* have a significant influence on iron and manganese solubility. A portable probe similar to a *pH* probe is used to measure ORP. It is important to read and understand the instructions that come with the probe. A probe-specific correction factor is required to convert the raw *mV* reading into E_H (calculated oxidation-reduction potential).

When data are recorded, it should be clear whether it is the raw reading or the corrected E_H value. Use standard Redox solutions to calibrate the electrode system at the expected temperature of measurement. Also, it should be distinguished from “ pE ” which is the measure of the availability of electrons in solution.

Assimilative capacity is an estimate of the potential mass of petroleum hydrocarbons per unit volume of ground water that can be metabolized (or utilized) by aerobic and anaerobic biodegradation based on stoichiometric relationships. The biodegradation process and the methodology for evaluating the geochemical indicators and assimilative capacity associated with that process are described more completely in Appendices E and G of this guidance. Expressed assimilative capacity can be estimated by calculating the difference in geochemical indicators’ concentration measured between a background well and monitoring wells within the plume.

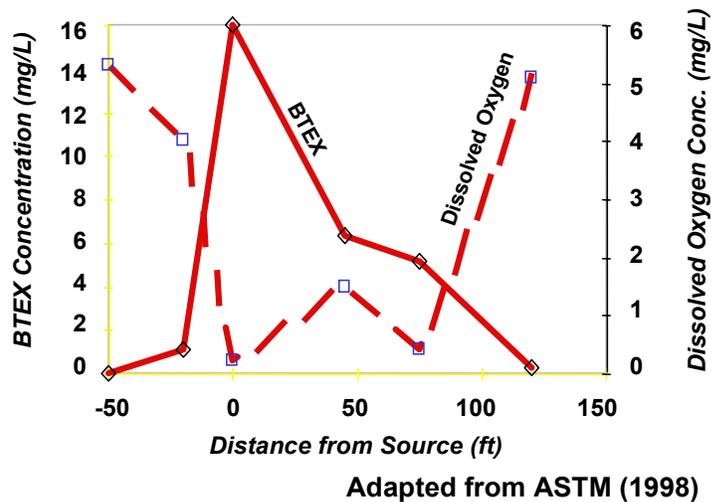
Another way of demonstrating that substantial biodegradation is occurring at a site is to estimate the biodegradation rate constants with solute transport models such as those provided in Appendix F of this document. These models incorporate advection, dispersion, sorption, and biodegradation. If the model prediction accurately simulates measured contaminant concentrations, the model confirms what is observed at the site and can be used to demonstrate the relative importance of biodegradation mechanisms.

The evaluation of the contaminant mass decrease due to biodegradation can be accomplished by the evaluation of geochemical indicators or by any combination of methods that include the evaluation of geochemical indicators:

- Evaluate the response of geochemical indicators (contour or isopleths map):
Use available ground water data to establish a correlation between the loss of contaminant vs. responses of at least one or two geochemical indicators that are consistent with known biodegradation reactions (e.g., increased alkalinity due to the production of CO_2 , reduced dissolved oxygen concentrations in source area wells) as shown in Table 3.3 and Figure 3.3. It is recommended the potential site-specific assimilative capacity of the system be estimated based on the geochemical indicators. The source area is likely to be the most reducing part of the contaminant plume. In conjunction with samples collected in the source area, samples collected in the dissolved plume down-gradient allow a determination to be made of whether or not the plume is degrading with distance along the flow path and to determine the distribution of geochemical indicators along the flow path.

Standard monitoring wells having 5- to 10-foot screened intervals can mix water from different vertical zones. Therefore, a field sampling program using these types of wells may yield data that indicate a general pattern of electron acceptor depletion, but not complete depletion, and overlapping of electron acceptors/metabolic by-products isopleths not predicted by thermodynamic principles. However, these general patterns of geochemical changes within the plume area can still provide evidence that multiple mechanisms of biodegradation are occurring at a site. It is also useful to compare geochemical indicators measured in monitoring wells within and outside the plume.

Figure 3.3. Geochemical Indicators Response
(Dissolved Oxygen and BTEX Concentration vs. Distance)



Contour maps can also be prepared for contaminants, electron acceptors consumed, and metabolic by-products produced during biodegradation to provide visual evidence of the occurrence of biodegradation in the field. Lines of equal concentration (isopleths) are drawn. Comparison of the contaminant contour map and the geochemical indicator contour map should be able to show that there is a strong correlation among areas with elevated contaminant concentrations and elevated total alkalinity, Mn^{+2} , Fe^{+2} , CH_4 , and depleted O_2 , NO_3^- , SO_4^{-2} , and lower Redox potential. These contour maps allow interpretation of data on the distribution (relationship) of geochemical indicators resulting from the microbial degradation of petroleum hydrocarbons and the relative transport and degradation rates of contaminants in the aquifer. Refer to Appendices C.2.2.5 and C.3.3.1 of US Air Force (1995) for more detail on the preparation and interpretation of contour maps.

- One-dimensional estimate of contribution ratio of plume contaminant mass removed to overall attenuation for stable plumes:
Estimate the biodegradation rate constant first and the contribution ratio of plume mass removed by biodegradation to the overall attenuation. This method (Buscheck and Alcantar, 1995) relies on a 1st-order biodegradation model but attempts to extract the biodegradation rate constants in a one-dimensional plume analysis by accounting for advection and dispersion. This method works only with stable plumes. Refer to Appendix F.3 of this document for more detail on the mathematical theory for this method.
- Two-dimensional estimate of contribution ratio of plume contaminant mass removed to overall attenuation for both shrinking and stable plumes:
Estimate the biodegradation rate constant across the plume using a two-dimensional analysis. This method uses two-dimensional analytical solute transport models (Domenico's analytical solution: Domenico, 1987) to predict plume extent. This method can be used for both shrinking and stable plumes. The biodegradation rate constant is calibrated with the field monitoring well concentrations observed. This method needs information on source

dimensions such as thickness, width, and mass. Refer to Appendix F.4 of this document for more detail on the mathematical theory for this method.

- Conduct conservative tracer study:
Generally, trimethylbenzene (three isomers of 1,2,3-TMB, 1,2,4-TMB, and 1,3,5-TMB) and tetramethylbenzene are present in sufficient quantities in fuel mixtures to be readily detectable when dissolved in ground water and are fairly recalcitrant to biodegradation under anaerobic conditions. These tracers have Henry's law constants and soil sorption coefficients that are similar to those of BTEX. After correcting measured BTEX concentrations for the effects of dispersion, dilution, and sorption using this tracer study, it is possible to estimate the amount of BTEX biodegraded (removed) from the aquifer. Refer to Appendix C.3.3.2 of US Air Force (1995) for more detail.
- Conduct microcosm studies:
Microcosm studies are laboratory assays to test whether those microorganisms from a contaminated site have the potential to degrade the hazardous substances. The biodegradation of major petroleum constituents such as BTEX is well documented. Thus, microcosm studies are not typically performed at petroleum release sites. However, they can be used to clearly demonstrate naturally occurring biodegradation if properly designed, implemented, and interpreted. Microcosm studies are inherently time consuming. Microcosm studies should be undertaken only at sites where there is considerable uncertainty concerning the biodegradation of petroleum hydrocarbons based on soil and ground water samples alone. In microcosm studies, small quantities of ground water and aquifer solids are placed into serum bottles. The decrease of electron acceptors and the production metabolic by-products are measured over time. Although microcosm studies can be used to estimate *in-situ* biodegradation rates, the most appropriate use of microcosm studies is to demonstrate biodegradation processes only. Refer to Appendix C.3.4 of US Air Force (1995) for more detail on the design, implementation, and interpretation of microcosm studies.
- Conduct biochemical testing:
There are two biochemical tests to indicate the biodegradation of petroleum hydrocarbons: volatile fatty acids and dehydrogenase tests. Volatile fatty acids are produced as metabolic by-products during the biodegradation of petroleum hydrocarbons. The production of these volatile fatty acids is a direct indication that biodegradation has occurred. The field dehydrogenase test is a qualitative method used if aerobic bacteria are present in aquifer in quantities capable of biodegrading petroleum hydrocarbons. If the dehydrogenase test gives a positive result, a sufficient number of microorganisms capable of aerobic and/or denitrification are present in the aquifer. Refer to Section 2.3.4 of US Air Force (1995) for more detail.
- Conduct stable carbon isotope testing for MTBE:
A new technique has been developed to evaluate the extent of MTBE biodegradation at field scale. The technique is based on the fractionation of the stable carbon isotopes in the remaining MTBE during the course of degradation. The fractionation of the stable carbon isotopes of MTBE can provide an unequivocal indication of MTBE biodegradation. This technique also could predict the extent of biodegradation from the measured stable carbon isotope ratio. Refer to Sections 5 and 6 of US EPA (2005a) for more detail.

Recommendation:

If, in addition to observed reductions in petroleum contamination, geochemical indicators clearly exhibit the expected trends (either decreases in reactants or increases in electron acceptors or metabolic by-products as shown in Table 3.3) compared to their background, then it can be concluded that substantial biodegradation is occurring at the site and this factor has been satisfied.

If geochemical indicators are insufficient to demonstrate biodegradation is substantially occurring, solute transport models may still be able to be used to calculate a biodegradation rate constant and demonstrate that biodegradation is a substantial mechanism in reducing contaminant mass. If neither technique can demonstrate biodegradation is occurring, then either additional source control needs to be conducted or other cleanup action alternatives evaluated.

3.2.1.3 Estimate and evaluate reasonableness of restoration time frame

| | |
|-----------------|---|
| Question: | What is the estimated restoration time frame and is that time frame reasonable compared to that of other more active cleanup action alternatives? |
| Evaluation: | <ol style="list-style-type: none"> 1. Estimate rate constants; 2. Estimate restoration time frame; and 3. Evaluate reasonableness of estimated restoration time frame. |
| Recommendation: | <ul style="list-style-type: none"> ✓ If the time frame is reasonable, then CONTINUE to evaluate other factors. ✓ If the time frame is unreasonable, then conduct MORE SOURCE CONTROL and/or EVALUATE OTHER CLEANUP ACTION ALTERNATIVES. |

To be considered a feasible cleanup action alternative, natural attenuation should not only be currently able to decrease contaminant concentrations and mass, but also able to achieve cleanup standards within a reasonable restoration time frame.

Evaluation:

Natural attenuation, either alone or in conjunction with other cleanup action components, should be evaluated to determine if it can meet ground water cleanup levels at the points of compliance within a reasonable time frame based on site-specific conditions without posing an unacceptable threat to human health or the environment.

The restoration time frame depends on four major components: the amount of source mass (and associated dissolution rate); bulk attenuation rates for the contaminants; the ground water cleanup levels needing to be met for the contaminants; and, the point of compliance at which the cleanup levels should be achieved. The lower the bulk attenuation rate, in general, the longer the restoration time frame. The bulk attenuation rate accounts for all natural attenuation mechanisms, both destructive and non-destructive. The biodegradation rate is not the same as the bulk attenuation rate. The biodegradation rate does not account for other attenuation mechanisms (e.g., dispersion and sorption) and therefore, by definition, will always be less than the bulk attenuation rate.

The restoration time frame also depends on the amount of source mass and the dissolution rate from the source into the ground water plume and hence on the amount of source control previously conducted to reduce that mass. The greater the amount of source mass, the greater the amount of contaminated mass leaching into the ground water requiring attenuation. The greater

the amount of contaminated mass requiring attenuation, the longer the restoration time frame. More detail on estimation of attenuation rate constants and restoration time frame is presented in Appendix F of this guidance.

An estimation of the probable range of the restoration time frame to achieve the cleanup goals should be made and then a determination made whether that time frame is reasonable. The bulk attenuation rate should be used to estimate the restoration time frame. To determine whether the estimated restoration time frame is reasonable, a comparative analysis of cleanup action alternatives should be conducted in accordance with WAC 173-340-360(4).

(1) Estimate Bulk Attenuation Rate Constants and then Restoration Time.

To estimate the actual restoration time frame, first estimate the bulk attenuation rate constant. To estimate the bulk attenuation rate, use one or more of the methods described in Appendix F of this document. Those methods include a simple regression method (involving the statistical analysis of contaminant concentrations over time and distance) and a more complex modeling approach. The bulk attenuation rates often vary at a site and with time. Changes in subsurface conditions can significantly change these rates. Rate changes can also occur due to depletion of reactants, changes in the nature or composition of a source area, or changes in the microbial community. Select the most appropriate method for the site, considering the specific conditions of the site. Other methods may also be developed to conduct the evaluation and demonstrate compliance, upon approval by Ecology. Recommended methods for estimating bulk attenuation rate constants and the restoration time frame are as follows:

- Estimate the restoration time with linear regression analysis for shrinking plumes (temporal analysis at a point in the plume):
Establish cleanup levels, the point of compliance at which those cleanup levels should be met, and the wells to be used to assess compliance. Graph measured ground water contaminant concentrations vs. time for each compliance well. Perform a linear regression analysis to estimate the point decay rate constant (k_{point}) for each well, including the lower bound for the regression line based upon an 85% (or greater) confidence level. The estimated restoration time for achieving compliance in each well is then the time at which the 85% (or greater) lower bound of the regression line reaches the cleanup level. Note that this requires extrapolation of the regression line beyond the measured data. Please refer to Section 3.3.3 and Appendix F.2 of this document and Section 7 of US EPA (2005a) for additional information on how to calculate the confidence interval on the slope. This method can be used only for a shrinking plume.
- Estimate the restoration time with two-dimensional analytical solute transport models for both shrinking and stable plumes:
These methods can be used for both shrinking and stable plumes. To conduct this analysis, extensive information is needed on the contaminant source mass and dimension and basic ground water flow parameters such as ground water velocity and direction, sorption, dispersivities, etc. Use the most recent and representative contaminant concentrations that are above detection limits in four or more consecutive wells sampled as described in Section 3.1 of this document (Remedial Investigation). First, calibrate the best-fitting biodegradation rate constant with field data, then estimate the restoration time to achieve cleanup standards at the

specified point of compliance, and compare concentration profiles generated for various time intervals in model simulations conducted with and without incorporating biodegradation kinetics. All hydrological parameters required in this method should be listed and be site-specific. More detail on the theoretical background for an analytical solute transport model is presented in Appendix F.4 of this document.

(2) Determine whether Estimated Restoration Time Frame is Reasonable.

Determinations regarding the “reasonableness” of the restoration time frame for any given cleanup alternative should be made on a site-specific basis. While natural attenuation may require a somewhat longer restoration time frame than other cleanup action alternatives, the restoration time frame for a remedy involving natural attenuation should **not be overly excessive** compared to that of other cleanup actions alternatives. Ecology has **not** established a default value for an acceptable and reasonable restoration time at petroleum-contaminated sites where natural attenuation, either alone or in conjunction with other cleanup action components, is proposed as a cleanup alternative.

To determine whether the estimated restoration time frame is reasonable, conduct a comparative analysis of cleanup action alternatives in accordance with WAC 173-340-360(4). A comparative analysis is necessary because the reasonableness of a particular restoration time is based on the practicability of achieving shorter time frames using alternative cleanup actions. A thorough evaluation is required before selecting a final cleanup action. In some cases, natural attenuation used as a sole cleanup action may not achieve cleanup standards within a reasonable period of time. However, one or more supplemental cleanup actions that are technically and economically feasible will significantly reduce the mass and concentration of contaminants and thus allow natural attenuation to achieve cleanup standards within a reasonable restoration time frame.

To determine whether a cleanup action provides for a reasonable restoration time frame, consider the factors set forth in WAC 173-340-360(4)(b). When evaluating whether natural attenuation achieves cleanup standards within a reasonable time frame, Ecology recommends consideration of the following specific factors, which are based on the factors set forth in the rule:

- Classification of the affected resource (e.g., drinking water source, agricultural water source) and value (e.g., cultural, subsistence, ecological) of the resource.
- Relative time frame in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies).
- Ability to fund monitoring and evaluation over the restoration time period.
- The degree of uncertainty related to the restoration time frame, which depends on:
 - The uncertainty related to the type and amount of source;
 - The uncertainty related to the geologic and hydrogeologic conditions;
 - The uncertainty related to the plume status; and
 - The uncertainty related to the natural attenuation rate.
- The practicability of additional source control, which would:

- Reduce contaminant mass and concentrations;
 - Shorten the restoration time frame; and
 - Reduce the risks posed by the contamination during the restoration time frame.
- The protectiveness of the remedy during the restoration time frame, which depends on:
 - Current and potential risk posed by the site to human and ecological receptors and environmental resources;
 - Proximity of contamination to receptors;
 - Presence of sensitive receptors and threatened or endangered species or habitats;
 - The extent to which contaminants could enter the interconnected aquifer, or discharge at the ground surface or into a surface water body; and
 - The risks posed to current receptors based on that use and the potential exposure pathways (e.g., vapors migration and soil direct contact).
 - The reliability of institutional controls to prevent use;
 - The reliability of monitoring to ensure the protectiveness of the remedy; and
 - The possibility of changes in use.
 - The effectiveness of the remedy during the restoration time frame, which depends on the amount of source control, and the reliability of performance monitoring with respect to:
 - The migration of hazardous substances; and
 - The progress of natural attenuation.
 - Public acceptance of the extended time for cleanup; and
 - The mobility, magnitude, potency, and toxicity of contaminants or their residual breakdown products.

Recommendation:

If natural attenuation is able to achieve cleanup standards within a reasonable restoration time frame under consideration of the above factors, then this factor is satisfied. If natural attenuation is not able to achieve cleanup standards within a reasonable restoration time frame, then additional source control may be required to reduce the source mass before relying on natural attenuation to achieve cleanup standards. If additional source control is not practicable, more aggressive cleanup actions may also be required.

3.2.1.4 Evaluate protectiveness during restoration time frame

| | |
|-----------------|---|
| Question: | Will the use of natural attenuation be protective of human health and the environment during the estimated restoration time frame? |
| Evaluation: | Identify and evaluate current and potential threats to receptors. |
| Recommendation: | <ul style="list-style-type: none"> ✓ If no unacceptable threats, then CONTINUE to evaluate other factors. ✓ If unacceptable threats, then EVALUATE OTHER CLEANUP ACTION ALTERNATIVES. |

To be considered a feasible cleanup action alternative, the cleanup action should not only be able to achieve cleanup standards within a reasonable restoration time frame, but also be able to

adequately protect human and ecological receptors during that time frame. If receptors are impacted by the contaminant, an active cleanup action will be necessary to remove or contain the contamination such that the receptor is adequately protected.

Evaluation:

Although ecological and human health risk assessments are discussed qualitatively in this guidance to assess the impacts on the actual or potential human and ecological receptors, it is **not** the intent of this document to address human health and ecological risk assessments in detail. In addition to information in the MTCA rule and other Ecology guidance on ecological risk assessment, see US EPA (1992c, 1997a, 1998c). For human health risk assessment, in addition to requirements in the MTCA rule, suggested references include EPA's Exposure Factors Handbook (1997b), EPA's Risk Assessment Guidance for Superfund (RAGS) (1989 and several updates and supplements), and ASTM Guide E1739 (1995b).

Risk assessment and natural attenuation are related. One of the key elements of risk assessment is to quantify the risks to receptors located some distance away from the source. To quantify this risk associated with ground water, usually the critical exposure pathway and the amount of attenuation occurring between the source and the receptors should be quantified by conducting surveys of sources, transport mechanisms, viable exposure pathways, and potential receptors. If risk-management strategies are not sufficient to prevent impacts to identified receptors, the remediation by natural attenuation is inappropriate as a stand-alone option.

Whether leaving contamination on the site during the restoration time frame poses an unacceptable threat to human or ecological receptors depends on whether and to what extent those receptors are impacted or have the potential to be impacted. Whether and to what extent receptors are impacted is dependent on the amount and concentration of the source mass, the rate of source dissolution, the rate of natural attenuation, exposure pathways, etc. Because natural attenuation relies on natural processes to prevent contaminants from migrating, it is important to determine the status of **plume stability** (i.e., either shrinking or stable plume) and whether receptors might be impacted by the release.

The decision process described in this section integrates risk and exposure assessment practices with remedial investigation activities (see Section 3.1 of this document) and cleanup action alternatives selection to ensure that the chosen cleanup action is protective of human health and the environment. Methods **other than a quantitative** site-specific risk assessment may also be used to determine if a cleanup action alternative is protective of human health and the environment. The key steps for evaluating protectiveness during restoration time frame include:

(1) Identify the Current and Potential Future Receptors and Exposure Points.

All down-gradient ground water and surface water receptors specified in Section 3.1.2 of this document should be identified as well as all potentially affected wells and surface waters/sediments. Site-specific conditions such as high ground water velocity or recalcitrant contaminants (e.g., MTBE) may require that receptors be identified beyond the distances listed in Section 3.1.2 of this document. Once receptors and environmental resources are identified, determine whether the contaminants pose a threat to the receptor, considering likely exposure pathways and site-specific factors.

(2) Refine the Site Conceptual Model (if necessary collect additional data).

An exposure assessment identifies the receptors (human and ecological) that could potentially come into contact with contamination and the pathways through which these receptors might be exposed. To have a completed exposure pathway, there should be a source of contamination, a potential mechanism(s) of release, a pathway of transport to an exposure point, an exposure point, and a receptor. If any of these elements do not exist, the exposure pathway is considered incomplete, and receptors will not come into contact with site-related contamination. When conducting this evaluation, consider both current conditions as well as likely potential future site conditions based on land and resource uses.

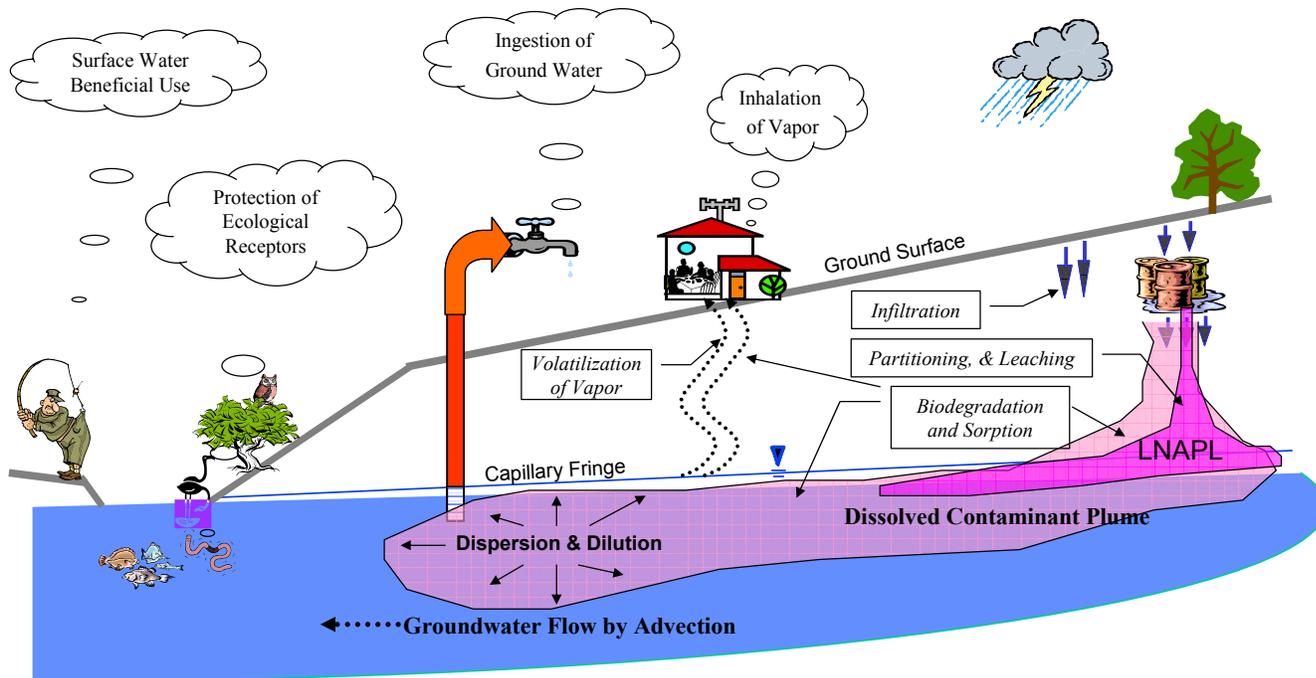
The purpose of refining the conceptual model is to consolidate site and regional data into the assessment of assumptions and concepts that can be evaluated quantitatively. Field data also should be used to refine the conceptual model that is ultimately chosen as the best site representation. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate representation of the hydrogeologic and contaminant transport system for use in fate and transport modeling.

The conceptual model evolves as additional data are collected and assessed. The site conceptual model should be refined by incorporating new data and reinterpreting site conditions. The foundation of a site conceptual model is always the site's hydrogeology. Knowing where and how ground water flows is therefore essential for tracking contaminants within the ground water and their geochemical indicators. This refined conceptual model can then be used for contaminant fate and transport modeling.

The site investigation should determine whether any exposure pathway is "complete", that is, that an actual (or potential) threat exists to human health and the environment. Figure 3.4 illustrates the concepts of natural attenuation mechanisms and the most common exposure pathways and receptors due to ground water contamination. Exposure pathways that need to be considered in a conceptual site model include:

- **Water supply wells:** identify all water supply wells as specified in Section 3.1.2 and assess any actual (or potential) impact on wells;
- **Surface water body:** evaluate the potential for degradation of surface water quality via surface run-off or ground water discharge to surface water. Identify all surface water discharge locations and assess the impact of the surface water discharge on contaminant movement;
- **Direct contact:** evaluate the potential for contact with shallow contaminated ground water and aquifer material;
- **Vapor migration to enclosed spaces:** assess enclosed spaces when buildings or utility lines are located near or over a shallow ground water plume; and
- **Additional evaluation if necessary:** assess any potential migration to off-site locations through utility line backfill, storm sewers, and other drainage systems.

Figure 3.4 Major Exposure Pathways and Natural Attenuation Processes of Petroleum Hydrocarbons in Ground Water



(3) Identify the Exposure Pathways Completed and Conduct Risk Assessment (if necessary use the fate and transport models).

Review the refined site conceptual model and determine whether the site data fit this conceptual model. If the data support the refined site conceptual model, then an exposure pathways analysis should be conducted. The data collected during the remedial investigation can be used to simulate the fate and transport of contaminants in the ground water. The modeling effort should be able to assess the potential for down-gradient receptors to be exposed to contaminant concentrations that exceed levels intended to be protective of human health and the environment.

Simulating natural attenuation allows prediction of the migration and attenuation of the contaminant plume through time and space. The results of solute fate and transport modeling are central to the exposure pathway analysis. The complexity of the modeling effort depends on site and contaminant characteristics. Relatively homogeneous sites and contaminants transformed by well-defined microbial reactions generally require less effort than do heterogeneous sites and contaminants affected by poorly defined microbial reactions or interactions with other contaminants or aquifer materials.

Any of following methods can be used to evaluate concentration profiles generated for various time intervals and various exposure locations in model simulations:

- Evaluate current and potential threat to receptors by extrapolation of the regression line: This type of evaluation can be used only for a shrinking plume. It is done by plotting ground water contaminant data over time for different well locations. A regression line is

constructed to extrapolate the distance where the ground water meets cleanup levels and the time required to meet cleanup levels at various exposure points.

- Evaluate current and potential threats to receptors with a two-dimensional analytical solute transport transient model:

This type of evaluation can be used for both shrinking and stable plumes. Transport models have an ability to generate contaminant concentration profiles (delineation of the plume behavior including the peak levels of contaminant concentration and the time to reach plume stabilization, etc.) at various existing and potential exposure points over time. The model can be used to demonstrate whether and to what extent receptors are (and will be) impacted. This method is also capable of estimating mass loading rate and the average concentration of contaminants coming from the ground water body entering into the adjacent surface water body, if any.

Vapor migration from shallow ground water is also of greater concern with the more volatile and flammable petroleum fuels (e.g., gasoline). Common vapor migration routes are in the coarse backfill around utility lines and conduits, in open conduits such as sewers, and through naturally permeable zones in the soil such as till fractures and gravel and sand stringers. Accumulations of vapors can present a safety threat from fire, as well as adverse health effects. Soil gas sampling results, ground water concentrations below a building, or vapor intrusion modeling results could indicate that contaminant vapors may be migrating into a building structure. Refer to Johnson and Ettinger (1991), US EPA (2002), and http://www.epa.gov/athens/learn2model/part-two/onsite/JnE_lite.htm for details.

(4) Evaluate the Protectiveness.

If a combination of assessment data and predictive modeling results predict that natural attenuation will be protective of human health and the environment, natural attenuation may be an appropriate cleanup action for the site. Document exposure pathways of contaminant movement, the location of existing and potential future receptors, and risk assessment results. Establish that existing and potential future receptors identified in step 1 are fully protected through the use of the selected remedy.

Recommendation:

A demonstration should be made that the attenuating plume currently does not and will not adversely impact drinking water supplies, other interconnected ground waters, surface waters, ecosystems, sediments, air, or other environmental resources if natural attenuation is the selected remedy. In addition, the protective measures taken to ensure that future exposures are prevented should be included in the remedy (e.g., deed restrictions to prohibit well placement, etc.). Model results should be verified through compliance monitoring.

If the model simulations predict that the on-site contamination currently poses an unacceptable threat to existing or potential human and ecological receptors, then additional remedial actions may be required as part of the cleanup action, including additional source control to reduce the source mass, and institutional controls to limit inappropriate use or incidental exposure to the ground water. If additional source control is not practicable or not effective in reducing the threat, evaluate and implement other more aggressive cleanup action alternatives.

Monitoring of other media (e.g., indoor air, soil gas, soils, surface water, and sediments) may also be necessary to determine possible impacts to receptors and other measures of remedy effectiveness. To aid in developing an effective monitoring network, US EPA provides guidance regarding the assessment of the indoor air exposure pathway (2002) and the assessment of the interactions of ground water and surface water (2000b). At many sites, the assessment of such cross-media transfers of contaminants is essential to design an appropriate verification monitoring network.

3.2.1.5 Evaluate whether source control is conducted to the maximum extent practicable

| | |
|-----------------|--|
| Question: | Has source control been conducted to the maximum extent practicable? |
| Evaluation: | <ul style="list-style-type: none"> ✓ Evaluate whether source control is conducted to the maximum extent practicable; ✓ If necessary, estimate extent of source mass and assess the amount of mass that should be removed from the current source zone in order to achieve the cleanup standards. |
| Recommendation: | <ul style="list-style-type: none"> ✓ If source control is enough, then CONTINUE to evaluate other factors. ✓ If source control is not enough, then conduct MORE SOURCE CONTROL and/or EVALUATE OTHER CLEANUP ACTION ALTERNATIVES. |

To be considered a feasible cleanup action alternative, source control should be conducted as part of the cleanup action to the maximum extent practicable before relying on natural attenuation to achieve ground water cleanup standards. Source control consists of any remedial action other than natural attenuation that reduces the source mass and the mass loading rate to acceptable levels. Source control may be conducted as part of an interim action and/or as part of the final cleanup action.

Remove or treat sources of existing or potential ground water contamination to the maximum extent practicable: those include hazardous substances from any leaking UST; product pipelines; NAPL; and soil containing contaminant concentrations that exceed the established levels. The following source control actions should be conducted:

- Remove hazardous substances from any leaking UST to the maximum extent possible;
- Remove any free product to the maximum extent practicable; and,
- Remove any readily accessible contaminated soils that may act as a long-term source of ground water contamination.

Evaluation:

A key component of the use of natural attenuation is that source control has been completed to the maximum extent practicable. The amount of product that will be able to be recovered is dependent on soil type, product type, age of product, extent of weathering, extent of attenuation rates, method of recovery, depth of contamination, and other site-specific factors.

Petroleum releases bulk petroleum hydrocarbons in the NAPL form, rather than dissolved in water or sorbed on soil particles. Petroleum in the form of NAPL is not readily degraded by

microorganisms and the dispersion, dilution by recharge, and sorption of the NAPL is very slow. Generally, natural attenuation is not expected to successfully remediate petroleum contamination if significant NAPL is present in the soil or ground water. Residual NAPL can be thought of as discrete blobs of NAPL in soil pores and may act as a long-term source of soluble contaminants impacting ground water.

A detailed evaluation of source control in relation to the “maximum extent practicable” is very site-specific. Factors that should be considered in conducting this evaluation include:

- Whether natural attenuation is actually able to significantly reduce contaminant concentrations (see Section 3.2.1.1 of this guidance) and contaminant mass (see Section 3.2.1.2 of this guidance) in the ground water. *The more source control that is conducted, the more effective natural attenuation will be in reducing contaminant concentrations and contaminant mass.*

Note: Peargrin (2000) examined the rate of attenuation of Benzene and MTBE in ground water in contact with residual gasoline at 23 gasoline release sites. Although the rates of natural attenuation in the smear zone varied widely, there is a clear difference between rates at sites where active source remediation has been completed, and sites with no active remediation. For Benzene and MTBE, the rate of attenuation at active source remediated sites is about 6 or more times higher than that for non-remediated sites with the same levels of initial concentrations of Benzene. This is especially true with larger and more recent releases.

- How much of the released product has actually been recovered through source control efforts. See Appendix C of this guidance to assess the amount of source contaminant mass at a site.
- Whether source control activities have caused shrinking or stabilization of the dissolved ground water concentrations at the site. See the earlier discussion in 3.2.1.1 on assessing plume status.
- Whether natural attenuation will be able to achieve ground water cleanup standards within a reasonable restoration time frame (see Section 3.2.1.3 of this guidance). *The more source treatment or removal that is conducted, the shorter the restoration time frame.*
- Whether natural attenuation will be adequately protective of human health and the environment during the restoration time frame (see Section 3.2.1.4 of this guidance). *The more source control that is conducted, the less likely on-site contamination will impact receptors or pose an unacceptable threat to impacted receptors, and less restrictive institutional controls will be required as part of the cleanup action.*

Often, residual NAPL will still be present even after costly source control activities have been completed at the site. Thus, further source control actions may still be necessary prior to utilizing natural attenuation.

If a solute fate and transport model has been prepared, it can be used to forecast the benefit of source control by predicting the time required to restore the aquifer to ground water cleanup levels and the reduction in contaminant loadings to any nearby surface water body.

Recommendation:

Source control actions should be conducted before relying on natural attenuation to achieve ground water cleanup standards. Whether and to what extent additional source control action is required beyond what has already been done at the site is dependent on an evaluation of the above identified factors.

3.2.2 Develop natural attenuation as a cleanup action alternative

If it is determined that a cleanup action alternative that uses natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water is feasible, then that alternative can be included as part of the comparative analysis of cleanup action alternatives (see Section 3.2.3 of this document). To appropriately conduct such an analysis, determine what would be required to implement natural attenuation as a component of the cleanup action and what additional remedial actions might be required if natural attenuation fails to perform as expected. This may require developing preliminary implementation plans, including both performance monitoring and contingency plans.

For technical guidance on how to develop natural attenuation as a cleanup action alternative including how to develop a site-specific performance monitoring plan and a site-specific contingency plan, please refer to Chapter 4.

3.2.3 Conduct comparative analysis of cleanup action alternatives

Even if it is determined that a cleanup action alternative that uses natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water is feasible, a comparative analysis of cleanup action alternatives (i.e., feasibility study) must still be conducted to enable the selection of a cleanup action.

To conduct such an analysis, first develop a range of cleanup action alternatives, including alternatives that use active remedial technologies instead of, or in addition to, natural attenuation to clean up the petroleum-contaminated ground water. Active remedial technologies include technologies such as:

- Additional source control such as contaminated soil and free product removal if any;
- Excavation and removal of contaminated aquifer material & ground water;
- *In-situ* air sparging;
- *In-situ* bioventing;
- Pumping and treating (or vacuum enhanced) the ground water;
- *In-situ* (or in-place) chemical treatment such as chemical oxidation;
- *In-situ* enhanced bioremediation; and
- Ground water containment systems such as a slurry wall, sheet piling, and membranes.

For additional information on other cleanup action alternatives, refer to the “REACH IT” program sponsored by US EPA: <http://www.epareachit.org>.

The comparative analysis involves the evaluation of each cleanup action alternative against the minimum requirements for cleanup actions set forth in WAC 173-340-360(2). As part of the comparative analysis, it must be determined which of the cleanup action alternatives is permanent to the maximum extent practicable. See WAC 173-340-360(2)(b)(i). To make that determination, a disproportionate cost analysis must be conducted consisting of a comparison of the costs and benefits of the different cleanup action alternatives. The costs and benefits that must be considered are described in the MTCA Cleanup Regulation. See WAC 173-340-360(3).

The purpose of this subsection is to supplement the evaluation criteria specified in WAC 173-340-360(3)(f) by providing additional technical guidance on factors to consider when conducting a disproportionate cost analysis for cleanup action alternatives that use natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water. This subsection, however, does not provide comprehensive guidance on how to conduct a comparative analysis of cleanup action alternatives (i.e., feasibility study).

When comparing the costs and benefits of natural attenuation against other alternatives, consider the potential advantages and limitations of natural attenuation discussed in Chapter 2 and the following factors that have been adapted from the MTCA Cleanup Regulation and ASTM (1998):

Protectiveness:

Consider the degree of risk posed during the restoration time frame and how quickly that risk will be reduced. Other cleanup action alternatives may be able to achieve cleanup standards within a shorter time frame, resulting in lower short-term risks and faster improvement of the overall environmental quality. Consequently, consider the marginal cost and benefit of alternatives that shorten the time frame by conducting more source control or more aggressive cleanup actions. Be careful, though, not to bias the comparison with unrealistic estimates of restoration time frames for the more aggressive cleanup actions. Section 3.2.1.4 provides some guidance on how to evaluate the protectiveness of a natural attenuation remedy.

Permanence:

Consider how much the natural attenuation is a result of destructive mechanisms (such as biodegradation) versus non-destructive mechanisms (such as dispersion and dilution). Other alternatives may rely less on non-destructive mechanisms. The analysis should consider the marginal costs and benefits of natural attenuation compared to other alternatives that rely less on non-destructive mechanisms.

Cost:

Natural attenuation is often assumed to be more cost-effective than other more active cleanup action alternatives; that assumption may not always be true. The analysis should carefully consider the long-term costs associated with natural attenuation or any other long-term cleanup action. Long-term costs include operation and maintenance costs, monitoring costs, equipment replacement costs, and the cost of maintaining institutional controls. Where water use is restricted, consider the long-term cost of providing alternative water supplies. Also, consider the cost of lost or restricted use of property or water use during the restoration time frame. The

longer the restoration time frame and the greater the demand for returning the land or water to productive use, the higher the cost of implementing natural attenuation.

Long-Term Effectiveness:

Consider not only how effective natural attenuation will be in significantly reducing contaminant concentrations within a reasonable restoration time frame, but also whether the ground water may be impacted by dissolved metals and other by-products of biodegradation and whether the remedy will effectively address those impacts. Even if it is determined that natural attenuation is able to significantly reduce contaminant concentrations, other cleanup action alternatives may provide greater reliability and predictability in fully restoring the ground water sooner and reduce the time frame that monitoring and institutional controls need to remain in place.

Management of Short-Term Risks:

Consider the effectiveness of measures that will be taken to limit exposure during the degradation process. Other cleanup action alternatives with shorter time frames may pose less of a risk to human and ecological receptors. Consequently, consider the marginal cost and benefit of alternatives that reduce the scope and level of contamination (and hence also the restoration time frame) by conducting more source control or more aggressive cleanup actions. Natural attenuation poses less of a risk where the land use is stable and changes in land use that may cause potential impacts to receptors are unlikely to occur without notice.

Technical and Administrative Implementability:

Consider whether it will be possible to maintain access for the long-term monitoring that will be necessary for a natural attenuation remedy. Also consider that if the natural attenuation remedy fails and a more aggressive cleanup action is needed, whether it will be possible to implement such remedies in the future in the face of changing land and resource use.

Public Acceptance:

Consider the concerns of the public and the degree to which the cleanup action alternative addresses those concerns. Concerns may be expressed by individuals, community groups, local governments, and tribes. Public involvement is particularly important at sites where natural attenuation is proposed as a cleanup action because of the unique concerns that community members may have about extending the cleanup time frame through use of natural attenuation as compared to more aggressive and engineered remedies.

3.3 Data Evaluation Methods and Tools

The purpose of this section is to provide an overview of the Data Analysis Tool Package and associated User's Manual (Ecology Pub. No. 05-09-091A), both of which are available separately. Also, this subsection provides guidance regarding:

- What is the purpose of the Tool Package;
- What is included as part of the Tool Package;
- How to handle uncertainty in rate constant calculation; and
- Whether methods or tools not included as part of this guidance may be used.

3.3.1 Data analysis tool package provided

The **Data Analysis Tool Package** provides several different and selected tools to evaluate the feasibility and performance of natural attenuation. Each tool is associated with a particular method or methods specified in the guidance. The associated **User's Manual** provides detailed instructions on how to use the tools provided in the Tool Package. Although Ecology has provided these methods and tools to assist in evaluating natural attenuation remedies, use of these specific methods and tools is **not** required to conduct the evaluations.

The Data Analysis Tool Package consists of the following **two packages**, each of which includes several different calculation modules for evaluating the feasibility and performance of natural attenuation:

- **Package A** which consists of **Modules 1-3**, provides the means to conduct a relatively simple “well-by-well” analysis; and
- **Package B** which consists of **Modules 4-6**, provides the means to conduct an integrated analysis of the “overall plume” using an analytical solute transport model.

Although the Data Analysis Tool Package is organized into two packages and the modules contained in Package B require more data collection and analysis compared to those in Package A, the Data Analysis Tool Package is **not** designed in a tiered approach. Select the most appropriate modules (i.e., tools) for the site, considering the specific conditions of the site and the advantages and limitations of each module. Furthermore, after using a module, review the results and decide whether more complex site-specific analysis is warranted.

While at some sites only those modules found in Package A may need to be used, at other sites modules from both packages may need to be used. For example, Module 2 (regression analysis for each well) may be used to estimate the plume stability and restoration time frame. If it is determined that Module 2 is not sufficient to definitely estimate the restoration time frame, Module 4 (source mass estimation) and Module 6 (analytical ground water Domenico model at transient mode) may need to be used or some other evaluation method not included in the Data Analysis Tool Package. Use of the modules in Package B can require a substantial incremental effort relative to Package A, as the evaluation is much more complex and requires additional site assessment.

The Data Analysis Tool Package provides tools for performing the following evaluations or calculations:

- Determining the plume status with non-parametric statistical tests, graphical and regression analysis;
- Estimating the bulk attenuation rate constant;
- Estimating the biodegradation rate constant;
- Estimating the restoration time;
- Estimating the amount of source mass and the amount of that mass that needs to be removed to achieve ground water cleanup standards within a specified restoration time frame;
- Evaluating the geochemical indicators of biodegradation;

- Calculating the expressed assimilative capacity; and
- Simulating contaminant transport using 1-D and 2-D (under steady and transient states) analytical solute transport models.

Please refer to Chapter 3 and Appendix A of the User's Manual for a brief description of each calculation module.

3.3.2 Other evaluation methods and tools

In general, use the simplest model that simulates the key natural attenuation processes that are occurring. At many sites, a simple analytical model can serve as a cost-effective approach for incorporating modeling into a natural attenuation demonstration as long as conservative assumptions are used. The use of complicated numerical models should be reserved for more complex sites.

Other fate and transport models and data evaluation methods **can** also be used to evaluate and monitor the effectiveness of the natural attenuation process. Whichever evaluation methods are used to assess the natural attenuation processes, the results should be verified by field data. For more detailed information on types of models, generic modeling guidance, verification procedures, uncertainty, model misuse/abuse, sensitivity analysis, suggested format for a ground water modeling report, a model review checklist, etc., please refer to US EPA (1992b), ASTM guidance documents (1995b and 1996) and Michigan State Department of Environmental Quality Ground Water Modeling Program Overview (http://www.michigan.gov/deq/0,1607,7-135-3313_21698---,00.html). A work plan for the use of different data evaluation methods other than those provided in this guidance should be submitted to the Ecology site manager for review and approval. The work plan should include the following information:

- The technical basis and merits of the alternative data evaluation method;
- The specific attenuation processes that the evaluation methodology is intended to evaluate; and
- The technical references supporting the proposed data evaluation method.

To detail the process by which an alternative model is selected, developed, calibrated, verified, and predicted, the ground water modeling documentation report should include the following information:

- a) Documentation of the historical hydrogeologic data used to characterize the site and the source of all input data used in the model, whether derived from published sources or measured or calculated from field or laboratory tests;
- b) Description of the model conceptualization including:
 - Governing equations;
 - Description of the boundary conditions, sources, sinks, calibration, and verification points; and
 - Identification of the model selected to perform the task and its applicability and limitations.
- c) Documentation of the modeling approach and all calculations;

- d) Summary of all model calibration, history matching, and sensitivity analysis results;
- e) Description of the quality control including documentation of the following:
 - The numerical stability of model solutions;
 - The mass balance percent discrepancy between inflow and outflow for each of the runs;
 - The closure criteria for each calculation run; and
 - The results of other numerical or analytical models used to cross-examine the major calculation result.
- f) Presentation of all model predictive simulation results as a range of probable results, given the range of uncertainty in values of model parameters.

Note: Item “e”, above, generally pertains to numerical models only.

3.3.3 Uncertainty in rate constant calculation

One of the important decision-making factors on whether or not natural attenuation is an appropriate cleanup action for a given site is the estimate of the rates of natural attenuation processes. Site characterization and monitoring data are typically used for estimating natural attenuation rates. Where these rates are used to evaluate natural attenuation or predict the future behavior of contamination, they should also be of adequate quality and usability. Statistical confidence intervals should be estimated for calculated attenuation rate constants, including those based on methods such as historical trend data analysis, analysis of attenuation along a flow path in ground water, and microcosm studies. When predicting a restoration time frame, sensitivity analyses may also be performed to indicate the dependence of the calculated restoration time frame on uncertainties in rate constants and other factors.

Sensitivity Analysis in the Model:

In reality, numerous factors will distort observed concentration profiles in comparison to those predicted by idealized models (McNab and Doohar, 1998). A partial list includes:

- Wrong assumption of plume conditions;
- Fluctuations in source strength with time and space;
- Non-ideal dispersion (Fick’s law) of solutes;
- Spatial variability in aquifer properties;
- Shift of flow direction;
- Placement of wells off the plume centerline when 1-D model is used;
- Dilution effects due to long well screen length; and
- Non-uniform degradation rate distribution spatially and temporally.

When there is a high degree of uncertainty regarding the magnitude of input parameters used in a model, the values of the parameters should be selected to err on the conservative side; i.e., tend to result in greater concentrations flowing at greater velocities. Sensitivity analysis could be performed by varying parameters used in the model to identify key input parameters having the greatest effect on predictions, and to quantify the uncertainty in the calibrated model. The results of sensitivity analysis should be presented in the report submitted to Ecology.

Confidence Interval on a Log-Linear Regression Analysis:

A statistical evaluation of rate constants estimated from investigations of ground water contamination reveals that the estimated rate constants contain considerable uncertainty (US EPA 1992a, 1999a, 1999b, 2000a; Washington State Department of Ecology, 1995; Newell et al., 2002).

Often the monitoring data are presented to Ecology site managers in a chart or table without any statistical evaluation of the data. If the data are examined, the evaluation is often cursory or incomplete. The report may provide Ecology with a chart showing a log-linear regression line of the monitoring data, with the slope of this line identified as the degradation rate constant. It may also provide the correlation coefficient (r^2) of the regression as an indication of the variability of the data. However, the value of r^2 in itself is **not a test for statistical significance**. The monitoring data should be further evaluated to determine if the concentrations are actually declining. More specifically, the data should be evaluated with conventional parametric statistics or non-parametric statistics such as the Mann-Kendall test to determine if the slope of the regression line is statistically significantly different from zero at a certain level of confidence (US EPA, 1999a and 2005a).

For this reason, a statistical confidence interval needs to be estimated for the calculated attenuation rates on all regression analyses. The level of confidence is the probability that the true rate is contained within the calculated confidence interval. Due to variability resulting from sampling and analysis, as well as plume variability over time, small apparent reductions are often insufficient to demonstrate that attenuation has in fact occurred at all. For example, analysis of natural attenuation rates from many sites indicates that a measured decrease in contaminant concentrations of at least one order of magnitude may be necessary to determine the appropriate rate law to describe the rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a certain level of confidence (US EPA, 1999a). Ecology recommends the use of **85%** or higher level of confidence as a guide for assessing the validity of a calculated degradation rate constant.

Please refer to US EPA (1999b), Newell et al. (2002), Appendix F.2 of this guidance, and Section 4.2 of the User's Manual for additional information on confidence intervals and for the discussion of uncertainty in rate constant calculations.

Chapter 4 Developing Natural Attenuation as a Cleanup Action

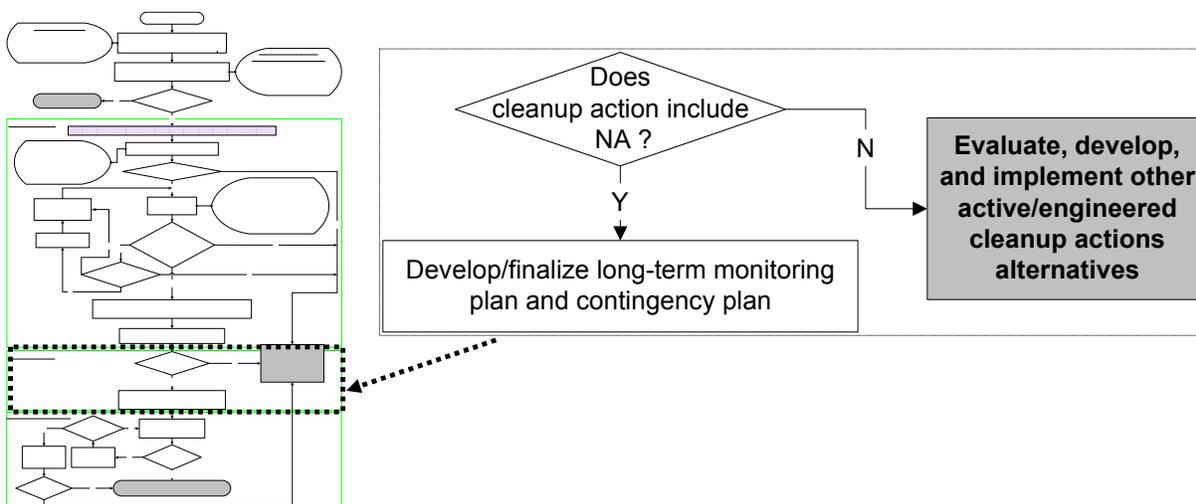
If it is determined that a cleanup action alternative that uses natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water is feasible, the alternative can be included in the comparative analysis of cleanup action alternatives (see Section 3.2 of this document).

If, based on the remedial investigation and feasibility study, a cleanup action that uses natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated ground water is selected, an implementation plan must be prepared. This plan will need to include both performance monitoring and contingency plans to verify predictions and to determine what additional remedial actions will be necessary if natural attenuation fails to perform as expected.

The purpose of this chapter is to provide technical guidance on how to develop natural attenuation as a component of a cleanup action, including how to develop a site-specific performance monitoring plan and a site-specific contingency plan. This chapter, however, does not provide guidance on how to develop the other plans that might be necessary to implement other components of the cleanup action (e.g., source control or active ground water remediation).

This step in the cleanup process is illustrated in Figure 4.1. Refer to Figure 1.1 for larger view.

Figure 4.1. Developing Natural Attenuation as a Cleanup Action



4.1 Developing a Performance Monitoring Plan

The general objectives of a performance monitoring program include:

- Ensuring that natural attenuation continues to be effective in achieving cleanup standards within the estimated restoration time frame, including demonstrating the remedy is
 - Effective in reducing contaminant concentrations and
 - Effective in reducing contaminant mass;
- Ensuring that human health and the environment continue to be protected during the restoration time frame; and
- Demonstrating compliance with cleanup standards.

The monitoring program developed for a site should specify the location, frequency, and type of samples and measurements necessary to achieve those objectives (Wiedemeier and Haas, 2002). The most important aspects of designing such a program are:

- Conducting adequate sampling and data analysis during the remedial investigation so that the nature and extent of contamination and the mechanisms and rates of natural attenuation are known with a high degree of certainty that good predictions can be made, and baseline conditions for comparison are well established.
- Selecting the number and locations of monitoring wells, sampling frequency, and analytical methods so that sufficient data are collected to assess whether natural attenuation is achieving its goals with a high degree of certainty.
- Developing a contingency plan, including appropriate triggers to enact the contingency plan, if needed, and identifying specific steps to be taken and in what time frame so the plan can be implemented without additional time-consuming negotiations.
- Performing site inspections for changes in exposure pathways.
- Developing clear reporting requirements that enable the collected information to be rapidly assessed.

The monitoring program should also include a provision that allows the amendment of the sampling plan during the implementation of the remedy based on changes in site conditions. Ecology approval is required for such amendments for sites at which cleanups are conducted under an order or decree.

4.1.1 Monitoring Plan Recommendations

To meet the objectives of the monitoring program, the program should ensure that natural attenuation continues to be effective and protective of human health and the environment during the restoration time frame. To meet those objectives, the following should be specified in the performance monitoring plan, as appropriate: the requisite number and location, screening interval, or depth of ground water monitoring wells; surface water and sediment monitoring points; vapor probe and/or air monitoring locations; ecological indicator monitoring; ongoing site inspections for changes in land or resource use or other physical changes that may affect site conditions (e.g., redevelopment, ground water use, utility construction, storm water infiltration systems); and any other types of monitoring needed. The plan should specify in detail the type

of samples and measurements, sampling frequency, and data analysis and evaluation procedures. Because ground water monitoring is a key element of the implementation of a natural attenuation remedy, this subsection focuses on recommendations for this aspect of the plan.

In addition to previously identified objectives, the ground water monitoring plan should:

- Verify the status of the ground water plume including the extent and direction of the plume, and the concentration and mass of contaminants within the plume;
- Verify the occurrence of natural biodegradation, and identify any by-products resulting from biodegradation;
- Verify the accuracy of the estimated restoration time frame;
- Detect any additional releases of contaminants to the environment that might reduce the efficacy of natural attenuation;
- Detect any changes in environmental conditions (e.g., hydrogeological and geochemical) that might reduce the efficacy of any natural attenuation mechanism;
- Identify any changes in exposure pathways;
- Identify and ensure adequate warning of potential impacts to down-gradient receptors; and
- Monitor surface water-ground water interaction -- where ground water plumes are or may discharge to a surface water body, the interface between the surface water and ground water system should be monitored.

Number and Location of Monitoring Wells:

Usually, a number of permanent monitoring wells are installed during the remedial investigation, and these wells may or may not subsequently be appropriate for use during the long-term monitoring phase to assess the progress of natural attenuation. Some monitoring wells installed during the remedial investigation may be useful while others could be decommissioned. At most sites where natural attenuation is a component of the selected cleanup action, additional monitoring wells will be needed. The long-term monitoring well network should allow a detailed understanding of ground water flow and geochemistry within the plume over time.

The number and location of performance monitoring wells should be sufficient to assess both the horizontal and vertical distribution of the plume and its predicted future movement. To achieve the goals of the performance monitoring program, the monitoring well network should include at least:

- One monitoring well up-gradient of the plume outside the plume boundary to detect changes in background water quality;
- One or more monitoring wells within the source or most impacted area (but outside any free-product zone) to determine changes in the source strength;
- Two or more monitoring wells, depending on plume length, near the contaminated plume centerline to assess the ability of natural attenuation processes; and
- One sentinel well beyond the leading edge of the plume and within a one-to-two-year ground water flow distance.

Where vertical migration of contamination is a concern, selected monitoring well locations will need to have more than one screened interval to assess vertical flow gradients and contaminant distribution.

A sentinel well provides an early warning that the plume is migrating. The location of sentinel well placement should be between the leading edge of the contaminant plume and possible receptors (e.g., drinking water well, surface water body). The sentinel well is used to trigger contingency action to control the plume so that the contaminants do not migrate beyond the sentinel well. As these sentinel wells can help in assessing whether the plume is expanding or is stable, sentinel wells should be close enough to the edge of the plume to determine plume behavior within a relatively short time (within a one-to-two-year ground water flow distance). Also, sentinel wells should be able to detect significant responses of geochemical indicators (e.g., high Fe^{+2} , low SO_4^{-2} , high alkalinity, etc.) migrating along with the plume.

As part of the contingency plan, additional monitoring wells may be necessary to monitor any unexpected plume migration that might pose a threat to receptors. Such wells should be placed between the plume and any potentially impacted receptors. The distance should be based on the rate of plume advance and the time necessary to implement the contingency plan. For specific recommendations regarding the design of a monitoring network including the number, location, and screen length of monitoring wells, please refer to Appendices G and H of this guidance. Also refer to US Air Force's MAROS system (Aziz et al., 2003), Optimal Well Locator (US EPA, 2004a) and other references (i.e., Wiedemeier and Haas, 2002 and US EPA 2005b) for a detail discussion of the optimization technique of cost-effective and long-term ground water monitoring plans. These references introduce tools to locate the most appropriate sampling points, minimize monitoring locations in the sampling network, and reduce sampling frequency without significant loss of information.

Monitoring Parameters (type of analysis and measurements):

The type of samples and measurements that should be collected should be sufficient to evaluate the performance of natural attenuation and to achieve the goals of the performance monitoring program. To achieve those goals, Ecology recommends the monitoring plan provide for the collection of the following parameters:

- Hazardous substances:
 - BTEX (Benzene, Toluene, Ethylbenzene, Xylenes);
 - Total Petroleum Hydrocarbons;
 - MTBE (Methyl tertiary-butyl ether) and other fuel additives if detected previously;
 - Other components if necessary as shown in Table 830-1 of WAC 173-340-900.

- Primary Geochemical indicators:
 - Dissolved Oxygen (O_2);
 - Redox Potential (E_H);
 - pH;
 - Specific Conductivity;
 - Temperature.

- Secondary Geochemical indicators:
 - Sulfate (SO₄⁻²);
 - Nitrate (NO₃⁻);
 - Ferrous Iron Soluble (Fe⁺²);
 - Manganese Soluble (Mn⁺²);
 - Methane (CH₄);
 - Alkalinity.

Ground water levels should be measured in all monitoring wells as often as ground water samples are collected at a site in order to assess if ground water elevation fluctuations affect the observed contaminant concentrations and to define the ground water flow direction. At a site where a deeper plume exists, changes in piezometric head with respect to ground water flow direction and vertical gradient should also be assessed.

Monitoring Frequency:

The appropriate frequency for ground water sampling depends on the rate with which contaminant concentrations change due to ground water flow and natural attenuation processes, the degree to which the causes of this variability are known, the types of evaluations to be performed, the location(s) of possible receptors, and the remediation goal for the site (US EPA 2004b). In situations where hydrologic, geochemical, and contaminant trends are stable and the conceptual site model is verified by measured site data, reductions in sampling frequency may be warranted. In situations where variability is high, increases in monitoring frequency and additional investigations to determine the source of the variability may be warranted. More frequent monitoring may be appropriate under circumstances where ground water flow is rapid and/or contaminant travel time to receptors is short.

The frequency of sampling should reflect the monitoring objectives and the type of sample or measurement. The sampling frequency should also consider the natural variability of contaminant concentrations, distance to receptors, and ground water seepage velocity. Natural variability refers to seasonal variations such as changes in the water table elevation or the recharge rate, as well as random events such as drought and flooding. Knowledge of natural variability may prevent a site from erroneously being triggered into the contingency phase or monitoring being terminated prematurely.

As recommended by US EPA (2004b), examples of factors influencing specification of the monitoring frequency are provided below. The actual monitoring frequency selected would be based on consideration of all the factors bearing on the given parameter and monitoring location.

- Possible contaminant travel time and threat to receptors:

The time it takes for contaminants to reach a potential down-gradient receptor and the time to bring a contingent remedy on line, should natural attenuation fail, needs to be considered when developing the monitoring plan. For example, consider a site with the following conditions: the travel time for ground water from the down-gradient plume boundary to a receptor was calculated as two years and the time required to design, construct, and bring an alternative remedy online to intercept the contaminant and protect the receptor is one year. This would leave only one year from the time contamination is confirmed to implement an

alternative, more active, remedy to prevent impacts to the receptor. In this situation, if more frequent monitoring isn't needed for another reason, monitoring should be conducted at least twice annually to allow time for confirmation of detections and action to be taken, should the initial round of sampling indicate the remedy is not working as planned. In this example, the travel time for ground water was used in the calculations to allow a more conservative estimate of the travel time than that obtained through use of a contaminant that may undergo sorption or biotransformation reactions and extend travel time, providing another factor of safety in the design.

- Evaluation of a cyclic change:

Most of Washington State experiences pronounced wet and dry seasons with associated changes in recharge rates and ground water flow characteristics. Thus sites will often display pronounced cyclical trends in ground water elevation, contaminant concentrations and plume boundaries. The historical variability in water levels and contaminant concentrations for the site and recorded climatic variability should be reviewed and considered when specifying the monitoring frequency. The monitoring frequency should be sufficient to prevent unmonitored expansion of the plume while avoiding collection of unnecessary data. Historical climatic data going back several decades can be obtained from the National Weather Service. Ground water monitoring data gathered over several years will likely be necessary to evaluate seasonal trends and determine if a different frequency of monitoring than that recommended in Table 4.1 is appropriate to capture changes related to seasonal trends.

- Relevance of parameters:

If a parameter is not expected to significantly influence evaluations of remedy performance at a site, monitoring frequency for that parameter could be reduced. If information gained from frequent sampling for a given parameter would not be reasonably expected to change site-related decisions, sampling for that parameter could be reduced in frequency. However, absent specific reasons for excluding a parameter, it generally would be expected that the entire suite of geochemical parameters relevant to the site, as well as contaminants and hydrogeological parameters, would be measured at all monitoring points on a set schedule. This allows an evaluation of continued stability in the geochemical setting and the potential for changes in biotransformation processes and attenuation rates to be performed.

- Information redundancy:

If over a period of several years data trends are consistent, a reduction in monitoring frequency may be warranted. Also, if two or more wells sampling the same zone are located close together and consistently produce similar data, changes in the monitoring frequency of one or more of the wells may be considered. For example, if the geochemical indicators at a given monitoring location are stable over a long period (e.g., within a range indicating suitable conditions for degradation of the contaminants), the monitoring for these geochemical indicators could be reduced in frequency, to the point of being measured annually, biennially, or at even greater intervals. If a sudden change in contaminant concentrations was noted, an increase in monitoring frequency may be warranted to provide information to facilitate understanding of the change and provide earlier warning of further change.

Data Analysis and Procedures:

The monitoring plan should include a sampling and analysis plan that describes the sample collection, handling, and analytical procedures to be used. To achieve the goals of the performance monitoring program, Ecology recommends the monitoring schedule shown in Table 4.1.

Table 4.1. Recommended Performance Monitoring Schedule for Petroleum-Contaminated Ground Water

| Type of Analysis | Number & Location of Monitoring Wells | Monitoring Frequency | |
|--|---|---|--|
| Hazardous Substances & Ground Water Table Elevation & Primary Geochemical Indicators | <ul style="list-style-type: none"> • One (1) well in up-gradient (not impacted) area • One (1) well within source (most impacted) area • Two (2) wells near contaminated plume center line | 1 st year | Quarterly |
| | | 2 nd & 3 rd years | Semi-annually, provided plume shrinking or stable during 1 st year and quarterly monitoring indicates semi-annual monitoring will provide sufficient data |
| | | Subsequent years | Annually, or less frequently, provided plume shrinking or stable for first 3 years and semi-annual monitoring indicates annual monitoring will provide sufficient data |
| Secondary Geochemical Indicators | <ul style="list-style-type: none"> • One (1) well in down-gradient “sentinel” area | 1 st & 2 nd years | Semi-annually |
| | | Subsequent years | Annually, or less frequently, to the extent necessary to assist performance monitoring |

Note: The monitoring schedule noted in Table 4.1. is the recommended sampling requirements for relatively simple sites that exhibit a well-defined source and plume within a simple hydrogeologic setting (e.g., single and shallow water table aquifer) with no potential to impact a drinking water well or surface water body.

Depending on the methods used to evaluate the performance of natural attenuation and the specific characteristics of the site, additional data may need to be collected, additional monitoring points may need to be established, and more frequent sampling may need to be conducted to achieve the goals of the performance monitoring program.

4.1.2 Protocols for demonstrating compliance

The monitoring program should enable a demonstration of compliance with ground water cleanup standards in accordance with WAC 173-340-720(9). For comprehensive guidance on what data must be collected and how to make decisions based on this data, please refer to

Appendix I: Section A6.0 – A6.2 of the following Ecology guidance document: *Guidance on Sampling and Data Analysis Methods*, Washington State Department of Ecology, Publication No. 94-49, 1995.

Where it is not practicable to meet the cleanup level throughout the site within a reasonable restoration time frame, a conditional point of compliance located as close to the source of the contamination as practicable may be utilized to demonstrate that natural attenuation is effectively remediating ground water to cleanup levels before crossing the conditional point of compliance. Use of a conditional point of compliance requires Ecology approval. Refer to WAC 173-340-720(8)(c) for more detail.

4.2 Develop a Contingency Plan

In addition to the performance monitoring plan, Ecology recommends development of a site-specific contingency plan that describes monitoring results that would require (“trigger”) additional more active remedial actions to be taken at the site and the additional remedial actions that would be required. This plan is used to help ensure protection of human health and the environment when a contaminant plume begins to migrate farther and/or faster than predicted based on the natural attenuation evaluation. In short, the contingency plan sets forth what constitutes failure of the selected remedy and what **backup** actions will be implemented in the event that the selected remedy fails to perform as anticipated.

The need for a contingency plan is not unique to cleanup actions involving natural attenuation. For example, contingency plans may be included as part of any cleanup action:

- Where there is significant uncertainty regarding the nature and extent of contamination at the time the cleanup action is selected;
- Where the selected cleanup action is not proven for the specific site application;
- Where there is uncertainty regarding whether a proven technology will perform as anticipated under site-specific circumstances; or
- When timely additional cleanup is necessary if performance monitoring demonstrates the chosen remedy is not performing as intended.

The plan should first describe the triggers that may require additional remedial action. The types of triggers that may require additional remedial action include, but are not limited to, the following:

- Evidence of increased contaminant concentrations within the plume (e.g., contaminant concentrations at specified locations within the plume exhibit an increasing trend);
- Evidence of plume expansion or plume migration to a sentinel well (e.g., contaminants are identified in monitoring wells located outside the original plume boundary);
- Evidence of new or renewed releases of contaminants (e.g., near-source wells exhibit large concentration increases indicative of a new or renewed release);
- Evidence that biodegradation is not occurring;
- Evidence that contaminant concentrations are not decreasing at a sufficiently rapid rate to achieve cleanup standards within the acceptable restoration time frame; and

- Evidence of changes in land, ground water, or other resource uses have occurred that could adversely affect the protectiveness of the remedy (e.g., ground water extraction alters direction of ground water flow).

When establishing the specific criteria for triggering additional remedial action, be careful to allow for sampling variability and seasonal fluctuations. For example, an anomalous spike (or, a drop) in concentrations might not be a true indication of a change in trend.

The contingency plan should describe the appropriate actions (contingency remedies) that would be taken if those contingencies were to occur. The plan may either specify a backup action or call for the modification of the selected remedy. The contingency plan could be **tiered** to respond to various scenarios of changed conditions at a site. Contingency remedies should be **flexible** enough to allow for the incorporation of new information about site risks and technologies. For example, a range of contingent remedies could be specified such as:

- Modify the performance monitoring plan to provide for additional wells and/or more frequent sampling or additional parameters to enhance the ability to evaluate the progress of natural attenuation and the threats posed to receptors;
- Conduct additional site investigation to reevaluate the conceptual site model;
- Conduct additional source control, such as removing additional contaminant mass, to reduce contaminant loading and enhance the effectiveness of natural attenuation; or
- Install a ground water pump and treat system or ground water barrier to intercept contamination before it impacts the receptor.

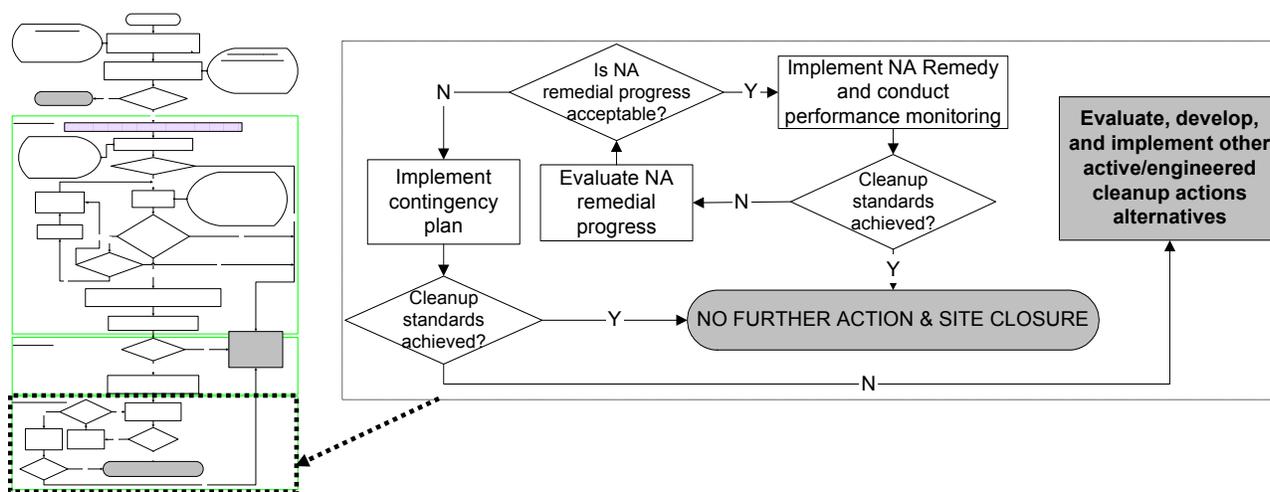
Chapter 5 Implementing Natural Attenuation as a Cleanup Action

The purpose of this chapter is to provide technical guidance on how to implement natural attenuation as a component of the selected cleanup action for a petroleum-contaminated site. This chapter, however, does not provide guidance on how to implement other components of the remedial action. The focus of the technical guidance provided in this chapter is limited to the following:

- How to implement the performance monitoring plan to monitor the performance of natural attenuation as a component of the cleanup action; and
- How to implement the contingency plan, should natural attenuation not meet identified performance measures.

This step in the cleanup process is illustrated in Figure 5.1. Refer to Figure 1.1 for larger view.

Figure 5.1. Implementing Natural Attenuation as a Cleanup Action



5.1 Implementation of Other Components of Cleanup Action (if required)

If the cleanup action requires the performance of additional source control actions before relying on natural attenuation, those actions should be conducted first.

5.2 Implementation of the Performance Monitoring Plan

After any additional source control actions are performed, next implement the performance monitoring plan (see Chapter 4 of this guidance). Monitoring data should be periodically

evaluated against the cleanup objectives to evaluate the progress of natural attenuation at the site. This includes periodic preparation of reports using appropriate evaluation methods to assess natural attenuation processes. Ecology recommends continued documentation of the following:

- Changes in environmental conditions that may reduce the efficacy of any of natural attenuation processes;
- Verification that the plume is shrinking or stable as expected;
- Detection of any new release or new sources of contamination;
- Verification of no unacceptable impact to down-gradient receptors;
- Verification that sentinel wells remain free of contamination;
- Verification of attainment of cleanup goals by evaluating performance and progress of natural attenuation toward achieving the cleanup levels; and
- Verification that the plume is not migrating to an extent greater than expected or in an unexpected direction/amount.

At a site where the cleanup is conducted under Ecology oversight, the documentation must be submitted to Ecology as required under the order or decree.

At a site where the cleanup is conducted without Ecology oversight, the documentation must be submitted as part of the independent remedial action report upon completion of the cleanup. Ecology also strongly recommends consultation with Ecology under the Voluntary Cleanup Program (VCP) throughout the cleanup process. There are significant benefits to requesting technical consultations with Ecology under the VCP. Consulting with Ecology at an early stage can provide greater assurance that the cleanup action involving natural attenuation is meeting the substantive requirements of chapter 173-340 WAC.

Note: When submitting any status or remedial action report to Ecology, a clear statement should be included at the beginning of the report as to whether the site is in compliance with cleanup standards and whether the remedial actions are functioning as predicted in the cleanup action plan. It is the responsibility of the person conducting the cleanup action to perform all the necessary evaluations and analyses required to assess compliance and to fully and truthfully report the conclusions to Ecology.

During the performance monitoring period, data plots should be updated after an appropriate monitoring round. If a change in trend is found, evaluate the change to assess what impact it may have on the overall cleanup process. Adjustments to the monitoring program can be made, if necessary.

If cleanup standards are not achieved within the estimated restoration time frame, evaluate the progress of natural attenuation and determine whether progress is acceptable in accordance with the following criteria. That evaluation should be conducted in accordance with Section 3.2 of this document.

- If the remedial progress is determined to be unacceptable, an alternative remedial solution and/or the contingency plan should be implemented at the site (see Figure 5.1).

- If the natural attenuation progress is considered acceptable, continue to implement that plan until cleanup standards are achieved.

5.3 Implement Contingency Plan (if necessary)

If one of the specified triggers set forth in the contingency plan (see Section 4.2 of this document) occurs during the course of performance monitoring, implement the requisite contingency plan specified in the contingency plan.

Chapter 6 Site Closure

The purpose of this chapter is to provide technical guidance on how to determine whether further remedial action is required to achieve ground water cleanup standards at sites where natural attenuation is used to clean up petroleum-contaminated ground water. This chapter, however, does not provide guidance on how to determine whether further remedial action is required at the remainder of the petroleum-contaminated site. The focus of the technical guidance provided in this chapter is limited to the following:

- How to determine compliance with ground water cleanup standards; and
- What data should be submitted to Ecology to document the performance of natural attenuation, and that no further action is required to clean up the ground water.

6.1 Determine Compliance with Ground Water Cleanup Standards

The progress of natural attenuation should continue to be monitored in accordance with the performance monitoring plan until the ground water cleanup standards have been achieved. The performance monitoring plan must enable a demonstration of compliance with ground water cleanup standards in accordance with WAC 173-340-720(9). Compliance must be met in each individual monitoring well at the point of compliance.

Once the cleanup standards have been achieved, as per WAC 173-340-410, conformational monitoring will need to be conducted to ensure that contaminant levels do not rebound and exceed the cleanup levels.

Generally, for petroleum-contaminated sites, Ecology recommends confirmational monitoring consist of at least three years of monitoring after the cleanup action achieves ground water cleanup standards, of which one to two of those years should have contaminant levels remaining below cleanup levels at the designated point of compliance. A shorter monitoring period can be used to demonstrate compliance with cleanup standards if the Ecology site manger approves this on a site-specific basis. This confirmational monitoring should be specified in the performance monitoring plan described in Section 4.1 of this guidance.

For comprehensive guidance on what data must be collected and how to make decisions based on the data collected, please refer to Appendix I: Section A6.0 – A6.2 of the following Ecology guidance document: *Guidance on Sampling and Data Analysis Methods*, Washington State Department of Ecology, Publication No. 94-49, 1995.

Under no circumstance should the results of any predictive modeling (including statistical trend analysis) be used to justify a decision to terminate performance monitoring and close the site. It is important to realize that these estimates are merely estimates and that the true natural attenuation rate is likely to change over time. The decision should be based only on adequate field data that convincingly demonstrate that contaminant levels have met cleanup standards.

6.2 Submit Documentation

At a site where the cleanup was conducted under Ecology oversight, the order or decree will specify what information must be submitted.

At a site where the cleanup was conducted without Ecology oversight, an independent remedial action report must be submitted to Ecology within ninety (90) calendar days of the completion of the action. See WAC 173-340-515(4). A determination may also be requested from Ecology under the Voluntary Cleanup Program as to whether further remedial action is required. See WAC 173-340-515(5).

For petroleum-contaminated sites where natural attenuation is used as part of the independent cleanup action, the following information should be included as part of the independent remedial action report, if not already reported:

- The results of all interim actions, including all source control actions taken;
- The remedial investigation work plan;
- The results of the remedial investigation, including all data regarding the nature and extent of contamination at the site and the hydrogeological, chemical, and biological characteristics of the site;
- The conceptual site model, including all assumptions and processes affecting contaminant fate and transport;
- The results of the methods used to evaluate the feasibility and performance of natural attenuation, including any tables or figures used to evaluate geochemical indicators, determine the status of the plume, calculate site-specific rate constants, and estimate the restoration time frame;
- The performance monitoring plan;
- The contingency plan, if implemented;
- The results of all performance monitoring conducted during the restoration time frame to demonstrate progress, including both the data and analysis of the data;
- The results of all performance monitoring conducted to evaluate the formation of degradation by-products (e.g., arsenic, nickel, and manganese);
- The results of all confirmational monitoring conducted to demonstrate compliance with cleanup standards after cleanup standards have been achieved, including both the data and analysis of the data;
- The results of any remedial action taken pursuant to the contingency plan; and
- The results of all other cleanup actions taken and conclusions.

Depending on what other remedial actions are conducted at the site, additional information may also need to be submitted to Ecology as part of the independent remedial action report. For additional guidance on the type of information that should be reported, please contact the Ecology site manager.

Appendix A

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Appendix B

Symbols and Abbreviations

Definition, abbreviation, and dimension of all symbols used in equations and tables of this document can be found in this Appendix B unless stated otherwise.

*Note: Unit of symbols is described as a dimension: T (time), M (mass), L (length);
 “Module” means a module contained in the Data Analysis Tool Package and a User’s Manual
 (Ecology Publication No. 05-09-091A)*

Abbreviations:

BTEX: Benzene, Toluene, Ethylbenzene, and Xylenes

C.L.: Confidence Level

CL_{calc}: Confidence Level; calculated for a specific data set

CL_{DecisionCriteria}: Predetermined Confidence Level; used as a decision criterion

CV: Coefficient of Variation; to account for the magnitude of scatter in the data

MTBE: Methyl Tertiary-Butyl Ether

NA: Not Applicable

NAPL: Non Aqueous Phase Liquid

TBA: Tertiary-Butyl Alcohol

TMB: Trimethylbenzene

Basic Hydrology Terms:

K : Hydraulic conductivity; (L/T)

i : Hydraulic gradient; (L/L)

n_e : Effective porosity; (dimensionless)

ρ_b : Dry soil bulk density; (M/L³)

Concentration Terms:

C_o : Initial dissolved contaminant concentration at source zone at “ $t = 0$ ”; (M/L³)

$C_{x,y,z,t}$: The concentration of the contaminant at location x, y, z from the source at time “ t ”;
 (M/L³)

C_{start} : Starting ground water concentration measured at a specific time and a specific monitoring well location; (M/L³)

C_{CUL} : Ground water cleanup level; (M/L³)

Dimension Terms:

1-D: One Dimension

2-D: Two Dimension

3-D: Three Dimension

Dispersion Terms:

α_x : Longitudinal (x-direction) dispersivity; (L)

α_y : Transverse (y-direction) dispersivity; (L)

α_z : Vertical (z-direction) dispersivity; (L)

D_x : Coefficient of hydrodynamic dispersion (x-direction); (L²/T)

D_y : Coefficient of hydrodynamic dispersion (y-direction); (L^2/T)

D_z : Coefficient of hydrodynamic dispersion (z-direction); (L^2/T)

Mathematical Functions:

erf: Error function

erfc: Complementary error function

exp: Exponential function

Mass and Mass Flux terms:

M : The mass of a contaminant introduced at the source; (M)

MF_s : Mass Flux near source (source control plane); (M/T)

MF_d : Mass Flux down-gradient from source (down-gradient control plane); (M/T)

MF_i : Mass Flux of contaminant within a cross sectional area, i ; (M/T)

C_i : Average contaminant concentration within a cross sectional area, i ; (M/L^3 or M/M)

C_{sw} : Contaminant concentration in supply well (at a receptor); (M/L^3 or M/M)

Q_{sw} : Supply well (at a receptor) pumping rate; (L^3/T)

A_i : Cross sectional area, i ; (L^2)

ρ_{water} : Density of ground water; (M/L^3)

Model Area terms:

W : Modeled area length; (L); Refer to Module 6 for a detailed discussion.

L : Modeled area width; (L); Refer to Module 6 for a detailed discussion.

L_p : Estimated plume length; (L)

Model Coordinate Terms:

x : Plume centerline distance from the source, x-direction; (L)

y : Off-centerline distance, y-direction; (L)

z : Vertical distance from the centerline, z-direction; (L)

Rate Constants:

k_{point} : Point decay rate (1st-order) constant; (1/T):

- calculated from the slope of plot log of concentrations vs. time for a single monitoring point, slope of best-fit line;
- under Module 2, rate and time to achieve the cleanup goal with both best-fit and pre-determined level of confidences will be calculated for each well;
- refer to Module 2 for a detailed discussion of this parameter.

k : Bulk attenuation rate (1st-order) constant; (1/T):

- calculated from natural log of concentrations vs. distance for a overall stable or shrinking plume;

- need the locations of multiple wells from the sources and site specific ground water seepage velocity and retardation factor;
- rate with both best-fit and pre-determined level of confidences will be used to estimate a plume trend (how far a plume will expand);
- refer to Modules 2 and 5 for a detailed discussion of this parameter.

λ : Biodegradation rate constant; (1/T):

- calculated from the calibration of a ground water solute transport modeling that includes dispersion and retardation by adjusting “ λ ”;
- refer to Modules 5 and 6 for a detailed discussion of this parameter.

k_{source} : 1st-order decay term for source concentration; (1/T):

- refer to Module 6 for a detailed discussion of this parameter.

Regression Terms (dimensionless):

n : Number of data used for log-linear regression

r^2 : Coefficient of determination of log-linear regression

r : Correlation coefficient of log-linear regression

CL: Confidence Level: refer to Module 2 for a detailed discussion of this term

CV: Coefficient of Variation: refer to Module 1 for a detailed discussion of this term

Sorption Terms:

R : Retardation Factor; (dimensionless)

$$R = 1 + \frac{K_{oc} f_{oc} \rho_b}{n_e} \quad (\text{Eq. B.1})$$

K_{oc} : Soil organic carbon-water partitioning coefficient; (L³/M)

f_{oc} : Soil fraction of organic carbon; (dimensionless)

Source Terms:

Y : Width of source area; (L)

Z : Depth of source area; (L)

Time Terms:

t : Travel or restoration time; (T)

Δt : Average travel time between two control planes; (T)

$t_{1/2}$: Half life of a contaminant (1st-order kinetics); (T)

$$t_{1/2} = \frac{\ln(2)}{\lambda} = 0.693/\lambda \quad (\text{Eq. B.2})$$

Velocity Terms:

v_{gw} : Ground water seepage velocity or average linear velocity; (L/T)

v_c : Contaminant velocity in ground water plume; (L/T):

$$v_c = v_{gw}/R \quad (\text{Eq. B.3})$$

Appendix C

Methods for Estimating Contaminant Mass

Various methods can be used to estimate the contaminant mass at a site. The following presents two methods, and the appropriate method should be selected based on site-specific considerations. Each equation shown throughout this appendix is directly followed by definition and dimension of symbols that are associated with the equation. The definition and dimension of symbols used in equations in this appendix are not defined in Appendix B of this guidance.

Note: Source mass estimates, especially based on direct sampling data, may underestimate or overestimate the true amount of mass present. The amount of under- or overestimation decreases as the sample density increases. Although source mass estimates can provide useful information to the decision-making process for a natural attenuation remedy, there is considerable uncertainty in any approach used to estimate mass present, and estimates should be considered to have an order-of-magnitude precision.

C.1 Estimating Source Mass Directly from Sampling Data

The following method was adapted from the State of Wisconsin (1999), Florida Petroleum Cleanup Program's RNA Tool Package Guidance Manual (1999), and Wiediemeier et al., (1999). The following only briefly summarizes the method described in these documents. See the original documents for additional information. Module 4 of the Data Analysis Tool Package can be used for computation of source mass. Refer to "User's Manual for Natural Attenuation Analysis Tool Package: Publication No 05-09-091A" for details.

This method presumes uniform stratigraphy, but can be used for non-uniform stratigraphy. The analysis is based upon defining a soil or saturated zone volume associated with each sampling point.

One procedure to estimate areas associated with each sampling point is the Thiessen Polygon Method. The method assumes that the concentration measured at a given point represents the concentration in the soil out to a distance halfway to all adjacent sampling points. The area associated with each sampling point is defined by constructing a Thiessen Polygon network.

The polygon network is formed by perpendicular bisectors of lines connecting adjacent sampling points (Chow et al., 1988). The mean area associated with each sampling point by the Thiessen Polygon method can be estimated with commercially available Geographic Information System (GIS) software such as ESRI's Arc/GIS or Arc/Info or preprocessors in numerical modeling software such as Groundwater Modeling System (GMS) (<http://www.gms.watermodeling.org/index.html>). Or, as illustrated by Fetter (1988), it can be calculated by hand as follows:

1. Draw lines between the closest sampling point measurements starting with a centrally located sampling point, and then expand the polygonal network outward;
2. Draw perpendicular bisectors at the midpoint of each line connecting two sampling points, and draw polygons around each sampling point by extending the perpendicular bisectors;
3. The boundary of the outermost polygon areas is formed by the "no detect" iso-contour line for each soil layer based on field data or conservative assumptions on the lateral extent of the parameter of concern; and

4. Determine the area of each polygon with a planimeter or calculate by trigonometry.

The following description divides the calculation into four (4) distinct layers: free product; unsaturated zone; smear zone; and dissolved in the ground water. Other approaches can be used. For example, the vertical sampling interval (the length of soil cores or well screen length) can be used to define the “layers” used in this method. Or, the soil/saturated zone layers used for the volume estimate can be based on site stratigraphy.

Mass in Free Product:

WAC 173-340-370(7) requires removal of free product to the maximum extent practicable. After removal of free product, a residual (or, entrapped) layer may remain that is hard to remove. These residual layers may vary from “sheen” to several inches of free product observed in monitoring wells depending on site and free product conditions. If free product is present, the mass of contaminant in the free product may need to be estimated. For methods to calculate volume of floating product and mass contained in the free product, see Lundegard and Mudford (1998); Farr, Houghtalen and McWhorter (1990); and, Huntley et al. (1994).

The Contaminated Soil in the Unsaturated Source Zone:

Collect and analyze soil samples to determine contaminant concentrations both laterally and vertically from the original release. For this analysis, the unsaturated (vadose) source zone extends in vertical depth from the ground surface to the seasonally high water table and laterally from the highest contamination to non-detectable levels. If detailed data needed to complete this method are not available, conservative assumptions may be used to estimate the extent and amount of the contaminant concentrations.

The following steps describe the process for estimating the mass in the unsaturated source zone:

1. Map the vadose zone based on vertical sampling intervals. Assume each soil sample represents a soil depth interval and a soil area.
2. Determine the thickness of each soil interval.
3. Use the Thiessen Polygon method to determine the area associated with each sample for each depth interval (soil layer).
4. Use the area-weighted average technique to determine the average contaminant concentration within the impacted area for each soil layer. In the area-weighted average technique, each data point is assigned an area represented by that data point. The equation (Eq. C.1) for the area-weighted mean for “n” data points each associated with an area “A_n” is:

$$\bar{c}_{soil} = \frac{(c_1 A_1 + c_2 A_2 + \dots + c_n A_n)}{(A_1 + A_2 + \dots + A_n)} \quad (\text{Eq. C.1})$$

Where:

\bar{c}_{soil} = area weighted average concentration (on dry weight basis) for a given depth interval in the given zone (M/M)

c_1, c_2, \dots, c_n = concentration of each sample within the depth interval (M/M)

A_1, A_2, \dots, A_n = area of soil represented by each sample in the depth interval (L²)

Figure C.1 presents a plan view of contaminant source with the Thiessen Polygon Network. Figure C.2 illustrates a cross-sectional view of contaminant source. Note that the location of data points may differ for each layer. The total soil area, area associated with each sample, and soil interval depth may differ for each layer.

5. Multiply, as shown in Eq. C.2, the average concentration by the total contaminated area for the depth interval and the depth of the soil layer.

$$\bar{c}_{soil} d_{soil} (A_1 + A_2 + \dots A_n) = \text{concentration} \cdot \text{volume for each depth interval} \quad (\text{Eq. C.2})$$

Where:

d_{soil} = thickness of sample interval (soil layer) (L)

6. Sum the concentration \times volume results for each layer. Multiply the result by dry soil bulk density to estimate the mass of contaminant in the vadose zone.

$$M_{soil} = \rho_b \sum_{i=1}^l \left[\bar{c}_{soil}^i d_{soil}^i (A_1^i + A_2^i + \dots A_n^i) \right] \quad (\text{Eq. C.3})$$

Where:

M_{soil} = mass of contaminant in unsaturated zone (M)

i = number of soil interval layer

l = total number of soil layer

ρ_b = dry soil bulk density of sample interval (soil layer) (M/L³)

d_{soil}^i = thickness of the i^{th} layer (L)

A_n^i = area represented by “n”th sample in “i”th soil layer (L²)

Figure C.1. Plan View of Source With Thiessen Polygon Network

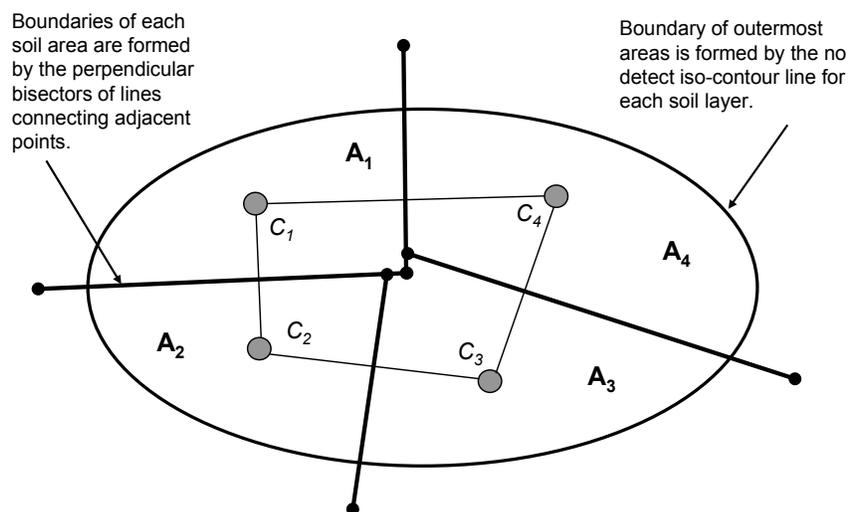
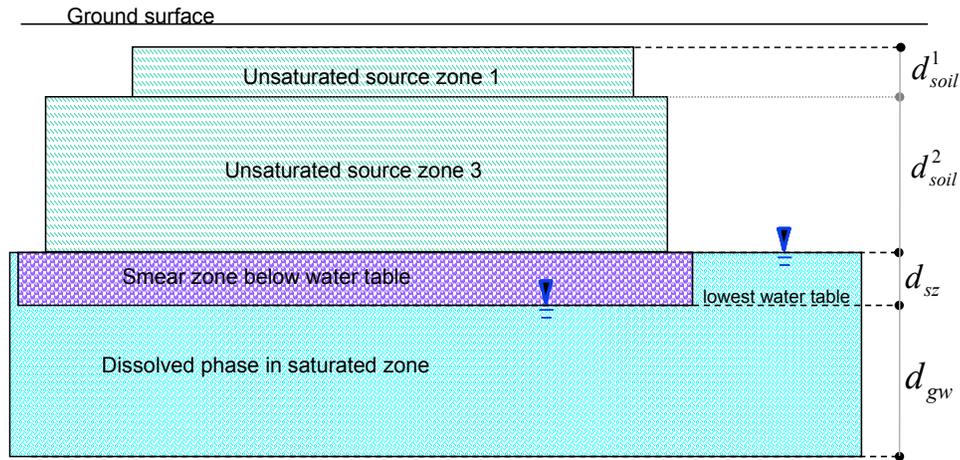


Figure C.2. Cross-Sectional View of Source



The Smear Zone Source below Water Table:

The smear zone is where NAPL (either as free product or as isolated blobs) is present in the soil or ground water and extends vertically from the highest water table to the lowest water table level. If the ground water has been pumped or otherwise significantly lowered, the lowest ground water level may define the lower bound on the vertical extent of the smear zone layer. If detailed data to complete this method are not available, conservative assumptions may be used to estimate the extent of the contaminant concentrations. For instance, these conservative assumptions for the lateral extent may be based on the area delineated by floating product, based on current or historical detection of free product, and that area with hydrocarbons above a calculated saturated soil concentration level (Gustafson, J.B., Tell, J.G, and Orem, D., 1977), C_{sat} .

$$C_{sat} = \sum_{i=1}^n S_i X_i \left(\frac{\theta_a H_i + \theta_w + K_{oc} f_{oc} \rho_b}{\rho_b} \right) \quad (\text{Eq. C.4})$$

Where:

C_{sat} = saturated soil TPH concentration (M/M)

S_i = aqueous solubility of component i (M/L³)

X_i = mole fraction of component i in the NAPL mixture (unitless)

H_i = dimensionless Henry's Law constant of component i (unitless)

K_{oc} = soil organic carbon to water partition coefficient of component i (L³/M)

f_{oc} = mass fraction of natural soil organic carbon within the soil matrix (unitless)

θ_a = the volumetric air content in soil (unitless)

θ_w = the volumetric water content in soil (unitless)

ρ_b = dry soil bulk density (M/L³)

The following steps describe the process for estimating mass in the smear zone:

1. Use the process described for unsaturated soils to determine the area weighted average soil concentration for the saturated zone.
2. Multiply the smear zone source concentration (\bar{c}_{sz}) by the area of the contaminated smear zone soils ($A_1, A_2, \dots A_n$) by the depth of smear zone soil contamination by the soil density to calculate a source mass for the smear zone.

$$M_{sz} = \rho_b d_{sz} \bar{c}_{sz} (A_1 + A_2 + \dots A_n) \quad (\text{Eq. C.5})$$

Where:

M_{sz} = mass of contaminant in smear zone materials (M)

ρ_b = dry density of smear zone materials (M/L³)

\bar{c}_{sz} = area weighted concentration (on dry weight basis) in smear zone materials (M/M)

$A_1, A_2, \dots A_n$ = individual area associated with each sample in smear zone materials (L²)

d_{sz} = depth of smear zone materials (L)

The Dissolved Phase in the Saturated Zone:

The dissolved phase zone in the saturated zone is that zone within the saturated zone where contamination is present in the ground water above detectable levels. It extends laterally where contamination has been detected and vertically from the seasonal high ground water table to the lowest elevation contamination has been detected. In general, the contaminant mass dissolved in the ground water is typically much smaller compared to that in the soil source zone. The contaminant mass contained in this compartment can be insignificant and frequently can be ignored when there is significant contamination of the unsaturated soil and smear zone media.

The following steps describe the process for estimating the dissolved mass in ground water.

1. Determine the area of the dissolved source zone. The area of source zone ground water corresponds to the area of ground water contamination above detectable levels.
2. Determine the depth of ground water contamination within the source area. Depth should be determined from the site characterization activities and extends to that depth above detectable levels.
3. Determine the area-weighted mean of the ground water contamination within the source zone, using the procedure listed above for unsaturated soils.
4. Multiply the mean ground water concentration (\bar{c}_{gw}), by the source area ($A_1, A_2, \dots A_n$), by the depth of ground water contamination at the source, by the porosity of the geologic media (n) to obtain dissolved contaminant mass.

$$M_{gw} = n \bar{c}_{gw} d_{gw} (A_1 + A_2 + \dots A_n) \quad (\text{Eq. C.6})$$

Where:

M_{gw} = mass of contaminant dissolved in source zone ground water (M)

n = porosity of saturated geologic media in source zone

\bar{c}_{gw} = area-weighted average concentration for ground water in the source zone ground water (M/L³)

A_1, A_2, \dots, A_n = individual area associated with each sample in the source zone ground water (L²)

d_{gw} = vertical depth of the contaminated source zone ground water (L)

C.2 Indirect Method to Estimate Smear Zone Mass

An estimate of source mass can still be made even if detailed soil contamination concentration data are not available for the saturated soil zone. The following indirect method to estimate smear zone mass was adapted from Wiedemeier et al. (1999) and Florida RBCA study (Groundwater Services Inc, 1997). The majority of the mass is assumed to be present as NAPL, with the size of the NAPL-saturated area based on plume size.

Begin by assuming that the width of the smear zone is half the width of the observed plume at the point of maximum ground water concentration. The length of the smear zone is assumed to be equal to the width. The thickness of the smear zone is assumed to be equal to the thickness of the contaminated ground water.

The following equation (Eq. C.7) may be used to calculate the source mass:

$$\text{SourceMass} = SZ * SA * n * S_o * M_f * \rho_c \quad (\text{Eq. C.7})$$

Where:

SourceMass = mass of dissolvable contaminants in source zone (M)

SZ = smear zone thickness (L)

SA = estimated smear zone area (L²): $SA = (0.5 * W_{plume})^2$

W_{plume} = plume width at highest concentration (L)

n = porosity (unitless)

S_o = residual saturation level: volume of NAPL/volume of voids (unitless)

M_f = mole fraction of contaminants of interest in NAPL (unitless)

ρ_c = pure-phase (NAPL) density of contaminant of interest (M/L³)

Appendix D

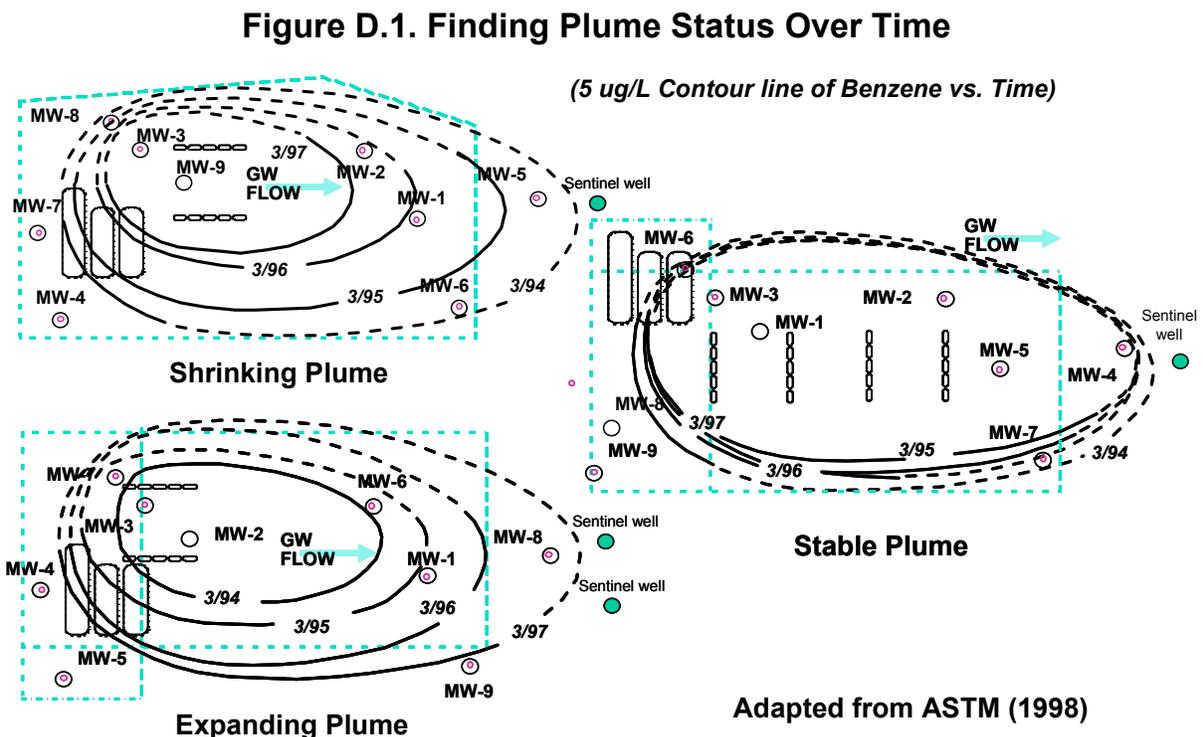
Methods for Evaluating Plume Status

For natural attenuation to be considered a feasible cleanup action alternative, the “plume status” needs to be defined; that is, whether the plume is stable or shrinking. The following presents several methods to visually and statistically evaluate plume status. It is not necessary to apply all of these methods when determining plume status. The appropriate method should be selected, depending on the site-specific conditions. It is important when evaluating the stability of the contaminant plume that the historical data demonstrate a clear and meaningful trend in contaminant mass and/or concentration.

D.1 Evaluating Plume Contours Over Time

One method of evaluating plume status is to plot plume concentrations from four or more events on the same figure. This approach requires sufficient data to delineate the plume and illustrate plume trends. The number and frequency of sampling events needed for this method depends on ground water flow velocity and well locations. This method is often most useful for stable plumes where evaluation of concentrations in single wells may provide confusing results while overall plume status is stable.

Figure D.1 illustrates plume contours for a shrinking, stable, and expanding plume. This graphic has been adapted from ASTM (1998).

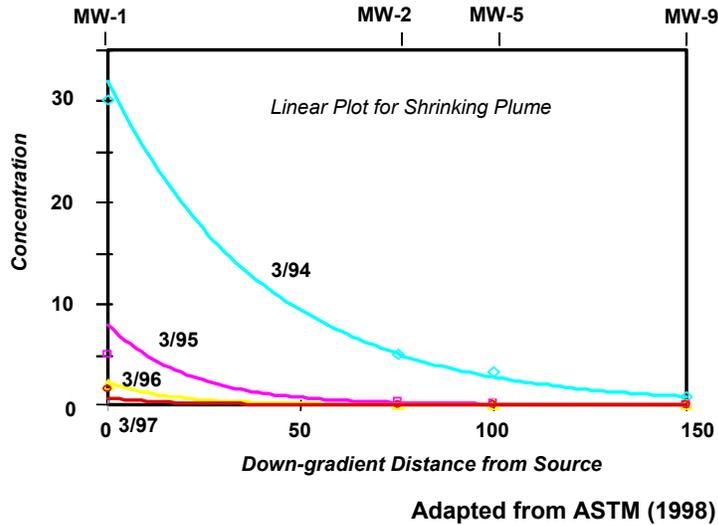


D.2 Graphical and Regression Analysis of Well Concentrations over Time

Ground water monitoring data from four or more sampling events are plotted for each site well. The data can be plotted on a linear scale, log scale, or natural log scale versus time. The

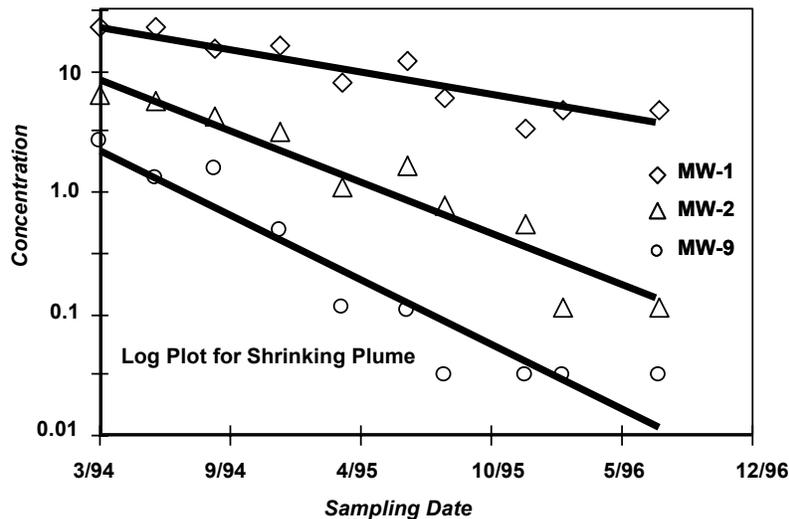
advantage of plotting on a linear scale is that if the data illustrate an exponential decay over time, it indirectly supports that 1st-order biodegradation may be occurring at the site. An example of a linear graph illustrating exponential decay is shown in Figure D.2 for a shrinking plume.

Figure D.2. Spatial and Temporal Analysis: Multiple Well Concentration vs. Multiple Time (normal-scale)



Plotting the concentrations on a log or natural log scale will often reduce scatter and more clearly illustrate concentration trends as shown in the following graph. Plotting the well data in log scale will relate more directly to calculation of attenuation rates using 1st-order decay. Generally, for each well, plot the best-fit line for the natural log of well data vs. time using a linear regression analysis to examine the goodness of fit to the data. Figure D.3 illustrates an example using the log of well concentration vs. time and distance graphs for a shrinking plume.

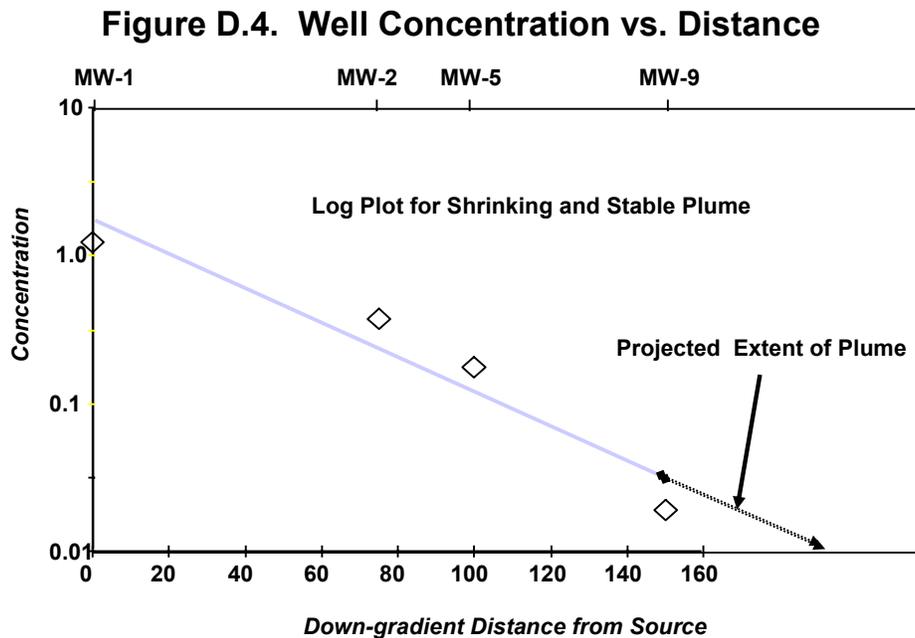
Figure D.3. Spatial and Temporal Analysis: Multiple Well Concentration vs. Multiple Time (log-scale)



Module 2 of the Data Analysis Tool Package along with this guidance allows plotting of well concentrations vs. time for multiple wells (along plume center line distance). It also calculates the best-fit line, r^2 value, and confidence level on slope for the data given. Refer to US EPA (1999b) and the procedure for calculating a confidence level found in Section 4.2 of the User's Manual.

D.3 Graphical and Regression Analysis of Well Concentration Versus Distance

Ground water data from four or more monitoring wells along the center line of the ground water plume is plotted by concentration vs. distance for several sampling events. An example of this approach is shown in Figure D.4. If the best-fit line based on the regression analysis (assuming that it has an acceptable confidence level) is extended to either the detection level or to intercept the x-axis, an estimate of plume length can be obtained from the graph, as shown in Figure D.4.



Adapted from ASTM (1998)

D.4 Non-parametric Statistical Tests for Plume Stability

If plume stability is visually unclear, non-parametric statistical approaches may be able to be used to evaluate if a shrinking or stable trend exists at the site. The Data Analysis Tool Package (Module 1) along with this guidance provides for the use of the Mann-Whitney U test or Mann-Kendall non-parametric tests. Since at very low concentrations successful application of this non-parametric statistical test may be difficult, selection of sampling events for the non-parametric statistical test is important.

To avoid biasing non-parametric statistical tests, the same number of significant figures should be consistently used to express the data for a given contaminant. This is to make sure that any

identified plume trends are true data trends and not trends of the laboratory's data reporting format.

The following describes how the Data Analysis Tool Package calculates these statistical tests.

Mann-Kendall Test:

The Mann-Kendall Test is a non-parametric test (Gilbert, 1987) that can be used to define the stability of a plume (i.e., stable, shrinking, or expanding) based on concentration trends at individual wells. To evaluate plume stability, four or more independent sampling events are required (Wedemeier et al., 1999). Caution should be exercised in evaluating data produced by this analysis. When using the Mann-Kendall test, well selection can play a critical role in determining if a plume is found to be stable or decreasing. Therefore, this type of test in conjunction with overall plume concentrations is a more reliable method of evaluating plume stability than just application of statistics at selected well locations.

The results from the first ground water sampling event are compared to all subsequent events,

- Concentration of event $x >$ event 1: Enter 1
- Concentration of event $x =$ event 1: Enter 0
- Concentration of event $x <$ event 1: Enter -1

Then, the results of the second ground water sampling event are compared to all subsequent events,

- Concentration of event $x >$ event 2: Enter 1
- Concentration of event $x =$ event 2: Enter 0
- Concentration of event $x <$ event 2: Enter -1

This process is repeated for all sampling events. The Mann-Kendall statistic "S" value for the data is calculated by the Data Analysis Tool Package for each well as the sum of all of the sums for each sampling event. The standard deviation and coefficient of variation are also calculated by the spreadsheet. If a clear trend is not shown at a pre-determined level of confidence and the calculated coefficient of variation is less than or equal to "one", the plume is determined to be stable.

Mann-Whitney U Test:

The Mann-Whitney U test (also called the Wilcoxon Rank-Sum Test) is another non-parametric statistical test (Mann and Whitney, 1947) that may be useful at a site. The outcome of the test is not determined by the overall magnitude of the data points, but depends on the ranking of individual data points. Therefore, if a higher concentration is detected during one of the last sampling events, even if an overall decreasing trend is evident from the site data, the analysis will not indicate a decreasing trend.

The Mann-Whitney U method tests the hypothesis that the two populations are statistically equivalent. The test is conducted by vertically ranking the eight data points from lowest to highest, with the lowest value on top and greatest value on the bottom. Eight consecutive

quarters of data are divided into two groups representing the first four quarters (designated with an “A”) and the last four quarters (designated with a “B”). For each individual “A” concentration, the numbers of “B” concentrations that occur below the “A” concentration are counted. The four values (either zero or some positive number) are summed together to obtain the U-statistic. For the purpose of the Mann-Whitney U method tests, non-detect values are considered zero. If two or more concentrations are identical, two vertical columns are constructed. In the first column, the tying “B” concentration is ranked first, and in the second column the tying A concentration is ranked first. An interim U is calculated for each column and the average of the interim U values is used as the final U value (Weidemeir et al., 1999).

If $U \leq 3$, the null hypothesis is rejected, and it is concluded with at least 90% confidence that the concentration for the individual contaminant has decreased with time at that well. If $U > 3$, the null hypothesis is accepted, and it cannot be concluded with at least 90% confidence that the concentration for the individual contaminant has decreased with time at that well.

D.5 Spatial Mass Flux Calculation Over Time

Contaminant mass flux is the rate at which a contaminant passes through a defined cross-sectional area in the ground water system per unit time. A mass flux calculation is a useful and cost-effective tool to evaluate the effectiveness of a natural attenuation remedy.

Once the contaminant mass leaves the source zone, the total flux within the plume should remain constant as the plume migrates down-gradient, unless mass is removed by natural attenuation processes. When the magnitude of the mass flux varies at different locations within a plume, this may be an indicator of natural attenuation. Mass flux calculations can provide insights into the nature, strength, and longevity of the source zone, and can be used for:

- Refining the conceptual site model;
- Evaluating plume status;
- Demonstrating contaminant mass loss;
- Estimating biodegradation rate constants; and
- Evaluating the potential impacts to receptors.

Several methods (Nichols and Roth, 2004) can be used to estimate contaminant mass flux. These include:

- Using multi-transects of monitoring wells across a plume as shown in Figure D.5;
- Capturing a plume by supply wells or remedial extraction wells;
- Using *in-situ*, down-hole flux meters; and
- Using solute transport modeling in combination with field data collection and interpretation.

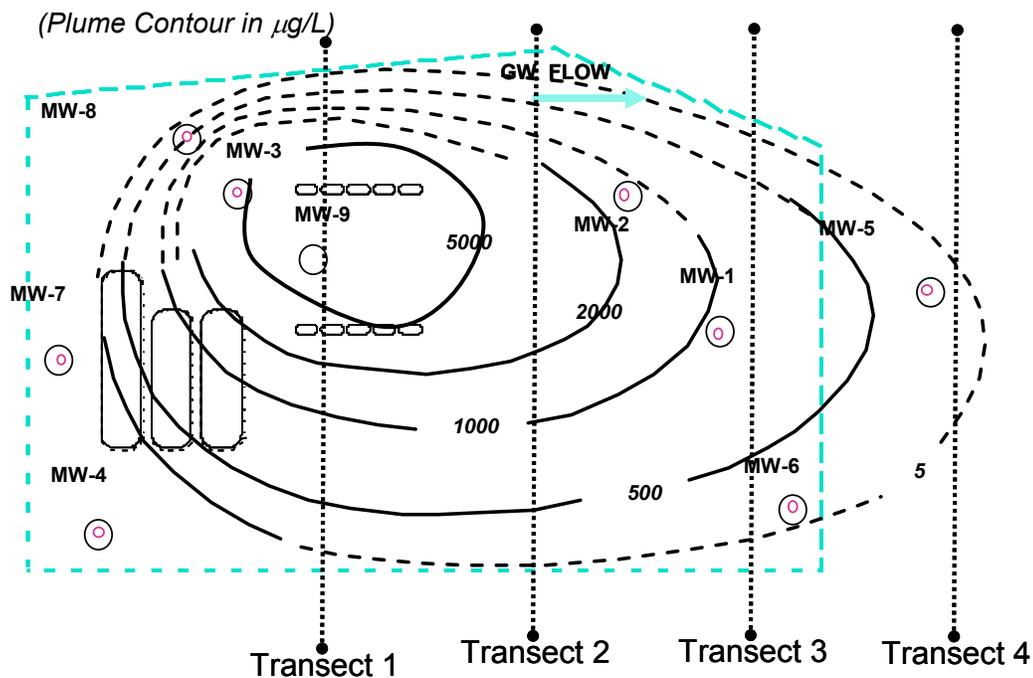
This guidance describes the mass flux method with multi-transects of monitoring wells. This method relies on ground water samples from single or multi-level monitoring well data interpolated along a transect across the plume, perpendicular to ground water flow. A vertical cross-section across the transect is divided into any number of sub-areas, each presenting a discrete area of uniform ground water concentration and flow. The total mass flux is the sum of

the fluxes from each of these sub areas, as illustrated in Figure D.5. Examples of mass flux methods can be found in Suarez and Rifai (2002), Wiedemeier et al. (1999), NRC (2000), Buscheck et al. (2003), and Nichols and Roth (2004).

Contaminant mass flux is the product of the rate of ground water discharge and the concentration of the contaminant at specified transects along the plume. The steps in a mass flux computation can be summarized as follows:

1. Drawing several transects (or lines) perpendicular to the flow and at various distances down-gradient from the source. These serve as control planes. Each transect of single or multi-level monitoring wells should extend sufficiently in distance both laterally and vertically, in order to define the width and thickness of the plume;
2. Determining the distance between two consecutive contours crossing each transect (within the study area);
3. Estimating volume (and mass) of ground water passing through each line between two consecutive contours for all the contaminant ground water concentrations along a transect;

Figure D.5. Mass Flux Method



4. Estimating the mass flux of the contaminant crossing a transect (i) using the following equation (Eq. D.1);

$$MF_i = C_i * (A_i n_e v_{gw} \rho_{water}) \quad (\text{Eq. D.1})$$

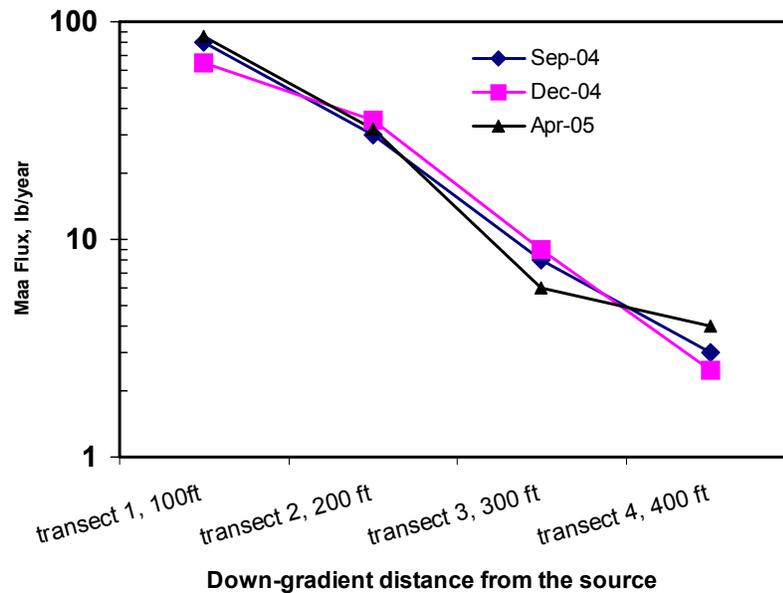
5. Calculating the contaminant mass for each two consecutive contour lines along the transect and adding up the mass; and
6. Comparing the mass flux change at each transect over time.

Although a lower-resolution approach with single-level monitoring wells can be applied, multi-level monitoring well data allow for a more refined, detailed concentration and flow profile.

Evaluating plume status:

Mass flux of the plume can help in assessing plume stability when multiple sampling events for multiple transects are conducted. This calculation involves contaminant mass flux (movement) across plume transects. To use this method, calculate the mass flux for each consecutive contour line along multiple transects as shown below and add up the mass annually as shown in Figure D.5, then compare the mass flux change at each transect to determine the trend in mass changes along the plume over time as shown in Figure D.6.

Figure D.6. Mass Flux versus Down-gradient Distance for Multiple Transects over Time



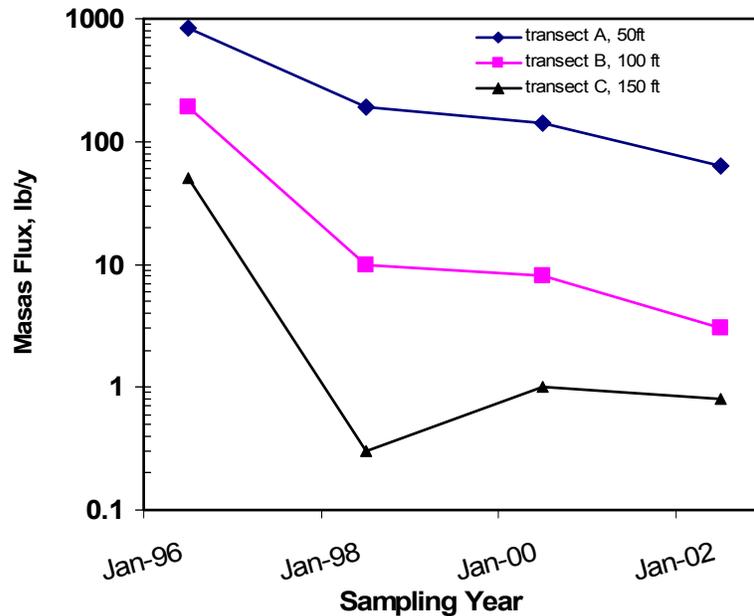
For example, the plots for mass flux versus distance over time shown in Figure D.6 demonstrate the stable plume. Figure D.7 indicates that the plume is shrinking, as exhibited by a mass flux that is declining spatially and temporally. The observed spatial and temporal loss of contaminant mass could be attributed to biodegradation and/or source decay.

Estimating biodegradation rate constants and demonstrating contaminant mass loss due to biodegradation:

An estimated biodegradation rate constant can be calculated by using a quantitative mass flux approach. The mass flux 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. See NRC (2000) and Bockelmann et al. (2003) for more details.

As ground water flows past a source area, it is loaded with dissolved petroleum hydrocarbons through contact with the free product and smear zone.

Figure D.7. Mass Flux versus Sampling Time over Multiple Transects



Therefore, the loading rate can be used as an estimate for the biodegradation rate constant for a stable plume. The mass of dissolved phase which enters the ground water system per unit of time will be the product of the average contaminant concentration in and below the source area and the flow of contaminated ground water in and below the source area. For an expanding plume, the actual biodegradation rate constant would be somewhat less than that calculated for a steady-state plume, and for a shrinking plume it would be somewhat more. The dissolved contaminant loading rate has two components:

- The dissolved phase added to the ground water that flows horizontally through the smear zone below the water table, and
- The dissolved phase added to the ground water beneath the smear zone, caused primarily by vertical dispersion and vertical advection.

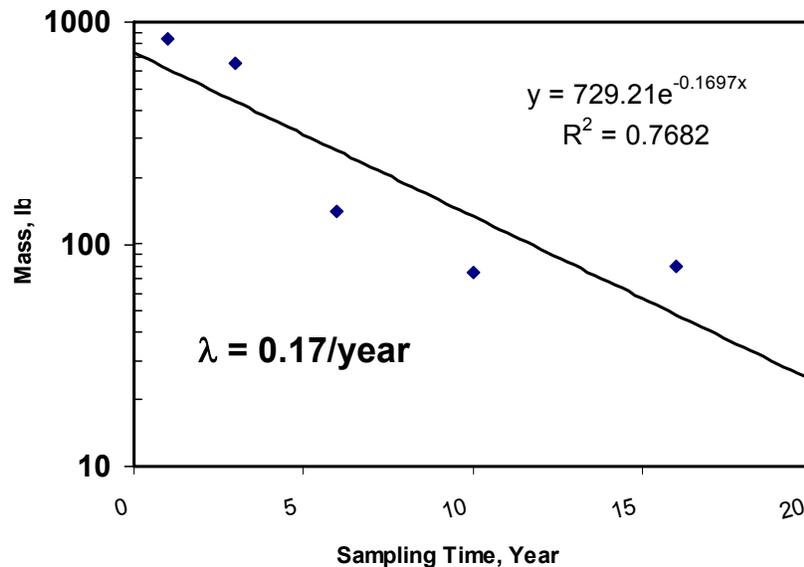
For both of these zones, an average concentration is estimated and multiplied by the ground water flow rate through the zone. The calculation results in the mass of dissolved petroleum hydrocarbons contributed for each zone. Based on stable plume conditions, this rate (Eq. D.2) can be equated to a biodegradation rate constant as shown below.

$$\lambda = -\ln\left(\frac{MF_s}{MF_d}\right) * \frac{1}{\Delta t} \quad (\text{Eq. D.2})$$

Biodegradation rate constant can be calculated by plotting the natural log of mass flux through different transects perpendicular to the flow as a function of the average ground water travel time between the adjacent transects. This method usually also requires a dense well network and accurate aquifer thickness. Mass flux method assumes the concentration associated with each sampling point is constant over the area represented by the sampling point. The greater the distance between monitoring wells (as well as the down-gradient distance between the control planes), the greater the uncertainty of both the contaminant concentration and mass and the contaminant travel time.

For a shrinking plume, biodegradation rate constant derived from mass changes is calculated from change in the total dissolved mass over time for a shrinking plume. A biodegradation rate constant for the contaminant plume is estimated using a plot of dissolved mass as a function of time (Suarez and Rifai, 2002). The rate is calculated as the slope of the best-fit line. Data from Figure D.8 indicate that biodegradation rate constant is occurring at the site at a rate of 0.17/year.

Figure D.8. Estimation of Biodegradation Rate Constant from Mass Change over Time



Evaluating the potential impacts to receptors:

At a site where there is the potential for receptor well impacts, mass flux estimates may be used to predict receptor well concentrations expected in the supply well using the equation – Eq. D.3 (Einarson and Mackay, 2001) below:

$$C_{sw} = \frac{MF_i}{Q_{sw}} \quad (\text{Eq. D.3})$$

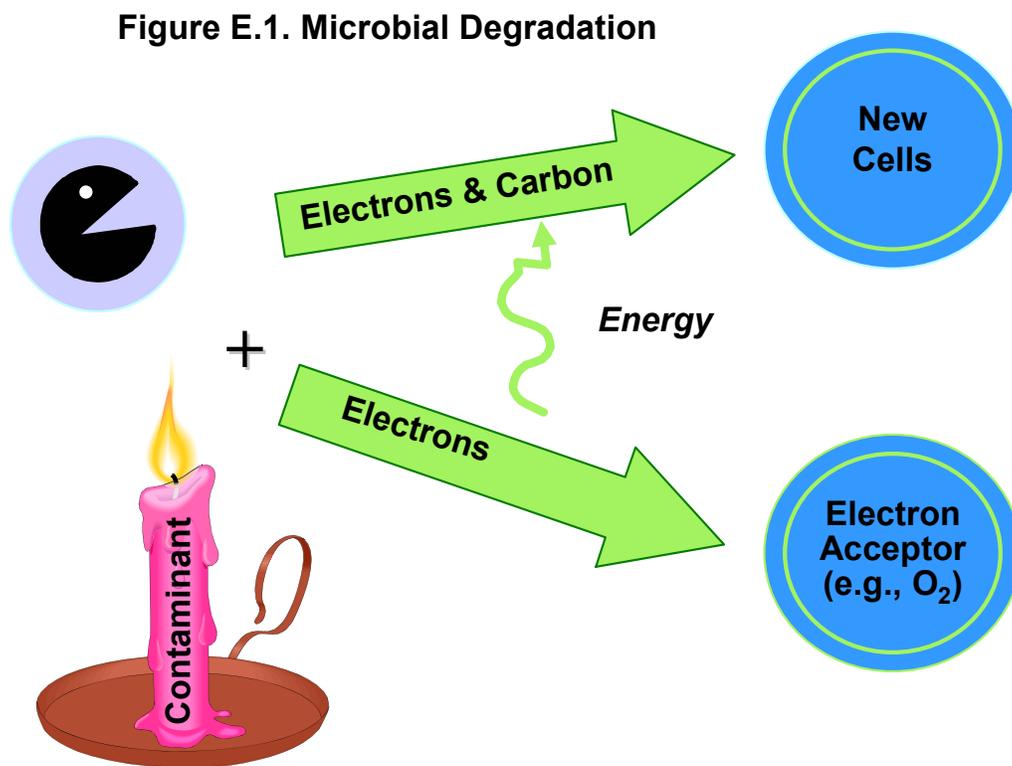
Appendix E

Methods for Evaluating Geochemical Indicators

Biodegradation is a destructive attenuation mechanism. Biodegradation by indigenous microbes can contribute significantly to the destruction of petroleum hydrocarbons. The energy acquired for cellular growth is obtained through the oxidation of petroleum hydrocarbons (an electron transfer process). Electrons are removed from the petroleum hydrocarbons (which are referred to as electron donors in this process) by the microbes during cellular growth. Electron acceptors must also be present to accept these removed electrons in order for the procedure to occur. Biodegradation or this electron donor reaction can occur under aerobic or anaerobic conditions. Some microbes can switch from aerobic to anaerobic biodegradation when dissolved oxygen in the ground water is depleted (NRC, 2000).

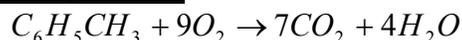
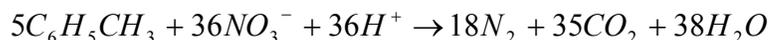
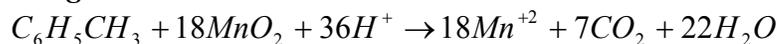
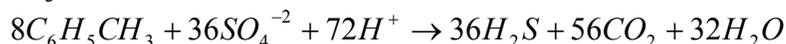
The end result of aerobic biodegradation of petroleum hydrocarbons is carbon dioxide, water, and cell mass. The end products of anaerobic biodegradation include simple organic acids, CO₂, H₂O, CH₄, H₂, N₂ and cell mass. The electron acceptors include oxygen under aerobic conditions, and nitrate, sulfate, ferric iron, and manganese under anaerobic conditions (ASTM, 1998).

Figure E.1 illustrates the fundamental concept of biodegradation.



Adapted from NRC (1993)

Evaluation of the geochemical indicators of biodegradation is an important piece of the evidence needed to demonstrate that significant biodegradation is occurring at a site and this evaluation is recommended for all sites. The following equations show the reactants and metabolic by-products involved in the aerobic and anaerobic metabolism of petroleum hydrocarbons.

Aerobic Respiration:**Anaerobic Respiration:*****Nitrate Reduction:******Manganese Reduction:******Iron Reduction:******Sulfate Reduction:******Methanogenesis:***

The reactions above are balanced based on toluene, but can be modified to address all petroleum hydrocarbons. Quantitatively, the balanced equations allow for a calculation of the ratio (Utilization Factor) of the mass of a terminal electron acceptor necessary to completely metabolize a given mass of hydrocarbons and the yield of reduced electron acceptor per mg of petroleum hydrocarbon metabolized (ASTM, 1998).

Assimilative capacity is used to estimate the capacity of the aquifer to degrade contaminants. By definition, assimilative capacity is the sum of all electron acceptor mass utilized in the biodegradation of contaminant mass at a site. When calculating the assimilative capacity at a site, it is normally assumed that a contaminant (or a mixture of contaminants) being evaluated is the only contaminant providing a demand for electron acceptors. However, the entire mass of organic materials (naturally occurring and anthropogenic contaminants) in the subsurface contributes to the electron acceptor demand. Caution should be exercised when estimating the restoration time of a specific contaminant of concern with assimilative capacity alone.

Measurement of the electron acceptors available in an aquifer can assist in identifying the predominant microbial and geochemical processes that are occurring or have already occurred at the time of sample collection. Dissolved oxygen is the first electron acceptor to be utilized during the biodegradation of many organic contaminants dissolved in ground water. Nitrate, Mn^{+4} , Fe^{+3} , sulfate, and carbon dioxide are found naturally in many ground water systems and are used as electron acceptors once the system becomes anaerobic. Concentrations of these natural electron acceptors can be measured in the field using probes or colorimetric techniques. Nitrate, sulfate, and carbon dioxide concentrations can also be determined in a fixed-base, off-site analytical laboratory. Because it can change in a relatively short time after sample acquisition, dissolved oxygen concentrations should be measured while in the field, and

sampling techniques should avoid aeration of the samples since this will affect the accuracy of the dissolved oxygen concentrations. The following summarizes these electron acceptors:

Dissolved Oxygen. Dissolved oxygen is the favored electron acceptor used by microbes for the biodegradation of many forms of organic carbon. During aerobic respiration, dissolved oxygen concentrations decrease. Thus, dissolved oxygen concentrations below background in areas with dissolved contamination provide evidence for biodegradation.

Nitrate. After dissolved oxygen has been depleted, nitrate may be used as an electron acceptor for anaerobic biodegradation via denitrification. During denitrification, nitrate concentrations measured in ground water decrease. Thus, nitrate concentrations below background in areas with dissolved contamination provide evidence for biodegradation. Nitrate is often analyzed by methods that measure nitrate (NO_3^-) and nitrite (NO_2^-). As nitrite is very unstable under most environmental conditions and makes up a very small percentage of total nitrogen at the majority of sites, nitrate alone can be used as a measure of nitrate.

Magnanese: When Mn^{+4} is used as an electron acceptor during anaerobic biodegradation of organic carbon, it is reduced to Mn^{+2} . Mn^{+2} concentrations can thus be used as an indicator that anaerobic biodegradation has occurred via Mn^{+4} reduction.

Iron: When Ferric iron (Fe^{+3}) is used as an electron acceptor during anaerobic biodegradation, it is reduced to Fe^{+2} , which is soluble in water. Ferrous iron (Fe^{+2}) concentrations can thus be used as an indicator that anaerobic biodegradation has occurred via Fe^{+3} reduction. Dissolved ferrous iron in ground water typically represents a minor fraction of the total assimilative capacity attributed to iron reduction. Most ferrous iron remains bound to insoluble ferric iron oxyhydroxide coating on soil. Measurement of bioavailable ferric iron in soil can be used as a baseline characterization for candidate natural attenuation sites. Please refer to Environmental Security Technology Certification Program (ESTCP) web-links (<http://www.estcp.org/projects/cleanup/200009o.cfm>).

Sulfate: After dissolved oxygen, nitrate, and biologically available Mn^{+4} and Fe^{+3} have been depleted in the microbiological treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegradation via sulfate reduction. During sulfate reduction, sulfate concentrations measured in ground water decrease. Thus sulfate concentrations less than background in areas with dissolved contamination provide evidence for biodegradation.

Methane: As implied by the name, *methanogenesis* results in the production of methane during the biodegradation of petroleum hydrocarbons. The presence of methane in ground water is indicative of strongly reducing conditions. Methanogenesis is a two-step process involving fermentation and respiration.

Metabolic By-Products: Metabolic by-products include Mn^{+2} , Fe^{+2} , hydrogen sulfide, methane, ethane, ethene, hydrogen, increased alkalinity, and lowered oxidation-reduction potential. Like electron acceptors, the measurement of metabolic by-products in an aquifer may be useful in identifying the predominant microbial and geochemical processes that are occurring or have already occurred at the time of sample collection. Of the readily measurable metabolic by-

products, only oxidation-reduction potential should be measured in the field; the remainder of the analytes can be measured in a fixed-base laboratory. As the sequential electron acceptors are utilized, CO₂ is produced at each metabolic step. Alkalinity can be expected to increase across a site where biological activity is occurring. Changes in alkalinity are an indication of microbial activity. Alkalinity is a measure of an ability of ground water to buffer changes in pH caused by the addition of biologically generated acids through both aerobic and anaerobic biodegradation processes.

Changes in specific geochemical indicators are in response to specific microbial metabolism of hydrocarbons. The energy received as microbes metabolize carbon determines the order in which the electron acceptors are used, as explained in Section 3.2.1.2 of this document.

Theoretically speaking, the concept of sequential use of an electron acceptor assumes competitive inhibition – that microbial metabolism will deplete oxygen, at first, then nitrate, then available iron, etc., resulting in definable zones of individual electron acceptors within a plume aquifer. However, as reduced products of electron acceptors such as ferrous iron, sulfide, and methane are transported down-gradient through plume advection and shifted by recharge, organic matter availability, hydraulic gradients and other factors, it makes it difficult to delineate a given redox zone and interpret electron acceptors at a contaminated site. In reality, iron, and sulfate reduction and methanogenesis may intermingle such that it is often difficult to determine the electron acceptor process that dominates at any given location and time within the plume aquifer.

Study results from the US Air Force Center for Environmental Excellence (Newell et al., 1995) and Sittler (2001) indicated that **anaerobic** processes **dominate** the biodegradation of petroleum-contaminated ground water during the natural attenuation processes. In particular, sulfate reduction and methanogenesis appear to be the major sink for petroleum hydrocarbons. Oxygen and nitrate serve as minor electron acceptors.

Appendix F

Methods for Estimating Rate Constants

Biodegradation (λ) and bulk attenuation (k) rate constants are used to calculate the fate and transport of the petroleum hydrocarbons dissolved in ground water and to calculate potential restoration time frames. Bulk attenuation refers to all of the natural attenuation processes (dispersion, sorption, volatilization, dilution by recharge, and biodegradation). Even though biodegradation usually is the majority of the bulk attenuation rate for dissolved petroleum hydrocarbon plumes, be careful using the bulk attenuation rate in fate and transport modeling, so that natural attenuation processes (e.g., dispersion and sorption) are not double counted in the calculations.

This appendix presents how to calculate both bulk attenuation rates and biodegradation rates. The Data Analysis Tool Package includes calculation of these types of site-specific rate constants. The user is cautioned to understand the assumptions used to calculate these rates and to design the monitoring plan accordingly. Any type of rate constant calculation should be verified by observed site conditions (ground water concentrations) during the performance monitoring period. Definition and dimension of symbols used in equations shown throughout this appendix can be found in Appendix B of this guidance unless specified otherwise.

F.1 Estimating Biodegradation Rate Constant Using a Mass Flux Approach

Refer to Appendix D.5 of this document for more detail.

F.2 Graphical and Regression Techniques to Calculate Point Decay Rate at a Well and Bulk Attenuation Rate Constants

The following graphical and regression techniques for concentration versus time (assuming shrinking trends) and concentration versus distance (assuming shrinking or stable trends) have been adapted from ASTM (1998) to determine rate constants.

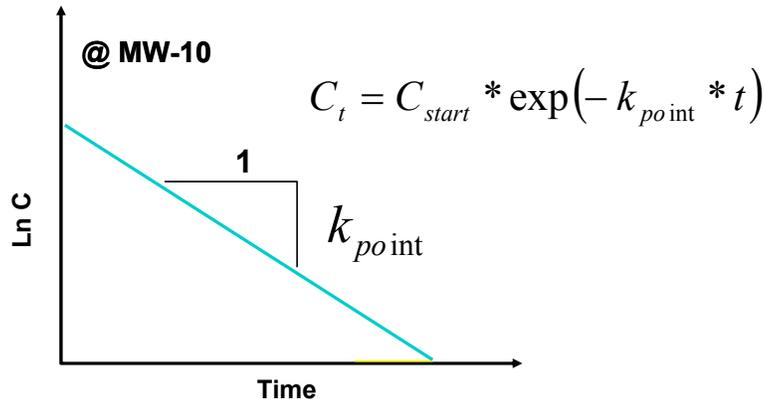
Concentration vs. Time Approach (temporal analysis at a point in the plume):

This technique is based on the point decay rate (assuming 1st-order) equation (Eq. F.1).

$$C_t = C_{start} * \exp(-k_{point} * t) \quad (\text{Eq. F.1})$$

For a shrinking plume, the natural log of the ground water concentrations can be plotted versus time at each well selected. The slope of the best-fit line of the regression analysis is an approximation of the bulk attenuation rate. Three or more wells in the plume should be used for this technique. The r^2 value of the regression analysis and the level of confidence on the slope of the log-linear regression line should be evaluated. Figure F.1 for a shrinking plume illustrates this technique.

Point decay rate constant derived at a single monitoring location provides information regarding the potential plume lifetime at that particular well location, but cannot be used to evaluate the distribution of contaminant mass within the ground water system. To adequately assess the entire plume, monitoring wells should be available that adequately delineate the entire plume, and an adequate record of monitoring data should be available for each well.

Figure F.1. Temporal Analysis at a Well in the Plume

k_{point} = Point decay rate constant: Slope of natural log ground water concentration ($\ln C_t$) vs. time plot at a well

Adapted from ASTM (1998)

For each well within the plume, the time to reach the cleanup goal for that well can be estimated using the following equation (Eq. F.2):

$$t = \frac{\ln\left(\frac{C_{CUL}}{C_{start}}\right)}{-k_{point}} \quad (\text{Eq. F.2})$$

As described in Section 3.3.3 of this document and Section 7 of US EPA document (2005a), a rate of attenuation can be extracted from field data and used to evaluate the data to determine whether the rate is statistically significant from zero. This rate can also be used to determine how soon the concentration will reach a cleanup level at a monitoring well. This approach relies on parametric statistics, specifically, the “Student’s *t*-statistic” on the rate of attenuation. When using the Student’s *t*-statistic in this manner, a confidence level of at least 85% and probability error of 15% may be used. The probability of error (α) is the probability that a calculated rate constant will be accepted as a statistically significant rate, even though the calculated rate was a result of random variation and was not truly from zero. The confidence level is one minus the probability of error.

In order to account for the uncertainty in the estimate of the point decay rate constant (k_{point}) and in the projected restoration time frame to achieve cleanup goals in a monitoring well, confidence intervals are calculated for each estimate of the point decay rate. The level of confidence is the probability that the true rate (or a project restoration time) is contained within the calculated confidence interval (Newell et al., 2002 and US EPA, 2005a). The statistical confidence is based on the variance of the data and the square root of the number of samples when the reduction of contaminant concentration is to be determined by “least square analysis”. Please refer to US

EPA (1999b) and Section 4.2 of the User's Manual for additional information on confidence interval and for the discussion of uncertainty in rate constant calculations.

In a least square regression analysis, the correlation coefficient "r" is a function of the degree of freedom; that is, the number of observations minus two. For example, if a well is sampled quarterly for two years, the degree of freedom would be "6" which requires a correlation coefficient of about 0.8 to demonstrate statistical significance at 98% level of confidence for a least square regression analysis. The level of confidence as a decision criterion for a log-linear regression analysis can be used to:

- Determine whether there is sufficient evidence to conclude that there is a linear correlation between sampling time and log contaminant concentration at a designated well; and
- Estimate the low boundary value of slope (calculated with log-linear regression analysis) and consequent calculations for prediction of plume behavior.

If there are strong seasonal effects on the recharge of precipitation to ground water, these effects may be reflected in the measured concentrations of contaminants in monitoring wells. When there are strong seasonal effects, it may be useful to extract the rate of attenuation of seasonal maximum concentrations, and compare that rate to the overall rate of attenuation (US EPA 2005a).

Concentration vs. Distance Approach (spatial analysis):

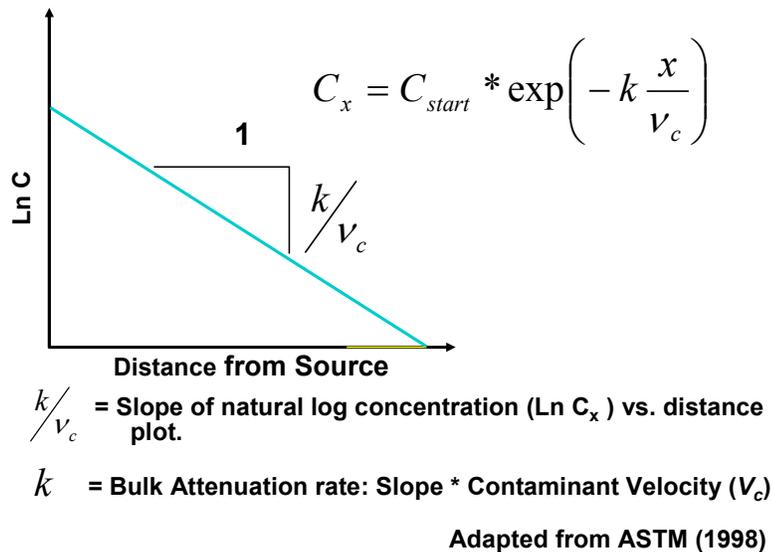
The natural log of the ground water concentration versus distance can be plotted for shrinking or stable plumes. Time, t, can be described in terms of contaminant velocity in ground water, v_c and distance traveled, x.

$$t = \frac{x}{v_c} \quad (\text{Eq. F.3})$$

The term x/v_c is the residence time for the contaminant to move some distance, x, from the source. So the 1st-order decay rate equation (Eq. F.4) can be re-written as:

$$C_x = C_{start} * \exp\left(-k \frac{x}{v_c}\right) \quad (\text{Eq. F.4})$$

The slope of the best-fit line of the regression analysis in a natural log of concentration vs. time plot is k/v_c , the reciprocal of the attenuation distance. To determine k , the slope of the line from the log-linear regression analysis of concentration along a plume path (at a particular time) should be multiplied by the contaminant velocity v_c as shown in Figure F.2. A minimum of four ground water wells along the centerline of the plume should be used when applying this technique. If ground water concentrations from multiple events are available for a stable plume, average concentrations per well could be used. Caution that this approach depends on accurate ground water velocities to obtain reliable bulk attenuation rates.

Figure F.2. Spatial Analysis

A single bulk attenuation rate derived does not provide enough information with regard to the variation of contaminant mass over time and therefore cannot be used to estimate the time required for the plume concentration to be reduced to cleanup levels. These bulk attenuation rate constants incorporate all attenuation mechanisms (sorption, dispersion, biodegradation, etc.) after they leave the source. The distance the contamination would travel down-gradient from the source to reach a certain ground water concentration (e.g., cleanup levels) can be calculated using the following equation (Eq. F.5):

$$x = -\ln\left(\frac{C_{CUL}}{C_{start}}\right) * \frac{v_c}{k} \quad (\text{Eq. F.5})$$

If the plume currently has not traveled this distance, then this rate analysis suggests the plume may expand to that point. If the plume has extended beyond that point, this rate analysis suggests the plume may shrink in the future.

F.3 Method of Buscheck and Alcantar (1995)

This method allows for calculation of a 1st-order biodegradation rate constant (λ) for stable plumes based on the 1-D steady state analytical solution to the advection dispersion equation presented by Bear (1979) and use of the concentration vs. distance regression analysis. This approach assumes steady state conditions and negligible volatilization. This approach uses an analytical solution that accounts for advection, dispersion, sorption, and biodegradation. This method is the basis of the biodegradation rate calculation in Module 5 of the Data Analysis Tool Package. For a stable (steady state) plume, the 1st-order biodegradation rate (Eq. F.6) is given by Buscheck and Alcantar (1995) based on steady state conditions as:

$$\lambda = \frac{v_c}{4\alpha_x} * \left\{ \left[1 + 2\alpha_x \left(\frac{k}{v_{gw}} \right) \right]^2 - 1 \right\} \quad (\text{Eq. F.6})$$

It is important to confirm that the plume is stable (see Section 3.2 of the feasibility study of this guidance) before calculating a biodegradation rate using this approach. The slope of the best-fit line is equal to k/v_{gw} which then is entered into the equation listed above. The r^2 value and the level of confidence on the slope generated by regression analysis should be evaluated to see if data are appropriate to calculate a biodegradation rate. The retarded contaminant velocity is entered into equation above as v_c , the dispersivity in main ground water flow direction is entered into the equation as α_x . Then the equation is solved for the biodegradation rate constant (λ). If all of the appropriate parameters have been entered, the Data Analysis Tool Package will do this calculation automatically. The calculated biodegradation rate will be only as accurate as the parameters input into the equation. If there is insufficient site-specific data to assign a value to these parameters, use of bulk attenuation rate constants or text book value rate constants may be used. However, the predicted plume extent should be verified by the performance monitoring program.

F.4 1, 2, and 3-D Analytical Models

Analytical solute transport 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 of the plume. Steady-state solutions can be used to estimate the extent of a plume and select the appropriate locations of down-gradient monitoring wells. The justification for a 1-, 2-, or 3-D model should be based on the availability of data. Two of the more sensitive input parameters are rate constants 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 1st-order rate constants, the rate constants are not necessarily interchangeable due to the differences in model assumptions and the lumped nature of the parameter (ASTM, 1998). The following presents the 1-, 2- and 3-D partial differential equations that describe solute transport by the processes of advection, dispersion, sorption and biodegradation.

The 1-D partial differential equation (Eq. F.7) describing transient solute transport with 1st-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_{gw}}{R} \frac{\partial C}{\partial x} - \lambda C \quad (\text{Eq. F.7})$$

Assuming the following initial and boundary conditions, Bear (1979) solved the equation above as a function of time and distance in x-direction (plume centerline) as below:

$$C_{x,t} = \left(\frac{C_o}{2}\right) * \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} * \operatorname{erfc}\left\{\frac{\left[x - v_c t \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]}{2\sqrt{\alpha_x v_c t}}\right\} \quad (\text{Eq. F.8})$$

$$C_{x,0} = 0 @ x \geq 0$$

$$C_{0,t} = C_o @ t \geq 0$$

$$C_{\infty,t} = 0 @ t \geq 0$$

where “erfc” represents the complementary error function which can be found in most ground water textbooks, at a steady-state, the solution (Eq. F.9) becomes:

$$C_x = C_o * \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} \quad (\text{Eq. F.9})$$

The 2- and 3-D partial differential equations (Eqs. F.10 and 11) describing transient solute transport with 1st-order biodegradation in the saturated zone are, respectively:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R} \frac{\partial^2 C}{\partial y^2} - \frac{v_{gw}}{R} \frac{\partial C}{\partial x} - \lambda C \quad (\text{Eq. F.10})$$

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R} \frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R} \frac{\partial^2 C}{\partial z^2} - \frac{v_{gw}}{R} \frac{\partial C}{\partial x} - \lambda C \quad (\text{Eq. F.11})$$

As an example of a solution to the advection-dispersion equation in three dimensions, assume the contaminant to originate as an instantaneous slug (Baetsle, 1969) at an instantaneous point source at $x = 0, y = 0, z = 0$. The mass of contaminant is then carried away from the source by transport in a steady-state uniform flow field moving in the x -direction in a homogeneous isotropic medium. As the contaminant mass is transported through the flow system, the concentration distribution of the contaminant mass at time t is given by:

$$C_{x,y,z,t} = \frac{M}{8(\pi)^{3/2} \sqrt{D_x D_y D_z}} * \exp\left(-\frac{(x - v_{gw}t)^2}{4D_x t} - \frac{y^2}{4D_y t} - \frac{z^2}{4D_z t}\right) - \lambda t \quad (\text{Eq. F.12})$$

Where M is the mass of contaminant introduced at the point source. It is apparent from the equation above that the maximum concentration is located at the center of gravity of the

contaminant cloud, where $x = 0$, $y = 0$, and $z = 0$. The peak concentration (Eq. F.13) that occurs at the center of gravity of the contaminant plume is given by:

$$C_{\max} = \frac{M * \exp(-\lambda t)}{8(\pi t)^{3/2} \sqrt{D_x D_y D_z}} \quad (\text{Eq. F.13})$$

The zone in which the majority of the contaminant mass occurs is described by the ellipsoid with dimensions, measured from the center of mass, of $\sigma_x = \sqrt{2D_x t}$, $\sigma_y = \sqrt{2D_y t}$, $\sigma_z = \sqrt{2D_z t}$ where σ is the standard deviation of the concentration distribution. $3\sigma_x$, $3\sigma_y$, $3\sigma_z$ represent three spreading lengths within which about 99.7% of the mass is contained. At low velocities, molecular diffusion is the dominant dispersive mechanism, in which case the migrating contaminant cloud is circular. Because these equations are based on idealized conditions such as the instantaneous point source and uniform flow, they have limited use in the analysis of most field situations. In simple hydrogeologic settings, however, they can be used to obtain preliminary estimates of the fate and transport (Freeze and Cherry, 1979).

Another example of a 3-D solution (Domenico, 1987) to the advection-dispersion equation (Eq. F.14) with biodegradation under the assumption of continuous and planar source is given below:

$$C_{x,y,z,t} = \frac{C_0}{8} \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} * \operatorname{erfc}\left\{\frac{\left[x - v_c t \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]}{2\sqrt{\alpha_x v_c t}}\right\} * \left\{\operatorname{erf}\left[\frac{\left(y + \frac{Y}{2}\right)}{2\sqrt{\alpha_y x}}\right] - \operatorname{erf}\left[\frac{\left(y - \frac{Y}{2}\right)}{2\sqrt{\alpha_y x}}\right]\right\} * \left\{\operatorname{erf}\left[\frac{\left(z + \frac{Z}{2}\right)}{2\sqrt{\alpha_z x}}\right] - \operatorname{erf}\left[\frac{\left(z - \frac{Z}{2}\right)}{2\sqrt{\alpha_z x}}\right]\right\} \quad (\text{Eq. F.14})$$

For a full discussion of how these models can be derived, the reader is referred to Wiedemeier et al. (1999) and US Air Force (1995). The 3-D solution shown above is the basis of the biodegradation rate calculation in Module 6 of the Data Analysis Tool Package that can be used for any types (stable, shrinking, and expanding) of plume by incorporating a transient-state mode calculation with decaying source.

Appendix G

Developing Remedial Investigation Work Plan & Data Collection Needs

The purpose of this appendix is to discuss the site data that may assist in a natural attenuation evaluation. The information in this appendix is adapted from Tables X2.1 and X4.1 of ASTM (1998). This appendix may not cover all information that may be required in a site characterization, but it does include most of the site characterization data that can be used in evaluating natural attenuation. For a more detailed description of what data may need to be collected to evaluate the feasibility of using natural attenuation as a cleanup action alternative, reasons for collecting those data, and sampling and analytical methods, please refer to API (1998) and the web references identified in Section 3.1 of this guidance.

Table G-1 lists the remedial investigation (site characterization) data needed to evaluate natural attenuation as a cleanup action, and as noted in this guidance.

Table G-2 serves as a guide for selection of geochemical indicators under natural attenuation to be evaluated 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 geochemical indicators.

Table G-1: Data Collection Items for Natural Attenuation at Petroleum-contaminated Sites

NOTE – This table describes the typical site characterization information recommended to evaluate natural attenuation. Only 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. The following information is adapted from ASTM, 1998.

| Data Collection Needs | Application | Sources/Methods/Protocols |
|---|--|---|
| 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. | NWTPH-HCID (see Washington State DOE, 1997), EPA 3550/8015/5030, directly from knowledge of type released. |
| Date of release and date discovered | Needed for calculation of expected plume travel distance and evaluation of time required to reach stability (often not available for older sites). | 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, regional confining units, and regional flow patterns. | State and federal government agencies and technical publications. |
| Definition of site lithology and stratigraphy | Address 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 ASTM 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. | Tax maps, site plans, site reconnaissance, GIS coverage, water billing records, state and local health departments, and Ecology water resource program records. |
| Locations of potential receptors | Identify potential exposure pathways of concern. | Tax maps, land use plans and zoning maps, site plans, site reconnaissance, GIS coverage, water billing records, local health department, and Ecology records. |
| Identify high conductivity pathways, natural or anthropogenic | Determine if natural geologic conditions or utility trenches, ditches, or subsurface utilities may impact ground water 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 and other utility records on subsurface utilities. |

| Data Collection Needs | Application | Sources/Methods/Protocols |
|--|--|---|
| 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. | Hydrogeologic textbooks/handbooks. |
| Range of seasonal water level fluctuations | Estimate ground water smear zone; Estimate 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) or textbook values based on soil type when appropriate. |
| 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 indicates a reasonable potential for vertical migration. | Multilevel piezometers and sampling points with relatively short screened intervals are recommended for evaluating vertical gradients and extent, if necessary. |
| Effective porosity | Calculate ground water seepage velocity and retardation factors. | Typically determine 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, and regional hydrogeology. |
| Collect biological indicator data such as terminal electron acceptors and environmental conditions | Evaluate secondary line of evidence. | See next Table G-2. |

| Data Collection Needs | Application | Sources/Methods/Protocols |
|---|--|---|
| 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 NAPL? phase and sorbed phase hydrocarbon | The extent of residual hydrocarbon impact is needed for evaluation of soluble plume attenuation. Wells at the down-gradient edge of the source should be used to represent source concentrations, and distances to other wells should be determined from the down-gradient edge of the source. The extent of the source area data on the presence of free product is 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, as necessary | 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 and hydrogeologic information. |
| Organic carbon content of saturated zone soils | Determine retardation factor for components of soluble plume to estimate rates of transport. | Laboratory procedure. |

Table G-2: Sampling Parameters, Methods, and Special Considerations for Evaluating Remediation by Natural Attenuation in Ground Water for Petroleum Release Sites

Note: Geochemical indicators are collected as apparent indicators of biodegradation. These indicators are used as indicators of potential aerobic and anaerobic biodegradation. This table has been adapted from ASTM (1998).

| Indicator | Field or Laboratory Method | Use of Data |
|-------------------------------|-----------------------------------|--|
| Conductivity | Field | Conductivity can be used as an indicator that samples taken from separate sampling points are from the same hydrogeological zone. |
| pH | Field | Difference in pH between contaminated and uncontaminated ground water may indicate biological activity is occurring. |
| Temperature | Field | Oxygen solubility is dependent on ground water temperature. Biodegradation rates may depend on temperature. An increase in temperature may be seen within the solute plume. |
| Dissolved Oxygen (DO) | Field | An inverse correlation of dissolved oxygen to a contaminant (or a mixture of contaminants: BTEX) concentration indicates aerobic biodegradation is occurring. This relationship may also be expressed as depressed or non-detectable levels of DO throughout the plume. |
| Ferrous Iron | Field | Increased concentrations of Fe^{+2} may indicate Fe^{+3} 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 | Increased dissolved Fe may indicate Fe^{+3} is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons; Also useful in assessing feasibility of other corrective action alternatives. Needed to assess compliance with cleanup standards. |
| Oxidation Reduction Potential | Field | Define regions of the plume under oxidizing and reducing conditions; Evaluate potential for biologically mediated redox reactions to occur; Helps validate DO measurements. |
| Nitrate | Field/Lab | Decreased nitrate concentrations in anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons. Needed to assess compliance with cleanup standards. |
| Sulfate | Field/Lab | Decreased sulfate concentrations in anaerobic portion of the plume may indicate use of sulfate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons. Needed to assess compliance with cleanup standards. |

| Indicator | Field or Laboratory Method | Use of Data |
|------------------|-----------------------------------|---|
| Manganese | Field/Lab | Increased Mn ⁺² may indicate that Mn ⁺⁴ is being used during anaerobic biodegradation as a terminal electron acceptor. Needed to assess compliance with cleanup standards. |
| Alkalinity | Field/Lab | Typically, total alkalinity is due primarily 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 CO ₂ is being produced. |

Additional Indicators:

| Indicator | Field or Laboratory Method | Use of Data |
|--------------------|-----------------------------------|---|
| Methane | Field or Lab GC | Elevated concentrations may indicate anaerobic degradation using carbon dioxide as an electron acceptor. |
| Carbon Dioxide | Lab GC or Field | Elevated carbon dioxide levels may indicate aerobic biodegradation or depleted levels may indicate methanogenesis is occurring. Carbon dioxide data should be collected and reviewed carefully due to complex geochemical interactions. |
| Dissolved Sulfides | Field/Lab | Increased levels above background may indicate sulfate-based anaerobic respiration. |

Appendix H

Developing a Performance Monitoring Plan

In any natural attenuation program, the placement of monitoring wells and the development of a monitoring protocol will be site-specific. The following discussion addresses monitoring requirements directly related to evaluating the lines of evidence for natural attenuation, performance monitoring, and subsequent site closure. Other wells and monitoring requirements may be necessary to fully evaluate ground water flow direction, seepage velocity, and other site characterization requirements. In addition, other methods and requirements may be necessary in complex systems.

For the evaluation of natural attenuation performance, monitoring point locations should include at least an up-gradient monitoring point, three or more monitoring points within the dissolved plume but outside any free product zone, and a down-gradient monitoring point near the centerline of the plume (UG-1, MW-1, MW-2, MW-3, and MW-4 in the following Figure H.1, illustrate these points). Other monitoring points and monitoring requirements may be necessary to fully evaluate ground water flow direction, seepage velocity, and plume extent (MW-5 and MW-6). Fewer monitoring wells could be selected due to restricted site access.

An up-gradient well can be used to establish the quality of ground water entering the site, both in terms of regulated contaminants and in terms of the concentrations of terminal electron acceptors and their reduction products. A down-gradient well outside the plume can be used 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 wells should be situated in a manner that will allow the gathering of data to determine the following:

- Plume type (stable, shrinking, or expanding);
- Attenuation rate constants; and
- Warning of impact on sensitive receptors.

In order to define the plume as stable, shrinking, or expanding, wells should be positioned in a manner that will allow plume characterization. This can be accomplished in one of following ways:

- Wells should be positioned in a manner that will allow the drawing of concentration contour maps. The map should extent to a non-detect or compliance level (for example, drinking water criterion) contour if possible. Based on changes (or lack of changes) in the contours over time, the plume can be characterized as expanding, shrinking, or stable.
- Alternatively, the concentration(s) in four or more wells located within the plume and down-gradient of the source and oriented along the direction of ground water flow can be monitored over time.
- Warning of impact on sensitive receptor(s): One or more sentinel wells should be installed between the impacted ground water and a sensitive receptor (for example, a drinking water well). Such wells will ensure that there will be time for other remediation steps to be taken, if the plume does spread beyond predicted boundaries.

The wells within the plume should contain measurable contaminant levels. The trend in 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, Geo-probe type investigations, or other approaches.

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 “big holes” exist in the monitoring network that would allow contamination to escape undetected. It is assumed, however, that these considerations have been addressed during the site remedial investigation phase. No rules of thumb exist for the absolute and appropriate number of wells needed; best sound professional judgment based on site data and experience is the best guide. Additional wells may also be required to determine the depth 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 might 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. It is important to note that a high degree of care must be taken when drilling a ground water monitoring well where confining layers are present to minimize the potential for creating a pathway for cross-contamination between different aquifers. Refer to WAC 173-160 for minimum standards for construction and maintenance of wells.

Screen Lengths (US EPA 2004b):

The screen length for a given monitoring well constitutes an important part of the three-dimensional monitoring location. The screen is sized to sample the interval of interest. The interval may be defined by stratigraphy, contaminant loadings, or geochemistry, based on the site characterization data. Factors to consider in determining screen length include the following:

- Well screens can be matched to stratigraphic intervals if the intervals are relatively small and the geochemical and contaminant values are similar throughout the vertical extent of the interval intersected by the well screen. For instance, a five-foot-thick sand layer within which contaminated water migrates could be sampled with a five-foot screen to intersect the entire interval. Any interval of significantly different conductivity could be targeted by a specific screen length. Well clusters can be used to provide coverage of the entire contaminated unit, as needed.
- Monitoring wells typically should screen comparable intervals. For example, suppose that dissolved petroleum contaminants (e.g., benzene, toluene, ethylbenzene, and xylenes) were transported primarily within a five-foot to ten-foot-thick interval of a 30-foot-thick sandy unit. In this situation, a monitoring well screen could be sized to sample the most contaminated part of the unit to help determine attenuation of the contaminants in that interval. The use of longer screens may result in artificially lower measured containment concentrations, or even lack of detections, due to the mixing of water with different chemical compositions. Calculated attenuation rates or estimated plume boundaries may reflect variations in screen length and placement rather than actual attenuation if monitoring well screen intervals are not matched to contaminant distribution in the contaminated stratigraphic interval.

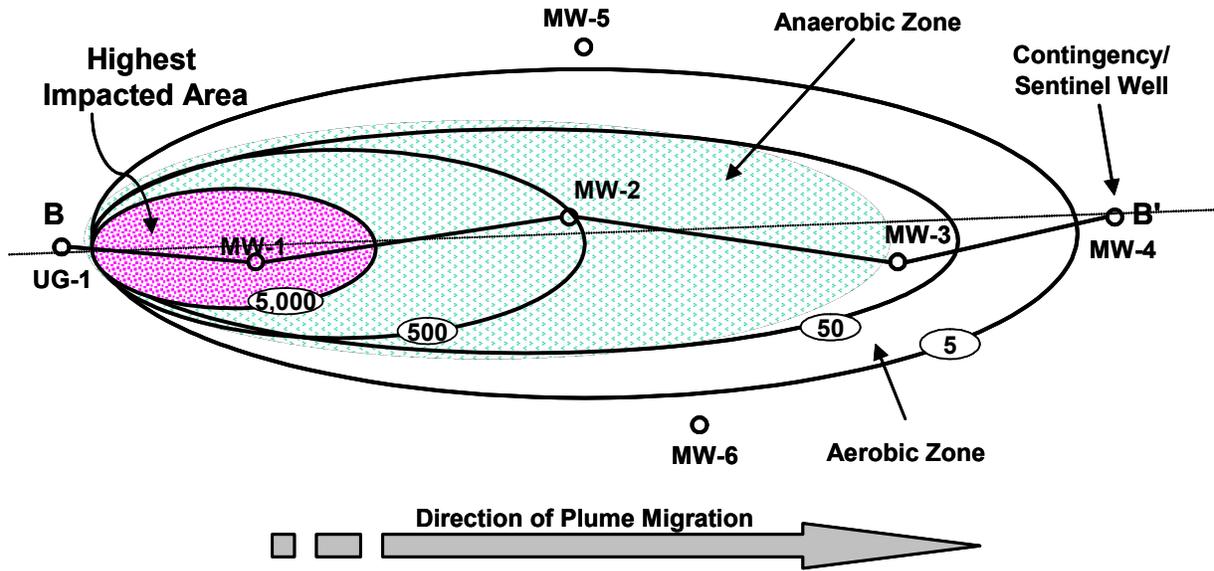
- Well screen lengths can be matched to geochemistry, to sample a zone where a particular geochemistry prevails. Because attenuation of some contaminants is highly sensitive to the geochemical environment, it is often desirable to be able to accurately identify and discretely sample locations in the plume where a particular geochemistry prevails.

Monitoring Natural Attenuation at Pre-Existing Sites:

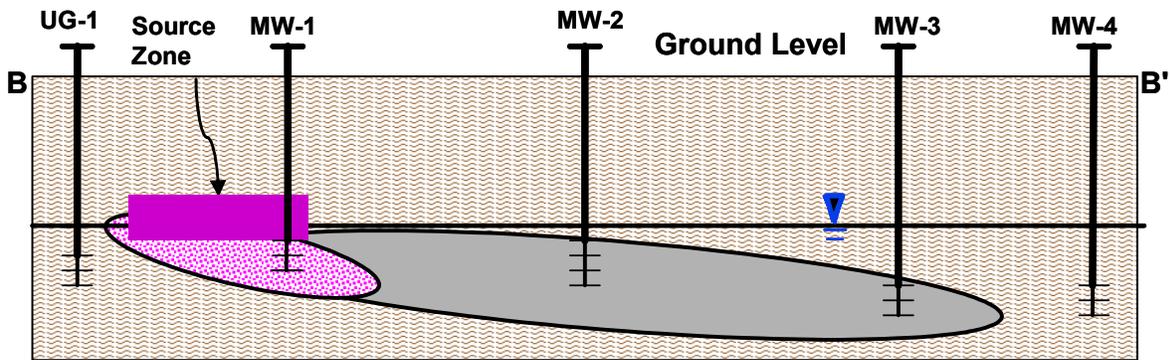
It should be noted that at sites with historical contamination, large numbers of wells may already have been installed and several years of monitoring data may exist. In such cases, further installation of wells may not be necessary if the extent of the hazardous substances, hydrogeological settings, sources, and rate constants are well defined.

Figure H.1. Recommended Performance Monitoring Network for Natural Attenuation Evaluation

Plan View



Cross-Sectional View through Plume Center Line



Not to scale

-  Highest Impacted Area
-  Contaminated Ground Water Plume
-  MW-1: Performance Monitoring Well
-  50 Iso-gradient Contour Line (e.g., Benzene concentration ($\mu\text{g/L}$))

