NAVAL FACILITIES ENGINEERING COMMAND
Washington, DC 20374-5066

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# NFESC
# USER'S GUIDE
# UG-2042-ENV

# USER'S GUIDE FOR IMPLEMENTING REMEDIATION BY NATURAL ATTENUATION AT PETROELUM RELEASE SITES

Prepared for:

Naval Facilities Engineering Command's

Naval Facilities Engineering Service Center
Southwest Division Naval Facilities Engineering Command
Engineering Field Activity, Northwest
Northern Division Naval Facilities Engineering Command
Atlantic Division Naval Facilities Engineering Command
Pacific Division Naval Facilities Engineering Command
Engineering Field Activity, Chesapeake
Engineering Field Activity, West

Contract Number N47408-95-D-0730

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September 2000

# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | September 2000 | May 1999-May 2004 |

4. TITLE AND SUBTITLE
**USER'S GUIDE FOR IMPLEMENTING REMEDIATION BY NATURAL ATTENUATION AT PETROLEUM RELEASE SITES**

5. FUNDING NUMBERS

6. AUTHOR(S)
Battelle

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Battelle
505 King Ave.
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8. PERFORMING ORGANIZATION REPORT NUMBER
UG-2042-ENV

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
NFESC
1100 23rd Ave.
Port Hueneme, CA 93043

10. SPONSORING/MONITORING AGENCY

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This operations manual describes when and how remediation by natural attenuation (RNA) should be implemented to remediate groundwater contaminated with petroleum hydrocarbons. The user is guided through the decision-making process to ensure that RNA will be protective of human health and the environment and that it will meet site cleanup goals for the intended use of the site, within a time frame that is reasonable compared to other remediation methods. This manual provides guidance on how to compare RNA to other technologies. However, the technical advantages and limitations of other technologies are beyond the scope of this manual. Comparisons of intrinsic remediation with other potentially applicable technologies for petroleum contamination are required under many regulatory programs to validate the selection of RNA and generally must be done on an individual site basis. After RNA is demonstrated to be viable for the site, a detailed comparison with other technologies should be made on the basis of standard criteria such as cost, implementability, short-term and long-term risk reduction, and the time required to meet remediation goals.

| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| Natural Attenuation (NA), Intrinsic Remediation, remediation for fuel hydrocarbons, Remediation by Natural Attenuation (RNA), Monitored Natural Attenuation (MNA) | 237 |
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| U | U | U | U |

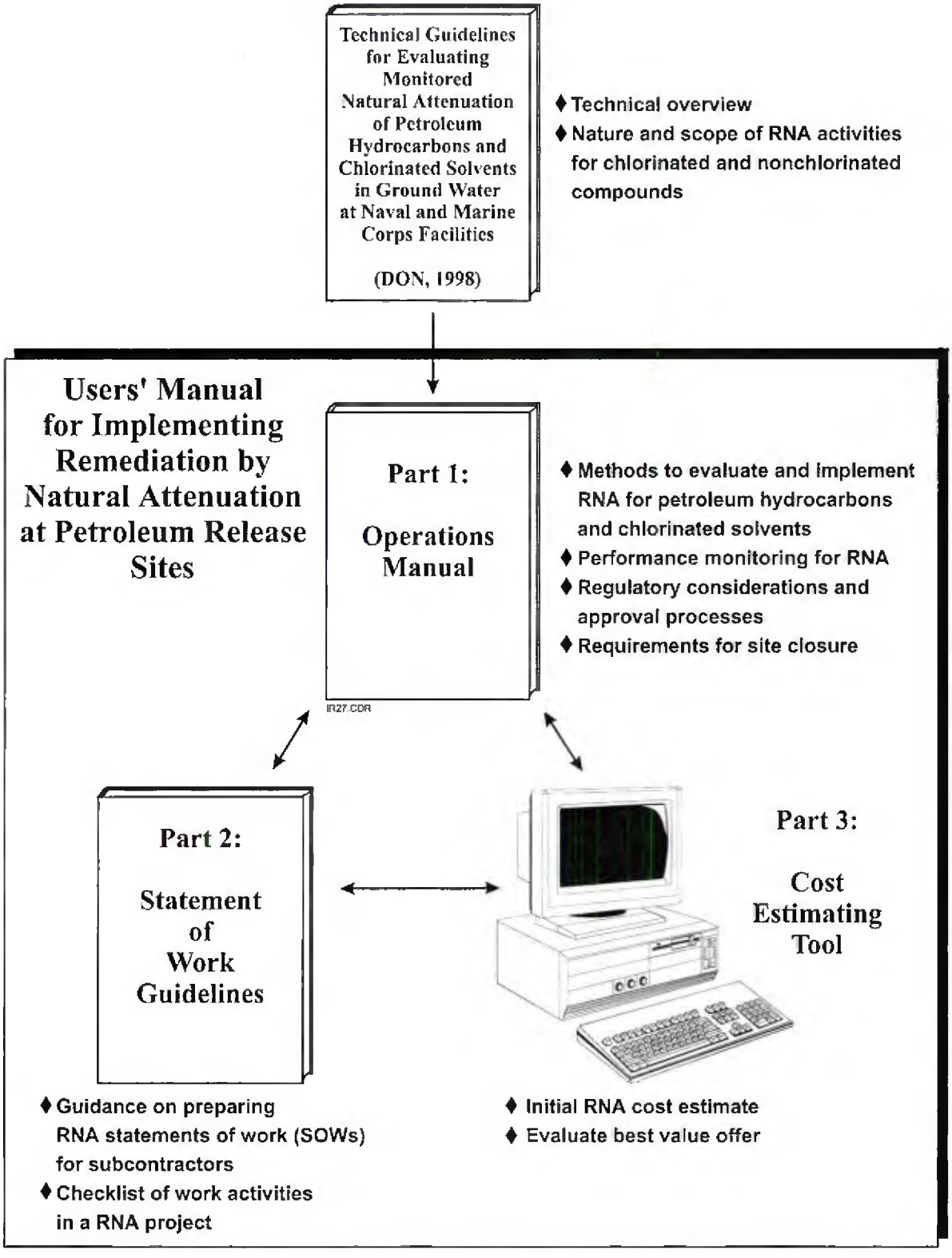


**Figure P-1. Tools for Implementing RNA at Navy and Marine Corps Sites.**

## PREFACE

Four tools on the subject of remediation by natural attenuation (RNA) have been developed by the Navy to assist Remedial Project Managers (RPM), Remedial Technical Managers (RTM), and other personnel responsible for selecting, designing, and implementing remediation of petroleum-contaminated groundwater at Navy and Marine Corps facilities.

***Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities*** (Department of the Navy [DON], 1998 (herein referred to as the Technical Gudielines). This document provides a concise overview of how RNA is used to remediate groundwater contaminated with fuel hydrocarbons or chlorinated solvents. The guidelines describe the biological processes involved in the degradation of petroleum hydrocarbons and chlorinated solvents, and explain how to recognize these processes in the field. This document was published separately, and can be obtained from the Naval Facilities Engineering Service Center (NFESC).

***User's Manual for Implementing Remediation by Natural Attenuation at Petroleum Release Sites – Part 1. Operations Manual*** (herein referred to as the Operations Manual). This document provides detailed instructions for implementing RNA at sites contaminated with fuel hydrocarbons, consistent with the Navy's companion *Technical Guidelines* document (DON, 1998).

***User's Manual for Implementing Remediation by Natural Attenuation at Petroleum Release Sites – Part 2. Statement of Work Guidelines*** (herein referred to as the Statement of Work Guidelines). This document assists RPMs, RTMs, and other Navy personnel in preparing the Statement of Work (SOW) that foster timely, concise, and cost-effective submissions from potential contractors, for RNA of fuel-contaminated groundwater.

***User's Manual for Implementing Remediation by Natural Attenuation at Petroleum Release Sites – Part 3. Cost Estimating Tool*** (herein referred to as the Cost Estimating Tool). This spreadsheet computer program provides a tool for developing a budget to implement RNA at sites with petroleum-contaminated groundwater.

The relationship between these documents is illustrated in Figure P-1. Although each of these documents was designed to stand alone, they should be used together to help Navy personnel and their contractors implement RNA at petroleum-contaminated sites.

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# USER'S GUIDE FOR IMPLEMENTING REMEDIATION BY NATURAL ATTENUATION AT PETROLEUM RELEASE SITES

## PART 1: OPERATIONS MANUAL

Prepared for:

Naval Facilities Engineering Command's

Naval Facilities Engineering Service Center
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May 1999

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 3-D | three-dimensional |
| AF | Air Force |
| AFB | Air Force Base |
| AFCEE | Air Force Center for Environmental Excellence |
| APHA | American Public Health Association |
| ARTT | Alternative Restoration Technology Team (of the Naval Facilities Engineering Command) |
| ASTM | American Society for Testing and Materials |
| BCF | bioconcentration factor |
| BRAC | Base Realignment and Closure |
| BTEX | benzene, toluene, ethylbenzene, and xylenes |
| CA | Corrective Action |
| CERCLA | Comprehensive Environmental Response, Compensation, and Liability Act |
| COC | contaminant of concern |
| CPT | cone penetrometer testing |
| DCA | dichloroethane |
| DO | dissolved oxygen |
| DOE | Department of Energy |
| EDB | ethylene dibromide |
| Eh | redox potential |
| EPA | U.S. Environmental Protection Agency |
| GC/MS | gas chromatography/mass spectrometry |
| GMS | Groundwater Modeling System |
| H | Henry's law constant |
| $H_2S$ | hydrogen sulfide |
| H&S | health and safety |
| IDW | investigation-derived waste |
| $K_d$ | soil or sediment sorption coefficient |
| $K_{oc}$ | organic carbon partition coefficient |
| $K_{ow}$ | octanol/water partition coefficient |
| LNAPL | light, nonaqueous-phase liquid |
| LTM | long-term monitoring |
| LUFT | leaking underground fuel tank |
| LUST | leaking underground storage tank |

| | |
|---|---|
| MCL | maximum contaminant level |
| MTBE | methyl-*tert*-butyl ether |
| mV | millivolt |
| NAPL | nonaqueous-phase liquid |
| NAS | Naval Air Station |
| NFESC | Naval Facilities Engineering Service Center |
| NRC | National Research Council |
| O&M | operations and maintenance |
| ORP | oxidation reduction potential |
| OSWER | Office of Solid Waste and Emergency Response |
| PAH | polycyclic aromatic hydrocarbon |
| PM | performance monitoring |
| POL | petroleum, oil, and lubricants |
| QA/QC | quality assurance/quality control |
| QAPP | Quality Assurance Project Plan |
| RBCA | Risk-Based Corrective Action |
| RCRA | Resource Conservation and Recovery Act |
| redox | oxidation-reduction |
| $R_f$ | retardation factor |
| RGD | reduced gas detector |
| RNA | remediation by natural attenuation |
| RPM | Remedial Project Manager |
| RTM | Remedial Technical Manager |
| S | solubility |
| SDWA | Safe Drinking Water Act |
| SOW | Statement of Work |
| SVE | soil vapor extraction |
| SVOC | semivolatile organic compound |
| TEAP | terminal electron acceptor process |
| TMB | trimethylbenzene |
| TOC | total organic compounds |
| TPH | total petroleum hydrocarbons |
| TPH-d | total petroleum hydrocarbons quantified as diesel |
| TPH-g | total petroleum hydrocarbons quantified as gasoline |
| USGS | U.S. Geological Survey |
| UST | underground storage tank |
| VFA | volatile fatty acid |
| VOC | volatile organic compound |

# 1.0 INTRODUCTION

This operations manual describes when and how remediation by natural attenuation (RNA) should be implemented to remediate groundwater contaminated with petroleum hydrocarbons. The user is guided through the decision-making process to ensure that RNA will be protective of human health and the environment and that it will meet site cleanup goals for the intended use of the site, within a time frame that is reasonable compared to other remediation methods. The manual is not intended to support RNA of chlorinated solvent plumes, plumes that contain mixtures of chlorinated solvents and petroleum hydrocarbons, plumes contaminated with heavy metals, or methyl-*tert*-butyl ether (MTBE) plumes.

This manual assumes that the user has completed an initial site characterization to identify contaminants of concern (COC) and determine the horizontal and vertical extent of contamination in soil and groundwater. If an initial site characterization has not been conducted, it should be the first step toward site remediation. While this manual does not directly address site characterization, it may serve as a useful guide for sites requiring characterization, to ensure that RNA-specific site data are collected.

This manual provides guidance on how to compare RNA to other technologies. However, the technical advantages and limitations of other technologies are beyond the scope of this manual. Comparisons of intrinsic remediation with other potentially applicable technologies for petroleum contamination are required under many regulatory programs to validate the selection of RNA and generally must be done on an individual site basis. After RNA is demonstrated to be viable for the site, a detailed comparison with other technologies should be made on the basis of standard criteria such as cost, implementability, short-term and long-term risk reduction, and the time required to meet remediation goals.

## 1.1 INTENDED AUDIENCE

This manual is intended for Navy Remedial Project Managers (RPM) and Remedial Technical Managers (RTMs) and for contractors involved with remediation of Navy and Marine Corps sites. The manual describes the necessary steps required to demonstrate and implement RNA at petroleum-release sites and provides guidance to RPMs and RTMs as they implement RNA directly or manage others to implement RNA for their sites.

## 1.2 ORGANIZATION OF THE RNA OPERATIONS MANUAL

The main text can be divided into two parts, the first consisting of Sections 1.0 and 2.0, which orient the reader to the document in particular and to the topic of RNA in general. The second part consists of Sections 3.0 through 6.0, which outline the process involved in implementing RNA at a site. Figures and sidebars appear throughout the document, highlighting important information and presenting specific examples. Checklists outlining the steps to be taken at each stage in the implementation of RNA can be found at the ends of Sections 4.0, 5.0, and 6.0. The contents of each section are described below.

***Section 1.0: Introduction to the RNA Operations Manual.*** This section introduces the reader to the operations manual. The manual objectives, intended audience, organization, and supporting sources of information on RNA are discussed.

***Section 2.0: Overview of Remediation by Natural Attenuation.*** This overview section introduces RNA to the user who may be unfamiliar with the technology. The application of RNA for petroleum-release sites is discussed to provide readers with sufficient background to understand the purpose of each activity described in this manual.

***Section 3.0: Overview of the Process for Implementing RNA at Navy Sites.*** Section 3.0 introduces the reader to the implementation process for RNA at petroleum release sites. A decision diagram that describes the overall implementation approach provides an overview of this process. The decision diagram divides the process into three major parts that are described in detail in Sections 4.0, 5.0, and 6.0.

***Section 4.0: Preliminary Assessment in Support of RNA.*** This section describes the preliminary assessment, which is the first step in implementing RNA at a site. The preliminary assessment is used to (1) screen out sites where RNA clearly is not appropriate, and (2) determine the need for additional field data and evaluation to verify RNA for the site. It involves the development of a conceptual site model to assess the need for interim corrective actions concurrent with or prior to implementing RNA, and to identify site-specific conditions that may preclude the use of RNA. This task concludes by developing a work-plan and establishing regulatory acceptance to proceed with a detailed evaluation of RNA.

***Section 5.0: Detailed Site Evaluation of RNA.*** The activities involved with conducting a detailed site evaluation and data collection in support of RNA are described in this section. Field data are collected to evaluate the status of the contaminant plume, verify the occurrence of contaminant reduction due to in-situ biodegradation, and demonstrate the protection of potential receptors. If the results demonstrate that RNA effectively protects receptors and reduces contamination to acceptable levels within a reasonable time frame, the site evaluation concludes by presenting the findings to regulatory authorities for acceptance of RNA.

***Section 6.0: Performance Monitoring and Site Closure.*** This section describes the final step in RNA, performance monitoring and site closure. Performance monitoring is required to ensure the protection of downgradient receptors, demonstrate a reduction in contaminant mass, compare measured COC levels with predicted levels, and demonstrate compliance with cleanup goals for site closure. In addition to performance monitoring, institutional controls such as land-use restrictions may be required while the site is undergoing remediation. Site closure involves documenting and reporting the performance monitoring results to regulatory authorities, establishing regulatory acceptance for closure, and documenting site closure in public records. Under some circumstances, site closure may be possible before final cleanup levels are achieved, provided that institutional controls are maintained.

***Section 7.0: References.*** This section provides complete references for the documents cited in the text.

***Appendices.*** *Appendix A* provides useful chemical and physical properties for common petroleum contaminants. *Appendix B* discusses modeling contaminant transport in support of RNA and the data requirements to support a contaminant transport model. *Appendix C* provides a statistical approach that can be used to evaluate historical contaminant data for statistically significant trends. *Appendix D* lists addresses and phone numbers for U.S. Environmental Protection Agency (EPA) regional underground storage tank (UST) offices and for state UST and leaking UST (LUST) offices.

## 1.3 RELATED SOURCES OF INFORMATION ABOUT RNA

A number of supporting references are available for the reader interested in learning more about RNA. Table 1-1 briefly describes several of these documents.

**Table 1-1. Selected Supporting Documents for RNA**

| Reference | Description |
|---|---|
| EPA. 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.* Directive 9200.4-17P. | Directive to U.S. EPA Regional Administrators clarifies EPA's policy regarding the use of monitored natural attenuation for the remediation of contaminated soil and groundwater at sites regulated under Office of Solid Waste and Emergency Response (OSWER) programs. |
| EPA. 1997. *Draft Region 4 Approach to Natural Attenuation of Chlorinated Solvents.* | Presents a technical protocol for data collection and analysis in support of RNA for groundwater contaminated with chlorinated solvents and mixtures of fuels and chlorinated solvents. |
| ASTM. 1997a. *Standard Guide for Remediation by Natural Attenuation at Petroleum Release Sites.* Draft Final. | Standard guide for determining the appropriateness of RNA and implementing RNA at petroleum-release sites. |
| Wiedemeier et al. 1995. *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater.* | Air Force (AF) protocol for data collection and analysis in support of RNA of petroleum-contaminated groundwater sites. Presents a technical course of action to scientifically document the occurrence and establish the effectiveness of RNA. |
| EPA. 1996. *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water.* | Proceedings of a 3-day symposium on natural attenuation of chlorinated solvents. Sponsored by the EPA, AF Armstrong Laboratory, and Air Force Center for Environmental Excellence (AFCEE). |
| EPA. 1994. *Symposium on Intrinsic Bioremediation of Ground Water.* | Proceedings of a 2-day symposium on Intrinsic Bioremediation. Sponsors included the EPA, the U.S. Geological Survey (USGS), and the AF. |
| NRC. 1993. *In Situ Bioremediation: When Does It Work?* | Presents technical requirements for intrinsic biodegradation. Compares requirements for RNA with requirements for engineered remediation. |
| McAllister and Chiang. 1994. "A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water." *Ground Water Monitoring and Review* | Gives hands-on guidance for monitoring of RNA sites. Describes primary indicators (plume status and background dissolved oxygen [DO] concentrations) and secondary indicators (geochemical data, microcosm studies, and modeling) used to evaluate RNA. |
| Buscheck and Alcantar. 1995. "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." | Presents case studies demonstrating two regression techniques for estimating first-order attenuation rates for shrinking plumes and first-order biodegradation rates for stable plumes, based on field data. |
| EPA. 1992a. *Bioremediation of Hazardous Wastes.* | Discusses bioremediation as an alternative to conventional methods of cleaning up hazardous wastes and presents a strategic plan for its acceptance and use by technical and regulatory communities. |
| EPA. 1995a. *Conducting Risk-Based Corrective Action for Federally Regulated UST Petroleum Releases.* | Specifies EPA Region 5 requirements for risk-based corrective actions (RBCA), including criteria for demonstrating the effectiveness of intrinsic remediation. |
| ASTM. 1995b. *Standard Guide for Risk-Based Corrective Action* (RBCA) *Applied at Petroleum Release Sites.* | Detailed guide for technical criteria to implement RBCA for environmental contaminants. Focuses on ecological and human-health risk-based decision making to establish and meet cleanup goals. |

## 2.0 OVERVIEW OF REMEDIATION BY NATURAL ATTENUATION

RNA is a passive remediation technology that can reduce the mass of petroleum hydrocarbons in groundwater to levels that do not pose an unacceptable threat to human health or the environment. It has been described by a variety of other terms, including intrinsic remediation, intrinsic bioremediation, monitored natural attenuation, passive remediation, and passive bioremediation. The use of the term RNA for this manual is taken from the ASTM *Standard Guide for Remediation by Natural Attenuation at Petroleum Release Sites* (ASTM, 1997a). In a directive describing the agency's policy for its use at Superfund and Resource Conservation and Recovery Act (RCRA) sites, the EPA recently referred to the technology as "Monitored Natural Attenuation," thereby emphasizing the need for careful site monitoring if implementation of RNA is to be successful (EPA, 1999).

For the purposes of this manual, RNA refers to the combined effect of several *naturally occurring processes*, including biodegradation, advection and dispersion, sorption, and volatilization, that act together to lower contaminant concentrations. The most important of these for petroleum hydrocarbons is biodegradation, because it is the only process that destroys contaminant mass. Through biodegradation, petroleum contaminants are degraded to $CO_2$ and $H_2O$, and the concentrations of the contaminants are significantly reduced. Although the other attenuating processes act to lower contaminant concentrations through physical and mechanical means, they do not destroy contaminant mass, and bring about only a limited reduction in contaminant concentrations. For this reason, RNA places greater emphasis on demonstrating *intrinsic biodegradation* of contaminants than on the physical/chemical attenuating mechanisms.

**Definition of remediation by natural attenuation (EPA, 1999)**

*A remedy where naturally occurring physical, chemical, and biological processes reduce contaminant levels to effectively protect human health and the environment and achieve remedial goals within a time frame that is reasonable compared to alternative technologies, without human intervention.*

This section provides the user with the following background information required to understand the tasks described in this operations manual and in the Navy's *Technical Guidelines* (DON, 1998) document:

- The advantages and limitations of RNA are described
- The COCs commonly associated with fuel-contaminated sites, and that are amenable to RNA, are identified.
- The regulatory framework in which RNA must be implemented is presented.
- The requirements for establishing the technical feasibility of RNA are described.
- Decision diagrams outlining the processes described in this manual for implementing RNA are provided.

The reader can refer to the Navy's companion document *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities* (DON, 1998) for further guidance on recognizing the occurrence of natural attenuation and evaluating natural attenuation processes.

## 2-1 ADVANTAGES AND LIMITATIONS OF RNA

As with any remedial technology, RNA has specific advantages and limitations. For treating petroleum contaminants, the advantages of RNA over active remediation methods include the following:

- ***RNA Results in the Destruction of Petroleum Hydrocarbons.*** RNA depends on the ability of microorganisms to degrade petroleum compounds to innocuous products such as $CO_2$ and $H_2O$. Thus, contaminant mass is reduced without being transferred to another medium such as granular activated carbon, and RNA does not result in the production of undesirable liquid or solid wastestreams that require additional treatment or disposal.

  The petroleum hydrocarbons that pose the greatest risk to human health and the environment due to their mobility and toxicity (i.e., benzene, toluene, ethylbenzene, and xylenes [the BTEX compounds]) tend to be the most strictly regulated petroleum hydrocarbon compounds. However, they also are easily biodegraded under aerobic conditions by microorganisms that occur naturally in the environment. Under anaerobic conditions, these compounds are degraded less readily.

- ***RNA Avoids Short-Term Risks.*** RNA reduces the potential for exposure of site workers and the public to contaminants during remediation compared to ex-situ treatment methods.

- ***RNA is Nonintrusive.*** RNA allows continuing use of the site infrastructure. RNA also may be used at inaccessible locations (e.g., below buildings) where engineered remedies could disrupt the existing infrastructure.

- ***RNA is Less Costly than Conventional Engineered Remediation Processes.*** Costs for conventional engineered processes typically are much higher than RNA costs.

- ***RNA Does Not Require Equipment Operations and Maintenance (O&M).*** Because RNA does not require equipment O&M, site remediation is not affected by equipment failure.

- ***RNA Can Be Combined with Other Remediation Technologies.*** RNA can be used effectively in conjunction with conventional remedial technologies such as pump and treat, air sparging, bioventing, bioslurping, and other technologies, thereby enhancing their performance and reducing overall remediation costs.

- ***RNA Can Be Evaluated Using Conventional Field Monitoring Methods.*** RNA can be evaluated by monitoring groundwater for easily measured chemical, biological, and hydrogeological parameters. If RNA alone cannot be used to protect receptors, the data collected for RNA can be used for conventional engineered processes.

The principal limitations of RNA for petroleum hydrocarbons include the following:

- ***Site Conditions Must Be Suitable for RNA.*** Prevailing site conditions must be suitable to support sufficient microbial activity so that contaminant concentrations are reduced to acceptable levels before potential receptors are affected.

- ***RNA May Require a Long Time to Meet Remediation Goals.*** Long periods may be required to achieve remediation objectives. In general, RNA is expected to take longer than active remediation.

- ***RNA Requires Performance Monitoring.*** Monitoring is required for several years, or until RNA meets remediation objectives for the site. Performance monitoring will prolong the owner's responsibility and expenditures for the site.

- ***The Groundwater Plume Characteristics and Site Hydrogeology Must Be Well Understood.*** The amount of site characterization required to demonstrate RNA effectiveness is greater than that required to implement most engineered technologies. Therefore, site characterization may be more costly for RNA. Insufficient information may preclude the use of RNA.

- ***Site Conditions Cannot Be Changed Significantly.*** Future land-use changes can affect the groundwater hydrogeology or otherwise increase the risk of human or environmental exposure to contaminants. Such changes may preclude RNA or require the reevaluation of RNA in the future. Thus, institutional controls may be necessary to ensure long-term protectiveness.

## 2-2 PETROLEUM CONTAMINANTS OF CONCERN (COC) AMENABLE TO RNA

In principle, RNA can be used for any contaminant that can be biodegraded to nontoxic byproducts or sufficiently attenuated by abiotic processes so that it does not pose an unacceptable threat to human health or the environment. In practice, RNA has been applied most commonly to remediate groundwater contaminated with petroleum hydrocarbons. The application of RNA for treatment of groundwater containing chlorinated compounds is increasing where biological transformation of these contaminants to nontoxic end products can be demonstrated. RNA also can be applied to soils and groundwater contaminated with inorganic contaminants where the existence of irreversible attenuating processes can be demonstrated (e.g., chemical precipitation during oxidation-reduction reactions).

This manual focuses on RNA of biodegradable petroleum hydrocarbons. However, it also applies to RNA for other organic contaminants that can be aerobically or anaerobically biodegraded. Table 2-1 shows the most common COCs occurring in the environment from uncontrolled petroleum releases. A more extensive list of petroleum contaminants is provided in Appendix A.

Due to their toxicity and mobility, the BTEX compounds tend to be among the most strictly regulated COCs at petroleum-release sites. However, because they are easily biodegraded in most environments, they are the most suitable candidates for RNA (ASTM, 1997a). Compared to the BTEX compounds, polycyclic aromatic hydrocarbons (PAH) are sparingly soluble and sorb strongly to soils, making them much less mobile in the environment. However, except for the two-ringed compound naphthalene, the in situ biodegradation of PAHs is very slow.

**Table 2-1. Common Contaminants of Concern Associated with Petroleum Releases**

| Contaminant | Unleaded Gasoline | Leaded Gasoline | Kerosene/ Jet Fuels | Diesel/Light Fuel Oils | Heavy Fuel Oils |
|---|---|---|---|---|---|
| Benzene | × | × | × | — | — |
| Toluene | × | × | × | — | — |
| Ethylbenzene | × | × | × | — | — |
| Xylenes (*m*-, *o*-, *p*-xylene) | × | × | × | — | — |
| Methyl-*tert*-butyl ether (MTBE) | when suspected | when suspected | — | — | — |
| Polycyclic aromatic hydrocarbons (PAH) | — | — | × | × | × |
| Lead, ethylene dibromide (EDB), 1,2-dichloroethane (DCA) | — | × | — | — | — |

From ASTM, 1995b; E1739-95)

MTBE is increasingly a cause for public and environmental concern, due to its potential toxicity, mobility in the environment, and relative recalcitrance to biodegradation under both aerobic and anaerobic conditions (Suflita and Mormile, 1993; Mormile et al., 1994). The presence of MTBE may render a site unsuitable for RNA. This manual does not specifically address RNA for MTBE. If MTBE is encountered, the reader should refer to the state or Federal requirements for MTBE remediation

Older gasoline spills also may include lead, ethylene dibromide (EDB), and/or 1,2-dichloroethane (DCA); historically, EDB and 1,2-DCA were commonly used as lead scavengers to reduce atmospheric emissions of lead and tetraethyl lead. RNA of lead and other heavy metals, 1,2-DCA, and EDB also are not discussed in this manual. If lead is encountered above background concentrations, the reader should refer to state or Federal requirements for lead remediation. For RNA of 1,2-DCA and EDB the reader is referred to the Navy's companion *Technical Guidelines* document (DON, 1998).

## 2.3 REGULATORY ACCEPTANCE OF RNA

In addition to establishing the technical basis for selecting RNA, the technology must be formally reviewed and accepted by regulators. Cleanup of petroleum hydrocarbon contamination resulting from USTs typically is regulated under state authority. Because many states do not have a formal policy for implementing RNA, the user should verify that the regulatory authority considers it to be an acceptable remediation method. If a site is regulated under a Federal UST or other program, RNA may have to meet provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or the RCRA Corrective Action (CA) process, which require screening and evaluation of several alternatives to support selection of a remedial alternative. The regulatory framework is determined by the nature of the waste, the spill event, and the regulatory assessment of the site. Typically, CERCLA addresses uncontrolled releases of hazardous substances often from facilities no longer in operation where contamination resulted from past practices; RCRA focuses on prevention and remediation for releases from currently operating facilities. For more information, refer to the U.S. Department of Energy (DOE) world-wide web site for RCRA and CERCLA guidance (http://www.em.doe.gov/rcracerc/index.html). The EPA released a directive that supports the use of RNA at federally regulated sites (EPA, 1997a).

The EPA generally finds RNA an acceptable remediation option if it can protect human health and the environment and can meet cleanup goals within an acceptable time frame (EPA, 1999). EPA's OSWER has developed an Interim Final Directive on RNA titled *Use of Monitored Natural Attenuation*

*at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (EPA, 1999). The directive includes the following key concepts:

- RNA is not a "do nothing" alternative and should not be considered a default or presumptive remedy at any contaminated site.

- RNA should be selected only where it meets all relevant remedy selection criteria, where it will be fully protective of human health and the environment, and where it will meet site remediation objectives within a time frame that is reasonable compared to other methods.

- In the majority of cases, RNA will be appropriate as one component of the total remedy, either in conjunction with active remediation or as a follow-up measure. Examples of appropriate active measures commonly required in combination with RNA include source control, treatment of media in high contaminant concentration areas while RNA is employed in the lower concentration areas, use of RNA as a follow-up to active remediation, and institution of controls.

- As with other remediation methods, RNA must be supported by detailed site-specific technical information that demonstrates the efficacy of this approach.

- Where the efficiency of RNA is highly uncertain, contingency measures should be incorporated into the remedy to ensure protection of potential receptors and attainment of the remediation objectives.

- Source control and performance monitoring (i.e., long-term monitoring) are fundamental components of any RNA program.

- Despite the relative ease with which BTEX contaminants tend to be biodegraded, other chemicals (e.g., MTBE) that are more resistant to biological or other degradation processes may also be present in petroleum fuels. In general, RNA is not an appropriate remediation option at sites where nondegradable contaminants are present at levels that pose an unacceptable risk to human health or the environment.

- EPA encourages the consideration of innovative approaches that may offer greater confidence and reduced remediation time frames at a modest additional cost.

The approach described in this manual requires evaluation of the applicability of RNA at multiple decision points. Because of the time, effort, and costs associated with evaluating and establishing a technical basis for RNA, early regulatory involvement is essential to gain approval for implementation. Appendix D includes a list of EPA regional UST program offices and state UST and LUST offices. Regulatory involvement is recommended at the following five points during an RNA project:

1. **Assess regulatory framework for RNA.** Determine whether there is a regulatory framework (formal or informal) for acceptance of RNA before implementing RNA. If no formal regulatory framework exists for RNA acceptance, determine whether the use of RNA can be negotiated with the regulatory authorities. RNA should be accepted in principle before investing time and resources into a technical evaluation of its effectiveness for site remediation.

2. **Gain early acceptance of RNA, based on a preliminary site assessment.** After conducting a preliminary, site-specific assessment of RNA, the results of the assessment should be presented for regulatory review and acceptance. Adequate data should be provided to demonstrate that contaminants do not pose an immediate or imminent threat to receptors and to show that site-specific physical and chemical conditions are amenable to RNA. This prevents the unnecessary expenditure of time, effort, and funds for detailed data collection and site evaluation without regulatory acceptance.

   If existing data are adequate to demonstrate that the plume is shrinking or stable, no further work may be required. Otherwise, the regulatory authority should be presented with a workplan that describes the technical approach proposed to document and establish the effectiveness of RNA at the site. Regulatory acceptance of the workplan for the evaluation of RNA ensures that an acceptable level of data will be collected and analyzed to support RNA.

3. **Gain acceptance of RNA based on a detailed site evaluation.** Upon receiving site-specific acceptance of RNA in principle, a detailed site evaluation involving field data collection and analysis is conducted in accordance with the approved workplan. If the data support the use of RNA, results of the detailed site evaluation must be presented to regulatory authorities for acceptance of RNA. Adequate data must be presented to demonstrate that the contaminants will not pose an adverse risk to human health and the environment, and that contaminant concentrations will be reduced to acceptable levels within a reasonable time frame.

4. **Gain acceptance of a performance monitoring plan.** Performance monitoring is required to demonstrate the long-term effectiveness of RNA. Regulatory acceptance of a performance monitoring program plan is generally required. The performance monitoring plan can be combined with the detailed site evaluation report (Item 3 above). Regulatory involvement throughout performance monitoring is necessary to keep authorities informed about the progress of RNA. A contingency plan also may be required as part of the plan.

5. **Gain acceptance for site closure.** After remedial goals have been met, regulatory acceptance will be required for final site closure.

## 2.4 EVALUATION OF IMMEDIATE OR IMMINENT THREATS TO RECEPTORS

A principal requirement for implementing RNA is that the site does not pose an immediate or imminent threat to receptors. An immediate threat occurs if a receptor already is impacted by contaminants at the site. An imminent threat occurs if a receptor potentially may be impacted within a short (e.g., 5-year) time period. If an immediate or imminent threat is perceived at the site, an interim remedial action may be required to reduce site risks to acceptable levels before RNA can be implemented. Interim actions could involve source removal and/or institutional controls to restrict land use and protect against human exposure to the contaminants while RNA is being implemented. Alternatively, interim actions could involve a more aggressive engineered remediation approach. Section 4.3 provides additional discussion of interim action requirements.

## 2.5 DEMONSTRATING THE TECHNICAL FEASIBILITY OF RNA

The effectiveness of RNA depends on a variety of site-specific factors, including the type of contaminant, its migration rate in groundwater, the proximity of receptors to the area of contamination, and the rate of contaminant attenuation. In general, the effectiveness of RNA is assessed by comparing the rate at which contaminant concentrations are attenuated to the rate at which the contaminants are

transported in the environment. Establishing the technical feasibility for RNA is incumbent upon the site owner before it can be implemented. Three primary requirements to establish the technical feasibility of RNA are (1) evidence that RNA is occurring, (2) a demonstration of the efficiency of RNA, and (3) a comparison of RNA with other remediation methods.

### 2.5.1 Demonstrating the Occurrence of RNA

To demonstrate the occurrence of RNA, a loss of contamination at the site must be documented, and the loss of contamination must be attributed to intrinsic biodegradation. There are two fundamental approaches for demonstrating a loss of contamination. One approach involves monitoring contaminant concentrations over time from wells inside the plume to demonstrate a statistically significant decrease in contamination at the site. This method provides the most convincing evidence of a loss of contamination. However, the time required to obtain sufficient data to demonstrate a meaningful trend varies among sites and may require several years of monitoring. The other approach involves collecting groundwater contaminant and geochemical data and correlating spatial characteristics of the contaminant plume with geochemical indicators of biological activity. These two approaches are not mutually exclusive and generally both are employed to demonstrate the occurrence and efficiency of RNA.

**Requirements to demonstrate the effectiveness of RNA**

1. *Demonstrate the Occurrence of Intrinsic Biodegradation*
   - Document loss of contamination
     - — Assess plume status as shrinking, stable, or expanding
     - — Compare measured to expected plume length
   - Link contaminant loss to biodegradation
     - — Correlate decrease in electron acceptors/increase in metabolic byproducts to contaminated area
     - — Measure spatial trends in other geochemical indicators (redox, alkalinity)
     - — Where primary field data are inconclusive, collect additional field data such as volatile fatty acids (VFA) or DO
     - — Where field data are inconclusive, conduct laboratory microcosms
2. *Evaluate the efficiency of RNA for the site*
   - Demonstrate long-term protection of human health and the environment
   - Estimate the time required to reach cleanup levels for the site
   - Verify that time to reach remediation goals is acceptable
3. *Compare RNA to alternative technologies*

**2.5.1.1 Demonstrate a Loss of Contamination.** A plume may be characterized as receding (shrinking), steady state (stable), or expanding. The first two characteristic plume configurations (shrinking and stable plumes) provide evidence that there has been a reduction in contaminant mass at the site. The third plume configuration (an expanding plume) requires additional evidence to establish that there has been a reduction in contaminant mass by demonstrating that the plume has migrated slower than would be expected without biodegradation.

**Shrinking plumes** are recognized by declining contaminant concentrations in monitoring wells and a decrease in the extent of the contaminated area. A shrinking plume provides evidence that the contaminant mass in the aquifer is decreasing and that RNA is occurring. Shrinking plumes occur after the source of contamination (i.e., free or residual nonaqueous-phase liquid [NAPL]) has been removed or substantially depleted, and bioremediation results in a net reduction in contaminant mass. If receptors are not at risk, a shrinking plume may be sufficient evidence to demonstrate RNA. Figure 2-1 shows an idealized example of a shrinking plume, recognizable from the decreasing plume size and the decreasing contaminant concentrations in a single well from three separate sampling events.

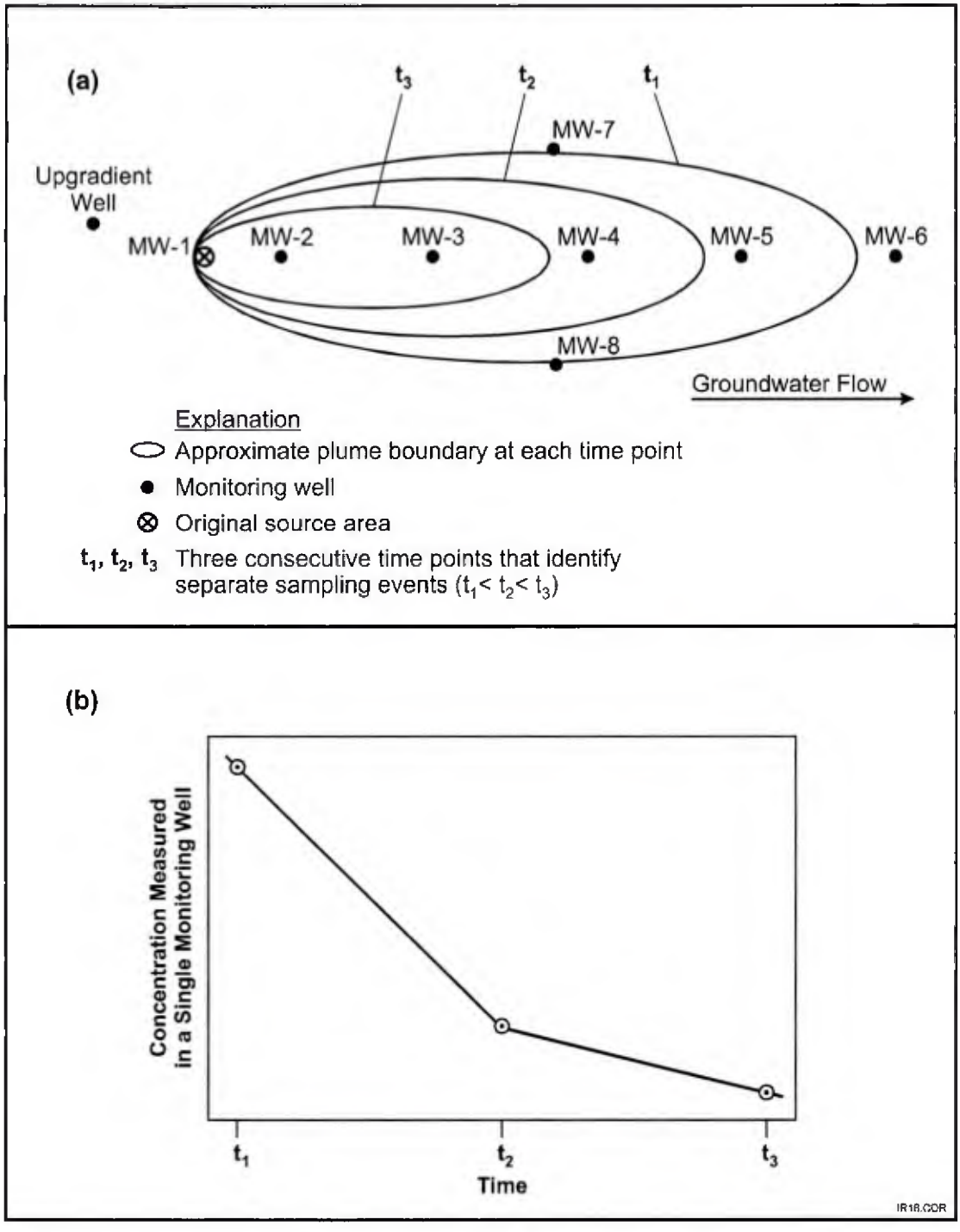



**Figure 2-1. Characteristic shrinking plume monitored on three separate sampling events ($t_1$, $t_2$, $t_3$). Part (a) shows that the plume boundaries recede over time. Part (b) shows that the contaminant concentrations in a single well decrease over time.**

**Stable plumes** are characterized by dissolved contaminant concentrations that remain constant over time in monitoring wells and by no observed change in the extent of the contaminated area. A stable plume develops when a contamination source releases COCs to the groundwater at the rate that the COCs are biodegraded, resulting in no net change in contaminant concentrations over time. This plume configuration provides evidence of intrinsic bioremediation, because without biodegradation the plume would continue to expand. Once the contamination source is exhausted, the plume will begin to recede and become a shrinking plume. A stable plume indicates that RNA is controlling plume migration and protecting downgradient receptors. Additional evidence may be required to verify the long-term protection of receptors, and to predict when the source of contamination will be depleted. Figure 2-2 shows an idealized example of a stable plume, recognizable from the stable plume size and stable contaminant concentrations in a single well from three separate sampling events.

**Expanding plumes** are recognized by increasing contaminant concentrations in monitoring wells and an increase in the extent of the contaminated area over time. An expanding plume indicates that the biodegradation rate is too slow to prevent contaminant migration, or that intrinsic biodegradation is not occurring. Figure 2-3 shows an idealized example of an expanding plume, recognizable from the increasing plume size and increasing contaminant concentrations in a single well from three separate sampling events.

Biodegradation in an expanding plume is demonstrated by comparing the measured plume length to the plume length that would be expected without biodegradation. Without biodegradation, the principal mechanisms that control contaminant migration and determine plume length are advection, dispersion, and sorption. If contaminants are being biodegraded, the plume will expand at a rate that is slower than would occur without biodegradation, and the resulting length of the plume will be smaller than what would be expected in the absence of biodegradation.

The plume length that would be expected without biodegradation can be estimated by means of a simple calculation if the approximate date of the release is known. In such a case, the length of the plume will be equal (roughly) to the velocity of the contaminant in the groundwater multiplied by the time that has elapsed since the release occurred (Equation 2-1), i.e.,

$$L = V_c \times T \qquad (2\text{-}1)$$

where: L = plume length without biodegradation
Vc = velocity at which the contaminant travels in the groundwater (L/T)
T = time since release occurred

The contaminant velocity can be estimated using the groundwater flowrate ($V_x$) at the site and the retardation factor ($R_f$) for the contaminant of interest. These terms are defined in Appendix B. If significant biodegradation is occurring, there should be an observable difference between the measured plume length and the expected plume length without biodegradation (Figure 2-4).

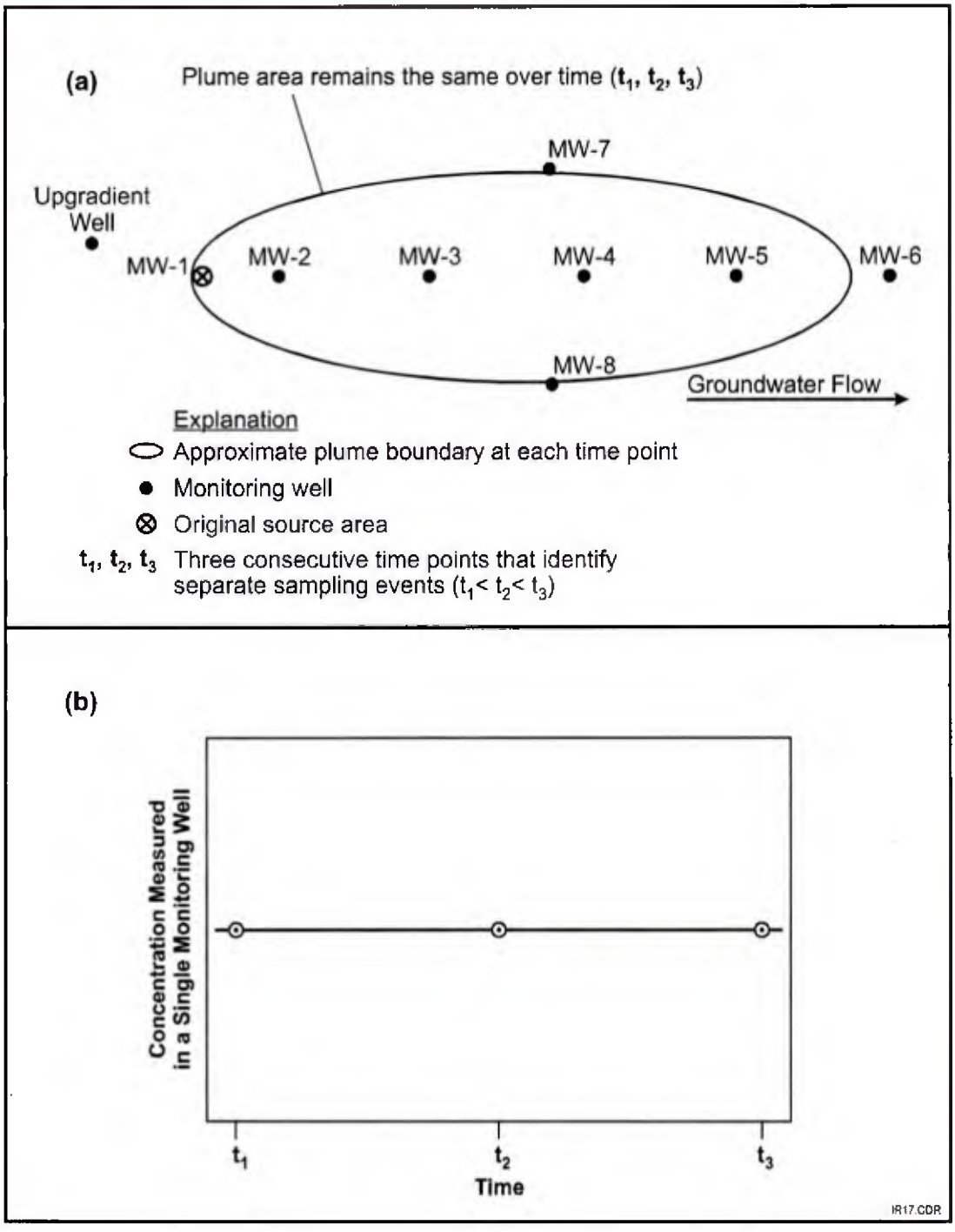



**Figure 2-2. Characteristic stable plume monitored on three separate sampling events ($t_1$, $t_2$, $t_3$). Part (a) shows that the plume boundaries remain constant over the three sampling events. Part (b) shows that the concentrations in a single well remain unchanged over time.**

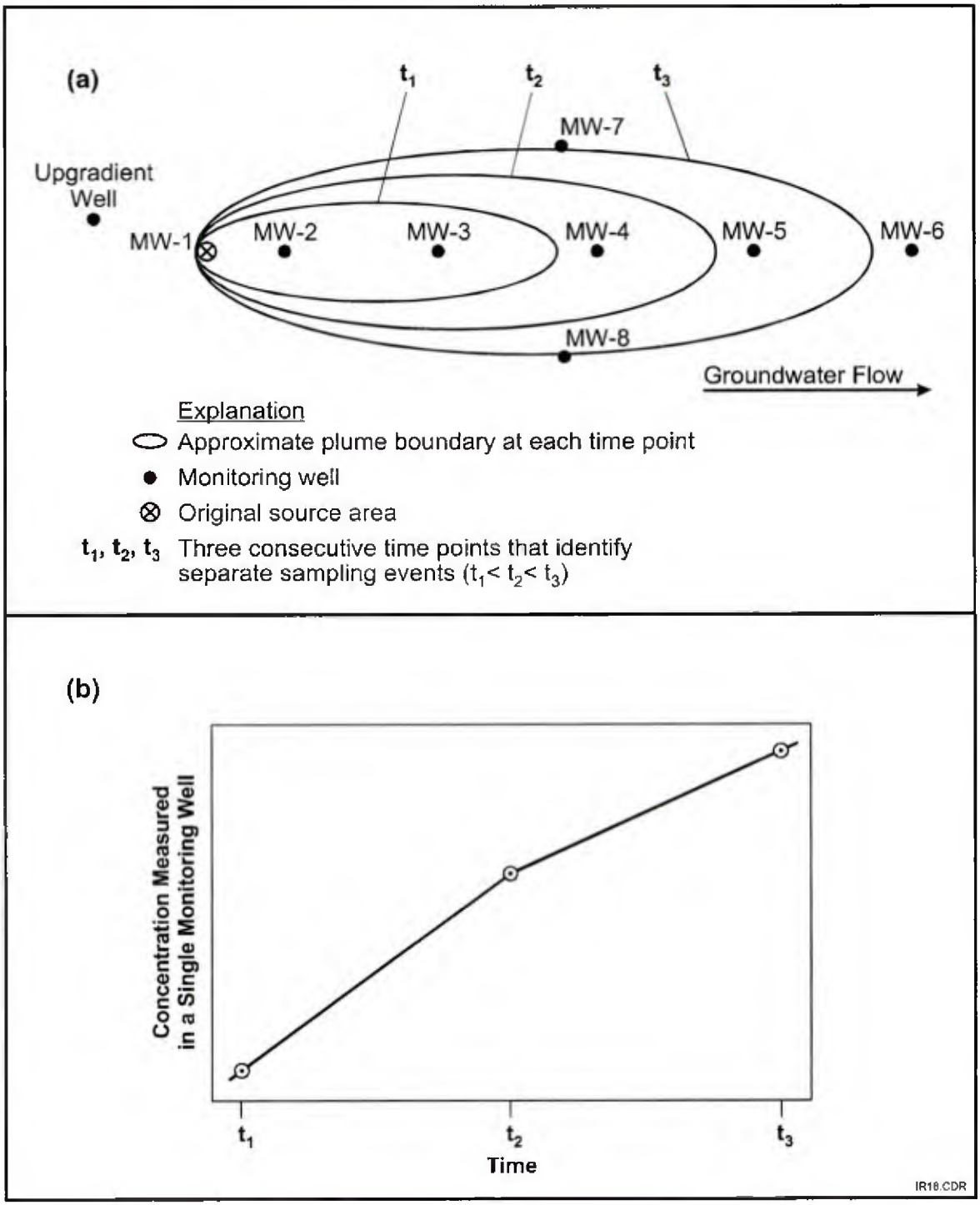



**Figure 2-3. Characteristic expanding plume monitored on three separate sampling events ($t_1$, $t_2$, $t_3$). Part (a) shows that the plume boundaries are expanding over time. Part (b) shows that the concentrations in a single well at the leading edge of the plume are increasing over time.**

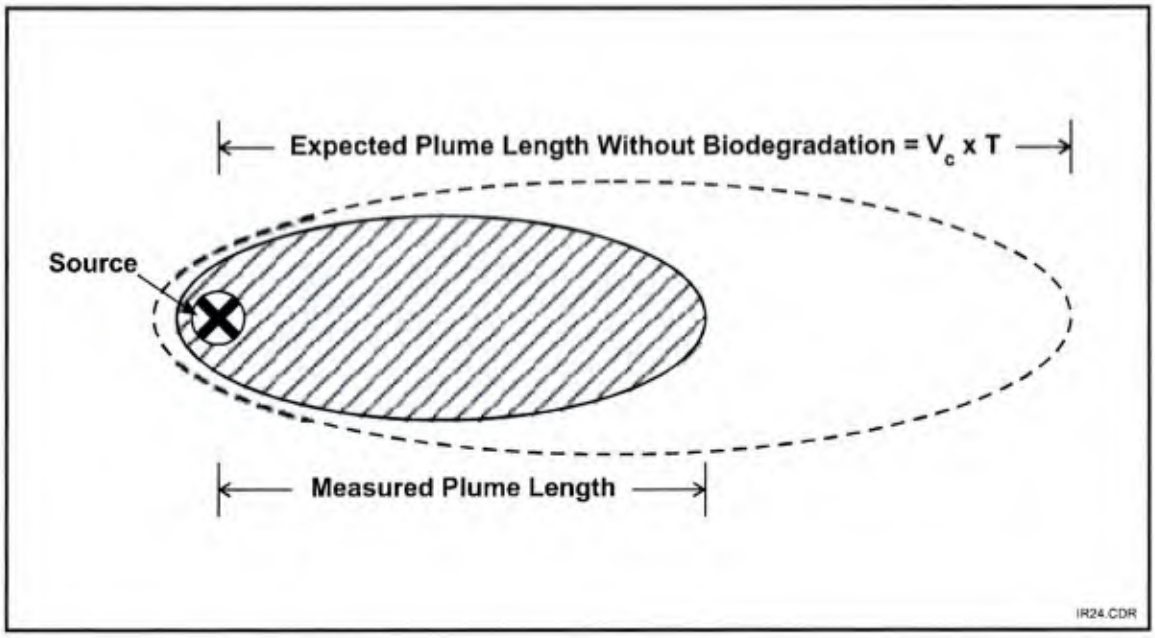



**Figure 2-4. Recognizing contaminant loss in an expanding plume.**

### 2.5.1.2 Demonstrate that COCs at the Site Are Being Biodegraded

***Geochemical Indicators of Biodegradation.*** Biodegradation brings about predictable changes in the chemistry of the groundwater as a result of microbial metabolism. For example, an observable loss of electron acceptors or accumulation of metabolic byproducts in the contaminated area of the aquifer provides compelling evidence that bioremediation is occurring in-situ. Therefore, a common goal of natural attenuation assessments is to determine if there is a spatial correlation between the concentrations of contaminants and these geochemical indicators (i.e., electron acceptors or metabolic byproducts) of biodegradation.

A detectable **loss of electron acceptors** in the contaminated area is a sign that biologically facilitated oxidation-reduction (i.e., redox) reactions have occurred. An oxidation reaction is defined as the removal of an electron, and a reduction reaction is defined as the addition of an electron to a chemical substrate. In petroleum-contaminated groundwater plumes, the contaminants serve as electron donors that are oxidized while compounds such as oxygen, nitrate, manganese, iron, sulfate, and carbon dioxide serve as electron acceptors and are reduced. As microorganisms consume contaminants, there is a corresponding consumption of the compounds that serve as electron acceptors. During aerobic respiration, oxygen serves as the terminal electron acceptor; consequently, the concentration of DO in the contaminated area will decrease when contaminants are biodegraded. Under anaerobic conditions, alternative compounds such as nitrate, manganese(IV), iron(III), sulfate, or carbon dioxide serve as the electron acceptors. Measurable depletions of nitrate or sulfate in the area of contamination indicate the use of nitrate or sulfate as an electron acceptor for contaminant degradation.

**Simplified equations for microbial metabolism of organic contaminants**

The general equation for contaminant biodegradation may be defined as:

organic contaminant (electron donor) + electron acceptor + nutrients + microorganisms
→ metabolic byproducts + growth of more microorganisms + $CO_2$ + $H_2O$ (2-2)

For example, BTEX degradation via sulfate reduction yields the following equation:

BTEX + sulfate + nitrogen and phosphorus + sulfate-reducing bacteria
→ $H_2S$ + more sulfate-reducing bacteria + $CO_2$ + $H_2O$ (2-3)

An **accumulation of metabolic byproducts** in the contaminated area can be another indication of contaminant biodegradation. Increased concentrations of reduced ferrous iron ($Fe^{2+}$) or reduced manganese ($Mn^{2+}$) in the contaminated portion of the aquifer indicate the use of ferric iron ($Fe^{3+}$) or manganese ($Mn^{+4}$) as electron acceptors for contaminant biodegradation, respectively. Similarly, hydrogen sulfide ($H_2S$) and methane accumulation may be used to demonstrate contaminant biodegradation under sulfate-reducing or methanogenic conditions, respectively. Methanogenesis will correspond to the most anoxic zones in the aquifer, resulting from intrinsic contaminant biodegradation in the aquifer.

Table 2-2 shows expected changes in electron acceptor or metabolic byproduct concentrations resulting from specific terminal electron acceptor processes (TEAP). At most petroleum-contaminated sites, both aerobic and anaerobic biodegradation processes will be active in different portions of the contaminated area. However, each TEAP requires a corresponding supply of electron acceptors in the groundwater; therefore, not all TEAPs will occur at every site. For example, Baedecker et al. (1993), Eganhouse et al. (1993), and Bennett et al. (1993) documented the occurrence of aerobic respiration, iron reduction, and methanogenesis as the primary mechanisms of biodegradation at the Bemidji, Minnesota crude oil spill. Nitrate reduction and sulfate reduction were not important anaerobic biodegradation mechanisms at this site due to low groundwater nitrate and sulfate concentrations.

**Table 2-2. Trends in Analyte Concentrations During Biodegradation**

| Analyte | Terminal Electron Acceptor Process | Concentration Trend During Biodegradation |
|---|---|---|
| **Electron Donor** | | |
| Contaminant (e.g., TPH, BTEX, etc.) | | Decrease |
| **Electron Acceptors** | | |
| Dissolved oxygen (DO) | Aerobic respiration | Decrease |
| Nitrate ($NO_3^-$) | Denitrification | Decrease |
| Sulfate ($SO_4^{=}$) | Sulfate reduction | Decrease |
| **Metabolic Byproducts** | | |
| Iron(II) ($Fe^{2+}$) | Iron(III) reduction | Increase |
| Manganese ($Mn^{2+}$) | Manganese reduction | Increase |
| Sulfide ($H_2S$) | Sulfate reduction | Increase |
| Methane ($CH_4$) | Methanogenesis | Increase |

Oversupply of an electron acceptor or chemical precipitation of electron-acceptor byproduct may preclude its use in verifying in-situ contaminant degradation. For example, sulfate concentrations are in excess of 5,000 mg/L at an ongoing RNA evaluation at the Naval Air Station Fallon (NAS Fallon),

Nevada. At this site, decreases in groundwater sulfate concentrations due to contaminant biodegradation are small compared to the variability in background concentrations, making it virtually impossible to correlate sulfate depletion with contaminant biodegradation. Furthermore, iron present at high concentrations results in the precipitation of sulfide, making hydrogen sulfide ($H_2S$) detection virtually impossible. As a result, alternative electron acceptors must be investigated to demonstrate BTEX biodegradation at this site.

**Other geochemical parameters** that can provide evidence of in-situ RNA include redox potential (Eh) and alkalinity. The Eh of groundwater is a measurement in millivolts (mV) of the relative tendency of a solution to accept electrons (Stumm and Morgan, 1996). Redox reactions in groundwater are influenced by groundwater chemistry or biologically active processes. In groundwater contaminated with petroleum hydrocarbons, biological activity will determine the Eh of the groundwater, ranging from –250 mV under methanogenic conditions to +800 mV under aerobic conditions. Figure 2-5 illustrates the Eh values at pH 7 and 25°C, for the different TEAPs discussed above.

Bacteria gain the most energy from aerobic respiration, and progressively less from each TEAP as Eh becomes more negative. In the environment, TEAPs typically proceed in the order of maximum energy gain for microorganisms, and begin with aerobic respiration, followed sequentially by nitrate, manganese, iron, and sulfate reduction, and ending with methanogenesis. This sequence of reactions can result in the characteristic sequential appearance of electron acceptor processes, as shown in Figure 2-6. Patterns like those shown in Figure 2-6 can be used to show that biodegradation of dissolved contamination is occurring. However, it should be noted that most sites will contain a wide variety of bacteria and TEAPs. In situ, TEAPs commonly overlap, and multiple overlapping TEAPs may be observed in a plume, particularly near the source area where biological activity is highest.

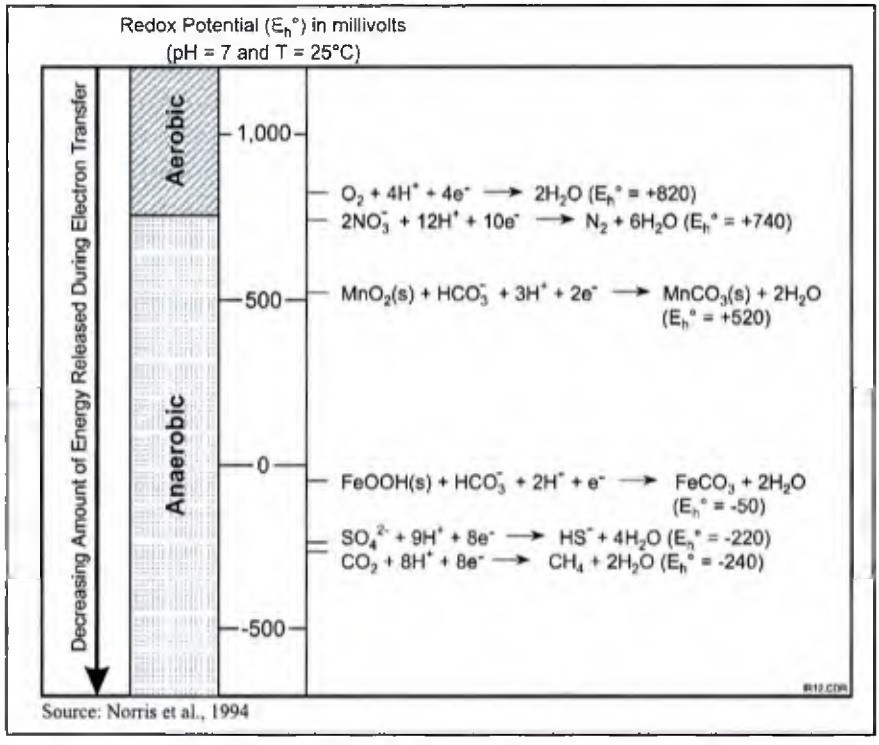



**Figure 2-5. TEAPs and corresponding redox potentials. (Modified from Norris et al., 1994)**

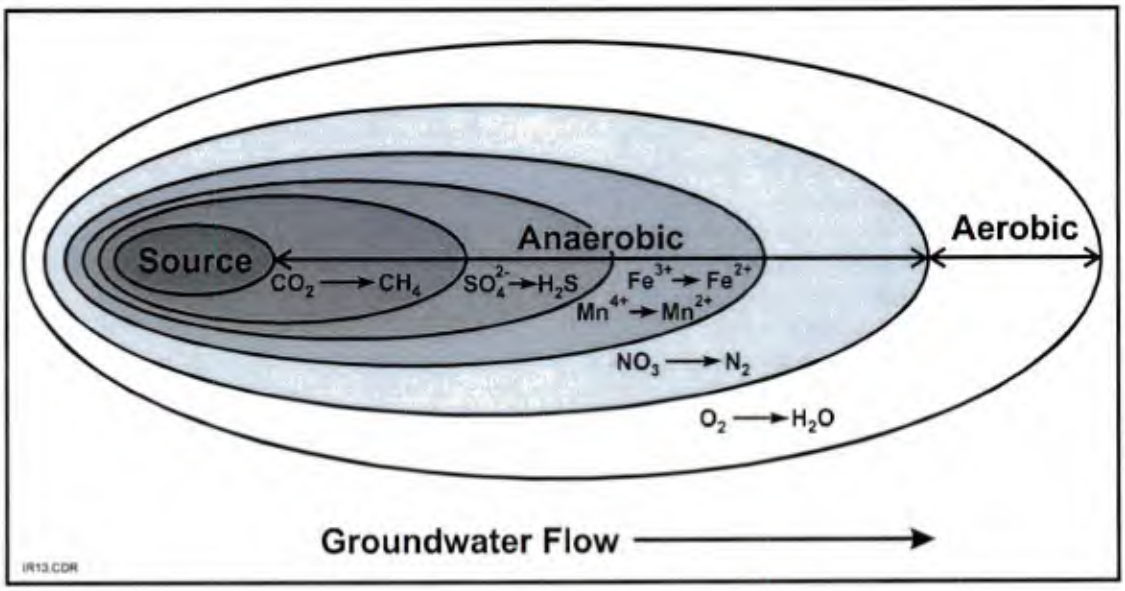



**Figure 2-6. Groundwater TEAP zones resulting from the preferred use of electron acceptors during contaminant biodegradation.**

Another indicator of biodegradation is alkalinity; in general, the total alkalinity will increase with the amount of BTEX oxidized under anaerobic conditions. Anaerobic processes such as nitrate, iron, manganese, and sulfate reduction will cause an increase in alkalinity due to the assimilation of hydrogen ions (see Table 2- 3). Consequently, alkalinity in the groundwater can be compared to the contaminant distribution to demonstrate a correlation between increased alkalinity and increased contaminant concentrations, as evidence of in situ contaminant biodegradation.

**Table 2-3. Biological Processes Affecting Alkalinity**

| Process | Alkalinity Change |
|---|---|
| Aerobic respiration<br>$O_2 + CH_2O \rightarrow CO_2 + H_2O$ | No net change in alkalinity per mole of oxygen reduced. |
| Denitrification<br>$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$ | Alkalinity increases by 1 equivalent per mole of nitrate reduced. |
| Iron reduction<br>$4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_2O$ | Alkalinity increases by 2 equivalents per mole of amorphous iron reduced. |
| Manganese reduction<br>$2MnO_2 + CH_2O + 4H^+ \rightarrow 2Mn^{2+} + CO_2 + 3H_2O$ | Alkalinity increases by 2 equivalents per mole of amorphous manganese reduced. |
| Sulfate reduction<br>$SO_4^= + 2CH_2O + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O$ | Alkalinity increases by 2 equivalents per mole of sulfate reduced. |
| Methanogenesis<br>$2CH_2O \rightarrow CH_4 + CO_2$ | No net change in alkalinity per mole $CH_4$ produced. |

***Laboratory Evidence of Intrinsic Biodegradation.*** Laboratory evidence of intrinsic biodegradation can be obtained using microcosm studies or microbial counts of heterotrophic and hydrocarbon-degrading bacteria. Laboratory microcosm studies provide strong evidence of in-situ biodegradation by demonstrating

that the microorganisms present at the site can degrade site contaminants. Typical microcosm studies involve taking representative aquifer samples from the site to the laboratory, spiking the samples with known amounts of the COCs, and monitoring the samples for contaminant loss. Control microcosms are used to ensure that the measured contaminant loss is biologically mediated.

In general, laboratory microcosm studies are used as a last resort because they are perceived as time consuming and expensive, and because they may not accurately represent site conditions. However, if the tests are properly conducted, they can provide very convincing supporting evidence of contaminant biodegradation.

Microbial counts of total heterotrophic bacteria can be used to indicate that RNA is taking place. In general, the proportion of heterotrophic degraders will be greater within the area of contamination than outside the plume boundaries due to biological growth stimulated by contaminant biodegradation. While microbial counts can provide indirect evidence of contaminant biodegradation, they are commonly used to supplement field data, along with laboratory microcosms, to provide evidence that contaminant losses are biological.

***Specialized Field Analyses.*** Specialized field analyses include monitoring for dissolved hydrogen ($H_2$) or VFA metabolites of petroleum degradation. Under anaerobic conditions, $H_2$ is produced continuously by fermentative microorganisms. The $H_2$ is then used by anaerobic respiring organisms, including, most commonly, organisms that use Fe(III), Mn (III) sulfate, and carbon dioxide as terminal electron acceptors (Chapelle et al., 1997). Each of these TEAPs has a unique affinity for $H_2$, producing predictable steady-state dissolved $H_2$ concentrations in the groundwater. Methanogens have the lowest affinity for $H_2$, resulting in the highest steady-state $H_2$ concentrations, followed by sulfate reducers, iron reducers, and lastly nitrate reducers. The expected steady-state $H_2$ concentrations in groundwater as a function of the terminal electron acceptor process is discussed in greater detail in Section 5.1.5.1.

Hydrogen can be used to indicate which anaerobic TEAPs are operating in the environment. The distribution of these processes can be correlated with contaminant concentrations in the environment to establish contaminant biodegradation by natural attenuation. The use of the $H_2$ may not be required, if geochemical indicators and other field data provide sufficient evidence of contaminant biodegradation and the corresponding TEAPs.

Like $H_2$, VFAs are produced during anaerobic fermentation of organic substrates (Grbic-Galic, 1990; Schink, 1992). Some VFAs are specific petroleum hydrocarbon metabolites, such as benzylsuccinate, which is a product of anaerobic benzene fermentation. Thus, the presence of VFAs, especially VFAs that can be *linked directly* to the anaerobic degradation of petroleum hydrocarbons, is a direct indication of anaerobic biological degradation of petroleum contaminants. However, unlike $H_2$, TEAPs do not result in predictable VFA concentrations, and VFA concentrations cannot be linked with specific TEAPs. The use of VFAs is relatively new, and few laboratories are equipped to analyze them. However, they provide strong qualitative evidence of intrinsic biodegradation and their use is gaining interest and attention. Their use is optional and should be considered only if other indictor parameters provide insufficient evidence of BTEX degradation.

### 2.5.2 Evaluating the Efficiency of RNA

This part of the evaluation involves demonstrating that RNA meets two criteria: RNA must protect human health and the environment, and it must meet cleanup requirements within a reasonable time frame compared to alternative technologies (EPA, 1999). These two components define the efficiency of RNA for a site. In other words, it is not sufficient to know only that natural attenuation is occurring at a site; RNA will be held to the same regulatory standards as any other remedial technology.

A model may be required to predict the future migration and concentrations of the COCs. Modeling tools vary in complexity from an easily applied analytical equation to sophisticated numerical groundwater flow and transport codes. The requirement for and choice of modeling tools depends on site-specific conditions (e.g., the variability of the aquifer hydraulic properties), the amount of data available to support the modeling analysis, and perceived risks to receptors. Modeling requirements and types of models are discussed in Section 5.2.2. The data required to establish contaminant fate-and-transport parameters and to construct a model are discussed in Appendix B.

**2.5.2.1 Demonstrate Long-Term Protection of Human Health and the Environment.** Establishing the long-term protection of human health and the environment using RNA requires an assessment of the potential for contaminants to reach sensitive receptors at unacceptable levels. Short-term (immediate and imminent) concerns must be addressed in order to allow sufficient time to evaluate the effectiveness of RNA for a site. Once the evaluation is completed and RNA is implemented, long-term protection of human health and the environment must be ensured by performance monitoring. Depending on the risk of long-term exposure, sites with demonstrable long-term risks may require alternative approaches in conjunction with RNA to adequately protect downgradient receptors.

Two methods may be used to demonstrate that RNA will be protective of human health and the environment. The first method involves historical monitoring, and the second involves contaminant fate-and-transport modeling. Historical data may be sufficient to demonstrate the protection of downgradient receptors. For example, using data from two sampling events in 1992 and 1994, Doyle et al. (1995) demonstrated a decrease in BTEX plume volume and mass, and strong correlations between the distribution of electron acceptors and the groundwater contaminant concentrations. These two pieces of information provided evidence of a shrinking plume caused by microbial activity, and were sufficient to convince regulatory authorities that contaminants would not migrate away from the site and impact potential receptors.

Models are the best tools for predicting the extent of contaminant migration when field data show that the plume has not stabilized. If modeling is necessary, an exposure assessment should be conducted to identify any potential receptors that could be affected by the migrating plume (see Section 4.2.3). The modeling should determine whether the contaminant plume will reach receptors before being degraded and may be used to estimate the time required for remediation using RNA. In spite of their usefulness for understanding the fate and transport of environmental contaminants, models should be used with discretion. As much as possible, field data should be used to establish trends in contaminant concentrations and plume migration.

**2.5.2.2 Estimate Time to Achieve Cleanup Requirements.** Often ignored as a remedial goal, an estimate of the overall time for RNA to meet remedial goals may be required to gain regulatory acceptance of RNA. RNA may take years or decades to achieve site remediation goals. Depending on the intended use of the site, this time frame may not be acceptable. RNA by itself may have limited application at some Navy Base Realignment and Closure (BRAC) sites. A recent EPA policy memorandum (EPA, 1999) states:

> "At some sites, natural attenuation may be sufficiently effective so as to be capable of achieving remediation objectives without the aid of other (active) remedial measures. [However], EPA encourages the consideration of innovative approaches which may offer greater confidence and reduced remediation timeframes at a modest additional cost.
>
> Contaminated groundwaters should be returned to "their beneficial uses wherever practicable, within a time frame that is reasonable given the particular circumstances of

the site." When restoration of groundwater is not practicable, EPA generally expects to "prevent further migration of the plume, prevent exposure to the contaminated groundwater, and evaluate further risk reduction."[1]

Thus, cost is not necessarily the prevailing consideration for technology selection. The time required to remediate the site also will impact the selection. Site remediation objectives must be met within a time frame that is reasonable and acceptable compared to other methods and for the intended use of the site.

## 2.6 COMPARISON OF RNA WITH OTHER TECHNOLOGIES

A comparison of RNA with other potentially applicable technologies is required under many regulatory frameworks and provides a baseline to validate the selection of RNA. Even if comparative screening is not required, there is a precedent for screening and evaluating technologies by comparison to clearly document the method and basis for selection. Technologies should be compared on the basis of effectiveness, implementability, and cost (EPA, 1988a; EPA, 1991e). Effectiveness measures the ability of the alternative to protect human health and the environment both during the remediation (short-term effectiveness) and after cleanup goals are achieved (long-term effectiveness), and includes time to achieve remediation objectives. Implementability measures the technical and administrative feasibility of installing and operating a technology. Cost includes capital and O&M costs, but may be of secondary importance compared to effectiveness and implementability.

The technology evaluation should consider the potential to apply natural attenuation alone or in combination with other technologies as part of a treatment train (EPA, 1999). Conditions at some sites may prevent RNA alone from achieving acceptable cleanup goals, whereas alternative remedial technologies may be able to correct the factor limiting the capabilities of RNA, but not achieve final cleanup. For example, natural attenuation alone is unlikely to be effective when free product is present, but most free-product recovery technologies can be combined with RNA. Sometimes, further source reduction by enhanced aerobic biodegradation (e.g., bioventing) will be required to reduce the risk of contaminant migration to downgradient receptors, or to reduce the remediation time. Combining other remediation alternatives with RNA may reduce the time required for cleanup without significantly impacting the cost of remediation; shortened time frames will reduce long-term operating costs incurred during performance monitoring for RNA.

[1] This is a general expectation for remedy selection in the Superfund program, as stated in the National Oil and Hazardous Substances Pollution Contingency Plan; Final Rule (NCP) at §300.430 (a)(1)(iii)(F).

# 3.0 OVERVIEW OF THE STEPS INVOLVED IN IMPLEMENTING RNA AT NAVY SITES

This operations manual includes four decision diagrams designed to aid the user in implementing each of the major steps in RNA. Figure 3-1 shows a decision diagram that describes the overall approach for RNA at petroleum release sites and divides the process into three parts, describing the major steps required to implement RNA. The major steps are described in detail in Sections 4.0, 5.0, and 6.0, where they are accompanied by the following decision diagrams: Preliminary Assessment in Support of RNA (Figure 4-1); Detailed Site Evaluation in Support of RNA (Figure 5-1); and Performance Monitoring and Site Closure for RNA (Figure 6-1). In the preliminary assessment the user must determine whether RNA is applicable and appropriate for the site using *existing* data. In the detailed evaluation the user must conduct a *detailed site evaluation* to demonstrate that RNA will meet cleanup objectives established for the sites. The last step involves *performance monitoring* of RNA followed by *site closure* once cleanup objectives have been met.

The preliminary assessment involves the careful review and analysis of existing data to identify COCs and the existing extent of contamination, to screen out sites where RNA clearly is not appropriate, and to determine the need for additional field data to verify RNA for the site. The preliminary assessment includes two decision points at which the user must decide whether to proceed with RNA. The first decision point asks the user whether RNA is applicable based on the existing data. While insufficient data may be available to positively confirm the applicability of RNA, the user should pay careful attention to conditions that may preclude the use of RNA, such as if a receptor is negatively impacted by contaminants, resulting in immediate and unacceptable risks to human health or the environment. The second decision point asks whether regulatory acceptance has been obtained to proceed with an RNA site investigation. Regulators at this stage will not necessarily approve RNA for the site but should accept it as a possibility so that the user may safely proceed with the detailed site investigation for RNA.

In the detailed evaluation, field data are collected to evaluate the status of the contaminant plume, verify the occurrence of contaminant reduction due to in-situ biodegradation, and demonstrate the protection of potential receptors. If the results demonstrate that RNA effectively protects receptors and reduces contamination to acceptable levels within a reasonable time frame, the evaluation concludes by presenting the findings to regulatory authorities for acceptance of RNA.

The detailed site evaluation includes two decision points, analogous to the decision points in the preliminary assessment. The first decision point asks the user whether RNA is expected to meet the remedial goals based on the data collected during the investigation. At this stage, the data should conclusively support the use of RNA and should demonstrate the protection of human and environmental receptors. The second decision point asks whether regulatory acceptance for RNA has been obtained, assuming the first decision point is answered affirmatively. If the regulators do not approve the use of RNA, the user must decide whether to collect additional data in support of RNA or to abandon RNA as a technology option.

Performance monitoring is required to ensure the protection of downgradient receptors, demonstrate a reduction in contaminant mass, compare measured COC levels with predicted levels, and demonstrate compliance with cleanup goals for site closure. In addition to performance monitoring, the site is monitored to ensure that it conforms with institutional controls established for the site. Site closure involves documenting and reporting the performance monitoring results to regulatory authorities, establishing regulatory acceptance for closure, and documenting site closure in public records.

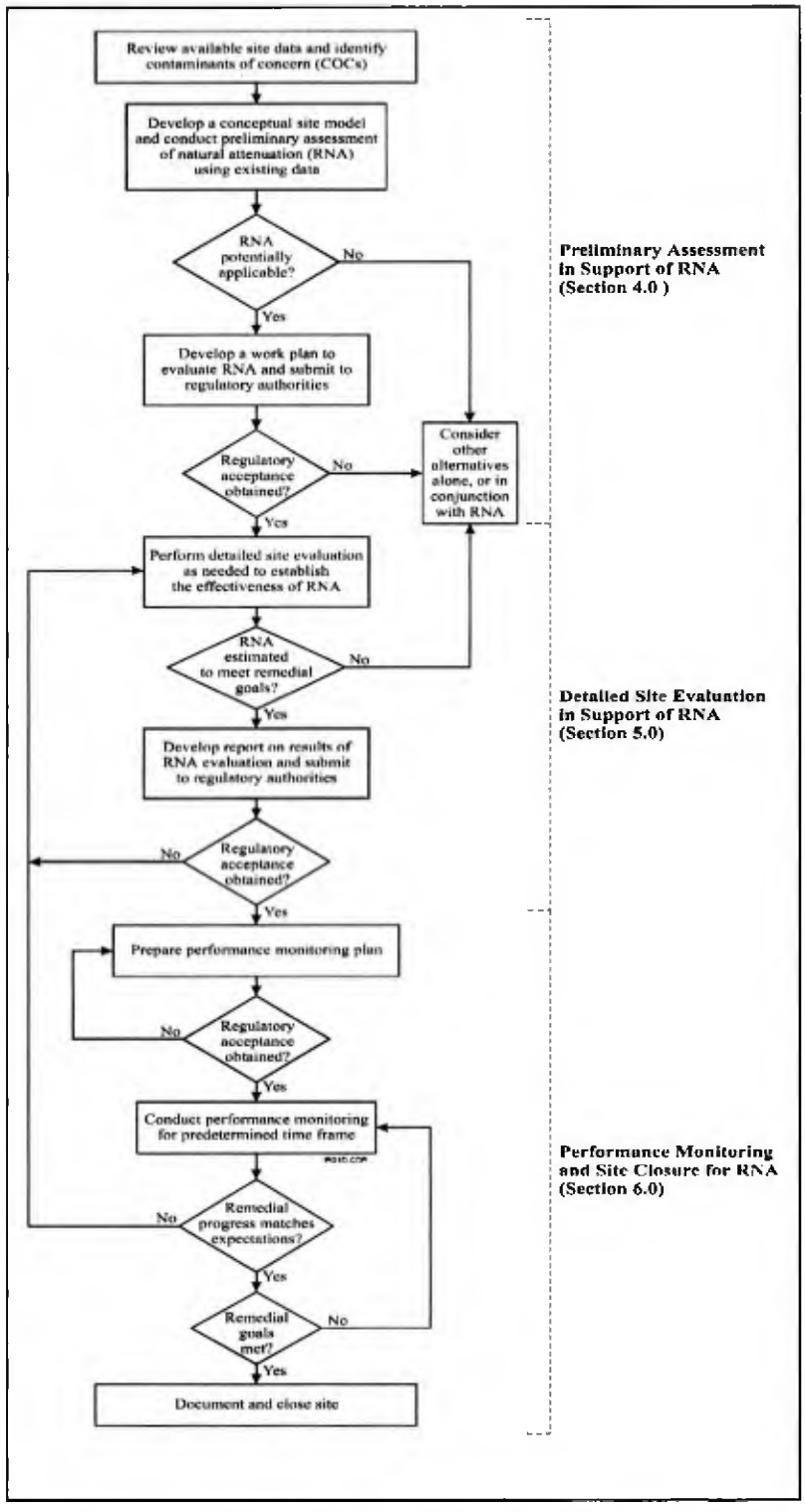



**Figure 3-1. Overall decision diagram for remediation by natural attenuation for petroleum-contaminated groundwater.**

Performance monitoring includes three decision points. The first decision point asks the user whether regulatory acceptance of the performance monitoring plan for RNA has been obtained. It is essential that the performance monitoring plan be approved by regulators to ensure that adequate data are collected to satisfactorily demonstrate the efficiency of RNA.

Performance monitoring plans commonly include internal review periods in which the performance of RNA is evaluated to assess whether it matches expectations established during the detailed site evaluation. The second and third decision points performance monitoring are addressed during these review periods. The second decision point asks the user whether RNA meets the expectations established during the detailed site evaluation. If the second decision point is answered negatively, the user must return to site evaluation and reevaluate RNA accounting for the data collected during performance monitoring; additional field data may be collected, if necessary. If the remedial progress of RNA matches expectations and the remedial goals are met, then the third decision point is answered affirmatively. The results then should be documented, and the site closed. If the remedial progress of RNA meets expectations but the remedial goals are not met, performance monitoring should continue for another predetermined period of time or until the goals are met.

# 4.0 PRELIMINARY ASSESSMENT IN SUPPORT OF RNA

This section of the operations manual expands upon the information presented in the Navy's companion document *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities* (DON, 1998) by describing the type and quantity of data required to assess the potential for RNA for petroleum-contaminated sites. Both of these documents may be used together to evaluate RNA on a site-by-site basis. A checklist to guide the reader through the preliminary assessment process is provided at the end of the section.

In the preliminary assessment, existing site data are used to determine whether conditions favor the use of RNA or if RNA should be precluded from further consideration. Although preliminary field data may be collected for this task, generally it presumes that the site has been characterized and it is limited to reviewing existing data and gathering information from literature to make an early, site-specific assessment of RNA. This section describes how to conduct the preliminary assessment. The decision diagram (Figure 4-1) shows the steps involved in the preliminary assessment in support of RNA. The steps can be summarized as follows:

1. Determine whether RNA is accepted within the existing regulatory framework.

2. Review existing site data and develop a conceptual model for RNA.

3. Based on the information assembled in the conceptual model, assess whether there are immediate or imminent threats to human or ecological receptors that require interim remedial actions such as free-product removal.

4. Determine whether existing data are adequate to demonstrate the effectiveness of RNA for the site or if a more detailed evaluation is required. To make this determination, it may be necessary to collect preliminary field data to support the development of a work plan.

5. Prepare a workplan for the detailed site evaluation in support of RNA.

6. Obtain regulatory acceptance to proceed with a detailed site evaluation of RNA.

## 4.1 EXAMINE REGULATORY ACCEPTANCE OF RNA

It is necessary to ensure that RNA is accepted within the existing regulatory framework governing remedial activities at the site. Each state and region may have unique requirements pertaining to RNA, and the acceptance of RNA by states is changing rapidly with updates in rules, regulations, and policies. Some states lack formal procedures to authorize RNA; therefore, it is prudent to involve regulators early in the process to ensure that no barriers exist that might prevent its use.

If the existing regulations rule out RNA for a site that otherwise may be amenable to RNA, it may be possible to negotiate the use of RNA and determine whether common ground can be found with the regulators. The requirements and attitudes towards RNA are changing rapidly, and it may be possible to negotiate the use of RNA after the preliminary assessment, when more evidence for the occurrence of RNA is established. The following items should be considered when negotiating RNA with regulators:

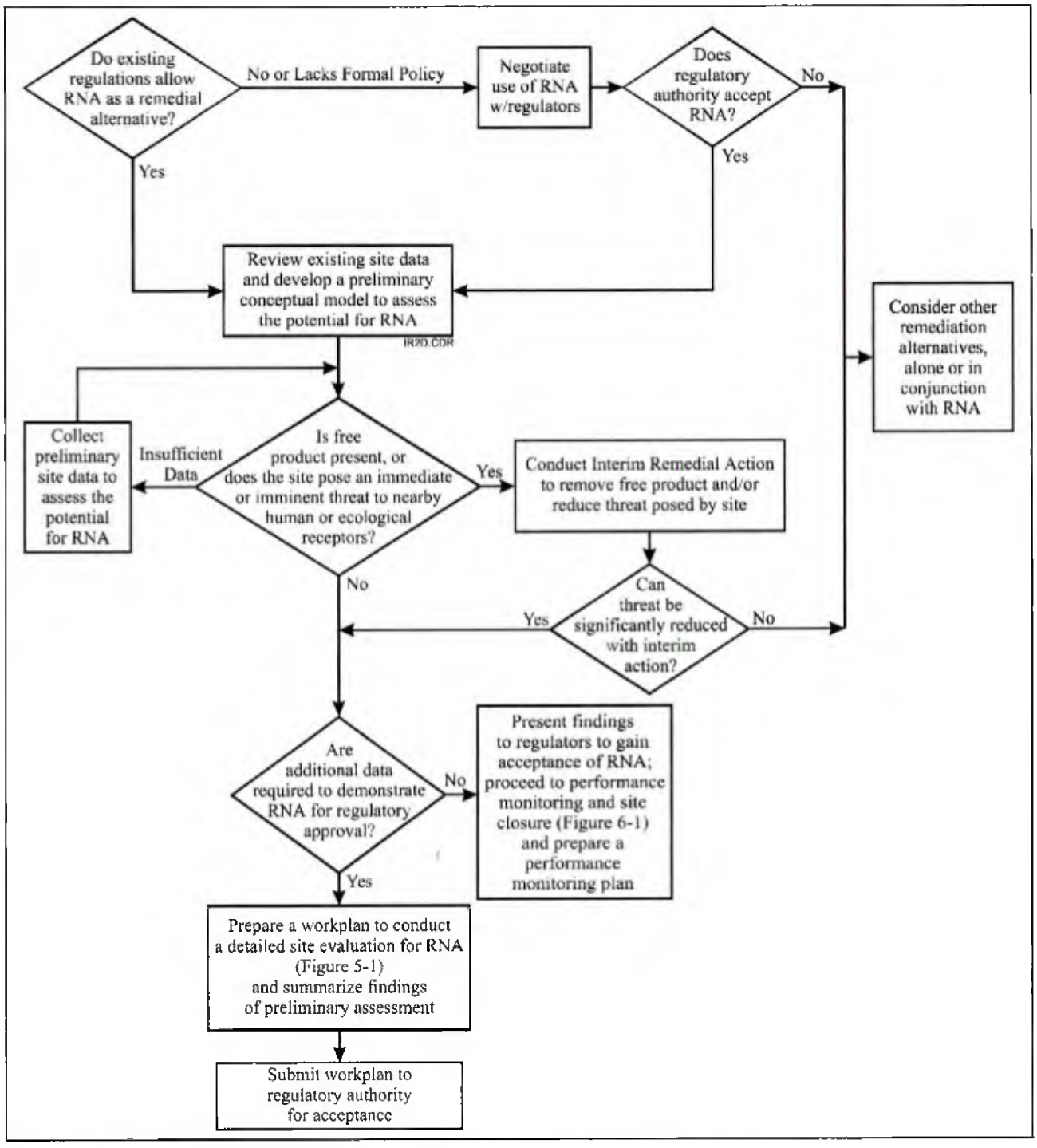



**Figure 4-1. Preliminary assessment in support of remediation by natural attenuation.**

1. Identify the regulator's concerns regarding RNA. Demonstrate how each concern will be addressed.

2. If possible, provide precedents (i.e., example cases) preferably within the regulator's region or state where RNA has been accepted and implemented successfully.

3. If possible, provide site-specific data supporting the use of RNA to the regulator.

4. Explain how a site-specific evaluation of RNA will determine whether RNA is protective of human health and the environment.

5. Identify how the regulator will be involved during each step of the decision-making process.

6. Consider combining RNA with another treatment technology to reduce the time required for cleanup while reducing the costs of the active remediation technology.

## 4.2 DEVELOP A PRELIMINARY SITE CONCEPTUAL MODEL

The first step toward evaluating existing data is the development of a conceptual model for the site. The site conceptual model is a compilation of basic site-specific information intended to help the user answer the following questions:

1. What is the potential for contaminant migration via the groundwater pathway and where are the nearest downgradient receptors (human and ecological) that must be protected?

2. Does the site pose an immediate or imminent threat that precludes the use of RNA or requires an interim remedial action prior to or in conjunction with RNA?

3. What site data exist that indicate that RNA might be technically feasible for the site? Are the existing data sufficient to begin implementing performance monitoring for RNA without further investigation or are more data required?

Despite the use of the term "model," this task does not rely on analytical or numerical modeling and is not intended to support a quantitative assessment of site risks or contaminant fate and transport. The conceptual model is often portrayed graphically, and it helps to identify data gaps because it requires the user to document existing information about the site and conceptualize the physical, chemical, and biological properties that affect RNA. The site conceptual model will continue to be refined during the detailed site evaluation of RNA (described in Section 5.0), after more site-specific information is collected.

The complexity of the site conceptual model should reflect the complexity of the site conditions, the extent of contamination, and available data (ASTM, 1995a; Standard E 1989-95). In general, the conceptual model should contain the following elements.

1. A map showing major site features, such as property boundaries, land use, populations, ecological features, and groundwater uses

2. A map showing the location of contamination source(s) and the horizontal and vertical extent of impacted soil and groundwater

3. An exposure pathway analysis documenting all potential contaminant release mechanisms and exposure pathways, and eliminating unlikely pathways

4. An estimate of the direction and rate of groundwater flow

5. A map showing the location of potential compliance points based on the potential for contaminants to migrate in groundwater.

Each of these five elements is described in detail below. For more information on developing conceptual models, refer to *Standard Guide for Developing Conceptual Site Models for Contaminated Sites* (ASTM, 1995; Standard E 1689-95).

### 4.2.1 Site Features

Common site features, including property boundaries, land uses, populations, ecological features, and groundwater uses, should be identified and documented on site maps.

**4.2.1.1 Property Boundaries.** Property boundaries are important legal demarcations and commonly serve as compliance points. Property boundaries can be obtained from legal records associated with the property (e.g., deeds), city or county plat maps, or previously published site drawings.

**4.2.1.2 Land Uses.** Land uses should be determined for the site and immediately surrounding areas. Major land-use categories include residential, industrial, commercial, agricultural, and recreational. A site visit is the best source of land-use information, but zoning maps, data from the U.S. Census Bureau, topographic maps, and aerial photographs also may provide land-use information. If known, potential future land uses should be noted. Possible information sources about future land uses include city or county master plans and U.S. Census Bureau projections. However, the determination of future land use is frequently based on professional judgment and experience. RNA may require the institution of land-use restrictions.

**4.2.1.3 Populations.** Populations are individuals or groups of people who have access to the site or the surrounding areas and have the potential to be exposed to contaminants originating from the site. Populations may include individuals as well as facilities such as schools and day care centers. A general description of the activity patterns of potentially exposed individuals and groups should be made, including an estimate of the amount of time and frequency spent in the contaminated areas.

**4.2.1.4 Ecological Features and Receptors.** Ecological features include habitat areas such as streams, rivers, wetlands, lakes, oceans, and ecologically protected areas. Ecological receptors are organisms, plants, or especially threatened and/or endangered species associated with these features.

**4.2.1.5 Groundwater Uses.** Groundwater uses in the vicinity of the site include wells that are used for private, municipal, industrial, or agricultural supplies. If no wells are located in the area, the *groundwater use classification* of the aquifer should be determined. Aquifers are commonly classified as beneficial or nonbeneficial. An aquifer classified for beneficial use may be suitable for one or more of the following uses: municipal (i.e., drinking water), agricultural, or industrial supply. Groundwater may not be classified as beneficial because of factors such as low yield or the presence of natural contaminants. For example, naturally occurring arsenic in surface aquifers in western states is a common natural contaminant that often precludes or limits an aquifer's beneficial use.

The groundwater use category for the impacted aquifer will be a major factor in determining final cleanup levels for the site. Not all states have implemented programs to identify beneficial groundwater uses.

In states that have not, the user will have to determine potential groundwater uses based on professional experience and judgment as well as input from the regulatory authority.

### 4.2.2 Contaminant Sources and Extent of Contamination

The locations of existing and historical sources of contamination should be identified and documented on a site map in the preliminary conceptual model. For petroleum hydrocarbons, the source generally will be light, nonaqueous-phase liquid (LNAPL). LNAPL may exist as free product on the water table surface and as residual product distributed in the capillary fringe and below the water table. As much as possible, the location, areal and vertical extent, and volume of the source should be documented on site maps and profile drawings. Dissolved groundwater contaminants should be plotted on a site map showing the magnitude and extent of the dissolved contaminant plume.

If the source of contamination has been removed, it is important to document when the source was removed and, if possible, how far the contaminants have migrated since its removal. Original spill sources such as existing or removed USTs, fire training pits, fueling areas, and other potential spill areas also should be identified.

### 4.2.3 Potential Exposure Pathways

Exposure pathways should be identified for all currently contaminated media (e.g., soil, groundwater). An *exposure pathway* consists of a contaminant migration route from a source of contamination to a receptor via soils, groundwater, or atmospheric transport. An exposure pathway is *complete* if the contaminant has the potential to reach a receptor; a *complete* exposure pathway does not necessarily imply that the contaminant has reached the receptor. The pathway is *incomplete* if a physical barrier or the contaminant's properties prevent migration to the receptor. Complete exposure pathways must contain the following elements (EPA, 1989a; ASTM, 1995a):

1. **A source of contamination (historical or ongoing).** Free product and residual product in soils are common types of sources.

2. **A contaminant migration pathway.** A *contaminant migration pathway* is a route by which contaminants can be *transported* through the environment or a mechanism by which contaminants can be *transferred* from one environmental medium to another. A migration pathway can include both a transfer mechanism and a transport process, including for example:

   - Dissolution of chemicals from free product followed by transport of the dissolved contaminants in groundwater

   - Volatilization of chemicals from soil or groundwater to the air followed by atmospheric transport.

A *pathway analysis* is performed to identify processes that have the potential to transport site contaminants in the environment and to identify media that may be impacted as a result of contaminant migration or intermedia transfer. The pathway analysis assembles basic chemical properties of the COCs and uses this information to make a qualitative assessment of their possible fate in the environment. Table 4-1 lists the principal chemical and physical properties that determine a contaminant's behavior in the environment. Literature values for some of these parameters are provided in Appendix A. Early

understanding of these parameters will help the investigator assess the potential for contaminant migration to potential receptors.

3. **An exposure point (i.e., a receptor).** An exposure point is a location where contact can occur between contaminants and human or ecological receptors. If a receptor is located at the source, exposure to the contaminants can occur without further transport through the environment. Examples of exposure points include drinking water wells, soils that are accessible to children, buildings where volatile chemicals can accumulate, and surface waters used for recreation or drinking water.

4. **Exposure routes.** Exposure routes for each potential receptor and exposure medium are the mechanisms by which receptors are likely to come into contact with contaminants. For example, ingestion, inhalation, and dermal absorption are common exposure routes. Table 4-2 lists principal exposure routes for contaminated environmental media.

Tracking contaminant migration from sources to potential receptors is one of the most important uses of the conceptual model (ASTM, 1995a). Exposure pathways should be identified both for current and for potential future conditions if land use changes are expected. Pertinent information on all possible exposure pathways at the site should be summarized, including the source media, potential transport/ transfer pathways, exposure media, exposure points, and exposure routes. To facilitate this process, exposure pathways are documented on an exposure pathway diagram, as shown in Figure 4.2.

Figure 4-2 also can be used as a checklist to make sure that all potential pathways are considered. This information provides the basis for a quantitative assessment of site risks or calculation of health-based cleanup goals later in the detailed site evaluation, if required.

### 4.2.4 Groundwater Flow Direction and Rate

The preliminary conceptual model should include a general assessment of groundwater occurrence at the site and an estimate of the direction and rate of groundwater movement. It is important to develop a general understanding of the groundwater movement to identify potential downgradient receptors that could be impacted by plume migration, and the time frame in which they could be impacted. This information is necessary to determine the need for interim action at the site, and to establish compliance points for RNA. The preliminary conceptual model will be refined during the detailed site evaluation to develop a better understanding of groundwater movement at the site.

The most common method for determining the direction of groundwater flow uses water-level measurements from wells and/or piezometers at the site. For isotropic aquifers, the groundwater flow direction is approximately equal to the direction of the hydraulic gradient, which is the slope on the water table (unconfined aquifers) or potentiometric surface (confined aquifers). The hydraulic gradient between two points is calculated as follows (Equation 4):

$$-dh/dl = \frac{-\Delta h}{\Delta l} \qquad (4\text{-}1)$$

## Table 4-1. Important Physical/Chemical Parameters Affecting Environmental Behavior of Contaminants

| Parameter | Significance |
|---|---|
| Soil or sediment sorption coefficient, $K_d$ | Provides a soil or sediment-specific measure of the extent of chemical partitioning between soil or sediment and water, and can be calculated as $K_d = K_{oc} \times f_{oc}$, where $K_{oc}$ is the organic carbon partition coefficient, and $f_{oc}$ is the fraction of organic carbon present in soil or sediment. The higher the $K_d$, the more likely a chemical is to bind to soil or sediment than to partition into water. (See Appendix B.1.4.2) |
| Organic carbon partition coefficient, $K_{oc}$ | Chemical-specific property that describes the tendency for chemicals to partition between organic carbon in soil or sediment and water at equilibrium. The higher the $K_{oc}$, the more likely it is that a chemical will bind to soil or sediment rather than partition into water. If measured values of $K_{oc}$ are not available, $K_{oc}$ can be estimated using methods in Lyman et al. (1992). |
| Octanol/water partition coefficient, $K_{ow}$ | Provides a measure of the extent of chemical partitioning between water and octanol at equilibrium. The greater the $K_{ow}$ the more likely it is that a chemical will partition to octanol rather than remain in water. Octanol is used as a surrogate for lipids (fat), and $K_{ow}$ can be used to predict bioconcentration in aquatic organisms. |
| Solubility, S | The upper limit on a chemical's dissolved concentration in water at a specified temperature. Aqueous concentrations approaching the contaminant solubility may indicate the presence of NAPL. |
| Henry's law constant, H | Provides a measure of the extent of chemical partitioning between air and water at equilibrium. The higher the Henry's law constant, the more likely it is that a chemical will volatilize rather than remain in the water. (See Appendix B.1.4.6) |
| Diffusivity in air and water | Describes the movement of a molecule in a liquid or gas medium as a result of differences in concentration. It contributes to the dispersive component of chemical transport. The higher the diffusivity, the more likely it is that a chemical will move in response to concentration gradients. (See Appendix B.1.4.4) |
| Bioconcentration factor (BCF) | Provides a measure of the extent of chemical partitioning at equilibrium between a biological medium, such as fish tissue or plant tissue, and an external medium such as water. The higher the BCF, the greater the accumulation in living tissue is likely to be. |
| Media- or chemical-specific half-life | Provides a relative measure of the persistence of a chemical in a given medium, although actual values can vary greatly depending on site-specific conditions. The greater the half-life, the more persistent a chemical is likely to be. |

Source: Modified from EPA, 1989a.

## Table 4-2. Principal Exposure Routes for Contaminated Environmental Media

| Exposure Media | Exposure Routes |
|---|---|
| Soil | Incidental ingestion<br>Dermal absorption<br>Inhalation of vapors[a]<br>Inhalation of windblown dust[a]<br>Bioaccumulation via plant uptake in plants/animals[a] |
| Subsurface Soil | Incidental ingestion<br>Inhalation of vapors[a]<br>Dermal absorption (during excavation activities)<br>Inhalation of windblown dust[a] |
| Groundwater | Ingestion<br>Dermal absorption (e.g., showering or direct contact with groundwater)<br>Inhalation of vapors[a] |
| Surface Water/Sediment | Incidental ingestion<br>Dermal absorption<br>Bioaccumulation in fish[a] |

Note: (a) Exposure route involves intermedia transfer of contaminants

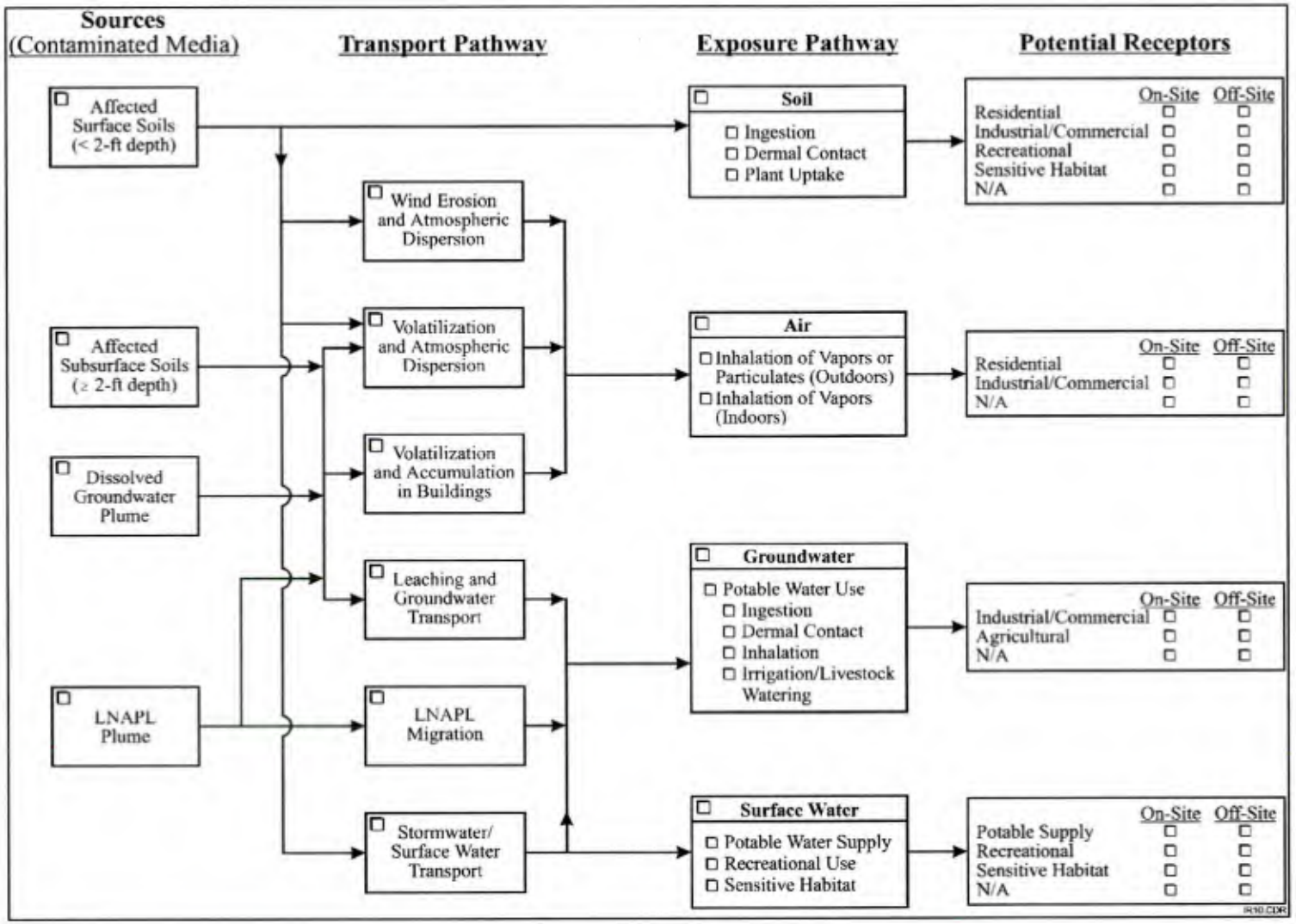



**Figure 4-2. Example exposure pathway diagram.**

where $\Delta h$ [L] is the difference between the hydraulic head (i.e., water-level elevations or piezometric levels) measured in each of two wells, and $\Delta l$ [L] is the distance between the two wells. Preferably, the hydraulic gradient should be determined with measurements of water-level elevation from a minimum of three wells arranged in a triangular pattern across the contaminated area to ensure that the direction corresponding to the maximum hydraulic gradient is determined. If elevations from more than three wells are available, a contour map of the water table or potentiometric surface can be constructed to determine the direction and magnitude of the hydraulic gradient.

In the absence of hydraulic head data, the direction of groundwater movement can be inferred from other site data. For example, a well-delineated contaminant plume provides a reliable indication of the predominant direction of groundwater movement.

Calculation of the groundwater flowrate requires knowing the hydraulic gradient, the hydraulic conductivity, and the effective porosity of the aquifer. For the preliminary conceptual model, the hydraulic conductivity and the porosity can be estimated; however, the hydraulic gradient should be calculated based on actual site data. Groundwater flowrate is calculated as follows (Equation 4-2):

$$V_x = \frac{-K}{n_e}\frac{dh}{dl} \qquad (4\text{-}2)$$

where: $V_x$ is the average linear groundwater velocity [L/T] in the "x" (i.e., principal) direction, K, is the hydraulic conductivity of the aquifer [L/T], and $n_e$ is the effective porosity of the aquifer. The groundwater flowrate can be used as a conservative estimate of the time required for dissolved contaminants to reach potential receptor points, because the actual travel time for dissolved contaminants will be longer than the groundwater travel time due to retardation by sorption.

Although not required for the preliminary conceptual model, other hydrogeologic information that can be compiled at this point includes the following:

1. Cross sections, fence diagrams, or three-dimensional (3-D) block models delineating geology and principal water-bearing strata (i.e., aquifers) and their physical boundaries

2. Hydraulic properties for the impacted aquifers, including hydraulic conductivity, porosity, storativity, bulk density, and organic carbon content

3. Water-level data for each aquifer compiled on water-table maps and/or hydrographs

4. Information about the location of recharge/discharge features and rates of inflow/outflow

5. Contaminant transport parameters that control the migration of contaminants at the site (e.g., retardation factors, dispersivities).

This information will be necessary if contaminant transport modeling is required. Any missing data may be obtained during the detailed site evaluation of RNA (described in Section 5.0).

### 4.2.5 Preliminary Compliance Points

Implementation of RNA requires long-term monitoring at compliance points to ensure that contaminants do not reach potential receptors. Compliance points are located downgradient of the dissolved plume and upgradient of the potential exposure points (i.e., human or environmental receptors) tentatively identified in the preliminary conceptual model. At the compliance points, contaminant concentrations in groundwater must remain below predetermined target levels that are protective of human health and the environment. If receptors are located off site and the contaminants have not reached the property boundaries, compliance points are commonly located at or immediately upgradient of the property boundaries. Compliance point locations are finalized when the performance monitoring plan is developed to ensure that they are properly located to provide for the long-term protection of receptors. When setting compliance points, it is important to consider the potential for contaminant migration based on the exposure pathway diagram for the site. Figure 4-3 is an example preliminary conceptual model showing compliance points located upgradient of a municipal drinking water well.

## 4.3 DETERMINE THE NEED FOR INTERIM OR ALTERNATIVE REMEDIAL ACTION

Certain site conditions will require that RNA be used in conjunction with another technology or may preclude the use of RNA all together. A primary objective of the preliminary assessment is to identify whether or not such conditions exist at the site. The information incorporated into the preliminary conceptual model should be sufficient to determine if these conditions exist at the site.

The primary criteria that determine whether or not an interim action is required are (1) the presence of LNAPL at the site; and (2) the severity of the threat posed by the site contamination. The presence of LNAPL will almost always trigger the need for an interim remedial action either prior to or in conjunction with the evaluation and implementation of RNA.

Common technologies used to remove LNAPL include bioslurping, skimming, passive absorption, and excavation. None of these technologies can remove all of the LNAPL. Therefore, once the LNAPL is removed to the maximum extent practicable, the site must rely on RNA or alternative technologies to remediate the residual product that cannot be cost-effectively removed using more conventional technologies. Potential alternative technologies for remediating residual product in the vadose zone or the saturated zone include bioventing, soil vapor extraction (SVE), and air sparging. Each application should have the following objectives: (1) remove the maximum amount of contamination possible to prevent ongoing contamination of the groundwater; (2) minimize the time required for overall site remediation; (3) protect potential receptors from exposure at the source; and (4) minimize the total cost of remediation. Additional information about free-product removal methods and technologies for remediating the vadose zone can be found in the following references: *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites* (EPA, 1995b); *Test Plan and Technical Protocol for Bioslurping* (Battelle, 1997); and *Soil Bioventing Principles and Practice* (Leeson and Hinchee, 1997).

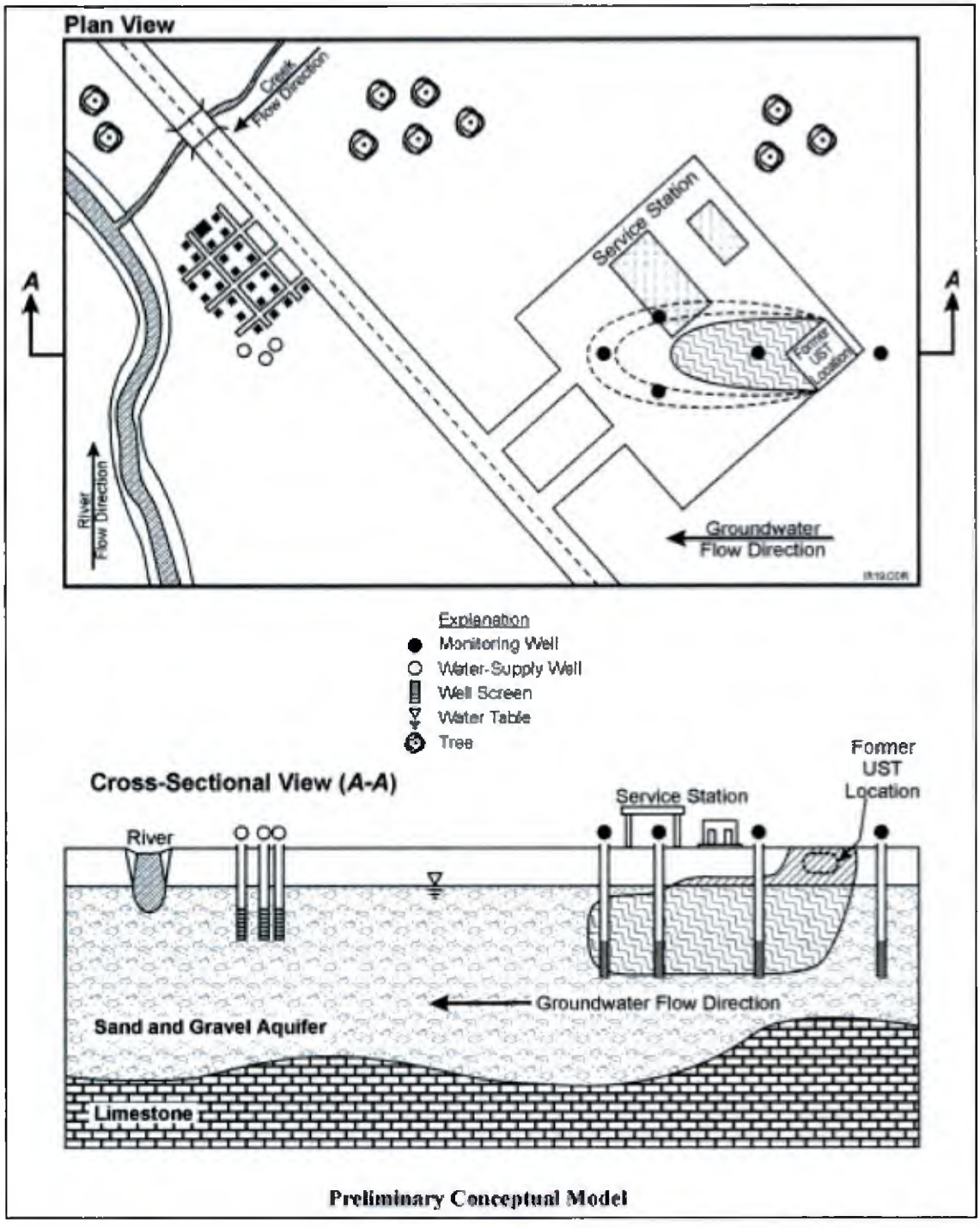



Figure 4-3. Preliminary site conceptual model.

A determination of the severity of the threat posed by site contamination is based on the urgency and the magnitude of the current and projected impact to human health and the environment. Threats can be classified as *immediate, short-term, long-term,* or *no reasonable potential threats* (ASTM, 1995b).

If an immediate or short-term threat exists, an interim remedial action will almost certainly be required to reduce the potential for adverse effects before RNA can be implemented. Interim actions may include engineered controls to control groundwater migration, alternative remediation technologies, or institutional controls that limit human and environmental exposure to contaminants. These interim actions may be conducted concurrently with the detailed site evaluation of RNA. The goal of the interim action should be to lower or eliminate the level of risk (i.e., risk reduction) posed to human health or the environment through active remediation or institutional controls.

**Severity of potential threats**

***Immediate Threat*** – An immediate threat occurs if an exposure pathway is complete and contaminants have reached human or environmental receptors. If the threat of human or environmental exposure is immediate, an interim action must be taken to reduce or eliminate continued exposure before RNA can be evaluated and implemented. An example of an immediate threat is a drinking-water supply that already is contaminated.

***Imminent Threat (0-5 Years)*** – An imminent threat occurs if a receptor will be impacted within a 5-year time period, based on groundwater travel time. Interim remedial actions may be required to address imminent threats and to provide sufficient time to evaluate the feasibility of RNA. If the risk cannot be eliminated immediately, institutional controls may be required to restrict land use and prevent exposure to the contaminants.

***Long-Term Threat (>5 Years)*** – If a receptor will not be impacted within a 5-year time period, based on groundwater travel time, the site does not pose an immediate or imminent threat. RNA may be evaluated without requiring interim actions. Five years provides adequate time to evaluate RNA, which generally requires about 2 years, before contaminants reach receptors.

***No Reasonable Long-Term Threat*** – No reasonable long-term threat implies that there are no potentially complete exposure pathways under existing or potential future conditions. RNA can be evaluated without interim actions. No reasonable long-term threat does not presume RNA acceptance.

Examples of threats for each of these four classifications are provided in Table 4-3, along with examples of possible interim actions to abate each threat. These examples are modified from the ASTM's *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites* (ASTM, 1995b) and may not be comprehensive or applicable for all sites. The user should note that not all interim actions described in the example involve active remediation. In many cases, the action is to monitor or further assess the site to ensure that risks posed by the site do not increase over time.

## 4.4 DETERMINE IF EXISTING SITE DATA SUPPORT RNA

Another goal of the preliminary assessment phase is to gather supporting data for RNA before it is formally proposed to the appropriate regulatory authority. For many sites, the existing data may be sufficient to propose RNA but may be insufficient to demonstrate that RNA can meet the remedial objectives of the site.

Presumably, at this stage of development there is no evidence of an immediate or imminent threat to receptors, and an interim action is not required. The amount of available historical data will vary from site to site: some sites will have little supporting evidence of RNA, whereas some may have enough evidence to proceed directly to performance monitoring. One outcome of this task will be to establish the additional data requirements needed to support RNA to obtain regulatory acceptance, and to plan the detailed site evaluation to follow.

**Table 4-3. Example Site Threats and Interim Remedial Actions**

| Criteria and Prescribed Scenarios | Example Interim Action |
|---|---|
| **1. Immediate threat to human health, safety, or sensitive environmental receptors**<br>• Explosive levels, or concentrations of vapors that could cause acute health effects, in buildings or subsurface utility system(s).<br>• An active public water supply is impacted or immediately threatened.<br>• A sensitive habitat or sensitive resources are impacted. | **1. Notify appropriate authorities, property owners, and potentially affected parties. Evaluate the need to do the following:**<br>• Evacuate building occupants.<br>• Initiate appropriate containment measures.<br>• Institute free-product recovery measures.<br>• Implement institutional controls. |
| **2. Imminent (0 to 5 years) threat to human health, safety, or sensitive environmental receptors**<br>• Shallow contaminated surface soils are open to public access.<br>• Groundwater is impacted, and a potable water supply well producing from the impacted aquifer is located within a 5-year groundwater travel distance from the plume.<br>• Impacted groundwater discharges to a sensitive habitat or surface water body within a 5-year groundwater travel distance from the plume. | **2. Notify appropriate authorities, property owners, and potentially affected parties. Evaluate the need to do the following:**<br>• Immediately assess the potential for groundwater or vapor migration to receptors.<br>• Initiate appropriate containment measures, if necessary.<br>• Implement institutional controls, if necessary.<br>• Initiate immediate monitoring of groundwater or vapors to protect against future impacts. |
| **3. Long-term (>5 years) threat to human health, safety, or sensitive environmental receptors**<br>• Groundwater is impacted, and potable water supply wells are located >5 years groundwater travel time from the dissolved plume.<br>• Impacted surface water, storm water, or groundwater discharges to a sensitive habitat or surface water body >5 years groundwater travel time from the dissolved plume. | **3. Assess the potential for future impact.**<br>• Notify appropriate authorities and assess potential to use RNA to remediate the site.<br>• Evaluate RNA or other appropriate technologies.<br>• Present results to regulatory authorities, property owners, and other potentially affected parties.<br>• Implement RNA or other appropriate technology.<br>• Monitor for long-term impacts to receptors and for technology performance. |
| **4. No demonstrated long-term threat to human health or safety or sensitive environmental receptors**<br>• Nonpotable aquifer with no beneficial use. | **4. Implement RNA to remediate the site.**<br>• Establish regulatory approval for RNA or long-term monitoring.<br>• Implement RNA of long-term monitoring, as required. |

Source: Modified from ASTM (1995b).

### 4.4.1 Plume Status

Historical data obtained from a consistent set of monitoring wells in the area of contamination may indicate whether the plume status is shrinking, stable, or expanding. If insufficient historical data are available to establish the plume status, time-series data will be one of the data requirements for the detailed site evaluation.

If the data unequivocally demonstrate a shrinking plume, and receptors are not immediately threatened, additional site data may not be required. A shrinking plume fulfills the requirements of RNA

by demonstrating a reduction in contaminant mass (implicitly through biodegradation), reduced groundwater contaminant concentrations, and immediate and long-term protection of receptors.

If possible, the evidence for a shrinking plume should be reported and presented to regulatory authorities for approval of RNA. Additional data, which are expensive to collect, should not be necessary unless the protection of receptors cannot be established confidently using the existing data alone. Although additional data may be of scientific interest, for example to determine the precise biological mechanisms of contaminant degradation, such data may be superfluous if it does not provide additional evidence for the protection of receptors. Thus, significant savings of time and remediation costs can be realized through early regulatory acceptance of RNA for sites with shrinking plumes. For this reason, the need for early regulatory involvement in the decision-making process cannot be over-emphasized. Once acceptance is achieved, the user should proceed to performance monitoring of RNA.

Protection of receptors from stable and expanding plumes will be less clear and may require additional monitoring and supporting data. Like the shrinking plume, a stable plume provides strong evidence that contaminant RNA is occurring at the site. If the RNA criteria (i.e., protection of receptors and contaminant reduction within a reasonable time frame) can be demonstrated to the satisfaction of the regulators, it may be possible to suggest immediate acceptance of RNA. Potential future environmental changes that may impact plume status must be considered to establish the long-term protection of receptors, and additional analyses may be required to predict the time for RNA to meet cleanup goals.

Virtually all expanding plumes will require additional information to demonstrate a loss of contaminant mass due to biodegradation, to ensure the protection of downgradient receptors, and to estimate the time required to remediate the site using RNA. This information usually requires a more detailed evaluation of contaminants, biological indicator parameters, and hydrogeologic conditions at the site, which are discussed in Section 5.0.

### 4.4.2 Biodegradation Potential

Aside from demonstrating a shrinking or stable plume, most sites will have little data supporting intrinsic contaminant biodegradation. Nevertheless, any existing supporting evidence of RNA, or evidence that may suggest that RNA is not occurring, should be gathered. Examples of supporting data include the following:

- **DO data from background samples and in the area of contamination.** If DO concentrations in the area of contamination are lower than background concentrations, DO data may be used to support RNA. Background DO concentrations also can be used to judge whether aerobic conditions at the site can support RNA.

- **Electron acceptor and metabolic byproduct data from background samples and from the area of contamination.** If electron acceptor concentrations can be correlated with contaminant concentrations, they may be used to support RNA. Background electron acceptor concentrations also may be used to determine which electron acceptors should be analyzed during the detailed site evaluation.

## 4.5 COLLECT SUPPORTING FIELD DATA

It may be helpful to collect preliminary field data to support RNA. At this stage, the user should not expect to gather enough data to fully demonstrate RNA; data collection in support of RNA is largely

deferred until the detailed site evaluation. However, at many UST sites, historical data may be minimal and may be insufficient to assess whether RNA should be considered. Conditions that may warrant immediate data collection during the preliminary assessment include the following:

- **Uncertain extent of contamination.** It may be necessary to sample along a plume transect to define the plume boundaries, especially if a receptor could be immediately impacted.

- **The presence of MTBE or other recalcitrant compounds is unknown.** Concern over the compound MTBE is increasing. If previous site investigations neglected to test for MTBE and other gasoline additives, groundwater samples should be analyzed for these compounds, because RNA may not be appropriate for these compounds. However, the presence of MTBE does not preclude the use of RNA for other petroleum compounds.

- **Unknown background DO concentrations.** To support aerobic biodegradation, background DO concentrations should be greater than 1.0 mg/L. Lower concentrations do not preclude RNA, but suggest that more extensive examination of the anaerobic pathways will be required. DO concentrations in the dissolved plume also should be measured. Depressed DO concentrations indicate RNA activity.

## 4.6 DEVELOP A WORKPLAN FOR EVALUATION OF RNA

For most sites, further site evaluation beyond the preliminary assessment will be required to demonstrate the feasibility of RNA to the regulatory authority. The process and data requirements for the detailed RNA evaluation are described in Section 5. The final step of the preliminary assessment is to develop a workplan outlining the proposed steps that will be undertaken during the detailed site evaluation. The workplan also should summarize the results of the preliminary assessment because they provide additional support for the use of RNA at the site. If necessary, the workplan should be submitted to the appropriate regulatory authority for preliminary acceptance of RNA and of the detailed evaluation-study objective.

The workplan should describe the types of samples that will be collected, the sampling frequency, and how the data will be analyzed to support RNA. If analytical or numerical modeling is anticipated, the data requirements for the model should be defined, and the field data should support the model development. If it is necessary to collect data over time, the sampling frequency and the study duration should be estimated. The workplan should identify which wells will be sampled, whether new wells/sampling points need to be installed, and the field sampling procedures. The workplan should also identify the analytical requirements for each sampling point, the analytical methods, holding times, preservation requirements, and quality assurance requirements. Finally, the workplan should be sufficiently flexible to accommodate unexpected changes encountered in the field and resulting from the data analysis.

**Example Outline for the Detailed Site Evaluation of RNA Workplan**

1.0 Introduction
- 1.1 Objectives of the RNA Evaluation
- 1.2 Site Background
  - 1.2.1 Operational History
  - 1.2.2 Previous Investigations
  - 1.2.3 Remediation History

2.0 Preliminary Assessment of RNA
- 2.1 Regulatory Acceptance of RNA
- 2.2 Preliminary Conceptual Model
  - 2.2.1 Site features
  - 2.2.2 Source(s) of Contamination
  - 2.2.3 Extent of Contamination
  - 2.2.4 Hydrogeology
  - 2.2.5 Potential Exposure Scenarios
- 2.3 Evidence for RNA

3.0 Data Requirements to Evaluate RNA
- 3.1 Contaminant Data
- 3.2 Geochemical Data
- 3.3 Hydrogeologic Data

4.0 Sampling and Analysis Plan
- 4.1 Soil Sampling and Monitoring Well Installation
- 4.2 Groundwater Sampling and Analysis
- 4.3 Aquifer Testing

5.0 Data Evaluation
- 5.1 Demonstrating Loss of Contamination
  - 5.1.1 Plume Status
  - 5.1.2 Conservative Tracer Analysis
- 5.2 Demonstrating Biodegradation
  - 5.2.1 Spatial Trends in Field Data
  - 5.2.2 Additional Field and Laboratory Data
- 5.3 Demonstrating Effectiveness
  - 5.3.1 Potential for Contaminant Migration
  - 5.3.2 Assessing Remediation Time

6.0 Quality Assurance/Quality Control (QA/QC)
- 6.1 On-Site QA/QC
- 6.2 Off-Site Laboratory QA/QC

7.0 Health and Safety Plan
- 7.1 Drilling and Installation
- 7.2 Sampling
- 7.3 On-Site Analytical Work

## Checklist for Preliminary Assessment in Support of RNA

| ITEM | TASK | PRELIMINARY ASSESSMENT GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 1 | Examine existing regulations concerning RNA | ❑ Does the existing regulatory framework accept RNA? If so, establish preliminary approval for RNA use, and proceed to Item 3<br>❑ For states that lack formal procedures, notify regulators of the interest in RNA, establish preliminary acceptance of RNA, pending further investigation, and proceed to Item 3<br>❑ For states that lack formal procedures, and the relevant agency does not readily accept RNA, proceed to Item 2 | Establish early regulatory acceptance of RNA, to streamline the regulatory process |
| 2 | Negotiate use of RNA with regulators | ❑ Identify regulatory concerns regarding RNA<br>❑ If possible, provide precedents for RNA use, preferably within the regulators' jurisdiction<br>❑ If available, provide site-specific supporting evidence of RNA<br>❑ Consider combining RNA with other treatment technologies to reduce the overall remediation cost | Establish the potential for using RNA with regulatory agencies by addressing site-specific and regulatory-specific requirements and concerns |
| 3 | Develop a preliminary conceptual model for RNA, using existing site data | ❑ Establish site features:<br>Establish property boundaries<br>Establish current and future land use<br>Define ecological features<br>Characterize current and potential future groundwater uses<br>Identify populations that may have access to the site or to the contaminated aquifer<br>❑ Identify the magnitude and extent of contamination<br>❑ Identify the magnitude and extend of an existing or historical source<br>❑ Conduct an exposure pathway analysis to identify potential exposure routes<br>❑ Calculate the groundwater flow direction and rate<br>❑ Establish preliminary compliance points<br>❑ Assemble information into a graphical and narrative conceptual model | The preliminary conceptual model is the foundation of the preliminary site assessment, and is used to assess relative risks to human and environmental receptors, and to establish the potential for RNA. The preliminary conceptual model will form the groundwork for the detailed site investigation in support of RNA |

## Checklist for Preliminary Assessment in Support of RNA (Cont.)

| ITEM | TASK | PRELIMINARY ASSESSMENT GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 4 | Determine the need for interim or alternative remedial actions | ❑ Evaluate the potential risks posed to receptors, based on information in the conceptual site model<br>If the site poses an immediate threat to human health or the environment, proceed to Item 5<br>If the site potentially poses an imminent threat, proceed to Item 6<br>If the site potentially poses a long-term threat, proceed to Item 7<br>If the site does not pose a reasonable long-term threat, proceed to Item 8 | Establish potential risks, based on historical data, to assess the potential for RNA |
| 5 | Necessary action, if an immediate threat is perceived | ❑ Notify appropriate authorities, property owners, and potentially affected parties of the risks posed by the site<br>❑ Take necessary precautions to protect human health, and implement appropriate actions | For sites with immediate risks, RNA may not be feasible without taking an interim action to protect receptors |
| 6 | Necessary action if an imminent threat is perceived | ❑ Notify appropriate authorities, property owners, and potentially-affected parties of the risks posed by the site<br>❑ Initiate measures to protect receptors<br>❑ Assess the potential for RNA in combination with alternative remediation measures, containment, or institutional controls | For sites with imminent risks, RNA may be possible, but interim measures may be required to protect receptors while RNA is evaluated |
| 7 | Necessary action if long-term threat is perceived | ❑ Assess the potential for future impact of receptors<br>❑ Evaluate the use of RNA or other potential remedies | For sites with long-term risks, RNA may be evaluated without posing undue risks to receptors during the evaluation |
| 8 | Necessary action if no reasonable threat is perceived | ❑ Establish regulatory approval for RNA or long-term monitoring | For sites where there is no demonstrable risk, RNA may be able to be implemented without further evaluation, pending regulatory acceptance |

## Checklist for Preliminary Assessment in Support of RNA (Cont.)

| ITEM | TASK | PRELIMINARY ASSESSMENT GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 9 | Determine whether existing data supports RNA | ❑ Establish biodegradation potential based on historical groundwater data<br>If there is conclusive evidence for RNA, establish plume status (next item)<br>If there is conclusive evidence that RNA is not occurring, proceed to Item 11<br>If there is insufficient evidence to draw a conclusion about intrinsic contaminant biodegradation, proceed to Item 10<br>❑ Establish plume status using available historical data<br>Determine whether the plume is shrinking, stable, or expanding<br>If the plume is expanding, evaluate the risk to receptors and whether RNA is suitable for the site | Historical data are evaluated to establish evidence for biodegradation and plume status as shrinking, stable, or expanding. Generally, historical data can be used to indicate whether RNA is potentially viable, but are insufficient to fully evaluate the efficiency of RNA. |
| 10 | If necessary, collect preliminary site data to assess the potential for RNA | ❑ If not already accomplished, establish plume boundaries<br>❑ If not already accomplished, assess the presence of MTBE<br>❑ If not already accomplished, establish DO concentration gradients in the area of contamination | Preliminary data, such as plume boundaries or groundwater dissolved oxygen levels, may be required to conduct the preliminary assessment. However, these data should not be confused nor overlap with data that will be collected during the detailed site investigation. |

## Checklist for Preliminary Assessment in Support of RNA (Cont.)

| ITEM | TASK | PRELIMINARY ASSESSMENT GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 11 | Summarize findings and prepare a workplan to conduct a detailed site investigation for RNA | ❑ Assemble data and establish the potential for RNA<br>❑ If results demonstrate that RNA should not be used, report results and proceed with an alternative or contingency remedial action<br>❑ If preliminary results demonstrate that RNA may be used, develop a workplan for a detailed evaluation of RNA | Data should be assembled and summarized for internal and external (i.e., regulatory) distribution. The summary should indicate whether RNA is expected to adequately remediate the site. If more data are necessary, a detailed site investigation will be conducted, for which a detailed workplan should be developed. Data needs should be established in the workplan. |
| 12 | Present findings and workplan to regulatory authorities, for preliminary acceptance | ❑ Gain regulatory acceptance to proceed with RNA<br>❑ Ascertain additional regulatory requirements for final RNA acceptance<br>❑ Submit the workplan for regulatory acceptance of proposed plans | Early regulatory involvement in the decision-making process, and early regulatory acceptance of RNA helps streamline the regulatory process. Regulatory review and acceptance of the workplan helps ensure that sufficient data will be gathered during the detailed site investigation, to maintain regulatory acceptance of RNA. |

# 5.0 DETAILED SITE EVALUATION OF RNA

After a preliminary assessment has been completed, the next step is to establish the occurrence of RNA and to evaluate its efficacy as a remedial approach. Presumably, at this stage the preliminary assessment will have verified that site conditions do not preclude the use of RNA, but that insufficient spatial or temporal data exist to establish that RNA is protective of human health and the environment. This step is divided into two primary objectives: the first involves collecting field data to establish the occurrence of RNA (Section 5.1); the second involves evaluating the data to establish the efficiency of RNA (Section 5.2), where efficiency is defined as the ability to protect human health and the environment and to remediate the site in an acceptable time frame. Figure 5-1 presents a decision diagram depicting the steps involved in the detailed site evaluation.

The framework for assessing the occurrence and efficiency of RNA for petroleum-contaminated sites also is outlined in the Navy's companion document, *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities* (DON, 1998). This section expands upon the step-by-step process for evaluating RNA of petroleum hydrocarbons discussed in Section 3.2 of the *Technical Guidelines* document by explaining how and where to collect field data and how to evaluate the data to fulfill the above two objectives of the detailed site evaluation. The investigator is shown how to calculate contaminant degradation rates, and how to use these rates in simple calculations to estimate the time for RNA to achieve site cleanup goals, or in models to demonstrate that RNA is protective of human health and the environment. Recommendations for comparing RNA with alternative technologies are provided, and reporting requirements are identified for summarizing and presenting the findings of the detailed evaluation for regulatory acceptance. A checklist to guide the reader through the detailed site evaluation is provided at the end of the section.

## 5.1 ESTABLISH THE OCCURRENCE OF RNA

Field data will be required to establish the occurrence of RNA if historical data from the preliminary assessment are insufficient to establish the plume status, if they indicate an expanding plume, or if contaminant biodegradation has not been established. The occurrence of RNA is established by correlating the contaminant data with indicators of biological activity at the site or in the laboratory as follows:

1. Field data are evaluated for spatial correlations between contaminants and geochemical or biological indicator parameters (e.g., electron acceptors or metabolic byproducts) that indicate in situ contaminant biodegradation.

2. If possible, internal tracers such as trimethylbenzenes (TMB) are measured to calculate the contaminant mass lost due to biodegradation.

3. Time series data are evaluated to establish the plume status as shrinking, stable, or expanding.

4. If necessary, optional field data such as dissolved $H_2$ concentrations, the presence of VFAs, or laboratory data from microcosm studies or microbial counts are collected in support of RNA.

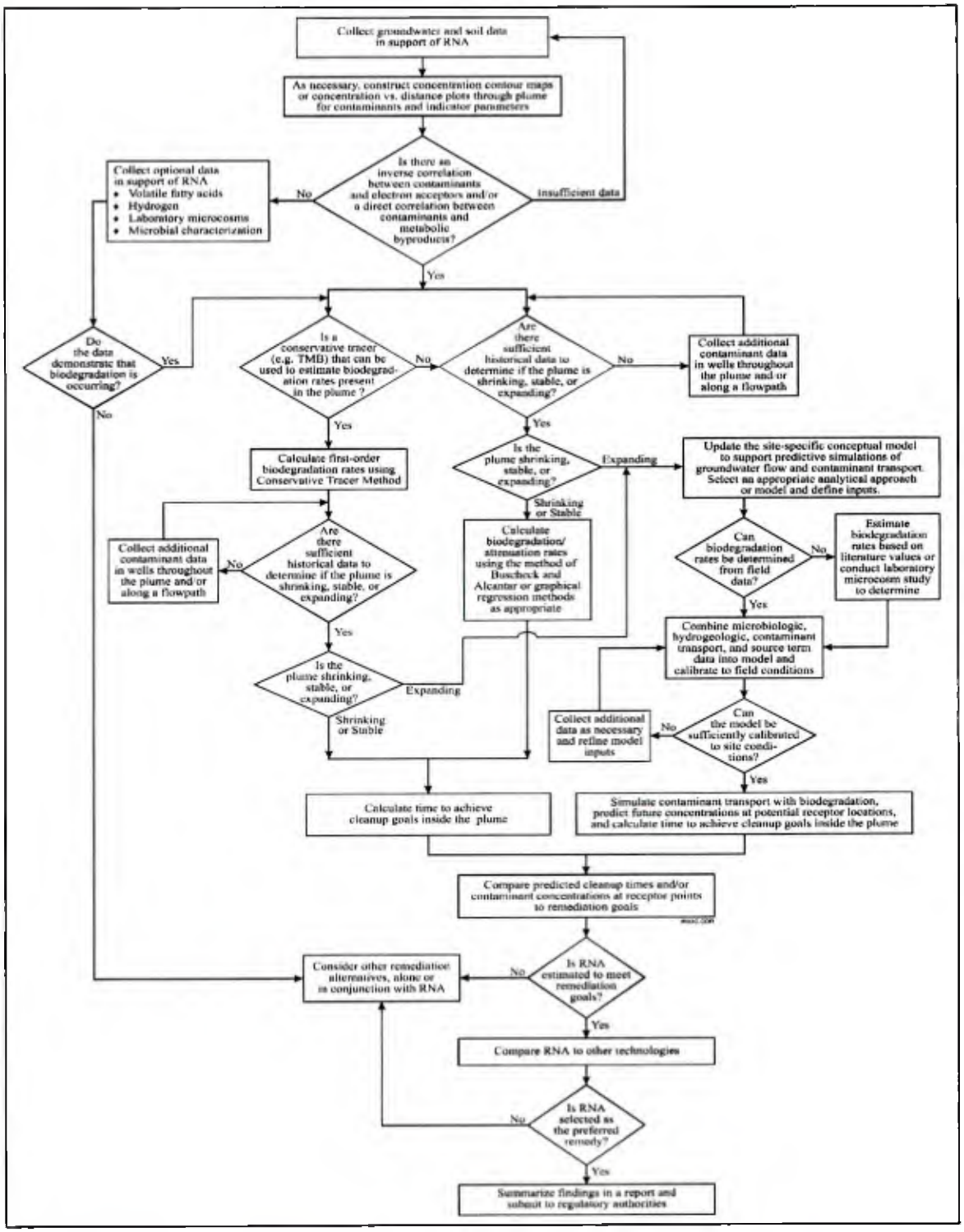



**Figure 5-1. Detailed site evaluation in support of remediation by natural attenuation.**

### 5.1.1 Collect Field Data in Support of RNA

Data collection for RNA focuses on demonstrating plume status, contaminant biodegradation, and protection of receptors. The type and frequency of data collection will depend on the site-specific hydrogeologic, geochemical, and contaminant conditions.

Soil and groundwater data are the principal data needed to evaluate RNA. Tables 5-1 and 5-2 show typical groundwater and soil analyses, respectively, with recommended methods and descriptions of where the samples should be taken and how the data should be used. Groundwater analyses are used to delineate the plume, characterize intrinsic biological activity at the site, and assess plume stability. Soil analyses are used to delineate the magnitude and extent of the contamination source and to estimate the total source mass. Source mass and source release calculations are discussed in Section 5.2.3.1 and Appendix B.2. To minimize the number of site visits, the groundwater and soil sampling events should be combined to the maximum extent possible.

There are no prescriptions for the minimum number of wells required to demonstrate RNA. However, to minimize the number of sample points, data can be collected along one or more plume transects rather than throughout the entire plume. This approach minimizes the number of samples by focusing the sampling along transects parallel and perpendicular to the direction of groundwater flow. Flowpath transects (i.e., parallel to flow) are the most useful because they can provide data for estimating biodegradation rates (see Section 5.2.1), and a flowpath transect along the plume centerline provides the most representative data regarding the plume status. Transect sampling is especially effective for sites where the direction of groundwater flow does not vary significantly throughout the year. Additional wells or multiple transects may be required if the groundwater flow direction is susceptible to changes. The plume transect approach is most effective for well-characterized plumes, where the longitudinal and lateral extent of the plume is understood. For poorly characterized plumes, transect plots may provide insufficient data to understand the dynamics of the entire plume.

Figure 5-2 shows an example soil sampling and groundwater monitoring well network for evaluating RNA. Wells are located along the plume centerline transect and transverse to the direction of groundwater flow. The transect includes sampling points located outside of the plume (i.e., upgradient and downgradient of the plume), as well as inside the plume. Three sampling points are included inside the plume. More wells will be required for larger plumes. An upgradient well is used to establish background concentrations for contaminants and geochemical parameters. Wells outside and downgradient of the plume are used to establish the plume boundaries and to monitor potential plume expansion. Multiple wells may be required at each sampling location if the plume has a significant vertical dimension.

For some sites where the direction of flow is unclear, samples may be collected from wells distributed throughout the plume and outside of the plume to generate contour maps. This approach is more time-consuming and expensive than collecting data along the transects, but it provides more comprehensive data for evaluating RNA.

## Table 5-1. Groundwater Analyses to Support RNA Demonstration

| Analysis | Recommended Method | Field or Off-Site Laboratory | Purpose | Field Location |
|---|---|---|---|---|
| Total petroleum hydrocarbons quantified as gasoline (TPH-g) BTEX | SW 846[(a)] 5030A/8015B | Off-site | Determine extent of contamination and monitor intrinsic TPH-g and BTEX biodegradation; establish plume status; correlate contaminants with indicators parameters | Dissolved plume area and/or plume transect |
| TPH quantified as diesel (TPH-d) | SW 846[(a)] 8015B | Off-site | Determine extent of contamination and determine TPH-d fraction; monitor TPH-d degradation. | Dissolved plume area and/or plume transect |
| 1,2,4- and 1,3,5-TMB | SW 846[(a)] 5030A/8010B | Off-site | Monitor TMB attenuation; use as internal tracers in anaerobic portion of the plume to establish mass loss and calculate biodegradation. | Dissolved plume area and/or plume transect |
| Semivolatiles for naphthalene and methylnaphthalene | SW 846[(a)] 5030A/8010B | Off-site | Monitor intrinsic degradation of PAHs only if PAHs are known or suspected to be present in groundwater. | Dissolved plume area and/or plume transect |
| Total organic compounds (TOC) | EPA 415.1[(b)] | Off-site | Supports calculation of contaminant retardation factor, $R_f$, for transport calculations | Dissolved plume area and/or plume transect and downgradient of plume |
| Dissolved oxygen (DO) | Field probe with direct reading meter[(c)] | Field | Indicator of hydrocarbon biodegradation if inversely correlated with hydrocarbon concentrations. DO concentrations below 1 mg/L suggest oxygen-limited conditions. | Dissolved plume area and/or plume transect, plus background |
| $NO_3^-/SO_4^{--}$ | EPA 300.0[(b)] | Off-site | Electron acceptors for nitrate and sulfate reduction. Indicators of anaerobic hydrocarbon biodegradation if inversely correlated with hydrocarbon concentrations. | Dissolved plume area and/or plume transect and background |
| Soluble iron ($Fe^{2+}$) and manganese ($Mn^{2+}$) | SW 846[(a)] 6010A | Off-site | Soluble products of iron and manganese reduction. Indicators of anaerobic hydrocarbon biodegradation if directly correlated with hydrocarbon concentrations. | Dissolved plume area and/or plume transect and background |
| Dissolved $CH_4$, propane | SW 846[(a)] 8000 | Off-site | The presence of $CH_4$ suggests hydrocarbon degradation by methanogenesis. Methane as natural gas will be contaminated with propane. | Dissolved plume area and/or plume transect and background |
| Dissolved $H_2S$, $HS^-$ | EPA 376.1[(d)] | Off-site | Byproduct of sulfate reduction. May be used as an indicator of hydrocarbon degradation. | Dissolved plume area and/or plume transect and background |
| Total alkalinity | Std. Methods[(d)] 2320B | Off-site | May be correlated directly with hydrocarbon concentrations as an indicator of biodegradation. | Dissolved plume area and/or plume transect and background |
| $H_2S$, $HS^-$, Nitrate, sulfate, $Fe^{2+}$, $Mn^{2+}$, alkalinity | Hach DREL/2000 Portable Laboratory[(d)] | Field | Used as indicators of biodegradation. Field analyses provide immediate results that are particularly useful when delineating plume areas. | Dissolved plume area and/or plume transect and background |
| Redox potential | Field probe with direct-reading meter | Field | Used as an indicator of the biological TEAP. Redox can range from +800 mV under aerobic conditions to –400 mV under methanogenic conditions. | Dissolved plume area and/or plume transect, and background |
| Conductivity, temperature, pH | Field probes with direct-reading meters | Field | General water quality parameters used during sampling, to ensure representative sample collection. | Dissolved plume area and/or plume transect, and background |

Note: (a) EPA, 1986
(b) EPA, 1995c
(c) Hach Catalog, 1999
(d) APHA et al., 1995

**Table 5-2. Soil Analyses to Support RNA Demonstration**

| Analysis | Recommended Method | Purpose | Field Location |
|---|---|---|---|
| TPH-G BTEX | SW 846[a] 5030A/8015B | Establish TPH-g and BTEX mass in the source area. Assess need for source remediation. Monitor TPH-g and BTEX degradation in soils. | Source |
| TPH-D | SW 846[a] 8015B | Establish TPH-d mass in the source area. Assess need for source remediation. Monitor TPH-d degradation in soils. | Source |
| PAHs | SW846[a] 8100 | Required only if PAHs are suspected. Monitor PAH degradation in soils. | Source |
| 1,2,4- and 1,3,5-TMB | SW 846[a] 5030A/8010A | Determine TMB content in source area. | Source |
| TOC | EPA 415.1[b] | TOC will affect contaminant sorption onto soils and the rate of contaminant transport. | Background |
| Volumetric moisture content | ASTM D2216[c] | Required to report results of chemical analyses on a dry-weight basis. Supports calculation of vertical mass flux rate through vadose zone. | Source |
| Bulk density | ASTM D2937[c] | Supports calculation of total mass in source zone. | Source |
| Grain-size distribution | ASTM D422[c] and D2487 | Used to estimate hydraulic conductivity if it is not measured. | Source |
| Saturated hydraulic conductivity | ASTM D5084[c] D2434-68(74) | Supports calculation of vertical flux rate through vadose zone. | Source |
| Specific gravity | ASTM D854[c] | Supports calculation of total porosity in vadose zone when bulk density is available. Total porosity is used to calculate total mass in source zone. | Source |

Note: (a) EPA, 1986
(b) EPA, 1995c
(c) ASTM, 1997c

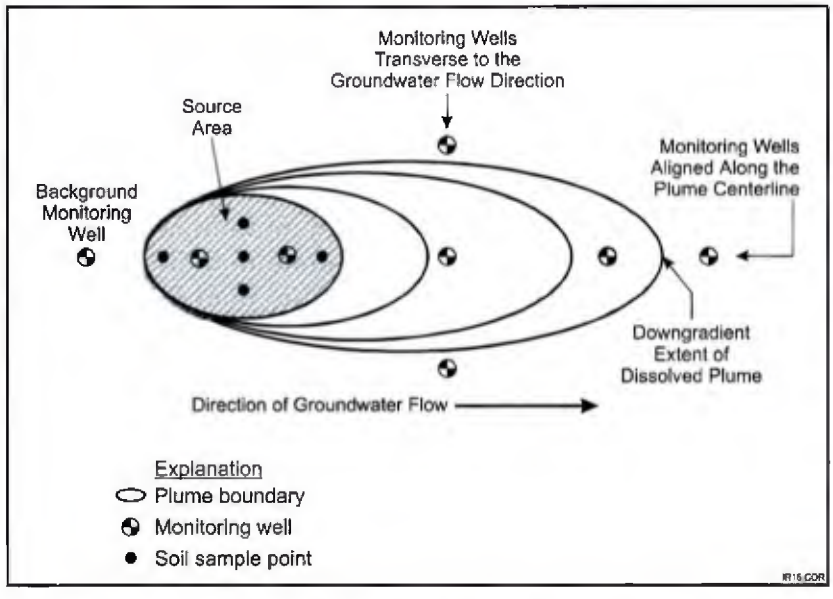



**Figure 5-2. Example well locations for evaluating RNA.**

### 5.1.2 Evaluate Data for Spatial Trends

A correlation between contaminants and electron acceptors or metabolic byproducts provides evidence that contaminant biodegradation is occurring. Contaminants and bioindicators should be plotted together and examined to determine if their spatial trends are correlated. Electron acceptors ($O_2$, $NO_3^-$, and $SO_4^-$) are depleted during hydrocarbon biodegradation, so concentrations should be inversely proportional to dissolved hydrocarbon concentrations. The concentration of metabolic byproducts of hydrocarbon biodegradation ($Fe^{2+}$, $Mn^{2+}$, $H_2S$, $CH_4$, and alkalinity) should be directly proportional to dissolved hydrocarbon concentrations. Figure 5-3 shows an example of two metabolic byproducts (manganese and methane) and alkalinity, all of which are indicators of biological activity, correlated with a dissolved BTEX plume at NAS Fallon, Nevada. The figure shows strong correlations between each indicator and BTEX, where the highest indicator concentrations correspond to the highest BTEX concentrations. The additional indicator plumes observed east of the BTEX plume are attributed to an adjacent TPH plume east and southeast of the BTEX plume.

### 5.1.3 Establish Biodegradation Using an Internal Tracer

Under certain conditions, the occurrence of contaminant biodegradation can be demonstrated if there is a conservative (i.e., nonbiodegradable) compound commingled in the BTEX plume. TMBs have been used as internal tracers to demonstrate biodegradation of BTEX compounds (Wiedemeier et al., 1995) because of the following properties:

1. TMBs are common cocontaminants of petroleum products.

2. TMBs have similar physical/chemical properties (i.e., similar sorption coefficients, Henry's law constants, and solubilities) to BTEX compounds. (It should be noted that this is only an approximation made to simplify the mathematical comparison between TMBs and BTEX compounds. Retardation factors for TMBs can be two to three times higher than for BTEX compounds, based on their relative octanol/water partition coefficients.)

3. TMBs are relatively recalcitrant to anaerobic biodegradation.

Because TMBs do not biodegrade significantly under anaerobic conditions, the amount that they attenuate between two points can be attributed primarily to physical/chemical mechanisms such as sorption, dispersion, diffusion, and volatilization.

Assuming that physical and chemical transport mechanisms affect TMB and BTEX compounds to the same extent, the relative decrease in BTEX concentrations between two points should be greater than the corresponding decrease in TMB concentrations, due to BTEX biodegradation. Equations 5-1 through 5-3 show how measured TMB concentrations can be used to correct BTEX concentrations measured between two points for the effects of dispersion, diffusion, sorption, and volatilization in order to detect concentration changes resulting from biodegradation. Given two points A and B, where Point B is located downgradient from Point A, Equation 5-1 is used to obtain the BTEX concentration at Point B that would be expected without dispersion, diffusion, sorption, or volatilization (i.e., due only to biodegradation between Points A and B). Thus, if BTEX is biodegraded, the corrected concentration at Point B should be less than the measured concentration at Point A.

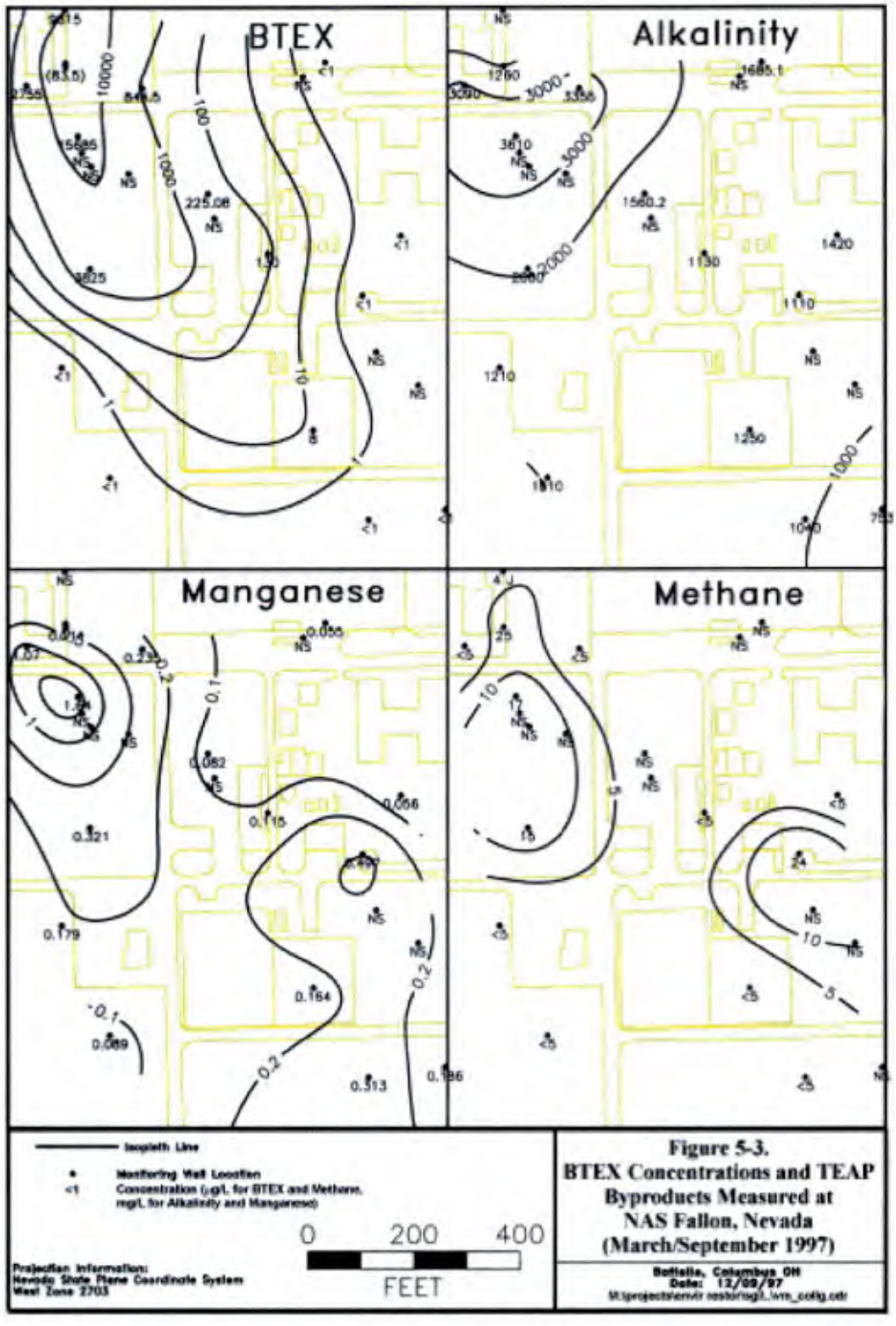



**Figure 5-3. BTEX concentrations and TEAP byproducts measured at NAS Fallon, Nevada.**

$$C_{B,Corr} = C_B\left(\frac{TMB_A}{TMB_B}\right) \quad (5\text{-}1)$$

where: $C_{B,Corr}$ = the corrected concentration of the BTEX compound at Point B (i.e., the concentration of the BTEX compound that would be expected without diffusion, dispersion, sorption, or volatilization)
$C_B$ = the measured concentration of the BTEX compound at downgradient Point B [$M/L^3$]
$TMB_A$ = the measured TMB concentration at upgradient Point A [$M/L^3$]
$TMB_B$ = the measured TMB concentration at downgradient Point B [$M/L^3$]

After correcting the measured BTEX concentrations for the nonbiological attenuating mechanisms, the difference in BTEX concentrations between Points A and B can be attributed to biodegradation (Wiedemeier et al., 1995). In Equation 5-2, $\Delta C_{Bio}$ describes the amount of contaminant loss due to biodegradation.

$$\Delta C_{Bio,AB} = C_{A,Obs} - C_{B,Corr} \quad (5\text{-}2)$$

where: $\Delta C_{Bio,AB}$ = the change in BTEX concentration between Points A and B, attributed to intrinsic biodegradation [$M/L^3$]
$C_{A,Obs}$ = the observed BTEX concentration at Point A [$M/L^3$]
$C_{B,Corr}$ = the corrected BTEX concentration at Point B [$M/L^3$].

The percent BTEX loss between Points A and B attributed to biodegradation and not to chemical/physical processes can be determined using Equation 5-3:

$$\Delta BTEX_{Bio} = \left(\frac{\Delta C_{Bio,AB}}{\Delta C_{Tot,AB}}\right) \bullet 100 \quad (5\text{-}3)$$

where: $\Delta BTEX_{Bio}$ = the percent BTEX lost to biodegradation
$\Delta C_{Tot,AB}$ = the observed change in BTEX concentration between points A and B, based on measured BTEX concentrations [$M/L^3$]

The total mass lost between Points A and B can be estimated by multiplying the BTEX concentration lost between the two points (i.e., $\Delta C_{Bio,AB}$) by the volume of water between these points (Wiedemeier et al., 1995).

An advantage of the internal tracer calculation is that it can be made with data from a single sampling event, so time-series data are not required to show evidence for contaminant loss due to biodegradation. Disadvantages of the internal tracer calculation are that the tracer compound must be present in the plume along with the contaminants, the tracer must have a similar distribution in the groundwater as the contaminants, and the assumption that TMBs have similar physical/chemical properties to BTEX compounds ignores the fact that octanol/water partition coefficients for TMBs are approximately three times higher than for BTEX compounds. Because of the higher octanol/water partition coefficients for the TMBs, they are expected to migrate more slowly than the BTEX compounds due to physical retardation. Thus, the magnitude and rate of BTEX degradation may be underestimated using this approach. Furthermore, the assumption that TMBs do not biodegrade under anaerobic

conditions also may lead to conservative estimates of BTEX degradation if anaerobic TMB biodegradation occurs.

### 5.1.4 Establish Plume Status

The occurrence of intrinsic biodegradation can be determined with time-series data (data collected over time) for the COCs. The contaminant plume can be identified as shrinking, stable, or expanding if the data collected over time indicate a statistically significant trend in contaminant concentrations. Shrinking or stable plumes provide evidence for a loss of mass over time due to biodegradation, whereas an expanding plume requires further evaluation to demonstrate that there has been a loss of contamination due to biodegradation. At sites where a statistically significant trend is not evident due to insufficient data, professional judgement and experience may be used. However, a statistical trend analysis (Appendix C) should be applied after adequate performance monitoring data are gathered.

Time-series data collected from the plume centerline wells should be plotted to assess whether or not there is a statistically significant trend present. Figures 2-1, 2-2, and 2-3 (Section 2.0) show the expected data trends for shrinking, stable, and expanding plumes when the data are plotted on log-linear plots of concentration versus time.

To establish if there is a significant trend in the data, short-term variations in monitoring well concentrations due to water table fluctuations, variability in groundwater flow direction, sampling variability, and analytical uncertainty should be distinguished from statistically significant concentration changes (ASTM, 1997a). This may be difficult because of the uncertainties inherent to environmental monitoring. Replicate and frequent sampling can statistically improve data interpretation, but will increase sampling and analytical costs. Although there is no prerequisite to the number of sampling events to establish a trend, ASTM (1996) recommends at least four monitoring events to establish the plume status. If possible, historical data or future performance monitoring data should be used to supplement the RNA study data to confirm or establish a significant trend.

The presence of a significant trend is not always immediately apparent based on visual inspection of data plots. Statistical methods can be used to further analyze the data to identify whether an increasing or decreasing trend is present. A statistical procedure using linear regression to detect a meaningful trend is provided in Appendix C. The method determines the confidence interval around the slope of a regression line to find out whether the observed trend is real or due to sample variability, and to identify whether contaminant concentrations are increasing or decreasing. The method is adopted from *Methods for Evaluating the Attainment of Cleanup Standards, Volume 2: Groundwater* (EPA, 1992b). A negative confidence interval indicates that concentrations are decreasing and a positive confidence interval indicates that concentrations are increasing. If the results do not suggest an increasing or decreasing trend, the plume can probably be considered to be at steady state provided there were several measurements made over time and there are no known data quality problems.

Some wells may show an increasing trend while others show a decreasing trend in contaminant concentrations. These results suggest that the plume is not stable but is "shifting." This "shifting" scenario may require additional monitoring to establish long-term trends. Additional monitoring may be conducted during performance monitoring for RNA, if permitted by the regulatory authorities.

### 5.1.5 Collect Additional Field/Laboratory Data for Evidence of RNA

Additional field and laboratory data are recommended only if the primary data (i.e., contaminants and biological indicator parameters) fail to provide conclusive evidence of contaminant biodegradation.

Additional data may include field $H_2$ analyses, laboratory analyses for VFAs and other BTEX metabolites, laboratory microcosms, or microbial counts and characterization.

**5.1.5.1 Hydrogen ($H_2$) Analyses.** Under anaerobic conditions, $H_2$ is produced continuously by fermentative microorganisms. The $H_2$ is then used by anaerobic respiring organisms, including, most commonly, organisms that use Fe(IV), Mn (III), sulfate, and carbon dioxide as terminal electron acceptors (Chapelle et al., 1997). Each of these electron acceptors has a unique affinity for $H_2$, producing predictable steady-state dissolved $H_2$ concentrations in groundwater. Methanogens have the lowest affinity for $H_2$, resulting in the highest steady-state $H_2$ concentrations, followed by sulfate reducers, iron reducers, and nitrate reducers. Table 5-3 shows the expected steady-state $H_2$ concentrations in groundwater as a function of the terminal electron acceptor process (Chapelle et al., 1997).

**Table 5-3. $H_2$ Concentrations in Groundwater and Corresponding Electron Acceptor Processes[(a)]**

| Electron Acceptor Process | Approximate Steady-State $H_2$ Concentration (nm) |
|---|---|
| Nitrate reduction | < 0.1 |
| Iron reduction | 0.2 – 0.8 |
| Sulfate reduction | 1 – 4 |
| Methanogenesis | 5 – 30 |

Note: (a)

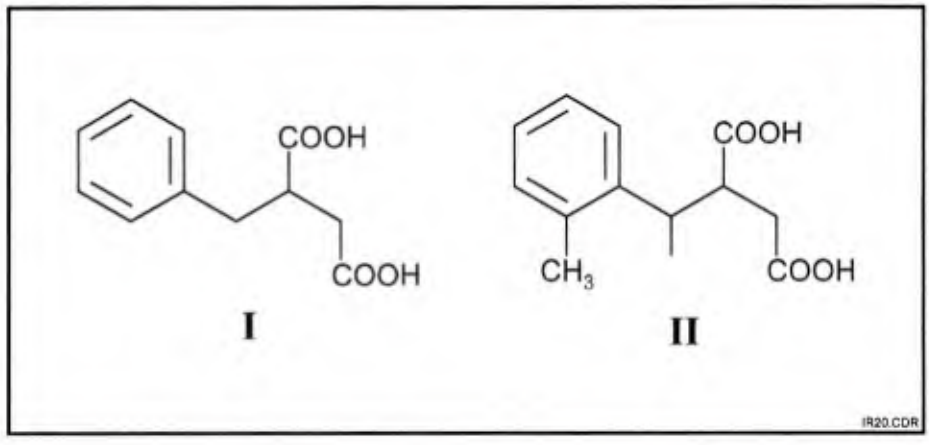
When $H_2$ is used as an indicator of the anaerobic electron acceptor processes occurring in groundwater, the distribution of these processes can be mapped and correlated with contaminant concentrations in the groundwater to establish the occurrence of intrinsic biodegradation.

As with many constituents measured in groundwater, $H_2$ can be affected by sampling and analytical errors. $H_2$ sampling is somewhat difficult, but innovative sampling techniques have been developed recently. For $H_2$ sampling methods, see Chapelle et al. (1997). Because of the instability of $H_2$ in groundwater samples, $H_2$ should be analyzed in the field using a gas chromatograph equipped with a reduced gas detector (RGD). This unique requirement and cumbersome sampling methods make $H_2$ less popular and more expensive than alternative analyses that provide similar information, such as measuring redox potential or electron acceptors. However, $H_2$ is gaining increasing favor and should be considered as an option on a site-by-site basis.

**5.1.5.2 Volatile Fatty Acid Analyses.** BTEX compounds are known to degrade anaerobically through a series of acidic, phenolic, and carboxylated intermediates (Barcelona et al., 1995). Common intermediates include *ortho*-, *meta*-, and *para*-toluic acids, salicylic acid, and a wide range of substituted benzoic acids. Identification of these compounds provides direct qualitative evidence of anaerobic BTEX biotransformation. The example below shows example VFA results from an ongoing RNA study for the Navy. However, because organic acid concentrations are difficult to correlate with specific in-situ redox processes, VFAs cannot be used to determine TEAPs.

## Example VFA Results from a BTEX Plume

In an ongoing Navy study, groundwater samples were collected and analyzed for aromatic VFAs according to methods described in Beller et al. (1995). Samples were extracted with diethyl ether, derivatized with diazomethane, and analyzed by gas chromatography/mass spectrometry (GC/MS). Benzylsuccinic acid (Structure I, below) and (2-methylbenzyl)succinic acid (Structure II, below) were measured at 110 and 220 µg/L, respectively, in monitoring well GTI14-2 (GTI14-2 is located within a BTEX plume, with approximately 16 mg/L BTEX). The significance of finding benzylsuccinic acid and (2-methylbenzyl)succinic acid in the groundwater is that these compounds are highly distinctive metabolites of the anaerobic microbial metabolism of toluene and *o*-xylene, respectively (Beller et al., 1995). They have no commercial or industrial sources and are unique to anaerobic (as opposed to aerobic) hydrocarbon metabolism (Beller et al., 1995). Additional samples, analyzed by the EPA laboratories in Ada, Oklahoma, showed relatively high concentrations of a wide variety of phenolic, benzoic, and other aromatic acids. These results provide strong supporting evidence of anaerobic BTEX degradation at this site. The VFA analyses were necessary because high pH (pH > 8.0), high dissolved salts (chloride > 10,000 mg/L), high sulfate concentrations ($SO_4^=$ > 5,000 mg/L), and complicated interpretation of electron acceptor and metabolic product distributions in groundwater raised questions about the site's suitability for anaerobic BTEX degradation.




Few contract laboratories perform analyses for aromatic organic acids because they are difficult and expensive. Thus, VFAs are not commonly analyzed to demonstrate RNA. They are most beneficial for sites where correlations between contaminant concentrations and electron acceptor or metabolic byproducts are uncertain. For analytical methods for VFA analyses, see Barcelona et al. (1995) and Beller et al. (1995).

**5.1.5.3 Laboratory Microcosm Studies.** Laboratory microcosm studies can be used to provide direct, qualitative evidence of intrinsic biodegradation. Typical microcosm studies involve taking aquifer samples from the site to the laboratory where they are spiked with known amounts of the contaminant(s) of interest and monitored over time for a decrease in contaminant concentration. Control microcosms ensure that contaminant losses can be attributed to biodegradation. Microorganisms responsible for biodegrading the contaminants generally are not identified during microcosm studies. Although historically laboratory microcosm studies have been used to estimate biodegradation rates, microcosm studies tend to overestimate actual field rates. Microcosms are most appropriately used as qualitative indicators of the potential for RNA, whereas in-situ field measurements are the preferred

method to determine actual fuel hydrocarbon degradation rates (Wiedemeier et al., 1995). Section 5.2.1 provides more information on field methods to determine biodegradation and natural attenuation rates.

Because laboratory microcosms studies can be costly, they are used as a last resort to demonstrate RNA. For most petroleum hydrocarbons, such as the BTEX compounds, laboratory microcosm studies are unnecessary because the conditions under which BTEX compounds biodegrade are well understood. Furthermore, BTEX-degrading bacteria are nearly ubiquitous in the environment, and their presence does not need to be demonstrated at every site. With respect to petroleum release sites, laboratory microcosm studies are most useful for compounds that are not easily degraded, such as some PAH compounds, and for sites where biodegradation of the contaminants of interest is uncertain.

## 5.2 ASSESS THE EFFICIENCY OF RNA

The efficiency of RNA is measured by its ability to protect receptors and to remediate the site within an acceptable time frame. Deciding on what constitutes an *acceptable* time frame compared to alternative remediation technologies may depend on a number of site-specific variables, including regulatory perspectives, public involvement, and the cost of RNA compared to the cost for the alternative technologies.

The level of analysis and the required amount of data to establish each of these objectives will depend on site-specific hydrogeologic and geochemical conditions, the magnitude and extent of contamination, the plume status (expanding plumes will require much more careful consideration than stable or shrinking plumes), the beneficial use of the impacted aquifer, and the potential risks posed by the contaminants. In general, the following actions are taken to determine RNA efficiency:

- Evaluate the potential for contaminants to impact downgradient receptors (using modeling for expanding plumes)

- Estimate the time to achieve final cleanup objectives using contaminant degradation rates and knowledge of contaminant transport parameters.

Both of these activities require knowing the rate of contaminant biodegradation or the total attenuation rate for the COC. Therefore, contaminant degradation rates must be determined as part of the assessment of RNA efficiency.

### 5.2.1 Practical Approaches to Determining In-Situ Contaminant Degradation Rates

In-situ biodegradation rates may be calculated for shrinking, stable, and expanding plumes to determine the following:

- For shrinking and stable plumes, the degradation rates are used to estimate how long it will take RNA to achieve cleanup goals that have been established for the site.

- For expanding plumes, the degradation rates are used in a fate and transport model that accounts for physical/chemical attenuating mechanisms (e.g., advection, dispersion, dilution due to recharge, and sorption) and biodegradation. The model may be used to determine the maximum distance the contaminants are expected to migrate, the maximum future concentrations at receptor points, or the time for RNA to achieve cleanup goals.

In-situ biodegradation rates can be divided into two categories, one for aerobic bacteria and one for anaerobic bacteria. Aerobic bacteria degrade hydrocarbons much faster than anaerobic bacteria, principally because they derive more energy from oxygen respiration than anaerobic bacteria derive from alternate electron acceptors.

For simplicity, and because in-situ aerobic degradation rates tend to be very fast relative to groundwater transport rates, aerobic biodegradation rates for petroleum hydrocarbons are commonly assumed to be instantaneous (Borden and Bedient, 1986). Aerobic respiration results in rapid oxygen depletion in areas of high groundwater contamination and rates are generally limited by the rate of oxygen diffusion into the groundwater. Thus, aerobic respiration tends to be significant only in areas of high groundwater recharge (where oxygen is rapidly replenished in the groundwater) and at the outer fringes of a hydrocarbon plume where there is ample oxygen available.

The remainder of the plume must rely on anaerobic processes for mass destruction, which cannot be assumed to be instantaneous. Instead, the anaerobic biodegradation rate is generally directly proportional to the contaminant concentration in groundwater. Thus, anaerobic biodegradation can be modeled as a first-order process, as shown in Equation 5-4:

$$\frac{dC}{dt} = \lambda C \tag{5-4}$$

where: $\frac{dC}{dt}$ = the change in contaminant concentration over time [$M/L^3$–T]
$C$ = the groundwater contaminant concentration at time t [$M/L^3$]
$\lambda$ = the first-order rate constant [1/T].

This approach makes a broad, simplifying assumption that the anaerobic portion of the plume can be defined by a single first-order rate.

**5.2.1.1 Aerobic Respiration (Instantaneous Reaction Rates).** The change in BTEX concentrations resulting from aerobic biodegradation is determined by the stoichiometric relationship between the BTEX compounds and oxygen. Equation 5-5 can be used to determine the concentration of BTEX consumed per unit concentration of DO available in the groundwater in contact with the BTEX:

$$\Delta C_{BTEX} = 0.32 \cdot C_{O_2} \tag{5-5}$$

where: $\Delta C_{BTEX}$ = the potential change in BTEX concentration due to aerobic BTEX degradation [$M/L^3$]
$C_{O_2}$ = the background or recharge $O_2$ concentration [$M/L^3$]
0.32 = the stoichiometric ratio of BTEX mass degraded per unit mass $O_2$ consumed.

This equation states that approximately 0.32 mg/L BTEX will be consumed per 1.0 mg/L oxygen. If we know the groundwater recharge volume, and recharge is the primary $O_2$ delivery mechanism, we can calculate the total BTEX mass consumed aerobically, using Equations 5-6 and 5-7:

$$M_{O_2} = V_{Recharge} \cdot C_{O_2} \tag{5-6}$$

$$\Delta M_{BTEX} = 0.32 \cdot M_{O_2} \quad (5\text{-}7)$$

where: $M_{O_2}$ = the $O_2$ mass introduced through groundwater recharge [M]
$V_{Recharge}$ = the volume of recharge [$L^3$]
$\Delta M_{BTEX}$ = the potential change in BTEX mass due to aerobic BTEX degradation [M]

Aerobic BTEX degradation also can be stimulated by oxygen diffusion into groundwater. However, oxygen diffusion is a relatively slow process and often limits the rate of aerobic biodegradation. For oxygen diffusion, the mass loss rate due to aerobic biodegradation can be calculated only if oxygen diffusion rates are considered.

**5.2.1.2 Anaerobic First-Order Degradation Rates.** Several methods based on field measurements of contaminant concentration are available to determine a total attenuation rate or a biodegradation rate under anaerobic conditions. The selection of the appropriate method depends on the status of the plume and the available data. These methods are discussed below and summarized in Table 5-4.

***Attenuation Rate for a Shrinking Plume (ASTM, 1997a).*** The temporal regression method is conducted by measuring a change in contaminant concentration over time in a single well and determining the first-order rate constant ($\lambda$) by solving the first-order differential rate equation (Equation 5-4). Solving Equation 5-4 yields Equation 5-8:

$$C(t) = C_0 e^{-\lambda} \quad (5\text{-}8)$$

Rearranging Equation 5-8 and solving for the first-order rate constant ($\lambda$) yields (Equation 5-9):

$$\lambda = -\frac{-\ln\left(\frac{C_t}{C_0}\right)}{t} \quad (5\text{-}9)$$

where: $C_t$ = the contaminant concentration at time t [$M/L^3$]
$C_0$ = the initial concentration at time t = 0 [$M/L^3$]
t = time [T]
$\lambda$ = natural attenuation rate constant [1/T]

The resulting first-order rate constant is an overall attenuation rate that includes advection, dispersion, dilution from recharge, sorption, and biodegradation. For a shrinking plume, $\lambda$ will be a positive number, whereas $\lambda$ will be zero for a stable plume. It is important to verify that the data conform to the first-order assumption for $\lambda$ to be valid. This can be easily done by inspecting the log-linear plot of concentration versus time. If the slope is linear (i.e., the regression coefficient [$r^2$] is close to 1.0), then the concentration data fit a first-order (exponential) pattern and Equation 5-4 can be assumed to be valid. The $r^2$ value for field analyses should be greater than 0.85, if possible. Lower $r^2$ values do not necessarily invalidate the first-order model, but raise uncertainty.

## Table 5-4. Methods to Determine Contaminant Degradation Rates[a]

| Plume Configuration | Method (Reference) | Rate Determination | Data Requirements |
|---|---|---|---|
| Shrinking plume | Temporal Regression (ASTM, 1997a) | A first-order natural attenuation rate is determined for single wells with decreasing concentrations over time. Divide the slope of the natural log concentration vs. time regression by time to determine the biodegradation rate. | • Concentration contaminant measured in monitoring well(s) over time<br>• Data must fit first-order assumption |
| Stable plume | Spatial Regression (ASTM, 1997a) | A first-order natural attenuation rate is determined using data from multiple wells aligned along a groundwater flowpath. Multiply the slope of the log concentration vs. distance regression by the groundwater velocity to determine the natural attenuation rate. | • Contaminant concentrations along the plume transect<br>• Distance between wells<br>• Groundwater flowrate (advection)<br>• Data must fit first-order assumption |
| | Analytical Solution (Buscheck and Alcantar, 1995) | A first-order contaminant biodegradation rate is determined using data from multiple wells aligned along a groundwater flowpath. Using an analytical solution for one-dimensional transport with first-order decay, solve for the first-order biodegradation rate. | • Contaminant concentrations along the plume transect<br>• Groundwater flowrate (advection)<br>• Longitudinal dispersivity<br>• Retardation coefficient<br>• Data must fit first-order assumption |
| | Mass Balance (ASTM, 1997a) | A natural attenuation rate (mass destroyed per day) is estimated by calculating the contaminant-loading rate into groundwater. The attenuation rate is equal to the loading rate in a stable plume. | • Data must fit first-order assumption<br>• Source mass (sorbed and free phase)<br>• Contaminant solid/liquid and fuel/liquid partition coefficients<br>• Vertical and horizontal hydraulic loading rates |
| Shrinking, stable, or expanding plume | Conservative Tracer Method (Wiedemeier et al., 1995) | A first-order biodegradation rate is determined between two wells for the BTEX compounds. | • Contaminant concentrations along the plume transect<br>• Tracer (i.e., TMB) concentrations along the plume transect<br>• Distance between wells<br>• Groundwater flowrate (advection)<br>• Data must fit first-order assumption |
| Expanding plume | Modeling Approach | Numerical or analytical models can be used to estimate biodegradation rates. Calibrate the model to reproduce the observed concentration distribution of a conservative compound in groundwater. Use the calibrated model to simulate the observed distribution of biodegradable contaminants. Adjust biodegradation rates used in the model until a good fit between observed and simulated concentrations is achieved. | • Contaminant and conservative tracer concentrations throughout plume, or along the transect<br>• Groundwater hydrogeologic parameters: recharge rates, hydraulic head, hydraulic conductivity<br>• Contaminant properties: retardation factors, dispersivities<br>• Source term data: contaminant mass flux rate into groundwater |

Note: (a) A natural attenuation rate does not distinguish between physical/chemical mechanisms and biodegradation.

***Natural Attenuation Rate and Biodegradation Rate for a Stable Plume.*** Three methods can be used to determine a degradation rate for a stable plume. The first method involves a *spatial regression* based on the first-order equation (Equation 5-4), where a linear regression of contaminant concentration versus distance along the plume transect

provides a natural attenuation rate due to physical, chemical, and biological attenuating mechanisms (ASTM, 1997a). The second method employs an *analytical solution* for steady-state, one-dimensional contaminant transport with first-order decay. This method, proposed by Buscheck and Alcantar (1995), is used to determine the *biodegradation* rate for a stable plume. The third method is based on a *mass balance* of contaminants entering a plume from a known source and the mass of contaminants removed through biodegradation. This method gives a zero-order natural attenuation rate.

The **spatial regression** method (ASTM, 1997a) involves plotting the log concentration versus distance for a minimum of three monitoring wells along a plume transect oriented in the direction of groundwater flow. A linear regression of the data provides an estimate of the natural attenuation rate. This method employs the following simple modification of Equation 5-8. First, the groundwater travel time, t, between two wells is calculated using Equation 5-10:

$$t = \frac{x}{v_x} \tag{5-10}$$

where: t = the travel time between two wells, A and B [T]
x = the travel distance between wells A and B [L]
$v_x$ = the average linear groundwater velocity (see Equation 4-2) [L/T]

Substituting $\left(\frac{x}{v_x}\right)$ for t in Equation 5-8 results in Equation 5-11:

$$C(x) = C_0 e^{-\left(\frac{\lambda}{v_x} x\right)} \tag{5-11}$$

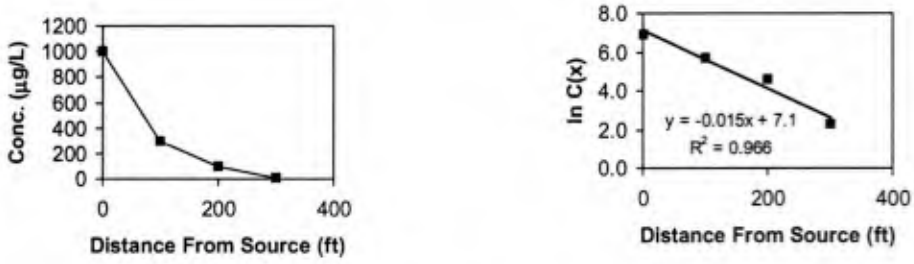
where: C(x) = the contaminant concentration as a function of distance x from an upgradient location [$M/L^3$]
$C_0$ = the concentration at the upgradient location (i.e., at x = 0) [$M/L^3$]
$\lambda$ = the first-order natural attenuation rate [1/T]

Equation 5-11 can be rearranged to yield:

$$\ln C(x) = -\frac{\lambda}{v_x}(x) + \ln C_0 \tag{5-12}$$

Equation 5-12 describes the line defined by the log concentration versus distance plot, where the slope of the line is $\frac{\lambda}{v_x}$ [1/L]. If the slope is multiplied by the groundwater pore velocity, $v_x$, we obtain the natural attenuation rate $\lambda$. Figure 5-4 demonstrates the spatial regression approach.

| Distance from Source, x (ft) | Conc. C(x) (µg/L) | Log Conc. ln C(x) |
|---|---|---|
| 0 | 1,000 | 6.9 |
| 100 | 300 | 5.7 |
| 200 | 100 | 4.6 |
| 300 | 10 | 2.3 |




The slope of the regression equals –0.015. Therefore, $\frac{\lambda}{v}$ = 0.015/ft. Assuming a groundwater flow velocity of 1 ft/day, $\lambda$ = (0.015/ft)(1 ft/day) = 0.015/day.

**Figure 5-4. Example spatial regression analysis.**

The **analytical solution** (Buscheck and Alcantar, 1995) employs the following one-dimensional transport equation with a first-order decay coefficient (Equation 5-13):

$$\frac{\partial C}{\partial t} = \frac{1}{R_f}\left[D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x}\right] - \lambda C \qquad (5\text{-}13)$$

where: $D_x$ = the dispersion coefficient [$L^2/T$]
$v_x$ = the average linear groundwater velocity [L/T]
$\lambda$ = the first-order natural attenuation rate [1/T].
$R_f$ = the retardation factor.

The retardation factor equals the ratio of the groundwater velocity to contaminant velocity and is calculated as (Equation 5-14):

$$R_f = 1 + \left(\frac{\rho_b}{n_e}\right) K_d \qquad (5\text{-}14)$$

where: $\rho_b$ = dry bulk density of the aquifer [$M/L^3$]
$n_e$ = the effective porosity of the aquifer
$K_d$ = the soil adsorption coefficient [$L^3/M$].

The soil adsorption coefficient can be calculated using Equation 5-15 (See Appendix B):

$$K_d = K_{oc} \cdot f_{oc} \quad (5\text{-}15)$$

where: $K_{oc}$ = the organic carbon partition coefficient (see Appendix A for $K_{oc}$ values for common petroleum contaminants) [$L^3/M$]
$f_{oc}$ = fraction of total organic carbon in soil.

Buscheck and Alcantar (1995) derive the following solution for Equation 5-13, which couples the spatial regression solution (Equation 5-12) with the analytical solution to Equation 5-13 to give a first-order biodegradation rate for a steady-state plume:

$$k = \frac{v_c}{4\alpha_x} \cdot \left( \left[ 1 + 2\alpha_x \left( \frac{\lambda}{v_x} \right) \right]^2 - 1 \right) \quad (5\text{-}16)$$

where: $k$ = the first-order biodegradation rate [1/T]
$v_c$ = the contaminant transport velocity ($v_c = v_x/R_f$) [L/T]
$\alpha_x$ = the longitudinal dispersivity [L/T] (see Appendix A for dispersivity values of common petroleum contaminants)
$\lambda/v_x$ = the slope of the spatial regression (see Equation 5-12, above).

Whereas $\lambda$ incorporates the effects of advection, dispersion, sorption, and biodegradation, k represents the first-order biodegradation rate, which does not include physical and chemical mechanisms.

The **mass balance** method calculates the mass loading rate to groundwater as an estimate of the overall mass removal rate for a steady-state plume. In a stable plume, concentrations are not changing over time, which is only possible if the contaminant mass loading rate to groundwater is approximately equal to the overall natural attenuation rate of the plume (ASTM, 1997a). Detailed methods to determine the mass loading rate are discussed in Appendix B. The loading rate provides a zero-order estimate of the natural attenuation rate in units of mass removed per time [M/T] that is applicable only under the steady-state condition. In general, this approach is useful only when well data are not available to allow using the spatial regression or analytical solution methods, or to corroborate biodegradation rates determined with the spatial regression method. At bes, source loading terms are rough estimates and therefore provide only rough estimates of the overall attenuation rate.

***Conservative Tracer Method (Wiedemeier et al., 1995).*** Section 5.1.3 describes how to calculate the amount of BTEX lost between two wells located along a groundwater flow path due to biodegradation using TMB as a conservative tracer. The tracer method uses the first-order rate equation (see Equation 5-8), where the TMB-corrected contaminant concentration in the downgradient well ($C_{corr}$), is substituted for C(t), and the measured concentration in the upgradient well ($C_{o,meas}$) is substituted for $C_o$. These two substitutions yield the following equation (Equation 5-17):

$$C_{corr} = C_{o,meas} e^{-kt} \quad (5\text{-}17)$$

where: $C_{corr}$ = the TMB-corrected contaminant concentration (see Equation 5-1) at the downgradient well [$M/L^3$]
$C_{o,meas}$ = the measured contaminant concentration at the upgradient well [$M/L^3$]
k = the first-order biodegradation rate [1/T]

Because TMB-corrected contaminant concentrations are used in the calculation, k represents the biodegradation rate separated from physical/chemical transport mechanisms. However, for reasons discussed in Section 5.1.3, the use of TMB compounds as internal tracers provided a conservative estimate of BTEX biodegradation rages and may underestimate the natural attenuation rate.

Solving for k gives (Equation 5-18):

$$k = \frac{-\ln\left(\frac{C_{corr}}{C_{o,meas}}\right)}{t} \qquad (5\text{-}18)$$

The time t equals the groundwater travel time from the upgradient well to the downgradient well (see Equation 5-10). Substituting the expression for t into Equation 5-18 and rearranging yields (Equation 5-19):

$$\ln C_{corr} = -\frac{\lambda}{v_x} \cdot x + \ln C_{o,meas} \qquad (5\text{-}19)$$

The log of the corrected concentrations in wells located along the plume transect are plotted versus distance along the transect and the slope, m, of the regression line is equal to the biodegradation rate constant divided by the average linear groundwater velocity (Equation 5-20):

$$m = \frac{k}{v_x} \qquad (5\text{-}20)$$

The biodegradation rate k is determined by multiplying the slope of the regression line by the average linear groundwater velocity, $v_x$.

***Modeling Method.*** Numerical and analytical models can be used to estimate biodegradation rates. The general approach is to first calibrate the model to correctly simulate groundwater flow conditions at the site. This step ensures that the values specified in the model for the hydrogeologic parameters, such as hydraulic conductivity and recharge, are appropriate. The next step is to calibrate the model to reproduce the observed concentration distribution of the contaminants in groundwater. This is achieved by adjusting the values specified in the model for key transport parameters, namely dispersion, biodegradation rate, and source concentrations.

Ideally, if a conservative tracer (i.e., a nonbiodegradable compound such as TMB having similar sorption behavior as the BTEX compounds) is present in the plume, the model can first be calibrated to match its concentration distribution in the groundwater. This way, the biodegradation rate is not involved in the calibration step. Then, the model is

recalibrated to match the concentration distribution of the biodegradable contaminant by adjusting the biodegradation rate-term in the model. Note that this applies only when biodegradation is represented in the model by a first-order decay term; however, this generally is acceptable for simulating biodegradation of petroleum hydrocarbons.

At many sites, a conservative tracer may not be comingled in the plume with the contaminants of concern. In this case, the model is calibrated to match the concentration distribution of a biodegradable contaminant. This requires simultaneously adjusting multiple model parameters, including biodegradation, retardation, dispersion, and source concentrations, until an acceptable match between simulated and measured concentrations is obtained. Because more parameters are used in the calibration, the biodegradation rate that is determined this approach will have a larger uncertainty.

As much as possible, the biodegradation rate should be calculated based on existing field data. Appendix B discusses groundwater modeling approaches and data requirements in greater detail.

**5.2.1.3 Laboratory Methods.** In addition to providing convincing evidence of the occurrence of RNA, laboratory microcosms also can be used to determine biodegradation rates. However, the following factors usually prevent their use in establishing degradation rates at most sites: (1) microcosms tend to be time consuming and expensive, and (2) it is difficult to simulate existing site conditions in the laboratory. Microcosms commonly overestimate biodegradation rates because well-mixed or blended soils are used, which can enhance nutrient availability to bacteria. However, if properly designed, implemented, and interpreted, microcosms can provide convincing evidence of the occurrence of intrinsic biodegradation, and they can be used to determine in-situ biodegradation rates if other methods are not available, or where there is considerable uncertainty concerning contaminant biodegradation rates based on soil and groundwater sampling.

The following guidelines should be followed for laboratory microcosm studies:

- As much as possible, the microcosms should simulate contaminant concentrations, localized TEAPs, electron acceptor concentrations, and redox conditions in the field. Thus, microcosm studies should not be conducted until the site hydrogeology, contaminant distribution, and geochemistry are well understood.

- Rate constants will vary according to the TEAP, type of contaminant, and contaminant concentration. Consequently, soils should be acquired at depths and locations that represent the prevailing local geochemical conditions. Time and cost may limit the number of microcosms.

- Anaerobic microcosms should not be exposed to oxygen during transport. Oxygen is toxic to most anaerobic microorganisms, except nitrate-reducing bacteria.

- Microcosms should be prepared in triplicate for statistical reasons. Sampling should reflect the observed rate of contaminant degradation. If the degradation rate is unknown, more frequent early sampling is recommended.

- Batch microcosms should have approximately the same ratio of solids to liquid as field soils. Microcosms should not be mixed or stirred during incubation, which may enhance the bioavailability of contaminants and electron acceptors, resulting in

overestimated degradation rates. However, mixing may be required during sampling to obtain a representative and homogeneous sample.

- During sampling, liquid may need to be replenished in the microcosm. For anaerobic microcosms, care should be taken not to introduce oxygen which may inhibit anaerobic microorganisms or enhance contaminant aerobic respiration by facultative bacteria.

**5.2.1.4 Literature Values.** In the absence of field data, literature values may be used as an estimate of the contaminant biodegradation rates for the site. When using literature values, conservative values (i.e., low degradation rates) should be used, so that concentrations at downgradient receptors and cleanup times are not underestimated. A conservative biodegradation rate that demonstrates protection of receptors strengthens the case to regulators for using RNA. Table 5-5 shows some rates reported in the literature. Additional literature values are provided in Appendix A.

**Table 5-5. Anaerobic Biodegradation Half-Lives for Petroleum Contaminants**

| Contaminant | Half-Life (weeks) |
|---|---|
| BTEX (total) | 0.53 – 10 |
| BTEX (total) | 10.4 – 33 |
| BTEX (total) | 23.5 – 99 |
| Benzene | 2.3 – 14 |
| Toluene | 2.6 – 4.3 |
| Ethylbenzene | 3.5 – 11.5 |
| Xylenes | 3.5 – 17.3 |
| Naphthalene | 8.4 – 15.75 |

Source: Weidemeier et al., 1995.

### 5.2.2 Calculate Future Concentrations at Downgradient Receptors Through Modeling

The feasibility of RNA relies on its ability to degrade contaminants before they migrate to downgradient receptors at levels that could cause an unacceptable impact to human health or the environment. For sites with a shrinking or stable plume, the long-term protection of downgradient receptors can be established with historical data that show that the contaminants are not migrating in the groundwater, therefore, this step is not required to demonstrate the effectiveness of RNA for shrinking or stable plumes. In these cases, the efficiency of RNA is assessed solely on the basis of the time required to cleanup goals for the site. However, for sites where there is an expanding plume or where the plume status is uncertain because of a lack of historical data, the protection of downgradient receptors is more difficult to establish. For these cases, modeling or analytical solutions will be required to determine if RNA is occurring at a rate that is sufficient to degrade the contaminants before they reach downgradient receptors.

This section discusses how modeling can be used to predict the extent of future contaminant migration to determine if downgradient receptors will be adversely impacted. Appendix B provides a detailed discussion of the modeling process, including the following:

- Development of a detailed conceptual model to support contaminant transport modeling
- Model input parameters

- Defining the source term
- Calibration of a contaminant transport model

If the model predictions demonstrate that the plume will not reach any receptors, then there is no demonstrable risk to human or ecological receptors. Under these circumstances, RNA meets the criteria of providing long-term protection of human health and the environment, provided land uses in the area of impacted groundwater do not change. This may be the case for many petroleum releases because dissolved BTEX plumes generally do not experience significant expansion due to intrinsic biodegradation. In a study of 271 leaking underground fuel tank (LUFT) sites in California, Rice et al. (1995) reported that benzene plume lengths rarely exceeded 250 feet. This generalization may not be accurate for all geologic settings and all fuel components, thereby requiring that each site be considered independently.

If modeling indicates that a contaminant is likely to reach an exposure point before it is completely degraded, there is a potential for an adverse impact to human health and the environment. The predicted future concentrations should be used in a risk assessment to quantify the magnitude of the impact for the likely exposure scenarios. If the resulting impacts are within acceptable limits, then RNA may be considered to be an acceptable remedy for the site. However, in these cases, more extensive sampling will be required during performance monitoring (see Section 6.0) to ensure that concentrations at the receptor point(s) agree with model predictions and to ensure the protection of potential receptors.

**5.2.2.1 Conditions Requiring Modeling.** Because modeling is perceived as an expensive task, the need for modeling should be clearly established on a case-by-case basis. The responses to the following questions aid the user to establish whether modeling is necessary and to determine the magnitude of the modeling effort (i.e., whether a steady-state or transient, one-, two-, or three-dimensional, analytical or numerical model is required) (Anderson and Woessner, 1992):

1. Is a modeling exercise the best way to answer the questions? For shrinking or stable plumes, modeling may not be required, and the time required for RNA to meet cleanup goals can be calculated using source attenuation and plume attenuation rates. Furthermore, modeling may not be required for *all* expanding plumes. For example, if an expanding plume poses no immediate, imminent, or long-term risk to a receptor, monitoring long-term trends may be sufficient.

2. Can an analytical model provide the answer, or must a numerical model be constructed? Analytical models generally are less expensive and provide results more quickly than numerical models. For many petroleum-contaminated sites, a simple analytical model may suffice, provided the site conditions fit the assumptions of the model.

3. Is the model to be constructed for prediction or system interpretation? Predictive modeling is used to estimate concentrations over time at downgradient receptors. Interpretive modeling is used to quantify one or more physical, chemical, or biological processes when direct data are not available (e.g., to estimate a biodegradation rate).

4. What specific questions will the model be constructed to answer? For example:
   a. How far will the plume expand before stabilizing?
   b. What will be the magnitude and extent of contamination in 5, 15, or 30 years?
   c. Will the contaminants reach a specific receptor? If so, when, and what is the maximum expected concentration?
   d. What is the approximate time required to achieve cleanup goals in the source area?

e. If the model will be used to estimate biodegradation rates, are the other RNA processes well enough defined to determine biodegradation rates with reasonable certainty?

As these questions suggest, the choice of modeling tools and the level of effort required depends on several factors, such as the complexity of the site conditions, the amount of data available to support the modeling analysis, and the degree of certainty required in the results. A clear understanding of these factors and of the purpose of the modeling task is necessary to focus the modeling efforts and conserve costs.

**5.2.2.2 Approaches to Modeling Contaminant Transport with Biodegradation.** Two general types of models are available, analytical and numerical. Both types of models solve a governing mathematical equation or set of equations that represent physical and chemical processes affecting contaminants in the groundwater environment. Generally, when assumptions used to derive an analytical solution are judged to be too simplistic and inappropriate for the site, a numerical model is selected (Anderson and Woessner, 1992). In general, the fewer the simplifying assumptions used to formulate a model, the more complex is the model.

Examples of models that can be used to simulate contaminant transport with biodegradation are shown in Table 5-6. These models incorporate zero-order (i.e., instantaneous), first-order, or Monod kinetics to simulate biodegradation. Standard contaminant transport models that use a general first-order decay term for natural attenuation are not listed in Table 5-6, but they too can be used to simulate contaminant transport with biodegradation. For example, Chapelle et al. (1996) used the SUTRA code (Voss, 1984) to model the fate of a hydrocarbon plume, substituting the first-order biodegradation rates determined in the laboratory and the field into the model's overall decay term.

### 5.2.3 Estimate the Time to Reach Cleanup Goals

The second component in establishing the efficiency of RNA is to demonstrate that RNA will meet site remediation objectives within a time frame that is reasonable compared to other remediation methods. This section presents analytical methods to estimate cleanup times for RNA for the following three plume configurations: shrinking plumes without a source; shrinking plumes with a source; and stable plumes. All three plume configurations require an estimate of the first-order biodegradation rates for the COCs. The latter two configurations also require an estimate of the contaminant mass in the source area and the rate of contaminant release to groundwater. Expanding plumes may require the use of a model to predict the time required to achieve cleanup goals (see Appendix B).

**5.2.3.1 Estimating the Source Mass.** The total source mass is an integral component of estimating the source life, and therefore, of time for remediation by RNA. Methods to calculate source life are discussed below for shrinking and stable plumes and in Appendix B for expanding plumes. Source mass is determined by measuring petroleum concentrations in soils. Similar to plume delineation, sampling for source delineation should be designed to establish the horizontal and vertical magnitude and extent of contamination. Samples can be analyzed for TPH per unit mass soil or for specific contaminants such as BTEX or PAH mass per unit soil, depending on the types of groundwater contaminants targeted for remediation. Analyses should distinguish between sorbed and free-phase TPH. If free-phase TPH is present, the relative mass of individual target contaminants should be measured. These measurements will be used to estimate the mass release of target contaminants into the dissolved plume (see Section B.2 in Appendix B).

**Table 5-6. Selected Models for Evaluating RNA[a]**

| Model | Model Description |
|---|---|
| BIOSCREEN (Newell and McLeod, 1996) | 2-D spreadsheet model based on the Domenico (1987) analytical model; first-order decay or instantaneous reactions (aerobic and anaerobic); multiple electron acceptors (oxygen, nitrate, sulfate); includes approximation for source decay. |
| BIOPLUME II (Rifai et al., 1987) | 2-D numerical model based on the USGS MOC model (Konikow and Bredehoeft, 1978); aerobic (instantaneous reaction); anaerobic (first-order decay); biodegradation from re-aeration is simulated as a first-order decay process. |
| BIOTRANS (ES&T, 1994) | 2-D numerical model; aerobic instantaneous reaction (oxygen limited); anaerobic constant first-order decay. |
| RT3D (Battelle, 1997)[b] | 3-D numerical model based on the MT3D code (Zheng, 1992); instantaneous (aerobic and anaerobic); kinetically limited biodegradation using multiple electron acceptors. |
| BIOF&T (Draper Aden, 1996) | Numerical 2-D planar, radially symmetric vertical section, or 3-D; aerobic instantaneous (oxygen limited) or Monod kinetics; anaerobic as first-order or modified Monod kinetics; both saturated/unsaturated flow regimes. |

Notes: (a) A comprehensive description of non-proprietary and proprietary flow and transport modeling codes can be found in the U.S. Environmental Protection Agency document entitled *Compilation of Ground-Water Models* (van der Heijde, 1996).

(b) RT3D is compatible with the Department of Defense Groundwater Modeling System (GMS) version 2.1.

Vertical soil profiles should account for smearing effects. At a minimum, soils should be sampled across the entire vertical range of the groundwater table. The source mass is calculated by estimating the contaminated soil volume and multiplying by the soil contaminant concentrations. For water-saturated soils, dissolved contaminants can significantly contribute to the total contaminant mass in the soil samples and the dissolved contaminant mass should be subtracted from the total mass in soil samples. Table 5-2 shows soil analyses commonly collected in support of RNA, and the purpose of each analysis.

**5.2.3.2 First-Order Decay for Shrinking Plumes Without a Source.** Most shrinking plumes will have some residual source that may prolong cleanup times. However, two conditions can result in the absence of a source: (1) the source has been remediated; or (2) a very old, weathered source may be depleted of soluble contaminants such as BTEX. Soils in the source area should be analyzed for BTEX and other soluble contaminants to determine if they are present at levels that could continue to leach to groundwater.

In the absence of a source, the time required to achieve cleanup goals in the plume can be determined by solving the first-order contaminant decay equation (see Equation 5-8). Solving Equation 5-8 for time yields Equation 5-21:

$$t = -\frac{\ln\left(\frac{C_g}{C_0}\right)}{\lambda} \qquad (5\text{-}21)$$

where: $C_g$ = the cleanup goal at a predetermined location in the plume [$M/L^3$]
$C_0$ = the initial contaminant concentration at t = 0 [$M/L^3$]

$\lambda$ = the first-order natural attenuation rate [1/T]

Example Problem 1 shows how the time for remediation can be calculated for a shrinking plume without a source.

**5.2.3.3 First-Order Decay for Shrinking Plumes With a Source.** Two time components define the time to reach cleanup goals for shrinking plumes with a source. One component is the expected lifetime of the source (i.e., source life). The other component is the time required to degrade the dissolved mass in the groundwater after the source is depleted. Although these components are not mutually exclusive, a simplifying approach is to treat them separately.

***Example Problem 1***: The groundwater cleanup standard is 5 µg/L for benzene. The plume has been determined to be shrinking, and analyses of soil samples from the source area show that BTEX is not present. The highest plume concentration is 10 mg/L and the first-order natural attenuation rate (determined, using the *temporal analysis*) is 0.10/week. The cleanup time can be determined as follows:

$$t = \frac{\ln\left(0.005/10\right)}{0.10/\text{week}} = 76 \text{ weeks } (1.5 \text{ years})$$

The estimated time for remediation is 1.5 years.

A source zone will contain a finite amount of soluble organic contamination. Thus, the source becomes depleted as organic compounds dissolve in fresh groundwater that passes through the source zone. The decrease in source mass due to contaminant dissolution into groundwater can be approximated as a first-order process (AFCEE, 1996), as shown in Equation 5-22:

$$\frac{dM}{dt} = k_{sz}M \tag{5-22}$$

where: dM/dt = the change in source mass over time [M/T]
$k_{sz}$ = the first-order rate constant for source zone depletion [1/T]

Equation 5-22 can be solved to provide the following exponential equation (Equation 5-23):

$$M(t) = M_0 e^{-k_{sz}t} \tag{5-23}$$

where: M(t) = the source mass at time t [M]
$M_0$ = the initial source mass at time zero [M]

The first-order source decay constant, $k_{sz}$, is not the same as the first-order biodegradation rate constant, k, or the natural attenuation rate constant, $\lambda$, used to calculate the amount of dissolved contaminant biodegraded in the plume. Equation 5-23 is rearranged to solve for the source life, resulting in (Equation 5-24):

$$t = -\frac{-\ln\left(\frac{M_f}{M_o}\right)}{k_{sz}} \tag{5-24}$$

where: $M_f$ = the final source mass [M].

At any time, t, dM/dt, which is equal to the mass loading rate to groundwater, is a constant. Thus, if the mass loading rate can be determined at a given time, it can be substituted into Equation 5-22 to solve for the first-order source decay rate, $k_{sz}$, as follows (Equation 5-25):

$$k_{sz} = \frac{\text{mass loading rate}}{M_0} \tag{5-25}$$

The source decay rate is then substituted into Equation 5-24 to determine the source life. Equation 5-24 conforms with the method used by the BIOSCREEN model (AFCEE, 1996). Methods to estimate the source mass [M] and the mass loading rate [M/T] to groundwater are described in Appendix B, and are based on field measurements of soil contaminant concentrations, an estimate of the groundwater recharge rate, and contaminant partition coefficients.

After the source is depleted, the time required to degrade the mass remaining in the plume after source depletion can be determined using Equation 5-21. Example Problem 2 shows how the time for remediation is calculated for a shrinking plume with a source.

**5.2.3.4 First-Order Decay for Stable Plumes.** As with shrinking plumes with a source, the time required to remediate stable plumes is a function of the time required to deplete the source plus the time required for concentrations in the dissolved plume to be reduced to the cleanup levels for the site. The time required for source depletion is expected to dominate the overall remediation time.

The same first-order equation (Equation 5-25) for the shrinking plume source life can be used to estimate the stable plume source life. However, in the case of a stable plume, two methods can be used to determine $k_{sz}$. Both methods involve dividing the groundwater mass loading rate by the total source mass (see Equation 5-25). The two methods differ only in the technique used to determine the mass loading rate to groundwater. The first method is the same as the one described above for the shrinking plume with residual source mass. The second method is based on the fact that, under steady-state conditions, the *contaminant loading rate to groundwater* is equal to the total plume attenuation rate, to yield the following sequence of equations (Equations 5-26 through 5-29).

***Example Problem 2***: The source for a shrinking plume is estimated to have1 kg of residual benzene mass. The groundwater cleanup standard for benzene is 5 µg/L throughout the plume. The target mass for benzene in the source zone is 1g. The first-order attenuation rate determined using the *temporal analysis* is 0.10/week. The mass loading rate is calculated to be 15 g/week. The total cleanup time, including the source life and plume attenuation time, can be determined as follows.

The source life first-order rate constant is determined as follows:

$$k_{sz} = \frac{15\ \text{g/week}}{1{,}000\ \text{g}} = 0.015/\text{week}$$

Source life:

$$t = \frac{-\ln\left(\frac{1\ \text{g}}{1{,}000\ \text{g}}\right)}{0.015/\text{week}} = 460\ \text{weeks (9 years)}$$

From *Example Problem 1*, the plume attenuation time is 1.5 years. Thus, the total remediation time is estimated as:

$$\begin{aligned} t_{TOT} &= \text{source life} + \text{plume attenuation} \\ &= 9\ \text{years} + 1.5\ \text{years} \\ &= 10.5\ \text{years} \end{aligned}$$

$$\frac{dM_s}{dt} = \frac{dM_p}{dt}, \text{ at steady state}$$

$$k_{sz} M_s = \lambda M_p \qquad (5\text{-}26)$$

$$k_{sz} = \frac{\lambda M_p}{M_s}$$

where: $M_s$ = the source mass [M]
$M_p$ = the total plume mass [p]
$\lambda$ = the first-order plume attenuation rate constant [1/T]

We can determine the plume mass by multiplying the plume volume by the average contaminant concentration in the plume, to yield:

$$Mp = V\bar{C} \qquad (5\text{-}27)$$

where: C = the average contaminant concentration in the plume [$M/L^3$]
V = the plume volume [L]

Substituting Equation 5-27 into Equation 5-26 yields:

$$k_{sz} = \frac{V\lambda\bar{C}}{M} \tag{5-28}$$

By substituting Equation 5-28 into 5-25, the source life can be determined as follows:

$$t = \frac{\ln\left(\frac{M_f}{M_s}\right)}{V\lambda\bar{C}/M_s} \tag{5-29}$$

Example Problem 3 shows how the time for remediation is calculated for a stable plume. The approach involves adding the time for source depletion and the time for plume degradation, assuming, for simplicity, that the plume begins shrinking after the source is depleted.

## 5.3 COMPARE RNA TO OTHER TECHNOLOGIES

A comparison of intrinsic remediation with other potentially applicable remediation technologies for petroleum contamination is required under many regulatory frameworks and provides a baseline to validate the selection of RNA. Provisions of CERCLA and the RCRA Corrective Action process require screening and evaluation of several alternatives to support selection of a remedial alternative. Cleanup of petroleum hydrocarbon contamination resulting from storage tanks usually will be regulated under state authority. The technology selection process under these state programs usually is less complex than the CERCLA or RCRA processes, but still may require consideration of alternative technologies. Even if comparative screening is not required, there is a precedent for screening and evaluating technologies by comparison to clearly document the method and basis for technology selection.

***Example Problem 3***: A site has a stable plume that measures approximately 1,000 feet by 100 feet by 10 feet. Estimates from soil sampling indicate remaining benzene mass in the source is approximately 100 kg. The total porosity of the aquifer is estimated to be 0.3. The groundwater cleanup standard for benzene is 5 µg/L throughout the plume and the target benzene mass for the source zone is specified as 1 g. The first-order natural attenuation rate for the plume, determined using the *spatial analysis* is 0.10/week. The average concentration throughout the plume is 1 mg/L, and the highest concentration is 10 mg/L. The total cleanup time, including the source life and plume attenuation time, is determined as follows.

Source life first-order rate constant: $k_{sz} = V\lambda C/M$:

$$V = (1{,}000)\,(100)\,(10)(0.3\%) = 300{,}000\ \text{ft}^3 = 8.496\times10^6\ \text{L}$$

$$k_{sz} = \frac{(8.496\times10^6\ \text{L})(0.10\ /\text{week})(1\ \text{mg/L})}{100\ \text{kg}\ (10^6\ \text{mg/kg})} = 0.0085/\text{week}$$

Source life:

$$t = \frac{-\ln\left(\dfrac{1\ \text{g}}{100{,}000\ \text{g}}\right)}{0.0085/\text{week}} = 1{,}354\ \text{weeks}\ (26\ \text{years})$$

From *Example Problem 1*, the plume attenuation time is 1.5 years. Thus, the total remediation time is estimated as follows:

$$\begin{aligned} t_{TOT} &= \text{source life} + \text{plume attenuation} \\ &= 26\ \text{years} + 1.5\ \text{years} \\ &= 27.5\ \text{years} \end{aligned}$$

As expected, the time required for source depletion dominates the total remediation time.

There is no established absolute basis for ranking technology performance. Lacking an absolute basis, comparison with other alternatives that have shown promising results in similar circumstances provides a method to evaluate technologies and describe the reasons for accepting or rejecting various alternatives. Examples of treatment alternatives that have been used for remediation of petroleum hydrocarbons in groundwater are summarized in Table 5-7.

The technology evaluation should also consider the potential to apply RNA in combination with other technologies as part of a treatment train (EPA, 1999). Conditions at some sites may prevent RNA from achieving acceptable cleanup levels, while another remedial technology may be able to correct the factor limiting the capabilities of RNA, but not achieve final cleanup. For example, RNA alone is unlikely to be effective when free product is present, but free-product recovery technologies can be combined with RNA. Free-product removal technologies such as bioslurping or skimming can be implemented prior to or during the evaluation and implementation of RNA. Table 5-8 shows examples of LNAPL recovery and soil remediation technologies that may be combined with RNA to enhance overall contaminant removal and reduce RNA treatment time.

Technology evaluation involves comparing each remedial alternative with respect to specific criteria. These criteria can be grouped into the categories of effectiveness, implementability, and cost and

## Table 5-7. Comparison of Common Groundwater Remediation Technologies

| Technology | Effectiveness for Hydrocarbons in Groundwater | Implementability | Typical Remediation Duration[a] | Cost |
|---|---|---|---|---|
| RNA | High when risk factors are suitable | Contaminants and conditions must favor biodegradation; requires monitoring and evaluation; may be applied to complex, heteorgeneous formations; does not require equipment installation; innovative technology | Several years | Low |
| Pump and treat | High | Works best in uniform formations with moderate to high permeability; uses simple, easily available equipment; commercial technology | Months to years | High |
| Biological or sparging barriers | Potentially high but not fully demonstrated; does not address entire plume | Works best in uniform formations with moderate to high permeability; should be keyed into an aquitard; difficult to place barrier deeper than 50 ft; emerging technology; anaerobic and nonbiological reactive barriers would be ineffective for petroleum contaminants; requires continuous oxygen supply (i.e., air sparging or oxygen-release compounds) | Several years | Moderate to high |
| Phytoremediation | High for shallow contaminants | Limited to remediation in root zone; emerging technology; could be used as a barrier method; relies on intrinsic contaminant biodegradation; innovative technology | Several years | Low |
| Groundwater circulating wells | Moderate | Works best in uniform formations with moderate to high permeability; uses moderately complex equipment; innovative technology | Months to years (not much faster than pump and treat) | Moderate to High |
| In-situ air sparging | Potentially high but performance effectiveness is variable | Works best in uniform formations with moderate to high permeability; uses in expensive, off-the-shelf equipment | Months to years | Moderate |
| In-situ (engineered) bioremediation | Potentially high, but not fully demonstrated | Works best in uniform formations with moderate to high permeability; effective delivery of oxygen- and nutrient-containing solution in situ can be difficult; uses simple, readily available equipment; innovative technology | Months to years | Moderate |

Note: (a) Time for remediation will depend on the size of the plume, contaminant concentrations, geology and hydrogeology, and water chemistry.

## Table 5-8. Comparison of Common LNAPL Recovery/Remediation and Vadose Zone Soil Remediation Technologies

| Technology | Effectiveness | | Implementability | Potential Impact on RNA | Typical Remediation Duration[a] | Cost |
|---|---|---|---|---|---|---|
| | Free LNAPL | Vadose Zone Residual | | | | |
| RNA | Low | High | Contaminants and conditions must favor biodegradation; applicable to low-risk sites with stable or shrinking groundwater plumes; extends duration of groundwater treatment; requires soil and groundwater monitoring and evaluation; minimal equipment and installation requirements; innovative technology | — | Years to decades | Low |
| Skimming | Moderate | Low to none | Works best in uniform formations with moderate to high permeability and significant LNAPL thickness; recovered oil may contain a small amount of water possibly requiring oil/water separation and disposal of water; uses simple, easily available equipment; commercial technology | Reduces source mass which will reduce RNA remediation time | Months to years | Moderate |
| Single-pump drawdown | High | Low to none | Works best in uniform formations with moderate to high permeability and significant LNAPL thickness; recovers an oil/water mixture requiring oil/water separation and disposal of water; risks spreading LNAPL in capillary fringe zone; uses simple, easily available equipment; commercial technology | Reduces source mass to reduce time for RNA. May increase spreading of LNAPL in the vadose zone, which could increase dissolved contamination | Months | Moderate |
| Dual-pump drawdown | High | Low to none | Works best in uniform formations with moderate to high permeability and significant LNAPL thickness; recovers an oil/water mixture requiring oil/water separation and disposal of water; risks spreading LNAPL in capillary fringe zone; uses simple, easily available equipment; commercial technology | | Months | Moderate |
| Bioslurping | High | High | Works best in uniform formations with moderate to high permeability; recovers an oil/water mixture requiring separation and disposal of water; off-gas must be collected and treatment may be required; provides horizontal flow path which can reduce flow resistance in stratified geology and LNAPL spreading in the capillary fringe zone; combines vadose zone stripping and bioremediation with free-product removal to enhance mass removal rates; uses simple, easily available equipment; commercial technology | Reduces source mass which will reduce time for RNA | Months | Moderate |
| Soil vapor extraction | Low | High | Works best in uniform formations with moderate to high permeability; off-gas must be collected and treatment may be required; uses simple, easily available equipment; commercial technology | Reduces residual source mass to reduce time for RNA | Months | Low to moderate |
| Bioventing | Low to none | High | Works best in uniform formations with moderate to high permeability; does not require off-gas collection or treatment; uses simple, easily available equipment; commercial technology | | Months to years | Low to moderate |
| In-situ (engineered) bioremediation | Low to none | High | Works best in uniform formations with moderate to high permeability; effective delivery of oxygen- and nutrient-containing solution in situ can be difficult; uses simple, easily available equipment; innovative technology | | Years | Moderate |
| Excavation and treatment | Moderate | High | Works best when contaminant concentration is high and the depth is shallow; commercial technology | Eliminates source to reduce time for RNA | Weeks to months | Moderate to high |

Note: (a) The time for remediation will depend on the nature of the contaminants in the source zone, the rate of contaminant release from the source zone either through attenuation or dissolution into the groundwater, and other factors such as the geology and soil chemistry.

the time required to achieve cleanup goals. Effectiveness measures the ability of the alternative to protect human health and the environment, both during the remediation (short-term effectiveness) and after cleanup goals are achieved (long-term effectiveness). Implementability measures the technical and administrative feasibility of installing and operating the technology. The capital and O&M costs of an alternative are considered, but often are of secondary importance compared to effectiveness and implementability. The time required for each technology to meet cleanup goals is usually considered as part of implementability and effectiveness criteria. Depending on the site characteristics, risk to receptors, and regulatory concerns about remediation time, this factor can have a significant impact on the technology comparison. The factors involved in evaluating a technology for short-term effectiveness, long-term effectiveness, implementability, cost, and time required to meet cleanup goals are summarized in Table 5-9.

**Table 5-9. Technology Screening Factors**

| Criteria | Factors Considered in Criteria Evaluation |
|---|---|
| Short-term effectiveness | Protection of the community during remedial activities<br>Protection of workers during remedial activities<br>Environmental impacts of remedial activities<br>Toxicity and volume of residuals produced by the technology<br>Time required to implement the technology |
| Long-term effectiveness | Ability to meet cleanup goals<br>Compliance with regulations<br>Residual risk at the site consistent with long-term land-use plans<br>Long-term reduction of mobility, toxicity, or volume of contaminants |
| Implementability | Ability to construct using conventional equipment, materials, and techniques<br>Ability to adapt to changing or unexpected site conditions<br>Reliability and maintainability of the technology<br>Ability to obtain required permits<br>State and public acceptance |
| Cost | Direct capital costs<br>Indirect capital costs<br>Annual O&M costs<br>Accuracy of the cost estimates for each alternative (generally, +50% to –30%) |
| Time required to meet cleanup goals | Time required for source reduction<br>Time required for plume attenuation<br>Comparisons can be made on the basis of a mass removal rate, avoiding potentially inaccurate estimates for complete cleanup |

Source/Reference: EPA, 1988a; EPA, 1991e; EPA, 1999.

## 5.4 SUMMARIZE FINDINGS OF THE DETAILED EVALUATION AND REPORT RESULTS TO THE APPROPRIATE REGULATORY AUTHORITIES

Most regulatory frameworks for site remediation require a formally documented decision point for technology selection. Thus, a formal documentation step is necessary to present the findings of the detailed site evaluation and to gain regulatory acceptance of RNA as the full-scale remediation technology for the site. The final report presentation should be the culmination of a consensus-building process conducted throughout the preliminary assessment and detailed site evaluation tasks.

The process for presenting the results of the detailed site investigation and for preparing the decision documentation varies significantly among different regulatory frameworks, but the general objectives are the same.

1. Document the cleanup goals
2. Describe and compare the remedial alternatives considered
3. Formally present the technical basis for selecting RNA based on the detailed site assessment
4. Obtain regulatory and public input

A report describing the results of the detailed site investigation and proposing RNA as the selected technology should be presented for regulatory review and acceptance of RNA. When presenting the technical basis for RNA, the report should clearly demonstrate that RNA will provide adequate protection of human health and the environment, and will remediate the site in an acceptable timeframe, based on the data collected during the detailed site evaluation.

**Example Report Outline for the Detailed Site Evaluation**

1.0 Introduction
- 1.1 Scope of the Detailed Site Investigation in Support of RNA
- 1.2 Site History
- 1.3 Ongoing Remedial Activities (e.g., interim actions)

2.0 Results of the Preliminary Site Assessment
- 2.1 Nature and Extent of Contamination
- 2.2 Potential Human Health and Environmental Risks
- 2.3 Preliminary Identification of Potential Receptors and Compliance Points
- 2.4 Preliminary Remediation Goals

3.0 Results of the Detailed Site Investigation
- 3.1 Geology and Hydrogeology
- 3.2 Supporting Evidence for RNA
  - 3.2.1 Plume Status
  - 3.2.2 Geochemical Data
  - 3.2.3 Tracer (i.e., TMB) Data
- 3.3 Biodegradation and Natural Attenuation Rates
  - 3.3.1 Calculated Rates
  - 3.3.2 Comparison of Calculated Rates with Literature-Reported Rates
- 3.4 Efficiency of RNA
  - 3.4.1 Protection of Human and Environmental Receptors
  - 3.4.2 Estimated Time Required to Meet Cleanup Goals

4.0 Comparison with Alternative Technologies
- 4.1 Short- and Long-Term Risk Reduction
- 4.2 Implementability (including time to meet cleanup goals)
- 4.3 Cost

5.0 Conclusions

6.0 References

**Checklist for Detailed Site Evaluation in Support of RNA**

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 1 | Establish the direction of groundwater flow and determine the location and quantity of groundwater monitoring wells | ❑ Establish the direction of groundwater flow using measured groundwater elevations or the direction of plume migration. This may require seasonal measurements.<br>❑ Is direction of flow clear?<br>If so, locate wells along plume centerline transect and transverse to the direction of groundwater flow.<br>If not, distribute wells throughout the plume and outside of the plume to generate contour maps.<br>Is groundwater flow direction susceptible to changes (e.g., due to seasonal or tidal influences)? If so, additional wells or multiple transects may be required.<br>❑ Locate at least one well upgradient of the contaminated area to establish background concentrations for contaminants and geochemical parameters.<br>❑ Locate at least one well near the downgradient plume boundary to monitor plume stability at the boundary.<br>❑ If there is a significant vertical dimension to the plume and a potential for vertical contaminant transport, establish vertically stratified wells at multiple sampling locations. | Obtain adequate data while minimizing the number of groundwater monitoring wells and potential sample points. |
| 2 | Establish analytical parameters and frequency | ❑ Identify appropriate groundwater analyses and analytical methods from Table 5-1.<br>❑ Identify the laboratory where analyses will be conducted<br>Make sure that the laboratory can support the necessary analyses and sample load.<br>❑ Establish the sample frequency for a 2-year study period. Sampling should be conducted two to four times per year, depending on diurnal groundwater fluctuations and project resources. | Obtain adequate data to identify whether intrinsic biodegradation is occurring and to establish the plume status. |

## Checklist for Detailed Site Evaluation in Support of RNA (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 3 | Identify whether there is an existing source | ❑ Review base history and previous site investigations for information on the source of contamination. If the source has not been removed completely and has not been delineated, identify sample locations for source area sampling.<br>❑ Select soil analyses and analytical methods from Table 4-2. | Delineate magnitude and extent of source area and estimate source release rate into groundwater and the source life |
| 4 | Collect groundwater and soil data | ❑ Collect groundwater data over the two-year investigation.<br>❑ Collect soil data to delineate the source area (temporal data not required). | Collect soil and groundwater data in support of RNA |
| 5 | Evaluate soil data | ❑ Based on the field data, identify whether there is an existing source and whether source removal is required.<br>❑ If source removal is not required, or following source removal, calculate the residual source mass.<br>❑ Calculate the approximate rate of release of the source to the plume and estimate the source life. | Delineate magnitude and extent of source area and estimate source release rate into groundwater and the source life |
| 6 | Evaluate field data for spatial correlations between contaminant and biological indicator concentrations | ❑ Determine whether electron acceptor concentrations are inversely proportional to hydrocarbon concentrations.<br>Electron acceptors include: $O_2$, $NO_3^-$, and $SO_4^{2-}$<br>❑ Determine whether metabolic byproduct concentrations are directly proportional to hydrocarbon concentrations.<br>Metabolic byproducts include: $Fe^{2+}$, $Mn^{2+}$, $H_2S$, $CH_4$, and alkalinity | Establish the occurrence of RNA |
| 7 | Establish biodegradation using an internal tracer | ❑ Is a conservative (i.e., nonbiodegradable) compound commingled in the BTEX plume?<br>❑ Is the tracer present in similar distribution with the contaminant?<br>❑ If the above questions are answered affirmatively, calculate corrected contaminant concentrations based on the proportional decrease in tracer compound due to diffusion, dispersion, sorption, or volatilization. Estimate the amount of reduced contaminant concentrations that can be attributed to biodegradation. | Establish the occurrence of RNA |

## Checklist for Detailed Site Evaluation in Support of RNA (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 8 | Establish plume status | ❑ Obtain time-series data for at least 4 monitoring events and for a minimum of 2 years<br>❑ Determine presence of significant trend using statistical methods described in Appendix C<br>Shrinking or stable plumes are evidence of biodegradation<br>Expanding plumes require further investigation<br>If trend is not evident due to insufficient data, professional judgment and experience may be used | Establish the efficiency of RNA |
| 9 | Collect additional data for evidence for RNA | ❑ Use $H_2$ analysis to identify TEAPs corresponding to the distribution of contaminants in groundwater<br>Sampling must be conducted in the field<br>❑ Use VFA analysis to identify unique anaerobic BTEX transformation mechanisms<br>VFAs cannot be used to determine TEAP<br>Analyses for aromatic organic acids are difficult and expensive<br>❑ Conduct microcosm studies to positively confirm the degradation of target contaminants under laboratory controlled conditions<br>Can be used to estimate biodegradation rates; tend to overestimate actual field rates | Provide conclusive evidence of RNA not provided by other data to establish the occurrence and the efficiency of RNA |

## Checklist for Detailed Site Evaluation in Support of RNA (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 10 | Determine in-situ contaminant degradation rates | ❑ Aerobic conditions: Assume zero-order rates for aerobic hydrocarbon degradation.<br>If possible, identify a DO front at the outer fringes of the plume. Estimate DO flux through groundwater recharge.<br>❑ Anaerobic conditions: Assume first-order rates for anaerobic hydrocarbon degradation. Various methods should be considered depending on the plume configuration and available data:<br>Shrinking plume<br>• Temporal regression<br>Stable plume<br>• Spatial regression<br>• Analytical solution<br>• Mass balance<br>Shrinking, stable, or expanding plume<br>• Conservative tracer<br>Expanding plume<br>• Modeling<br>❑ Laboratory microcosms<br>❑ Literature values | Establish the efficiency of RNA |
| 11 | Calculate future contaminant concentrations at downgradient receptors | ❑ Not required for stable or shrinking plumes<br>❑ Requires modeling or analytical solutions for expanding plumes<br>Estimate time for contaminants to reach receptors<br>Estimate maximum concentration at the receptor<br>Estimate time for RNA to reach cleanup goals | Calculate the efficiency of RNA for expanding plumes and the risk to downgradient receptors of contaminant exposure |

## Checklist for Detailed Site Evaluation in Support of RNA (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 12 | Calculate time to cleanup for shrinking plumes | ❑ Estimate source mass (see Items 3 and 5)<br>❑ For shrinking plumes without a source, use the first-order decay for shrinking plume (see Item 10) to estimate cleanup time<br>❑ For shrinking plumes with a source, use the first-order decay for shrinking plume (see Item 10) and source attenuation rate (see Item 5) to estimate cleanup time<br>❑ Estimate first-order decay for a stable plume | Establish that cleanup objectives can be met within a reasonable time frame for shrinking plumes |
| 13 | Calculate time to cleanup for stable plumes | ❑ Estimate source mass (see Items 3 and 5)<br>❑ Use the source attenuation rate (see Item 5) to estimate source cleanup time<br>❑ Use the first-order decay for shrinking plume (see Item 10) to estimate the plume cleanup time after source depletion | Establish that cleanup objectives can be met within a reasonable time frame for stable plumes |
| 14 | Calculate time to cleanup for expanding plumes that demonstrate an imminent or long-term risk to receptors | ❑ Estimate source mass (see Items 3 and 5)<br>❑ Use the source attenuation rate (see Item 5) and estimate source cleanup time using a model or analytical solution.<br>❑ Using a model or analytical solution, determine the maximum plume size and use an estimated first-order decay rate (see Item 10) to determine the plume cleanup time after source depletion. | Establish that cleanup objectives can be met within a reasonable time frame for expanding plumes |
| 15 | Compare RNA to other technologies | ❑ Compare RNA with other technologies using criteria such as effectiveness, implementability, cost, and time to achieve cleanup goals.<br>❑ Consider RNA in combination with other technologies. | Validate the selection of RNA |
| 16 | Summarize findings and report to authorities | ❑ Document the cleanup goals<br>❑ Formally present the technical basis for selecting RNA based on the detailed site assessment<br>❑ Validate the selection of RNA by comparison with alternative technologies (see Item 15)<br>❑ Obtain regulatory and public input<br>❑ Submit a final report documenting findings, for regulatory and public acceptance. | Document findings and establish regulatory approval for RNA as the remedial technology of choice |

## 6.0 PERFORMANCE MONITORING AND SITE CLOSURE FOR RNA

This section describes the requirements of performance monitoring and site closure. The sequence of steps in this process is illustrated in Figure 6-1 and includes the following:

1. Develop a performance monitoring (PM) plan
2. Establish cleanup objectives
3. Install additional monitoring wells/points (as necessary)
4. Implement institutional controls (as necessary)
5. Collect data and evaluate RNA progress
6. Develop contingency measures
7. Verify cleanup objectives
8. Prepare site closure documentation
9. Restore site (as necessary)

The Navy's companion document, *Technical Guidelines for Applying Monitored Natural Attenuation at Naval and Marine-Corps Facilities* (DON, 1998) also discusses the need for performance monitoring. The *Technical Guidelines* document describes factors that impact the placement of performance monitoring wells and the type of data to collect during performance monitoring. This section expands that discussion by describing the information to include a performance monitoring plan, technical considerations for implementing institutional controls, evaluating RNA progress, and verifying attainment of cleanup goals for site closure. A checklist to guide the reader through performance monitoring and site closure is provided at the end of the section.

Performance monitoring is a required element of all long-term response actions. It is especially critical for RNA due to the potential for long remediation time frames and the need to carefully monitor contaminant migration (EPA, 1999). Performance monitoring is necessary to accomplish the following objectives (EPA, 1999).

- Evaluate remedy effectiveness (demonstrate that RNA is occurring according to expectations).
- Ensure protection of human health and the environment (demonstrate no impact to downgradient receptors and verify that institutional controls are providing the desired level of protection).
- Verify attainment of cleanup goals.
- Detect contaminant migration/plume expansion.
- Detect new releases of contaminants to the environment.
- Detect changes in the hydrogeochemical environment that may decrease the effectiveness of RNA.

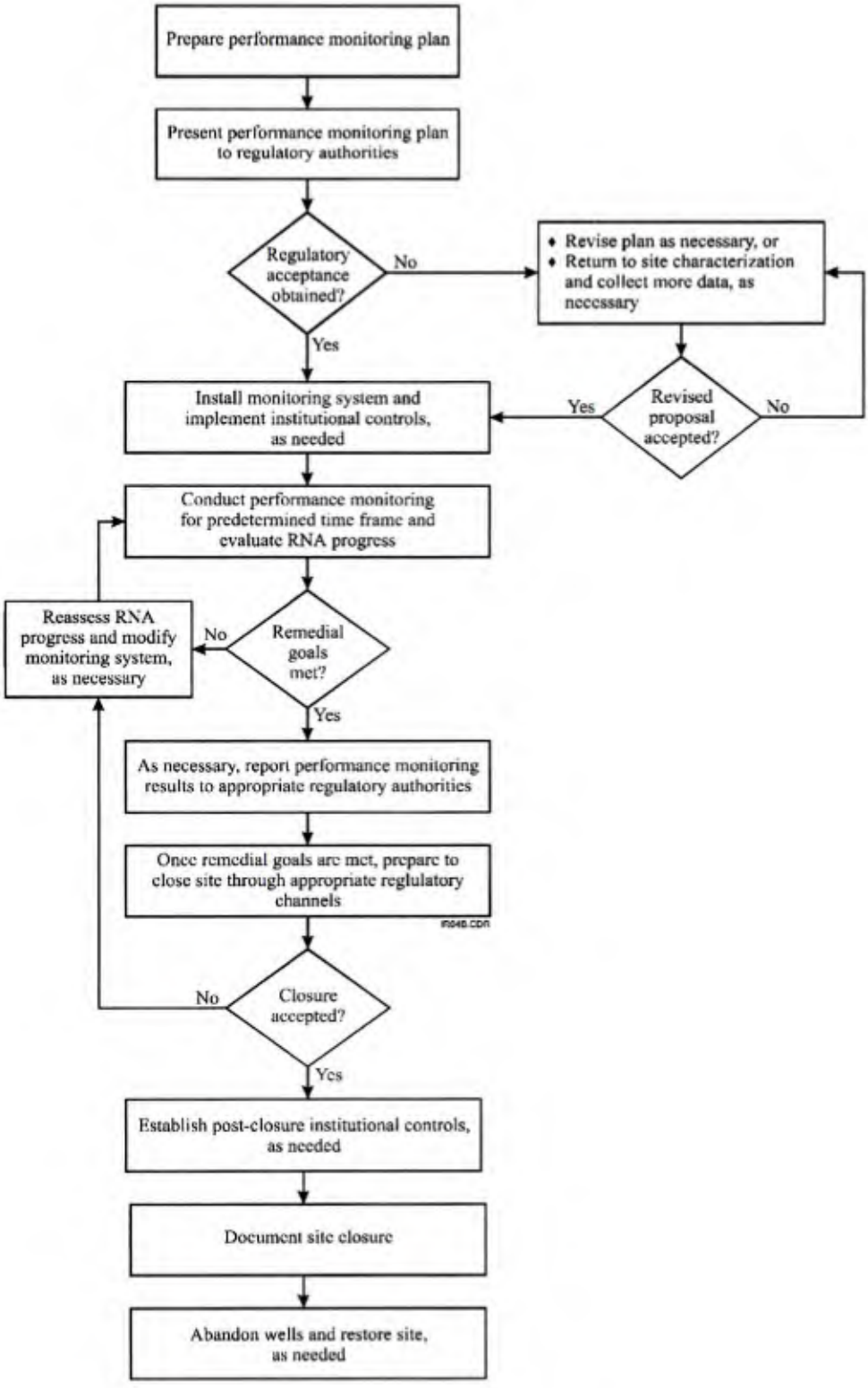



**Figure 6-1. Performance monitoring and site closure for RNA.**

Performance monitoring will most likely be required as long as contamination levels remain above required cleanup goals on any portion of the site. Additional monitoring (e.g., 1 to 3 years) may be required after cleanup goals are achieved to ensure that contaminant levels are stable and remain below target levels.

## 6.1 DEVELOP A PERFORMANCE MONITORING PLAN

The PM plan should specify the location, frequency, and types of samples and measurements necessary to evaluate RNA performance and it should define the performance objectives and decision rules for site closure. Procedures should be included in the PM plan for installing additional monitoring points (if needed), sample collection and analysis and reviewing and evaluating cleanup progress. The typical elements of a PM plan are summarized in Table 6-1. Cleanup objectives of contingency measures are discussed in more detail in this section.

**Table 6-1. Typical Elements of a Performance Monitoring Plan**

| Design Element | Information Required |
|---|---|
| Sampling and analytical requirements | Describe the location of monitoring points (These may be existing or proposed wells), construction details for proposed wells (well depth, screen interval, etc.), sample collection methods, target analytes, analytical methods, and sampling frequency and duration. |
| Institutional controls that are required during performance monitoring | Identify any institutional controls (e.g., land use restrictions) that are required to protect human health and the environment during performance monitoring. |
| Method for data reduction and evaluation of RNA progress | Describe how the monitoring data will be reviewed and evaluated to assess the ongoing effectiveness of RNA after each monitoring event and to determine compliance with cleanup levels. |
| Definition of final cleanup levels and applicable compliance points | Location of wells for compliance monitoring, and definition of protective action labels that apply at these locations. |
| Contingency measures if RNA progress deviates from expectation | Criteria that indicate unexpected performance of RNA and signal when to take corrective action or implement alternative (contingency) measures identification of one or more contingency measures. |
| Quality Assurance Project Plan (QAPP) | Information describing measures to be taken to ensure the performance monitoring data are of suitable quality to support making definitive statements about RNA progress and attainment of cleanup objectives for the site[a]. |
| Health and Safety Plan | Information describing how protection of worker health and safety will be ensured during performance monitoring[b]. |
| Schedule | Schedule of major project milestones, deliverables, and decision points. |
| Cost Estimate | Definitive cost estimate (+30% to –15%) of capital and operating and maintenance (O&M) costs. |

Notes: (a) For more information on preparing Quality Assurance Project Plans, see the following references: EPA 1991a, 1991b, 1991c, and 1991d.

(b) For more information on preparing a site-specific Health and Safety Plan to comply with 29 CFR 1910.120(b)(1)(iv) and (v), see the following reference: U.S. Dept. of Health and Human Services, 1985.

The PM plan should be provided to the regulatory authorities for review prior to initiating the PM program. The PM plan may be submitted alone or as part of the detailed site evaluation report (see Section 5.4). For large or complex projects or projects operating under more formal regulatory frameworks (e.g., CERCLA or RCRA CA), the performance monitoring may have to be presented for review at several stages

(e.g., preliminary [35 percent complete], intermediate [60 percent complete], pre-final [95 percent complete], and final) and may require public review.

### 6.1.1 Establish Cleanup Objectives

Site closure occurs after performance monitoring data demonstrate that concentrations have been reduced to levels below the site cleanup goals. One to three years of additional monitoring may be required after cleanup levels have been achieved, to ensure that concentration levels are stable and remain below target levels.

The site cleanup goal may be either a numerical standard or a performance criterion that protects human health and the environment. The *numerical standard* typically is defined as the maximum allowed concentration of specific contaminants in the groundwater within a defined area of attainment. For example, Safe Drinking Water Act (SDWA) maximum contaminant levels (MCL) apply when drinking water supplies are adversely affected. Health-based or ecological risk-based concentrations determined from site-specific conditions can be used, if drinking water is not affected. The *area of attainment* is the site volume where the cleanup standards must be met. The area of attainment may be the *entire plume* or a *portion of the plume*, depending on site conditions and risk scenarios.

*A performance-based standard* is a criterion that must be fulfilled to ensure the protection of human health and the environment. For example, a performance-based standard may be to demonstrate a shrinking plume over a predetermined time. Although a performance-based standard must ensure public safety and protection of the environment, the site may be closed before contaminants reach conventional numerical cleanup goals. Performance standards are appropriate for low-risk sites where the data demonstrate a clearly stable or shrinking plume. To date, performance standards have been less widely accepted than numerical standards. However, the potential for significant cost savings makes them attractive. Performance standards must be accepted by the appropriate regulatory authority. Also, performance standards likely will require institutional controls on land use. If the property changes ownership or if land use changes, the site may have to be reopened and characterized for the presence of residual contamination.

Compliance with standards should be evaluated using established statistical comparison methods. Guidance on the use of statistical methods for verifying attainment of cleanup levels can be found in ASTM (1997b), and EPA (1989b and 1992b).

### 6.1.2 Establish Contingency Measures

EPA recommends that remedies employing RNA be evaluated to determine the need for including one or more contingency measures that would be capable of achieving remediation objectives if RNA fails to perform as expected (EPA, 1999). This is especially important for sites where there is a large amount of uncertainty about the expected performance of RNA. On the other hand, contingency measures may not have to be included in the PM plan if there are ample historical data to show that contaminant concentrations are following a long-term decreasing trend (i.e., a shrinking plume). The selection of contingency measures will be a site-specific decision, and is beyond the scope of this operations manual.

Criteria should be established in the PM plan that will signal unacceptable performance of RNA and indicate when to implement a contingency measure. Examples of such criteria for RNA might include the following:

- Contaminants are detected in sentinel wells located between the source and the nearest downgradient receptor, indicating a potential threat to human health or the environment.

- The rate at which contaminant concentrations are decreasing is slower than required to meet cleanup levels within the desired time frame.

- Contaminant concentrations in performance monitoring wells exhibit an unexpected increasing trend indicating that RNA may not be occurring at a rate that is sufficient for the site.

- Changes in land and/or groundwater use that prevent RNA from providing adequate protection of human health or the environment.

## 6.2 INSTALL MONITORING SYSTEM AND CONDUCT PERFORMANCE MONITORING

Implementing RNA may require extensive monitoring and analysis, but unlike most active remedial alternatives, extensive equipment is not required. Existing groundwater monitoring wells and soil-gas monitoring points are used to the maximum extent possible. If additional monitoring points are required, they must be installed in accordance with state and local regulations and accepted practices for groundwater monitoring wells or soil-gas monitoring points (e.g., ASTM, 1997a).

A monitoring strategy is designed and implemented to consider appropriate sampling locations, frequency of sampling, and sampling parameters. Many of the details of a sampling program will have to be determined with regulatory input, because requirements vary from state to state. For example, a recent national survey showed that 15 states require a minimum number of monitoring locations that vary from as few as one to as many as six points, and 25 other states do not specify a minimum number of wells (UTTU, 1997). The following recommendation is provided for a performance monitoring network; however, it could exceed the minimum requirements of a state or local regulatory agency. The monitoring well network should include the following types of wells:

- ***Upgradient Well.*** One or more monitoring wells located upgradient of the plume to monitor the quality of water flowing into the contaminated area and to confirm that hydrogeochemical conditions remain favorable for intrinsic biodegradation.

- ***Plume Transect Wells.*** Three or more wells located along the plume transect to monitor changes in contaminant concentrations over time. One of these wells should be located near the source area to provide a means for detecting renewed releases.

- ***Periphery Wells.*** Three or more wells located immediately outside the plume boundary to detect plume expansion or contaminant migration. At least one of these wells should be positioned immediately downgradient of the leading edge of the plume, and preferably in the shadow of the plume where the concentrations of electron acceptors are below background levels to provide for better detection of plume migration.

- ***Sentinel (Point of Compliance) Wells.*** One or more wells located at negotiated compliance point(s). These wells should be positioned upgradient of any potential receptors. They should provide a minimum of 2 years of groundwater travel time to

the nearest receptor, to provide early detection of contamination before the receptor risks being impacted. If there are no nearby receptors, this should correspond to an agreed-upon location where regulatory standards must be met.

Compliance points must meet the following criteria:

- Compliance points must be located in a clean portion of the aquifer, downgradient of the contaminated portion of the aquifer and upgradient of the receptor.

- The locations, number of compliance wells, and screened intervals (depths) must ensure detection of contaminants that have the potential to migrate to a receptor.

- In the event that groundwater contaminants reach a compliance point, the compliance point location must provide adequate time to establish a contingency plan to protect receptors. A general rule of thumb is to locate compliance wells to provide a minimum of 2 years groundwater travel time to the receptor.[2] Nevertheless, the user must demonstrate that adequate time will be available to ensure the protection of the receptors.

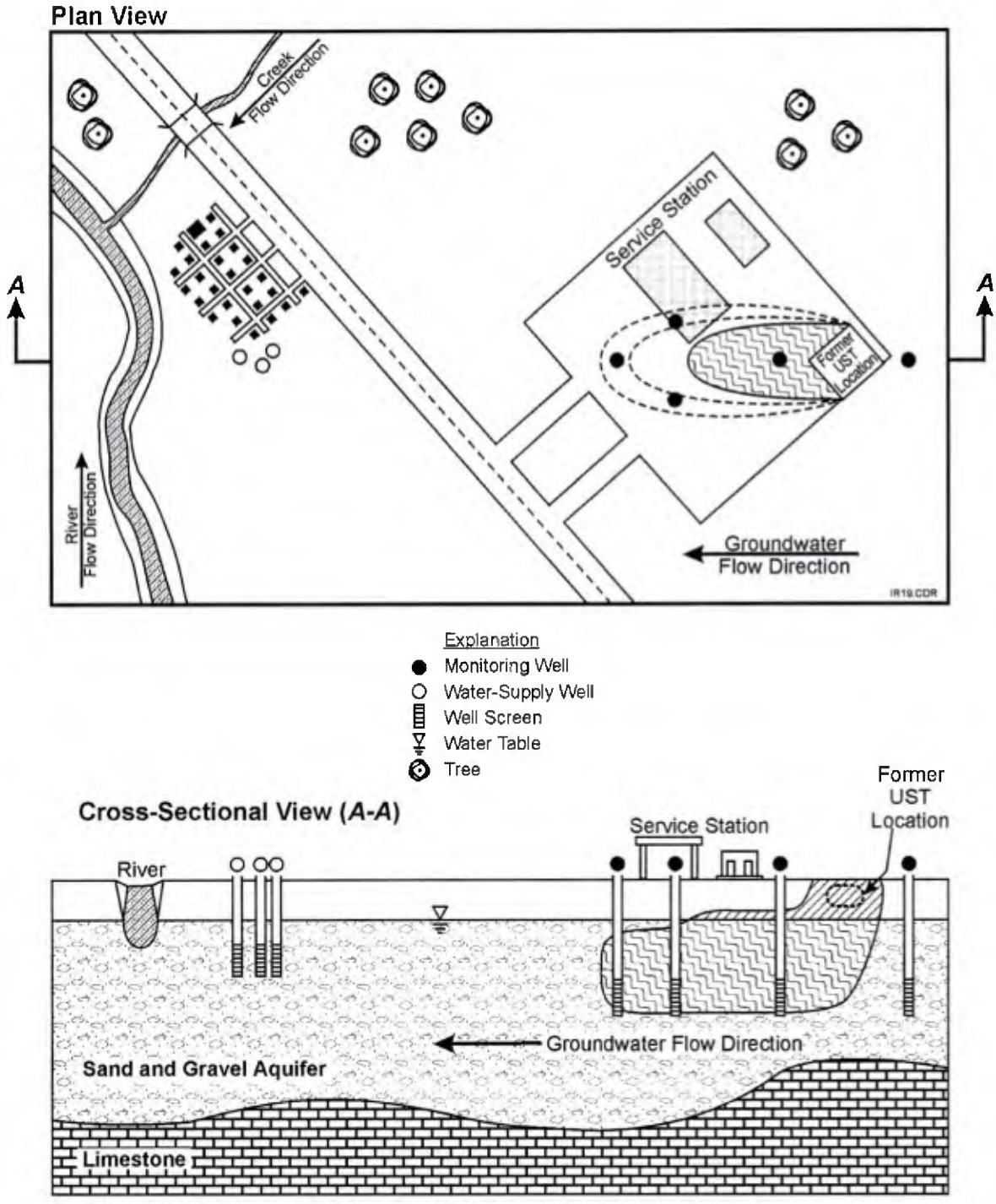
An example of a performance monitoring network for RNA is illustrated in Figure 6-2. The sentinel wells are located upgradient of the nearest downgradient receptor.

All of the performance monitoring wells must be located in the same vertical interval of the contaminated plume. To ensure that the downgradient wells are screened in the proper hydrogeolgic interval, stratigraphic data from the proposed monitoring well locations should be collected and correlated with the stratigraphy of the plume area. Geochemical data also can be collected to confirm that downgradient monitoring wells are screened in the same interval as the contaminant plume (DON, 1998). For example, a monitoring well that is located downgradient of the current plume boundary and that exhibits decreased concentrations of electron acceptors or elevated concentrations of metabolic byproducts relative to background levels for the site provides evidence that the well is screened within the same interval as the contaminant plume. Both stratigraphic data and geochemical analyses of groundwater samples can be collected using direct-push techniques (e.g., Geoprobe® or cone penetrometer testing [CPT]) prior to installing new monitoring points to avoid misplacing the monitoring wells.

The PM plan for the site specifies the information that will be collected throughout the period of operation. At a minimum, the following data should be obtained during each monitoring event:

- Concentrations of the COCs (e.g., BTEX) in performance monitoring wells.

[2] Because the spacing is based on a groundwater travel time, the actual time for contaminants to travel from a sentinel well to a receptor should be greater than 2 years, thereby providing sufficient time to implement a contingency remedial action. The actual contaminant travel time will be approximately equal to the groundwater travel time multiplied by the retardation factor, $R_f$, for the contaminant.




**Preliminary Conceptual Model**

**Figure 6-2. Well network for performance monitoring.**

- Concentrations of electron acceptors (DO, nitrate, sulfate), metabolic byproducts [Fe(II), Mn(II), and methane], and general water quality parameters (e.g., temperature, pH, alkalinity, and redox potential) in performance monitoring wells to track changes in ambient water quality and provide further evidence of ongoing remediation.

- Water level elevations so that water table maps can be prepared to monitor flow direction and velocity. If free product is present in wells, the thickness should be recorded and used to correct the water levels before constructing water table maps.

- Surface water samples to be analyzed for COCs if there is potential for the plume to discharge to a surface water body.

- Soil-gas samples to be analyzed for COCs if there is a potential for exposure due to volatilization.

Routine (i.e., annual) review of institutional controls and inspection of supporting engineering controls to ensure that they are being enforced as intended and are providing the required level of protection to human health and the environment.

Not all performance monitoring wells have to follow the same analytical protocol. The sentinel well(s) at the point of compliance may be located a considerable distance downgradient of the contaminant plume. Therefore, it may be necessary to analyze these wells only for COCs, whose presence could trigger a corrective action or a contingency measure. For wells in closer proximity to the plume, only those electron acceptors and metabolic byproducts that provide evidence for RNA should be measured. It is good practice to monitor DO, pH, temperature, conductivity, and redox in all wells during each sampling event. DO and redox data are useful for monitoring biological activity, while pH, temperature, and conductivity are used to ensure that representative samples are collected.

The frequency of sampling should be determined based on site-specific considerations and regulatory input. Sampling that is conducted too frequently should be avoided because it wastes money without providing useful information. Sampling that is conducted too infrequently creates the potential for undetected contaminant migration and possibly human or ecological exposure to contaminants. Except at sites with very low groundwater velocities, it will likely be necessary to monitor on a quarterly basis for the first year of performance monitoring to confirm that any new compliance monitoring well is properly located downgradient of the plume in the path of groundwater flow. The first year's sampling will provide a baseline for future sampling and for seasonal effects on contaminant migration. If a plume has not reached steady state, more frequent sampling will be required than if it has reached its maximum extent or has started decreasing in size. Other factors that will affect the frequency of sampling are the proximity of the downgradient point-of-compliance well(s) to the plume and the rate of groundwater movement. For example, more frequent sampling will be required at sites where the plume is in close proximity to the point-of-compliance well(s) or where groundwater velocities are high, while less frequent sampling will be required at sites where the plume is well characterized, plume status is well defined, and downgradient receptors are not at risk.

The first year of sampling its frequency should be decreased to semiannual or annual. The EPA (1997a) and most states recommend that performance monitoring continue as long as contamination levels remain above required cleanup goals. However, some states may have less stringent requirements. For example, at least two states require monitoring only until a definitive (decreasing) trend in concentrations is established (UTTU, 1997) (see Section 6.2 for cleanup objectives.) Specific decision

criteria should be established in the performance monitoring plan pertaining to the frequency and duration of performance monitoring sampling and to identify the criteria for site closure.

## 6.3 IMPLEMENT INSTITUTIONAL CONTROLS

Institutional controls are measures that limit human activities at or near a contaminated site to protect human health and the environment, or to ensure the continued effectiveness of the remedy over time (55 FR 46 at 8706). They are used to restrict the use of the property when contamination is left in place above the applicable cleanup standard (Kratina, 1997). Institutional controls may be required during performance monitoring and may have to remain in place after the RNA project is completed.

Institutional controls can provide notice of exposure elimination, system maintenance (e.g., engineering controls such as fencing), or land-use controls (e.g., zoning ordinance for commercial land-use only). Institutional controls are most often imposed as restrictive covenants in the form of a deed restriction. Deed restrictions may be used, for example, to prohibit installation of wells, digging/excavation, or even habitation of a property (Capuco, 1993). Examples of institutional controls that may be considered for use during or after completion of RNA are summarized in Table 6-2.

**Table 6-2. Example Institutional Controls**

| Institutional Control | Function |
|---|---|
| Restrict disturbance of ground cover | Avoid changes in evapotranspiration rate, infiltration rate, or erosion |
| Restrict irrigation | Avoid changes in evapotranspiration rate, infiltration rate, or erosion |
| Restrict disturbance of monitoring systems | Prevent changes or damage to monitoring system, and prevent unintended use of wells. |
| Limit or control construction | Restrict construction that would change groundwater flow regime, disturb the monitoring system, or expose workers to contaminated soils or groundwater |
| Construct access controls | Control access by means of fences and/or signs. |
| Control groundwater use | Restrict installation of new wells or changes in pumping rate that alter the groundwater flow regime |

Institutional controls require that the user record a control requirement (i.e., notice) with the appropriate government or regulatory agency where a "reasonable due diligent inquiry" would uncover the existence of such notice (Kratina, 1997). Once established, institutional controls should "run" with the land or property file so that they are passed on to the new owner if the property is transferred. This is accomplished by way of deed notices or by filing notice with the appropriate local/county/state agencies, depending on the type of institutional control that is implemented.

Enforcement of deed restrictions generally is left up to the individual property owner or the government agency that is responsible for recording deeds. If the property is transferred, enforcement responsibility is shifted to the lending agency or the title insurance company requiring a title search. The new owner must agree to abide by the restriction(s). If the new owner wishes to change the restrictions, the site may have to be reevaluated to determine if it meets, cleanup standards appropriate for the new land use.

Deed restrictions in the form of covenants that prohibit groundwater use or disturbance of soil are the most commonly used institutional controls for remedial actions that involve leaving waste on site for a significant period of time (Capuco, 1993). Deed restrictions that limit the future use of the land may be needed to ensure that land use remains consistent with the assumptions that were used in the risk assessment to establish cleanup goals for the site. This is especially true for sites where risk-based

cleanup levels assume nonresidential land use. Fences and signs to limit access and to specify acceptable uses may be required.

## 6.4 EVALUATE RNA PROGRESS

The effectiveness of RNA must be evaluated throughout performance monitoring to ensure that it is working as expected. The primary objectives of the evaluation are (1) to demonstrate that there is continued protection of human health and the environment and (2) to demonstrate that there is continued reduction in contamination over time. Demonstrating protection of human health and the environment is accomplished by monitoring at downgradient sentinel wells to show that contaminants do not migrate to receptor points, and by routine review and inspection of institutional and engineering controls to ensure that they provide the required level of protection. Land use should be evaluated on a routine basis during performance monitoring to ensure that it remains consistent with assumptions in the risk assessment used to establish cleanup goals.

As with other in-situ remediation methods, demonstrating a reduction in mass over time relies on making interpretations based on subsurface monitoring data. A reduction in contamination over time due to RNA can be demonstrated using a mass balance approach that calculates the total mass in the subsurface (i.e., dissolved mass in the plume plus sorbed and NAPL mass in the source area) for each sampling event. However, this method usually is not feasible because of the large amount of data required. Therefore, a simplified method is required to verify that there is an ongoing reduction in contamination due to RNA. The following approach is recommended for monitoring RNA progress for shrinking, stable, and expanding plumes.

For a shrinking plume, contaminant concentrations should exhibit a decreasing trend in monitoring wells within the plume. Contaminant data from each sampling event should be plotted to demonstrate a downward trend. Preferably, wells that are selected for performance monitoring should have historical data from earlier site investigations; historical concentration versus time plots for these wells can be updated with the performance monitoring data to show that concentrations are in decline. The analytical procedure in Appendix C should be used to establish a statistically significant decreasing trend. The evaluation also should confirm that the mass removal rate is similar to the expected rate (i.e., the rate that was determined during the detailed site evaluation). This is done by comparing the slope of the log concentration versus time regression line during performance monitoring sampling to the slope determined from previous sampling events. If the slope (i.e., rate) changes significantly, the estimated time required to achieve cleanup levels should be recomputed.

For a stable plume, mass removal is demonstrated by showing that contaminant concentrations in monitoring wells within the plume are not changing over time. At some point during performance monitoring, concentrations should begin to decline as the source becomes depleted and the plume begins to shrink. Plots of concentration versus distance should be constructed to demonstrate that the plume is relatively stable and not increasing. The analytical procedure in Appendix C should be used to verify that there is not a significant increasing trend in the data if conclusions cannot be made solely from visual inspection of the plots. Plots of concentration vs. distance also should be constructed using data from the performance monitoring wells that are located along the plume centerline transect to demonstrate that the plume has not expanded since the previous sampling event. The spatial regression line should be unchanged from previous events if the plume is at steady state, indicating a continued reduction of contaminant mass due to RNA. Both the concentration versus time plots and the concentration versus distance plots should be inspected following each sampling event for changes that indicate the plume has started to shrink.

Demonstrating that there is continued reduction in contamination over time is more difficult for an expanding plume than for stable or shrinking plumes. Presumably, modeling has demonstrated that the current rate of plume expansion is acceptable and concentrations will be sufficiently reduced before downgradient receptors are impacted. Therefore, performance monitoring for expanding plumes should demonstrate that the rate of plume expansion has not increased such that the model predictions are invalidated. This can be done by plotting log concentrations versus time for individual monitoring wells inside the plume and comparing the slope of the regression line for the most recent sampling events to the slope determined from previous events. If the slope appears to increase significantly during performance monitoring, corrective action should be taken that involves reassessing biodegradation rates and reevaluating model predictions to determine the potential for adverse impacts on downgradient receptors.

Performance monitoring data should be used to verify the accuracy of model predictions that show that downgradient receptors will not be adversely impacted. Measured concentrations at the performance monitoring wells should be compared to concentrations predicted with the model. This could require running additional model simulations to generate the concentration time-series data at these locations. If the predicted concentrations are substantially different than the measured concentrations, the model assumptions should be reevaluated, and, if necessary, the model should be recalibrated using this new information. Additional predictive simulations should be performed to reassess the potential for contaminants to reach downgradient receptors.

## 6.5 DOCUMENT SITE CLOSURE

The data and technical evaluation supporting achievement of cleanup goals and the acceptance of closure by the regulators and the public should be presented in a formal site closure document. The format and content of closure documentation will vary depending on the regulatory framework controlling the cleanup, but elements typically included are summarized in Table 6-3.

**Table 6-3. Typical Elements Included in Closure Documentation**

| Closure Documentation Elements | Function |
|---|---|
| Site history and description of contamination | Brief description of past site activities, the source of contamination, site conditions, and nature and extent of contamination |
| Establishment of cleanup criteria | Summary of conceptual model development and further analyses required to define the cleanup criteria. |
| Summary of remedial action | Description of sampling and analyses, showing contaminant reduction over time. |
| Comparison of contamination status with cleanup criteria | Analysis of data demonstrating that site cleanup criteria have been achieved. |
| Current contamination status | Description of current contamination at the site. |
| Certification statement | Documented acceptance of site cleanup by regulatory authority, with public comments. |
| Recommended restrictions | Documentation of restrictions on site use after cleanup is complete. |

## 6.6 ABANDON WELLS AND RESTORE SITE

Wells or monitoring equipment used during the natural attenuation project often have value for routine environmental monitoring after cleanup goals are reached. These wells may be left in place for future use. Any monitoring points that are not needed after site closure should be removed. Excess wells should be abandoned to fulfill the following performance criteria (ASTM, 1997c):

- Conform with local regulatory requirements
- Ensure that the well cannot be used for purposes other than intended
- Prevent migration of contaminants into an aquifer or between aquifers
- Reduce the potential for vertical or horizontal migration of fluids in or around the well.

RNA is less intrusive than most engineered remedial technologies, resulting in minimal environmental damage from site remediation. Therefore, post-closure restoration requirements for a natural attenuation project are limited in scope. Nevertheless, plans and funding should be included to restore the site consistent with its intended future use.

## Checklist for Performance Monitoring and Site Closure

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 1 | Develop performance monitoring goals. | ❑ Establish numerical- or performance-based standards<br>Numerical-based standard: the maximum allowed concentration of a specific contaminant within a defined area of attainment<br>Performance-based standard: a criterion that must be fulfilled to ensure protection of human health and the environment | Define performance objectives and decision rules for site closure |
| 2 | Establish locations of groundwater monitoring wells. | ❑ Identify monitoring well locations.<br>Upgradient wells: minimum of one for background data.<br>Plume transect wells: minimum of three to establish plume trends.<br>Periphery wells: minimum of one at the plume boundary to identify early plume migration.<br>Sentinel (point of compliance) wells: one or more wells located at a negotiated compliance point with a minimum of 2 years of travel time to the nearest receptor.<br>❑ For plumes with a significant vertical dimension, vertically stratified wells may be required at various sampling locations.<br>Identify locations that require vertically stratified wells.<br>Identify the number of screened intervals and their depths.<br>Soil-gas monitoring points should be established if there is a potential for exposure due to volatilization.<br>❑ Describe construction details for newly installed groundwater monitoring points.<br>Well depth<br>Screened interval<br>Bentonite and grouting requirements<br>Surface mounting requirements | Establish a monitoring well network. |

## Checklist for Performance Monitoring and Site Closure (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 3 | Establish sampling and analytical requirements based on site-specific considerations, performance monitoring goals, and regulatory input. | ❑ Establish the sampling frequency and duration.<br>Baseline sampling during the first year, to account for seasonal effects.<br>If a plume has not reached steady state, more frequent sampling may be required than if it has reached its maximum extent or has started decreasing in size.<br>More frequent sampling will be required at sites where the plume is in close proximity to the point-of-compliance well(s) or where groundwater velocities are high.<br>❑ Identify target analytes, sample collection methods, and analytical methods.<br>Concentrations of the contaminants of concern<br>Concentrations of electron acceptors (DO, $NO_3^-$, $SO_4^{=}$), metabolic by-products ($Fe^{2+}$, $Mn^{2+}$, and $CH_4$), and general water quality parameters (pH, temperature, alkalinity, and ORP)<br>Water-level elevations to monitor flow direction and velocity. If free product is present, record the thickness and correct water table elevations.<br>COCs in surface water samples if there is potential for the plume to discharge to a surface water body.<br>COCs in soil-gas if there is a potential for exposure due to volatilization.<br>❑ Develop appropriate PM plans.<br>Establish a PM work plan.<br>Establish data reduction and collection methods<br>QAPP<br>Health and Safety Plan<br>Performance monitoring schedule; major milestones, deliverables, and decision points. | A monitoring strategy should consider the appropriate sampling frequency, and sampling and analytical parameters. The monitoring strategy should be designed to track changes in ambient water quality and provide further evidence of ongoing remediation. |
| 4 | Develop a PM plan | ❑ Prepare the PM plan, to include Items 1, 2, and 3 of this checklist and Table 6-1.<br>❑ Obtain regulatory approval. | The PM plan should receive regulatory acceptance before field activities are begun. |

## Checklist for Performance Monitoring and Site Closure (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 5 | Establish institutional controls required during performance monitoring and after site closure. | ❑ Identify any institutional controls (e.g., land use restrictions) that are required to protect human health and the environment during performance monitoring.<br>Describe how these controls will be monitored and enforced: e.g., routinely inspect and review institutional controls and supporting engineering controls to ensure that they are being enforced as intended and are providing the required level of protection to human health and the environment. | Limit human activities at or near the site to protect human health and the environment, or to ensure the continued effectiveness of the remedy over time. |
| 6 | Implement institutional controls. | ❑ Construct access controls (e.g., fencing, sign posting, etc.)<br>❑ Deed restrictions<br>Land-use controls (e.g., zoning ordinance for commercial land use only)<br>Drilling, digging, or excavation restrictions<br>Restrictions on groundwater use<br>Irrigation restrictions or restrictions on ground cover disturbance<br>Restrictions on disturbance of monitoring systems | Limit human activities at or near the contaminated site to protect human health and the environment, or to ensure continued effectiveness of the remedy. |

## Checklist for Performance Monitoring and Site Closure (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 7 | Evaluate RNA progress. | ❑ Demonstrate that there is continued protection of human health and the environment.<br><br>Monitor downgradient sentinel wells to show that contaminants do not migrate to receptor points.<br><br>Routinely assess contaminant transport rates to ensure protection of downgradient receptors.<br><br>Routinely evaluate land use to ensure that it remains consistent with deed restrictions and with the assumptions used to establish cleanup goals.<br><br>❑ Demonstrate that there is continued reduction in contamination over time.<br><br>Establish plume trends as shrinking, stable, or expanding.<br><br>Compare mass removal rates established during performance monitoring with expected rates established during the detailed site evaluation for RNA.<br><br>o Shrinking plume: Contaminant concentrations should exhibit a decreasing trend in monitoring wells with time.<br><br>o Stable plumes: Contaminant concentrations in monitoring wells should not change over time. Stable plumes will begin shrinking after the source is depleted.<br><br>o Expanding plumes: The rate of plume expansion should meet expectations based on the detailed site evaluation; contaminant concentrations should be sufficiently reduced before downgradient receptors are impacted; eventually, the plume should stabilize and transition to the stable plume configuration. | Describe how the monitoring data will be reviewed and evaluated to assess the ongoing effectiveness of RNA after each monitoring event and to determine compliance with cleanup goals. |

## Checklist for Performance Monitoring and Site Closure (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 8 | Compare RNA progress with established performance monitoring objectives. | ❑ At predetermined intervals, compare RNA performance with expected performance based on the detailed site evaluation.<br>❑ Compare RNA performance with performance objectives.<br>If performance objectives are met, discontinue monitoring and prepare to close the site.<br>If performance objectives are not met, but RNA is meeting expectations, continue monitoring.<br>If performance monitoring objectives are not met and RNA is not meeting expectations, reassess RNA progress and efficiency. | Assess RNA progress and, if performance monitoring objectives are met, prepare to close the site. |
| 9 | If necessary, implement contingency measures | ❑ Establish criteria that would signal unacceptable performance of RNA and indicate when to implement contingency measures.<br>Contaminants are detected in sentinel wells at unacceptable concentrations.<br>The rate of contaminant migration exceeds expectations and threatens downgradient receptors.<br>Changes in land and/or groundwater use prevent RNA from providing adequate protection of human health and the environment.<br>❑ Identify the contingency measure.<br>❑ Implement the contingency measure as necessary, if specific, predetermined criteria are exceeded. | The EPA recommends assessing the need for including one or more contingency measures that would be capable of achieving the remediation objectives, if RNA fails to perform as expected. |
| 10 | Document Site Closure. | ❑ Describe the site history and a description of the historical extent of contamination.<br>❑ Describe previously approved cleanup criteria.<br>❑ Summarize the remedial action, including results from the detailed site investigation.<br>❑ Present performance monitoring data and results.<br>❑ Compare contaminant status with cleanup criteria.<br>❑ Document acceptance of site cleanup by regulatory authority, with public comments.<br>❑ Identify restrictions of site use after cleanup is complete. | Performance monitoring data and a technical evaluation supporting the achievement of cleanup goals and acceptance of site closure by regulators and the public should be presented in a formal site closure document. |

## Checklist for Performance Monitoring and Site Closure (Cont.)

| ITEM | TASK | DETAILED SITE INVESTIGATION GUIDANCE AND TASK CHECKLIST | BASIS |
|---|---|---|---|
| 11 | Close site | ❑ Abandon existing monitoring wells, as necessary<br>Conform with regulatory requirements<br>❑ Restore site as required. | Restore site to meet future site uses. |

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# APPENDIX A
# Physical, Chemical, and Biological Parameters for Petroleum Fuel Contaminants

## Table A-1. Physical and Chemical Properties of Example Fuel Components

| Chemical Class | Compound | Formula | Molecular Weight | Melting Point (°C) | Boiling Point (°C) | Vapor Pressure mm Hg (at °C) | Solubility in Water mg/L (at °C) | Diffusivities | | Henry's Constant | | Koc | Kow |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | air | water | atm-$m^3$/mol | dimension-less | | |
| Alkylbenzenes | Benzene | $C_6H_6$ | 78.11 | 5.5 | 80.1 | 76 (20) | 1,800 (20) | 8.80E-02 | 9.80E-06 | 5.50E-03 | 2.30E-01 | 6.50E+01 | 134.89 |
| | Toluene | $C_6H_5CH_3$ | 92.10 | -95.1 | 110.8 | 22 (20) | 640 (25) | 7.80E-02 | 8.60E-06 | 6.60E-03 | 2.70E-01 | 2.60E+023 | 489.78 |
| | Ethylbenzene | $C_6H_5C_2H_5$ | 106.17 | -94.4 | 136.2 | 10 (25.9) | 100 (15) | 7.50E-02 | 7.80E-06 | 7.90E-03 | 3.20E-01 | 2.20E+02 | 1413 |
| | *o*-Xylene | $C_6H_4(CH_3)_2$ | 106.17 | -25 | 144.4 | 5 (20) | 187 (25) | 4.90E-03 | 1.00E-05 | 4.90E-03 | 2.00E-01 | 2.40E+02 | 1413 |
| | *m*-Xylene | $C_6H_4(CH_3)_2$ | 106.17 | -47.3 | 139.3 | 6 (20) | 166 (25) | 6.90E-03 | 7.80E-06 | 6.90E-03 | 2.80E-01 | 2.40E+02 | 1585 |
| | *p*-Xylene | $C_6H_4(CH_3)_2$ | 106.17 | 13 | 138.4 | 6.5 (20) | 175 (25) | 7.00E-03 | 8.40E-06 | 7.00E-03 | 2.90E-01 | 2.40E+02 | 1413 |
| Selected PAHs | Naphthalene | $C_{10}H_8$ | 128.16 | 80.2 | 217.9 | 0.0082 (25) | 30 (25) | 6.90E-02 | 7.50E-06 | 1.30E-03 | 5.20E-02 | 1.30E+03 | 2344 |
| | 2-Methylnaphthalene | $C_{10}H_7CH_3$ | 142.19 | 35 to 36 | 241 to 242 | 0.068 (25) | NA | NA | NA | 4.00E-04 | NA | 2.51E+03 | 7244 |
| | Acenaphthene | $C_{12}H_{10}$ | 154.21 | 90 to 95 | 279 | .0027 (20) | 3.5 –7.4 (25) | 640E-02 | 7.70E-06 | 1.20E-03 | 4.90E-02 | 4.60E+03 | 8318 |
| | Anthracene | $C_{14}H_{10}$ | 178.23 | 216.2 to 216.4 | 340 | 0.000196 (20) | 1.29 (25) | 5.80E-02 | 7.70E-06 | 3.40E-05 | 1.40E-03 | 1.30E+04 | 23184 |
| | Benzo(a)anthracene | $C_{18}H_{12}$ | 228.00 | 158 | 437 | 5.0E-9 (20) | 0.044 (24) | NA | NA | 5.10E-05 | NA | 3.31E+04 | 407380 |
| | Benzo(a)pyrene | $C_{20}H_{12}$ | 252.30 | 177 | 495 | 5.25E-9 (25) | .002 (25) | NA | NA | 7.99E-06 | NA | 5.50E+06 | 1148154 |
| | Chrysene | $C_{18}H_{12}$ | 228.20 | 254 | 488 | 6.3E-7 (20) | 0.0006 (25) | 4.60E-02 | 6.20E-06 | 6.20E-06 | 4.30E-05 | 2.00E+05 | 870964 |
| | Fluoranthene | $C_{16}H_{10}$ | 202.00 | 107 | 250 | 6.0E-6 (20) | 0.265 (25) | NA | NA | 5.40E-05 | NA | 3.80E+04 | 213796 |
| | Pyrene | $C_{16}H_{10}$ | 202.26 | -149 to -151 | 360 | 6.85E-7 (20) | 0.16 (26) | 2.70E-02 | 7.20E-06 | 7.20E-06 | 4.10E-04 | 1.20E+05 | 75858 |
| Fuel Addtives | Methyl-*tert*-butyl ether (MTBE) | $C_5H_{12}O$ | 88.15 | -109 | 55.2 | 245 (25) | 51.26 (25) | NA | NA | 5.50E-04 | NA | 1.23E+01 | 17.37 |
| | *tert*-butyl alcohol (TBA) | $(CH_3)_3COH$ | 74.10 | 25 | 83 | 31 (20) | miscible (20) | NA | NA | 1.19E-05 | NA | 3.72E+01 | 2.29 |
| | Ethanol | $CH_3CH_2OH$ | 46.07 | -114 to -117 | 78.4 | 43.9 (20) | miscible (25) | NA | NA | 6.29E-06 | NA | 1.58 | 0.49 |
| | Methanol | $CH_3OH$ | 32.04 | -98 | 65 | 92 (20) | miscible (20) | NA | NA | 4.60E-06 | NA | 2.75 | 0.17 |

Note: NA = not available.

## Table A-2. Biodegradation Results from Field and Laboratory Studies at Intrinsic Bioremediation Sites

| SITE | Contaminant | V (m/d) | Field Results | Laboratory Results |
|---|---|---|---|---|
| Borden, Ontario (Baker et al., 1967) | BTX stock injected into uncontaminated aquifer | 0.09 | Zero-order decay rates from mass balance method:<br>benz. = 30 mg $d^{-1}$<br>tol. = 37 mg $d^{-1}$<br>*m*-xyl. = 47 mg $d^{-1}$<br>*p*-xyl. = 55 mg $d^{-1}$<br>*o*-xyl. = 33 mg $d^{-1}$ | Zero-order decay rates (per 1,800 L) from aerobic microcosms:<br>benz. = 58 mg $d^{-1}$<br>tol. = 61 mg $d^{-1}$<br>*m*-xyl. = 50 mg $d^{-1}$<br>*p*-xyl. = 65 mg $d^{-1}$<br>*o*-xyl. = 54 mg $d^{-1}$ |
| Borden, Ontario (Barbaro et al., 1992) | Stock solution contacted with gasoline then injected into leachate plume | 0.09 | % loss over 4 m travel | |
| Rocky Point, NC (Borden et al., 1995) | Residual gasoline from UST | 0.08 | Rates from conc. vs. travel time:<br>benz. = 0.0002 $d^{-1}$<br>tol. = 0.0021 $d^{-1}$<br>e-benz. = 0.0015 $d^{-1}$<br>*m,p*-xyl. = 0.0013 $d^{-1}$<br>*o*-xyl. = 0.0021 $d^{-1}$ | Rates from $Fe/SO_4$ reducing microcosms:<br>benz. = 0.024 $d^{-1}$<br>tol. = 0.045 $d^{-1}$<br>e-benz. = 0.002 $d^{-1}$<br>*m,p*-xyl. = 0.02 $d^{-1}$<br>*o*-xyl. = 0.056 $d^{-1}$ |
| Kalkaska, MI (Chiang et al., 1989)<br>Columbus, MS (MacIntyre et al., 1993) | Natural gas condensate-BTEX stock solution of benzene, *p*-xylene, naphthalene, *o*-dichlorobenzene | 0.2 | Rates for mass balance:<br>benz. = 0.0095 $d^{-1}$<br>Tritium used as nonreactive tracer. Mineralization proven using $^{14}C$-*p*-xyl. Rates from mass balance:<br>benz. = 0.0070 $d^{-1}$<br>*p*-xyl. = 0.0107 $d^{-1}$<br>naphthalene = 0.0064 $d^{-1}$<br>*o*-DCB = 0.0046 $d^{-1}$ | Rates from aerobic microcosms:<br>BTX = 0.01 to 0.1 $d^{-1}$ |
| Sleeping Bear, MI (Wilson et al., 1994b; Schafer, 1994) | Residual gasoline from UST release – BTEX | 0-0.4 | Rates from conc. vs travel time using 2,3-dimethylpentane as an internal standard: benz. = N.S.<br>tol. = 0.02 – 0.07 $d^{-1}$<br>e-benz. = 0.03 – 0.011 $d^{-1}$<br>*m*-xyl. = 0.004 – 0.014 $d^{-1}$<br>*p*-xyl. = 0.002 – 0.010 $d^{-1}$<br>*o*-xyl. = 0.004 – 0.011 $d^{-1}$ | Rates from methanogenic microcosms: benz. = N.S.<br>tol. 0.007 – 0.04 $d^{-1}$<br>e-benz. = N.S.<br>*m,p*-xyl. = N.S.<br>*o*-xyl. = N.S.<br>12 to 16 mg/L $CH_4$ produced in lab microcosms |

**Table A-2. Biodegradation Results from Field and Laboratory Studies at Intrinsic Bioremediation Sites (Cont.)**

| SITE | Contaminant | V (m/d) | Field Results | Laboratory Results |
|---|---|---|---|---|
| Indian River, FL (Kemblowski et al., 1987) | Gasoline from UST – BTEX | 0.06 | Conc. vs. travel time: benz. = 0.0085 $d^{-1}$ | 1st-order rates from aerobic microcosms: benz. = 0.02 to 0.2 $d^{-1}$ |
| Morgan Hill, CA (Kemblowski et al., 1987) | Gasoline – BTEX | 0.05 | Rates from conc. vs. travel time: benz. = 0.0035 $d^{-1}$ | |
| Eglin AFB, FL (Wilson et al., 1994a) | JP-4 from POL depot | 1.3 | Rates from conc. vs. travel time using 1,2,4-trimethylbenzene as internal standard: benz. = B.D. tol. = 0.05 to 0.013 $d^{-1}$ e-benz. = 0.03 to 0.05 $d^{-1}$ *m*-xyl. = 0.02 to 0.1 $d^{-1}$ *p*-xyl. = 0.02 to 0.08 $d^{-1}$ *o*-xyl. – 0.21 $d^{-1}$ | |
| Hill AFB, UT (Wiedimeier et al., 1994) | JP-4 from POL depot | 0.5 | Rates from conc. vs. travel time using total trimethyl-benzene as internal standard: benz. = 0.03 to 0.09 $d^{-1}$ e-benz. = 0.01 to 0.08 $d^{-1}$ *p*-xyl. = 0.01 to 0.03 $d^{-1}$ *m*-xyl. = 0 to 0.03 $d^{-1}$ *o*-xyl. = 0 to 0.02 $d^{-1}$ Toluene rate not calculable. | |
| Patrick AFB, FL (Wiedemeier et al., 1994) | 700 gal (2,650 L) unleaded gasoline from UST | 0.13 | Rates from conc. vs. travel time using total methane as internal standard: benz. = 0 to 0.004 $d^{-1}$ tol. = 0.0006 to 0.004 $d^{-1}$ e-benz. = 0.0001 to 0.004 $d^{-1}$ *p*-xyl. = 0.001 to 0.003 $d^{-1}$ *m*-xyl. = 0.001 to 0.004 $d^{-1}$ *o*-xyl. = 0.004 to 0.02 $d^{-1}$ | |
| Fairfax, VA (Buscheck et al., 1993) | 700 gal (2,650 L) unleaded gasoline from UST | 0.015 | Rates from conc. vs travel time: benz. = 0.00055 $d^{-1}$ tol. = 0.00045 $d^{-1}$ e-benz. = 0.00045 $d^{-1}$ *m,p, o*-xyl. = 0.00040 $d^{-1}$ | |

**Table A-2. Biodegradation Results from Field and Laboratory Studies at Intrinsic Bioremediation Sites (Cont.)**

| SITE | Contaminant | V (m/d) | Field Results | Laboratory Results |
|---|---|---|---|---|
| San Francisco, CA (Buscheck et al., 1993) | Gasoline – BTEX | 0.03 | Rates from conc. vs. travel time: benz = 0.0028 $d^{-1}$<br>tol. = 0.0022 $d^{-1}$<br>e-benz. = 0.0033 $d^{-1}$<br>*m,p, o*-xyl. = 0.0023 $d^{-1}$ | |
| Alameda County, CA (Buscheck et al., 1993) | Gasoline – BTEX | 0.01 | Rates from conc. vs. travel time: benz = 0.0020 $d^{-1}$<br>tol. = 0.0017 $d^{-1}$<br>e-benz. = 0.0020 $d^{-1}$<br>*m,p, o*-xyl. = 0.0017 $d^{-1}$ | |
| Elko County, NV (Buscheck et al., 1993) | Gasoline-BTEX | 0.04 | Rates from conc. vs. travel time: benz. 0.001 $d^{-1}$ | |
| Sampson Co., NC (Borden, personal communication, 1995) | Gasoline from UST – BTEX/MTBE | 0.04 | High nitrate concentrations in groundwater may enhance biodegradation 1st – order rates from mass flux:<br>MTBE = 0.0006 $d^{-1}$<br>benz. = 0.0006 $d^{-1}$<br>tol. = 0.0021 $d^{-1}$<br>e-benz. = 0.0023 $d^{-1}$<br>*m,p*-xyl. = 0.0016 $d^{-1}$<br>*o*-xyl. = 0.0009 $d^{-1}$ | Toluene and ethylbenzene rapidly degraded in denitrifying microcosms after a 56-d lag period. |
| Traverse City, MI (Wilson et al., 1990) | Aviation gasoline from UST – BTEX | 1.5 | Rates from conc. vs. travel time:<br>benz. = 0.001 $d^{-1}$<br>tol. = 0.2 $d^{-1}$<br>*m,p,o*-xyl. = 0.004 $d^{-1}$ | Anaerobic microcosm rates:<br>benz. = 0.07 $d^{-1}$<br>tol. = 0.04 $d^{-1}$<br>*m,p* xyl. = 0.06 $d^{-1}$<br>*o*-xyl. = 0.07 $d^{-1}$<br>Methane produced in microcosms. |
| Broward Co., FL (Caldwell et al., 1992) | Gasoline from UST — BTEX and MTBE | 0.1 | Anaerobic decay rate from matching BIOPLUME for total BTEX = 0.00012 $d^{-1}$. Aerobic decay will increase net biodegradation. | |
| Pensacola, FL (Bekins et al., 1993) | Creosote-phenols | 0.3 to 1.2 | Selected phenols were completely degraded over a 100-d travel time through methanogenic aquifer. | Selected phenols were completely degraded over 100 to 200 d in methanogenic microcosms. |

## Table A-2. Biodegradation Results from Field and Laboratory Studies at Intrinsic Bioremediation Sites (Cont.)

| SITE | Contaminant | V (m/d) | Field Results | Laboratory Results |
|---|---|---|---|---|
| Bemidji, MN (Baedecker et al., 1993) | Crude oil — BTEX | 0.25 | tol. and *o*-xyl. depleted over 20 m (200 d travel time); benz, and e-benz. depleted over 100 m. Downgradient migration was limited by mixing with uncontaminated water. | 98% benz. loss in 125 d and 99% tol. loss in 45 d in anaerobic microcosms. |
| Perth, Australia (Thierrin et al., 1993) | Gasoline from UST — BTEX | 0.4 | Rates from conc. vs. travel time:<br>benz. = N.S.<br>tol. = 0.006 $d^{-1}$<br>e-benz. = 0.003 $d^{-1}$<br>*m,p*-xyl. = 0.004 $d^{-1}$<br>*o*-xyl = 0.006 $d^{-1}$<br>naphthalene = 0.004 $d^{-1}$ Field (plume scale) rates closely match rates from tracer test using deuterated compounds. | Anaerobic columns with 14 mg/L $SO_4$:<br>benz. = N.S.<br>tol. = 2.3 d<br>e-benz. = N.S.<br>*o*-xyl. = N.S. |
| Manufacturing Plant (Davis et al., 1994) | Benzene only | 0.16 | BIO1D match to field data showed benzene decay rate >0.01 $d^{-1}$ | Over 90% benzene loss over 77 d in methanogenic and sulfate-reducing microcosms. |
| Cliffs-Dow (Klecka et al., 1990) | Charcoal wastes, phenols, naphthalene | 0.2 to 0.46 | All organics degraded within 100 m of source. | All organics degraded in aerobic microcosms within 30 to 60 d. |
| Hill AFB-2, UT (Dupont et al., 1994) | 18,000 gal (68,137 L) UST | 0.14 | Rates from mass balance: 1st order for TPH = 0.005 $d^{-1}$<br>Zero order for:<br>benz. = 0.02 kg/d<br>e-benz. = 0.06 kg/d<br>*p*-xyl. = 0.06 kg/d | |
| Gas Plant (Piontek et al., 1994) | NAPL released from natural gas plant-BTEX | | 105 reduction in BTEX over 100 m. | |
| Picatinny Arsenal, NJ (Martin and Imbrigiotta, 1994) | TCE, 1,1,1-trichloroethane and metals from plating wastewater | 0.3 to 1.0 | Spatial distribution of TCE, DCE, and VC indicate reductive dechlorination. | Anaerobic microcosms:<br>TCE = 0.0001 to 0.003 $d^{-1}$ |
| St. Joseph, MI (Wilson et al., 1994b) | TCE from lagoons/dry wells | 0.1 | Rates from mass flux:<br>TCE = 0.001 to 0.003 $d^{-1}$ | |

**Table A-2. Biodegradation Results from Field and Laboratory Studies at Intrinsic Bioremediation Sites (Cont.)**

| SITE | Contaminant | V (m/d) | Field Results | Laboratory Results |
|---|---|---|---|---|
| Finger Lakes, NY (Major et al., 1994) | TCE, acetone, methanol | | Spatial distribution of TCE, DCE, VC, and ethene were indicative of reductive dechlorination. | |

Note: (a) benz. = benzene, tol. = toluene, e-benz. = ethylbenzene, xyl. = xylenes, TPH = total petroleum hydrocarbons, N.S. = not significant, POL = petroleum, oil, and lubricans; TCE = trichloroethylene; DCE = dichloroethylene; VC = vinyl chloride.

Adoped from Rifai et. al., 1995.

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# APPENDIX B
# Modeling Fate and Transport of Fuel Hydrocarbons in Groundwater

The feasibility of RNA relies on its ability to degrade contaminants before they migrate to sensitive receptors at levels that will cause unacceptable risk. Expanding plumes generally require the use of a model to predict future COC migration. In order for a model to adequately predict the fate and transport of an expanding dissolved hydrocarbon plume, it must consider the following influences:

- Contaminant dissolution (release) to groundwater from a source
- Groundwater hydrogeology
- Contaminant transport properties such as dispersion, sorption, and biodegradation

To maintain brevity, this appendix focuses on the data and information required to establish contaminant fate and transport parameters and to construct a fate and transport model. It does not include analytical solutions to 1-, 2-, and 3-dimensional partial differential fate and transport equations, which can be found in the following sources: *Applied Groundwater Modeling: Simulation of Flow and Advective Transport* (Anderson and Woessner, 1992); *Physical and Chemical Hydrogeology* (Domenico and Schwartz, 1990); and *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Wiedemeier et al., 1995). Specifically, this appendix discusses the following modeling tasks:

- Develop a detailed conceptual model, and define the following terms:
  - The physical framework of the model
  - The geologic and hydrogeologic framework
  - The nature and extent of contamination
  - Contaminant transport parameters
- Determine the source volume and mass, and the contaminant dissolution rate into groundwater
  - Construct a fate and transport model
  - Calibrate the model and conduct sensitivity analyses
  - Perform predictive simulations
  - Report modeling results

The investigator who will construct and execute the model is expected to have in-depth knowledge and experience with fate and transport modeling. This appendix should be used to evaluate the site-specific data requirements for a model, and to ensure that the proper type and amount of data are collected during the detailed site evaluation.

## B.1 REFINE CONCEPTUAL MODEL FOR GROUNDWATER FLOW AND CONTAMINANT TRANSPORT MODELING

Development of a detailed conceptual model is an integral step in the modeling process. A complete conceptual model to support groundwater flow and contaminant transport modeling should include information describing the geologic framework, the hydrogeologic framework, the nature and extent of contamination, and the parameters that control the migration of contaminants through the flow system. This detailed conceptual model, which is intended to support groundwater flow and contaminant transport modeling, is more detailed than the preliminary assessment conceptual model discussed in Section B-4. However, the information assembled in the preliminary conceptual model will provide the foundation for the detailed conceptual model.

The purpose of the detailed conceptual model is to simplify the problem and organize all the pertinent physical, hydrologic, and contaminant data so that the physical system can be analyzed more easily. The detailed conceptual model should present all available site-specific data and should be integrated into a complete three-dimensional representation of the hydrogeologic and contaminant transport system of the site. It should include a graphical representation of the flow system, as shown in Figure B-1. Additional elements of the detailed conceptual model should include:

- Land use, potential receptors, and general descriptions of the climate, geology, hydrogeology, geochemistry, and contamination (from the preliminary site conceptual model)

- A detailed description of the geologic framework based on geologic maps, lithologic logs, hydrogeologic cross sections, and hydrostratigraphic unit surface and isopach maps

- The hydrogeologic framework defined by interpretations of the flow system based on water levels and hydrographs, water-table elevation maps, the direction of groundwater flow, hydraulic gradients, hydraulic conductivities, flow velocities, recharge and discharge points, and flow boundaries and budgets

- The nature and extent of contamination as defined by analytical results from groundwater sampling and interpreted through the construction of contaminant contour maps and maps of pertinent biological indicators

- The contaminant transport parameters that control the migration of contaminants at the site, including retardation coefficients, hydrodynamic dispersion coefficients, volatilization factors, and biodegradation rates

Using the available information in the preliminary site conceptual model and the information obtained from the detailed site evaluation, the detailed conceptual model can be developed to meet the data requirements of a groundwater flow and contaminant transport model. Table B-1 is a summary of the specific information that should be included in the detailed conceptual model.

### B.1.1 Define the Physical Framework of the Model

The physical framework sets the physical boundaries of the model. It refers to the distribution and configuration of the aquifer of interest and any related stratigraphic units, such as confining layers. Of particular interest are the thickness, continuity, lithology, and geologic structure of contaminated units and other units that are relevant to the study. The physical framework of a flow system can be defined using the concept of hydrostratigraphic units, which consist of geologic units or formations of similar hydrogeologic properties. Several geologic formations may be combined into a single hydrostratigraphic unit, or a geologic formation may be subdivided into aquifers and confining units.

The physical framework and hydrostratigraphic units can be define using the following traditional geologic techniques:

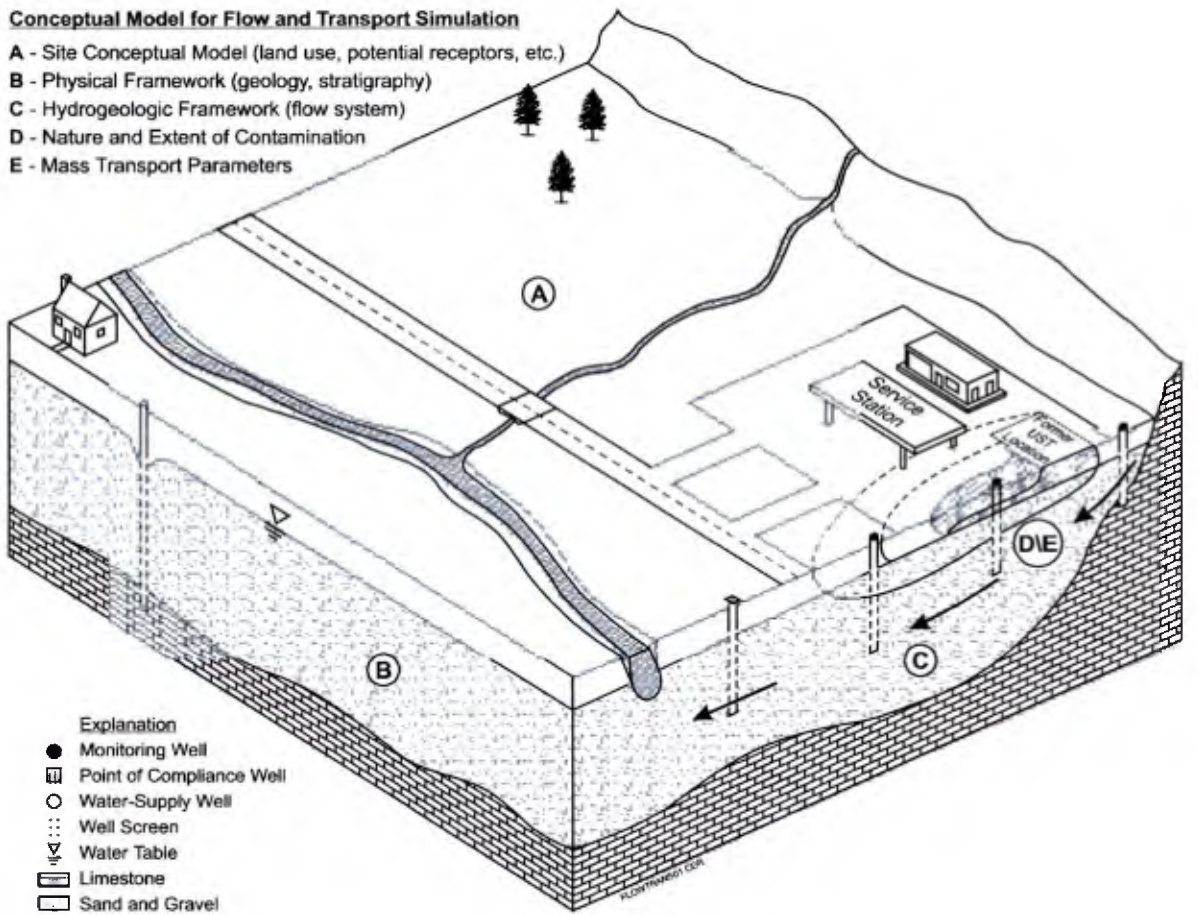


**Figure B-1. Graphic three-dimensional representation of a detailed conceptual model.**

## Table B-1. Information Required to Complete a Detailed Conceptual Model

| Parameter/Data | Application | Test Methods (References) | Measurements Needed |
|---|---|---|---|
| *Physical Framework* | | | |
| • Lithologic logs<br>• Geologic and topographic maps<br>• Cross sections<br>• Isopach maps | Needed to define the physical framework and identify hydrostratigraphic units of interest. Also needed to define model domain and layers. | Based on logging and descriptions made during drilling. | Number determined by the size of site, professional experience, and site complexity |
| *Hydrogeologic Framework* | | | |
| Water-level measurements | Needed to construct hydrographs, water-table maps, calculate hydraulic gradients, and define groundwater flow directions. Also needed to define saturated thickness of aquifer. | Field measured with oil-water interface probe or water-level meters (Fetter, 1994). | Number determined by the size of site, professional experience, and site complexity. Measurements should be taken in as many wells as possible. |
| Hydraulic conductivity (K) | Needed to calculate groundwater flow velocities. | Field measured with aquifer – pumping or slug tests. May be estimated from literature values (ASTM D 4043; ASTM D 4044-96; Fetter, 1994; Domenico and Schwartz, 1990; Kruseman and de Ridder, 1991). | Aquifer testing typically is performed either as one pumping test, or as several slug tests in as many wells as possible. |
| Hydraulic gradient (dh/dl) | Needed to calculate groundwater flow velocities and determine lateral and vertical flow directions. | Calculated from water-level data and water-table maps depicting groundwater flow directions (Fetter, 1994). | Should be calculated for several areas across the site, particularly for sites with irregular flow patterns. |
| Groundwater flow velocity (v) | • Needed to determine rate of groundwater movement and calculate migration rate of contaminants.<br>• May be specified as a model input parameter, particularly for analytical models. Alternatively, k maybe calculated within the model based on hydraulic conductivities, gradients, and porosity. | Calculated from hydraulic gradient, hydraulic conductivity, and effective porosity (Fetter, 1994). | Should be calculated for several areas across the site, particularly for sites with irregular flow patterns. |
| Porosity (n, $n_e$) | • Needed to calculate groundwater flow velocities and retardation factors.<br>• May be specified as a model input parameter. | Measured in the laboratory or estimated from literature (Domenico and Schwartz, 1990). | Should be measured or estimated for each different lithology at the site. |
| *Contaminant Transport Parameters* | | | |
| Nature and extent of contamination and biological indicators<br>• Contaminant distribution maps<br>• Biological indicator maps | Needed to determine concentrations and distribution of contaminants and biological indicator compounds (electron acceptors, metabolic byproducts, geochemical parameters). | Based on laboratory analysis of groundwater samples and field measurements performed during sampling. | As needed to characterize the extent and distribution of contaminants and biological indicator compounds at the site. |

| Parameter/Data | Application | Test Methods (References) | Measurements Needed |
|---|---|---|---|
| Source term | Needed to determine mass loading rate from hydrocarbon contamination to the groundwater. Also needed to predict source lifetime and plume status. | Based on field and contaminant characterization data. | Must be calculated for each specific contaminant compound. |
| Retardation factor ($R_f$) | Needed to calculate the rate of contaminant migration relative to the groundwater flow velocity. May be a model input parameter. | Calculated based on the distribution coefficient ($K_d$), the soil bulk density ($\Delta_b$), and the effective porosity ($n_e$) (Domenico and Schwartz, 1990). | Must be calculated for each specific contaminant compound and for each different lithology at the site. |
| Distribution coefficient ($K_d$) | Needed to determine the amount of sorption occurring during contaminant migration. Used to calculate the retardation factor. May be a model input parameter. | Calculated based on the sorption coefficient ($K_{oc}$) and the soil organic carbon fraction ($f_{oc}$). May be determined directly using laboratory batch experiments and sorption isotherms (Domenico and Schwartz, 1990). | Must be calculated for each specific contaminant compound and for each different lithology at the site. |
| Sorption coefficient ($K_{oc}$) and soil organic carbon fraction ($f_{oc}$) | Needed to calculate the distribution coefficient. May be a model input parameter. | • Sorption coefficient ($K_{oc}$) can be determined from the octanol-water partitioning coefficient ($K_{ow}$) found in the literature.<br>• Organic carbon fraction ($f_{oc}$) can be measured in the laboratory. | Must be determined for each specific contaminant compound and for each different lithology at the site. |
| Bulk density ($\Delta_b$) | Needed to calculate the retardation factor. May also be a model input parameter. | Measured in the laboratory. | Must be determined for each different lithology at the site. |
| Hydrodynamic dispersion ($D_x$) | Needed to determine contaminant migration rate and potential plume spreading. Model input parameter for both analytical and numerical transport models. | Can be determined in the field using a tracer test, but typically estimated based on plume length or literature values (Domenico and Schwartz, 1990). | Determined or estimated for the entire flow system. |
| Biodegradation rates | Needed to determine rate of contaminant depletion due to biological activity. May be a model input parameter or calculated by the model based on the distribution of electron acceptors. | Determined by:<br>• Regression of field data<br>• Analysis of conservative tracer concentrations<br>• Laboratory microcosm studies. | Must be determined for each contaminant. |
| Volatilization factors | Needed to determine amount of contaminant loss from partitioning from free- or dissolved-phase plume. Generally contributor to less than 5% of the total plume attenuation rate (Chiang et. al., 1989) | Based on literature values for partial pressures and Henry's law constants | Must be determined for each contaminant. |

- Geologic maps and cross sections showing the areal and vertical extent and boundaries of the formations are necessary to identify the hydrostratigraphic units of interest and to define the physical extent of the system.

- Topographic maps showing surface water bodies and potential hydrologic divides provide information regarding potential surface water/groundwater interactions.

- Contour maps depicting the elevation of the base of the aquifers and confining beds and isopach maps showing the thickness of the aquifers and confining beds aid in defining the physical extent of the hydrostratigraphic units.

Geologic and topographic maps of the site of interest are typically available through state or federal resources, including the state geological survey and the United States Geological Survey (USGS). Additional references may be available including reports from previous studies. Site-specific information such as lithologic logs, geophysical logs, and soil boring descriptions should be used to develop site-specific hydrogeologic cross sections, contour maps depicting the physical boundaries of the system, and isopach maps defining the thickness of the units of interest. If this information is not available, it is recommended that several boreholes be drilled and continuous sediment/rock cores be collected and logged to adequately characterize the stratigraphy of the site.

### B.1.2 Define the Hydrogeologic Framework

Definition of the hydrogeologic framework is dependent on the description of the physical framework. Where the physical framework, or hydrostratigraphy, is used to form the physical structure of the conceptual model, the hydrogeologic information is used to conceptualize the movement of groundwater through the system. Information and interpretations needed to describe the movement of groundwater include:

- Measurement of water-level elevations and the construction of hydrographs
- Development of potentiometric-surface or water-table maps to assess groundwater flow direction
- Measurement of the hydraulic conductivity of the aquifer materials
- Estimation of the porosity of the aquifer materials
- Calculation of the groundwater flow velocity
- Identification and quantification of recharge, discharge, and flow boundaries
- Calculation of an overall water budget

**B.1.2.1 Water-Level Measurements and Hydrographs.** Water-level measurements from wells and piezometers within the area of interest are used to construct water table maps and/or potentiometric surface maps to determine the direction of groundwater flow, the location of recharge and discharge points, the connection between individual aquifers, and the hydraulic communication between aquifers and surface-water bodies. It is essential to have measurements from as many wells and piezometers at the site as possible, because water-table elevations, hydraulic gradients, and groundwater flow directions can change considerably over a short distance in an aquifer. Repeated measurements also are needed from several time periods throughout the year because water-table elevations often fluctuate temporally as a result of changes in precipitation, recharge, surface-water elevations, and pumping stresses. Hydrographs

are plots of water-level elevation over time and are used to assess the amount of variability in the water-table elevation in a particular well over time.

**B.1.2.2 Potentiometric-Surface or Water-Table Maps to Assess Groundwater Flow Direction.** Potentiometric-surface or water-table maps are essential in determining the gradients and directions of groundwater flow. These maps are comprised of contoured water-table elevations determined from water-level measurements. The contours, or equipotential lines, represent values of equal hydraulic potential (i.e., equal hydraulic head). Groundwater flows from areas of relatively high potential to areas of low potential, and these maps can be used to determine the direction of groundwater flow within the area of interest. Groundwater flows in a direction that is perpendicular to the equipotential lines on a water-table elevation map.

The vertical component of groundwater flow can be assessed by plotting water-table elevations on a hydrogeologic cross section showing the hydrostratigraphic units of interest. Using the premise that groundwater flows from areas of relatively high potential to areas of low potential, the hydraulic heads measured in different units can be used to determine the vertical direction of groundwater flow.

The hydraulic gradient is the change in hydraulic head (water-table elevation) divided by the length of groundwater flow along a flowpath. Accurate assessment of the hydraulic gradients across a site is dependent on the measurement of water levels in as many monitoring wells and piezometers as possible. Because hydraulic gradients can vary spatially and fluctuate temporally, it is essential to have sufficient data to assess the flow variability over space and time. Sites near surface water bodies, such as lakes or rivers, are more likely to be affected by seasonal variations in water-table elevations, changes in hydraulic gradients, and changes in groundwater flow directions. Sites near oceans or harbors may be influenced by tidal patterns that can impact water-table elevations and hydraulic gradients.

**B.1.2.3 Hydraulic Conductivity.** Hydraulic conductivity is required to calculate the groundwater flow velocity and the rate that dissolved contaminants migrate in groundwater. Hydraulic conductivity is a measure of an aquifer's ability to transmit water and is expressed as the rate at which water can move through the porous medium. Hydraulic conductivity is perhaps the most important parameter governing groundwater flow. Conceptually, the hydraulic conductivity of an aquifer is the volumetric flowrate that the aquifer will permit through a unit surface area under a specified hydraulic gradient. The units used to describe hydraulic conductivity are derived from units of volumetric flow normalized to surface area, or $(L^3/T)/L^2$, which reduces to L/T. Common units for hydraulic conductivity are cm/s and ft/d. Table B-2 is a list of representative hydraulic conductivity values for various rock and sediment types.

Darcy's law describes the relationship between the volumetric flowrate and hydraulic conductivity, hydraulic gradient, and surface area associated with the flow of water through a porous medium and can be expressed as (Equation B-1):

$$Q = -K\frac{dh}{dl}A \qquad \text{(B-1)}$$

where: Q = volumetric flowrate ($L^3/T$)
K = hydraulic conductivity (L/T)
dh/dl = hydraulic gradient
A = cross-sectional area of flow ($L^2$).

**Table B-2. Representative Hydraulic Conductivity Values for Various Rock Types**

| Material | Hydraulic Conductivity (cm/s) |
|---|---|
| ***Sedimentary Deposits*** | |
| Gravel | $3 \times 10^{-2}$ to 3 |
| Coarse sand | $9 \times 10^{-5}$ to $6 \times 10^{-1}$ |
| Medium sand | $9 \times 10^{-5}$ to $5 \times 10^{-2}$ |
| Fine sand | $2 \times 10^{-5}$ to $2 \times 10^{-2}$ |
| Silt, loess | $1 \times 10^{-7}$ to $2 \times 10^{-3}$ |
| Till | $1 \times 10^{-10}$ to $2 \times 10^{-4}$ |
| Clay | $1 \times 10^{-9}$ to $4.7 \times 10^{-7}$ |
| Unweathered marine clay | $8 \times 10^{-11}$ to $2 \times 10^{-7}$ |
| ***Sedimentary Rocks*** | |
| Karst and reef limestone | $1 \times 10^{-4}$ to 2 |
| Limestone, dolomite | $1 \times 10^{-7}$ to $6 \times 10^{-4}$ |
| Sandstone | $3 \times 10^{-8}$ to $6 \times 10^{-4}$ |
| Siltstone | $1 \times 10^{-9}$ to $1.4 \times 10^{-6}$ |
| Salt | $1 \times 10^{-10}$ to $1 \times 10^{-8}$ |
| Anhydrite | $4 \times 10^{-11}$ to $2 \times 10^{-6}$ |
| Shale | $1 \times 10^{-11}$ to $2 \times 10^{-7}$ |
| ***Crystalline Rocks*** | |
| Permeable basalt | $4 \times 10^{-5}$ to 2 |
| Fractured igneous and metamorphic rock | $8 \times 10^{-7}$ to $3 \times 10^{-7}$ |
| Weathered granite | $3.3 \times 10^{-4}$ to $5.2 \times 10^{-3}$ |
| Weathered gabbro | $5.5 \times 10^{-5}$ to $3.8 \times 10^{-4}$ |
| Basalt | $2 \times 10^{-9}$ to $4.2 \times 10^{-5}$ |
| Unfractured igneous and metamorphic rocks | $3 \times 10^{-12}$ to $2 \times 10^{-8}$ |

Source: after Domenico and Schwartz, 1990.

The velocity of groundwater flow is directly related to the hydraulic conductivity in the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence contaminant transport by providing preferential pathways for contaminant migration.

The most common field methods used to determine hydraulic conductivity are aquifer pumping tests and slug tests. A complete description of the theory and application of pumping tests can be found in Domenico and Schwartz (1990) and Fetter (1994). A complete description of pumping tests and the various methods that can be used in the analysis of data collected during a pumping test is provided in Kruseman and de Ridder (1991). In addition, "*Standard Guide for Selection of Aquifer-Test Method in Determining of Hydraulic Properties by Well Techniques*" (ASTM, 1991) is available to aid in the selection of the proper aquifer test techniques for a given aquifer type.

Pumping tests involve pumping water from a well at a constant rate and monitoring the impact of that stress on the aquifer. A 4-inch-diameter well generally is required to conduct pumping tests in highly transmissive aquifers because small-diameter pumps are not capable of producing flowrates adequate to induce significant drawdown. Although aquifer pumping tests generally give reliable information on hydraulic conductivity, the tests may be difficult to conduct in contaminated areas because the water produced during the test generally must be contained and treated as investigation-derived waste (IDW). In areas with fairly uniform and homogeneous aquifer materials, pumping tests may be conducted in uncontaminated areas and the results can be used to estimate hydraulic conductivity in the contaminated area.

Slug withdrawal or injection tests are commonly used as alternatives to pumping tests and may be conducted in the absence of a pumping test, although they tend to be much less accurate then pumping tests. Slug tests can be used to determine the hydraulic conductivity of an aquifer in the immediate vicinity of a well. A slug test is performed by adding (or removing) a "slug" of known volume to (or from) a well, and monitoring the water level in the well as it falls (or rises) back to the equilibrium water level. A complete description of slug tests and the various methods that can be used in the analysis of slug test data is provided in Kruseman and de Ridder (1991). A standard test method for performing slug tests also is available (ASTM D 1996).

Advantages of slug tests include their relative simplicity and short duration (which make them fast [typically lasting minutes to a few hours] and inexpensive), and the fact that no pumping is required and the amount of IDW is minimized. The primary disadvantage of slug tests is that they provide information only for the area in the immediate vicinity of the monitoring well and they are less much accurate than pumping tests. Consequently, it is not advisable to rely only on data from slug tests. Furthermore, slug tests should be performed in triplicate for multiple monitoring wells at the site. As with pumping tests, slug tests should be conducted in wells that are properly screened in the aquifer.

**B.1.2.4 Porosity of the Aquifer Materials.** Porosity is needed to calculate average linear groundwater velocity and to predict the rate of contaminant migration. Porosity is defined as the ratio of the void spaces in a unit of soil or rock to the total volume of that unit. Porosity usually is expressed either as a percent or in decimal fraction. Table B-3 lists representative ranges of porosity for different rock and soil types.

**Table B-3. Ranges of Porosity for Various Soil and Rock Types**

| Soil or Rock Type | Porosity (%) |
|---|---|
| Unconsolidated Deposits | |
| Gravel | 25 - 40 |
| Sand | 25 - 50 |
| Silt | 35 - 50 |
| Clay | 40 - 70 |
| Rocks | |
| Fractured basalt | 5 - 50 |
| Karst limestone | 5 - 50 |
| Sandstone | 5 - 30 |
| Limestone, dolomite | 0 - 20 |
| Shale | 0 - 10 |
| Fractured crystalline rock | 0 - 10 |
| Dense crystalline rock | 0 - 5 |

Source: Freeze and Cherry, 1979.

The ability of a rock or soil to transmit water is dependent on the porosity and the permeability (i.e., interconnectedness) of the pore spaces. Well-cemented sedimentary, chemically precipitated metamorphic, and igneous formations all typically have low primary porosities, and these formations depend more on secondary porosity resulting from fractures and joints to transmit groundwater. Shales and some clays have relatively high primary porosities, but the clay minerals are plate-like and overlap to the degree that pore spaces are not interconnected, resulting in very low permeabilities. Consequently, shales and some clays must be fractured or jointed to function as aquifers. Unconsolidated formations are

characterized by the lack of cementation binding individual grains of the matrix. Unconsolidated formations range from well-sorted alluvial and outwash deposits to poorly sorted glacial tills. Well-sorted deposits have high primary porosities and the pore spaces are more interconnected than in poorly sorted materials.

The effective porosity is the volume of the void spaces through which water or other fluids can travel divided by the total volume of the rock or sediment. Effective and total porosities are determined in the laboratory using samples collected during drilling (Fetter, 1994).

**B.1.2.5 Groundwater Flow Velocity.** The average linear groundwater flow velocity is directly related to the hydraulic conductivity, the hydraulic gradient, and the effective porosity of the aquifer materials. The velocity of groundwater flow is an important parameter in the understanding of contaminant transport in an aquifer. Groundwater flow velocities can be calculated for site-specific conditions using the following equations (Equations B-2):

$$V_x = \frac{-K}{n_e}\frac{dh}{dl} \qquad \text{(B-2)}$$

where: $V_x$ = average linear groundwater flow velocity in the X direction (L/T)
$K$ = hydraulic conductivity (L/T)
$dh/dl$ = hydraulic gradient
$n_e$ = effective porosity.

**B.1.2.6 Recharge/Discharge Points and Flow Boundaries.** Identification of all recharge and discharge points, as well as the relevant flow boundaries, is an important consideration in determining the area that must be included in the model. If possible, the model area should be bounded by natural hydrologic features such as rivers, streams, lakes, hydrologic divides, and no-flow boundaries. Recharge to groundwater may occur from precipitation, from overland flow, or as infiltration from surface-water bodies. Discharge from a groundwater system may occur as springflow, as baseflow to streams, as evapotranspiration, or through pumping. Underflow, or flow occurring beneath the site or beneath surface-water bodies, also can occur and must be accounted for in the conceptual model.

Flow boundaries can consist of physical or geologic limitations to flow or of hydrologic controls. Physical boundaries to groundwater flow may include faults, changes in the stratigraphy, or physical limits of an aquifer. Hydrologic boundaries typically consist of hydrologic divides, areas of the water-table surface where groundwater flows in opposite directions. Hydraulic divides are commonly created by the regional topography.

**B.1.2.7 Water Budget—Inflows and Outflows.** The sources of water to the flow system and the expected flow directions and exit points should be included in the conceptual model. A water budget quantifies all inflows and outflows. A water budget should be prepared from the field data to summarize the magnitudes of these flows and potential changes in aquifer storage. The water budget can be used during the calibration of the groundwater flow model by comparing the water budget computed by the model with the manually-calculated budget based on field data.

### B.1.3 Define the Nature and Extent of Contamination and Biologic Indicators

As part of the detailed assessment of RNA, contour maps of contaminant concentrations, electron acceptors, and metabolic byproducts should be constructed. These maps should be available as a result of the preliminary and detailed site investigation (i.e., Sections 4.0 and 5.0, respectively). A review of the data used to construct these maps should be performed to evaluate their applicability to model construction and calibration. Sufficient contaminant characterization data should be included in these maps to describe the spatial and temporal trends in contaminant, electron acceptor, and metabolic byproduct concentrations. Any data gaps should be identified and addressed, and additional groundwater sampling should be performed as needed to further define the nature and extent of contamination and/or characterize the distribution of the biological indicator parameters.

### B.1.4 Define Contaminant Transport Parameters

Contaminant transport parameters refer to the factors that describe the processes controlling the fate and potential migration of contaminant compounds within a flow system. These parameters include the retardation factor and retarded contaminant transport velocity, the distribution coefficient, the contaminant sorption coefficient, the soil bulk density, the hydrodynamic dispersion coefficient, contaminant biodegradation rates, and relevant volatilization factors.

**B.1.4.1 Retardation Factor and Retarded Contaminant Transport Velocity.** Many contaminants dissolved in groundwater travel at a rate that is slower than the average linear groundwater velocity; this is known as retarded contaminant transport. The migration of contaminants is impeded by contaminant partitioning from the dissolved phase to the sorbed phase on aquifer sediments. The retardation factor, or coefficient of retardation, describes this phenomenon and is defined in Equation B-3:

$$R_f = \frac{v_x}{v_c} \qquad \text{(B-3)}$$

where: $R_f$ = retardation factor
$v_x$ = average linear groundwater velocity [L/T]
$v_c$ = average velocity of dissolved contaminant [L/T].

The ratio of $v_x/v_c$ describes the relationship between the velocity of the groundwater and the dissolved contaminant. The retardation factor ($R_f$) can be calculated in terms of the contaminant's solid-liquid distribution coefficient ($K_d$) and the bulk density and porosity of the aquifer. For soils where the fraction of organic carbon ($f_{oc}$) > 0.001, the retardation factor for a dissolved contaminant can be described by:

$$R_f = 1 + \frac{\rho_b K_d}{n} \qquad \text{(B-4)}$$

where: Rf = retardation factor
ρb = bulk density (M/L3)
Kd = distribution coefficient (L3/M)
n = total porosity.

**B.1.4.2 Distribution Coefficient.** The coefficient $K_d$, is a commonly used method for expressing the tendency for an organic compound to partition between the aqueous phase and the aquifer matrix. $K_d$ is defined as the ratio of the sorbed contaminant concentration to the dissolved contaminant concentration at equilibrium as shown in Equation B-5:

$$K_d = \frac{C_s}{C_l} \tag{B-5}$$

where: $C_s$ = sorbed concentration (mass contaminant/mass soil) [M/M]
$C_l$ = concentration dissolved in the liquid phase [$M/L^3$].

The migration and partitioning of a contaminant is highly dependent on the compound's distribution coefficient and its aqueous solubility. The higher the distribution coefficient, the greater the potential for contaminant sorption to the aquifer matrix and the greater the retardation of contaminant migration.

Sorption occurs as a complex phenomenon and may be caused by several mechanisms, including physical and chemical processes. Hydrocarbons most often sorb to aquifer sediments through hydrophobic bonding. Consequently, sorption is controlled primarily by the amount of organic matter in the aquifer matrix and the hydrophobicity of the organic compound. For organic compounds, the sorption coefficient can be measured with bench-scale experiments using Equation B-5, or predicted using the following relationship:

$$K_d = K_{oc} * f_{oc} \tag{B-6}$$

where: $K_{oc}$ = sorption coefficient normalized for total organic carbon content [$L^3/M$]
$f_{oc}$ = fraction of total organic carbon (mass organic carbon/mass soil).

Values of $K_{oc}$ have been determined for a wide range of chemicals, and are provided in Table B-4 for the BTEX compounds and TMB isomers and also in Appendix A for a wider range of petroleum hydrocarbons. The fraction of total organic carbon ($f_{oc}$) can be determined in the laboratory using soil/sediment samples collected from the site.

**B.1.4.3 Bulk Density.** The bulk density of a soil or sediment ($\rho_b$) describes the ratio of the mass of soil to the total soil volume.

The bulk density is defined as follows (Equation B-7):

$$\rho_b = \frac{M_s}{V_T} \tag{B-7}$$

where: $M_s$ = mass of solid in the sample [M]
$V_T$ = total volume in the sample [$L^3$].

## Table B-4. Values of Aqueous Solubility and $K_{oc}$ for the BTEX Compounds and TMB Isomers

| Compound | Solubility (mg/L) | $K_{oc}$ (L/kg) |
|---|---|---|
| Benzene | 1,750[a] | 87.1[a] |
| Benzene | 1,780[c] | 190[c,j] |
| Benzene | 1,780[c] | 62[c,j] |
| Benzene | 1,780[h] | 72[h] |
| Benzene* | 1,780[h] | 79[h,j] |
| Benzene | 1,780[c,h] | 89[k] |
| Toluene | 515[a] | 151[a] |
| Toluene | 537[c] | 380[c] |
| Toluene | 537[c] | 110[c] |
| Toluene* | 537[c] | 190[k] |
| Ethylbenzene | 152[a] | 158.5[a] |
| Ethylbenzene | 167[c] | 680[c] |
| Ethylbenzene | 167[c] | 200[c] |
| Ethylbenzene | 140[h] | 501[h,i] |
| Ethylbenzene* | 140[h] | 468[h,j] |
| Ethylbenzene | 167[c] | 398[k] |
| *o*-xylene | 152[a] | 128.8[a] |
| *o*-xylene* | 152[a] | 422[k] |
| *m*-xylene | 162[c] | 720[c] |
| *m*-xylene | 162[c] | 210[c] |
| *m*-xylene* | 162[c] | 405.37[k] |
| *p*-xylene | 198[a] | 204[a] |
| *p*-xylene* | 198[a] | 357[k] |
| 1,2,3-trimethylbenzene* | 75 | 884[b]* |
| 1,2,4-trimethylbenzene | 59[l] | 884[b] |
| 1,2,4-trimethylbenzene* | 59[l] | 772[k]* |
| 1,2,5-trimethylbenzene* | 72.60[g] | 676[k]* |

Notes: (a) From Knox et al., 1993.

(b) From Jeng et al., 1992; temperature = 20°C.

(c) From Lyman et al., 1992; temperature = 25°C.

(g) From Lyman et al., 1992; temperature 20°C.

(h) From Fetter, 1993.

(k) Average using equations from Kenaga and Goring (1980), Means et al. 1980), and Hassett et al. (1983) to estimate $K_{oc}$ from solubility.

(l) From Sutton and Calder (1975).

* Recommended value.

The bulk density can also be expressed as it relates to the particle density by:

$$\rho_b = (1-n)\,\rho_s \qquad \text{(B-8)}$$

where: $\rho_s$ = particle density of soil [$M/L^3$]
$n$ = total porosity.

Bulk density can be measured in the laboratory using soil/sediment samples collected from the site.

**B.1.4.4 Hydrodynamic Dispersion Coefficient.** Hydrodynamic dispersion is the process through which a contaminant plume spreads out in directions parallel (longitudinal) and perpendicular (transverse) to the direction of groundwater flow and plume migration. Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical dispersion of solutes travelling through a porous medium. Molecular diffusion occurs due to concentration gradients, causing solutes to migrate from zones of higher concentration to zones of lower concentration, even in the absence of groundwater flow. Molecular diffusion is considered to be an important process at low groundwater velocities. Mechanical dispersion is the result of mechanical mixing, when groundwater and solutes disperse through pores in the aquifer. The effects of hydrodynamic dispersion are the spreading and mixing of the contaminant plume with uncontaminated water surrounding the plume and contaminant migration at a faster rate than the average linear groundwater velocity.

The coefficient of hydrodynamic dispersion (D) is the sum of the coefficients of effective diffusion ($D_d$) and mechanical dispersion (DN). Effective diffusion is chemical dependent and can be determined from literature values. Mechanical dispersion is the product of the dispersivity ($\alpha$) and the average linear groundwater velocity ($v_x$). Dispersivities are commonly required input parameters for contaminant transport models. Hydrodynamic dispersion can be described by (Equation B-9):

$$D_x = \alpha_x v_x + D_d \qquad \text{(B-9)}$$

where: $D_x$ = coefficient of hydrodynamic dispersion in the x direction [$L_2/T$]
$\alpha_x$ = dispersivity in the x direction [L]
$v_x$ = average linear groundwater velocity in the X direction [L/T]
$D_d$ = effective molecular diffusion [$L^2/T$].

Dispersion can be determined by conducting a tracer test in the field. Tracer tests are considered to be the most appropriate method of evaluating the potential effect of hydrodynamic dispersion on a contaminant plume, but these tests are rarely conducted in small- to moderate-size studies because of time and monetary constraints. In place of performing a tracer test in the field, it is common to use literature values or to make assumptions. A common rule of thumb is that the longitudinal dispersion equals approximately 0.1 times the length of the contaminant plume (Wiedemeier et al., 1995; Lallemand-Barres and Peaudecerf, 1978).

**B.1.4.5 Biodegradation Rates Using an Analytical Solution.** Biodegradation rates are a vital component of groundwater fate and transport models for biodegradable contaminants. Various methods to determine first-order biodegradation and natural attenuation rates based on field-monitoring data are described in Section 5.0. However, except for the TMB-tracer method, the methods shown in Section 5.0 only apply to shrinking and stable plumes, not expanding plumes. Biodegradation rates for expanding plumes can be determined by using one of the following methods:

1. A TMB tracer can be used to determine a first-order biodegradation rate (see Section 5.0).

2. Laboratory microcosms can be used to determine biodegradation rates (see Section 5.0).

3. Natural attenuation or biodegradation rates published in the literature for similar sites can be used. The use of literature rates is discussed in Section 5.0 and literature rates are provided in Appendix A.

4. A contaminant transport model can be calibrated to match the observed contaminant distribution by varying the biodegradation rate parameter. This method is discussed below and in Section B.3.

Model calibration involves varying input parameters such as the source term, the anaerobic decay coefficient, the coefficient of retardation, the dispersivity or biodegradation rates until the solution matches historical conditions. Although this approach does not provide a unique solution, it can be used in combination with sensitivity analyses to establish a theoretical range in magnitude of each contaminant transport parameter. Another approach to determining an approximate biodegradation rate is to use an analytical solution to Equation B-10 the general fate and transport equation.

$$\frac{\partial C}{\partial t} = \frac{1}{R_f}\left[D_x \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}\right] - \lambda C \qquad \text{(B-10)}$$

where: $D_x$ = the dispersion coefficient [$L^2/T$]
$v$ = the groundwater velocity [L/T]
$R_f$ = the retardation factor, which equals the ratio of the groundwater velocity to contaminant velocity (i.e., $R_f = v/v_c$)
$\lambda$ = the first-order biodegradation rate.

The general solution to Equation B-10 is shown below (Domenico and Schwartz, 1990). More complicated analytical solutions are available for 2- and 3-dimensional fate and transport equations, and can be found in Anderson and Woessner (1992), Domenico and Schwartz (1990), and Wiedemeier et al. (1995).

$$C(x,t) = \frac{C_o}{2}\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1-\left(1+\frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right\}\operatorname{erfc}\left(\frac{x - v_c t\left(1+\frac{4\lambda\alpha_x}{v_c}\right)^{1/2}}{2(\alpha_x v_c t)^{1/2}}\right) \qquad \text{(B-11)}$$

where: $C(x,t)$ = the contaminant concentration in the x direction at time t[M/L3]
$C_o$ = the initial contaminant concentration at t = 0 [$M/L^3$]
$\lambda$ = the first-order biological degradation rate [1/T]
$v_c$ = the contaminant transport velocity ($v_c = v/R_f$) [L/T]
$\alpha_x$ = the longitudinal dispersivity [L]
$\lambda$ = the first-order biodegradation rate constant [1/T].
$t$ = time [T]
erfc = error function, found in mathematical tables or in most statistical programs.

This rather complex analytical solution can be simplified for a steady-state plume, where the error function approaches –2, resulting in Equation B-12. This is the approach used by Buscheck and Alcantar (1995) to determine the biodegradation rate for a steady-state plume by solving Equation B-12 for the biodegradation rate, λ.

$$C(x) = -C_o \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1-\left(1+\frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right\} \qquad \text{(B-12)}$$

Unfortunately this simplification cannot be made for non-steady-state (i.e., or shrinking) expanding plumes, for which λ must be determined iteratively. If one knows the values of $\alpha_x$, $v_c$, $C_o$, and C(x), a simple, publicly available analytical model such as BIOSCREEN (AFCEE, 1996) can be used to help determine λ for non-steady state plumes. The approach would involve inputting all of the contaminant transport parameters, as directed in the model's user manual, and varying λ until the solution matches historical data. Arguably, this approach is similar to varying the parameters in a more complicated numerical model. However, a simple analytical model has the advantage of being much faster, easier to implement and understand, and more cost-effective than most numerical models. Once a range of biodegradation rates is established, the rates can be used in more complex models.

**B.1.4.6 Volatilization Factors—Raoult's and Henry's Law Constants.** Volatilization is a process of liquid-phase evaporation that occurs when contaminants present either as NAPL or dissolved in water contact a gas phase. This phenomenon can occur with organic contaminants in the saturated and unsaturated zones. The process is controlled by the vapor pressure of the organic compound, which represents a compound's tendency to evaporate. Raoult's law describes the equilibrium partial pressure of a volatile organic compound in the atmosphere above a solvent (such as LNAPL) (Domenico and Schwartz, 1990) (Equation B-13).

$$P_{org} = x_{org} P^o_{org} \qquad \text{(B-13)}$$

where: $P_{org}$ = partial pressure of the vapor in the gas phase
$x_{org}$ = mole fraction of the organic solvent in the LNAPL
$P^o_{org}$ = vapor pressure of the pure organic solvent.

Volatilization of dissolved organic compounds removes contaminants from the groundwater by partitioning the contaminant between the liquid and gaseous phases. The partitioning process is governed by Henry's law, which defines a chemical-specific constant that describes the tendency of a compound to volatilize from its dissolved phase. Henry's law states that at equilibrium the concentration of a contaminant in the gaseous phase is directly proportional to the contaminant's concentration in the liquid phase:

$$H = \frac{C_a}{C_l} \qquad \text{(B-14)}$$

where: H = Henry's law constant (atm • $m^3$/mole)
$C_a$ = concentration of compound in air (atm)
$C_l$ = concentration of compound in water (mole/$m^3$).

A theoretical Henry's law constant can be calculated from the compound's vapor pressure and solubility, as follows (Equation B-15):

$$H = \frac{P^{o}_{org}}{S} \qquad \text{(B-15)}$$

where: $H$ = Henry's law constant (atm • $m^3$/mole)
$P^{o}_{org}$ = compound-specific vapor pressure (atm)
$S$ = compound-specific solubility (mole/$m^3$).

Henry's law constants can be obtained from literature values and do not need to be measured experimentally. Appendix A lists vapor pressures and Henry's law constants for selected hydrocarbons.

Volatilization typically does not play a large role in the reduction of the dissolved contaminant mass because the surface area of the contaminated groundwater flow system exposed to soil gas is relatively small compared to the total plume volume. Consequently, volatilization of BTEX compounds from groundwater is a relatively slow process that generally can be neglected when modeling biodegradation. Chiang et al. (1989) demonstrated that less than 5 percent of the mass of a dissolved BTEX plume is lost to volatilization in the saturated groundwater environment. Nonetheless, many models include volatilization, and Henry's law constants are required input parameters for these models. Volatilization from LNAPL may be a more significant source of contaminant mass reduction and most be considered if volatilized contaminants pose a risk to receptors.

## B.2 SOURCE VOLUME, MASS, AND DISSOLUTION INTO GROUNDWATER

Source-term calculations are an important part of the modeling investigation. Determination of the source term is an essential part of evaluating the feasibility of applying RNA for expanding plumes, because these plumes are the result of contaminant loading in excess of the natural attenuation processes. The discussion provided in this section focuses on the estimation of hydrocarbon loading from residual NAPL contamination in the smear zone and from sorbed hydrocarbon contamination in the unsaturated zone. Residual contamination assumed to be the remaining contamination following free-phase NAPL removal by bioslurping, product skimming, or other LNAPL removal technologies. This section gives "back-of-the-envelope" calculations that can be used to estimate the source release rate from residual LNAPL sources. If contaminant loading from free-phase LNAPL is a concern, the reader is referred to the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Wiedemeier et al., 1995).

### B.2.1 Estimating the Source Mass

The total source mass is an integral component of estimating the source life, and therefore of time for remediation by RNA. The best way to determine the source mass is by measuring petroleum concentrations in soils in the field. Similar to plume delineation, source delineation requires multiple sampling in the source zone to establish the horizontal and vertical magnitude and extent of contamination. Samples usually are analyzed for total petroleum hydrocarbons (TPH), and quantified as mass TPH per unit mass soil. Analyses should distinguish between sorbed and free-phase TPH. As much as possible, the relative mass of individual target contaminants (e.g., BTEX) also should be distinguished from TPH. For wet soils, dissolved contaminants can contribute significantly to the total contaminant mass in the soil samples. The dissolved contaminant mass should be subtracted from the total mass in soil samples.

Vertical soil profiles should account for smearing effects, and soils should be sampled across the entire vertical range of the groundwater table. The source mass is calculated by estimating the contaminated soil volume and multiplying by the soil contaminant concentrations.

### B.2.2 Contaminant Dissolution from "Smear Zone" into Groundwater

Dissolved hydrocarbon mass loading to an aquifer may occur from the "smear zone" that forms as a result of water-table fluctuations and the vertical spreading of hydrocarbon contaminants. Dissolved hydrocarbon loading from the smear zone has two components:

- Dissolved hydrocarbons added to groundwater flowing horizontally through or beneath the smear zone.
- Dissolved hydrocarbons added to the groundwater through vertical dispersion and vertical advection (i.e., infiltration).

An average concentration is estimated and multiplied by the groundwater flowrate through the smear zone both inside and beneath the smear zone. The calculation results in the mass of dissolved hydrocarbon (e.g., BTEX) contributed for each area (ASTM, 1997). The calculation of hydrocarbon mass added to the groundwater flowing through the smear zone involves the following steps:

1. Estimate the cross-sectional area of the smear zone below the water table ($A_{sz}$), perpendicular to the direction of groundwater flow. $A_{sz}$ may be estimated by assuming that the average thickness of the smear zone is equal to one-half the thickness of the zone of seasonal water-table fluctuations. The width of the zone can be determined from field data describing the nature and extent of the source area (Equation B-16).

$$A_{SZ} = \frac{1}{2} T_{WF} \, W_{SZ} \qquad \text{(B-16)}$$

where: $A_{sz}$ = cross-sectional area of smear zone beneath water-table [$L^2$]
$T_{WF}$ = thickness of zone of annual water-table fluctuation [L]
$W_{sz}$ = width of smear zone perpendicular to the direction of groundwater flow [L].

2. Estimate the hydraulic conductivity of the smear zone ($K_{sz}$). The hydraulic conductivity in the smear zone will be less than the regional hydraulic conductivity (K) due to the presence of residual NAPL trapped in the pores of the aquifer matrix. Information on determining $K_{sz}$ can be found in ES&T (1994), ASTM (1997), and Parker et al. (1987).

3. Calculate the groundwater flowrate through the smear zone. The groundwater flow through the smear zone ($Q_{sz}$) is calculated as follows (Equation B-17):

$$Q_{SZ} = K_{SZ} \left( \frac{dh}{dl} \right) A_{SZ} \qquad \text{(B-17)}$$

where: $Q_{sz}$ = groundwater flow through the smear zone ($L^3/T$)
$K_{sz}$ = estimated relative hydraulic conductivity for water in the smear zone (L/T)
dh/dl = hydraulic gradient across the smear zone
$A_{sz}$ = cross-sectional area of the smear zone beneath the water table ($L^2$).

4. Determine the mass flux of dissolved hydrocarbons entering the groundwater. The mass flux of dissolved hydrocarbons (e.g., $BTEX_{sz}$) [M/T] entering the groundwater through the smear zone due to lateral flow is calculated using the following expression (Equation B-18):

$$BTEX_{sz} = C_{sz}Q_{sz} \tag{B-18}$$

where: $BTEX_{sz}$ = mass flux of dissolved BTEX entering the groundwater through the smear zone due to lateral groundwater flow [M/T]
$C_{sz}$ = theoretical solubility for BTEX in groundwater in contact with gasoline components. Approximately 100 mg/L is based on immiscible partitioning (Shiu et al., 1988) [$M/L^3$]. However, this value should be adjusted based on the relative concentration of BTEX in the NAPL phase.
$Q_{sz}$ = groundwater flow through the smear zone [$L^3/T$].

Calculation of hydrocarbon mass added to the groundwater flowing beneath the smear zone involves an estimate of both the thickness of the dissolved plume below the smear zone and the average concentration of the plume. The calculation of BTEX mass loaded to the groundwater that flows beneath the smear zone involves the following steps:

1. Estimate the cross-sectional area of the dissolved plume beneath the smear zone ($A_{bsz}$) perpendicular to the direction of groundwater flow as follows (Equation B-19):

$$A_{bsz} = \frac{1}{2}T_{bsz}W_{sz} \tag{B-19}$$

where; $A_{bsz}$ = cross-sectional area of contaminant plume beneath smear zone [$L^2$]
$T_{bsz}$ = thickness of contaminant plume beneath smear zone ([L], if unknown, assumed to be approximately 10 ft)
$W_{sz}$ = width of smear zone [L].

2. Calculate the groundwater flowrate beneath the smear zone ($Q_{bsz}$) as follows (Equation B-20):

$$Q_{bsz} = K\left(\frac{dh}{dl}\right)A_{bsz} \tag{B-20}$$

where: $Q_{bsz}$ = groundwater flowrate beneath the smear zone [$L^3/T$]
K = hydraulic conductivity of the aquifer [L/T]
dh/dl = hydraulic gradient
$A_{bsz}$ = cross-sectional area of contaminant plume beneath smear zone [$L^2$].

3. Estimate the average BTEX concentration ($C_{bsz}$) for the contaminant plume beneath the smear zone. This can be done with analytical data from groundwater samples collected beneath the smear or NAPL zone.

4. The mass flux of dissolved BTEX contributed to the groundwater flowing beneath the smear zone ($BTEX_{bsz}$) is calculated using the following expression (Equation B-21):

$$BTEX_{bsz} = C_{bsz}Q_{bsz} \tag{B-21}$$

where: $BTEX_{bsz}$ = mass flux of dissolved BTEX beneath the smear zone [M/T]
$C_{bsz}$ = average BTEX concentration for the contaminant plume beneath the smear zone [$M/L^3$]
$Q_{bsz}$ = groundwater flowrate beneath the smear zone [$L^3/T$].

The estimation of total dissolved BTEX loading rate ($BTEX_{tot}$) is determined by (Equation B-22):

$$BTEX_{tot} = BTEX_{sz} + BTEX_{bsz} \quad \text{(B-22)}$$

where: $BTEX_{tot}$ = total dissolved BTEX loading rate [M/T]
$BTEX_{sz}$ = mass flux of dissolved BTEX entering the groundwater through the smear zone due to lateral groundwater flow [M/T]
$BTEX_{bsz}$ = mass flux of dissolved BTEX beneath the smear zone [M/T].

The residual contamination above the water table will continue as a source until it is depleted. The total time of source addition can be estimated using the first order decay method described in Section 5.0.

### B.2.3 Vertical Loading of Contaminants from Groundwater Infiltration

Loading of hydrocarbons to the groundwater from sorbed hydrocarbon contamination in the unsaturated zone can be estimated by calculating the volumetric flux of water and the mass flux of hydrocarbons in the unsaturated zone. This process can be defined by the following steps:

1. Estimate the average recharge rate to the unsaturated zone at the site, as follows (Equation B-23):

$$R = P - RO - ET \quad \text{(B-23)}$$

where: R = recharge [L/T]
P = precipitation [L/T]
RO = runoff, overland flow [L/T]
ET = evapotranspiration [L/T].

Values for R, P, RO, and ET can be determined from existing regional hydrologic studies and from climate and precipitation records.

2. Estimate the pore water velocity in the unsaturated zone and calculate a water flux through the contaminated area in the unsaturated zone. The pore water velocity in the unsaturated zone can be determined using the relationship (Equation B-24):

$$v_{pw} = q/\theta \quad \text{(B-24)}$$

where: $v_{pw}$ = interstitial groundwater (pore water) velocity [L/T]
q = average recharge rate (equivalent to R in equation B-23) [L/T]
$\theta$ = volumetric moisture content of the unsaturated zone (decimal fraction, representing volume of water per volume of soil).

Volumetric moisture contents can be estimated from Table B-5.

**Table B-5. Representative Values for Saturated Moisture Contents and Field Capacities of Various Soil Types**

| Soil Type | Number of Soils | Saturated moisture content ($\theta_s$) Mean | ± 1 Standard Deviation |
|---|---|---|---|
| Sand | 762 | 0.437 | 0.347 - 0.500 |
| Loamy sand | 338 | 0.437 | 0.368 - 0.506 |
| Sandy loam | 666 | 0.453 | 0.351 - 0.555 |
| Loam | 383 | 0.463 | 0.375 - 0.551 |
| Silt loam | 1,206 | 0.501 | 0.420 - 0.582 |
| Sandy clay loam | 498 | 0.398 | 0.332 - 0.464 |
| Clay loam | 366 | 0.464 | 0.409 - 0.519 |
| Silty clay loam | 689 | 0.471 | 0.418 - 0.524 |
| Sandy clay | 45 | 0.430 | 0.370 - 0.490 |
| Silty clay | 127 | 0.479 | 0.425 - 0.533 |
| Clay | 291 | 0.475 | 0.427 - 0.523 |

Source: U.S. EPA, 1988b.

The total flux of water in the contaminated portion of the unsaturated zone can be calculated by (Equation B-25):

$$Q_w = v_{pw} A_{cuz} \quad \text{(B-25)}$$

where: $Q_w$ = volumetric flowrate of water through the contaminated portion of the unsaturated zone ($L^3/T$)
$v_{pw}$ = pore-water velocity in the unsaturated zone (L/T)
$A_{cuz}$ = plan area of the contaminated unsaturated zone [$L^2$].

3. Estimate the mass flux of hydrocarbons ($Q_{mass(i)}$) from the calculated pore water concentration, based on the relevant contaminant distribution (i.e., sorption) coefficient ($K_d$). This can be done using the following relationships (Equation B-26):

$$Q_{mass(i)} = Q_w C_{w(i)} \quad \text{(B-26)}$$

where: $Q_{mass(i)}$ = mass flux of hydrocarbons from the contaminated portion of the unsaturated zone [M/T]
$Q_w$ = volumetric flowrate of water through the contaminated portion of the unsaturated zone [$L^3/T$]
$C_{w(i)}$ = contaminant-specific soil-water concentration based on soil-water partitioning [$M/L^3$]

where:

$$C_{w(i)} = C_s K_d \quad \text{(B-27)}$$

where: $K_d$ = contaminant-specific distribution (sorption) coefficient [$L^3/M$]
$C_{s(i)}$ = sorbed contaminant mass (mass contaminant/mass soil) [M/M].

## B.3 CONSTRUCT FLOW AND TRANSPORT MODEL

Model construction consists primarily of converting the conceptual model into the input files for the numerical model. In both finite-difference (such as MODFLOW) and finite-element models, a model grid is constructed to divide (i.e., discretize) the lateral and vertical space that the model is to represent. The grid is based on the conceptual model, which is divided into units known as *hydrostratigraphic* units. The different hydrostratigraphic units are represented by model layers, each of which is defined by an array of grid cells. Each grid cell is defined by a unique set of the following hydraulic and contaminant transport parameters:

- Cell coordinates (cell top, bottom, and sides)
- Permeability
- Porosity and cell storage capacity
- Hydraulic conductivity
- Contaminant partitioning coefficients
- Dispersivity (including dispersion and diffusion)
- Biodegradation rates.

These units define the physical framework or grid mesh of the numerical model.

### B.3.1 Define Initial Conditions

Initial conditions are used to describe conditions at the start of a simulation. For steady-state flow and transport models, initial conditions need not be specified, because steady-state models represent systems that do not change over time. However, initial conditions must be specified for transient groundwater flow and transport problems, in which the plume is shrinking or expanding. Transient problems often are initiated with the results of a steady-state simulation used as the initial conditions. In contaminant transport simulations, initial conditions typically are determined based on one of the following three objectives (Zheng and Bennett, 1995):

- Reconstruct the evolution of an existing plume from its origin to the present
- Evaluate future response of an existing plume to various proposed remedial options
- Predict contaminant concentrations at downgrade receptors.

To predict contaminant concentrations at downgradient receptors, the model must either reconstruct the evolution of an existing plume and predict its potential future migration, or base the simulation on existing conditions without knowledge of historical migration.

### B.3.2 Define Boundary Conditions

Model boundaries are simulated by specifying boundary conditions that define the head or flux of water that occurs at the model grid boundaries or edges. Boundary conditions describe the interaction between the system being modeled and its surroundings. Boundary conditions are used to include the effects of the hydrogeologic system outside the area being modeled while at the same time allowing the isolation of the desired model domain from the larger hydrogeologic system. Three types of boundary conditions generally are utilized to describe groundwater flow: specified-head (Dirichlet, Type I), specified-flux (Neumann, Type II), and head-dependent flux (Cauchy, Type III) (Anderson and Woessner, 1992). Internal boundaries or hydrologic stresses, such as wells, rivers, drains, and recharge, also may be simulated using these conditions.

With ***Type I*** boundary conditions, the hydraulic head and/or contaminant concentration values are specified along a model boundary. This condition is used if the hydraulic head or contaminant concentration at the model boundary is independent of flow conditions in the model domain. The Type I boundary condition commonly is used to describe the interaction between surface water bodies and groundwater. For example, an aquifer may be bounded by a lake, reservoir, or river. If the surface water body elevation is relatively constant over time, the head is expressed as a function of position. This is known as a constant-head boundary. If the surface water body elevation fluctuates over time, the head is expressed as a function of position and time. This is known as a specified-head boundary.

A constant concentration boundary specifies that, at a specified location, the contaminant concentration remains unchanged over time. A common example of a constant concentration boundary is a continuous source. Once the source is removed, the residual source mass will diminish over time due to weathering and dissolution into groundwater, resulting in transient contaminant concentrations at the source boundary.

The ***Type II*** boundary condition specifies the flux of water or contaminants across a model boundary (i.e., perpendicular to the model boundary). For flow models, the specified-flux boundary represents a flux of water specified as a function of position and time. A no-flow boundary has a specified flux of zero. For contaminant transport models, the specified-flux boundary is described a function of position and time. A constant horizontal flow of groundwater or a no-flow boundary could represent a constant hydraulic flux, whereas vertical recharge often is represented by a time-dependent flux.

The concentration gradient Type II boundary is represented like the hydraulic flux boundary, and is defined by space and time. The simplest case is one where the flux across a boundary is constant, one which also could represent a stable plume. However, eventually the plume will recede, in which case the boundary can no longer be considered constant over time.

The ***Type III*** boundary condition represents groundwater or mass flux across a boundary that is dependent on changes in the hydraulic head or concentration gradient across the boundary. This type of boundary condition is used to describe a flux that changes in response to changes in the hydraulic head within the aquifer. Head-dependent boundaries typically are used to model leakage across semipermeable boundaries, such as lake bottoms that tend to accumulate silt and clay (Wiedemeier et al., 1995). For example, the hydraulic gradient through an aquifer in contact with a lake will vary with the lake elevation.

The concentration-dependent flux boundary condition is used when the concentration gradient across a boundary is dependent on the difference between a specified concentration on one side of the boundary and the solute concentration on the opposite side (Wiedemeier et al., 1995, from Wexler, 1992).

It is important to note that boundary conditions may also refer to internal model boundaries, as well as to those surrounding the edge of the model domain. These internal boundaries may include sources and sinks of water and/or mass and may include pumping wells and, injection wells. More thorough discussions of boundary conditions can be found in Anderson and Woessner (1992) for groundwater flow models and in Zheng and Bennett (1995) for solute transport models. Each modeling code has specific names and methods of specifying boundary conditions and user manuals should be referred to for a complete understanding of the means by which the code addresses boundary conditions.

### B.3.3 Determine the Discretization of Space and Time

Numerical groundwater flow and transport simulations must consider the discretization (i.e., partitioning) of space and time. *Discretization of space* refers to division of physical space into cells and nodes (i.e., into a model grid). The model grid allows the definition of model parameters for each grid element, node, or cell. Typically, finer resolution in the model grid is warranted near the plume source and other areas of interest, to provide a more representative simulation of contaminant transport in these areas. The model grid may consist of regular- or irregular-shaped cells or elements. Irregular cells are used to better represent the physical framework of the system.

*Discretization of time* refers to the total simulation time, stress periods, and the time steps used in the iterative solution process. Total simulation time is determined by the simulation objectives, the groundwater flow velocity, the rate of contaminant migration, and the size of the model domain. Stress periods are used to simulate blocks of time over which the hydraulic and contaminant stresses (i.e., sources, sinks, and boundary conditions) are constant. Changes in these stresses are incorporated by modeling over individual stress periods and combining the results of these periods. Time steps are used to subdivide the stress periods into smaller increments of time to aid in the solution process. More complete discussions of how to develop model grids and define stress periods and time steps for groundwater flow and transport models can be found in Anderson and Woessner (1992) and Zheng and Bennett (1995).

## B.4 CALIBRATE THE MODEL AND CONDUCT SENSITIVITY ANALYSIS

Calibration of a groundwater flow model refers to the demonstration that the model is capable of producing field-measured heads and flows that are used as the calibration values or targets. Calibration of a fate and transport model refers to the demonstration that the model is capable of representing the horizontal and vertical magnitude and extent of contamination over time. Groundwater flow calibration is accomplished by finding a set of hydraulic parameters, boundary conditions, and stresses that, when used in the model, produce simulated heads and fluxes that match field-measured values within a preestablished range of error (Anderson and Woessner, 1992). Groundwater calibration flow can be evaluated through the statistical comparison of field-measured and simulated conditions.

Fate and transport model calibration requires the simulation of existing or known historical contaminant conditions. Consequently, this calibration step requires historical contaminant data, and the model should be reevaluated periodically, as more groundwater field data become available. To calibrate the model for the flow of groundwater contaminants, model input parameters are modified until model predictions match dissolved contaminant concentrations. Model runs are made using the calibrated hydraulic model with predetermined initial contaminant concentrations. Plume calibration is achieved by varying the source term, the anaerobic decay coefficient, the coefficient of retardation, or the dispersivity until the model reasonably predicts historical plume concentrations. Preferably, the model should be calibrated between two time points, where the contaminant distribution is known at both time points.

Model calibration is often difficult because values for aquifer parameters, hydrologic stresses, and contaminant transport parameters typically are known in relatively few locations and their estimates are influenced by uncertainty. If multiple parameters are varied to calibrate the model (e.g., boundary conditions, the source term, the anaerobic decay coefficient, the coefficient of retardation, and/or the dispersivity) the solution will not be unique. Therefore, the more information that can be obtained to firmly establish each of the hydrogeologic, contaminant transport, and biodegradation parameters, the closer the model will represent the actual conditions at the site.

The uncertainty in a calibrated model and its input parameters can be evaluated through the performance of sensitivity analyses in which the aquifer parameters, stresses, and boundary conditions are

varied within an established range. The impact of these changes on the model output provides a measure of the uncertainty associated with the model parameters, stresses, and boundary conditions used in the model. Uncertainty results from the inability to define the exact spatial and temporal distribution of the aquifer and contaminant transport parameters for a specific site. A sensitivity analysis establishes the effect of each parameter on the model output by varying model-input parameters over reasonable and acceptable ranges and running the model for each variation. During groundwater flow model calibration, model parameters that are varied may include hydraulic conductivity, hydraulic loading or heads, and soil porosity. Once the flow model is calibrated, these values generally are held constant while the fate and transport parameters are varied for the sensitivity analysis. The fate and transport parameters that are varied commonly include the contaminant loading rates, dispersivity, retardation coefficients, and biodegradation rates.

## B.5 PERFORM PREDICTIVE SIMULATIONS

After a model has been calibrated to historically observed conditions, the model can be used for predictive simulations. In a predictive simulation, the parameters determined during calibration are used to predict future contaminant concentrations and plume distributions. The model also can be used to predict the response to changes in the flow system, such as an increase or decrease in hydraulic conductivity or hydraulic gradients over time or the effect of pumping in the plume vicinity.

Initial simulations should be performed without including biodegradation processes to assess the theoretical extent of plume migration without biodegradation. Subsequent simulations should incorporate biodegradation to predict the future magnitude and extent of contamination and the rate of hydrocarbon contaminant migration.

### B.5.1 Simulate Plume Migration without Biodegradation

The simulation without biodegradation should assess the maximum potential extent of contaminant migration and the time required before the hydrocarbon plume reaches steady state. These provide a conservative baseline estimate in which biodegradation does not contribute to natural attenuation. In the absence of biodegradation, a plume that reaches steady state before intercepting a point of compliance will provide the maximum possible protection for the receptor.

### B.5.2 Simulate Plume Migration with Biodegradation

After completing the simulation without biodegradation, subsequent simulations should focus on incorporating the appropriate aerobic and/or anaerobic degradation rates and conditions, based on site-specific data. These simulations must focus on at least two objectives.

1. Predict future contaminant concentrations at potential receptor locations and point-of-compliance wells.

2. Predict the time needed to achieve cleanup goals inside the dissolved hydrocarbon plume.

## B.6 DOCUMENT MODEL RESULTS

As with any investigation or study, thorough documentation should describe the decision to model, the model selection process, the inherent model assumptions, the model methods, the input parameter definitions, the model calibration process, and the performance of simulations. Documentation of the modeling process provides the only means by which the model can be interpreted and applied to make decisions affecting site remediation. All modifications to the initial model should be recorded, and results of the changes on model output should be documented. A thorough explanation of the sensitivity analysis also should be provided.

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11. Freeze and Cherry, 1979

12. Knox et al., 1993

13. Jeng, et al., 1992

14. Lyman et al., 1992

15. Fetter, 1993

16. Kenga and Goring, 1980

17. Means et al., 1980

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20. Lallemand-Barres and Peaudecerf, 1978

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22. AFCEE, 1996

23. ASTM, 1997

24. ES&T, 1994

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26. Shiu et al., 1988

27. Zheng and Bennett, 1995

28. Wexler, 1992

# APPENDIX C
## Statistical Method to Determine a Meaningful Trend in a Set of Concentration Measurements Collected Over Time

The following method is used to determine if an increasing or decreasing trend in groundwater contaminant concentrations is statistically significant. The method involves determining the confidence interval around the slope of a regression line defined by concentration and time measurements. The user is referred to *Methods for Evaluating the Attainment of Cleanup Standards, Volume 2: Groundwater* (U.S. EPA, 1992) for an in-depth explanation of the method. For the purpose of this appendix, the steps required to calculate the confidence interval around the slope are provided, along with an example problem. This analysis can easily be performed on a computer spreadsheet; also, statistical software packages generally have the ability to perform this analysis.

This method can be used to assess an increasing or decreasing trend within a single monitoring well. If the upper limit of the confidence interval is negative, the trend is negative and the concentration at the well is decreasing. A positive confidence interval implies a positive trend and an increasing concentration at the well. If similar trends are observed in other wells throughout the plume or along the plume transect, the plume can be established as shrinking or expanding, respectively.

There are two possibilities for confidence intervals that span zero. There may be insufficient evidence to establish a statistically significant trend (e.g., there may be too much data scatter) or the plume is at steady state (i.e., the regression analysis establishes a horizontal line with a zero slope). Distinguishing between these two options requires experience and judgment, and additional data may be required. The resulting action should be to continue monitoring and to repeat the analysis after more data are collected.

Another possibility is that some wells may show increasing trends while others show decreasing trends. These results suggest that the plume is not stable but is "shifting." This "shifting" scenario also will require additional monitoring to establish long-term trends.

The following example illustrates how the confidence interval is calculated and discusses the interpretation of the results to determine if a statistically significant trend exists in the data set of monitoring well concentrations over time.

Step 1. Given monitoring well data, conduct regression analysis to obtain the following equation (Equation C-1):

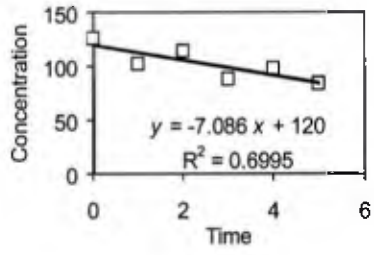
$$y = mx + b \qquad \text{(C-1)}$$

where: $y$ = the log concentration at time t, ln(C(t)) [$M/L^3$]
m = the slope of the regression line
$x$ = time [T]
b = the y-intercept of the regression line [$M/L^3$]

**Example Step 1**

**Time-Series Data**

| Time | Concentration |
|---|---|
| 1 | 126 |
| 2 | 102 |
| 3 | 114 |
| 4 | 88 |
| 5 | 98 |
| 6 | 84 |




Example regression of concentration data versus time

Step 2. Calculate five basic quantities for use in simple linear regression analysis.

| Parameter | Basic Quantities for Use in Simple Linear Regression Analysis |
|---|---|
| Sum of the $x$ values | $S_x = \sum_{i=1}^{N} x_i$ |
| Sum of the $y$ values | $S_y = \sum_{i=1}^{N} y_i$ |
| Sum of the $x^2$ values | $S_{xx} = \sum_{i=1}^{N} x_i^2 - \frac{S_x^2}{N}$ |
| Sum of the $y^2$ values | $S_{yy} = \sum_{i=1}^{N} y_i^2 - \frac{S_y^2}{N}$ |
| Sum of the $x/y$ cross products | $S_{yx} = \sum_{i=1}^{N} y_i x_i - \frac{S_y S_x}{N}$ |

**Example Step 2**

| | $x_i$ values | $y_i$ values | $x_i^2$ | $y_i^2$ | $x_i y_i$ |
|---|---|---|---|---|---|
| | 0 | 126 | 0 | 15876 | 0 |
| | 1 | 102 | 1 | 10404 | 102 |
| | 2 | 114 | 4 | 12996 | 228 |
| | 3 | 88 | 9 | 7744 | 264 |
| | 4 | 98 | 16 | 9604 | 392 |
| | 5 | 84 | 25 | 7056 | 420 |
| | **15** | **612** | **55** | **63680** | **1406** |

| Basic Quantities for Use in Simple Linear Regression Analysis | Example Problem Step 2 |
|---|---|
| $S_x$ | 15 |
| $S_y$ | 612 |
| $S_{xx}$ | 55 – 37.5 = 14.5 |
| $S_{yy}$ | 63,680 – 62,424 = 1,256 |
| $S_{xy}$ | 1406 – 1530 = –124 |

Step 3. Calculate the estimated regression parameters.

| Parameter | Equation | Example Problem Step 3 |
|---|---|---|
| Slope | $m = \frac{S_{yx}}{S_{xx}}$ | –7.09 |
| y-intercept | $b = \frac{S_y}{N} - m\frac{S_x}{N}$ | 119.7 |
| Sum of squares due to error (SSE) | $SSE = S_{yy} - \frac{S_{yx}^2}{S_{xx}}$ | 377.37 |

Step 4. Calculate the mean square error (MSE):

$$MSE = \frac{SSE}{N-2}$$

**Example Step 4**

MSE = 377.37/(6–2)

= 94.34

Step 5. Calculate the coefficient of determination, $R^2$:

$$R^2 = 1 - \frac{SSE}{S_{yy}}$$

**Example Step 5**

$R^2$ = 1–377.37/1256

= 0.70

Step 6. Calculate the standard error of the estimated slope (s(m)):

$$s(m) = \sqrt{\frac{MSE}{S_{xx}}}$$

**Example Step 6**

$S(m) = (94.34/14.5)^{1/2}$

= 2.32

Step 7. Calculate the confidence interval around the slope (CI):

$$CI = m \pm t_{1-\alpha/2;N-2} \cdot s(m)$$

where: CI = the confidence interval around the slope

$t_{1-\alpha/2;N-2}$ = the 1-$\alpha$/2 percentage point of a t distribution, with N-2 degrees of freedom (see attached table; $t_{1-\alpha/2;N-2} = 2.776$)

**Example Step 7**

CI = –7.09 ± (2.776 * 2.32)

CI = –13.53 and –0.65

Conclusion: Because the interval (-13.53, -0.65) does not include zero, we can conclude that the observed downward trend is significant at the ∀ = 0.05 level. That is, we have confidence that the observed downward trend is real, and is not just the result of sample variability.

This statistical analysis should be used cautiously when working with very small sample sets, such as the one used in this example. When a significant increasing or decreasing trend is present, the likelihood that the CI includes zero will decrease with larger sample sets. The investigator should balance professional experience and judgment with the results of this analysis to establish the presence of an increasing or decreasing trend. When the existing data are insufficient to establish whether the trend is statistically significant, the analysis should be revisited using additional data collected during performance monitoring.

## REFERENCE

1. EPA, 1992

# Appendix D
# Federal and State Regulatory Offices

## Federal EPA Regional Offices

### EPA Region 1
1 Congress Street, Suite 1100
Boston, MA 02114-2023
Phone: (617) 918-1111

Connecticut, Massachusetts, Maine, New Hampshire, Rhode Island, Vermont

### EPA Region 2
290 Broadway, 26th Floor
New York, NY 10007-1866
Phone: (212) 637-5000
Fax: (212) 637-3526

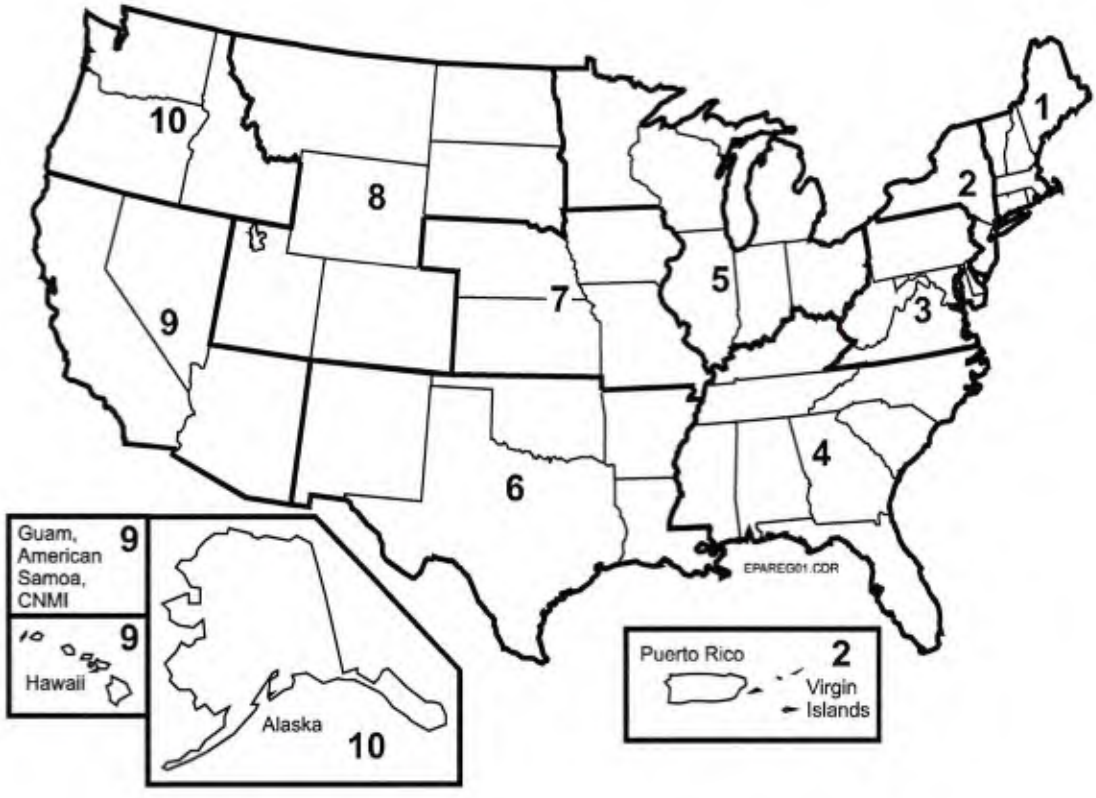
New Jersey, New York, Puerto Rico, Virgin Islands

### EPA Region 3
1650 Arch Street
Philadelphia, PA 19103-2029
Phone: (215) 814-5000

Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, West Virginia

### EPA Region 4
Atlanta Federal Center
61 Forsyth Street, SW
Atlanta, GA 30303-3104
Phone: (404) 562-9900

Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee



**EPA Region 5**
77 West Jackson Blvd.
Chicago, IL 60604
Phone: (312) 353-2000
Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin

**EPA Region 6**
1445 Ross Avenue
Dallas, TX 75202
Phone: (214) 665-2200
Fax: (214) 665-7263
Arkansas, Louisiana, New Mexico, Oklahoma, Texas

**EPA Region 7**
726 Minnesota Avenue
Kansas City, KS 66101
Phone: (913) 551-7003
Iowa, Kansas, Missouri, Nebraska

**EPA Region 8**
999 18th Street, Suite 500
Denver, CO 80202-2466
Phone: (303) 312-6312
Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming

**EPA Region 9**
75 Hawthorne Street
San Francisco, CA 94105
Phone: (415) 744-1305
Arizona, California, Hawaii, Nevada, American Samoa, Guam, Trust Territories of the Pacific

**EPA Region 10**
1200 Sixth Avenue
Seattle, WA 98101
Phone: (206) 553-1200
Fax: (206) 553-1280
Alaska, Idaho, Oregon, Washington

**EPA Information on the World Wide Web:**
http://www.epa.gov

## Additional Sources of Information

### PHONE & HOTLINE INFORMATION

**RCRA/Superfund Hotline**
1-800-424-9346
(in Washington, DC: 703-412-9810)

**Safe Drinking Water Act Hotline**
1-800-426-4791

**EPA Small Business Ombudsman Hotline**
1-800-368-5888
(in Washington, DC: 202-557-1938)

**National Response Center**
1-800-424-8802

**Hazardous Materials Information Center**
1-800-467-4922
(in Washington, DC: 202-366-4488)

**Toxic Substances Control Act (TSCA) Assistance Service**
202-554-1404

## STATE ENVIRONMENTAL REGULATORY AGENCIES

**ALABAMA**
Alabama Dept. of Environmental Management
Land Division
1751 Congressman Dickinson Drive
Montgomery, AL 36109-2608
334-271-7700

**ALASKA**
Dept. of Environmental Conservation
410 Willoughby Avenue, Suite 105
Juneau, AK 99801-1795
907-465-5010

Northern Regional Office
610 University Avenue
Fairbanks, AK 99709
907-451-2360

**ARIZONA**
Arizona Dept. of Environmental Quality
Waste Programs Bureau
3033 North Central Avenue
Phoenix, AZ 85012
602-207-2300

**ARKANSAS**
Dept. of Environmental Quality
8001 National Drive
Little Rock, AR 72209-8913
501-682-0744

**CALIFORNIA**
California EPA
Dept. of Toxic Substances Control
400 P Street, 4th Floor
P.0. Box 806
Sacramento, CA 95812-0806
916-322-0504

California EPA
State Water Resources Control Board
901 P Street
Sacramento, CA 95812-0100
916-657-1444

**COLORADO**
Dept. of Public and Environment
Hazardous Materials and Waste Management Division
4300 Cherry Creek Drive South
Denver, CO 80246-1530
303-692-3300

**CONNECTICUT**
Dept. of Environmental Protection
Bureau of Waste Management
Waste Engineering and Enforcement Division
79 Elm Street, 4th Floor
Hartford, CT 06106
860-424-3023

**DELAWARE**
Dept. of Natural Resources and Environmental Control
Division of Air and Waste Management
Hazardous Waste Office
89 Kings Highway
Dover, DE 19901
302-739-4764

**DISTRICT OF COLUMBIA**
Environmental Regulation Administration
Dept. of Consumer and Regulatory Affairs
Pesticides and Hazardous Waste Management Branch
2100 Martin Luther King Jr. Avenue SE, Suite 203
Washington, DC 20020
202-404-1167

**FLORIDA**
Dept. of Environmental Protection
Waste Management Division
3900 Commonwealth Blvd.
Tallahassee, FL 32399-3000
850-487-3299

**GEORGIA**
Dept. of Natural Resources
Environmental Protection Division
Hazardous Waste Management Branch
Floyd Towers East, Suite 1154
205 Butler Street, SE
Atlanta, GA 30334
404-656-7802

**HAWAII**
Dept. of Health
Solid and Hazardous Waste Branch
919 Alamoana Boulevard, Room 212
Honolulu, HI 96814
808-586-4226

**IDAHO**
Dept of Health and Welfare
Division of Environmental Quality
1410 N Hilton
Boise, ID 83706-1255
208-373-0502

**ILLINOIS**
Dept. of Commerce and Community Affairs
325 West Adams Street, Room 300
Springfield, IL 62704
217-524-1266
800-252-8955

**INDIANA**
Dept. of Environmental Management
Office of Solid and Hazardous Waste Mgmt.
100 North Senate Avenue
Indianapolis, IN 46206-6015
317-233-3656

**IOWA**
Dept. of Natural Resources
Waste Management Assistance Division
Wallace State Office Building
502 East 9th Street
Des Moines, IA 50319-0034
515-281-4367

**KANSAS**
Dept. of Health and Environment
Bureau of Waste Management
Forbes Field, Building 740
Topeka, KS 66620
913-296-1600

**KENTUCKY**
Natural Resources and Environmental
Protection Cabinet
Division of Waste Management
14 Reilly Road
Frankfort, KY 40601
502-564-6716

**LOUISIANA**
Dept. of Environmental Quality
Hazardous Waste Division
7290 Bluebonnet Boulevard
Baton Rouge, LA 70810
225-765-0355

**MAINE**
Dept. of Environmental Protection
Bureau of Remediation and Waste
Management
17 State House Station
Augusta, ME 04333
207-287-2651

**MARYLAND**
Dept. of the Environment
Waste Management Administration
2500 Broening Highway
Baltimore, MD 21224
410-631-3000

**MASSACHUSETTS**
Dept. of Environmental Protection
Bureau of Waste Site Cleanup
One Winter Street
Boston, MA 02108
617-292-5500

**MICHIGAN**
Michigan Dept. of Environmental Quality
Waste Management Division
503 N. Euclid Ave.
Bay City, MI 48706
517-684-9141

**MINNESOTA**
Pollution Control Agency
Hazardous Waste Division
520 Lafayette Road
St. Paul, MN 55155-4194
612-296-6300
800-657-3864

**MISSISSIPPI**
Dept. of Environmental Quality
Hazardous Waste Division
2380 Highway 80 West
Jackson, MS 39204
601-354-6612

**MISSOURI**
Dept. of Natural Resources
Division of Environmental Quality
Solid Waste Management Program
P.O. Box 176
210 Hoover Drive
Jefferson City, MO 65102
573-751-5401

**MONTANA**
Dept. of Environmental Quality
Remediation Division
2209 Phoenix Avenue
Helena, MT 59620-0901
406-444-1420

**NEBRASKA**
Dept. of Environmental Quality
P.O. Box 98922
Atrium Building, 4th Floor
1200 N Street, Suite 400
Lincoln, NE 68509-8922
402-471-2186

**NEVADA**
Dept. of Conservation and Natural Resources
Division of Environmental Protection
Bureau of Waste Management
123 West Nye Lane, Room 120
Carson City, NV 89706-0851
702-687-4670

**NEW HAMPSHIRE**
Dept. of Environmental Services
Waste Management Division
Health and Welfare Building
6 Hazen Drive
Concord, NH 03301
603-271-2900

**NEW JERSEY**
Dept. of Environmental Protection and Energy
Division of Solid and Hazardous Waste
120 S. Stockton St., CN 414
Trenton, NJ 08625-0414
609-984-6510

**NEW MEXICO**
Environment Dept.
Hazardous and Radioactive Materials Bureau
2044 Galisteo Street
Santa Fe, NM 87502
505-827-1557

**NEW YORK**
Dept. of Environmental Conservation
Division of Solid and Hazardous Materials
50 Wolf Road
Albany, NY 12233
518-457-6934

**NORTH CAROLINA**
Dept. of Environment, Health, and Natural Resources
Division of Waste Management
Hazardous Waste Section
401 Oberlin Road
Raleigh, NC 27605
919-733-2178

**NORTH DAKOTA**
Dept. of Health, Environmental Health Section
Division of Waste Management
P.O. Box 5520
1200 Missouri Avenue, Rm. 302
Bismarck, ND 58506-5520
701-328-5166

**OHIO**
Ohio Environmental Protection Agency
Division of Hazardous Waste Management
122 S. Front St.
Columbus, OH 43215
614-644-2917

**OKLAHOMA**
Dept. of Environmental Quality
Hazardous Waste Management Division
707 N. Robinson
Oklahoma City, OK 73102
405-702-5100

**OREGON**
Dept. of Environmental Quality
Hazardous Waste Division
811 SW Sixth Avenue
Portland, OR 97204
503-229-5913

**PENNSYLVANIA**
Dept. of Environmental Resources
Bureau of Land Recycling and Waste Management
Director's Office
400 Market Street
Harrisburg, PA 17105
717-783-2388

**RHODE ISLAND**
Dept. of Environmental Management
Division of Waste Management
235 Promenade Street, Rm. 425
Providence, RI 02908
401-222-2771

**SOUTH CAROLINA**
Dept. of Health and Environmental Control
Bureau of Land and Waste Management
8901 Farrow Road
Columbia, SC 29223
803-896-4000

**SOUTH DAKOTA**
Dept. of Environment and Natural Resources
Office of Waste Management
523 East Capital Avenue
Pierre, SD 57501-3181
605-773-3153

**TENNESSEE**
Dept. of Environment and Conservation
Division of Solid/Hazardous Waste Management
5th Floor, L & C Tower
401 Church Street
Nashville, TN 37243-1535
615-532-0780

**TEXAS**
Natural Resource Conservation Commission
Office of Waste Management
12100 Park 35 Circle
Austin, TX 78711-3087
512-239-2104

**UTAH**
Dept. of Environmental Quality
Division of Solid and Hazardous Waste
288 North 1460 West
Salt Lake City, UT 84114-4880
801-538-6170

**VERMONT**
Agency of Natural Resources
Dept. of Environmental Conservation
Waste Management Division
West Office Building
103 South Main Street
Waterbury, VT 05671-0404
802-241-3888

**VIRGINIA**
Natural Resources Office
Dept. of Environment Quality
629 East Main Street
Richmond, VA 23219
804-698-4000

**WASHINGTON**
Dept. of Ecology
Solid Waste and Financial Assistance Program
300 Desmond Drive, S.E.
Lacey, WA 98503
360-407-7455

**WEST VIRGINIA**
Division of Environmental Protection
Office of Waste Management
1356 Hansford Street
Charleston, WV 25301
304-558-5929

**WISCONSIN**
Dept. of Natural Resources
Bureau of Waste Management
MacKenzie Environmental Center
W7303 Co. Hwy. CS
Poynette, WI 53955-9690
608-266-2111

**WYOMING**
Dept. of Environmental Quality
Solid and Hazardous Waste Division
Herschler Building
122 West 25th Street
Cheyenne, WY 82002
307-777-7752

NAVAL FACILITIES ENGINEERING COMMAND
Washington, DC 20374-5066

NAVFAC

# USER'S GUIDE FOR IMPLEMENTING REMEDIATION BY NATURAL ATTENUATION AT PETROLEUM RELEASE SITES

## PART 2: STATEMENT OF WORK

Prepared for:

Naval Facilities Engineering Command's

Naval Facilities Engineering Service Center
Southwest Division Naval Facilities Engineering Command
Engineering Field Activity, Northwest
Northern Division Naval Facilities Engineering Command
Atlantic Division Naval Facilities Engineering Command
Pacific Division Naval Facilities Engineering Command
Engineering Field Activity, Chesapeake
Engineering Field Activity, West

Contract Number N47408-95-D-0730

Prepared by:

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## CONTENTS



## TABLES

## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| CA | corrective action |
| CERCLA | Comprehensive Environmental Response, Compensation, and Liability Act |
| COC | contaminant of concern |
| GIS | Geographic Information System |
| HASP | Health and Safety Plan |
| OSHA | Occupational Safety and Health Administration |
| QA/QC | quality assurance/quality control |
| QAPP | Quality Assurance Project Plan |
| RCRA | Resource Conservation and Recovery Act |
| RNA | remediation by natural attenuation |
| RPM | remedial project manager |
| SOW | Statement of Work |
| TMB | trimethyl benzene |
| U.S. EPA | United States Environmental Protection Agency |
| UST | underground storage tank |
| VFA | volatile fatty acid |
| WBS | Work Breakdown Structure.0-1 |

# 1.0 INTRODUCTION

This Statement of Work (SOW) Guide outlines, in tabular form, the technical information required to define tasks and performance standards. All of the work elements that might be required to assess and implement remediation by natural attenuation (RNA) under any one of a wide range of regulatory frameworks are listed in the tables. Potentially applicable regulatory frameworks include the following:

- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
- Corrective action (CA) provisions of the Resource Conservation and Recovery Act (RCRA)
- Underground storage tank (UST) provisions of the RCRA (Federally regulated)
- State-regulated or administered UST cleanup programs.

This document will assist in preparing a SOW that fosters timely, concise, cost-effective submissions from potential contractors. Project tasks are grouped into the following five phases:

- Project planning and management
- Preliminary assessment of RNA
- Site characterization and detailed evaluation of RNA
- Performance monitoring
- Project closeout

Some of the tasks described may not be required for a particular site because of site conditions or the regulatory framework being applied. The personnel preparing the SOW must select applicable tasks in the tables in Section 3.0 and use the tabulated information to assist in preparing a SOW.

This SOW Guide can be used to develop a SOW that describes the technical requirements for the project and to define the basis for evaluating the technical quality and value of a contractor's proposal. Preparing an effective SOW requires careful thought and planning to identify the key tasks that must be performed and the criteria that must be met without limiting the contractor's flexibility to provide their best value option. The criteria must be clearly stated so that the quality of the result can be determined and must be sufficiently demanding to provide an acceptable result, but not so demanding as to be uneconomical or impractical. More detailed information on preparing a performance-based SOW is available on the internet (see Appendix A) and in U.S. Environmental Protection Agency (EPA) guidance (U.S. EPA, 1995).

A typical RNA project starts with a review of existing data followed by data collection and interpretation leading to performance monitoring and finally site closure. Data collection, interpretation, and regulatory and public reviews are repeated with increasing levels of resource commitment and detail. Tasks in the SOW must be defined to allow input from regulators and, where necessary, the public through formal and informal forums frequently throughout the evaluation and implementation process. The SOW should require a staged approach to the evaluation and implementation of RNA with periodic decision points to allow for review of the applicability of RNA before each phase that requires a significant commitment of new resources. The complexity of the site and contaminant conditions determine the number of iterations needed to complete site cleanup using RNA.

The SOW clearly defines the roles and responsibilities of the participants in the work. Related work that has been completed as part of a prior project or is to be performed in parallel under a separate SOW must be described, and the relation to the planned work explained. Key decision points and interfaces must be clearly described so that all participants understand who is to perform each work element, what is to be done, and where the authority lies for accepting the results.

The SOW requires the contractor to provide separate costs for each task specified using the Work Breakdown Structure (WBS) specified by the Navy. Having detailed cost information for each task allows more effective comparison of the bids. The Users' Manual for Implementing *Remediation by Natural Attenuation at Petroleum Release Sites – Part 3: Cost Estimating Program* will assist Naval personnel in estimating costs so they can evaluate the value offered by each proposal.

This SOW Guide is organized to cover the sections that appear in a typical SOW, as shown in Table 1.

**Table 1-1. Organization of a Typical Statement of Work**

| | |
|---|---|
| 1.0 | Scope |
| | 1.1 General |
| | 1.2 Background |
| 2.0 | Reference Documents |
| 3.0 | Requirements of the RNA Project |
| | 3.1 Program Planning and Management |
| | 3.2 Preliminary Assessment of RNA |
| | 3.3 Site Characterization and Detailed Evaluation of RNA |
| | 3.4 Performance Monitoring |
| | 3.5 Project Closeout |
| 4.0 | Government-Furnished Property |
| 5.0 | Government-Furnished Facilities |
| 6.0 | Deliverables |

## 1.1 SCOPE

## 1.2 GENERAL

Table 1-2 shows an example of a typical scope statement for a project to implement RNA.

**Table 1-2. Example SOW Scope Statement**

The purpose of this Statement of Work (SOW) is to set forth the requirements for implementing remediation by natural attenuation (RNA) in accordance with the provision of _____ (decision document, e.g., permit issued by the state or regional water control board, Record of Decision [ROD], or permit modification or order) issued on _____ (date). The required efforts will include the following:

- Project management and planning
- Preliminary assessment of RNA
- Site characterization and detailed evaluation of RNA
- Performance monitoring
- Project closeout

RNA, which may also be referred to as intrinsic remediation or monitored natural attenuation, is defined as follows:

> "A remedy where naturally occurring physical, chemical, and biological processes will effectively protect human health and the environment and will achieve remedial goals within a time frame that is reasonable compared to alternative technologies, without human intervention."

This SOW provides the framework for conducting remediation of petroleum-contaminated groundwater at _____ (date). The goal is to complete remedial design by _____ (date) and site closure by _____(date).

## 1.3 BACKGROUND

A SOW is required when the facility has identified the need to remediate a site that has groundwater contaminated with petroleum hydrocarbons and is interested in using RNA. The SOW must clearly summarize any completed site characterization, review of regulatory constraints, and technical analyses to establish site-specific remediation goals. Table 1-2 lists the typical background information summarized in the SOW. This SOW Guide assumes that efforts under the contract make maximum use of the existing data and monitoring points installed at the site. Necessary background information often is contained in project reports, manuals, and photographs summarizing the current state of knowledge. These reports can be attached to the SOW or otherwise be made available to the contractor. If possible, the SOW should allow time for a site visit by contractors during proposal preparation.

**Table 1-3. Example of Site Information Typically Summarized in the SOW**

- Initial site conditions
  - Location and physical layout
  - Availability of utilities
  - Restrictions on access or road use
- Documentation of state concurrence with RNA application to site
- Relevant documents prepared by the local water control board
- Existing permits
- Cleanup standards and regulatory requirements
- Nature and extent of contamination
- Approximate volume to be remediated
- Geomorphology and surface water hydrology
- Geology and geohydrology
  - Location and types of strata
  - Depth to groundwater
  - Direction of groundwater flow
- Unresolved issues

The SOW must define the regulatory constraints applicable to the site. In particular, the lead regulatory agency must be identified. Other interested regulatory and public interest groups and their relationships to the project must be summarized in the SOW.

## 2.0 REFERENCE DOCUMENTS

The SOW provides a listing of documents that describe the data, methods, or requirements applicable to the work necessary for evaluating and/or implementing RNA at petroleum hydrocarbon-contaminated sites. Examples of documents that may be applicable for sites planning to implement RNA for petroleum contamination include the following:

***RNA Assessment***


a. Wiedemeier, T.H. and F.H. Chapelle. 1997. Technical Guidelines for Applying Monitored Natural Attenuation at Naval and Marine Corps Facilities. Draft report prepared for the Naval Facilities Engineering Command, Alternative Restoration Technology Team (ARTT).

b. U.S. Environmental Protection Agency. 1997. *Directive: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.* OSWER Directive 9200.4-17. Office of Solid Waste and Emergency Response, Washington, DC.

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# 3.0 REQUIREMENTS

The following subsections provide the technical background about the tasks that are specified in a SOW to obtain a proposal for implementing RNA. The project is divided into the following five phases:

- Project planning and management
- Preliminary assessment of RNA
- Site characterization and detailed evaluation of RNA
- Performance monitoring and site closeout

The tasks specifically related to implementing RNA are tabulated for each phase. Guidance documents are available describing aspects of the remedial design, implementation, and closeout process that are not technology-specific (U.S. EPA, 1995; Tri-Service/U.S. EPA Working Group, 1998.) Tasks that are appropriate for a particular site should be selected and the SOW should then be prepared based on the scope and typical preparation time, as stated in the tables. The information provided under the heading "Task Guidance and Information" in each table can be used to assist in preparing the SOW and evaluating responses from the bidders.

## 3.1 PROJECT PLANNING AND MANAGEMENT

The purpose of this project phase is to provide overall management to maximize the effectiveness of expenditures throughout the project. The SOW requires the contractor to provide the labor, equipment, materials, and facilities to prepare the required plans and effectively manage the RNA project. The major tasks included in this phase are summarized in Table 3-1.

Contractors are required to furnish a description of each of the following project management components as part of their proposal:

- Overall organizational structure proposed for the project
- Qualifications of the project management team
- Project management system to be used
- Subcontracting systems to be used
- Relevant corporate experience.

Contractors are required to furnish, as a part of their proposal, a current corporate Quality Assurance/Quality Control (QA/QC) Program Plan setting forth their QA/QC capabilities. The QA/QC Program Plan must address, at a minimum, the following topics:

- A statement of the corporate QA/QC policy
- An organization chart showing the position of the QA/QC function in the organization
- A delineation of the authority and responsibility of the QA/QC function
- A description of the organization's total concept, requirements, and scope of effort for achieving and verifying quality

**Table 3-1. Statement of Work Requirements for RNA: Project Planning and Management**

| Task Name | Task Scope | Task guidance and Information | Typical Performance Time |
|---|---|---|---|
| Project management plan[a] | Document overall strategy, budget, and schedule for performing the design, installation, performance monitoring, and close out of RNA project. | • Document responsibility and authorities of all organizations<br>• Identify key personnel<br>• Document qualifications of key personnel | 1 to 3 months |
| Community relations plan[a] | Plan for information transfer and consensus building with local representatives, as necessary | • Reflect knowledge of citizen concerns<br>• Provide for citizen involvement<br>• Often not required for UST remediation projects<br>• Typically performed as a revision of community relations plan | • 1 to 3 months<br>• Prepared in parallel with project management plan |
| Permitting | Obtain permits or comply with substantive requirements , as applicable | • Provide for installing new monitoring wells<br>• Provide for management of investigation-derived material<br>• Projects conducted under CERCLA are not required to obtain permits, but must meet substantive permitting requirements | • As needed usually prior to the detailed site characterization of RNA<br>• 1 to 4 months |
| Reporting | Provide adequate documentation of project activities, status, problems, and corrective actions | • Provide written monthly reports<br>• Perform site trips and provide verbal progress updates, as required<br>• Document significant decisions with written telephone record<br>• Provide meeting agenda and minutes | Continues throughout the project |

Note: (a) Only required under CERCLA of RCA CA regulatory framework

## 3.2 PRELIMINARY ASSESSMENT IN SUPPORT OF RNA

The purpose of the preliminary assessment is to allow the contractor to establish an understanding of the conditions and challenges at the site based on existing data and reports, to evaluate the feasibility of RNA, and to prepare a plan for the detailed assessment, if needed. The major tasks included in the preliminary assessment are summarized in Table 3-2. The SOW requires the contractor to provide the labor, equipment, materials, and facilities to accomplish the following objectives:

- Review available data, develop a conceptual model, and assess site conditions
- Make a preliminary determination of the feasibility of RNA for the site
- Develop a workplan for the detailed site characterization and assessment.

## 3.3 DETAILED SITE EVALUATION OF RNA

The purpose at this stage is to collect site data and document site conditions to allow definitive assessment of the feasibility of RNA, document the basis for recommending RNA, build a consensus

with.3-3 regulators and the public for using RNA, and document the acceptance of RNA at the site. The major tasks included in the detailed site evaluation are summarized in Table 3-3. The SOW requires the contractor to provide the labor, equipment, materials, and facilities to accomplish the following objectives:

- Develop all required assessment information to demonstrate the occurrence of RNA based on field data
- Develop all required assessment information to demonstrate that RNA will adequately protect human health and the environment at the site
- Refine the site conceptual model
- Demonstrate that cleanup objectives for the site can be achieved within a reasonable timeframe
- Establish and document a consensus among the technical and regulatory community and the public that RNA will adequately protect human health and the environment at the site.

## 3.4 PERFORMANCE MONITORING AND SITE CLOSURE

The purpose of this stage is to collect site data and perform technical analyses to quantitatively evaluate the performance of RNA; then when site-specific remediation goals have been achieved, to document the completion of remediation activities. The major tasks included under performance monitoring and site closure are summarized in Table 3-4. The SOW requires the contractor to provide the labor, equipment, materials, and facilities to accomplish the following objectives:

- Develop a Performance Monitoring Plan, including a Contingency Plan (and obtain regulatory acceptance)
- Install any required facilities (e.g., monitoring wells)
- Establish/implement institutional controls (if needed)
- Periodically collect performance monitoring data until remedial action goals are achieved
- Periodically evaluate the progress of RNA with respect to predicted behavior
- Make recommendations for continued monitoring, reassessment of the conceptual model, alternative remedial action (i.e., implementation of contingency plan) or site closure, as appropriate
- Report progress of RNA to regulators, as appropriate
- Document compliance with remediation goals
- Establish institutional controls (if needed)
- Complete site closure activities, including a site closure report.

## Table 3-2. Statement of Work Requirements for RNA: Preliminary Assessment in Support of RNA

| Task Name | Task Scope | Task Guidance and Information | Typical Performance Time |
|---|---|---|---|
| Review regulatory acceptance of RNA | Determine if existing regulations in the applicable jurisdiction allow RNA as a remedial alternative | The contractor should demonstrate specific experience with regulator status of RNA under the applicable jurisdiction and regulatory framework | 1 to 2 months |
| Collect and organize existing data | Review and organize existing data into a usable format | • Organize data into a comprehensive database consistent with the Geographic Information System (GIS) or other format specified by the Navy<br>• Perform QA review to validate data for completeness and accuracy | 1 to 3 months |
| Develop a preliminary conceptual model to assess applicability of RNA based on risk factors | Use existing data top develop an understanding of site location, history, description, climate, demography, and land use | Develop maps(s) showing major site features such as property boundaries, land use, populations, ecological features, and groundwater uses | 1 to 4 months |
| | Use existing data to develop an understanding of the contaminants of concern (COC) and nature and extent of contamination | Review/develop maps and figures defining the location of sources and the distribution of contaminants in the environment above regulatory limits and conservative risk-based concentrations | |
| | Use existing site geology and hydrology data to develop an understanding of groundwater flow regimes | • Document current status of information about site geology and hydrology<br>• Define groundwater flow regimes, including principal aquifers and direction and rate of groundwater flow | |
| | Use existing data to identify potential exposure pathways and assess the presence of immediate or imminent threats that could preclude RNA | • Develop a basic understanding of contaminant behavior in the environment and identify potential migration pathways, exposure points, exposure routes and receptors<br>• Identify potential compliance points | |
| | Determine of the presence of free product or other site factors constrain the ability to implement RNA | • Identify technical constraints that eliminate RNA as an alternative<br>• Consider supplemental technologies to mitigate constraints<br>• Ensure that releases have been adequately assessed and that sources are understood and controlled | |
| | Establish a conceptual model with sufficient detail to allow a preliminary assessment of the applicability of RNA | Assess immediate and/or imminent effects of contaminants on potential human and environmental receptors | |
| Assess applicability of RNA based on the potential for biodegradation | • Use site data to determine if there is evidence for the occurrence of RNA<br>• Determine the extent of additional characterization required | Stable or shrinking plume conditions provide evidence for RNA and may be sufficient to allow bypassing of detailed site characterization | • 1 to 2 months<br>• Performed in parallel with conceptual model development |

## Table 3-2. Statement of Work Requirements for RNA: Preliminary Assessment in Support of RNA (Continued)

| Task Name | Task Scope | Task Guidance and Information | Typical Performance Time |
|---|---|---|---|
| Prepare preliminary assessment report and workplan and submit to regulatory agencies | Prepare a report describing the conceptual model, preliminary evaluation, and plans for collecting data required for detailed evaluation; incorporate regulatory input | • Document site status<br>• Define technical basis supporting applicability of RNA<br>• Document extent of additional characterization required<br>• Detailed assessment may not be required if existing data indicate that the plume is shrinking | 1 to 4 months |
| Prepare preliminary data collection Quality Assurance Project Plan (QAPP) | Prepare a plan to control the quality of preliminary data collection | • Define QA/QC organization, responsibilities, and authorities<br>• Specify definable features or work and quality measures<br>• Describe field QA/QC<br>• Describe sampling and analytical QA/QC<br>• Describe equipment maintenance QA/QC<br>• Describe change control methods<br>• Describe corrective action methods | • 1 to 2 months<br>• Performed in parallel with workplan preparation |
| Prepare preliminary data collection Health and Safety Plan (HASP) | Prepare a plan to maintain safe working conditions during preliminary data collection | Compliance with Occupational Safety and Health Administration (OSHA) requirements; specifically 29 CFR 1910.120, 29 CFR 1910.1200, and 29 CFR 1026 | • 1 to 2 months<br>• Performed in parallel with workplan preparation |
| Support public meetings | Prepare materials and attend public meetings | • Prepare presentation materials, technical summaries, and handouts<br>• Attend public meetings to support Naval personnel<br>• Allow for two-way communication and response to community concerns in project plans | As required |

## Table 3-3. Statement of Work Requirements for RNA: Site Characterization and Detailed Evaluation of RNA

| Task Name | Task Scope | Task Guidance and Information | Typical Performance Time |
|---|---|---|---|
| Install required wells and monitoring points | Install wells as needed to ensure samples can be collected to evaluate status of RNA | • Obtain applicable permits<br>• Comply with applicable rules and regulations<br>• Wells in plume at compliance point typically required | 1 to 2 months |
| Establish occurrence of RNA | Demonstrate that the in-situ conditions at the site promote biodegradation of COCs | • Collect primary data (geochemical parameters and contaminant concentrations) throughout the plume and along flowpath transects<br>• Construct contour maps for each electron acceptor, metabolic byproduct and biological indicator<br>• Evaluate data for spatial trends that indicate RNA (i.e., inverse correlations with contaminants and electron acceptors and/or direct correlations with contaminants and metabolic byproducts)<br>• Evaluate conservative tracer (e.g., trimethyl benzene [TMB] data to show biodegradation of contaminants<br>• Identify needs for optional studies to support RNA | Performed in parallel with evaluating plume status |
| Evaluate plume status | Characterize plume chemistry and geochemistry to demonstrate occurrence of RNA and support evaluation of the efficiency of RNA | Collect time-series data throughout the plume and along flowpath transects<br>Evaluate significant trends<br>Construct contaminant contour maps<br>Establish if there ahas been a loss of contaminant over time | 1 to 2 years of field monitoring with at least four sampling events |
| Perform optional studies as needed to establish occurrence of RNA | Use optional studies to establish occurrence of RNA | Plan and perform the following: analysis of volatile fatty acids (VFA), analysis of hydrogen in groundwater, laboratory microcosm studies, and microbial characterization, as needed | 2 to 6 months |
| Quantify RNA efficiency | Determine if RNA will protect human health and the environment and achieve site-specific remediation goals within a time frame that is reasonable compared to other remedial alternatives | • Determine biodegradation rates for COCs<br>• Determine if a conservative tracer can be used to quantify plume dynamics and biodegradation rates<br>• Determine if historical time-series data indicate a shrinking, stable, or expanding plume<br>• If no tracer is present and plume is shrinking or stable, calculate biodegradation rates using Buscheck and Alcantar method or spatial regression methods, as appropriate<br>• If plume is expanding, perform laboratory microcosm studies or modeling to quantify biodegradation rates, or consult literature<br>• Calculate time to achieve site-specific remediation goals, if possible | 1 to 3 months |

## Table 3-3. Statement of Work Requirements for RNA: Site Characterization and Detailed Evaluation of RNA (Continued)

| Task Name | Task Scope | Task Guidance and Information | Typical Performance Time |
|---|---|---|---|
| Perform fate and transport modeling as needed to demonstrate protection of human health and the environment and determine the time required to achieve site-specific remediation goals | Perform modeling to predict the time-dependent behavior of contaminant concentrations with an without biodegradation | • Refine site specific conceptual model<br>• Select model and define inputs<br>• Construct and calibrate model to site conditions<br>• Perform predictive simulations to estimate concentrations at compliance points and time to reach remediation goals | Performed in parallel with evaluation of plume status |
| Compare RNA to other remediation alternative | Conduct a technology screening to ensure that RNA offers the best balance of effectiveness, implementability, and cost | • Identify a comprehensive listing of candidate technologies<br>• Perform technology screening using criteria required by regulations | 1 to 2 months |
| Prepare RNA evaluation report and submit to regulatory agencies (and public if necessary) | Prepare a report describing the RNA demonstration/evaluation program, recommending (or rejecting) RNA as an effective remedial alternative, and incorporating regulatory and public input | • Document evidence for occurrence of RNA<br>• Document information and technical analysis used to demonstrate that RNA will protect human health and the environment<br>• Document information and technical analysis used to determine time to reach remediation goals<br>• Provide technical basis for setting compliance points and actin levels to ensure protection of human health and the environment<br>• Provide technical basis for setting remediation goals for RNA close out<br>• Project future trends to be used to evaluate performance during performance monitoring<br>• Quantify uncertainties in predictions<br>• Recommend RNA, if appropriate, and obtain regulatory and public consensus<br>• Document results of alternative screening | 1to 4 months |
| Support public meetings | Prepare materials and attend public meetings | • Prepare presentation materials, technical summaries, and handouts<br>• Attend public meetings to support Naval personnel<br>• Allow for two-way communication and response to community concerns in project plans | As required |

## Table 3-4. Statement of Work Requirements for RNA: Performance Monitoring and Site Closure

| Task Name | Task Scope | Task Guidance and Information | Typical Performance Time |
|---|---|---|---|
| Prepare Performance Monitoring Plan and submit to regulatory agencies | Develop a plan, cost estimate, and schedule for performance monitoring and evaluation to implement RNA at the site and obtain regulatory acceptance | • Define scope and objectives of performance monitoring<br>• Arrange wells to make maximum use of existing facilities and equipment<br>• Establish analytical requirements<br>• Establish sampling frequency and duration<br>• Specify location of compliance points and protective action limits<br>• Describe data reduction and evaluation of RNA progress<br>• Specify data format consistent with GIS requirements<br>• Plan for actions if RNA progress deviates from expectations (Contingency Plan)<br>• Provide quantitative definition of remediation goal<br>• Identify institutional controls that are required during performance and monitoring<br>• Develop project schedule and definitive cost estimate (+15% to −5%) | 2 to 5 monthsd |
| Prepare monitoring QA/QC program Plan | Prepare a plan to control the quality of performance monitoring | • Define QA/QC organization, responsibilities, and authorities<br>• Specify definable features of work and quality measures<br>• Describe field QA/QC<br>• Describe sampling and analytical QA/QC<br>• Describe equipment maintenance (QA/QC<br>• Describe change control methods<br>• Describe corrective action methods | • 1 to 3 months<br>• Performed in parallel with preparing the Performance Monitoring Plan |
| Prepare monitoring HASP | Prepare a plan to maintain safe working conditions during performance monitoring | Ensure compliance with OSHA requirements: specifically 29 CFR 1910.120, 29 CFR 1910.1200, and 29 CFR 1926 | • 1 to 3 months<br>• Performed in parallel with preparing the Performance Monitoring plan |
| Install required wells and monitoring points | Install wells as needed to ensure samples can be collected to evaluate progress of RNA | Comply with applicable rules and regulations | 1 to 2 months |
| Establish institutional controls as required | Provide institutional controls to protect human health and the environment during performance monitoring, if needed | Place access restrictions, deed restrictions, easement, and other controls as needed during performance monitoring | • 1 to 3 months<br>• Performed in parallel with well installation |
| Provide construction quality assurance | Provide on-site inspection and documentation to ensure compliance with quality requirements | • Perform daily inspections<br>• Identify and correct deficiencies<br>• Document results | Daily during construction |
| Conduct performance monitoring | Collect and analyze samples to support evaluation of the progress of RNA | • Collect samples in and around the plume and at compliance points until remedial action goals are achieved<br>• Comply with Performance Monitoring Plan, QA/QC program Plan, and HASP | 1 to 5 years |

## Table 3-4. Statement of Work Requirements for RNA: Performance Monitoring and Site Closure (Continued)

| Task Name | Task Scope | Task Guidance and Information | Typical Performance Time |
|---|---|---|---|
| Evaluate progress of RNA | Determine if RNA is proceeding as expected and recommend corrective action for unexpected results | • Compare plume status to site-specific remediation goals and expected progress and recommend continued monitoring (expected progress), corrective action (significant unexpected results), or closeout (remediation goals achieved)<br>• Update conceptual model and revise model predictions<br>• Update remediation time predictions | Performed in parallel with performance monitoring |
| Prepare performance monitoring and performance assessment reports | Report results and obtain regulatory approval | Document methods, results, and QA activities for monitoring period. | 1 to 2 months preparation time Performed periodically as defined in Performance Monitoring Plan |
| Prepare closure report | Prepare a report documenting remediation activities and results and formal acceptance of site closure | Demonstrate protection of human health and the environment<br>Quantify, on a statistical basis, the attainment of site-specific remediation goals and level of confidence | 2 to 5 months |
| Establish institutional or administrative controls | Establish any required institutional or administrative controls | • Conform with local regulatory requirements for closing unneeded wells<br>• Ensure that any wells left in place cannot be used for purposes other than intended<br>• Abandon unneeded wells using methods that prevent migration of contaminants into an aquifer or between aquifers and reduce the potential for vertical or horizontal migration of fluids in or around the well | 2 to 5 months |
| Restore and close site | Perform well abandonment as required | • Conform with local regulatory requirements for closing unneeded wells<br>• Ensure that any wells left in place cannot be used for purposes other than intended<br>• Abandon unneeded wells using methods that prevent migration of contaminants into an aquifer or between aquifers and reduce the potential for vertical or horizontal migration of fluids in or around the well | 2 to 5 months |

## 4.0 GOVERNMENT-FURNISHED PROPERTY

The SOW must specify that the contractor is expected to be self-sufficient for all work to be performed, unless specific site conditions require use of government-furnished property.

## 5.0 GOVERNMENT-FURNISHED FACILITIES

Facility personnel must provide the implementing contractor access to the site to be remediated. The SOW must define the requirements for contractor personnel to enter the facility and work at the site.

The work elements required to perform RNA frequently involve the use of existing sampling wells and monitoring points. The SOW must provide a description of the number, location, and construction of wells and monitoring points in and around the area to be remediated.

The SOW must clearly define responsibilities for managing investigation-derived wastes. Existing waste management facilities located at the site that are appropriate for managing investigation-derived wastes, if any, and facility limitations must be described.

## 6.0 DELIVERABLES

A list of the deliverable items to be produced during the project, with a clear indication of the due date for each item, appears in the SOW. Table 6-1 is provided as an example to assist in preparation of the deliverables list. The number of days to complete each deliverable is project-specific and should be defined as the SOW is prepared. The number of copies, print and electronic format, and addresses of recipients should be defined in the SOW.

### Table 6-1. Example Deliverable for an RNA Project

| Deliverable | Applicable Task | Number of Copies | Due Date |
|---|---|---|---|
| Draft program management plan[b] | Planning and management | 5 | [Number] days after project start |
| Final program management plan[b] | Planning and management | 10 | [Number] days after receiving comments on the draft plan |
| Draft community relations plan[b] | Planning and management | 5 | [Number] days after project start |
| Final community relations plan[b] | Planning and management | 10 | [Number] days after receiving comments on the draft plan |
| Input for permit applications (e.g., well construction permits) | Planning and management | 5 | As required |
| Monthly reports | Planning and management | 1 | [Number] days after the first of each month |
| Meeting agendas | Planning and management | 15 | [Number] days before the event |
| Telephone records, trip reports, and meeting minutes | Planning and management | 1 | [Number] days after the event |
| Draft assessment report and workplan for detailed evaluation[c] | Preliminary assessment | 5 | [Number] days after approval of project management plan |
| Final assessment report and workplan for detailed evaluation[c] | Preliminary assessment | 10 | [Number] days after receiving comments on draft workplan |
| Public meeting support | Preliminary assessment | -- | As required |
| Draft detailed evaluation report | Detailed assessment | 5 | [Number] days after approval of the final site technology evaluation report |
| Final detailed evaluation report | Detailed assessment | 10 | [Number] days after receiving comments on the draft report |
| Public meeting support | Detailed assessment | -- | As required |
| Draft Performance Monitoring Plan[c] | Performance monitoring | 5 | [Number] days after approval of the final site technology evaluation report |
| Final Performance Monitoring Plan[c] | Performance monitoring | 10 | [Number] days after receiving comments on the draft plan |
| Construction QA Report | Performance monitoring | 1 | Daily during field activities |
| Performance monitoring/performance assessment reports | Performance monitoring | 5 | Periodically as required in the Performance Monitoring Plan |
| Draft site closure report | Project closeout | 5 | [Number days after approval of the final Performance Monitoring Plan |
| Final site closure report | Project closeout | 10 | [Number] days after receiving comments on the draft report |

Notes: (a) Tables in Section 3 indicate typical task durations
(b) These deliverables are only required under CERCLA, or RCRA CA regulatory frameworks
(c) Includes site-specific QA/QC Program Plan and HASP

## 7.0 REFERENCES


Department of the Navy. 1998. *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents at naval and marine Corps Facilities.* Naval Facilities Engineering Command.

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U.S. EPA, see U.S. Environmental Protection Agency.

# APPENDIX A

# PERFORMANCE-BASED STATEMENT OF WORK.

NAVAL FACILITIES ENGINEERING COMMAND
Washington, DC 20374-5066

NAVFAC

# USER'S GUIDE FOR IMPLEMENTING REMEDIATION BY NATURAL ATTENUATION AT PETROLEUM RELEASE SITES

## PART 3: COST ESTIMATING PROGRAM

Prepared for:

Naval Facilities Engineering Command's

Naval Facilities Engineering Service Center
Southwest Division Naval Facilities Engineering Command
Engineering Field Activity, Northwest
Northern Division Naval Facilities Engineering Command
Atlantic Division Naval Facilities Engineering Command
Pacific Division Naval Facilities Engineering Command
Engineering Field Activity, Chesapeake
Engineering Field Activity, West

Contract Number N47408-95-D-0730

Prepared by:

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## CONTENTS



### *FIGURES*



### *TABLES*

## *ACRONYMS AND ABBREVIATIONS*

| | |
|---|---|
| ARTT | Alternative Restoration Technology Team |
| BTEX | benzene, toluene, ethylbenzene, and xylenes |
| CAD | computer-assisted design |
| CPT | cone penetrometer testing |
| DO | dissolved oxygen |
| GW | groundwater |
| HSA | hollow-stem auger |
| MTBE | methyl-tert-butyl ether |
| NFESC | Naval Facilities Engineering Service Center |
| ORP | oxidation reduction potential |
| PAH | polycyclic aromatic hydrocarbon |
| PVC | polyvinyl chloride |
| QA/QC | quality assurance/quality control |
| RNA | remediation by natural attenuation |
| RPM | Remedial Project Manager |
| RTM | Remedial Technical Manager |
| TOC | total organic carbon |
| TPH-D | total petroleum hydrocarbons quantified as diesel |
| TPH-G | total petroleum hydrocarbons quantified as gasoline |
| TPH-JP5 | total petroleum hydrocarbons quantified as jet propellant #5 |
| TPH-MO | total petroleum hydrocarbons quantified as motor oil |
| VFA | volatile fatty acid |
| VGA | video graphics adapter |

# 1.0 INTRODUCTION

This user's guide provides instructions on the use of the Remediation by Natural Attenuation (RNA) Cost Estimating Program. This user's guide is provided both in hard copy form and as a help file that can be accessed from the cost estimating program. This document and the associated cost estimating program fulfill objectives relating to the scope of work under Delivery Order 0039 of the U.S. Naval Facilities Engineering Service Center (NFESC) Contract No. N47408-95-D-0730.

The RNA Cost Estimating Program is intended for use by Navy Remedial Project Managers (RPM) and Remedial Technical Managers (RTM) and by contractors involved with remediation of Navy-owned sites. The cost estimating program provides the RPMs and RTMs with a practical tool for developing budgets to implement RNA at petroleum-contaminated sites. This cost estimating program should be used in conjunction with the following documents:

- *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities* (DON, 1998) (hereby referred to as the Technical Guidelines)

- *Users' Manual for Implementing Remediation by Natural Attenuation (RNA) at Petroleum Release Sites – Part 1: Operations Manual.* (hereby referred to as the Operations Manual)

- *Users' Manual for Implementing Remediation by Natural Attenuation at Petroleum Release Sites – Part 2: Statement of Work Guidelines.* (hereby referred to as the Statement of Work Guidelines)

The RNA Cost Estimating program has been developed using Microsoft® Visual Basic™ programming language and runs on the Microsoft® Excel platform. Microsoft® Excel version 5.0 or higher is required to use this cost estimating program. The program is basically a spreadsheet file with several custom-built options including dialog boxes, menus, and buttons. The file extension associated with Microsoft® Excel and all RNA Cost Estimating Program files is "xls."

The RNA Cost Estimating Program has been developed concurrently with the *Operations Manual* and *Statement of Work Guidelines*, and follows the same organizational structure as these documents. The program has been developed to guide the user in developing costs for the three main stages of RNA system design and operation presented in the *Operations Manual*:

- Section 4.0 – Preliminary Assessment in Support of RNA
- Section 5.0 – Detailed Site Evaluation of RNA
- Section 6.0 – Performance Monitoring and Site Closure.

## 1.1 SCOPE

This RNA Cost Estimating Program User's Guide provides guidance on the use of the RNA Cost Estimating Program. The program has been developed to aid in the determination of costs associated with the implementation of RNA at petroleum-contaminated sites. RNA, which may also be referred to as intrinsic remediation or monitored natural attenuation, is defined as follows:

> "A remedy where naturally occurring physical, chemical, and biological processes will effectively protect human health and the environment and will achieve remedial goals

within a time frame that is reasonable compared to alternative technologies, without human intervention (DON, 1999a)."

## 1.2 COMPUTER SYSTEM REQUIREMENTS

The RNA Cost Estimator can be used on any IBM compatible computer that operates under Windows 3.1™ or Windows 95™. Microsoft® Excel version 5.0 or higher is required to run this program. Minimum hardware requirements for this program (in addition to those required to run Microsoft® Excel) are 2 megabytes of hard-disk space, a regular video graphics adapter (VGA) color monitor, and a mouse.

## 1.3 INSTALLATION PROCEDURE

Installation of the RNA Cost Estimator involves copying the files associated with the program to a directory of your choice. It is recommended that you set up a separate directory, such as "c:\RNA\," to install the program. The program consists of the spreadsheet file, "RNACEv1.xls," and the help file, "RNACEv1.hlp."

## 1.4 DEFINITION OF TERMS

The following selected terms are used to describe elements of Visual Basic™ programming.

**Dialog Box** – A pop-up window used to input text, select a button, or bring up another window. It is usually invoked by a menu, a button, or another dialog box. Figure 1-1 is an example of the "Save As" dialog box.

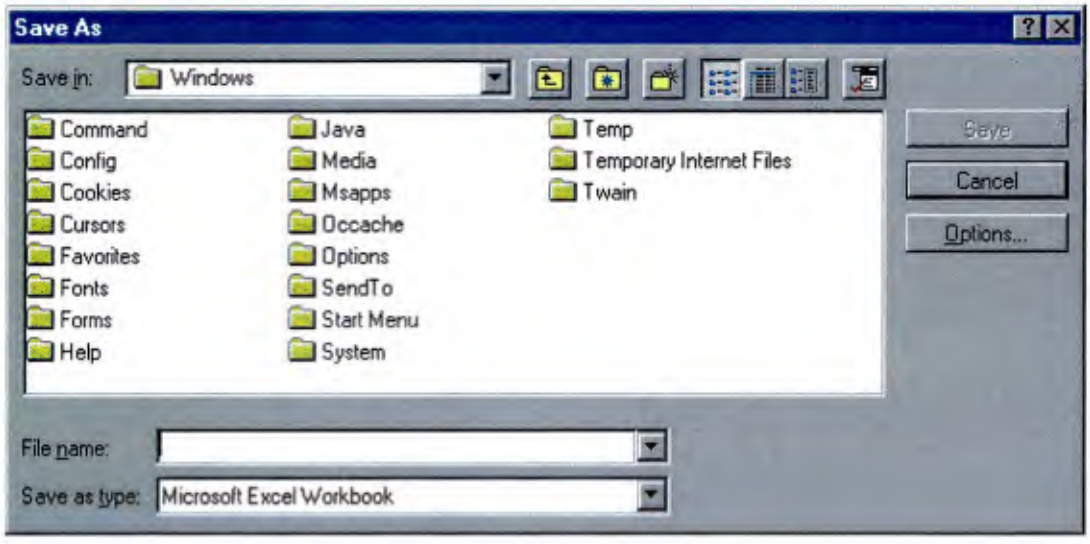



Figure 1-1. "Save As" Dialog Box.

**Dropdown Box** – A box used to select one item from two or more listed choices. The boxes to the right of the "Save in:," "File name:,",and "Save as type:, text in Figure 1-1 are examples of dropdown boxes.

**Button** – Usually a box containing text that, when selected using the mouse, performs an action or executes a program. Figure 1-1 contains three buttons labeled "Save," "Cancel," and "Options."

## 1.5 PROGRAM STRUCTURE

As stated previously, the RNA Cost Estimating Program closely follows the structure of the *Operations Manual*. Therefore, the user can prepare a detailed cost estimate by estimating costs for the three major stages of RNA system design and operation: Preliminary Assessment, Detailed Site Evaluation, and Performance Monitoring and Site Closure. Also, the user has the option of preparing a general cost estimate, which is a much less extensive method of costing.

Whether preparing a detailed cost estimate or a general cost estimate, the user is prompted for input through the use of custom dialog boxes (Section 5.0 provides a complete description of every custom dialog box associated with the program). After providing cost parameters through a series of dialog boxes, the section detail worksheet for each aspect of RNA presents itemized costs for material and labor. A summary sheet also can be accessed that provides a summary of costs for each aspect of RNA.

After estimating costs using the general cost estimate option, the cost summary sheet is displayed. The user can access cost summary charts from the cost summary sheet to view the costs graphically. Figure 1-2 shows the organizational structure of the RNA Cost Estimating Program.

## 1.6 PROGRAM FEATURES

The RNA Cost Estimating Program contains some user-friendly features drawn from previous Battelle-developed cost estimating programs, as well as several new features not available in previous cost estimating programs. Program features include the following:

- **User-Friendly Graphical Interface** — Guides the user through the cost estimating process. Common Windows™ components, such as menus, dialog boxes, and buttons, are used to create a program that is familiar and easy-to-use.

- **Detailed and General Cost Estimating Procedures** — Gives the user the option of developing a general cost estimate requiring input on only a few of the most cost-sensitive parameters or a detailed cost estimate requiring more extensive user input.

- **Unrestricted Access to Microsoft® Excel Functions and Menus** — Utilizes all of Excel's capabilities and spreadsheet functions.

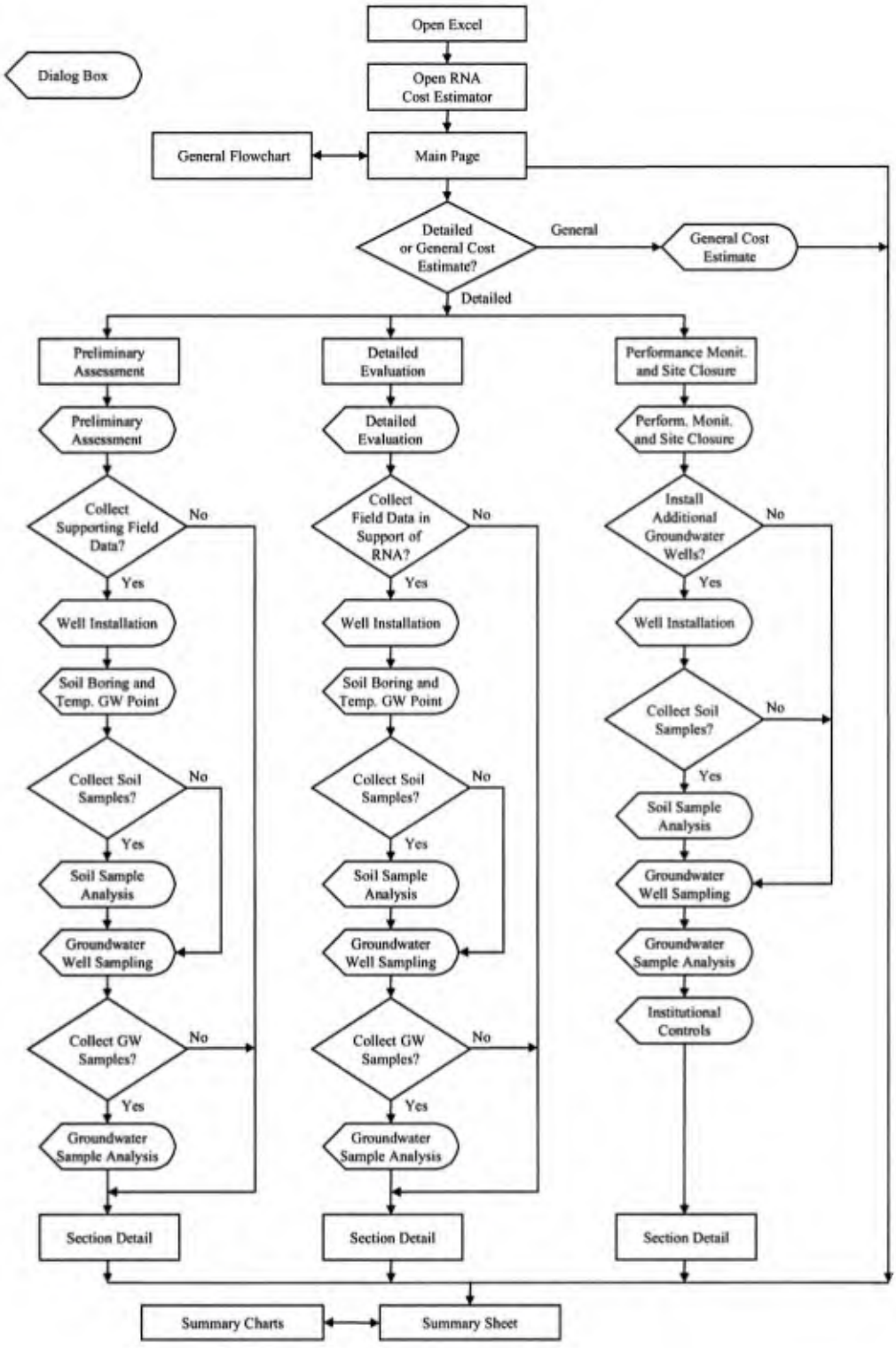



Figure 1-2. Organizational structure of the RNA cost estimating program.

- **Unrestricted Access to the Microsoft® Excel Spreadsheet** — Estimates costs based on required input parameters, and then generates a detailed list of costs on an Excel spreadsheet. This cost detail sheet can be modified just like any Excel spreadsheet, thus providing the user with greater control over the cost estimation process. For example, quantities can be adjusted, items can be added or deleted, and unit costs can be changed. Also, the tables created by the program can be reformatted by the user as well as copied to another spreadsheet.

- **Step-Wise Costing Dialog Boxes** — Takes the user through a sequence of dialog boxes to estimate costs. Therefore, the user is prompted only for input on required data. Steps in the costing sequence that are not requested by the user are skipped.

- **Help File** — Allows quick access to information about the cost estimating program.

## 2.0 BEGINNING A COST ESTIMATING SESSION

To begin a cost estimating session, start the Microsoft® Excel program. Within Excel, select the Open submenu from the File menu to access the Open dialog box. Select the file "RNACEv1.xls" by either typing in the file location and file name or browsing the file hierarchy. After the file is selected, click on the Open button to begin.

Upon entering the program, the dialog box shown in Figure 2-1 will appear. The user must enter a file name to proceed with the program. It is recommended that users work with and save only one file per site, and that the original name of the file (RNACEv1.xls) is not used as a filename for specific sites. Entering project information is optional; however, this information will be included in the footer of all printouts. When the user reopens a project file, the file and project information will be displayed. If the information is to remain the same, simply click the "OK" button.

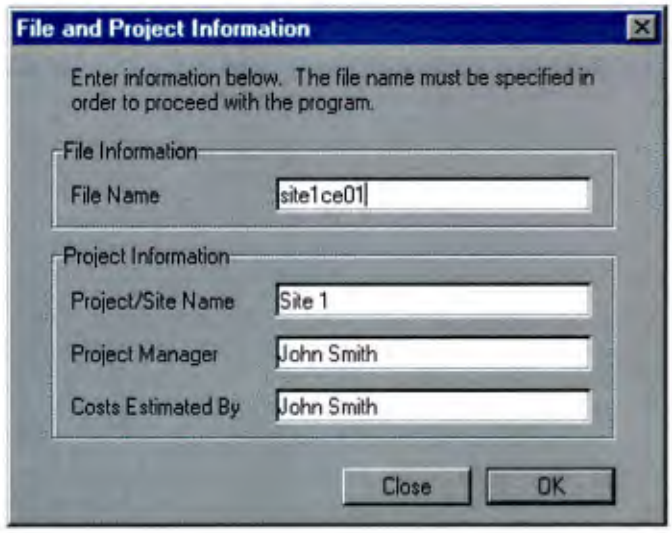



Figure 2-1. "File and Project Information" dialog box.

After inputting the desired file and project information and clicking "OK," the main screen, depicted in Figure 2-2, will be displayed. Costing worksheets for each stage of RNA (Preliminary Assessment, Detailed Site Evaluation, and Performance Monitoring and Site Closure) can be accessed from the main screen, as can the general cost estimate dialog box, the cost summary worksheet, and the general RNA flowchart from the *Operations Manual*. Access to these worksheets and program features is available through either the associated buttons on the main screen or the "Goto" menu function.

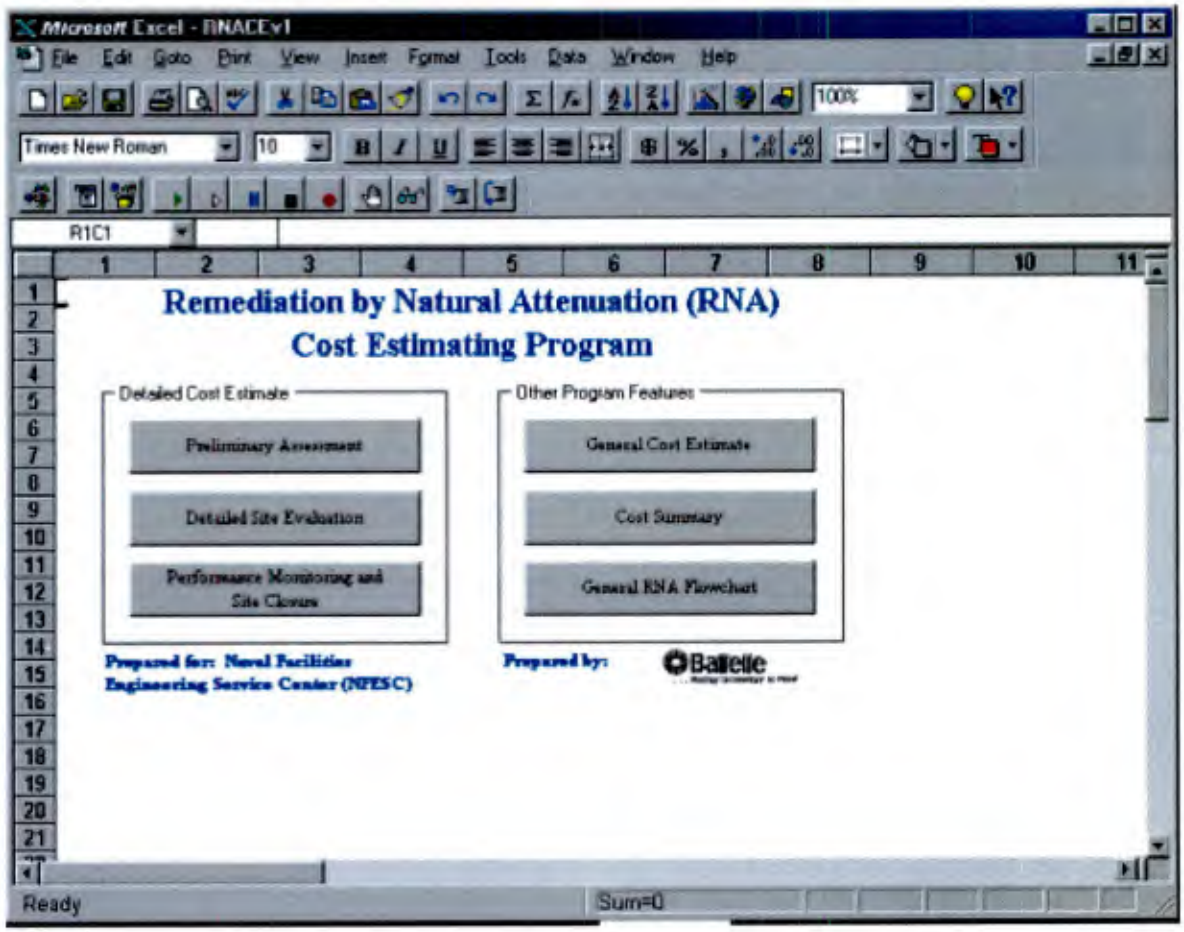



Figure 2-2. Main screen.

## 3.0 COSTING METHODS

This program features two methods for costing RNA. The first costing method is a detailed cost estimate with which the user estimates costs for each of the three stages of the RNA process (Preliminary Assessment, Detailed Site Evaluation, and Performance Monitoring and Site Closure). A costing worksheet for each stage of RNA can be accessed by clicking on the appropriate button located in the left column of the main screen or through the Goto menu function. Costing worksheets also can be accessed from the general RNA flowchart by clicking in the associated area of the flowchart.

After accessing one of the costing worksheets, the user must select the button labeled "Estimate Parameters" to prepare a cost estimate. After selecting the estimate parameters button, a series of dialog boxes will prompt the user for input on cost parameters. The button labeled "Next," located at the bottom of each dialog box, should be selected after input of the appropriate cost parameters. The "Next" button is disabled in the last dialog box in the series, and the button labeled "Finish" should be selected upon completion. If the "Finish" button is selected prior to completing all steps of the estimating process, then default values presented in Section 5.10 will apply to all remaining parameters in that section.

The second costing method is a general cost estimate, accessible through the button of the same name or through the submenu labeled "General Cost Estimate" under the "Goto" menu function. This option requires much less user input than the first option and provides a reasonable cost estimate for RNA. However, assumptions are made using this cost estimating option that may or may not be appropriate for your site. Refer to Section 5.10 of this document for a complete description of the assumptions used for the general cost estimate.

## 4.0 SECTION DETAIL AND COST SUMMARY WORKSHEETS

In this program, each of the three main stages of RNA (Preliminary Assessment, Detailed Site Evaluation, and Performance Monitoring and Site Closure) produces a separate and detailed worksheet that displays the costing information. Costing information consists of the cost category, cost subcategory, a description of the item, the unit of measure, the unit cost, the quantity, and the total price. Costing parameters are estimated using a series of dialog boxes that prompt the user to input information that determines costs.

Estimating costs is initiated by clicking the button labeled "Estimate Parameters" on each section detail worksheet, as explained in Section 3.0 of this document. Also, each worksheet displays three additional buttons in the upper left corner of the screen and labeled "Main," "Clear Page," and "Print." The function of each button is defined as follows:

- **Estimate Parameters** – Accesses cost estimate input screens
- **Main** – Takes the user back to the main screen (Figure 2-2)
- **Clear Page** – Clears the costing information displayed on the worksheet
- **Print** – Prints the costing information displayed on the worksheet. Printing also can be accomplished using the "Print" custom menu item located to the right of the "Goto" custom menu item.

After estimating costs for each phase of RNA or by using the general cost estimating method, the user can view the cost summary worksheet. To access this worksheet, use the "Goto" menu function or click the button labeled "Cost Summary" located on the main screen (Figure 2-2). Like information worksheets, this summary worksheet can be printed using the button located in the upper left corner of the screen or from the "Print" menu function. Also, cost summary charts can be accessed from the cost summary worksheet by clicking on any of the option buttons located at the top of the worksheet. Costs associated with the entire project as well as preliminary assessment, detailed evaluation, and performance monitoring and site closure can be viewed on separate cost summary charts.

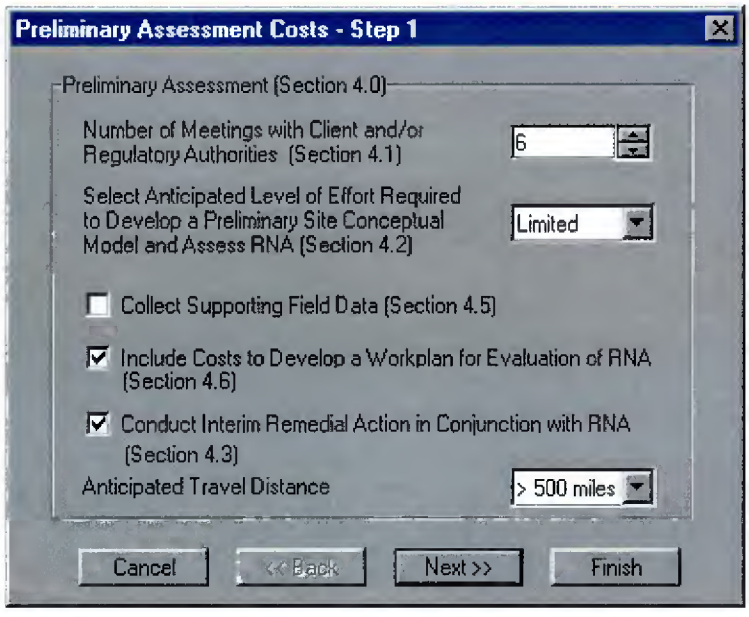
The section detail and cost summary worksheets can be edited. The user can modify, for example, unit costs, change quantities, insert cells, reformat, or copy and paste to further refine and customize the cost estimate.

# 5.0 COSTING DIALOG BOXES

This section describes the custom dialog boxes associated with the RNA Cost Estimating Program by presenting an image of the dialog box, describing the dialog box location in the program, explaining the features of the dialog box, and outlining any assumptions that influence the way specific tasks associated with the dialog box operate. To the extent possible, common dialog boxes are used throughout the program. For example, the dialog box that prompts the user for input on groundwater sample analysis is the same whether the user is estimating costs for the preliminary assessment, detailed evaluation, or performance monitoring and site closure.

When applicable, the section number from the RNA *Operations Manual* is referenced in the dialog box text, so users can refer to that section of the operations manual at their convenience for detailed information on the referenced subject.

## 5.1 PRELIMINARY ASSESSMENT DIALOG BOX




*Location*

This preliminary assessment dialog box is the first that appears when the user selects the "Estimate Parameters" button in the Preliminary Assessment Worksheet.

*Features and Assumptions*

- **Number of Meetings with Client and/or Regulatory Authorities (Section 4.1).** Estimate the number of meetings with the client and/or regulatory authorities that are anticipated during the preliminary assessment. The default value is two meetings. Each meeting includes costs for one project manager and one project scientist to attend a 1-day meeting (8 hours of effort each).

- **Select the Anticipated Level of Effort Required to Develop a Preliminary Site Conceptual Model and Assess RNA (Section 4.2).** The user must estimate the anticipated level of effort required to develop a preliminary site conceptual model and assess RNA at the site. The options for level of effort are "none," "limited," and "extensive." "None" should be selected if a preliminary site conceptual model has already been prepared and RNA at the site has already been assessed. "Limited" and "extensive" should be selected based on a qualitative estimate of the level of effort required. "Limited" typically would apply when working on a site with a single source of contamination with a well-defined extent. "Extensive" typically would apply to sites with multiple sources of contamination and multiple receptors. Table 5-1 lists the assumed labor associated with the selected level of effort.

**Table 5-1. Labor Associated with Developing a Preliminary Site Conceptual Model and Assessing RNA**

| Labor Category | Labor Hours (None) | Labor Hours (Limited) | Labor Hours (Extensive) |
|---|---|---|---|
| Project Manager | 0 | 16 | 32 |
| Project Scientist | 0 | 40 | 80 |
| Staff Scientist | 0 | 40 | 80 |
| Draftsman/Computer-Assisted Design (CAD) Operator | 0 | 20 | 40 |

- **Collect Supporting Field Data (Section 4.5).** If supporting field data need to be collected during the preliminary assessment, this box should be checked. If this box is checked, a series of dialog boxes will follow that will guide the user in selecting data collection methods and sample analyses.

- **Include Costs to Develop a Workplan for Evaluation of RNA (Section 4.6).** If a workplan for evaluating RNA needs to be developed, this box should be checked. Labor hours estimated for preparing a workplan are listed in Table 5-2.

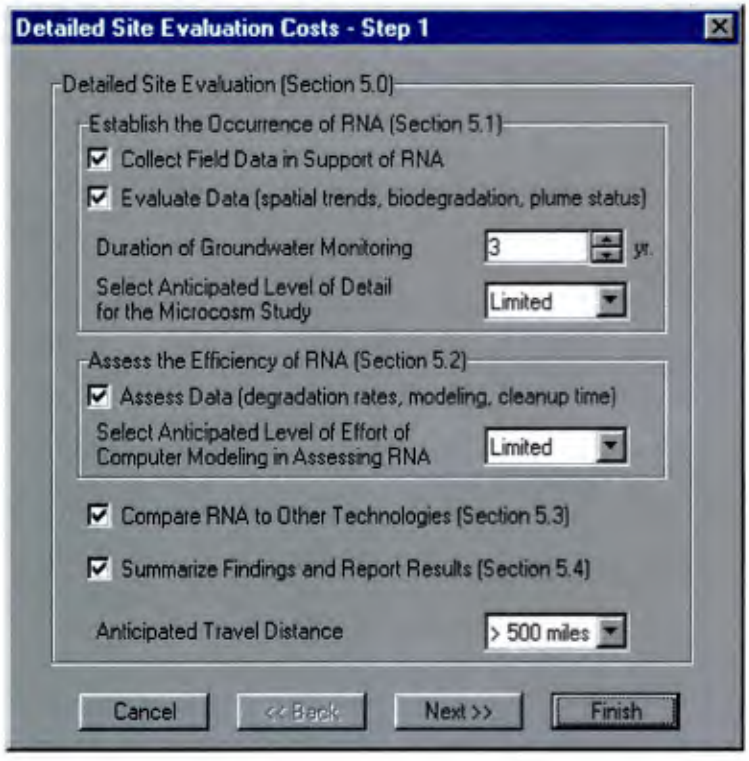
- **Conduct Interim Remedial Action in Conjunction with RNA (Section 4.3).** Check this box to indicate that interim remedial action is selected but that costs are not contained in this program.

- **Anticipated Travel Distance.** Specify the anticipated travel distance required for this project to estimate costs associated with travel. Options for anticipated travel distance are "local," "<500 miles," and ">500 miles." For costing purposes, it is assumed that local travel incurs no per diem or airfare costs. Travel <500 miles incurs a $100/day per diem and a $400 round trip airfare. Travel >500 miles incurs a $100/day per diem and a $700 round trip airfare.

**Table 5-2. Labor Associated with Developing a Workplan for Evaluation of RNA**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 8 |
| Quality Assurance/Quality Control (QA/QC) Officer | 20 |
| Senior Project Engineer | 40 |
| Project Scientist | 80 |
| Staff Scientist | 160 |
| Draftsman/CAD Operator | 80 |
| Word Processing/Clerical | 40 |

## 5.2 DETAILED EVALUATION DIALOG BOX




*Location*

This detailed evaluation costs dialog box is the first that appears when the user selects the "Estimate Parameters" button in the Detailed Evaluation worksheet.

*Features and Assumptions*

- **Collect Field Data in Support of RNA (Section 5.1).** If field data will be collected during the detailed evaluation, this box should be checked. If this box is checked, a series of dialog boxes will follow that will guide the user in selecting data collection methods and sample analyses.

- **Evaluate Data (spatial trends, biodegradation, plume status) (Section 5.1).** If the box associated with evaluating data is checked, labor hours estimated to complete this task will be incorporated into the cost estimate. This task includes labor costs for data reduction associated with evaluating data for spatial trends, establishing biodegradation using an internal tracer, and establishing plume status. Table 5-3 presents the labor estimates used for this task.

**Table 5-3. Labor Associated with Evaluating Data**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 8 |
| Project Scientist | 40 |
| Staff Scientist | 80 |
| Draftsman/CAD Operator | 80 |

- **Duration of Groundwater Monitoring (Section 5.1).** Estimate the duration of groundwater monitoring anticipated during the detailed evaluation. The recommended duration is 2 years. Groundwater monitoring duration is only applicable if the box associated with collecting field data in support of RNA has been checked.

- **Select Anticipated Level of Effort for a Microcosm Study (Section 5.1).** Estimate the anticipated level of effort required for a laboratory microcosm study. The options for level of effort are "none," "limited," and "extensive." A limited level of effort estimates that a 12-week-long study will be conducted. An extensive level of effort estimates that a 24-week-long microcosm study will be performed. Estimates include costs for the following items:

  - Materials (limited = $500, and extensive = $1,000)

  - Weekly laboratory analysis of benzene, toluene, ethylbenzene, and xylenes (BTEX); total petroleum hydrocarbons quantified as gasoline (TPH-G); and total petroleum hydrocarbons quantified as diesel (TPH-D)

  - Weekly laboratory analysis of nitrate, sulfate, sulfide, iron, manganese, methane, and carbon dioxide

  - Labor hours for a project scientist (2 hours/week), a staff scientist (4 hours/week), and a laboratory technician (8 hours/week).

- **Assess Data (degradation rates, modeling, cleanup time) (Section 5.2).** If the box associated with this task is checked, the program estimates labor hours required to determine in situ contaminant degradation rates, calculate future concentrations at downgradient receptors, and estimate times to reach cleanup goals. The estimated labor hours associated with this task are presented in Table 5-4.

**Table 5-4. Labor Associated with Assessing Data**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 40 |
| Senior Project Engineer | 40 |
| Project Scientist | 160 |
| Staff Scientist | 160 |
| Draftsman/CAD Operator | 80 |

- **Select Anticipated Level of Effort of Computer Modeling in Assessing RNA (Section 5.2).** The user must estimate the anticipated level of effort required for computer modeling in assessing RNA. The options for level of effort are "none," "limited," and "extensive," Selecting "none" assumes that modeling will not be performed. "Limited" should be selected for sites with a single source of contamination and data collected from fewer than 15 monitoring wells. "Extensive" should be used for sites containing multiple sources of contamination and/or data collected from more than 15 monitoring wells. Labor estimates for each level of effort are presented in Table 5-5.

**Table 5-5. Labor Associated with Computer Modeling**

| Labor Category | Labor Hours (None) | Labor Hours (Limited) | Labor Hours (Extensive) |
|---|---|---|---|
| Project Manager | 0 | 16 | 32 |
| Project Scientist | 0 | 80 | 160 |
| Staff Scientist | 0 | 80 | 160 |
| Draftsman/CAD Operator | 0 | 40 | 80 |

- **Compare RNA to Other Technologies (Section 5.3).** Check this box if a comparative analysis of RNA to other technologies is required. Labor estimates for comparing RNA to other technologies are presented in Table 5-6.

- **Summarize Findings and Report Results (Section 5.4).** Check this box if the findings from the detailed evaluation must be summarized and reported. Labor hours associated with this task are presented in Table 5-7.

**Table 5-6. Labor Associated with Comparing RNA to Other Technologies**

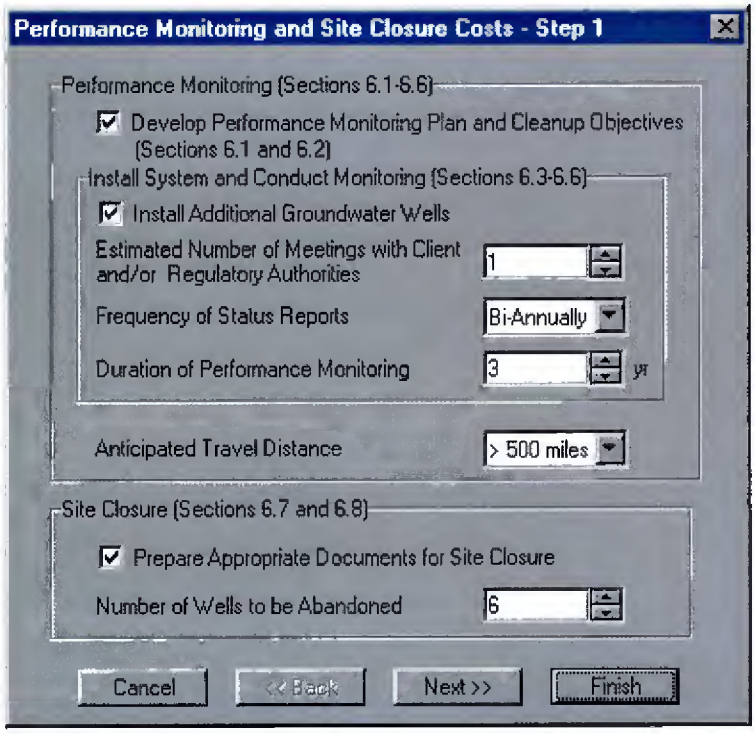
| Labor Category | Labor Hours |
|---|---|
| Project Manager | 8 |
| Senior Project Engineer | 40 |
| Project Scientist | 80 |
| Staff Scientist | 160 |

**Table 5-7. Labor Associated with Summarizing Findings and Reporting Results of the Detailed Evaluation**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 8 |
| QA/QC Officer | 20 |
| Senior Project Engineer | 40 |
| Project Scientist | 160 |
| Staff Scientist | 160 |
| Draftsman/CAD Operator | 80 |
| Word Processing/Clerical | 40 |

- **Anticipated Travel Distance.** Specify the anticipated travel distance required for the project to estimate costs associated with travel. Options for anticipated travel distance are "local," "<500 miles," and ">500 miles." For costing purposes, it is assumed that local travel incurs no per diem or airfare costs. Travel <500 miles incurs a $100/day per diem and a $400 round trip airfare. Travel >500 miles incurs a $100/day per diem and a $700 round trip airfare.

## 5.3 PERFORMANCE MONITORING AND SITE CLOSURE DIALOG BOX




*Location*

This dialog box is the first that appears when the user selects the "Estimate Parameters" button in the Performance Monitoring and Site Closure worksheet.

*Features and Assumptions*

- **Develop Performance Monitoring Plan and Cleanup Objectives (Sections 6.1 and 6.2).** Check this box if preparing a performance monitoring plan prior to performance monitoring is required. Labor hours associated with this task are presented in Table 5-8.

- **Install Additional Groundwater Wells (Sections 6.3-6.6).** Check this box if additional groundwater monitoring wells need to be installed prior to performance monitoring. If this box is checked, a series of dialog boxes will follow that guide the user in selecting data collection methods and sample analysis.

- **Estimated Number of Meetings with Client and/or Regulatory Authorities (Sections 6.3-6.6).** Estimate the anticipated number of meetings with the client and/or regulatory authorities throughout performance monitoring. The default value is five meetings. Each meeting includes costs for one project manager and one project scientist to attend a one-day meeting (8 hours of effort each).

**Table 5-8. Labor Associated with Developing a Performance Monitoring Plan**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 8 |
| QA/QC Officer | 20 |
| Senior Project Engineer | 20 |
| Project Scientist | 80 |
| Staff Scientist | 80 |
| Draftsman/CAD Operator | 40 |
| Word Processing/Clerical | 40 |

- **Frequency of Status Reports (Sections 6.3-6.6).** Input the required frequency of status reports. The estimated labor hours required per status report are presented in Table 5-9. Options are "monthly," "quarterly," "bi-annually," and "annually."

**Table 5-9. Labor Associated with Preparing a Project Status Report**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 4 |
| QA/QC Officer | 8 |
| Project Scientist | 40 |
| Staff Scientist | 40 |
| Draftsman/CAD Operator | 8 |
| Word Processing/Clerical | 40 |

- **Duration of Performance Monitoring (Sections 6.3-6.6).** Estimate the duration of performance monitoring. Reasonable time frames range between 5 and 15 years.

- **Anticipated Travel Distance.** Specify the anticipated travel distance required for this project to estimate costs associated with travel. Options for anticipated travel distance are "local," "<500 miles," and ">500 miles." For costing purposes, it is assumed that local travel incurs no per diem or airfare costs. Travel <500 miles incurs a $100/day per diem and a $400 round trip airfare. Travel >500 miles incurs a $100/day per diem and a $700 round trip airfare.

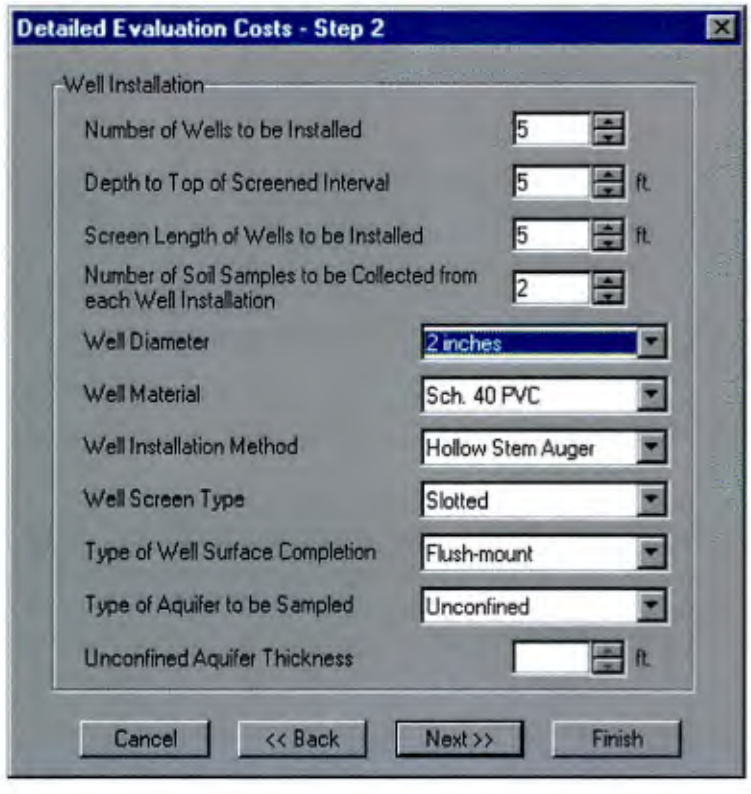
- **Prepare Appropriate Documents for Site Closure (Sections 6.7 and 6.8).** Check this box if preparing site closure documents will be necessary. Estimated labor hours associated with this task are presented in Table 5-10.

**Table 5-10. Labor Associated with Preparing Site**

| Labor Category | Labor Hours |
|---|---|
| Project Manager | 8 |
| QA/QC Officer | 40 |
| Senior Project Engineer | 40 |
| Project Scientist | 160 |
| Staff Scientist | 160 |
| Draftsman/CAD Operator | 80 |
| Word Processing/Clerical | 40 |

- **Number of Wells to be Abandoned (Sections 6.7 and 6.8).** Estimate the number of wells that will require abandonment following closure of the site. Abandonment costs consist of well removal, fill materials, and disposal of wastes. Costs are based on abandonment of a 4-inch-diameter well.

## 5.4 WELL INSTALLATION DIALOG BOX



*Location*

This dialog box appears when estimating costs for well installation during Preliminary Assessment, Detailed Site Evaluation, and/or Performance Monitoring and Site Closure.

*Features and Assumptions*

- **Number of Wells to be Installed.** Input the number of wells to be installed during the associated task.

- **Depth to Top of Screened Interval.** Input the depth from ground surface to the top of the screened interval. If the depth is unknown, use the depth to groundwater as an estimate.

- **Screen Length of Wells to be Installed.** Input the estimated length of the screened interval to be used for all well installations. If screen length is unknown, use a 5-foot screened section as an estimate.

- **Number of Soil Samples to be Collected from each Well Installation.** Input the estimated number of soil samples to be collected from each well installation. If sampling requirements are unknown, use two samples per well installation as an estimate.

- **Well Diameter.** Use the dropdown box to select the well diameter. The options for well diameter are "¾- to 1-inch," "2 inches," "4 inches," and "6 inches." Table 5-11 lists the assumptions that are associated with selection of well diameter.

**Table 5-11. Assumptions Associated with Well Diameter**

| Well Diameter | Installation Options | HSA Borehole Diameter (inches) | Unconfined Aquifer Casing Diameter (inches)[a] |
|---|---|---|---|
| ¾ to 1 inch | Direct push or HSA | 8 | 8 |
| 2 inches | Direct push or HSA | 8 | 8 |
| 4 inches | HSA | 11 | 10 |
| 6 inches | HSA | 13¾ | 12 |

Note: (a) Refers to the casing diameter used to protect the unconfined aquifer when installing wells into a confined or semi-confined aquifer.
HSA = Hollow-stem auger.

- **Well Material.** Use the dropdown box to select the material that will be used to construct the well. The options for well material are "schedule 40 (PVC [polyvinyl chloride])," "schedule 80 PVC," and "stainless steel."

- **Well Installation Method.** Use the dropdown box to select the method for well installation. The options for the well installation method are "direct push" or "hollow-stem auger." The program only allows wells of ¾- to 1-inch-diameter or 2-inch-diameter to be installed if the user selects the direct push method of well installation.

- **Well Screen Type.** Use the dropdown box to select either "slotted" or "continuous slot" well screens. Continuous slot screen is more expensive but may allow higher recharge rates.

- **Type of Well Surface Completion.** Use the dropdown box to select either "flush-mount" or "aboveground" surface completions for all wells to be installed.

- **Type of Aquifer to be Sampled.** Use the dropdown box to select either "unconfined" or "semi-confined/confined" for the type of aquifer to be sampled. Well installations into confined or semi-confined aquifers typically require a protective casing to be installed around the well through the unconfined aquifer. Therefore, installation of wells into confined or semi-confined aquifers requires additional stainless steel casing (diameters are indicated in Table 5-11) and larger augers for the drilling equipment.

- **Unconfined Aquifer Thickness.** Input thickness only if wells are to be installed in a confined or semi-confined aquifer. This parameter specifies the length of the protective outer casing.

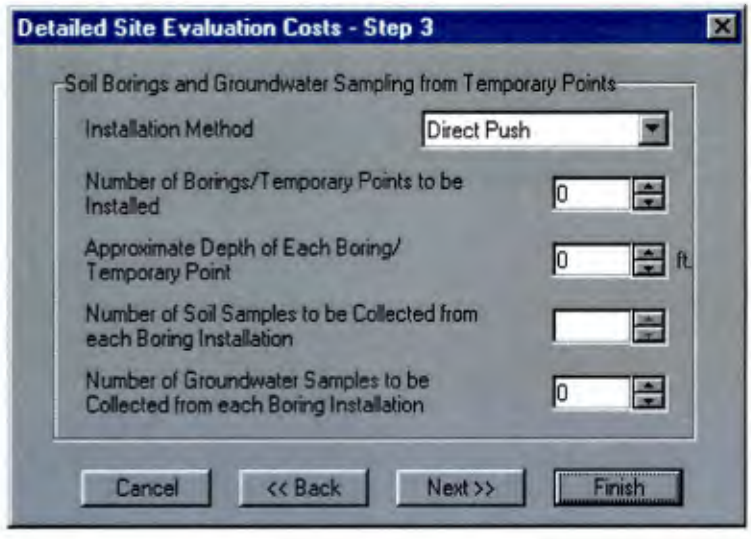
*Additional Comments*

The number of drums required to contain the drill cuttings are estimated using the following equation:

$$\text{Number of drums} = L \times BF \times \frac{\pi D^2}{4} \times 7.481 \frac{\text{gal}}{\text{ft}^3} \times \frac{\text{drum}}{55\ \text{gal}} \qquad (5\text{-}1)$$

where: L = Total length of drilling = (depth to top of screened interval + screen length of wells to be installed) × number of wells
BF = Bulking factor = 1.3
D = Borehole diameter (see Table 5-11).

## 5.5 SOIL BORINGS AND GROUNDWATER SAMPLING FROM TEMPORARY POINTS DIALOG BOX



*Location*

This dialog box appears when estimating costs for soil borings and groundwater sampling from temporary points during Preliminary Assessment, Detailed Site Evaluation, and/or Performance Monitoring and Site Closure.

*Features and Assumptions*

- **Installation Method.** Select the method for soil borings and temporary groundwater sampling installations and to select the lithologic data collection method. The options are "direct push," "hollow stem auger," and "CPT [cone penetrometer testing]," If CPT is chosen, no soil analytical samples can be collected and no input value will be accepted by the program for that parameter.

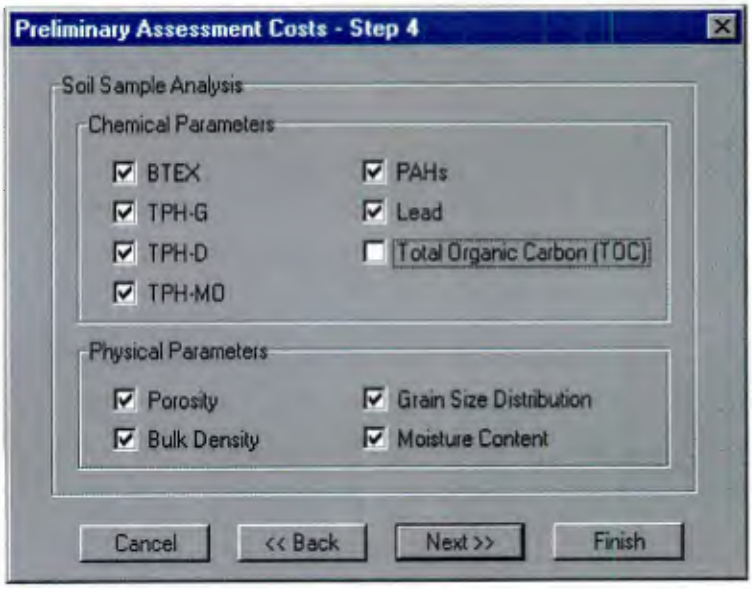
- **Number of Borings/Temporary Points to be Installed.** Input the number of soil borings and/or temporary groundwater sampling points to be installed.

- **Approximate Depth of Each Boring/Temporary Point.** Input the approximate depth of each boring/temporary point to be drilled.

- **Number of Soil Samples to be Collected from each Boring Installation.** Input the estimated number of soil samples to be collected from each boring installation. If sampling requirements are unknown, use two samples per boring installation as an estimate.

- **Number of Groundwater Samples to be Collected from each Boring Installation.** Input the number of groundwater samples to be collected from each boring or temporary groundwater sampling point location. If sampling requirements are unknown, use one sample per boring/temporary point as an estimate.

## 5.6 SOIL SAMPLE ANALYSIS DIALOG BOX



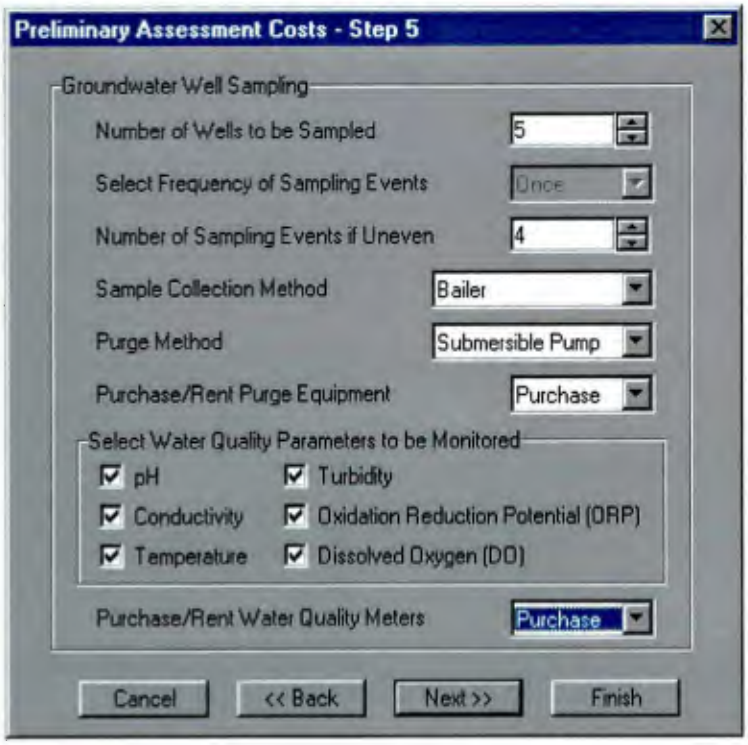
*Location*

This dialog box appears when estimating costs during Preliminary Assessment, Detailed Site Evaluation, and/or Performance Monitoring and Site Closure. If no soil samples are specified in both the Well Installation dialog box and the Soil Borings and Groundwater Sampling from Temporary Points dialog box, this dialog box will not appear.

*Features and Assumptions*

Check the box next to each chemical and/or physical soil analysis parameter required for the cost estimate. It is assumed that soil samples will be collected using a split-spoon sampling device.

## 5.7 GROUNDWATER WELL SAMPLING DIALOG BOX




*Location*

This dialog box appears when estimating costs for groundwater well sampling during Preliminary Assessment, Detailed Site Evaluation, and/or Performance Monitoring and Site Closure.

*Features and Assumptions*

- **Number of Wells to be Sampled.** Input the estimated number of wells that will be sampled during the associated task.

- **Select Frequency of Sampling Events.** Use the dropdown box to select the frequency of groundwater well sampling. Options for frequency of sampling are "once", "monthly", "quarterly", "bi-annually", and "annually". For the Preliminary Assessment, the program requires and automatically inputs a frequency selection of once.

- **Number of sampling events if uneven.** Use this function if sampling frequency is uneven.

- **Sample Collection Method.** Use the dropdown box to select either "bailer" or "peristaltic pump" as the sample collection method.

- **Purge Method.** Use the dropdown box to select the well purging method. The options for purging the wells prior to sampling are "bailer", "submersible pump", or "peristaltic pump".

- **Purchase/Rent Purge Equipment.** Use the dropdown box to indicate how to cost the groundwater purging equipment. The options given in the program are "rent", "purchase", or "don't need". If bailer is selected as the purge method, the program automatically assumes that the bailers will be purchased.

- **Select Water Quality Parameters to be Monitored.** Check the box next to each water quality parameter that is to be monitored while purging the groundwater well. It is recommended that all parameters be monitored because they may help to support the occurrence of RNA.

- **Purchase/Rent Water Quality Meters.** Use the dropdown box to indicate how to cost the water quality meters. The options given in the program are "rent," "purchase," or "don't need." The program automatically selects the most cost-efficient combination of meters to be rented or purchased, although the user may change the input as required or preferred.

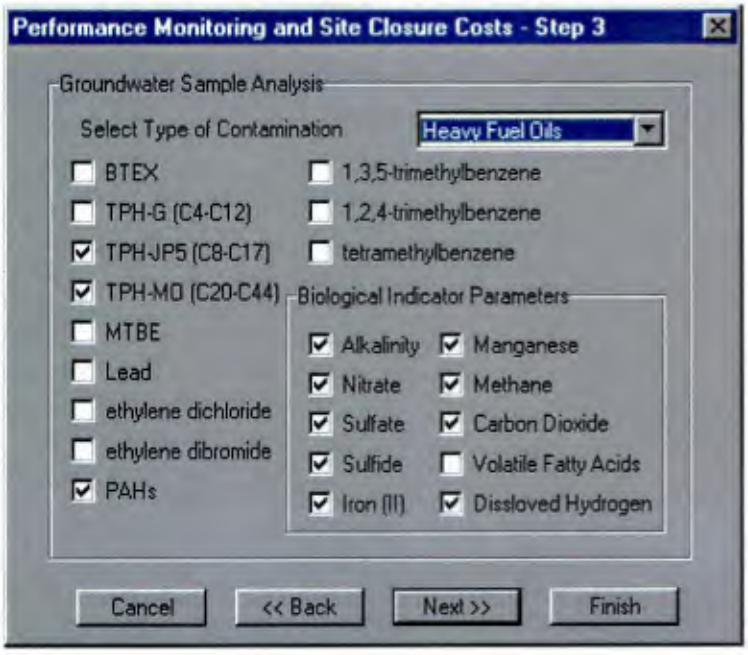
***Additional Comments***

The number of drums required to contain the purge water are estimated using Equation 5-2:

$$\text{Number of drums} = L \times PV \times \left[ \left( PS \times \left( \frac{\pi D_B^2}{4} - \frac{\pi D_W^2}{4} \right) \right) + \frac{D_W^2}{4} \right] \times \frac{7.481\,\text{gal}}{\text{ft}^3} \times \frac{\text{drum}}{55\,\text{gal}} \qquad (5\text{-}2)$$

Where:
- $L$ = Length of screened section = 10 feet if not specified previously
- $PV$ = Number of borehole volumes to be purged = 2
- $PS$ = Pore space in sand pack = 0.3
- $D_B$ = Borehole diameter (see Table 5-11)
- $D_W$ = Well diameter = 4 inches if not specified previously.

## 5.8 GROUNDWATER SAMPLE ANALYSIS DIALOG BOX




*Location*

This dialog box appears when estimating costs during Preliminary Assessment, Detailed Site Evaluation, and/or Performance Monitoring and Site Closure. If no soil samples are specified in both the Groundwater Well Sampling dialog box and the Soil Borings and Groundwater Sampling from Temporary Points dialog box, then this dialog box will not appear.

*Features and Assumptions*

- **Select Type of Contamination.** Use the dropdown box to select the type of petroleum contamination that exists at the subject site. Options provided in the dropdown box are "unleaded gasolines," "leaded gasolines," "diesel/jet fuel," and "heavy fuel oils." Each dropdown box selection corresponds with a different set of chemical analytical parameters, as indicated in Table 5-12.

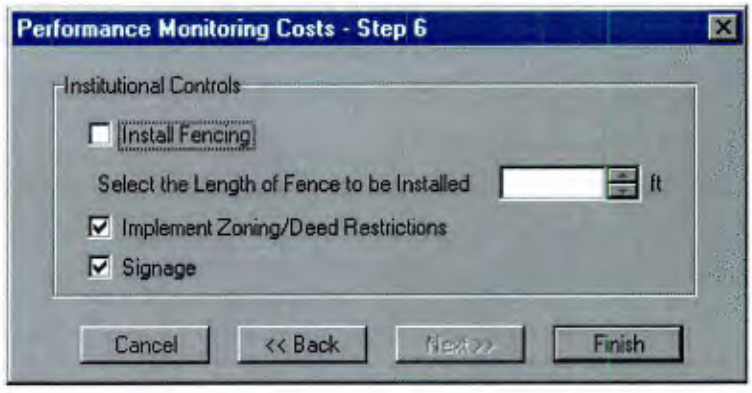
- **Chemical and Biological Indicator Parameters.** Check the box next to each groundwater analysis chemical or biological indicator parameter required for the cost estimate. Default settings assume that analyses will be performed for all biological indicator parameters except volatile fatty acids (VFA) and dissolved hydrogen.

**Table 5-12. Type of Petroleum Contamination**

| Chemical Parameter | Unleaded Gasolines | Leaded Gasolines | Diesel/ Jet Fuel | Heavy Fuel Oils |
|---|---|---|---|---|
| BTEX | x | x | x | |
| TPH-G (C4-C12) | x | x | x | |
| TPH-JP5 (C8-C17) | x | x | x | x |
| TPH-MO (C20-C44) | | | x | x |
| MTBE | x | x | | |
| Lead | x | x | | |
| Ethylene dichloride | | x | | |
| Ethylene dibromide | | x | | |
| PAHs | | x | x | x |
| 1,3,5-trimethylbenzene | | | | |
| 1,2,4-trimethylbenzene | | | | |
| Tetramethylbenzene | | | | |

TPH-MO = Total petroleum hydrocarbons quantified as motor oil.
MTBE = Methyl-*tert*-butyl ether.
PAH = Polycyclic aromatic hydrocarbon.

## 5.9 INSTITUTIONAL CONTROLS DIALOG BOX




### *Location*

This dialog box appears when estimating costs during Performance Monitoring and Site Closure.

### *Features and Assumptions*

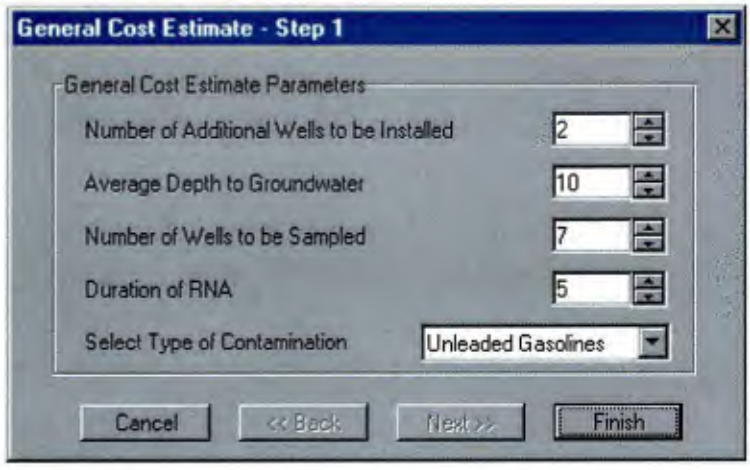
- **Install Fencing.** If fencing is required, check this box. The assumed fencing material is 6-foot-high chain link.

- **Select the Length of Fence to be Installed.** Input the estimated linear feet of fencing to be installed. This box can be accessed only if the "Install Fencing" box is checked.

- **Implement Zoning and Deed Restrictions.** Check this box if zoning and deed restrictions require implementation. Costs for this activity assume 40 hours of labor for an attorney.

- **Signage.** Check this box if installation of signs is required to control access or to warn others of hazards present at the site. Costs for this activity are estimated as a lump sum of $5,000.

## 5.10 GENERAL COST ESTIMATE DIALOG BOX




### *Location*

This dialog box appears when estimating costs for a general cost estimate.

### *Features and Assumptions*

- **Number of Additional Wells to be Installed.** Input the estimated number of additional wells to be installed. Costs associated with well installations will be included within the section detail worksheet for the Detailed Evaluation.

- **Average Depth to Groundwater.** Input the average depth from ground surface to the top of the groundwater table. This parameter helps determine costs for well installations.

- **Number of Wells to be Sampled.** Input the estimated number of wells that will be sampled. This estimate applies to both the Detailed Site Evaluation and to Performance Monitoring.

- **Duration of RNA.** Input the anticipated duration that RNA will be implemented. Costs for the first 2 years will be included within the section detail worksheet for the Detailed Site Evaluation. Costs associated with all remaining years will be included within the section detail worksheet for Performance Monitoring and Site Closure.

- **Select Type of Contamination.** Use the dropdown box to select the type of petroleum contamination that exist at the subject site. Options provided in the dropdown box include

"unleaded gasolines," "leaded gasolines," "diesel/jet fuel," and "heavy fuel oils." Each dropdown box selection corresponds with a different set of chemical analytical parameters, as indicated in Table 5-12.

- **Anticipated Travel Distance.** Specify the anticipated travel distance required for this project to estimate costs associated with travel. Options for anticipated travel distance are "local," "<500 miles," and ">500 miles." For costing purposes, it is assumed that local travel incurs no per diem or airfare costs. Travel <500 miles incurs a $100/day per diem and a $400 round trip airfare. Travel >500 miles incurs a $100/day per diem and a $700 round trip airfare.

### *Additional Assumptions*

Preliminary Assessment

- Two (2) meetings with the client and/or regulatory authorities
- A "limited" level of effort will be required to develop the preliminary site conceptual model and assess RNA
- No supporting field data will be collected during the Preliminary Assessment
- Costs will be incurred to develop a workplan for evaluation of RNA

Detailed Site Evaluation

- Additional field data will be collected with the following assumptions:
    - Screen length of all wells will be 5 feet
    - Two soil samples will be collected from each well installation
    - Two-inch-diameter schedule 40 PVC with slotted screen will be used for well installations
    - Wells will be installed using a hollow-stem auger
    - Flush-mount well surface completions will be used
    - Aquifer being sampled is unconfined
    - No soil borings or groundwater sampling will be done from temporary points
    - Soil sample analysis on soil samples collected during well installations will include the following: BTEX, TPH-G, TPH-D, TPH-MO, PAHs, lead, total organic carbon (TOC), porosity, bulk density, grain size distribution, and moisture content
    - The frequency of sampling events during the Detailed Site Evaluation will be bi-annual

- Will use peristaltic pump for sample collection
- Will use submersible pump for purge method
- Purge pump will be rented
- During sampling the following water quality parameters will be monitored: pH, conductivity, temperature, turbidity, oxidation reduction potential (ORP), and dissolved oxygen (DO)
- Water quality meters will be rented
- The following groundwater biological indicator parameters will be analyzed: alkalinity, nitrate, sulfate, sulfide, iron (II), manganese, methane, and carbon dioxide

- Data will be evaluated for spatial trends, biodegradation, and plume status
- A laboratory microcosm study will not be performed
- Data will be assessed for degradation rates, modeling, and cleanup times
- A "limited" level of effort is anticipated for computer modeling
- RNA will be compared to other technologies
- Findings from the Detailed Site Evaluation will be summarized and results reported

Performance Monitoring and Site Closure

- A Performance Monitoring Plan will be developed
- No additional groundwater wells will be installed
- Two meetings will be held with the client and/or regulatory authorities
- Status reports will be submitted annually
- Appropriate documents will be prepared for site closure
- The same number of wells that are being sampled will be abandoned
- Annual sampling events will be conducted during the Detailed Site Evaluation
- Will use peristaltic pump for sample collection
- Will use submersible pump for purge method
- Purge pump will be rented

- During sampling the following water quality parameters will be monitored: pH, conductivity, temperature, turbidity, ORP, and DO
- The following groundwater biological indicator parameters will be analyzed: alkalinity, nitrate, sulfate, sulfide, iron (II), manganese, methane, and carbon dioxide
- No fencing will be installed
- Zoning/deed restrictions will be implemented
- Appropriate signage will be installed

## 6.0 REFERENCES

Department of Navy. 1998. *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities.*

Department of the Navy. 1999.

## Table of Contents (continued)