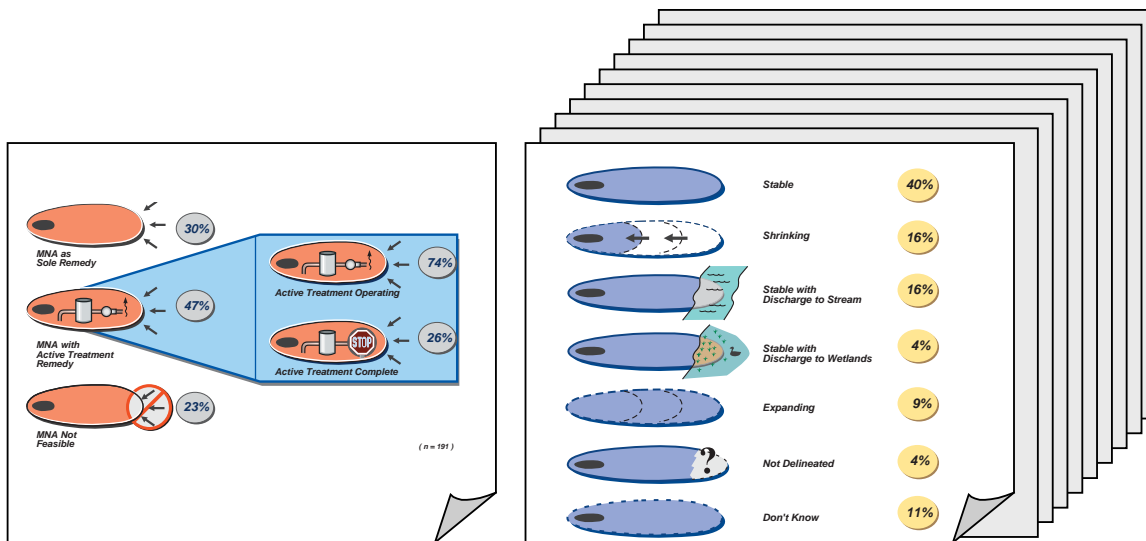


Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents

March 9, 2004



Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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March 9, 2004

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Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents

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1. Recent Historical Development of MNA/EPR for Petroleum Hydrocarbons and Chlorinated Solvents (modified from Wiedemeier and Barden, 2002)

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Overview

The Department of Energy (DOE) is sponsoring an initiative to facilitate efficient, effective and responsible use of Monitored Natural Attenuation (MNA) and Enhanced Passive Remediation (EPR) for chlorinated solvents. This Office of Environmental Management (EM) “Alternative Project,” focuses on providing *scientific and policy support for MNA/EPR*. A broadly representative working group of scientists supports the project along with partnerships with regulatory organizations such as the Interstate Technology Regulatory Council (ITRC) and the Environmental Protection Agency (EPA). The initial product of the technical working group was a summary report that articulated the conceptual approach and central scientific tenants of the project, and that identified a prioritized listing of technical targets for field research. This report documented the process in which: 1) scientific ground rules were developed, 2) lines of inquiry were identified and then critically evaluated, 3) promising applied research topics were highlighted in the various lines of inquiry, and 4) these were discussed and prioritized. The summary report will serve as a resource to guide management and decisionmaking throughout the period of the subject MNA/EPR Alternative Project. To support and more fully document the information presented in the summary report, we are publishing a series of supplemental documents that present the full texts from the technical analyses within the various lines of inquiry (see listing). The following report – documenting our “Historical and Retrospective Survey of Monitored Natural Attenuation” -- is one of those supplemental documents.

Summary Report:

Natural and Passive Remediation of Chlorinated Solvents: Critical Evaluation of Science and Technology Targets, WSRC-TR-2003-00238

Supplemental documents:

Baseline Natural Attenuation Processes: Lines of Inquiry Supporting Monitored Natural Attenuation of Chlorinated Solvents, WSRC-TR-2003-00329

Potential Enhancements to Natural Attenuation: Lines of Inquiry Supporting Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00330

Multiple Lines of Evidence Supporting Natural Attenuation: Lines of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00331

Potential Enhancements to the Characterization and Monitoring of Natural Attenuation: Lines of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00332

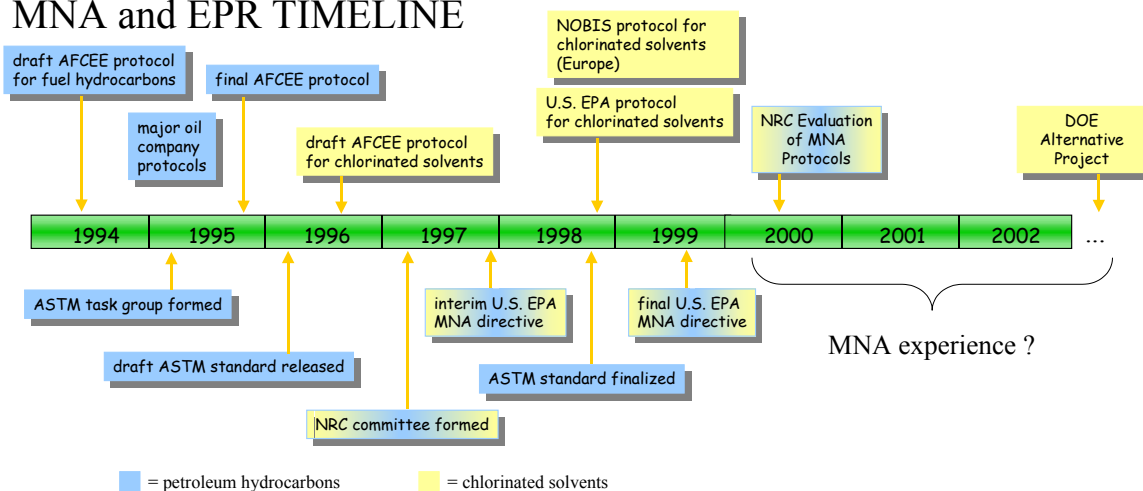
Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00333

Historically, the recognition, evaluation and reliance on natural processes for remediation and final polishing of contaminated sites has been problematical. Over the past fifteen years, however, significant progress has been made due to the efforts of regulatory and federal agencies such as the Environmental Protection Agency (EPA) and the Department of Defense (DOD), and others. This progress has taken the form of regulatory protocols and case studies from attempted implementation. To be successful, the DOE Alternative Project must link to, and build upon, this progress. A critical component of responsibly advancing the technical basis for the use of MNA/EPR was documenting this historical development and assessing, using a retrospective survey, what has worked and where there are barriers to implementation.

Early variants took the form of “alternate concentration limits” (ACLs) or “mixing zones”. These concepts provided a useful tool for relatively low risk sites and were based on modeling – the goal was to calculate a target concentration in the plume that would not result in an exceedence of an applicable or appropriate standard at an agreed exposure location. The guidelines for ACL modeling did not emphasize the full range of natural attenuation and remediation mechanisms. As a result, scientists, regulators and policymakers began a process to develop improved guidelines that would encourage responsible and disciplined use of remediation and site management strategies that rely on natural processes. These efforts were squarely focused on natural attenuation processes and lead to the definition and understanding of the term “MNA” (EPA, 1998 and EPA, 1999). The efforts were customized, as appropriate, to major classes of common contaminants. This allowed the most applicable mechanisms to be identified and specific guidelines and protocols to be established for the most widespread problems. It is particularly instructive to examine the timing of protocol development efforts for various classes of organic contaminants.

Figure 1 provides a time line for the development and regulatory protocol development for monitored natural attenuation (MNA) for petroleum hydrocarbons and for chlorinated solvents. It is clear from the timeline that development of MNA for petroleum hydrocarbons, because the underlying processes are inherently more robust and simple, occurred earlier than the development of MNA for chlorinated volatile organic contaminants (CVOCs). Moreover, MNA of petroleum hydrocarbons is now widely accepted and used. Protocol development for CVOCs has proven to be more complex and the viability, robustness and utility of the CVOC protocols has not been documented. How have they worked? How many sites have they been applied to? What percentage of those sites met the requirements? What parts of the protocol have been most useful in practice? What parts of the protocol have been least useful? Obtaining answers to these types of questions is an absolute requirement for any effort whose goal is to build on and contribute to this historical process and to the positive evolution of MNA/EPR. The answers to key questions are key input that will help determine the most promising research and regulatory path. Of particular interest are experiences in the period since 1998/1999 – after the EPA regulatory protocols and directives were released. A few historical evaluations have been performed – normally covering a case study or a few sites. To assist in developing a target list of critical science and technology needs and issues to support advancing CVOC protocols, a general historical survey was performed.

MNA and EPR TIMELINE



Modified from chart provided by Todd Wiedemeier (2000)

Figure 1. Recent Historical Development of MNA/EPR for Petroleum Hydrocarbons and Chlorinated Solvents (modified from Wiedemeier and Barden, 2002)

A retrospective “Historical Analysis of MNA” survey was developed to gain a better understanding of the application of MNA at sites affected with chlorinated solvents. The survey sought to provide insights into the remediation professional’s general experience with MNA and to gather site-specific data regarding the implementation of MNA as a remedy of a particular CVOC plume. The survey was distributed to approximately 230 remediation professionals in industry, government, and academia with experience in the field of MNA.

The survey was divided into two parts: part A) general request for information about MNA experiences and B) more detailed data on a specific site. Part A consisted of four questions and attempted to gather high level information. How many sites? How successful? Typical size? Typical cost? Part B consisted of 39 questions requesting data for a specific plume where MNA was applied as the remedy, either solely or as a component of other active treatment. These questions explored many topics including the types of monitoring and modeling, the status of the effort, and the like.

Survey data was received from 30 individuals for a total of 178 waste sites; all respondents provided Part A data, and site-specific data was received for 42 individual chlorinated solvent plumes. Data from Part A and Part B are summarized in and interpreted in the attached report that contains the full text and interpretation from this line of inquiry. The results provided interesting and useful insights as summarized below.

Part A:

- MNA was determined to be feasible as a remedy at over 75% of the sites where the application of MNA was evaluated (30% sole remedy, 47% with other treatment). Importantly, MNA was determined to be infeasible at about 23% of the sites and follow-up contacts will be conducted to elicit the reasons.
- At sites where MNA is used with an active treatment, the active treatment is still in operation at approximately 74% of those sites.
- The average cost of the entire initial MNA study was reported to be about \$177,000 and results ranged from \$10,000 to \$750,000.
- The average annual cost for monitoring an MNA site was found to be \$33,000 with a range of \$3,000 to \$150,000.
- Nearly half of the respondents reported that the typical size of a chlorinated solvent plume where MNA is utilized in the remedial scheme is 10 to 50 acres, while 30% and 23% reported the average size to be less than 10 acres and greater than 50 acres, respectively.

Part B:

- MNA is used as a remedy at a variety of industrial sites with a broad range of processes.
- The 1998 EPA protocol (EPA, 1998 and 1999) was most often referenced as the guideline for MNA implementation (36%). Notably, almost 27% used a site specific protocol. Other protocols used as the basis for the reported sites included: 16% state protocol, 18% other, and 4% National Research Council (NRC) MNA review (NRC, 2001).
- Slightly more than 70% of respondents stated that anaerobic degradation is the primary natural attenuation process occurring in the plume, while the remaining attenuation processes each accounted for less than 7%
- A variety of geochemical indicators are reportedly used to assess MNA, but over 90% rely on the presence of biodegradation daughter products.
- Computer models of various types were used to evaluate MNA at 56% of the sites. The most common model used was BIOCHLOR.

-
- The timeframe for remediation was estimated at over 60% of the sites, and most (68%) expect remediation goals to be achieved in less than 30 years. This result was surprising to the technical working group (TWG) and suggests that current conceptual models of MNA may be overly optimistic.
 - For approximately half the plumes reported, TCE is the original contaminant released. PCE follows at 36% of sites, with releases of cis-DCE, vinyl chloride, 1,1,1-TCA and 1,2-DCA also reported.
 - Most plumes evaluated have a maximum length of 1000 to 5000 feet, an area of 1 to 10 acres.
 - 34% of the MNA sites were less than 100 feet from a downgradient discharge.
 - The respondents classified the plumes as stable or shrinking at 56% of the sites. Interestingly, the plumes were classified as expanding for 9% of the sites and discharging for 20% of the sites.
 - The most important lines of evidence in documenting MNA were concentration decreases and geochemical footprints of daughter products.

In addition to the survey, past regulatory and peer review perspectives related to MNA/EPR were evaluated. Several key milestones where regulatory protocols and guidance directives, as well as independent scientific evaluations, were completed are evident in the MNA/EPR timeline presented above (Figure 1). These critically important enabling documents are discussed below as they relate to future science and technology development / prioritization efforts.

The first step in the decision-making process for use of MNA/EPR at a particular site is to determine the regulatory program or programs under which the cleanup will be conducted and to establish what the cleanup goals are for that site. Cleanup goals will typically include both intermediate (shorter-term) goals as well as the ultimate (final and/or longer-term) cleanup goals for the site. For federal cleanup programs, such as RCRA Corrective Action or Superfund, *intermediate goals* will typically include preventing contaminants from reaching human and environmental receptors, controlling sources, preventing plume migration, and other goals needed to protect human health or the environment. *Ultimate goals* for these federal programs will typically include returning the contaminant plume to cleanup levels appropriate for potential beneficial uses of the ground water, which in most cases are federal and state drinking water standards. (Note that the term “cleanup goal” can sometimes be misinterpreted as a desired target rather than a regulatory requirement. For this reason, the term remedial action objective (RAO) is used in EPA Superfund guidance when referring to a required outcome. In this document, “cleanup goal” is intended to have the same meaning and is used in place of the term “remedial action objective.”)

EPA’s Office of Solid Waste and Emergency Response (OSWER) finalized the policy directive: “Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites” in April 1999, as shown on the timeline in Figure 1. In developing this DOE document, the authors have assumed that federal and state cleanup programs will consult and follow the guidelines established in the EPA policy when evaluating proposals for use of MNA as a component of the remedy at a particular site. For this reason,

users of this document are encouraged to become familiar with the EPA directive. Also, key elements of the EPA policy directive are highlighted below:

- MNA should *not* be considered a “no action,” “default” or “presumptive” remedy.
- Use of MNA should *not* result in plume migration or impacts to receptors that would be “*unacceptable to the overseeing regulatory authority.*”
- Selection of MNA should be based on thorough site characterization and comparison with other cleanup methods.
- In general, MNA should be used with other cleanup measures or as follow-up to such measures (e.g., source control, pump and treat [P&T] of plume hot spots).
- The time frame for MNA to attain site-specific cleanup goals should be “reasonable” when compared to the time required by active methods.
- A contingency remedy should be included when selection of MNA was based mostly on predictive analysis.
- Progress of an MNA remedy should be carefully monitored.
- A remedy is *not* considered complete until cleanup objectives have been met.

A review by the National Research Council of the National Academy of Sciences (NRC, 2001) generally supported the concepts of MNA as articulated by EPA. Some of the key chlorinated solvent related conclusions emerging from this independent effort, and some of the alternative recommendations included:

- Community groups are generally wary of MNA as a remedy. Stakeholders often want to be convinced that dilution is not the primary process and that some form of contaminant destruction is in place.
- Community groups should be involved early in the decision process.
- Decreases in concentration may not provide sufficient basis for selecting MNA. Data documenting attenuation mechanisms are also needed.
- Greater level of effort is needed to document MNA at complex sites.
- A long-term monitoring plan, including a contingency plan, should be specified for every MNA remedy.
- Future protocols should minimize use of "scoring systems" for decisions on MNA remedies.

It is clear, from the historical survey and from the regulatory and review documentation that MNA is a promising tool and that there has been significant success in implementation since the publication of protocols in 1998 and publication of an OSWER Directive in 1999. The retrospective analysis provided some clear indications of approaches that have worked, approaches that have not worked, and the regulatory framework that govern any MNA implementation. This information, in turn is a critical factor in determining and prioritizing future science and technology efforts.

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Attachment
Full Text of Line of Inquiry

Performance of MNA Remedies at Chlorinated Solvent Sites

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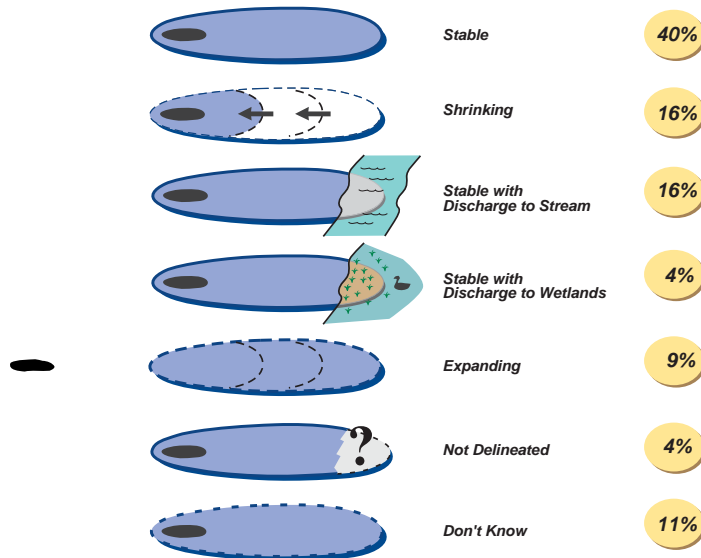
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PERFORMANCE OF MNA REMEDIES AT CHLORINATED SOLVENT SITES



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**PERFORMANCE OF MNA REMEDIES AT
CHLORINATED SOLVENT SITES**

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Aiken, South Carolina

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PERFORMANCE OF MNA REMEDIES AT CHLORINATED SOLVENT SITES

Savannah River Technology Center
Aiken, South Carolina

LIST OF ACRONYMS AND ABBREVIATIONS

AFCEE	Air Force Center for Environmental Excellence
BTEX	benzene, toluene, ethylbenzene, xylenes
CAH	chlorinated aliphatic hydrocarbon
COC	constituent of concern
COD	chemical oxygen demand
CVOC	chlorinated volatile organic compound
DCA	dichloroethane
DCE	dichloroethene
DCP	dichloropropane
DGGE	denaturing gradient gel electrophoresis
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DOE	Department of Energy
LNAPL	light nonaqueous phase liquid
MCL	Maximum Contaminant Level
mg/L	milligrams per liter
MNA	monitored natural attenuation
NA	natural attenuation
ORP	oxidation reduction potential
OSWER	Office of Solide Waste and Emergency Response
PCA	tetrachloroethane
PCE	perchloroethene
rDNA	recombinant deoxyribonucleic acid
TCA	trichloroethane
TCE	trichloroethene
TOC	total organic carbon
ug/L	micrograms per liter
US EPA	United States Environmental Protection Agency
VC	vinyl chloride
VOC	volatile organic compound

1.0 EXECUTIVE SUMMARY

As requested by the Savannah River Technology Center, Groundwater Services, Inc. (GSI), has conducted a historical analysis of Monitored Natural Attenuation (MNA) application at chlorinated solvent sites. The objective of the analysis was to document trends, characteristics, successes, and barriers in the use of MNA as a remedy at chlorinated solvent sites. The analysis consisted of the following: i) a review of recent literature regarding application of natural attenuation at chlorinated solvent sites, ii) a review of regulatory and industry guidance directing evaluation and implementation of MNA as a remedy at chlorinated solvent sites, and iii) a historical survey distributed to MNA experts, which requested data relating to the evaluation and implementation of MNA at chlorinated solvent sites.

Case Study Review. An extensive search of online journals, government program websites, scientific literature databases, and internet search engines generated 20 case studies on MNA of chlorinated solvents at field sites. Efforts were focused on studies issued following release of the US EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* in September 1998 (US EPA, 1998). Review of the case studies produced the following key points:

- Anaerobic biodegradation processes were a key factor at nearly all case study sites;
- A “lines of evidence” approach, as described in the US EPA protocol, was used to evaluate natural attenuation at most sites;
- Computer modeling was implemented as part of the MNA evaluation at half the case study sites, and was typically used to predict plume stability or estimate remediation time frame;
- Only 2 sites of the 20 sites reviewed indicated the MNA remedy had been approved by regulators, however 4 additional sites suggested MNA would be applied as the proposed remedy;
- MNA was excluded as a potential remedy at 3 case study sites because of unacceptable remediation time frames;
- *cis*-DCE “stall” was reportedly a problem at 2 of the 3 case study sites where the estimated remediation time frame was considered too long.

Protocol Review. The literature search generated 12 protocols providing guidance on policy and/or technical elements of applying Monitored Natural Attenuation as a remedy at chlorinated solvent sites. Review of the protocols produced the following key points:

- Nearly all protocols are modeled after the US EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*;
- Three lines of evidence described in the US EPA protocol should be used to demonstrate the occurrence of natural attenuation at field sites. The three lines of evidence include:
 - i) demonstration of concentration trends that indicate temporal decreases in contaminant mass or concentration;
 - ii) geochemical and hydrogeologic data evidencing the natural attenuation processes active at the site; and the rate at which natural attenuation processes reduce CVOC concentrations; and

- iii) data from field or microcosm studies that demonstrate natural attenuation processes and their ability to degrade contaminants at the site;
- Many protocols also implement the analytical screening system, described in the US EPA protocol, as an initial assessment of the likelihood of using MNA as a remedy.

Historical Survey. The historical survey was intended to gain insights on how MNA projects at chlorinated solvent sites were being conducted and how successful MNA had been. A two-part survey approach was utilized:

- Part A of the survey requested information regarding the respondent's general experience in evaluation of how MNA was applied to the entire portfolio of chlorinated solvent sites where MNA was considered;
- Part B requested detailed data from a specific solvent site where MNA was applied either as the sole remedy or was incorporated into a remedial scheme.

A short follow-up survey was also conducted to satisfy data gaps existing from the initial questionnaire. Results from the historical survey are summarized below:

PART A:

- 34 MNA experts provided general data regarding MNA evaluation for 191 chlorinated solvent sites.
- MNA was determined a possible remedy, either solely or as a component of the remedy, at over 75% of all sites evaluated (sole remedy at 30%, with active treatment at 47%).
- Plume instability and unacceptable remediation time frame were leading factors excluding use of MNA.
- Average cost of an initial MNA evaluation was \$177,000, while annual monitoring costs averaged \$33,000 per year.

PART B:

- Site-specific data was provided for 45 chlorinated solvent plumes where MNA was being used either as a sole remedy or part of a multi-technology remedy.
- The 1998 US EPA protocol was most often referenced as the guideline for MNA implementation (36%). Notably, about 27% used a site specific protocol.
- Over 70% of respondents stated that anaerobic biodegradation is the primary natural attenuation process occurring in the plume.
- A variety of geochemical indicators are reportedly used to assess MNA, but over 90% rely on the presence of biodegradation daughter products.
- Computer models of various types were used to evaluate MNA at 60% of the sites. The most commonly used model was BIOCHLOR.
- The timeframe for remediation was estimated at nearly 60% of the sites, and most (68%) expect site remediation goals to be achieved in less than 30 years.
- Most plumes evaluated have a maximum length of 1000 to 5000 feet, an area of 1 to 10 acres, and contain maximum chlorinated solvent concentrations of 10 to 100 mg/L.
- 34% of the MNA sites were less than 100 feet from a downgradient surface water discharge, with 20% actually discharging.

- The respondents classified the plumes as stable or shrinking at 56% of the sites. The plumes were classified as expanding for 9% of the sites.
- Sites with maximum solvent concentrations exceeding 10 mg/L often relied on an active treatment remedy to enhance natural attenuation.
- MNA was most commonly used as a sole remedy at sites with groundwater seepage velocities less than 20 feet/year and plumes less than 500 feet in length.
- MNA has been approved by regulators at nearly half the sites (22 sites), while the remedy is still being considered at 44% of sites.

2.0 INTRODUCTION

Natural attenuation processes, such as dispersion, sorption, biodegradation, hydrolysis, volatilization, and dilution, occur to varying degrees at every site affected with chlorinated solvents. These processes occur naturally, in-situ, and act to decrease the mass or concentration of contaminants in the subsurface. Considerable research and evaluation of natural attenuation processes in recent years has led to an increased understanding of chlorinated solvent attenuation, and therefore an increasing number of sites relying on these processes to achieve site-specific remedial goals in a reasonable time frame.

As the understanding of natural attenuation processes increased and the incidence of Monitored Natural Attenuation (MNA) remedies being applied to contaminated sites also increased, regulatory and other agencies began to issue guidance on the application of MNA for specific classes of organic compounds. Protocols were first issued regarding the implementation of MNA as a remedy at sites affected with fuels and their related hydrocarbons since natural attenuation processes for these compounds were well documented and understood. A variety of protocols have since been issued that define procedures for applying MNA at chlorinated solvent sites. Due to the complexity of natural attenuation processes governing the fate of chlorinated solvents, considerable benefit would result from a review of application of the protocols at actual field sites where MNA was being applied to remedy chlorinated solvent contamination. In order to continue moving forward in the evaluation and implementation of MNA at chlorinated solvent sites, a historical analysis documenting trends, characteristics, successes, and barriers in the application of MNA as a remedy was performed.

A detailed survey of experts in the application of natural attenuation at chlorinated solvent sites was conducted. The survey was comprised of a two-part electronic questionnaire distributed via email. Part A of the survey requested information regarding the respondent's general experience in evaluation of how MNA was applied to the entire portfolio of chlorinated solvent sites where MNA was considered, while Part B requested detailed data from a specific solvent site where MNA was applied either as the sole remedy or was incorporated into a remedial scheme. A short follow-up survey was also conducted to satisfy data gaps existing from the initial questionnaire. In addition to the survey, a review of recent literature regarding application of MNA at chlorinated solvent sites and protocols issuing guidance on the implementation of MNA at chlorinated solvent sites at both the national and state levels was also conducted.

Of approximately 230 survey recipients, 34 individuals replied and provided general information for 191 sites where MNA was evaluated, and site-specific data for 45 chlorinated solvent plumes being managed by MNA. Data from 20 case studies on MNA of chlorinated solvents at field sites, and 12 technical protocols on the subject were reviewed. Data from Part A of the survey indicates that MNA was a feasible remedy (either as a sole remedy or part of a larger remedy) at over 75% of the sites evaluated. Several trends from the site-specific Part B data included: i) most sites used either the US EPA technical protocol or a site-specific protocol to evaluate MNA; ii) observance of degradation products and concentration trends of parent products were relied on heavily to indicate natural attenuation; iii) anaerobic biodegradation was the most important process at over 70% of sites, with other attenuation processes each being dominant at less than 7% of sites; iv) computer models were used to evaluate the plume at over 40% of MNA sites; and v) remediation timeframe was estimated as less than 30 years for 68% of sites.

The organization of this report is as follows:

- Section 3.0 provides a review of literature relevant to the subjects of MNA application at chlorinated solvent sites, and technical protocols issuing guidance on evaluation and implementation of MNA;
- Section 4.0 details survey methods utilized to collect MNA related data from experts in the field;
- Section 5.0 presents results of the survey;
- Section 6.0 summarizes key conclusions;
- Section 7.0 lists references cited;
- Appendix A provides a copy of the original questionnaire; and
- Appendix B lists references of MNA reports that have been issued by survey respondents.

3.0 LITERATURE REVIEW

A review of case studies documenting the application of Monitored Natural Attenuation (MNA) at chlorinated solvent sites in published literature was conducted. In addition, protocols issuing guidance on the implementation of MNA at chlorinated solvent sites at both the national and state levels were examined. The goals of this review are: i) to examine trends in MNA evaluation and implementation in the published literature; ii) to evaluate successes and failures in MNA evaluation at affected sites; and iii) to compare and contrast various protocols establishing guidelines for implementation of MNA at chlorinated solvent sites.

An extensive search of online journals, government program websites, scientific literature databases, and internet search engines (see complete list of databases and websites searched on Table 3.1) was performed. The search focused on studies published following the issuance of the US EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* in September 1998 (US EPA, 1998).

3.1 Case Study Review

A review of recent scientific literature generated 21 case studies documenting the evaluation and/or implementation of MNA as a remedy at sites affected with chlorinated volatile organic compounds (CVOCs) that have been published following the 1998 US EPA Technical Protocol. Key information from each case study (i.e., site location, primary CVOC released, primary natural attenuation process occurring, MNA indicators evaluated, and key findings) is summarized on Table 3.2. Additionally, particular attention in the "Key Findings" of each case study listed on Table 3.2 was given to: i) lines of evidence used to evaluate MNA; ii) protocols referenced; iii) computer models used to evaluate the plume; and iv) regulatory approval.

Most sites documented in the literature review are located in the continental United States, with exceptions being, a site in Alaska, a site with a plume extending from the US into Canada, and a site located in northern Italy.

All but four sites reviewed listed trichloroethene (TCE), either solely or mixed with other chlorinated solvents, as the primary solvent released at the site. TCE was the sole contaminant released at nearly 40% of sites, and was mixed with 1,1,1-trichloroethane (TCA) at 25% of sites, with perchloroethene (PCE) at 10% of sites, and with TCA, PCE, and 1,1,2,2-tetrachloroethane (PCA) at one site. PCE was the primary CVOC at two sites, while PCA, 1,2-dichloroethane (DCA), and 1,2-dichloropropane (DCP) were the primary CVOC released at one site each.

18 of the 21 sites reviewed provided maximum CVOC concentration data for the site. The maximum CVOC concentrations ranged from less than 1 mg/L to nearly 10,000 mg/L. Only three sites (17%) indicated maximum concentrations greater than 100 mg/L, while 5 sites reported less than 1 mg/L (28%) and 6 sites listed between 10 and 100 mg/L (33%). The remaining 22% (4 sites) indicated maximum CVOC concentrations ranging from 1 to 10 mg/L.

Anaerobic biodegradation processes (i.e. reductive dechlorination) overwhelmingly accounted for the primary mechanism of natural attenuation at the sites reviewed (95%). Several studies indicated that aerobic biodegradation also accounted for substantial attenuation, particularly of the lesser chlorinated compounds *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (Lenczewski,

TABLE 3.1
MNA LITERATURE REVIEW:
DATABASES AND WEBSITES SEARCHED

Performance of MNA Remedies at Chlorinated Solvent Sites
 Savannah River Technology Center, Aiken, South Carolina

<i>Online Journals</i>
Environmental Science and Technology
Bioremediation Journal
Ground Water
<i>Government Program Websites</i>
U.S. EPA Clu-In
U.S. EPA Record of Decision System (RODS)
Remediation Technologies Development Forum (RTDF)
Air Force Center for Environmental Excellence (AFCEE)
Strategic Environmental Research and Development Program (SERDP)
Environmental Security Technology Certification Program (ESTCP)
U.S. Army Environmental Center (USAEC)
Interstate Technology Regulatory Council (ITRC)
U.S. Department of Energy Office of Environmental Management
<i>STN Databases</i>
National Technical Information Service (NTIS)
Computerized Engineering Index (COMPENDEX)
PASCAL
Chemical Engineering and Biotechnology Abstracts (CEABA-VTB)
Federal Research In Progress (FEDRIP)
Biotechnobase (BIOTECHNO)
<i>International Databases and Websites</i>
Network for Natural Attenuation in Groundwater and Soil (NNAGS)
NATO Committee on the Challenges of Modern Society (CCMS)
Network for Industrially Contaminated Land in Europe (NICOLE)
<i>Books</i>
Natural Attenuation of Fuels and Chlorinated Solvents (Wiedemeier et al, 1999)
Natural Attenuation of Environmental Contaminants (Leeson et al, 2001)
<i>Internet Search Engines and Other Websites</i>
Google
Bioremediation Discussion Group

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Lenczewski et al., 2003	Oak Ridge, TN	TCE; Max conc. = 0.01 mg/L	Anaerobic and aerobic biodegradation	Organic degradation products, methane, ethane, ethene, DO, Fe (II), sulfide, sulfate, chloride, microbial counts and 16s rDNA analysis	Natural Attenuation of TCE in fractured shale bedrock was demonstrated through multiple lines of evidence including: i) VOC concentration and distribution, ii) appropriate redox conditions, and iii) microbial evidence. Data from approximately 30 wells were collected over a 1-yr period. VOC concentration and distribution evidence for NA was based on observation of daughter product plumes (cDCE and vinyl chloride) extending beyond the TCE plume, and increased concentrations of daughter products relative to TCE. However, a decreasing or stable concentration trend over time for TCE, a key indicator of NA, was not observed at the site. Redox conditions were determined favorable for anaerobic reductive dechlorination based on presence and distribution of Fe (II) and sulfide (i.e., same size and shape of plumes as vinyl chloride and ethene plumes). Additionally, the authors suggest that aerobic degradation occurs in localized areas, including fractured zones receiving storm water recharge and a seep near a stream.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Clement et al., 2002	Baton Rouge, LA	Various chlorinated ethenes and ethanes (incl. 1,1,2,2-tetra-chloroethane, 1,1,2-trichloro-ethane, PCE, and TCE); Max CVOC conc. > 100 mg/L	Anaerobic biodegradation	Organic degradation products, TOC, methane, ethane, ethene, dissolved H ₂ , DO, ORP, pH, alkalinity, Fe (II), sulfate, sulfide, CO ₂ , chloride, volatile fatty acids, BTEX	The use of MNA as a remedy for a chlorinated solvent site affected with significant DNAPL accumulation was evaluated according to the U.S. EPA screening protocol (US EPA, 1998). Data from 4 monitoring wells located within the source area over a period of 3 years was used in the evaluation. Geochemical indicators at all monitoring points indicated that conditions were favorable for biological anaerobic reductive dechlorination. A detailed conceptual site model was developed, and site-specific hydrogeologic data, chemical data, and biological first-order decay rates were generated for use in the BIOCHLOR fate-and-transport model. Results from three BIOCHLOR simulations indicated that the chlorinated constituents were attenuating at a rate faster than would be expected from adsorption-related attenuation processes, and that the dissolved plume would become stable prior to constituents reaching identified exposure points. Based on EPA screening criteria, MNA was determined to be a feasible remedy at the site.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Dinicola et al., 2002	Naval Undersea Warfare Center (OU 1), Division Keyport, WA	TCE; Max conc. = ~100 mg/L	Anaerobic biodegradation	Organic degradation products, TOC, methane, ethane, ethene, dissolved H ₂ , DO, Eh, pH, alkalinity, Mn, Fe (II), total Fe, H ₂ S, sulfate, chloride, oxygen-18, hydrogen-2	MNA was assessed over a 10-year period (1991-2000) as a remedy for treatment of a TCE plume beneath a former landfill that discharges to surface water. MNA was evaluated by examining temporal trends in chlorinated VOC data over the 10-year period, and by examining changes in VOC concentrations and redox sensitive compounds along groundwater flowpaths. Both lines of evidence indicated that natural attenuation was occurring at the site; however, natural attenuation alone was determined to be not effective to meet remediation goals for the site. Two poplar plantations were planted on the landfill in 1999 in attempt to enhance remediation of the shallow groundwater, but the effect of phytoremediation on chlorinated VOCs has not yet been determined.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Witt et al., 2002	Dover AFB, Dover, DE	PCE and TCE; Max PCE = 2.5 mg/L; Max TCE = 3.1 mg/L	Anaerobic biodegradation in anaerobic zone; Aerobic biodegradation in aerobic zone	Organic degradation products, TOC, total inorganic carbon, methane, ethane, ethene, propane, dissolved H ₂ , DO, Eh, ORP, pH, Fe (II), Mn, sulfide, sulfate, chloride, nitrogen- ammonia, nitrogen- nitrate, BTEX	MNA as potential remedy of a PCE and TCE plume was demonstrated using the three-tier documentation guidance issued by EPA (US EPA, 1999). The lines of evidence required by this EPA guidance are: i) field-scale loss of contaminants, ii) proper geochemical indicators of NA; and iii) microbiological evidence. Data was collected from approximately 40 monitoring points over a 2-yr period to support the MNA study. Concentration vs. distance data, statistical analysis, and stable carbon isotope data indicate that PCE and TCE are both degrading at the field-scale. Geochemical and biogeochemical indicators at the site evidenced two distinct zones where biological attenuation is occurring. An anaerobic zone near the source of contamination supports reductive dechlorination of chlorinated ethenes, while an aerobic zone downgradient of the source supports co-oxidation of lesser chlorinated species. Finally, reports of companion studies provide evidence through microcosm studies using groundwater from the site, that microbes at the site are capable of complete PCE and TCE transformation via the hypothesized pathways.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
US EPA, 2002	Plymouth, ME (West Site/ Hows Corner Superfund Site)	PCE; Max conc. = 32 mg/L	Anaerobic biodegradation	Not listed	This Record of Decision document reports MNA as the remedy for non-source area groundwater (defined as groundwater with VOC concentrations below 10 mg/L) underlying a former waste oil storage facility. The remedy also includes extraction and treatment of source area groundwater, long-term monitoring of nearby surface water, sediments, and groundwater to assess NA progress, residential well monitoring with a public water contingency, institutional controls preventing use of affected groundwater, and five-year reviews. The ROD was determined as interim due to a highly uncertain estimated remediation timeframe, which ranged from a minimum of 35 years to over 1,000 years.
Buss et al., 2001. In: Leeson et al., 2001.	Upper Midwest US	TCE; Max conc. = 78 mg/L	Anaerobic biodegradation and sorption	Organic degradation products, methane, ethane, ethene, DO, pH, ORP, nitrate, ammonia, nitrogen, ferrous iron, potassium, chloride, phospholipid fatty acid (PLFA) analysis, denatured gradient gel electrophoresis (DGGE)	The natural attenuation of a TCE plume in peat was evaluated. The concentrations of chloroethenes on either side of the peat deposits showed 100,000-fold reductions due to degradation and sorption. A decrease in the ratio of TCE to DCE was used to indicate reductive dechlorination. Geochemical lines of evidence were presented to demonstrate reduced conditions. Dissolved oxygen decreased from 0.6 mg/L at the edge of the peat to 0.2 mg/L inside the peat. Redox showed a strong negative shift from the background to the center of the plume. Ferric iron reduction, sulfate reduction, and methanogenesis were observed within the plume in the peat compared to background conditions.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Downey et al., 2001	England AFB, LA	TCE; Max conc. = <1 mg/L	Anaerobic biodegradation	Organic degradation products, ORP, DO, TOC, Fe (II), Mn (partial list)	A Corrective Measures Study was conducted to evaluate MNA as a remedy of a 245-acre TCE plume. Geochemical site data indicated that conditions were favorable to support complete reductive dechlorination, and an evaluation of plume lifetime suggested that remediation by MNA would require about 48 years of institutional controls and monitoring. Based on these results, LDEQ and US EPA Region 6 approved MNA as sole remedy of the plume contingent upon a 5-year monitoring and verification period to assure plume stability and degradation rates.
Lacko et al., 2001	Sanford, FL	PCE; Max conc. = 0.16 mg/L	Anaerobic biodegradation	Organic degradation products, methane, ethane, ethene, soluble organic carbon, DO, ORP, pH, CO ₂ , dissolved H ₂ , alkalinity, Fe (II), total Fe, nitrogen, nitrate, nitrite, sulfate, sulfide, chloride	Natural Attenuation was evaluated as a remedy for a PCE groundwater plume following source removal activities. Data from 15 to 25 monitoring wells sampled in 1994 and 1999 indicate decreases in PCE, TCE, and DCE concentrations with an increase in vinyl chloride, indicating microbial reductive dechlorination was active at the site. Sampling of geochemical indicators from 1999 through 2000 (six events) demonstrate favorable conditions to support anaerobic dechlorination. Based on the geochemical and organic concentration data, the authors suggest natural attenuation is occurring at the site via a combined Type 1 and Type 2 behavior, as described in EPA guidance (US EPA, 1999).

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Meregaglia et al., 2001	Northern Italy	TCE; Max conc. = 0.25 mg/L	Anaerobic biodegradation	Organic degradation products, methane, ethane, ethene, TOC, pH, ORP, DO, Fe (II), nitrate, sulfate, chloride	Evaluation of a MNA remedy following source removal at a TCE affected site in Northern Italy was conducted by examining four lines of evidence: i) presence of anaerobic conditions, ii) loss of electron donors/acceptors, iii) loss of TCE mass and presence of daughter products, and iv) presence of geochemical indicators. Seven wells were monitored over a 6-month period to establish chemical/geochemical trends. DO below 1 mg/L, low ORP, and methane concentrations indicated the aquifer was anaerobic. cis-DCE and vinyl chloride were detected at concentrations higher than TCE, however, the concentration of TCE increased slightly over the 6-month period in downgradient wells. The occurrence of cis-DCE "stall" was observed and the authors suggest this may be a result of limited electron donor (evidenced by low TOC). Based on these lines of evidence, MNA as a follow-up remedy to source removal was approved by Italian Authorities.
Morrill et al., 2001. In: Leeson et al., 2001	Not available	TCE and 1,1,1-TCA; Max conc. < 1 mg/L and < 10 mg/L, respectively	Anaerobic biodegradation	Organic degradation products, TOC, DO, ORP, COD, nitrate, sulfate, sulfide, methane, dissolved H ₂	Natural attenuation of a TCE and 1,1,1-TCA plume was demonstrated by presenting daughter product concentrations (cis-1,2-dichloroethylene, vinyl chloride, and ethene for TCE and 1,1-DCA, chloroethane, and ethane for 1,1,-TCA) that were elevated or higher than parent compound concentrations. DO, ORP, and methane levels were representative of a reduced environment that would support NA. Despite the presence of natural attenuation processes, the high contaminant concentrations did not permit the attainment of clean up levels in a reasonable time frame. Other remedial processes are being investigated.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Norris et al., 2001. In: Leeson et al., 2001	Various	PCE and TCE	Anaerobic biodegradation	Organic degradation products, DO, nitrate, sulfate, Fe(II), Mn, ethene	Natural attenuation of solvent plumes emanating from landfills was discussed. Case studies were presented to show that conditions favorable to natural attenuation of chlorinated solvents typically occurs within and downgradient of landfills. The presence of co-contaminants that act as electron donors and reduced methanogenic conditions create an environment conducive to reductive dechlorination. Chloroethene data were provided for the Shope's Landfill Superfund Site in Girard, Pennsylvania, which showed non-detect levels of TCE, and elevated levels of cis-DCE, vinyl chloride, and ethene. Historic vinyl chloride data were also presented to show a decreased concentration trend as evidence of NA. VOC data from the Upstate New York Landfill was also presented. The ratio of daughter to parent products was used to demonstrate active reductive dechlorination.
Richmond et al., 2001	Six Mile Village, Alaska	TCE, TCA, BTEX; Max TCE conc. = 0.066 mg/L	Dilution	Organic degradation products, ferrous iron, sulfate, nitrate, alkalinity, TOC, DO, hydrogen, methane, ethane, ethene, microbial counts, anaerobic heterotrophic activity	MNA was assessed over a 4 to 6 year period (1994-2000) as a remedy for treatment of an approximately 50 acre TCE/TCA mixed plume. Dilution was determined to be the primary NA process occurring at the site. Although TCE biodegradation products were detected at the site, observance of stable ratios of parent compound to degradation products over time and direct microbiological measurements supported the conclusion that reductive dechlorination was no longer actively occurring at the site. The authors suggest that reductive dechlorination likely occurred when BTEX was still present at the site (TEX has not been detected since MNA monitoring began). Temporal trends in TCE concentration (determined by Mann-Kendall analysis) were inconsistent among

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
					the 25 wells sampled, but most indicated decreasing TCE concentration or no concentration trend. Pseudo-first order decay calculations indicated that TCE concentrations would decrease below the MCL in 15 to 25 years at the site.
Tesoriero et al., 2001	Northern Washington, U.S./ Southwestern British Columbia, Canada	1,2-Dichloropropane (DCP); Max DCP conc. = 0.0194 mg/L	Anaerobic biodegradation	Organic degradation products, ferrous and ferric iron, nitrate, DO, microcosm studies	MNA was assessed over a 2-year period (1997-1998) as a remedy for treatment of a 1,2-dichloropropane plume. Data from 59 wells were evaluated. Due to the nonpoint source nature of the contamination, a site-specific MNA protocol was developed that evaluated MNA according to the following lines of evidence: 1) frequency of detection and concentrations of DCP relative to dominant terminal electron-accepting process(es); 2) application of a 2-D groundwater flow and solute transport model to compare observed plume extent to predicted plume extent (Visual MODFLOW); and 3) microcosm studies using aquifer material from different redox zones. Anaerobic biodegradation of DCP was shown to be the primary NA process only in the more reduced (iron-reducing) zones of the aquifer.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
US EPA, 2001	Twin Cities Army Ammunition Plant, St. Paul, MN	TCE and 1,1,1-TCA; Max TCE = 1.1 mg/L	Anaerobic biodegradation (limited)	Organic degradation products, methane, ethane, ethene, DO, Eh, Fe (II), Mn, nitrate, sulfate	The US EPA (1998) Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water was verified by applying the guidelines to a TCE/TCA plume where use of natural attenuation as a sole remedy had been predetermined unfeasible. The existence of a 5-mile long plume in a consolidated fractured dolomite and sandstone, and 10 years of monitoring established that natural attenuation would not provide adequate remediation. Applying the US EPA 1998 Protocol to the groundwater plume accurately predicted the exclusion of natural attenuation as the sole remedy. This was accomplished by evaluating parent compound concentration trends over time and along groundwater flow paths, comparing geochemical data at the site to conditions conducive to reductive dechlorination, determining rates of natural biodegradation of parent and daughter products, and conducting fate-and-transport modeling of the plume (using BIOSCREEN and BIOPLUME III models).

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Huff et al., 2000 In USGS Report 00-4121	Harris County, TX	TCE, 1,1,2 -TCA; Max TCE conc. =	Anaerobic biodegradation	Organic degradation products, DO, Fe (II), H ₂ , methane, carbon dioxide, chloride, sulfide, ethene, sulfate, DOC, nitrate, alkalinity	Natural attenuation of chlorinated ethenes and ethanes in a sand channel beneath a petroleum reclamation site was evaluated. Hydrogen data were used to show that the plume was in a sulfate-reducing to methanogenic environment. BIOCHLOR, a semi-analytical model, was used to simulate the plume concentrations and determine apparent first order biodegradation rate constants using field data. Evidence supporting reductive dechlorination included biogenic cis-1,2-DCE, an increase in the ratio of 1,2-DCA to 1,1,2-TCA, and elevated ethene and methane concentrations within the plume area relative to background levels. Because lateral and vertical inhomogeneity in the distribution of chlorinated ethenes and ethanes may have affected the determination of apparent decay rate coefficients, it was concluded that additional information might be needed for a more quantitative assessment for the potential of natural attenuation as a remedy.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
AFCEE 1999	Various (14 US Air Force sites in continental US)	TCE; Max conc. range \cong <1 mg/L to >25 mg/L	Anaerobic and aerobic biodegradation	Organic degradation products, methane, ethane, ethene, ORP, DO, nitrate, nitrite, sulfate, sulfide, Fe (II), total iron, CO ₂ , alkalinity, chloride, dissolved H ₂	The effectiveness of natural attenuation as a remedy for chlorinated solvent plumes at 14 US Air Force sites was evaluated. Only sites exhibiting some degree of intrinsic bioremediation were selected for the study to provide a better understanding of the role of biological processes in NA. All sites were characterized according to the Type 1, 2, or 3 rating as described by US EPA (1998). Concentration trends over time at the sites indicated that 5 contaminant plumes were stable or shrinking, 6 plumes were stable or slowly expanding, and 3 plumes appeared to be expanding. MNA was recommended as the sole remedy at 2 sites, with 2 other sites warranting additional data prior to determining the need for active remediation. At other sites, MNA in conjunction with active treatment was proposed. The average cost for the MNA studies was \$122,000, and the annual monitoring cost was estimated at almost \$23,000.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Lorah and Olsen, 1999	Aberdeen Proving Ground, Maryland	1,1,2,2- PCA; Max PCA conc. = ~1.0 mg/L	Anaerobic biodegradation	Organic degradation products, ferrous and ferric irons, DO, manganese, ammonia, sulfide, methane, microcosm studies	MNA was assessed over a 2-year period (1995-1996) as a remedy for treatment of a 1,1,2,2-tetrachloroethane plume (PCA) that discharges into wetland sediments and a creek. Data from 25 piezometers were evaluated. Microcosm experiments were also conducted to evaluate PCA degradation pathways and rates under anaerobic conditions. Two anaerobic biodegradation pathways, hydrogenolysis and dichloroelimination, were determined to dominate natural attenuation processes occurring at the site. Accumulation of vinyl chloride was observed and further reduction of vinyl chloride occurred only in the presence of strongly reduced (i.e. methanogenic) conditions.
Lee et al., 1999	Lake Charles, LA	1,2-DCA; Max conc. = 9200 mg/L	Anaerobic biodegradation	Organic degradation products, dissolved iron, sulfate, chloride, ammonia-N, TOC, DO, Eh, pH, total phosphorus, microcosm studies	MNA was assessed over a 3-year period (1995-1997) as a remedy for treatment of a 1, 2-dichloroethane plume (DCA). Data from more than 70 wells were evaluated. Efficacy of MNA was also evaluated through microcosm experiments. The following three lines of evidence were used to evaluate MNA at the site (based on the AFCEE protocol, Weidemeier et al. 1996): i) reduction in contaminant concentrations along the groundwater flowpath, ii) documented loss of contaminant using chemical/geochemical data, and iii) microcosm data to evaluate biodegradation rates. All three lines of evidence demonstrated that NA of DCA was occurring at the site. MNA with verification through long term monitoring coupled with shallow recovery and hydraulic containment of DCA were chosen as preferred remedies.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Swanson, 1999. In: Weidemeier et al., 1999	Cape Canaveral Air Station, FL (Site CCFTA-2)	TCE; Max conc. = 15.8 mg/L	Anaerobic biodegradation	Organic degradation products, TOC, DO, ORP, nitrate, sulfate, dissolved H ₂ , Fe (II), methane, ethene, ammonia, alkalinity, chloride	MNA was assessed as a remedy for treatment of a TCE plume emanating from a multicomponent LNAPL. The mobile LNAPL was excavated from the site to reduce remediation time. MNA was evaluated according to the AFCEE protocol. MODFLOW and MT3D modeling was performed to determine time required to achieve surface water and groundwater standards. Geochemical and contaminant data evidenced that non-chlorinated components of the former LNAPL (i.e., BTEX) were supporting reductive dechlorination of TCE and its daughter products. Slow reduction of vinyl chloride (VC) to ethene (compared to TCE reduction to cis-DCE and subsequently VC) cause accumulation of cis-DCE and VC. A horizontal air sparging system was installed adjacent to a canal downgradient of the plume to reduce the mass of VC discharging to surface water. Modeling results indicate that MNA, in conjunction with the source removal and air sparging system, should effectively reduce chlorinated VOC concentrations at the site.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Buscheck, 1999. In: Weidemeier et al., 1999	San Francisco, CA	TCE; Max conc. = 35 mg/L	Anaerobic biodegradation	Organic degradation products, TOC, COD, ORP, sulfate, methane, ethane, ethene	The natural attenuation of a PCE and TCE plume within 2 shallow water bearing zones was evaluated. A groundwater monitoring program has been in place since 1986, and was augmented for MNA study in 1996. The lines of evidence used at this site consist of: i) loss of parent contaminants and appearance of breakdown products, ii) redox geochemistry to support anaerobic conditions, and iii) availability of electron donor. The decline of parent compounds with simultaneous increase in daughter products indicates that reductive dechlorination is the primary NA process. Redox geochemistry data indicate site conditions that are suitable for reductive dechlorination. COD and TOC data were used to evaluate the presence of suitable electron donors, and results indicated that reductive dechlorination was feasible at the site.

**TABLE 3.2
LITERATURE REVIEW SUMMARY
OF MNA CASE STUDIES**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Reference	Site Location	1° CVOC	1° NA Process	MNA Indicators	Key Findings
Moutoux, 1999. In: Weidemeier et al., 1999	Offutt AFB, NE	TCE; Max conc. = 25 mg/L	Anaerobic biodegradation (limited)	Organic degradation products, TOC, DO, ORP, pH, nitrate, sulfate, sulfide, Fe(II), methane, ethane, ethene, temperature, CO ₂ , alkalinity, chloride, dissolved H ₂ , fatty acids	The natural attenuation of a 3000 ft long plume of mixed chlorinated aliphatic hydrocarbons (CAHs), composed primarily of TCE, was evaluated for incorporation into an active remediation program. There are indications that limited biodegradation of TCE is occurring, primarily evidenced by the presence of DCE. Further reductive dechlorination of DCE to VC and ethene does not appear to occur at the site. The lines of evidence used to evaluate CAH attenuation include: i) the distribution of TCE and metabolites, ii) the redox conditions of the groundwater, iii) presence of electron donors, and iv) alternative electron acceptors and their metabolic by-products. Groundwater monitoring performed since 1991 does not indicate overall decreases in dissolved TCE concentrations. This observation suggests that the rate of natural attenuation is not great enough to overcome the rate at which TCE partitions from the source into the groundwater. Daughter products are only found in the source area and one other area suggesting that reductive dechlorination at the site is localized. MODFLOW and MT3D model simulations indicate that even with optimum decay rates the plume will continue to expand. Furthermore, all simulations suggest that dissolved TCE concentrations substantially higher than 5 ug/L will persist in groundwater for more than 200 years.

Notes:

- 1) 1° = primary; CVOC = chlorinated volatile organic compound; NA = Natural Attenuation; MNA = Monitored Natural Attenuation
- 2) TOC = total organic carbon; DO = dissolved oxygen; ORP = oxidation-reduction potential
- 3) PCE = tetrachloroethene; TCE = trichloroethene; DCE = dichloroethene; VC = vinyl chloride; PCA = tetrachloroethane; TCA = trichloroethane; DCA = dichloroethane; DCP = dichloropropane

2003; Witt et al., 2002; AFCEE, 1999). Additionally, one site also suggested retardation via sorption added significantly to reductive dechlorination in the attenuation of TCE in a peat environment (Buss et al., 2001).

Dilution was stated as the primary attenuation process at the one site where anaerobic biodegradation was not the primary attenuation process (Richmond et al., 2001). This site was located in a subarctic region of Alaska, and the extreme cold groundwater conditions coupled with a lack of organic carbon apparently excluded the growth of reductive dechlorinating bacteria.

In nearly all of the studies reviewed, groundwater was analyzed for a minimum of the following chemical/geochemical indicators to develop lines of evidence in support of the MNA assessment:

- organic degradation products;
- methane, ethane, and ethene;
- dissolved oxygen;
- pH;
- oxidation-reduction potential (ORP);
- ferrous iron;
- nitrate and nitrite;
- sulfate and sulfide; and
- total organic carbon (TOC).

Several studies also indicated using parameters such as alkalinity, carbon dioxide, chloride, dissolved hydrogen, and manganese in their MNA evaluation. To a lesser extent, parameters specifically targeting the detection of dechlorinating microorganisms or anaerobic microbial activity were evaluated. These microbe-specific parameters included microbial counts (Lenczewski et al., 2003; Richmond et al. 2001), 16s rDNA analysis (Lenczewski et al., 2003), anaerobic heterotrophic activity analysis (Richmond et al. 2001), volatile fatty acid data (Clement et al., 2000; Moutoux, 1999), phospholipids fatty acid analysis, and denatured gradient gel electrophoresis analysis (Buss, et al., 2001).

Interestingly, only three studies indicated the use of microcosm data to aid in evaluating the role of microbiological processes in natural attenuation at their sites (Tesoriero et al., 2001; Lorah and Olsen, 1999; Lee et al., 1999). In all three cases, microcosm experiments were conducted to elucidate biodegradation pathways and determine degradation rates at sites where the primary CVOC released was not PCE, TCE, or TCA. The specific CVOCs present at the sites where microcosms were used were DCP (Tesoriero et al., 2001), PCA (Lorah and Olsen, 1999), and DCA (Lee et al., 1999). Microcosm data from sites affected with less commonly studied CVOCs, such as these, is likely needed to fully understand the potential for natural attenuation at the site.

The case study analysis indicated that several technical protocols, dominated by the 1998 US EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*, were followed in evaluation of MNA at field sites. Most studies that did not explicitly state the US EPA protocol was followed still used a "lines of evidence" approach in their assessment similar to that outlined in the US EPA protocol. In general, the lines of evidence approach used to support MNA evaluation included demonstration of the following concepts: i) demonstration of concentration trends that indicate temporal decreases in contaminant mass or

concentration; ii) geochemical and hydrogeologic data evidencing the natural attenuation processes active at the site; and the rate at which natural attenuation processes reduce CVOC concentrations; and iii) data from field or microcosm studies that demonstrate natural attenuation processes and their ability to degrade contaminants at the site.

Implementation of another concept from the 1998 US EPA protocol, a screening process in which points are accumulated based on chemical/geochemical data to determine whether conditions are favorable for reductive dechlorination (see Table 3.3 and Section 3.2 for detailed description), was generally limited only to sites explicitly following the US EPA protocol or the similar AFCEE protocol (AFCEE, 1999).

Fifty percent of case studies indicated the use of computer modeling in their evaluation of CVOC plumes at potential MNA sites. The various computer models used included the analytical models BIOCHLOR, BIOSCREEN, and BIOPLUME III, as well as numerical flow and solute transport models such as MODFLOW and MT3D. Modeling was typically used to predict plume characteristics (i.e. length and stability) and/or estimate remediation timeframe (AFCEE, 1999; Moutoux, 1999; Swanson, 1999; Norris et al., 2001; US EPA, 2001). Other modeling objectives included estimation of first-order decay rates using site data (Huff et al., 2000), and comparison of predicted plume extent to observed plume extent for determining the occurrence and rate of natural attenuation (Tesoriero et al., 2001; Clement et al., 2002).

Only two studies (10%) indicated that MNA had been approved as a site remedy by the respective regulatory agency. Regulators at Louisiana Department of Environmental Quality (LDEQ) and US EPA Region 6 each approved MNA as the sole remedy of a 245-acre TCE plume at England Air Force Base, LA following a Corrective Measures Study that predicted a remediation timeframe of 48 years (Downey et al., 2001). Approval was contingent upon a 5-year monitoring and verification period designed to assure plume stability and verify degradation rates. Characteristics of the England AFB site that likely aided in gaining regulatory approval included: i) maximum TCE concentrations less than 1 mg/L; ii) complete, 3-D plume delineation; iii) geochemical conditions favoring reductive dechlorination; iv) highly organic soils to supply electron donor; and v) *cis*-DCE "stall" does not occur (i.e. reduction of TCE degradation products is complete). MNA was also approved by the Italian Authorities as a follow-up remedy to achieve site closure following active source zone remediation at a TCE site in northern Italy (Meregaglia et al., 2001). Regulatory approval followed a one year demonstration program and agreement to continue monitoring for verification that remedial goals are met, and that microbial processes are sustainable.

Four additional studies stated that MNA would be the proposed remedy for the affected plume based on data generated in the MNA evaluation. MNA was proposed as the sole remedy at two of the four sites (Clement et al., 2002; Buscheck et al., 1999), and would be part of an active remediation scheme at the two other sites (Lee et al., 1999; Swanson, 1999). Three studies concluded that MNA would likely not be a feasible remedy at the sites (Moutoux, 1999; Morrill et al., 2001; US EPA 2001). All three studies suggest the timeframe for remediation via MNA was estimated to be too long compared to other remedial alternatives. The condition of *cis*-DCE "stall" was observed at two of the three sites (Moutoux, 1999; US EPA 2001), indicating limited capacity for microorganisms naturally present at the site to substantially enhance natural attenuation. The remaining studies either provided no indication as to whether MNA would be pursued as a remedy for the site, or indicated a need for additional data prior to making a decision.

The AFCEE case study (AFCEE, 1999) evaluated the potential for MNA as a remedy at 14 individual sites selected based on prior evidence that microbiological processes were attenuating the CVOC plumes. Results of Treatability Studies at the sites indicated that MNA alone was likely a sufficient remedy at 2 sites, with 2 other sites warranting additional data collection before determining the need for active remediation. At the remaining 10 sites, MNA was proposed in conjunction with active remediation. This was the only case study providing cost data on MNA evaluation and monitoring. The average cost for evaluation of MNA at the sites was reportedly \$122,000, while the annual monitoring costs were estimated at almost \$23,000.

3.2 Protocol Review

A review of the databases and websites listed on Table 3.1 produced 12 protocols issuing guidance on the evaluation/implementation of MNA at CVOC sites. Several main parameters from each protocol, including: i) the issuing agency/organization; ii) specific contaminants addressed; iii) models required or recommended; iv) geochemical/chemical indicators required; and v) other supporting lines of evidence required, are summarized on Table 3.3. A summary of key information from the protocol is also included on Table 3.3.

As evident from Table 3.3, many protocols share some similarity with the 1998 US EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (US EPA protocol). Therefore, the focus of this review will be on the US EPA protocol and key differences between it and other protocols. The reader is referred to the National Research Council's *Natural Attenuation for Groundwater Remediation* (NRC, 2000) for additional information regarding review of technical protocols.

While the US EPA protocol is primarily a technical protocol aimed at providing guidance for data collection and analysis to evaluate MNA, the protocol also contains limited policy information taken from the EPA document *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (US EPA, 1999). One of the main policy issues relates to the lines of evidence that should be provided to demonstrate natural attenuation, and guidance on proper interpretation of each line of evidence. Three lines of evidence are identified that should be used to support a natural attenuation remedy at a CVOC site: i) historical data that demonstrates a decreasing temporal trend in contaminant mass or concentration; ii) geochemical and hydrogeologic data evidencing the natural attenuation processes active at the site, and the rate at which natural attenuation processes reduce CVOC concentrations; and iii) data from field or microcosm studies that demonstrate natural attenuation processes and their ability to degrade contaminants at the site.

EPA directs that the first line of evidence, concentration trends over time, may be sufficient to support natural attenuation as a site remedy if the data record is of sufficient quality and duration as judged by the regulatory agency. However, if the first line of evidence is determined not to meet regulatory standards, then the responsible party should demonstrate the second and/or third lines of evidence to determine whether natural attenuation is a proper remedy for

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
US EPA, 1998	Chlorinated solvents	Detailed conceptual site model; Solute fate-and-transport computer model (recommends BIOSCREEN and BIOPLUME III)	Contaminant and degradation products concentration, pH, temperature, conductivity, ORP, DO, nitrate, nitrite, sulfate, sulfide, ferrous iron, total iron, methane, ethane, ethane, CO ₂ , alkalinity, chloride, dissolved hydrogen (optional)	Requires demonstration of decreasing mass or concentration of CVOCs; and/or geochemical evidence demonstrating NA processes and rates; and/or data from field or microcosm studies directly evidencing NA processes	Technical protocol issuing guidance on the application of MNA at chlorinated solvent sites based on policy set forth in the document <i>Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites</i> (US EPA, 1997 (draft), Final 1999). The protocol is directed at project managers, consultants, scientists, and regulators involved in remedial programs utilizing MNA. Institutes the use of an analytical screening system designed to indicate the likelihood of a successful MNA remedy at the site. The screening system rates site potential to support anaerobic biodegradation based on a variety of chemical and geochemical indicators. The document emphasizes demonstration of biological processes that result in contaminant destruction, and provides ample information on the assessment of such processes at field sites.

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
Navy, 1998	Chlorinated solvents and petroleum hydrocarbons	Dispersion-biodegradation analytical model	See US EPA, 1998	Historical data record demonstrating groundwater plume stabilization and/or loss of contaminant mass over time; and geochemical data documenting active biological processes and favorable conditions to sustain these processes	Provides a thorough discussion of the chemical and geochemical data used to evaluate site characteristics and determine if MNA is a suitable remedy. Specific attention is given to implications of geochemical data on biological degradation of chlorinated solvents. An 8-step process for evaluating natural attenuation is proposed. This protocol also provides and assessment of the effects of active remediation technologies on natural attenuation processes. Case studies on MNA application at fuel sites and chlorinated solvent sites are presented.

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
US EPA, 1999a	Chlorinated solvents, petroleum-related compounds, inorganic compounds	None specified (see US EPA, 1998)	None specified (see US EPA, 1998)	1) Historical data that demonstrates a decreasing temporal trend in contaminant mass/concentration; 2) Geochemical/ hydrogeologic data evidencing the natural attenuation processes active at the site; and 3) Data from field or microcosm studies that demonstrate NA processes and their ability to degrade contaminants at the site	Provides EPA policy regarding implementation of MNA as a remedy for contaminated sites regulated by the EPA Office of Solid Waste and Emergency Response. Directs that for MNA to be used as a remedy, time frame for remediation must be comparable to active treatment alternatives. Recognizes dispersion, dilution, sorption, volatilization, biotic chemical reactions, and abiotic chemical reactions as attenuation mechanisms potentially occurring at sites; however, mechanisms resulting in chemical degradation are preferred at sites using MNA. Source control, detailed site characterization and analysis are emphasized; however technical guidance is not provided (refers to US EPA, 1998). States MNA will likely be most appropriate when used in conjunction with, or following, source control measures. Recommends contingency remedies be included as part of the MNA remedy, particularly if MNA remedy selection is based on predictive analysis.

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
US EPA, 1999b	Chlorinated solvents	Recommended: MT3D, BIOMOD3D, BioREDOX, RT3D	See US EPA, 1998	See US EPA, 1999a Suggests microcosm studies should be performed only at sites where there is considerable uncertainty concerning the biodegradation of contaminants due to the expense and time requirements of these studies.	This US EPA Region 4 document was originally released to complement the US EPA OSWER Policy Directive. Suggests a natural attenuation demonstration report should include the following elements: 1) a complete site characterization; 2) remedial action for the source; 3) a long term monitoring (including O&M) plan; 4) a comparison of the MNA remedy to an active treatment remedy; 5) the enumeration of institutional controls that are currently operational and enforceable for the site; and 6) determination of the carbon source and demonstration of sustainability for chlorinated solvent degradation. Employs the analytical screening system designed to indicate the likelihood of a successful MNA remedy detailed in the US EPA Technical Protocol (US EPA, 1998)

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
US DOE, 1999	General	Recommends use of fate-and-transport modeling	See US EPA, 1998	See US EPA, 1998, 1999a	This document is intended to complement the EPA OSWER Policy Directive as a decision-making framework for evaluation and selection of MNA at DOE sites. Emphasizes the use of other department guidance, such as the MNA Toolbox software, in conjunction with the document. The MNA Toolbox, developed for the DOE, is designed to rate the likelihood of a successful MNA program at contaminated sites. The decision-making framework consists of 3 tiers: Tier 1 is a planning phase where the conceptual model of the site is developed; Tier 2 involves comparison of MNA to active treatment technologies; and Tier 3 is an evaluation of risk management issues with respect to the regulatory program governing the site including MNA effectiveness, implementability, and cost.
ITRC, 1999	Chlorinated solvents	See US EPA, 1998	See US EPA, 1998	See US EPA, 1998, 1999a	Provides a general, step-by-step framework for evaluating and understanding natural attenuation based on the lines of evidence approach advocated by the USEPA technical protocol. Uses a question-and-answer approach to discuss principles and implementation of MNA.

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
MPCA, 1999	Chlorinated solvents	Simple modeling may be used for the screening phase; Solute fate-and-transport models for the verification phase (recommends BIOCHLOR and BIOSCREEN)	Contaminant and degradation products, pH, temperature, conductivity, ORP, DO, hydrogen, nitrate, nitrite, sulfate, sulfide, ferrous iron, reduced manganese, total iron, methane, ethane, ethane, CO ₂ , alkalinity, chloride, TOC	None specified	Provides guidance for use of MNA as a remedy at sites in Minnesota. Defines a phased approach to evaluating MNA: Phase 1 involves a screening system similar to that in the US EPA Technical Protocol (US EPA, 1998); Phase 2 includes a thorough site characterization, or feasibility study; and Phase 3 is the implementation and verification phase, which includes long-term monitoring and contingency plans. Contains a very thorough discussion of modeling requirements and the limitations of models in the decision-making process.
NHDES, 1999	Volatile organic compounds	Solute fate-and-transport model (recommends BIOCHLOR, BIOSCREEN, and BIOPLUME III)	Organic degradation products, DO, nitrate, sulfate, methane, ferrous iron, soluble manganese, ORP, TOC, pH	See US EPA, 1998, 1999a	Guidance for utilization of remediation by natural attenuation is provided. Requires demonstration of multiple lines of evidence similar to USEPA technical protocol. States that natural attenuation will not be selected as a sole remedy for any site with non-aqueous phase liquids present. A 10 year remediation timeframe is stated as the acceptable value for approval of a MNA remedy, however exceptions to the default may be proposed.

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
AFCEE 2000	General	Mann-Whitney or Mann-Kendall statistical analysis to show plume stability	Contaminant and degradation products, pH, temperature, conductivity, ORP, DO, nitrate, nitrite, sulfate, sulfide, ferrous iron, total iron, methane, ethane, ethane, CO ₂ , alkalinity, chloride	See US EPA 1998, 1999a	Provides guidance on design of an effective monitoring program for evaluation of MNA as required by US EPA (US EPA, 1998, 1999a). Emphasizes designing the monitoring network to monitor temporal and spatial concentration trends and verify attenuation rates needed to protect potential receptors. Describes use of Performance Monitoring Wells (PMWs) and Contingency Monitoring Wells in the monitoring network. For use in conjunction with EPA and AFCEE protocols. PMWs are designed to achieve the two goals stated above, while contingency wells confirm that plume constituents are not migrating to receptors.
NCDWM, 2000	Chlorinated Organics	BIOCHLOR model for estimation of remediation time frame; BIOPLUME III for demonstration of attenuation processes	Contaminant and degradation products, pH, temperature, conductivity, ORP, DO, nitrate, nitrite, sulfate, sulfide, ferrous iron, total iron, methane, ethane, ethane, CO ₂ , alkalinity, chloride	See US EPA 1998, 1999a	This document provides guidance on implementation of MNA at chlorinated solvent sites in the state of North Carolina, and is largely reflective of the US EPA Technical Protocol (US EPA, 1998). Institutes analytical screening method, and natural attenuation demonstration based on the lines of evidence approach. Stresses demonstration of attenuation processes that degrade contaminants, and source control or removal in conjunction with an MNA remedy. Provision for public involvement through a public review and comment period is a unique element of the protocol. Public comments are considered by regulators prior to selecting the remedy.

**TABLE 3.3
LITERATURE REVIEW SUMMARY OF
MNA PROTOCOLS**

Performance of MNA Remedies at Chlorinated Solvent Sites
Savannah River Technology Center, Aiken, South Carolina

Agency / Date	Contaminant	Models Req'd	Indicators Required	Lines of Evidence	Key Findings
KDHE, 2001	General	See US EPA, 1998	DO, pH, ORP, temperature, alkalinity, sulfate, sulfide, methane, ethane/ethane, TOC, chloride, iron, nitrogen, nitrate, nitrite, COC and degradation products, CO ₂ , manganese, hydrogen, conductivity	See US EPA, 1998, 1999a	US EPA Technical Protocol (1998) is used as a basis for the guidance document; this policy provides further clarification of additional Kansas requirements to the guidance provided by EPA. Requires a "Source Control Plan" be developed to address source zones or high concentration zones. Additionally, a contingency plan must be developed and institutional controls must be placed on all impacted property with MNA approved as the remedy. MNA as the plume remedy requires demonstration that the contaminant plume is stable or shrinking. Impacts to surface water or drinking water wells exclude MNA as a potential plume remedy. Also limits the use of MNA as a remedy for contaminated soil.
TCEQ, 2001	General	Solute fate-and-transport modeling	See US EPA, 1998	See US EPA, 1998, 1999a	This document provides guidance on the application of MNA at affected properties in Texas. If evaluation of site conditions indicates MNA may be applicable, then contaminant data from at least four sampling events is required to establish a concentration trend before proceeding with an MNA remedy. If MNA is determined applicable, several state specific guidelines for choosing and implementing MNA are provided. Specifies which lines of evidence are required under various implementation strategies.

Notes:

- 1) CVOC = chlorinated volatile organic compound; COC = constituent of concern; NA = Natural Attenuation; MNA = Monitored Natural Attenuation
- 2) TOC = total organic carbon; DO = dissolved oxygen; ORP = oxidation-reduction potential

the site. The US EPA protocol cautions, however, that even despite reductions of contaminant concentrations at a site, the second or third lines of evidence will need to be pursued at most sites to demonstrate mass destruction. The US EPA protocol provides guidance regarding proper data gathering and interpretation to satisfy these policy requirements.

The complete MNA evaluation/implementation process as described by the US EPA protocol consists of seven primary steps:

- 1) Conduct initial site screening;
- 2) Collect site characterization data;
- 3) Refine conceptual site model to include MNA specific data;
- 4) Use fate-and-transport computer modeling to simulate natural attenuation;
- 5) Evaluate potential exposure pathways;
- 6) Evaluate source removal options to supplement natural attenuation; and
- 7) Establish long-term monitoring and contingency plans.

To facilitate the initial site screening process, EPA proposed an analytical screening system to rate a site for its potential to support anaerobic reductive dechlorination, which is the dominant microbial process responsible for the destruction of many CVOCs. The screening system involves the accumulation of points based on geochemical data indicating an anaerobic environment and the observance of CVOC biodegradation daughter products. A score above 15 suggests that conditions are favorable for reductive dechlorination, and that the MNA evaluation should continue. Similar screening methods are described in other protocols (US DOE, 1999; MPCA, 1999; NCDWM, 2000). The practice of using an analytical screening system to evaluate potential for natural attenuation is not agreed upon by all experts and decision-makers however, as the National Research Council suggests the scoring systems do not account for the complexity of attenuation processes and may be misused (NRC, 2000).

Once site-specific MNA characterization data has been collected and the conceptual model of the site is refined, EPA suggests using fate-and-transport computer modeling to compare the rate of contaminant transport to the rate of natural attenuation. This comparison provides a determination as to whether the site can be restored in a timeframe comparable to other remedial alternatives. Analytical models such as BIOSCREEN (which has been superseded by the chlorinated solvent-specific analytical model BIOCHLOR) and BIOPLUME III are recommended in the US EPA protocol.

KEY POINTS

- 20 case studies documenting natural attenuation in recent literature were reviewed
- Anaerobic biodegradation processes were a key factor at nearly all sites
- A “lines of evidence” approach, as described in the US EPA protocol, was used to evaluate natural attenuation at most sites
- Computer modeling was implemented as part of the MNA evaluation at half the sites, and was typically used to predict plume stability or estimate remediation time frame
- Only 2 sites indicated a MNA remedy had been approved by regulators, however 4 additional sites suggested MNA would be the proposed remedy
- MNA was excluded as a potential remedy at 3 sites and all stated an unacceptable remediation time frame as the reason
- cis-DCE “stall” was reported at 2 of the 3 sites where remediation time frame was unacceptable

4.0 DATA COLLECTION METHODS

4.1 Survey Distribution and Recipients

An initial list of experts in the field on natural attenuation was generated from a list of attendees of the 1996 "Symposium on Natural Attenuation of Chlorinated Organics in Ground Water" co-sponsored by the US EPA. The list included approximately 650 attendees, and about 240 of those listed an email address in their contact information. An additional 160 contacts were added from various other sources including: i) authors of case studies and protocols; ii) contact lists of Groundwater Services, Inc. personnel; and iii) the 2003 National Ground Water Association membership directory.

The survey was distributed via email to the 400-person contact list, as well as to Anja Sinke of TNO Environment in the Netherlands for distribution to European contacts. The survey was automatically rejected by approximately 170 recipients, most likely due to expired email accounts. Therefore, the approximate number of survey recipients was 230.

4.2 Survey Overview

The goal of the Monitored Natural Attenuation (MNA) survey was to gain insights on how MNA projects at chlorinated solvent sites were being conducted and how successful MNA had been. A two-part approach was utilized:

- **Part A** requested information regarding the respondent's general experience in evaluation of how MNA was applied to the entire portfolio of chlorinated solvent sites where MNA was considered, and
- **Part B** requested detailed data from a specific solvent site where MNA was applied either as the sole remedy or was incorporated into a remedial scheme. The electronic survey was constructed in the Microsoft Excel platform due to its programming simplicity and widespread use.

A copy of the entire survey can be found in Appendix A.

4.2.1 Part A

Four questions aimed at obtaining data related to the respondent's general experience in evaluating MNA were posed in Part A of the survey. The first question (A.1) asked if one or more chlorinated solvent sites had been characterized to determine if MNA was a feasible remedy. If yes was answered, several additional questions were asked as follows:

- At how many total sites was MNA evaluated?
- How many where MNA was shown not to be feasible for any purpose at the site?
- How many where MNA alone was selected as the remedy?
- How many where MNA was used together with active treatment?
- How many where the details of the MNA portion (including monitoring) been fully approved by the applicable regulatory agency?
- How many sites has the active treatment system been completed?
- How many sites is the active treatment system still operating?

The second question (A.2) asked for the typical plume size at sites where MNA had been approved by regulators. Plume size was ranked according to an area greater than 50 acres (large), an area between 10 and 50 acres (medium), or a plume area less than 10 acres (small).

The third and fourth questions (A.3 and A.4) of Part A dealt with typical costs associated with MNA evaluation and implementation. Question A.3 asked the respondent to estimate the typical cost of the initial MNA characterization including MNA-specific monitoring, data analysis, modeling, report writing, and other related expenses. The final question (A.4) asked for the estimated cost of annual MNA monitoring for a typical site.

4.2.2 Part B

Part B was comprised of thirty-nine questions that requested detailed data from a specific CVOC site where MNA was applied either as the sole remedy or was incorporated into a remedial scheme. Questions were grouped into 5 general categories as follows: i) where was the site; ii) how was MNA applied at the site; iii) what contaminants are present and what are the contaminant trends; iv) when did certain events related to MNA implementation take place; and v) who is completing the survey.

The first three questions (B.1 through B.3) focused on site location (i.e. state and city or county for US sites, and city and country for European sites). The respondent was also asked to select primary industries and processes carried out at the site. Finally, the hydrogeologic setting for sites in the United States, based on the DRASTIC system, was selected. Alternatively, sites in Europe selected vadose zone and saturated zone soil types based on the Unified Soil Classification System.

The next section, inquiring as to how MNA was implemented at the site, consisted of 18 questions (B.4 through B.21). Questions B.4 and B.5 asked how MNA was implemented at the site (i.e. as sole remedy, with source treatment, with plume treatment, and/or with a containment system), and which protocol was referenced in evaluating and implementing MNA. Question B.6 had the respondent select and rank the importance of parameters used in the evaluation of MNA from an extensive list that included concentration trend data, chemical data, and geochemical data.

The next two questions, B.7 and B.8, asked for listing of all natural attenuation processes active at the site, and then had the respondent chose the primary attenuation mechanism. The physical location(s) in the subsurface (i.e. throughout the vadose zone, throughout the saturated zone, at surface water/groundwater interface, at vadose zone/groundwater interface) where natural attenuation processes are occurring was then selected.

Several questions (B.9 through B.11) regarding number of wells used to evaluate MNA, total number of wells at the site, and years of groundwater data analyzed for the MNA study were asked. Questions B.12 through B.16 concerned the use of microcosms, geochemical footprints, statistics, and models to support the MNA evaluation. Then question B.17 asked the respondent to rank lines of evidence used for their importance in the MNA evaluation. A question (B.18) regarding evaluation of anaerobic biodegradation sustainability was asked, followed by a question (B.19) concerning whether an analysis of remediation timeframe had been performed. Finally, questions B.20 and B.21 asked for cost estimates of the MNA evaluation study and annual monitoring, respectively.

The nine questions (B.22 through B.30) in the following section, concern trends and other data pertaining to the contaminant released at the site. The primary parent CVOC released, the distribution of parent compound and breakdown products, and the maximum total CVOC concentration in a monitoring well were asked in questions B.22, B.23, and B.24, respectively. The length of the longest plume (B.25), the area of longest plume (B.26), and the groundwater seepage velocity at the site (B.27) were then asked. Question B.28 asked the respondent to select the trend for the length of the longest CVOC plume (i.e. shrinking, stable, stable with discharge to surface water, or expanding). The occurrence of *cis*-DCE “stall”, the condition of where it appears biodegradation beyond *cis*-DCE to vinyl chloride does not occur resulting in *cis*-DCE accumulation, was surveyed for in question B.29. The final question of this section (B.30), asked for estimated distances of the plume edge to a drinking water well and to a surface water discharge point.

Questions in the next section requested data regarding the temporal record of MNA evaluation and implementation at the site. Questions B.31 and B.32 requested the number of years ago groundwater data was first collected, and MNA specific data was first collected, respectively. The following questions (B.32 and B.33) requested the number of years ago the primary MNA report was issued and when regulators approved the MNA remedy. The final question of the section (B.34) asked how long MNA had been used as a remedy at the site.

The final section of the questionnaire contained questions relating the respondent’s professional background and experience conducting MNA investigations, as well as contact information (see Appendix A for complete survey).

4.2.3 Follow-up Survey

A short follow-up survey of respondents was conducted via email to gather additional information related to each section, Part A and Part B, discussed above. The questions posed in the follow-up survey are listed below:

- 1) *If you have evaluated MNA at sites where MNA was determined to be not feasible, please indicate the primary reason MNA was not feasible at the site based on the following selections:*

A = site hydrogeology is prohibitive

B = plume is not stable

C = non-destructive processes are primary attenuation mechanisms (e.g. dilution, dispersion, sorption)

D = remediation timeframe was estimated to be too long

E = geochemical footprints of biodegradation not present

F = plume is outcropping to surface water

G = other (please describe)

- 2) *What regulatory program governs the site where MNA is being used as a remedy?*

A = CERCLA (if CERCLA, has a 5 year review of remedy been performed)

B = RCRA

C = State program (dry cleaner, underground storage tank, etc.)

D = other (please specify)

- 3) *What is your best estimate for the year(s) the primary chlorinated solvent release occurred?*

- 4) *Has a report, or reports, for the MNA project been issued? If so, please provide a citation for the report(s) if available.*
- 5) *There was some confusion about concentration units in the original survey question. Please confirm the maximum concentration of all chlorinated solvents at the well with the highest total concentration at this site (for your convenience, the ranges are provided in two common units):*

A = <0.01 mg/L (<10 ug/L)

B = 0.01 to 0.1 mg/L (10 to 100 ug/L)

C = 0.1 to 1 mg/L (100 to 1000 ug/L)

D = 1 to 10 mg/L (1,000 to 10,000 ug/L)

E = 10 to 100 mg/L (10,000 to 100,000 ug/L)

F = >100 mg/L (> 100,000 ug/L)

G = don't know

KEY POINTS

- The initial survey contact list consisted of approximately 400 experts in chlorinated solvent natural attenuation
- An electronic survey was distributed to the contact list via email
- The survey was received by an estimated 230 people on the contact list
- The survey was comprised of two parts:
 - Part A requested general information regarding evaluation of MNA at all sites
 - Part B requested detailed data from a specific plume being managed by MNA
- A follow-up survey of respondents was conducted to fill gaps in data from the original survey

5.0 SURVEY RESULTS

5.1 Part A – General MNA Application Data

Thirty-four experts in the field of Monitored Natural Attenuation (MNA) provided data regarding applicability of MNA as a remedy at 191 chlorinated solvent sites. As shown in Figure 5.1, MNA was determined a viable remedy at over 75% of the sites evaluated, with MNA sufficient as the sole remedy at 30% of sites. At the 47% of sites requiring some type of active treatment, the active treatment technology applied is currently operating at nearly three-quarters of the sites. Additionally, 51% of sites using an active remedy in conjunction with MNA indicate that the details of the MNA portion have been fully approved by the regulatory agency.

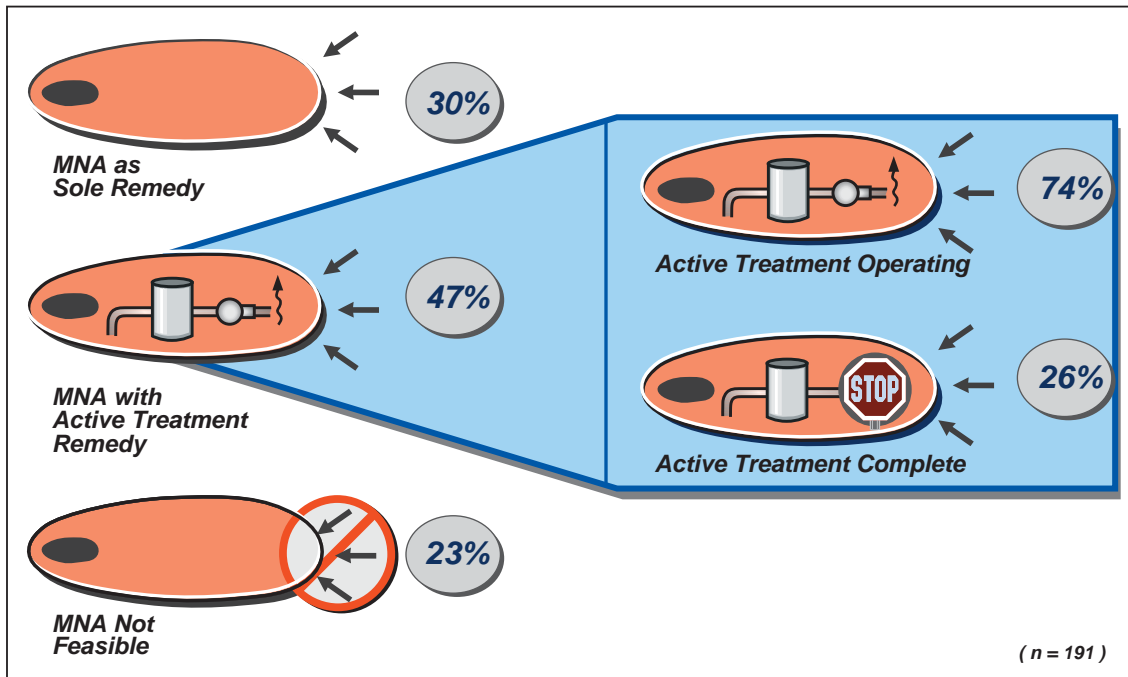


Figure 5.1
Evaluation of MNA Feasibility at Chlorinated Solvent Sites

A follow-up question sought to elucidate factors that contributed to MNA not being a feasible remedy at sites where it was evaluated. Figure 5.2 indicates that a variety of hydrogeologic, geochemical, and plume characteristics influence MNA applicability; however, the leading factors that were reported to prohibit use of a MNA remedy were plume instability and an unreasonable time frame for remediation using MNA. Interestingly, plume discharge to surface water was the least often cited factor prohibiting a MNA remedy.

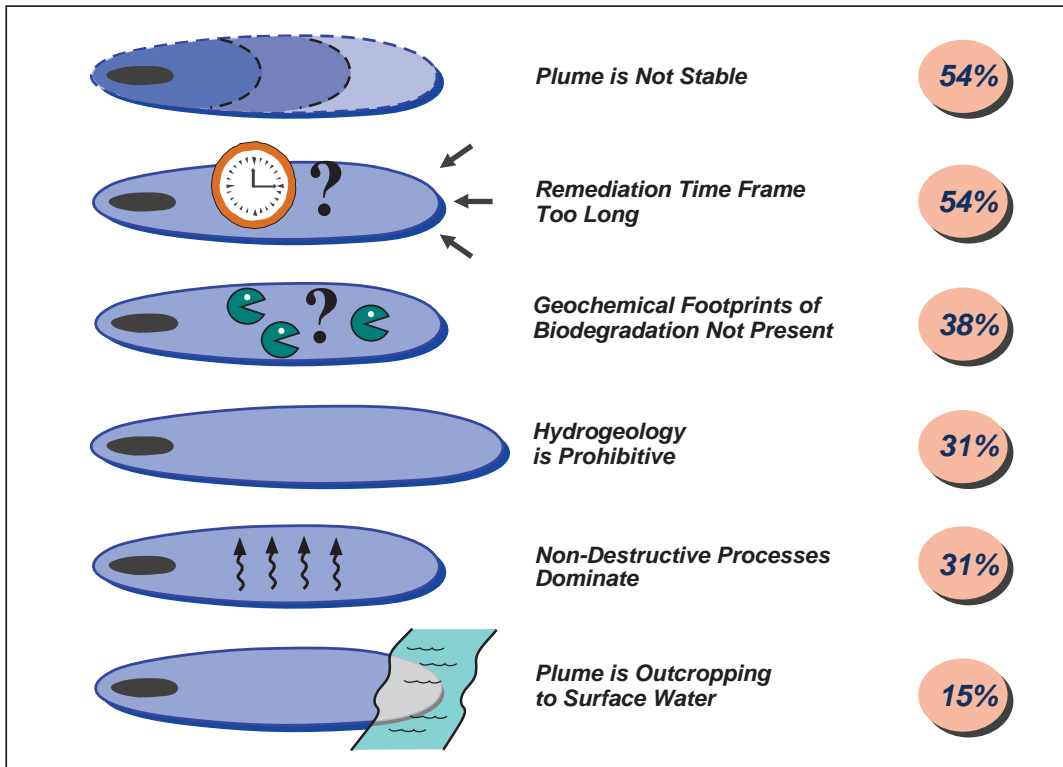


Figure 5.2
Factors Prohibiting Use of MNA as a Remedy (n=23)

An evaluation of typical plume sizes at sites where MNA is currently managing the plume indicated most plumes are approximately 10 to 50 acres in area (Figure 5.3). Significant application of MNA is also observed for plumes greater than 50 acres, and less than 10 acres.

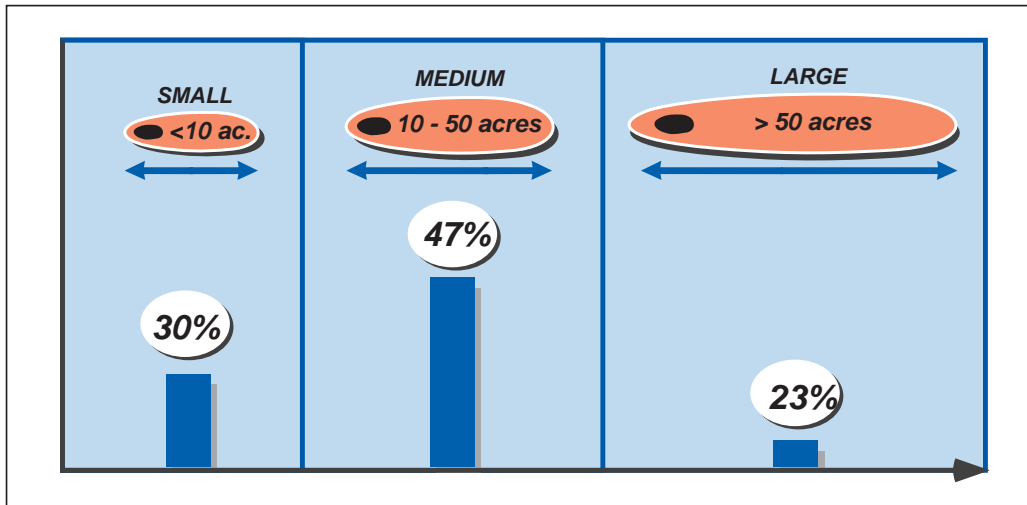


Figure 5.3
Typical Plume Size at MNA Sites (n=32)

Results of typical costs associated with initial MNA evaluation studies and annual monitoring of plumes being managed by MNA are presented in Figure 5.4. As evident from Figure 5.4, cost

of initial characterization studies range widely, with an average of \$177,000 and minimum and maximum values of \$10,000 and \$750,000, respectively. In contrast, annual monitoring costs associated with MNA do not vary as widely, and average \$33,000 per year.

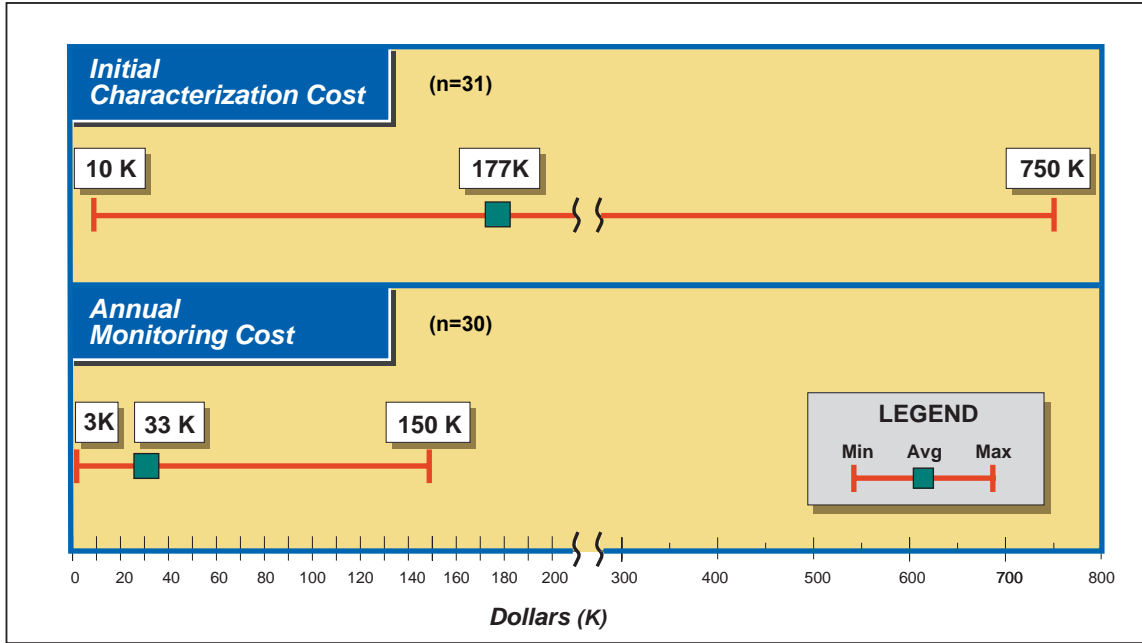


Figure 5.4
Typical Costs Associated with MNA

5.2 Part B – Site-Specific MNA Data

Site-specific data from 45 chlorinated solvent plumes were gathered from the survey. Extensive data from two of the case studies (Lee et al., 1999; Meregaglia et al., 2001) reviewed in Section 3.1 were used to complete surveys for the plumes described in each study. Survey sites were distributed across the continental United States as shown in Figure 5.5. Results were also obtained for 1 site in Alaska, and 10 sites in Europe. Figure 5.6 indicates that MNA is an applicable remedy at sites of varying industries where a range of processes are performed.

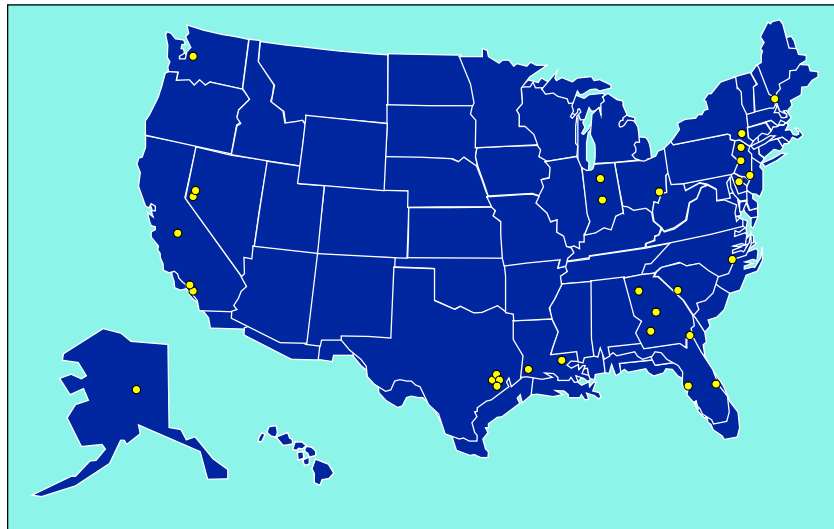


Figure 5.5
Locations of Survey Sites in the United States

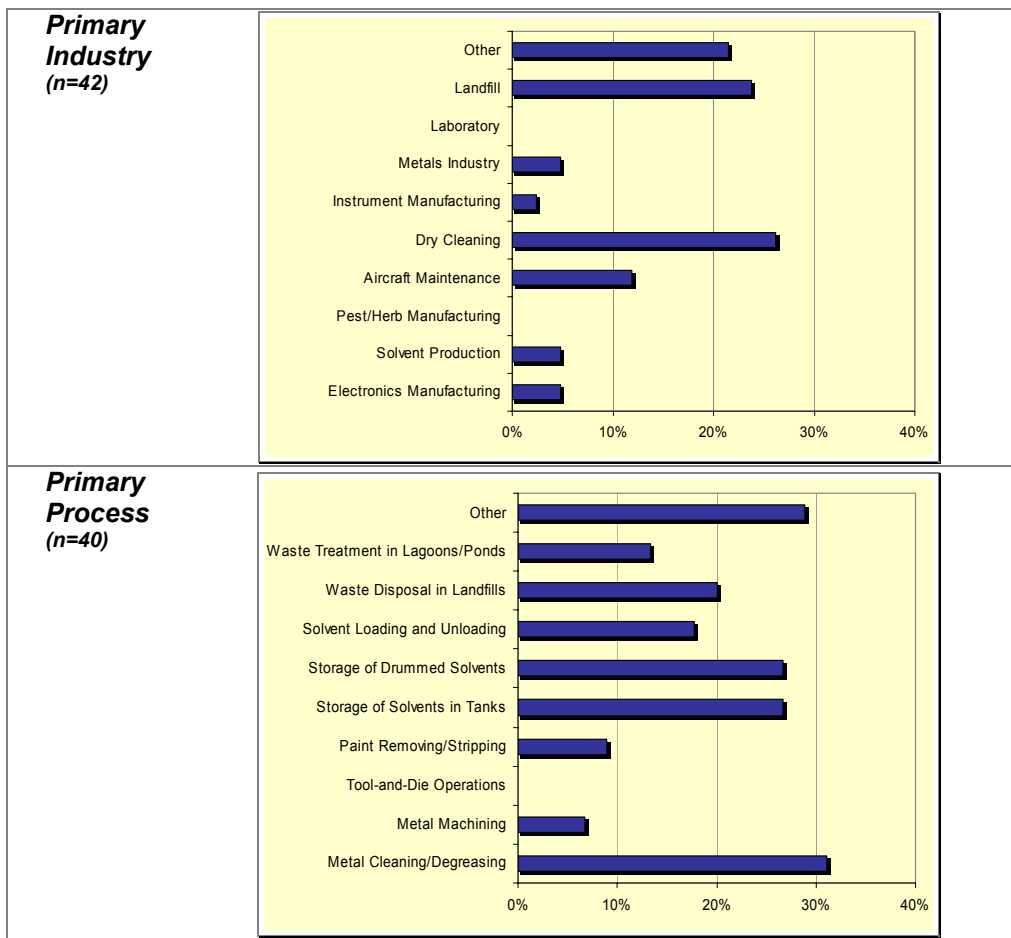


Figure 5.6
Primary Industries and Processes at Chlorinated Solvent Sites Implementing MNA

Most sites where MNA is being applied have had or plan to have some type of source remediation to enhance the effectiveness of MNA (Figure 5.7). However, many sites indicate that MNA will continue as the sole remedy.

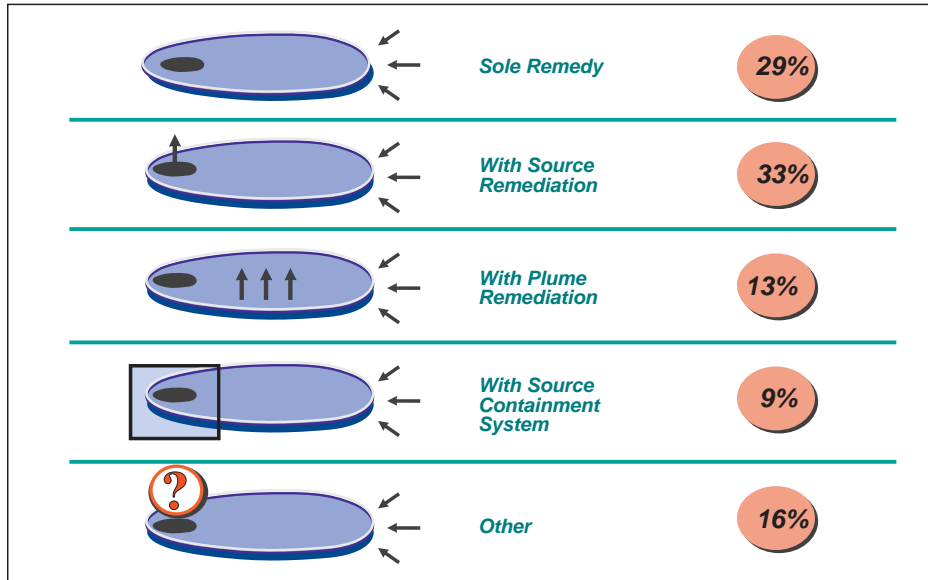


Figure 5.7
MNA Use as a Remedy (n=45)

The US EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (US EPA, 1998) was the most often referenced guidance document used to evaluate MNA. Additionally, state protocols and site-specific protocols were frequently used as shown in Figure 5.8. Reliance upon the EPA protocol is likely even higher than Figure 5.8 illustrates since, as discussed in Section 3.2, many protocols issued by other organizations are similar to the EPA protocol.

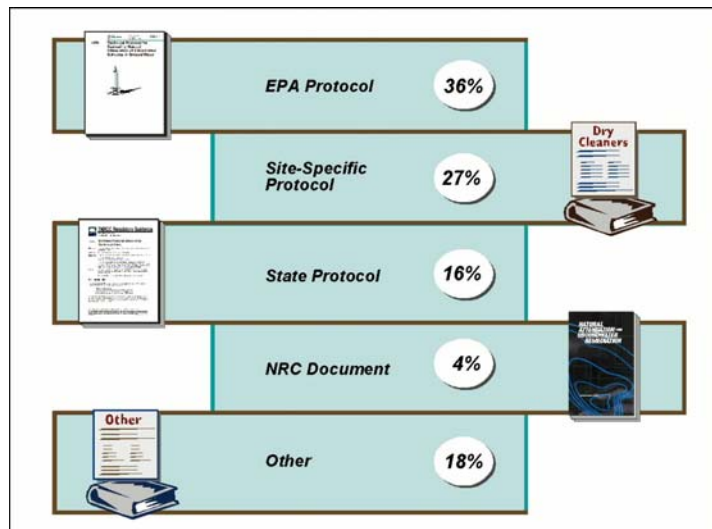


Figure 5.8
Protocols Referenced for MNA Evaluation (n=45)

Figure 5.9 illustrates the variety of field data and the relative importance of the data used to evaluate MNA. Data relating to concentrations and trends of the contaminants and degradation

products were found most important in MNA evaluation. Geochemical indicators often listed as very important or moderately important included: i) dissolved oxygen; ii) total organic carbon; iii) oxidation-reduction potential; iv) ferrous iron; and v) methane. Least important data collected for evaluating MNA were temperature, pH, alkalinity, chloride, and manganese. Dissolved hydrogen data was frequently not collected (61%), which is not surprising since the US EPA technical protocol says collection of dissolved hydrogen data to identify groundwater where reductive dechlorination may occur is “optional”. Only two sites indicated collection of microbe specific data, which included detecting the presence of *Dehalococcoides ethenogenes* and conducting DGGE analysis.

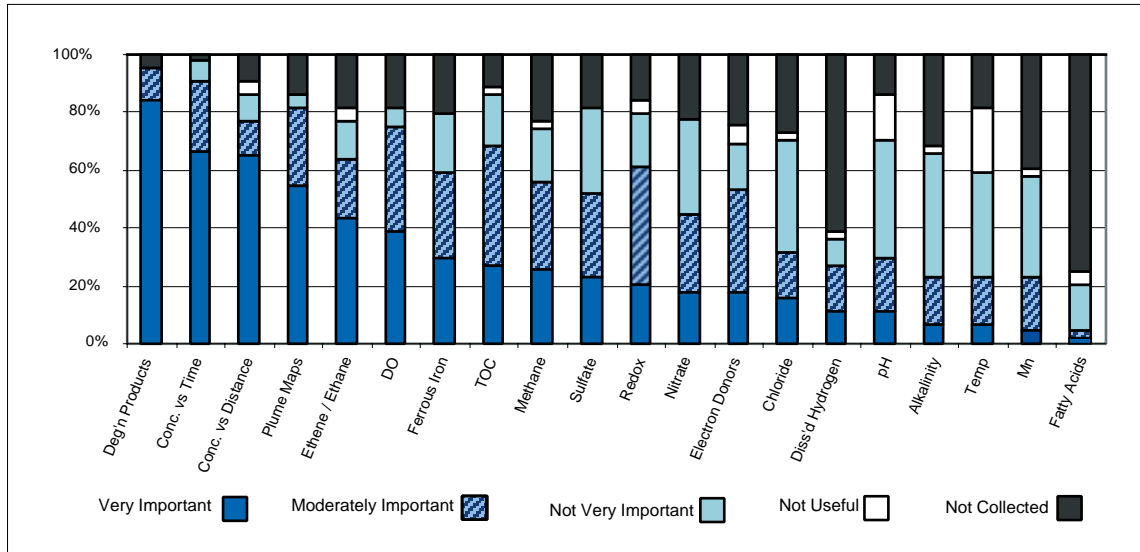


Figure 5.9
Data Collected to Evaluate MNA and Relative Importance

A variety of natural attenuation processes were obviously active at most sites, with anaerobic biodegradation active at over 90% of sites. However, as illustrated in Figure 5.10, anaerobic biodegradation dominated as the most important process over the others. Since anaerobic biodegradation processes dominate natural attenuation mechanisms at most sites, it is not surprising that most sites indicated the occurrence of natural attenuation is primarily in the saturated zone (Figure 5.11).

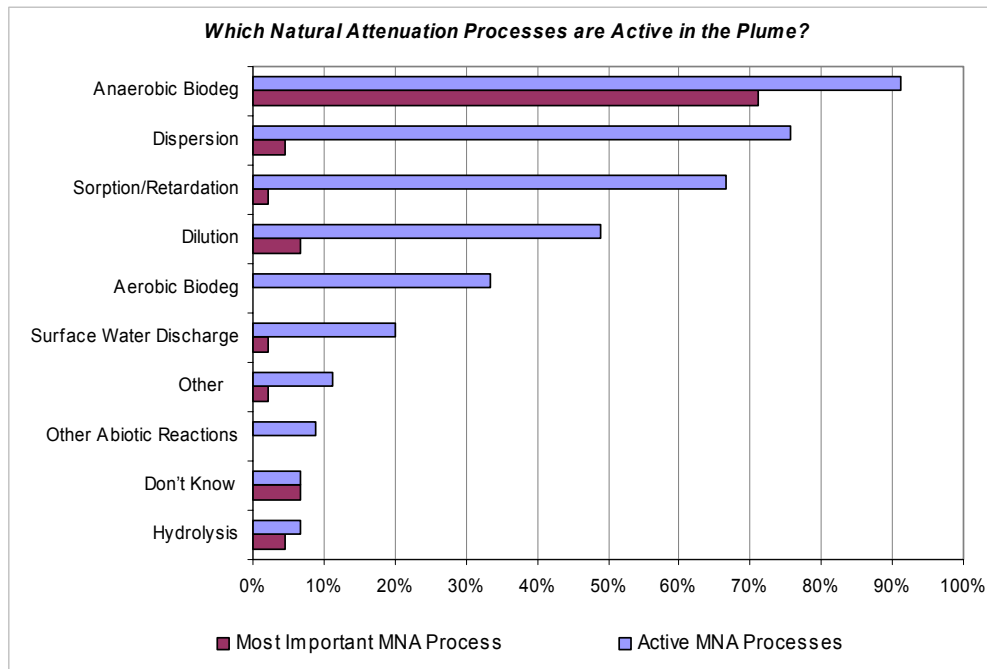


Figure 5.10
Attenuation Processes Active at Chlorinated Solvent Sites (n=45)

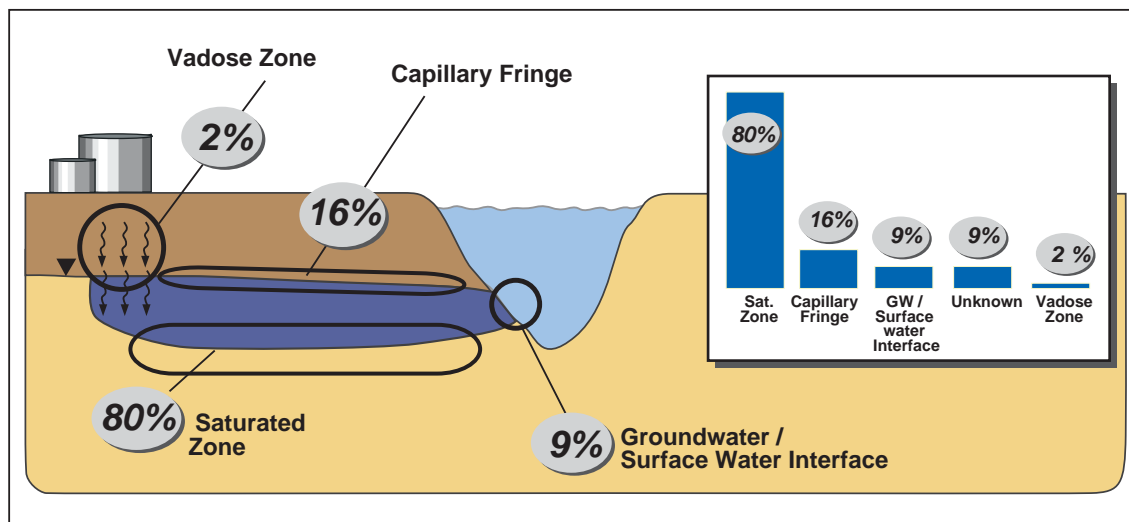


Figure 5.11
Primary Subsurface Location of Attenuation Processes (n=45)

The number of wells used to evaluate MNA varied from less than 10 to greater than 50, although most sites did incorporate less than 50 wells. In contrast, many sites contain a total of greater than 50 wells as indicated on Figure 5.12.

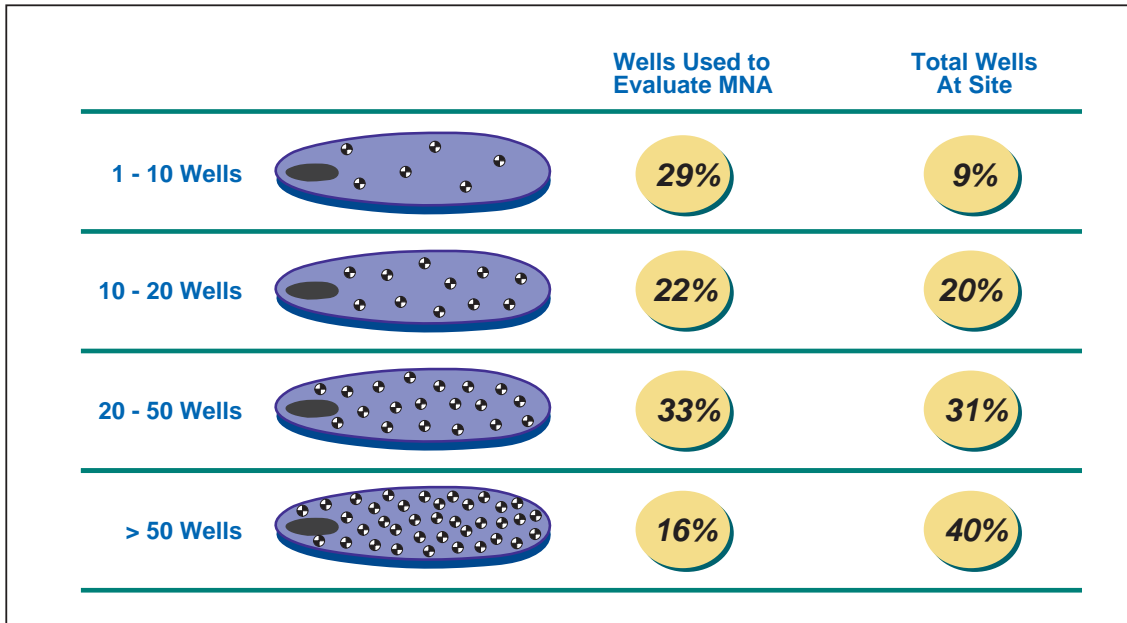


Figure 5.12
Number of Monitoring Wells Used to Evaluate MNA (n=45)

Methods of evaluating MNA, or demonstrating “lines of evidence” as described in the US EPA and other technical protocols, are summarized on Figure 5.13. Approximately three-quarters of sites indicated using statistics and/or calculations to analyze spatial and/or temporal concentration trends. The most frequently used methods included concentration versus distance to obtain bulk degradation rates and concentration versus time plots to get point decay rates (see Newell et al., 2002 for a through discussion of the use of different types of rate calculations for MNA studies). 24% of sites used a trend analysis such as Mann-Kendall statistics. Geochemical footprints of biodegradation often evaluated included the presence of biodegradation daughter products, appropriate redox conditions and/or dissolved oxygen data, and concentrations of sulfate, nitrate, and/or ferrous iron. Only 1 site indicated that geochemical indicators were not evaluated. Computer models were used to predict a variety of parameters and/or gain a better understanding of attenuation mechanisms at 60% of sites. The primary use of modeling was found to be prediction of plume stability. When asked to rank six lines of evidence from most important to least important in the MNA evaluation process, respondents indicated that favorable geochemical indicators were most important. However, observed decrease in chlorinated solvent concentrations was most often ranked either first or second. Data also demonstrate that microcosm studies are rarely used to evaluate MNA.

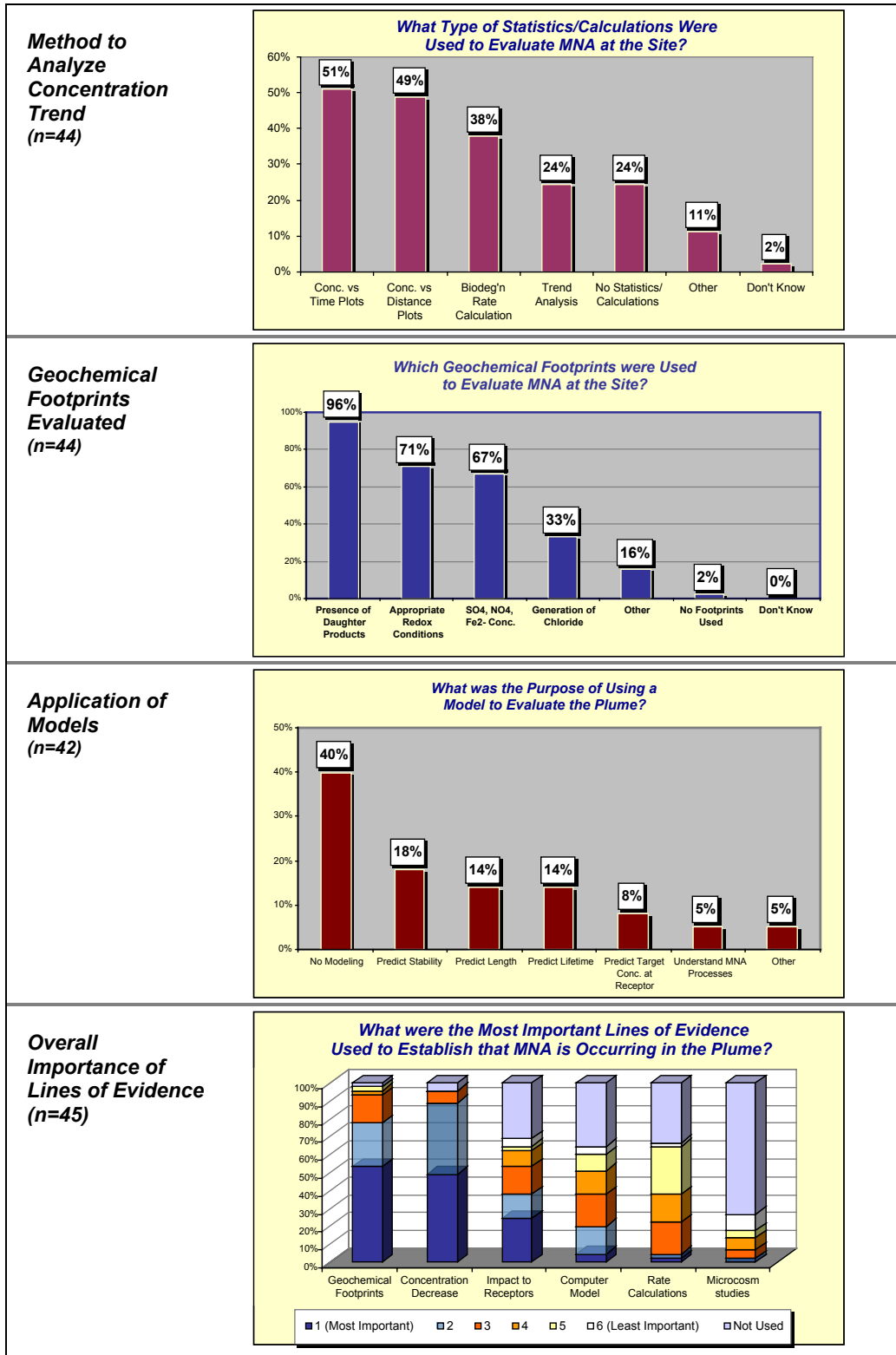


Figure 5.13
Methods Used to Evaluate MNA

Few respondents indicated the use of studies to evaluate the sustainability of anaerobic biodegradation as shown in Table 5.1. A lack of guidance on methods to evaluate sustainability in the US EPA and other technical protocols is likely the reason for the low occurrence.

Were Studies Performed to Evaluate Sustainability of Anaerobic Biodegradation within the Plume?	
Response	% of Sites
Yes	27
No	67
Anaerobic Biodegradation does not Occur	4
Don't Know	2

Table 5.1
Evaluation of Natural Attenuation Sustainability (n=45)

Estimation of remediation time frame is an important factor in determining the likelihood of an MNA remedy as the US EPA technical protocol and many state protocols require demonstration that MNA will likely attain remedial objectives in a reasonable period compared to other technologies (US EPA, 1998; KDHE, 2001; TCEQ, 2001; NHDES, 1999). Figure 5.14 illustrates that 57% of respondents estimated the remediation time frame. Extrapolated concentration versus time trends and computer modeling were most often utilized in the time frame evaluation, and 36% used more than one method to estimate the time to reach remedial objectives. Additionally, the analytical model BIOCHLOR was the computer model most frequently used for time frame estimation. Estimated remediation time frames are presented on Table 5.2 and show that most sites predict remedial goals to be met in less than 30 years using MNA. However, no questions were asked about the uncertainty associated with the time frame estimate. Additionally, remedial objectives for the primary CVOC, shown on Table 5.3, indicate that most sites are remediating to Maximum Contaminant Levels (MCLs).

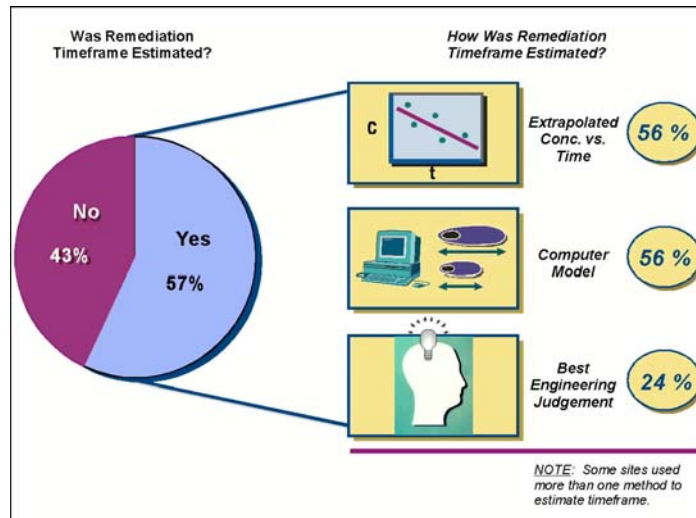


Figure 5.14
Methods of Estimating Remediation Time Frame (n=44)

What is the Estimated Remediation Time Frame?	
Estimated Time Frame	% of Sites
< 5 yrs	4
5 to 10 yrs	8
11 to 20 yrs	44
21 to 30 yrs	12
> 30 yrs	32

Table 5.2
Remediation Time Frame Estimation (n=25)

What are the Cleanup Concentration Goals for the Primary Chlorinated Constituent?	
Concentration Goal	% of Sites
< 0.005 mg/L	64
0.005 to 0.1 mg/L	20
> 0.1 mg/L	12
Don't Know	4

Table 5.3.
Remedial Concentration Goals (n=25)

Cost data, categorized into the initial MNA study and annual monitoring, specific to the site was requested. Results, presented in Table 5.4, are consistent with the data obtained from Part A of the study.

Cost Range (K)	Initial Characterization	Annual Monitoring
	% of Sites	% of Sites
< \$50	17	71
\$50 to \$100	26	10
\$100 to \$200	24	10
> \$200	26	10
Don't Know	7	0

Table 5.4
Costs Associated with MNA (n=42)

Figure 5.15 summarizes characteristics of the chlorinated solvent plumes observed at surveyed sites. TCE or PCE was listed as the primary solvents originally released at most sites, and the maximum solvent concentration detected in a well was 10 to 100 mg/L at nearly 40% of sites. A follow-up question confirmed that units were not misinterpreted in the original question. Since the solubility of PCE and TCE are approximately 200 mg/L and 1100 mg/L, respectively, these results indicate that many sites may have DNAPL present based on maximum concentrations that exceed 1% solubility of primary constituents. Results also demonstrate that almost all

solvent plumes being managed by MNA are less than a mile long and 100 acres in area. Typical groundwater seepage velocities of the contaminant plumes are presented in Figure 5.16. By comparison, the median seepage velocity for 290 groundwater sites (representing a mixture of fuel, solvent, metals, and inorganic plumes) reported by Newell et al. (1990) was 88 feet per year.

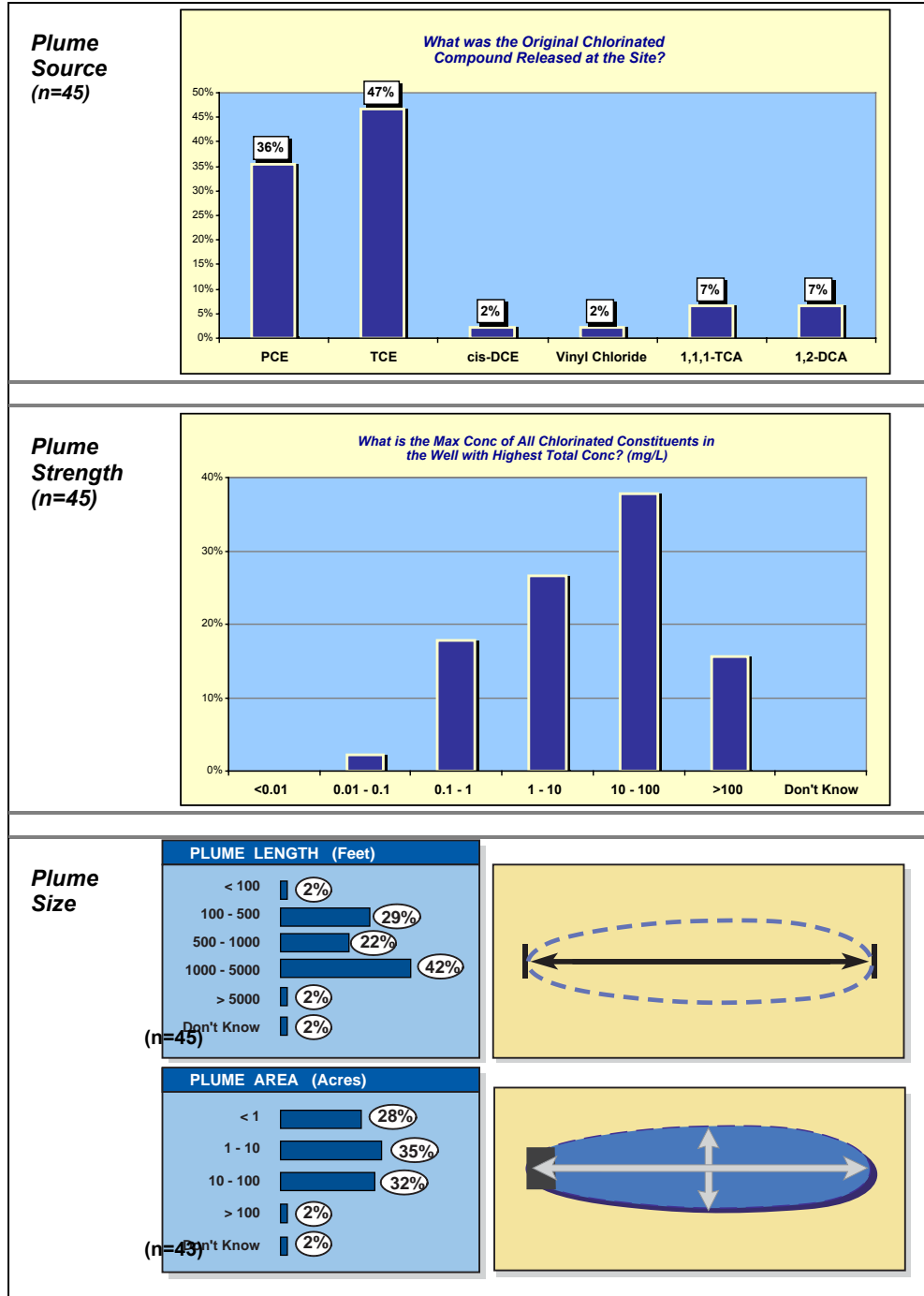


Figure 5.15
Characteristics of Solvent Plumes Managed by MNA

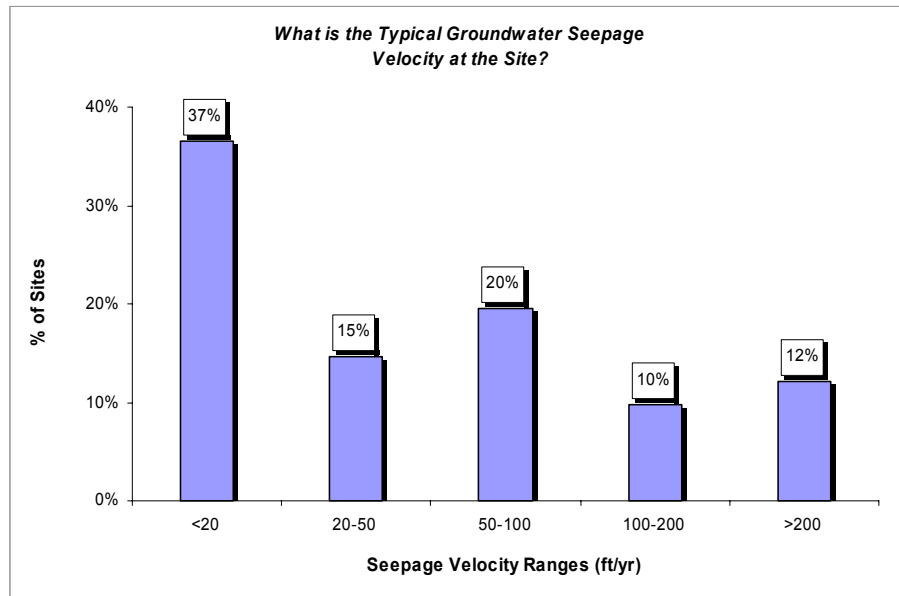


Figure 5.16
Typical Groundwater Seepage Velocities at MNA Sites (n=41)

Another very important characteristic of a plume that often determines the possibility of a MNA remedy is plume stability. Plume stability is evaluated by examining the trend of the plume length (i.e. shrinking, expanding, stable, stable with discharge to surface water, etc.). Most protocols require demonstration that a plume is either stable or shrinking prior to applying MNA as a final control measure. Figure 5.17 illustrates that 56% of sites currently applying MNA indicate a stable or shrinking plume. Four of the seven sites with a shrinking plume report a 10 to 50% reduction in plume length, while two sites report a reduction of less than 10%. An additional 20% of sites have a stable plume that is discharging either to wetlands or a stream. Interestingly, MNA is being applied at 9% of sites with an expanding plume.

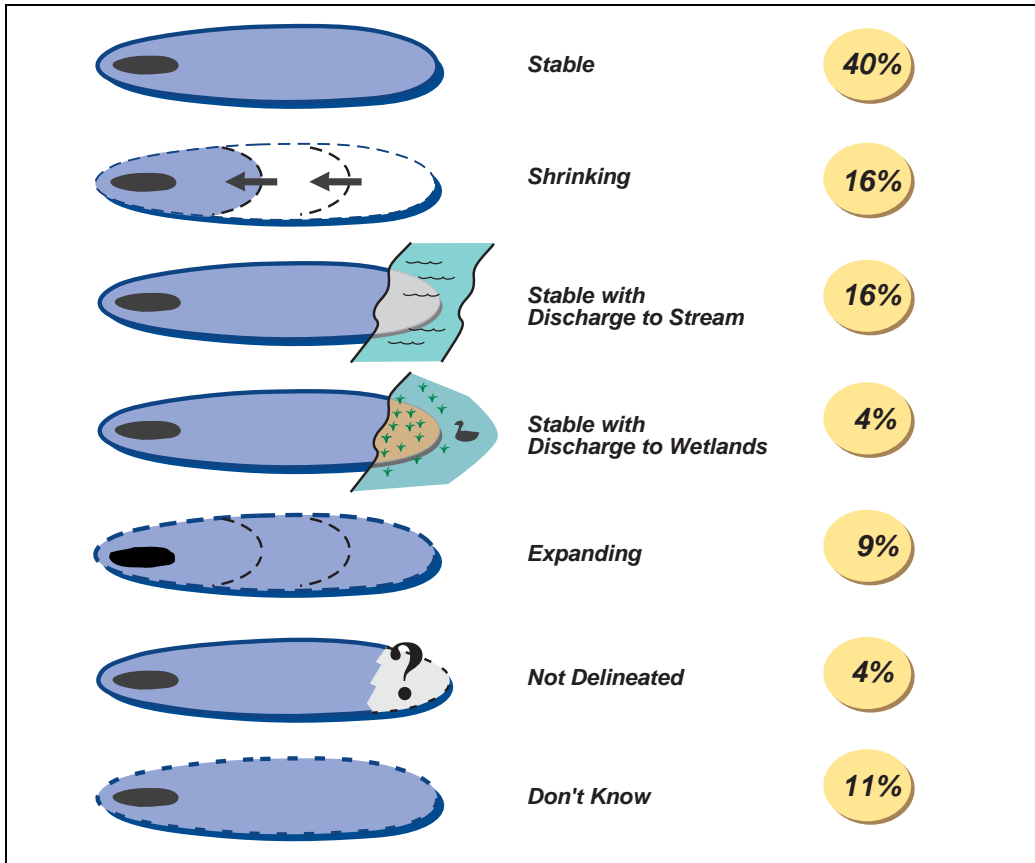
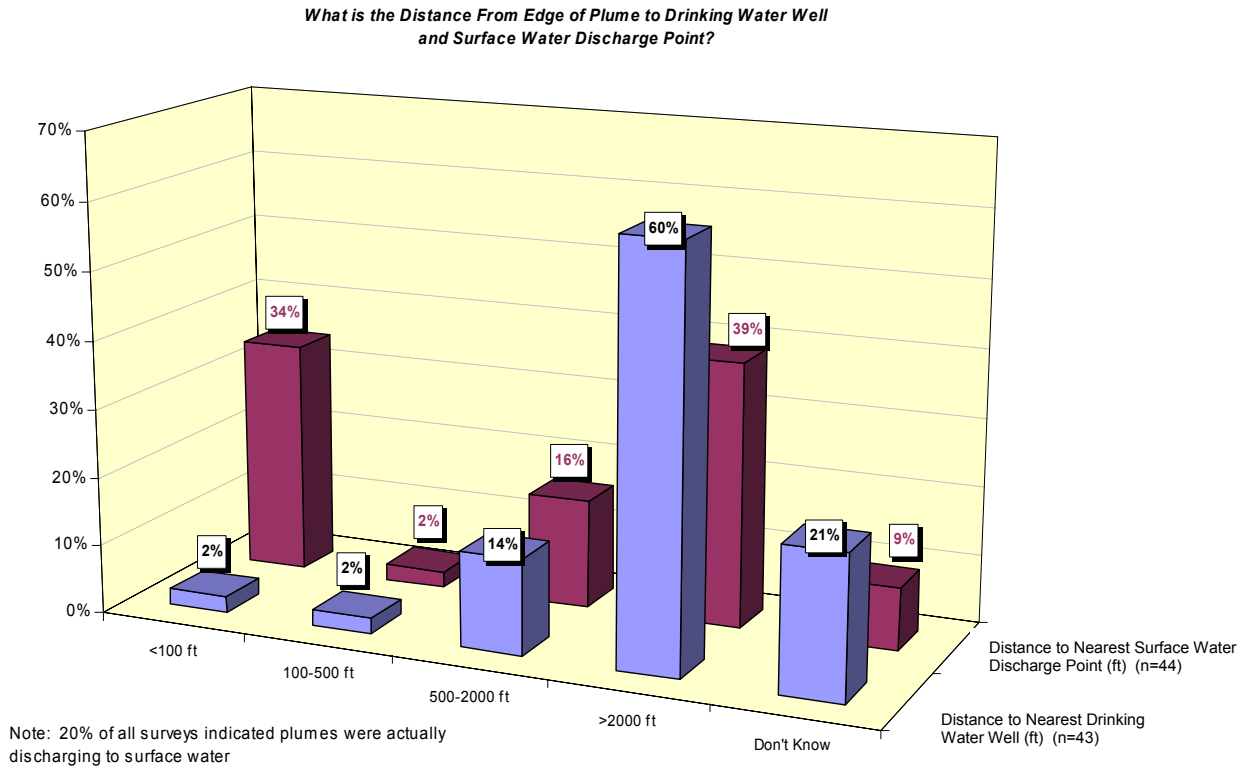


Figure 5.17
Evaluation of Plume Stability (n=45)

The downgradient edge of most solvent plumes was found to be greater than 2,000 feet from the nearest drinking water well as indicated in Figure 5.18. However, distances to surface water discharge points varied, and as stated previously, 20% are actually discharging to surface water.



**Figure 5.18
Distance of Plume Edge to Receptors**

Many studies at chlorinated ethene sites have observed accumulation of the *cis*-DCE isomer evidenced by concentrations of *cis*-DCE higher than parent compounds and other degradation products. This condition of *cis*-DCE “stall” may occur for several reasons: i) slower rate of *cis*-DCE reduction compared to other chlorinated ethenes due inappropriate redox conditions; ii) microorganisms that reduce PCE/TCE to *cis*-DCE out compete those that degrade *cis*-DCE to vinyl chloride and ethene resulting in a slower growth rate of the latter organisms; and/or iii) rapid degradation of vinyl chloride via direct oxidation is occurring, and therefore does not accumulate as would be predicted if degradation occurred via reductive dechlorination (Wiedemeier et al., 1999). Less than one-quarter of those surveyed indicated the condition of *cis*-DCE “stall” was a problem as shown in Table 5.5.

Does the Condition of <i>cis</i>-DCE “Stall” Appear to be a Problem at the Site?	
Response	% of Sites
Yes	23
No	57
Not a <i>cis</i> -DCE Site	7
Don't Know	13

Table 5.5

Occurrence of *cis*-DCE Stall (n=44)

Table 5.6 displays the timing of several critical events in the MNA evaluation and implementation process. Several interesting findings include: i) 56% of sites indicated that the MNA remedy has been approved by the applicable regulatory agency, and is still being considered as a remedy at the remainder; ii) the primary report documenting MNA was released 1 to 5 years ago at over 75% of sites (report references provided by respondents are found in Appendix B); and iii) the primary solvent release began in the 1960's or 1970's and ended in the 1970's or 1980's at most sites. Interestingly, 10% of sites indicated releases continuing into the 1990's.

(n=20)	When did Primary CVOC Release Begin?	5%	5%	15%	35%	25%	10%	5%							
(n=20)	When did Primary CVOC Release End?				10%	45%	35%	10%							
(n=45)	When was Groundwater First Collected?	<i>Don't Know</i> 4%			9%		49%	33%			4%				
(n=45)	When was MNA Data First Collected?	<i>Don't Know</i> 4%			38%			33%			24%				
(n=45)	When was Primary MNA Report Issued?	<i>Don't Know</i> 4%			9%			40%			36%		11%		
(n=39)	When was MNA Approved by Regulators?	<i>Don't Know</i> 8%			<i>Still Being Considered</i> 44%			8%			18%			13%	10%
	Year / Decade	1930's	1940's	1950's	1960's	1970's	1980's	1993	1998	1999	2000	2001	2002	2003	
	Years Ago						20	10	5	4	3	2	1	0	

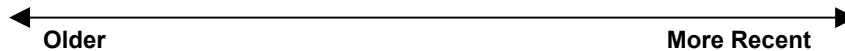


Table 5.6
Time Table of Critical Events

Finally, the professional background of survey respondents is listed in Table 5.7. Respondents, on average, stated they have been conducting MNA evaluations at chlorinated solvent sites for 7 years.

What is Your Professional Background?	
Response	% of Respondents
Geology	43
Environmental Engineering	23
Other	23
Hydrology	13
Civil Engineering	7

Table 5.7
Professional Background of Respondents (n=34)

5.2 Correlation of Survey Data

Several correlations of survey data, primarily relating to how MNA was implemented at sites as a function of various plume characteristics, were performed. Figure 5.19 presents the fraction of several MNA implementation strategies for sites where the maximum solvent concentration in a well exceeds 10 mg/L. As evident, most sites within this category rely on some active treatment process, often targeting the source of contamination, to complement the MNA remedy.

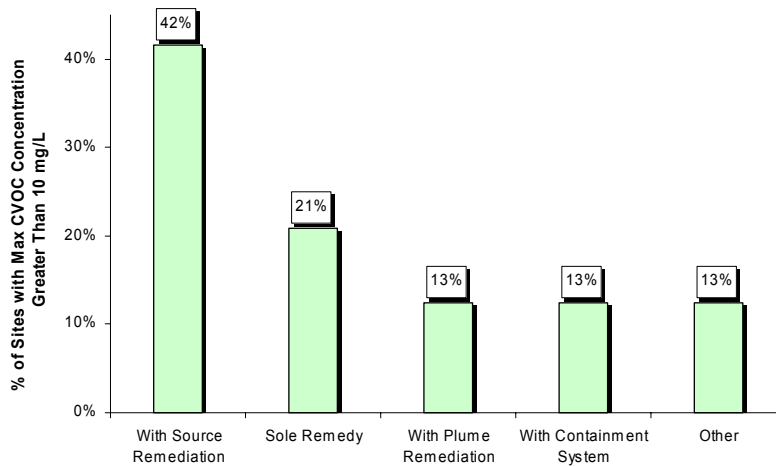


Figure 5.19
MNA Use at Sites with Maximum CVOC Concentration Exceeding 10 mg/L

Next, MNA implementation was compared to groundwater seepage velocity and plume length. Results, shown in Figure 5.20, demonstrate that at over half the sites where MNA is implemented as the sole remedy, groundwater seepage velocity is less than 20 feet per year. Additionally, many sites implementing MNA as the sole remedy exhibit solvent plumes less than 500 feet long.

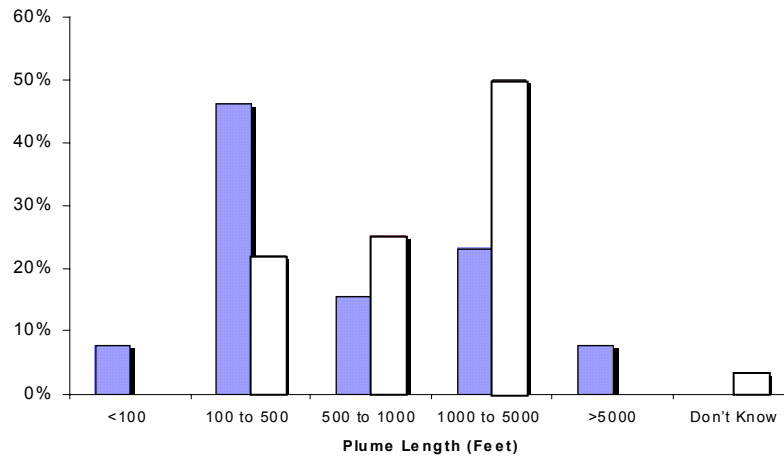
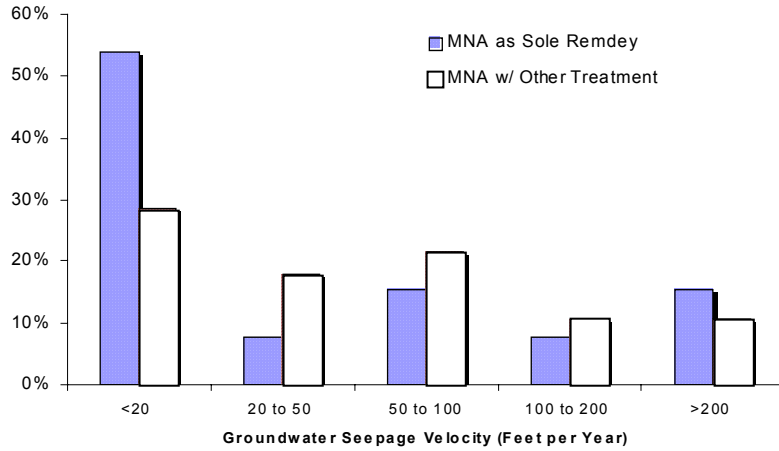


Figure 5.20
Use of MNA as a Function of Groundwater Seepage Velocity and Plume Length

Many sites indicated the estimated time frame for remediation was less than 20 years (see Table 5.2). An analysis of various parameters was conducted to better understand site and/or plume conditions that may influence a short remediation time frame. The most dominant trend emerging from this analysis was the occurrence of a shrinking or stable plume at over 80% of sites estimating remediation time frame as less than 20 years (Figure 5.21).

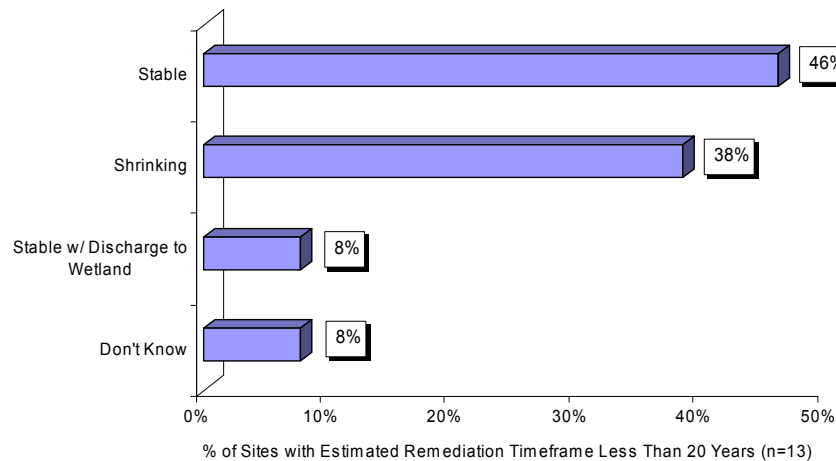


Figure 5.21

Plume Stability of Sites with an Estimated Remediation Time Frame of 20 Years or Less

KEY POINTS

PART A:

- 34 MNA experts provided general data regarding MNA evaluation at 191 chlorinated solvent sites.
- MNA was determined a possible remedy, either solely or as a component of the remedy, at over 75% of all sites evaluated (sole remedy at 30% of sites, with active treatment at 47% of sites).
- Plume instability and unacceptable remediation time frame were leading factors excluding the use of MNA.
- Average cost of the initial MNA evaluation was \$177,000, while annual monitoring costs averaged \$33,000 per year.

PART B:

- Site-specific data was provided for 45 chlorinated solvent plumes being managed by MNA.
- The 1998 US EPA protocol was most often referenced as the guideline for MNA implementation (36%). Notably, about 27% used a site specific protocol.
- Over 70% of respondents stated that anaerobic biodegradation is the primary natural attenuation process occurring in the plume.
- A variety of geochemical indicators is reportedly used to assess MNA, but over 90% rely on the presence of biodegradation daughter products.
- Computer models of various types were used to evaluate MNA at 60% of the sites. The most commonly used model was BIOCHLOR.
- The timeframe for remediation was estimated at nearly 60% of the sites, and most (68%) expect remediation goals to be achieved in less than 30 years.
- Most plumes evaluated have a maximum length of 1000 to 5000 feet, an area of 1 to 10 acres, and contain maximum chlorinated solvent concentrations of 10 to 100 mg/L.
- 34% of the MNA sites were less than 100 feet from a downgradient discharge.
- The respondents classified the plumes as stable or shrinking at 56% of the sites. Interestingly, the plumes were classified as expanding for 9% of the sites and discharging for 20% of the sites.
- MNA has been approved by regulators at nearly half the sites, while the remedy is still being considered at 44% of sites.

6.0 CONCLUSIONS

The objective of the historical survey of MNA at chlorinated solvent sites was to document characteristics, trends, successes, and barriers in the application of MNA as a remedy. This objective was accomplished through the distribution of a two-part, electronic survey to over 200 experts in the field. Thirty-four respondents provided general information regarding the evaluation of MNA at over 190 chlorinated solvent sites, and provided site-specific data on the implementation of MNA as a remedy for 45 solvent plumes. In addition to the survey, a review of case study literature generated site-specific data for approximately 20 additional sites.

An evaluation of site characteristics where MNA is being applied as a remedy revealed that MNA is typically applicable at a variety of sites. Survey respondents indicated application of MNA at a wide variety of industrial sites with a broad range of processes. MNA was most often implemented at sites with slower groundwater seepage velocities (i.e. less than 100 feet/year). High chlorinated solvent concentrations were found not to preclude use of MNA, as more than half the sites indicated maximum chlorinated constituent concentrations exceeding 10 mg/L. However, most sites with high CVOC concentrations relied upon active treatment remedies to enhance the effectiveness of natural attenuation. Very few respondents indicated use of MNA to manage very large solvent plumes (i.e. greater than 5000 feet in length, greater than 100 acres in area) or plumes where the downgradient edge is within 500 feet of a drinking water well.

Several trends related to application of MNA at chlorinated solvent sites emerged from the study including:

- The 1998 US EPA protocol was most often referenced as the guideline for MNA implementation (36%). Notably, about 27% used a site specific protocol.
- Over 70% of respondents stated that anaerobic biodegradation is the primary natural attenuation process occurring in the plume.
- A variety of geochemical indicators are reportedly used to assess MNA, but over 90% rely on the presence of biodegradation daughter products to demonstrate MNA occurrence.
- Computer models of various types were used to evaluate MNA at 60% of the sites. The most commonly used model was BIOCHLOR.
- The timeframe for remediation was estimated at nearly 60% of the sites, and most expect remediation goals to be achieved in less than 30 years.

Successful demonstrations of MNA would include those sites where MNA is being applied as the sole remedy and those sites where MNA has been approved by the applicable regulatory agency. Therefore, characteristics and trends documented at such sites were examined. The two following plume characteristics were found to dominate sites where MNA is being applied as the sole remedy: i) a groundwater seepage velocity of less than 20 feet per year, and ii) a maximum plume length of less than 500 ft. Conversely, MNA was infrequently used as the sole remedy at sites with maximum CVOC concentrations exceeding 10 mg/L. No dominant trends were evident for sites where MNA has been approved by regulators. Sites with short estimated remediation time frames are another indicator of successful MNA application. Examination of sites with an estimated remediation time frame of less than 20 years revealed that almost 85% of such sites demonstrate a stable or shrinking plume trend (however, no questions regarding the uncertainty in time frame estimates were asked).

Survey results indicated that less than one-quarter of all sites evaluated for MNA application found MNA was not a feasible remedy. Additionally, only three of the sites reviewed as part of the case study analysis indicated MNA was not applicable. Nearly all of these sites specified an unacceptable remediation time frame as a primary reason for this determination. Survey respondents also cited plume instability, lack of geochemical indicators of biodegradation, prohibitive site hydrogeology, and dominance of non-destructive attenuation processes as other factors contributing to exclusion of MNA at chlorinated solvent sites.

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APPENDIX A
MNA HISTORICAL SURVEY

Performance of MNA Remedies at Chlorinated Solvent Sites

Savannah River Technology Center
Aiken, South Carolina

"HISTORICAL PERSPECTIVE OF MNA" QUESTIONNAIRE FOR CHLORINATED SOLVENT SITES



We would greatly appreciate your help with this questionnaire! **The deadline to respond is June 27, 2003**

If you don't know the answer or if the question does not apply, leave it blank. To save time, approximate answers are OK.

If you don't have time, just fill out Part A!

If you complete Part A and Part B, then you will receive a **\$25 honorarium** in appreciation of your efforts.

Savannah River Technology Center appreciates your help with this important project! **Thanks!**

Upon completion of the questionnaire, please SAVE the file, attach the file to an email, and send to mnasurvey@gsi-net.com

Questions? Contact Travis McGuire at (713) 522-6300 or tmmcguire@gsi-net.com

(If this email was forwarded to you, or you want to fill out more than 1 questionnaire, please contact Travis McGuire at 713-522-6300 or tmmcguire@gsi-net.com)

PART A - YOUR GENERAL EXPERIENCE WITH MNA (TIME: 5 MINUTES)

A.1 Have you characterized one or more CHLORINATED SOLVENT contaminated sites to determine if MNA is feasible?

If yes, MNA feasibility was evaluated at:

How many total sites?

How many where MNA was shown NOT to be feasible for any purpose at the site?

How many where MNA alone was selected as the remedy?

How many where MNA was used together with active treatment?

How many where the details of the MNA portion (including monitoring) been fully approved by the applicable regulatory agency?

→ For sites where MNA was used with active treatment:

How many sites has the active treatment system been completed?

How many sites is the active treatment system still operating?

A.2 What is the typical size of the plume at your approved MNA remediation sites?

- Large (> 50 acres) (50 acres: approx. 2000 by 1000 ft)
- Medium
- Small (< 10 acres) (10 acres: approx. 1000 by 500 ft)

A.3 About how much did the typical MNA initial characterization effort cost? (Including MNA-specific monitoring, data analysis, modeling, report writing, and other related expenses)

A.4 About how much does the typical annual monitoring of an MNA site cost?

If you do not wish to complete Part B, please scroll to the bottom of the questionnaire for reply instructions. **Thanks!**

PART B - YOUR KNOWLEDGE ABOUT A SPECIFIC MNA SITE (TIME: <1 HOUR)

If you have data for a chlorinated solvent site where MNA was evaluated as a remedy, then please complete Part B.

WHERE

B.1 What is the name of the site? (Optional)

Please select the primary **INDUSTRIE(S)** and **PROCESS(ES)** carried out at the site.

- Industries
- Electronics manufacturing
 - Solvent production
 - Pesticide/Herbicide manufacturing
 - Aircraft maintenance
 - Dry cleaning
 - Instrument manufacturing
 - Metals industry
 - Laboratory
 - Landfill
 - Other

- Processes
- Metal cleaning/degreasing
 - Metal machining
 - Tool-and-die operations
 - Paint removing/stripping
 - Storage of solvents in underground or above ground storage tanks
 - Storage of drummed solvents
 - Solvent loading and unloading
 - Disposal of mixed chemical wastes in landfills
 - Treatment of mixed chemical wastes in lagoons or ponds
 - Other

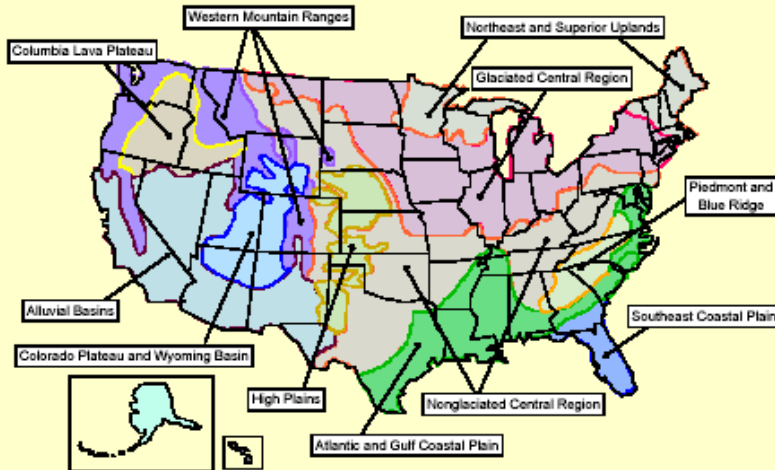
B.2 Where is the site located?

-Select State- ▼

County/Parish or City

Latitude (Optional)

Longitude (Optional)



B.3 Select the hydrogeologic setting of the water-bearing unit based on the DRASTIC hydrogeologic settings listed below for the thirteen regions in the United States as depicted in the figure above. (Please select only ONE region and setting)

Western Mountain Ranges ▼

Columbia Lava Plateau ▼

-Select Colorado Plateau and Wyoming Basin-

-Select Nonglaciated Central Region-

B.7 What natural attenuation processes are active in this plume? (answer both questions below)

	What MNA Processes Were Active At This Site? <i>(check ONE OR MORE boxes)</i>	Which Single Process Was the Most Important For MNA At This Site? <i>(select ONE from the following list)</i>
Dispersion	<input type="checkbox"/>	<input type="checkbox"/>
Sorption/Retardation	<input type="checkbox"/>	<input type="checkbox"/>
Aerobic Biodegradation	<input type="checkbox"/>	<input type="checkbox"/>
Anaerobic Biodegradation	<input type="checkbox"/>	<input type="checkbox"/>
Hydrolysis	<input type="checkbox"/>	<input type="checkbox"/>
Other abiotic reactions	<input type="checkbox"/>	<input type="checkbox"/>
Discharge to surface water	<input type="checkbox"/>	<input type="checkbox"/>
Dilution	<input type="checkbox"/>	<input type="checkbox"/>
Other	<input type="checkbox"/>	<input type="checkbox"/>
Don't Know	<input type="checkbox"/>	<input type="checkbox"/>

B.8 Where was the primary natural attenuation process occurring throughout the system? (check one or more boxes)

- throughout the vadose zone
- throughout the saturated zone
- at the groundwater / surface water interface
- at the vadose / groundwater interface
- don't know

B.9 How many wells were used to evaluate MNA at the site?

-Select Number of Wells- ▼

B.10 How many total wells are present at the site?

-Select Number of Wells- ▼

B.11 How many years of groundwater data were analyzed for the MNA study?

-Select Years of Data- ▼

B.12 Were microcosms used to help evaluate MNA? (select one from the following list)

Yes. If yes, How many?

No

Don't Know

B.13 What type of geochemical footprints were used to evaluate MNA at the site? (check one or more boxes)

- Presence of daughter products from reductive dechlorination (i.e., cis-DCE, Vinyl Chloride, 1,1-DCA, ethene, ethane, etc.)
- Appropriate redox conditions and/or dissolved oxygen concentration
- Concentrations of sulfate, nitrate, and/or ferrous iron
- Generation of chloride
- Other Describe Other:
- No geochemical footprints were used in the MNA study
- Don't know

B.14 What type of statistics / calculations were used to evaluate MNA at the site? (check one or more boxes)

- Concentration vs. distance plots to get bulk degradation rate

B.15 What type of models were used to evaluate MNA at the site? (check one or more boxes)

- Simple conceptual model of site
- Mass flux calculations at one or more points in plume
- Analytical model (such as BIOCHLOR, Domenico model, etc.)
- Numerical flow model and solute transport model (such as MODFLOW and MT3D)
- Research model for chlorinated solvent sites (such as RT3D)
- No modeling was performed
- Don't know

If a computer model was used, why was that particular model selected:

B.16 What was the purpose for using a model to evaluate the plume? (check one or more boxes)

- Predict if plume is shrinking, stable, or expanding
- Predict ultimate plume length
- Predict lifetime of plume (how many years it will take until groundwater is restored)
- Predict that a target concentration will not be exceeded at a receptor or compliance point
- Understand which natural attenuation processes are important at the site
- Other Describe Other:
- Don't know

B.17 In your opinion, what were the most important lines of evidence in establishing that MNA was occurring in the plume? (Rank from 1 to 6 with 1 being most important, or select "Not Used")

- Rank from 1 to 6-

 Observed decrease in concentrations of chlorinated solvents as shown in concentration history in wells, change in plume maps, etc.
- Rank from 1 to 6-

 Presence of geochemical footprints (such as redox conditions, presence of daughter products)
- Rank from 1 to 6-

 Computer modeling results
- Rank from 1 to 6-

 Rate calculations
- Rank from 1 to 6-

 Microcosm studies
- Rank from 1 to 6-

 No impact to receptors

B.18 Did you perform an analysis to evaluate whether anaerobic biodegradation processes in the plume were sustainable over a long time period?

Yes, we used the following approach:

No

There was no anaerobic biodegradation at this site

Don't know

B.19 Did you perform an analysis to estimate the remediation timeframe at this plume (in other words, an estimate for how many years MNA would take to restore the aquifer to meet site cleanup goals)?

Yes (see below) No Don't know

If Yes, how did you estimate remediation timeframe? (check one or more boxes)

WHAT

B.22 What was the main parent compound at the site? (the original contaminant that was released)

-Select Chlorinated Constituent- ▼

B.23 What is the approximate percentage of solvents by compound, based on the well with highest total concentration? (This can be very approximate. Leave blank if not chlorinated ethene or ethane site)

<p>If chlorinated ethene site:</p> <p><input type="checkbox"/> % PCE</p> <p><input type="checkbox"/> % TCE</p> <p><input type="checkbox"/> % cis-DCE</p> <p><input type="checkbox"/> % Vinyl chloride</p> <p><input type="checkbox"/> Don't know</p>	<p>If chlorinated ethane site:</p> <p><input type="checkbox"/> % 1,1,1-TCA</p> <p><input type="checkbox"/> % 1,1-DCA</p> <p><input type="checkbox"/> % 1,1-DCE</p> <p><input type="checkbox"/> Don't know</p>
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B.24 What is maximum concentration of ALL chlorinated solvents at the well with the highest total concentration?

-Select Max. Conc. of ALL Chlorinated COCs- ▼

B.25 How long is the longest chlorinated solvent plume at the site?

-Select Max. Chlorinated COC Plume Length- ▼

B.26 What is the approximate area of the largest chlorinated solvent plume in acres?

-Select Max. Chlorinated COC Plume Area- ▼

B.27 What is the typical groundwater seepage velocity at the site?

-Select Typical Seepage Velocity- ▼

B.28 What is the trend for the length of the longest chlorinated solvent plume at the site?

Shrinking. If shrinking, what percent is the plume length now compared to initial characterization? -Select Plume Reduction %- ▼

Stable in aquifer. No discharge to surface water.

Stable but discharges to stream, ditch, creek, or river.

Stable but discharges to wetland.

Expanding. If expanding, what percent is the plume length now compared to initial characterization? -Select Plume Expansion %- ▼

Have not delineated downgradient edge of plume.

Don't know.

B.29 Does cis-DCE stall (the condition where it appears that biodegradation past cis-DCE to vinyl chloride does not occur) appear to be a problem at the site?

Yes

No

Don't know

No cis-DCE at site

B.30 What is the distance between the downgradient edge of the longest plume to:

- An actual drinking water well -Select Distance- ▼
- A discharge point to a stream or wetland -Select Distance- ▼

WHEN

B.31 When was groundwater data first collected at the site? -Select Year- >

WHO

B.36 What is your professional background?

<input type="checkbox"/> Geology	<input type="checkbox"/> Hydrology	<input type="checkbox"/> Environmental Engineering
<input type="checkbox"/> Civil Engineering	<input type="checkbox"/> Other	<input type="text"/>

B.37 What is your job title?

B.38 How many years have you been conducting MNA remedies/studies?

B.39 May we contact you for a short follow-up interview if necessary? Yes No

Please provide contact information:

Name	<input type="text"/>
Organization	<input type="text"/>
Address	<input type="text"/>
Phone Number	<input type="text"/>

Thank you for completing our questionnaire. Please **SAVE** file and email to: mnasurvey@osl-net.com

If you completed Part A and Part B of the questionnaire, then a \$25 honorarium will be sent to you at the address above.

If you have another site, or know someone else that might want to participate, then please contact Travis McGuire at 713-522-6300 or tmm@osl-net.com for confirmation! Thanks!

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APPENDIX B
MNA REPORT REFERENCES
PROVIDED BY SURVEY RESPONDENTS

Performance of MNA Remedies at Chlorinated Solvent Sites

Savannah River Technology Center
Aiken, South Carolina

- Feasibility Study - Somersworth Landfill, Somersworth, New Hampshire Canonic Environmental. Prepared for Somersworth Landfill Trust. March 1993.
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