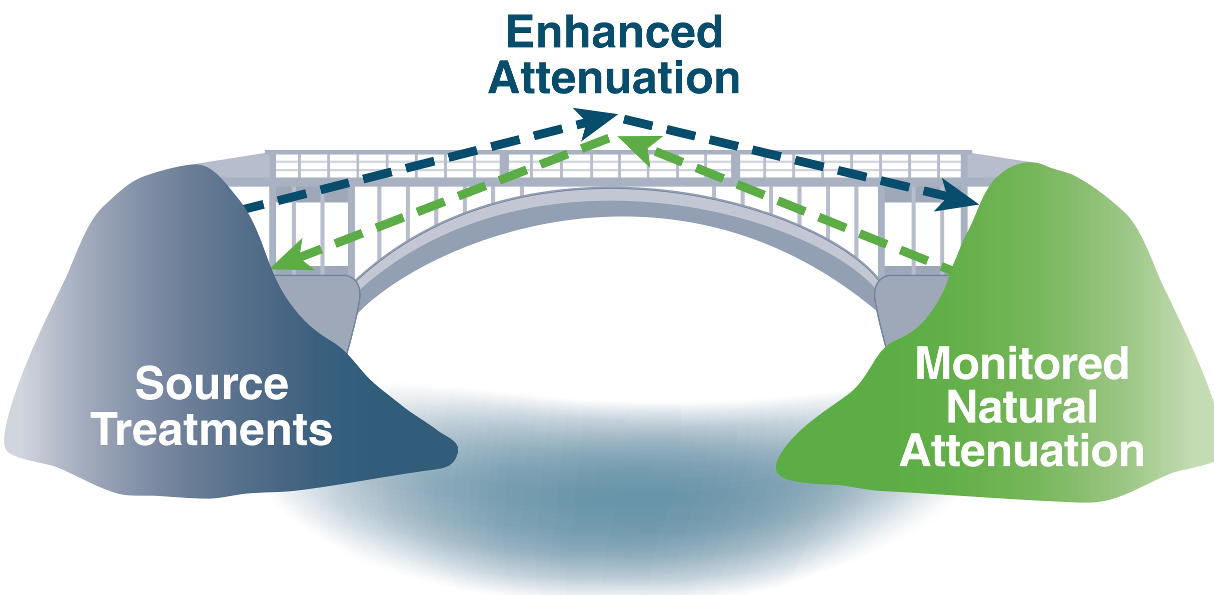
Technical and Regulatory Guidance

Enhanced Attenuation: Chlorinated Organics



April 2008

Prepared by
The Interstate Technology & Regulatory Council
Enhanced Attenuation: Chlorinated Organics Team

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Established in 1995, the Interstate Technology & Regulatory Council (ITRC) is a state-led, national coalition of personnel from the environmental regulatory agencies of all 50 states and the District of Columbia, three federal agencies, tribes, and public and industry stakeholders. The organization is devoted to reducing barriers to, and speeding interstate deployment of better, more cost-effective, innovative environmental techniques. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers. More information about ITRC and its available products and services can be found on the Internet at www.itrcweb.org.

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EXECUTIVE SUMMARY

Many sites with chlorinated organic contamination in groundwater throughout the nation have gone through extensive remedial evaluations and actions. The remedial alternatives for many of these sites include high-energy treatments such as pump-and-treat systems. After years of operation, the effectiveness of these high-energy processes has begun to diminish without remedial objectives being met. Other more effective remedial alternatives need to be implemented; however, there is a lack of guidance available to regulators and the environmental community regarding how and when to transition these sites to lower-energy remedial alternatives and eventually to monitored natural attenuation (MNA). To answer this need, the ITRC Enhanced Attenuation: Chlorinated Organics (EACO) Team developed this guidance, which includes a protocol to assist in a smooth transition (or a bridge) between aggressive remedial actions and MNA, and thus the concept of enhanced attenuation (EA) was born.

> **Enhanced attenuation** is a plume remediation strategy to achieve groundwater restoration goals by providing a "bridge" between source-zone treatment and MNA and/or between MNA and slightly more aggressive methods.

EA is that "bridge," incorporating three important features: the evaluation of mass balance, defined as the relationship between mass loading and attenuation capacity of an aquifer; a decision framework that provides guidance for site decisions, and a toolbox of potential EA technologies (known as "enhancements") that optimize aquifer conditions to provide a sustainable treatment or, at least, minimize the energy needed to reduce contaminant loading and/or increase the attenuation capacity of an aquifer. The decision framework, in the form of a flowchart presented in Chapter 2, provides direction to regulators and practitioners on how to integrate EA into the remedial decision process. The EA approach is consistent with the current regulatory environment and can be accommodated within a broad range of regulatory programs such as those that follow the Comprehensive Environmental Resource Conservation Liability Act or state dry cleaner regulations. This new remedial framework and decision process will accelerate the environmental cleanup progress on a national scale and may reduce overall costs, while still providing protection to human health and the environment.

Briefly, the EA decision framework achieves the following:

- facilitates transition of contaminated sites through the remediation process
- complements MNA and expands remediation opportunities
- encourages energy efficiency and develops the best solutions for the environment

EA provides an organized, scientific, and structured yet broadly usable approach to implement specific treatment technologies ("enhancements") at appropriate sites and at appropriate times. Chapter 3 of this guidance discusses contaminant mass loading, aquifer attenuation capacity, and remediation treatment sustainability. These concepts and working methodology support all EA processes. While the underlying EA principles are not new, the EA concept was developed to address situations where natural attenuation processes, rates, or capacity are not sufficient to meet remedial goals. Specific elements considered in the EA decision framework include risk, remediation time frame, and cost criteria. Transitioning between source-zone treatment and MNA and/or between MNA and slightly more aggressive methods can be sequenced spatially as well as temporally. The EA decision framework also allows for situations where a site currently undergoing MNA may require enhancements due to changes in acceptable remediation time frames, cost, risk, or other conditions at the site.

The basic premise of EA is that, for some sites, source mass flux reductions due to natural attenuation processes may not be sufficient to meet regulatory criteria, causing MNA alone to be an unacceptable treatment option. The concept of EA essentially asks the question, "Is it possible through enhancements to augment the natural attenuation processes so that they operate more effectively and sustain themselves without further intervention?" Thus, the goal is an accelerated reduction in mass flux of contaminants sufficient to meet regulatory requirements using MNA as the final treatment. It is important to bear in mind that meeting acceptable remediation time frames for MNA may require consideration of other risk-reduction strategies either preceding or in tandem with an MNA remedy. More importantly, it may require establishing interim remediation goals to measure MNA remedy success.

Enhancements, discussed in Chapter 4, are lower-energy remediation technologies falling into two broad categories that either reduce the mass flux of contaminants from the source zone or increase the natural attenuation capacity of the aquifer downgradient from the source. They also have additional requirements regarding their capacity to achieve or maintain plume stability and eventual shrinkage, their ability to be monitored/validated, and their sustainability for a time sufficient to meet remediation goals.

Chapter 5 presents a detailed example of the application of EA with illustrated discussions of contaminant mass flux and aquifer attenuation capacity. Also included in this section is summary information from a database developed as a repository for sites throughout the country where EA technologies were used for chlorinated organics remediation. This Web-based database contains case studies of both successful and unsuccessful applications of EA technologies.

The team worked extensively with the U.S. Department of Energy (DOE) MNA/EA Technical Working Group through the entire EA decision framework development process. Both the DOE Technical Working Group and the ITRC team believe that the objective of the effort was to provide key scientific and technical aspects related to natural and enhanced attenuation of chlorinated organics and to provide a framework to encourage creative implementation of technologies based on defensible designs centered on contaminant mass loading and attenuation rates. The focus of this document is on chlorinated solvents due to the prevalence of groundwater contamination caused by this type of chlorinated organic. This resulted in the general affirmation of the approaches and guidance in the U.S. Environmental Protection Agency chlorinated solvent MNA directive and protocol of 1998 and 1999, OSWER Directive 9200.4-17P (1999, www.epa.gov/OUST/oswermna/mna_epas.htm). In addition, specific areas were identified for technical advances: mass balance as the framework for evaluating the attenuation processes and scientific techniques which integrate attenuation remedies for contaminated sites.

Following the MNA/EA Decision Flowchart offers regulators and the entire environmental community the tools necessary for successful characterization, remedy selection and implementation, site closure, and long-term monitoring. The team believes that through the use of this guidance, EA processes can successfully transition sites from active remediation to natural attenuation, with the ultimate goal of matching and optimizing the remedial strategy to the needs of the site.

GLOSSARY

Glossaries are traditionally located at the end of ITRC guidance documents. In this case, however, the team felt it more valuable to offer the reader the opportunity to review potentially unfamiliar terms prior to reading the guidance.

abiotic—Chemical and physical processes occurring without the involvement of living organisms. In some cases, such attenuation processes do not involve microorganisms or plants at all, while in other cases, biological and abiotic processes occur simultaneously and/or serve to enhance each other.

adaptive management (AM)—Also known as "adaptive resource management" (ARM), a structured, iterative process of optimal decision making in the face of uncertainty, with an aim to reducing uncertainty over time via system monitoring. In this way, decision making simultaneously maximizes one or more resource objectives and, either passively or actively, accrues information needed to improve future management. AM is often characterized as "learning by doing."

advection—Transport of a solute by the bulk motion of flowing groundwater.

aerobic—Conditions for growth or metabolism in which the organism is sufficiently supplied with molecular oxygen.

aerobic respiration—Process whereby microorganisms use oxygen as an electron acceptor to generate energy.

aliphatic compounds—Acyclic or cyclic, saturated or unsaturated carbon compounds, excluding aromatic compounds.

amendment—Substrate introduced to stimulate the in situ microbial processes (vegetable oils, sugars, alcohols, etc.).

anaerobic respiration—Process whereby microorganisms use a chemical other than oxygen as an electron acceptor. Common substitutes for oxygen are nitrate, sulfate, iron, carbon dioxide, and other organic compounds (fermentation).

anoxic—An environment where there is no free oxygen and where microbial and chemical reactions use other chemicals in the environment to accept electrons. Often such an environment is referred to as "anaerobic" because of the anaerobic respiration which occurs there.

anthropogenic—Derived from human activities, as opposed to those occurring in natural environments without human influences.

attenuation—The reduction of contaminant concentrations. The term applies to both destructive and nondestructive contaminant removal.

attenuation rate—The rate at which a contaminant is removed. This is not a rate constant but a rate, with typical units of µg per L per year.

bioaugmentation—The addition of beneficial microorganisms into groundwater to increase the rate and extent of anaerobic reductive dechlorination to ethene.

biodegradation—Breakdown of a contaminant by enzymes produced by bacteria.

biogeochemical reductive dechlorination (BiRD)—A process that involves both biological and chemical reactions to effect the abiotic reduction of chlorinated solvents, such as trichloroethene and tetrachloroethene. Indigenous sulfate-reducing bacteria are stimulated through the addition of a labile organic and sulfate, if not already present at high concentrations. The stimulated bacteria produce reductants that react in conjunction with minerals in the aquifer matrix. Moreover, the reducing conditions necessary to produce such reactions most often are created as a result of microbial activity.

biomass—Material produced by the growth of microorganisms.

bioremediation—Engineered treatment processes that use microorganisms to biodegrade contaminants. For MNA and EA, these processes occur in soil and groundwater.

biostimulation—Adding chemical amendments, such as nutrients or electron donors, to soil or groundwater to support bioremediation.

biotransformation—Biologically catalyzed transformation of a chemical to some other product.

capillary force—A force due to capillary action that "pulls" water and/or waterborne contaminants toward a substance that attracts them, leading to the production of thin trails of contamination and the incorporation of contamination into the inner windings of a soil particle.

chlorinated ethene—Chemical substances, such as trichloroethene and tetrachloroethene that have been used in industry as solvents.

chlorinated solvent—Organic compounds with chlorine substituents that commonly are used for industrial degreasing and cleaning, dry cleaning, and other processes.

chloromethanes—Chemical substances, such as carbon tetrachloride and chloroform that have been used in industry as solvents.

co-metabolism—A reaction in which microorganisms transform a contaminant even though the contaminant cannot serve as an energy source for growth, requiring the presence of other compounds (primary substrates) to support growth.

compliance monitoring—The collection of data which, when analyzed, can evaluate the condition of the contaminated media against standards such as soil and or water quality regulatory standards, risk-based standards of remedial action objectives.

conceptual site model (CSM)—A hypothesis about how releases occurred, the current state of the source zone, and current plume characteristics (plume stability).

dehydrohalogenation—A process by which a halogenated alkane loses a halogen from one carbon atom and a hydrogen from the adjacent carbon atom, producing the alkene and an acid (e.g., 1,1,2,2-tetrachloroethane dehydrohalogenates to produce trichloroethene and HCl).

dense, nonaqueous-phase liquid (DNAPL)—An immiscible organic liquid that is denser than water (e.g., tetrachloroethene).

desorption—The converse of sorption, i.e., when a compound slowly releases from a surface(s) that it has previously accumulated upon or within.

diffusion—The process of (net) transport of solute molecules from a region of high concentration to region of low concentration caused by their molecular motion and not by turbulent mixing.

dilution—A reduction in solute concentration caused by mixing with water at a lower solute concentration.

dispersion—The spreading of a solute from the expected groundwater flow path as a result of mixing of groundwater.

electron—A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions.

electron acceptor—Chemical substances, such as oxygen, nitrate, sulfate, and iron, that receive the electrons during microbial and chemical reactions. Microorganisms need these compounds to obtain energy. For MNA and EA, these electron acceptors often compete with chlorinated solvents and reduce the attenuation rates.

electron donor—Chemical substances, such as molecular hydrogen or organic substrate, that yield an electron as they are oxidized, producing energy to sustain life and for the subsequent degradation of other chemicals, in this case, chlorinated solvents.

enhanced attenuation—Any type of intervention that might be implemented in a source-plume system to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. Enhanced attenuation is the result of applying an enhancement that sustainably manipulates a natural attenuation process, leading to an increased reduction in mass flux of contaminants.

enhanced bioremediation—An engineered approach to increasing biodegradation rates in the subsurface.

evapotranspiration—In addition to the ability of plants to stabilize or take up inorganics as well as promote the enhanced biodegradation of organics, plants also significantly affect the local hydrology. Specifically, plants have the ability to intercept a significant portion of rain on their leaf surfaces.

flux—Rate of flow of fluid, particles, or energy through a given surface.

halorespiration—The use of halogenated compounds (e.g., trichloroethene) as electron acceptors. This is the essential processes of biological reductive dechlorination.

hydraulic conductivity—A measure of the capability of a medium to transmit water.

hydraulic gradient—The change in hydraulic head (per unit distance in a given direction) typically in the principal flow direction.

hydrogenolysis—The conversion of an alkene (e.g., cis-dichloroethene) to an alkane (e.g. 1,2,-dichloroethane) by the addition of a hydrogen molecule across the double bond of the alkene. This does not reduce the degree of chlorination of the subject molecule, but it does change its properties.

hydrolysis—Decomposition of a chemical compound by reaction with water, such as the dissociation of a dissolved salt or the catalytic conversion of starch to glucose.

inorganic compound—A compound that is not based on covalent carbon bonds, including most minerals, nitrate, phosphate, sulfate, and carbon dioxide.

in situ—Literally meaning "in place," refers to treating a compound where it is rather than first mechanically removing it (by excavation, pumping, venting, etc.) and then treating it.

integrated mass flux (IMF)—The total quantity of a migrating substance that moves through a planar transect within the system of interest and oriented perpendicular to the direction of movement. If the transect is at the entry point to the system, the integrated mass flux is the loading. If the transect is at the exit point from the system, the integrated mass flux is the discharge. Note that these terms have units of mass per time (kg/year, g/day, or the like) and represent an extension of the traditional engineering definition of flux (e.g., kg per year per m^2) in which the transect area is accounted for to allow mass balance calculation of plume- or system-scale behavior.

irreversible sorption—A hysteresis effect in which a chemical species becomes more strongly bound over time. The term sometimes appears to be used to describe a situation where, once sorbed, the contaminant is removed from the plume and remains associated with the soil.

mass balance—Assessment includes a quantitative estimation of the mass loading to the dissolved plume from various sources, as well as the mass attenuation capacity for the dissolved plume.

mass loading—Contaminant released to the environment (in this case the aquifer or unsaturated zone) from the source material.

mass transfer—The irreversible transport of solute mass from the nonaqueous phase (i.e., DNAPL) into the aqueous phase, the rate of which is proportional to the difference in concentration.

metabolism—The chemical reactions in living cells that convert food sources to energy and new cell mass.

methanogen—Strictly anaerobic Archaeabacteria able to use only a very limited substrate spectrum (e.g., molecular hydrogen, formate, methanol, carbon monoxide, or acetate) as substrates for the reduction of carbon dioxide to methane.

microarray—A multifaceted tray or array of DNA material. Microarrays are expected to revolutionize medicine by helping pinpoint a very specific disease or the susceptibility to it. Sometimes called "biochips," microarrays are commonly known as "gene chips."

microbe—A microorganism.

microcosm—A batch reactor used in a bench-scale experiment designed to resemble the conditions present in the groundwater environment.

microorganism—An organism of microscopic or submicroscopic size, including bacteria.

mineralization—The complete degradation of an organic compound to carbon dioxide and other inorganic compounds, such as water and chloride ions.

natural attenuation—Naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media.

oxidation—Loss of electrons from a compound.

passive flux meter—Sampling device that uses the absorption and desorption properties of the sampling media to collect and measure the movement of contaminants through the device over a set period of time. These results are then used to estimate the rate at which the contaminants will move through the associated groundwater system for an extended period of time.

performance monitoring—The collection of information which, when analyzed, evaluates the performance of the system on the environmental contamination.

permeable reactive barriers—Subsurface walls composed of reactive materials that will either degrade or alter the state of a contaminant when that contaminant in a groundwater plume passes through the wall.

phytodegradation—Plants metabolically degrade the contaminant to a nontoxic form in roots, stems, or leaves.

phytoextraction—The removal of a substance original located in the soils and groundwater surrounding the roots of a plant through that plant's vascular system.

phytovolatilization—Plants translocate contaminants into the atmosphere via normal transpiration.

plume—A zone of dissolved contaminants. A plume usually originates from a source and extends in the direction of groundwater flow.

pool—An accumulation of DNAPL above a capillary barrier.

process monitoring—The collection of information documenting the operation of a system's engineered components.

rebound—After contaminant concentrations in groundwater have been reduced through in situ treatment and the treatment is terminated or reduced, concentrations return to elevated levels from the continued release of mass from a source zone beyond the natural attenuation capacity of the groundwater system.

reductive dechlorination—The removal of chlorine from an organic compound and its replacement with hydrogen.

response boundary (control plane)—A location within the source area, or immediately downgradient of the source area, where changes in the plume configuration are anticipated due to the implementation of the in situ bioremediation DNAPL source zone treatment. Not to be confused with "point of compliance."

rhizodegradation—Plants promote a soil environment suitable for microbes that can degrade or sequester contaminants.

saturated zone—Subsurface environments in which the pore spaces are filled with water.

sorption—The uptake of a solute by a solid.

source loading—The flux of a substance leaving the original disposal location and entering the water migrating through the soil and aquifer.

source zone—The subsurface zone containing a contaminant reservoir sustaining a plume in groundwater. The subsurface zone is or was in contact with DNAPL. Source zone mass can include sorbed and aqueous-phase contaminant mass as well as DNAPL.

stakeholder—A person other than regulators, owners, or technical personnel involved in the environmental activity of concern, who has a vested interest in decisions related to those particular activities.

substrate—A molecule that can transfer an electron to another molecule. Organic compounds, such as lactate, ethanol, or glucose, are commonly used as substrates for bioremediation of chlorinated ethenes.

sulfate reducer—A microorganism that exists in anaerobic environments and reduces sulfate to sulfide.

sustainable enhancement—An intervention action that continues until such time that the enhancement is no longer required to reduce contaminant concentrations or fluxes.

sustainability—The ability of a system to maintain the important attenuation mechanisms through time. In the case of reductive dechlorination, sustainability might be limited by the amount of electron donor, which might be used up before remedial goals are achieved. When analyzing data from a natural attenuation site, a key question often is whether the mechanisms that destroy or immobilize contaminants are sustainable for as long as the source area releases them to the groundwater. More specifically, whether the rates of the protecting mechanisms will continue to equal the rate at which the contaminants enter the groundwater may be a concern. Sustainability is affected by the rate at which the contaminants are transferred from the source area and whether or not the protecting mechanisms are renewable.

transcription—Transfer of information in DNA sequences to produce complementary messenger RNA (mRNA) sequences. It is the beginning of the process by which the genetic information is translated to functional peptides and proteins.

transect—A cross section through which groundwater flows.

translation—The decoding of mRNA occurs after transcription to produce a specific polypeptide according to the rules specified by the genetic code.

volatilization—The transfer of a chemical from its liquid phase to the gas phase.

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ENHANCED ATTENUATION: CHLORINATED ORGANICS

1. INTRODUCTION

Many sites throughout the United States with chlorinated organic groundwater contamination have gone through extensive remedial evaluations and actions. The remedial technologies for many of these sites include high-energy treatments such as pump-and-treat systems. After years of operation, the effectiveness of these high-energy processes has begun to diminish without remedial objectives being met. Regulators and site managers often had not anticipated a need to transition sites from high-energy systems to other less energy-consumptive alternatives and eventually to monitored natural attenuation (MNA). To help fill the gap between aggressive source treatment and MNA, the Interstate Technology & Regulatory Council (ITRC) Enhanced Attenuation: Chlorinated Organics (EACO) Team developed this technical and regulatory guidance document, which describes a smooth transition or "bridge" between aggressive remedial actions and MNA.

Enhanced attenuation (EA) is the use of low-energy, long-acting (sustainable) technologies when MNA is not sufficiently effective or acceptable. EA can provide an effective and efficient "bridge" from higher-energy remedies to MNA with technologies that either increase the attenuation of the contaminants within the affected aquifer or reduce contaminant loading to the downgradient aquifer. EA features the evaluation of mass balance (defined as the relationship between mass loading and attenuation capacity of the aquifer), a decision framework that provides guidance for site decisions, and a "toolbox" of potential EA technologies that optimize aquifer conditions to provide a sustainable treatment or, at least, minimize the energy needed to reduce contaminant loading and/or increase the attenuation capacity of an aquifer. The decision framework (Appendix A) provides direction to regulators and practitioners on how to integrate EA into the remedial decision process.

> **Mass balance** is the quantitative estimate of the mass loading to the dissolved plume from various sources vs. the mass attenuation capacity within the dissolved plume.

The ITRC EACO Team was formed in January 2004 to address a high-priority need for additional guidance on natural attenuation processes and the development of strategies for enhancing natural attenuation processes at chlorinated organic–contaminated sites. The key accomplishments of the EACO Team are the development of the EA concept and a decision framework that provides guidance for the use of enhancements to transition remediation of chlorinated organic–contaminated sites from initial treatments to a final treatment of MNA and site closure. EA can just as easily be applied at sites where MNA is not meeting the remediation goal. The focus of this document is on chlorinated solvents due to the prevalence of groundwater contamination caused by this type of chlorinated organic.

Enhanced attenuation does the following:

- **Facilitates transition of contaminated sites through the remediation process.** Many sites require a combination of remedies over time (i.e., treatment-train approach). Implementing EA using the concepts of plume stability, and mass balance facilitates the transition of the

site to MNA, especially for sites with ongoing treatment and for sites where plumes are currently nearing stability.
- **Complements MNA and expands remediation opportunities.** Using a tailored approach—a successful site strategy based on the decision framework—enables sites to realize some of the benefits of MNA. The type of technology depends on site-specific conditions.
- **Encourages energy efficiency and helps to develop the best solutions for the environment.** Deploying technologies based on the decision framework results in sustainable treatments that require less energy and investment to reach environmental cleanup goals. As a result, sustainable treatments are often less disruptive to property and the environment and can potentially reduce the time required to clean up the site. These sustainable treatments can be implemented to reduce residual contamination in source treatment areas as well as contaminants in associated subsurface groundwater plumes.

Enhanced attenuation addresses the following challenges:

- Efforts undertaken to understand the balance between source loading and mass attenuation rates in the plume are typically limited, resulting in remedies that have longer remediation time frames and less than optimal cleanup costs.
- Little guidance is available regarding when to transition from energy-dependent remedies such as source control to a MNA.
- MNA remedies are sometimes ruled out because naturally occurring attenuation rates appear too slow. This approach translates into unacceptably long remediation time frames or plumes that are expanding or that pose unacceptable risks to downgradient receptors.

This guidance document provides a decision framework that can be applied to identify site-specific areas of concern and then identify innovative remedial strategies. This framework enables the matching of potential remedial technologies to the specific conditions and treatment requirements of a chlorinated organic–contaminated site. Remedies can offer a "bridge" between active source or plume remediation and MNA. The framework also can be used to evaluate the overall performance of existing MNA remedial actions and identify enhancement opportunities. It is anticipated that this document will assist regulators and site managers in selecting a preferred methodology from a wide array of innovative approaches.

1.1 EACO Team

The EACO Team consists of regulators from five states, representatives of the U.S. Department of Defense (DOD), U.S. Environmental Protection Agency (EPA), U.S. Department of Energy (DOE), industry, academia, and stakeholders. The EACO Team has collaborated with the DOE's MNA/EA Technical Working Group (TWG) to include current, valuable scientific information and to provide a forum for the introduction of new technical concepts and tools.

The team initially conducted a national survey of state regulators to gain valuable insights on the perspective of regulators with respect to the use of MNA and the conceptual use of new tools for site remediation. The insights gained from this survey helped the EACO Team to develop an appropriate path forward with specific team goals. The survey results confirmed that there was a lack of guidance available to state regulators and project managers on how to transition contaminated sites from aggressive source treatment to MNA. Team members noted that many chlorinated solvent–contaminated sites get trapped in an endless circle of characterization and monitoring that results in substantial costs without progressing toward cleanup. At the other end of the spectrum, contaminated sites using MNA may see little or no progress within the anticipated cost and time frame, and there is no guidance on how to provide innovative remedial options to move the site from MNA to a more productive remediation strategy. To move past these roadblocks, the EA concept and the decision framework were developed and incorporated into this guidance.

1.2 EACO Team Products

The ITRC EACO Team developed several products which provided building blocks for this guidance document. Concurrently, the team provided outreach activities which helped bring the conceptual ideas into the national environmental field. The decision framework is in this document; additional information is available on the ITRC EACO Public Resource Page (www.itrcweb.org/teamresources_50.asp):

- **Fact Sheet**—"Enhanced Attenuation: A Solution to a Common Groundwater Remediation Problem" is a one-page information sheet developed in 2004 by the EACO Team to document and clarify the definition of enhanced attenuation.

- **National Survey of State Regulators**—"A National Overview of Monitored Natural Attenuation and Enhanced Attenuation—Results of an Interstate Technology & Regulatory Council Survey" documents results of the team's survey to gain a clear understanding of the national regulatory framework for the use of MNA and to introduce technical concepts such as attenuation capacity, mass balance, and mass flux.

- **A Decision Flowchart**—"The Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation at Sites with Chlorinated Organic Plumes" is the core building block for this guidance document. It includes a short narrative describing the use of the decision flowchart.

- **Resource Guide**—"The Enhanced Attenuation of Chlorinated Organics: Resource Guide" compiles relevant scientific and technical literature on natural attenuation and EA. In that regard, the resource guide is designed to provide a consistent approach to the basic principles, terminology, and technical features of natural attenuation and EA.

- **Database—**The "EACO Case Study Database" provides a repository for information from sites throughout the country where EA technologies were used for chlorinated organics remediation. Chapter 5 of this document summarizes the database information.

1.3 Current State of MNA as a Groundwater Remedy

MNA is an important environmental management strategy that recognizes the affects of natural mechanisms in the subsurface which stabilize or shrink a contaminant plume. During the past 20 years, MNA for chlorinated organics has advanced rapidly, supported by improved scientific information and clear policy developments. EPA formally recognized the use of natural attenuation for chlorinated solvents and the use of the term "MNA" with issuance of two documents, a protocol (EPA 1998) and a directive (EPA 1999). These encouraged the use of MNA, in combination with other actions, to achieve remediation goals. According to EPA (1999), the processes that contribute to attenuation include "a variety of physical, chemical, or biological processes that under favorable conditions, act without human intervention to reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater." MNA is continuing to be applied at chlorinated solvent sites; however, it is challenged by the lack of a clear strategy for its appropriate application.

Requirements for environmental strategies that rely on natural attenuation typically include the following:

- documenting that the plume poses minimal risk
- documenting that the plume is stable or collapsing
- monitoring to ensure environmental protection
- triggers to implement contingency plans as needed

MNA is a remedial strategy that specifies no human intervention. It has been described as "watchful waiting"; however, MNA remedies are intended to move toward remediation goals that minimize risks at an acceptable rate. There are a variety of issues and challenges to broader implementation of MNA of chlorinated solvents. For example, current protocols for MNA of chlorinated solvents single out reductive dechlorination as the primary mechanism that should be documented at virtually every site. There may, however, be other attenuation mechanisms, such as oxidative processes, which may be operating at some sites under appropriate conditions.

Challenges to implementing an MNA remedy may include the following:

- limited understanding of site-specific natural attenuation processes
- limited characterization, including site-specific geochemical conditions
- unreasonably long remediation time frames
- insufficient natural attenuation rates relative to the mass loading entering the plume from the source area(s)

In cases where natural attenuation mechanisms are not sufficient to achieve remediation goals—because of risk/exposure to receptors, plume growth, or long time frames—additional actions are required. Targeted approaches are necessary to overcome the conditions(s) that cause MNA alone to be inadequate for site remediation. Innovative strategies that couple high-energy remediation techniques with natural attenuation and the consideration of EA are discussed in the context of the decision flowchart in Chapter 2.

As can be seen on the timeline in Figure 1-1, national experience with natural attenuation of chlorinated solvents has a significant time lapse when compared to the natural attenuation of hydrocarbons. Thus, there are considerably fewer case studies and less literature to rely on.

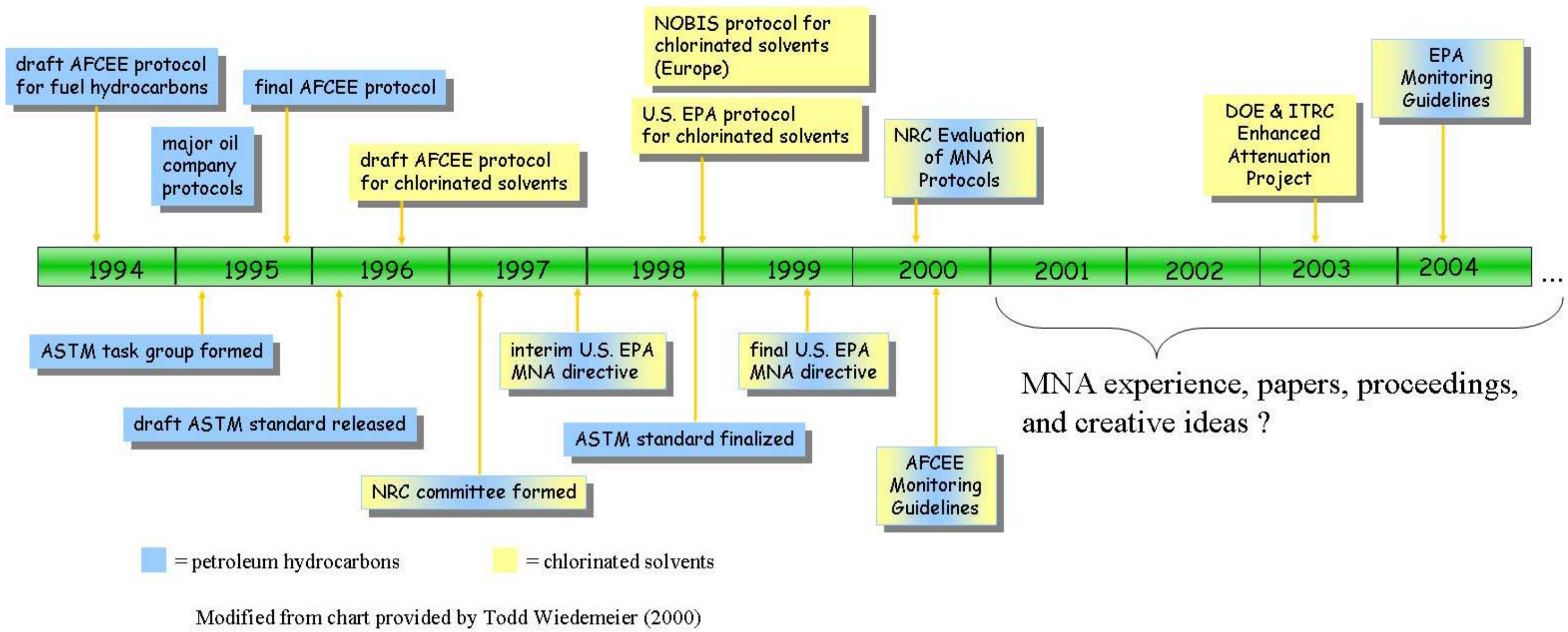


Figure 1-1. Timeline of natural attenuation of hydrocarbons and chlorinated solvents.

1.4 Enhanced Attenuation

EA relies on technologies that have been increasingly used for remediation even though they have not always been used specifically as transition technologies. The technical and regulatory difficulties in applying EA result not from a lack of confidence in the technologies themselves, but from the lack of guidance on how and when to apply these types of technologies. The level of site characterization must be sufficient to evaluate whether MNA alone can be sufficiently effective, as well as to assess how well various technologies can reduce the source strength or increase the attenuation rates.

> EA is a plume remediation strategy to achieve groundwater restoration goals by providing a "bridge" between MNA and aggressive source-zone or dissolved-phase treatment and/or between MNA and slightly more aggressive methods.

> Selection of EA remedies should be based on a mass flux analysis to best assess how to balance the source strength and the attenuation capacity.

EA refers to sustainable enhancements designed to be an effective bridge between high-energy treatment and an MNA remedy or to accelerate the naturally occurring attenuation mechanisms of the subsurface. EA applications are different from conventional remedies because they involve a strong emphasis on balancing the relationship between mass loading from the source area(s) and the rate of mass attenuation (attenuation capacity) in the plume. This relationship defines the stability of the plume. The sustainability of the conditions that provide a stable or shrinking plume based on a mass balance evaluation is the fundamental outcome of a successful EA application.

Remediation of chlorinated organic–contaminated sites typically requires a combination of technologies to meet remediation goals. Enhanced attenuation involves "managing all or part of the contaminant plume in soil and groundwater by initiating and/or augmenting natural and sustainable mechanisms" (Early et al. 2006). Enhanced attenuation is an active human intervention that can "jump start" or "accelerate" the natural attenuation processes or that "regulates" the contaminant loading such that the attenuation capacity of the subsurface system is sufficient to support MNA as an appropriate action. Enhancements fall into two categories:

- source strength reduction technologies—technologies that reduce the mass flux of contaminants from the source zone (e.g., capping, hydraulic diversion)
- attenuation capacity enhancement technologies—technologies that increase the natural attenuation capacity of the aquifer downgradient from the source (e.g., permeable reactive barriers or phytoremediation)

> **Sustainability**—The ability of a system to maintain the important attenuation mechanisms through time. In the case of reductive dechlorination, sustainability might be limited by the amount of electron donor, which might be used up before remedial goals are achieved. When analyzing data from a natural attenuation site, a key question often is whether the mechanisms that destroy or immobilize contaminants are sustainable for as long as the source area releases them to the groundwater. More specifically, whether the rates of the protecting mechanisms will continue to equal the rate at which the contaminants enter the groundwater may be a concern. Sustainability is affected by the rate at which the contaminants are transferred from the source area and whether the protecting mechanisms are renewable.

EA results from a planned scientific and engineered approach that augments the natural subsurface properties at appropriate locations and at appropriate times to degrade or immobilize groundwater contaminants. Various remediation technologies can be designed to reduce the source flux and/or increase the attenuation capacity/rate in the plume to ensure the plume will stabilize and shrink.

Both MNA and EA recognize the importance of source zone remediation whenever practicable and also depend on the sustainable attenuation mechanisms to reduce the mass flux of contaminants or increase the attenuation capacity of the subsurface. While MNA is based on natural attenuation processes with "no human intervention," EA requires human intervention to boost existing attenuation processes. This intervention enables less energy-intensive attenuation processes to achieve cleanup goals where natural attenuation processes are insufficient to reach those goals in the required time frame.

1.5 Mass Flux

This document makes frequent use of the term "mass flux." Mass flux is the total mass of particles which move across a surface per unit time (mass/unit area/unit time). Sections 3.1.1 and 3.2.1 discuss mass flux, integrated mass flux, and the mass flux tools. The EACO Team believes it extremely important to bring the mass flux concept into this document, although there will certainly be new information generated in the future as the use of mass flux is fully evaluated. While the definition presented here represents the team's current understanding of mass flux, additional work will be initiated by the ITRC BioDNAPL Team in late 2008 to further research important mass flux aspects, such as the usefulness of mass flux for performance monitoring (see www.itrcweb.org/teampublic_BioDNAPLs.asp).

The use of mass flux provides a new approach since existing techniques to evaluate a plume's spatial existence include analytical concentration data. While a groundwater concentration measurement can be valid for a single point in space and time, mass flux surveys can provide information on aquifer mass loading. These surveys consist of numerous discrete measurements throughout the aquifer that can integrate both velocity and flux distributions. Results of mass flux monitoring can be used to generate mass flux balance information throughout the entire plume. This is certainly a new approach and, in the context of site conceptual remediation models, represents a progressive extension of plume characterization which will enhance future remediation techniques.

1.6 General Flow and Structure of EA

A decision framework in the form of a flowchart is the central element in this guidance document. The flowchart provides an important roadmap for decision making. Figure 1-2 displays a familiar sequence and parallels many existing guidance documents and protocols. The initial efforts at a contaminated site (blue boxes I and II) represent the initial discovery, characterization, source treatment, and active remediation. These result in characterization data as well as decision-making information describing risk, evaluating technology performance, treatment time, and treatment cost (green circles). These criteria, in turn, are inputs to a series of questions related to the viability of MNA (yellow diamonds). This portion of the process encourages implementation of MNA according to the existing regulatory protocols with added emphasis on mass balance-based assessment of plume stability and with documentation of treatment sustainability. This sustainability requirement, which for example is applicable to sites that may have codisposed hydrocarbons serving as electron donors to facilitate attenuation, represents an additional level of documentation and rigor. The following chapter explains and demonstrates the application of this decision framework. Note that there can be spatial as well as temporal sequencing of all the elements in the following decision framework.

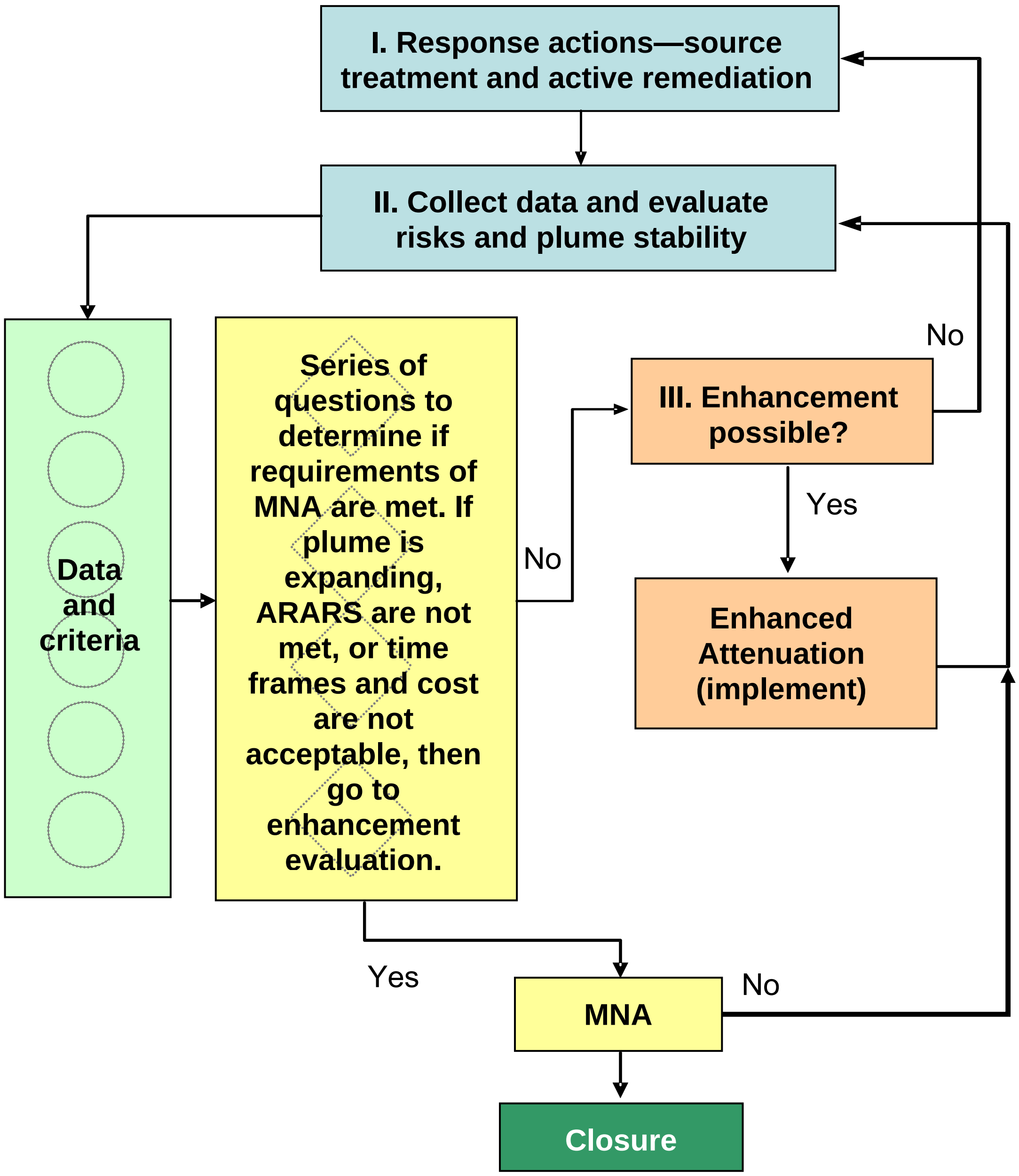


Figure 1-2. General structure and logic of MNA/EA Decision Flowchart.

2. ENHANCED ATTENUATION DECISION FLOWCHART

The overarching goal of the MNA/EA Decision Flowchart is to depict a decision process that is both innovative and disciplined and that encourages the identification and implementation of appropriate remedial alternatives. The flowchart provides a mechanism for transitioning sites through the complete remediation process for not only the regulator but also the site manager. The decision process is not cumbersome or technically complicated, and it supports the goal of documenting site remediation decisions with an efficient scientific evaluation process. It is important to note that this decision flowchart can also be used to support site remedial transitions from ineffective MNA back to high-energy remediation or EA technologies.

As a site is approaching MNA but does not meet the requirements of MNA, Sections II A–E (i.e., it does not pass the gauntlet of requirements expanded on the left side of the Figure 2-1), the decision flowchart provides an additional potential option of EA (Section III). Sections II A–E provide specific requirements to be considered in evaluating the mass balance to optimize long-term plume stability/reduction (shrinking) and in selecting and designing an EA treatment. In this case, the scientist/engineer determines whether there is a sustainable action that will modify the risk, plume stability, or remediation time frame and allow for implementation of that action. The types of enhancement evaluated and the objectives of the enhancements are developed based on the specific issues identified in the MNA questions. For example, if the remediation time frame is determined to be too long, then enhancements that increase degradation rates will be identified; if conditions are not sustainable then enhancements to further sustain the attenuation process will be identified and evaluated. Chapters 3 and 4 describe the evaluation of plume stability and sustainability and the classes of enhancements.

The supplemental loop within the decision flowchart entitled "III. Evaluate Enhancement Options" requires an iterative process for a smooth, efficient, and defensible transition to MNA from source and plume treatments. If enhancements are not viable, then traditional treatment continues. If enhancement is viable and has the potential to be more effective than the current treatment, then it is implemented and monitored to document that the desired change was achieved so that the site can transition to MNA or to identify that the desired change was not achieved such that further enhanced treatment is required. The selection of the preferred response action or the decision to transition from high energy to natural or enhanced attenuation typically requires an analysis of a short list of remedial alternatives, collaboratively developed by technical specialists working with the site owner, regulators and stakeholders. The remainder of this chapter describes the various actions and decisions within the flowchart and documents how to implement this technical/regulatory paradigm.

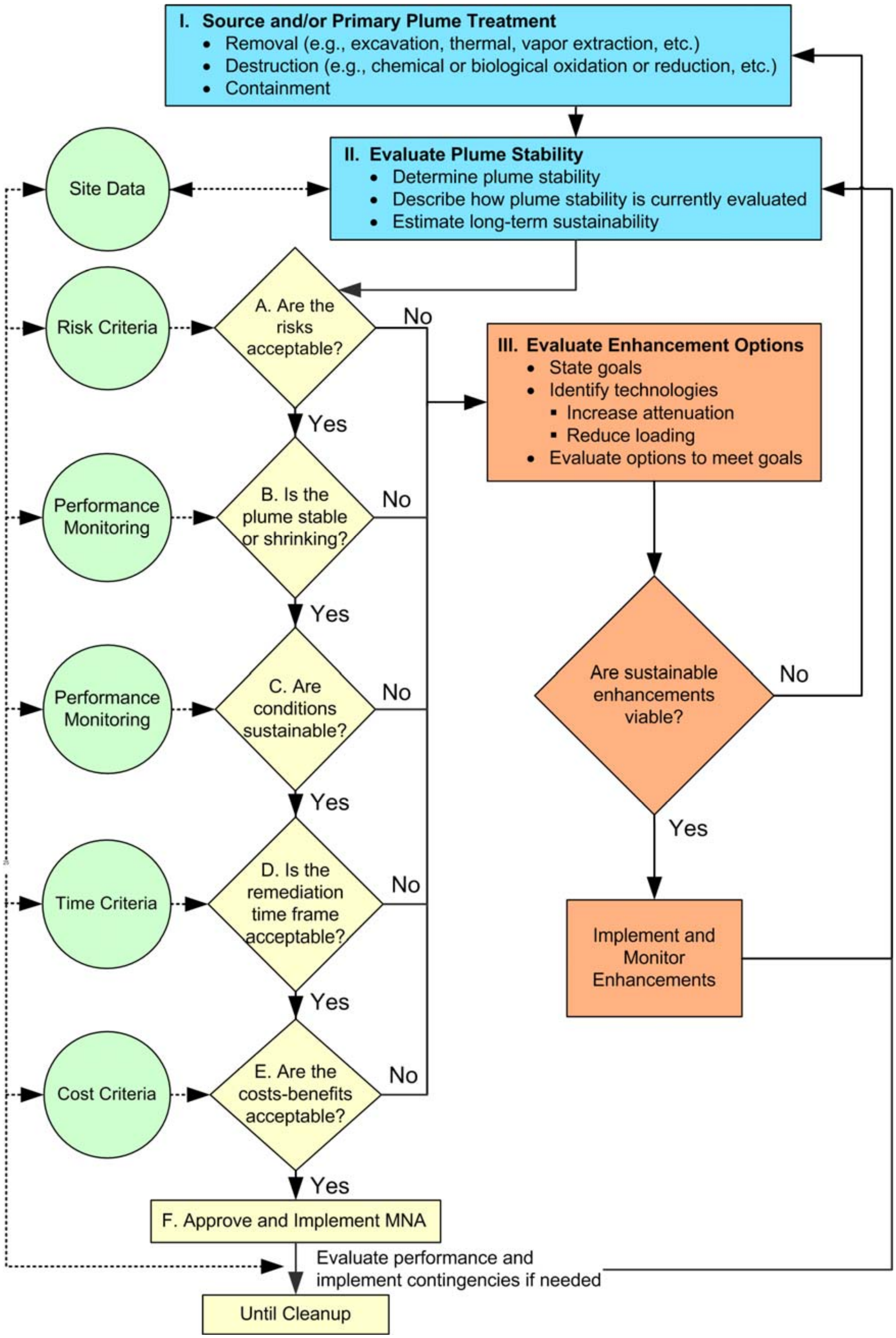
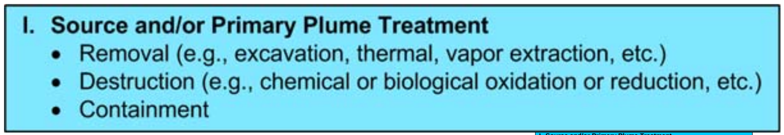
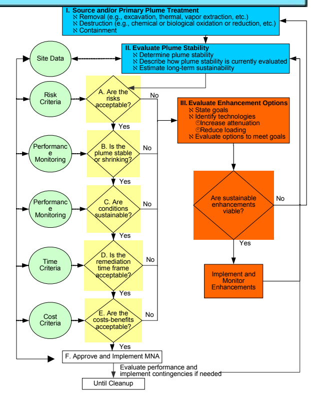


Figure 2-1. Expanded MNA/EA Decision Flowchart.

2.1 Source and/or Primary Plume Treatment





When a source/primary plume is present, essentially all regulatory guidance recommends, and regulators require, source/primary plume treatment. Based on current trend analysis, many chlorinated organic–contaminated sites require the use of several technologies that combine aggressive and passive technologies to reach cleanup goals.

Two key issues to consider for source and plume treatment in the context of the EA evaluation process are how to integrate the source area remedy with a current or future MNA/EA remedy and how to develop an understanding of the effects of the source area remedy on aquifer conditions that affect the entire plume remedial efforts. Note that there can be spatial as well as temporal sequencing. See *In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies* (ITRC 2007b) for a more thorough discussion of dense, nonaqueous-phase liquid (DNAPL) source zone relationships to remediation of the dissolved plume phase.

The first objective is to develop a decision process that provides knowledge of when to stop operation of the active remedy in the source zone and transition and implement into other appropriate MNA/EA remedies. In addition, a site manager needs to be able to decide whether it is appropriate to implement an MNA/EA approach for a different area of the plume while the source area remedy is still operating. Appropriate decisions for both aspects of this issue can be made as long as an adequate performance assessment program is in place. Performance metrics that would help determine when the action is complete or can no longer be equally effective with the same level of effort should be identified early in the process.

The second issue for consideration with regard to source area remediation in the context of an MNA/EA evaluation is the potential collateral effects of the technology on the aquifer. Rather than approaching site remediation as a series of isolated steps, consideration should be given to potential collateral effects on possible later attenuation goals. The evaluation of these collateral effects can be performed using a "subsurface ecological assessment"[1] approach. This assessment can be defined by evaluating three major areas: hydrological impacts, microbial population changes, and electron donor/electron acceptor activity changes.

2.1.1 Hydrological Impacts

Remedial processes that directly or indirectly impact groundwater flow may impact the existing risk management conditions (such as diverting or increasing flow to a receptor or discharge

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[1] The subsurface ecological assessment concept recognizes the interrelatedness of the living and geochemical components of the subsurface environment. A subsurface ecological assessment is an evaluation of the direct impact on subsurface conditions, or potential change in conditions, associated with a remedial technology and how those conditions will directly or indirectly impact biotic-biotic and biotic-abiotic interactions.

point) or other attenuation processes (such as decreasing flux of biologically available electron donor/acceptor). Examples of hydrological impacts include the following:

- hydraulic or physical containment of the source, which may change groundwater flow characteristics
- biomass growth and gas generation due to bioremediation, which may reduce porosity locally

2.1.2 Microbial Population Changes

Remedial processes may create conditions that inhibit or enhance biological processes. Examples include the following:

- Pump-and-treat can introduce oxygen into the subsurface that will benefit aerobic processes but inhibit the growth of anaerobes.
- Thermal treatment may reduce the activity of chlororespiring microorganisms, delaying the onset of reductive dechlorination.
- It was previously thought chemical oxidation would cease biological activity, but recent work (Chapelle, Bradley, and Casey 2005; Rowland et al. 2001; Rowland and Golden 2003) has shown that aquifer conditions following chemical oxidation may be favorable for future reductive dechlorination.
- Geochemistry changes, such as pH conditions, sulfide/sulfate, etc., may occur.

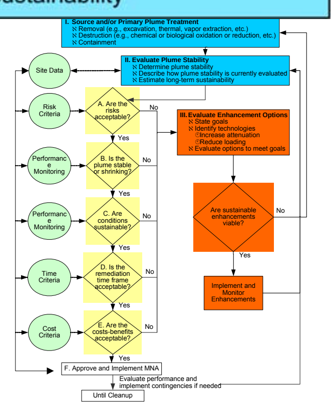
2.1.3 Electron Donor/Acceptor Activity Changes

Processes that change the availability of oxidizable or reducible chemical species may impact future remedy implementation. Examples include the following:

- Injection of oxidizing agents such as peroxide or permanganate can change redox conditions and introduce new electron acceptors to the local and downgradient aquifer.
- Residual co-solvents from a flushing operation can act as electron donors for reductive dechlorination.

The above considerations, included in Section I of the decision flowchart, as well as physical containment or mass reduction activities in the source area will reduce the availability of anthropogenic substrates in the downgradient plume if a supply is present in the source area.

II. Evaluate Plume Stability
- Determine plume stability
- Describe how plume stability is currently evaluated
- Estimate long-term sustainability



2.2 Evaluate Plume Stability

2.2.1 Determine Plume Stability

The question of plume stability is a key factor in the regulatory decision process. Generally speaking, plume stability indicates that the plume is no longer expanding in size, nor is its footprint moving. It is also useful to consider a more academic definition of plume stability, such as the following from DOE's *Decision-Making Framework Guide for Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* (1999), which is based on contaminant attenuation and mass flux:

> Plume [stability] occurs when the perimeter of the plume attains sufficient size or location such that attenuative mechanisms equal or exceed the mass flux [from the source].

2.2.2 Describe How Plume Stability Is Currently Evaluated

Traditionally, various documents such as EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (1998) cite "lines of evidence" to assess the degree to which natural attenuation is occurring and whether it could be a suitable remedy. Although geochemical, biochemical, and microbiological lines of evidence may exist, most regulatory agencies consider a stable or shrinking plume to be the critical line of evidence for determining whether MNA alone is an appropriate remedy.

Determining plume stability can be difficult, particularly if data resolution is low throughout space and time. Currently, most regulations require the comparison of concentration data (i.e., mass per volume) to regulatory standards as opposed to evaluation of mass flow or mass flux (i.e., mass per area per time). When used in combination, both concentration data and mass flux may provide a truly scientific approach acceptable to regulators to support transitioning between technologies and ensure that compliance is maintained and measured via a concentration standard.

Assessing plume stability relies on the emplacement of a representative monitoring network to provide the spatial and temporal data necessary to evaluate whether the plume is stable, shrinking, or expanding. EPA's *Performance Monitoring of MNA Remedies for VOCs in Ground Water* (2004) offers in-depth discussion regarding monitoring for plume stability.

Assessment of plume stability may also include the following:

- assessment of in situ attenuation rates
- mass balance assessment to evaluate the natural attenuation capacity and how it will be affected by implementation of a particular remedy near the source and farther downgradient

2.2.3 Estimate Long-Term Sustainability

Until recently, most evaluations of plume stability focused on the question of current stability as indicated by spatial and temporal trends in existing monitoring data. With the advent of evaluation mechanisms of the MNA remedy, the importance of understanding the likelihood of achieving future long-term plume stability/reduction is starting to be considered by responsible parties and regulatory agencies as a necessary component for acceptance of an MNA remedy. Evaluation of long-term plume stability/reduction can start with the mass balance evaluation on attenuation mechanisms vs. mass loading.

When biodegradation is an active attenuation mechanism, it is important to determine how sustainable it will be over the expected life of the plume (i.e., whether there will be sufficient electron donor to sustain an adequate biodegradation rate for continuous plume stability). Ultimately, the mass balance should demonstrate whether the plume is likely to remain stable, shrink in size, or expand over the long term. In the "real world" of site remedial efforts, it is difficult in many cases to estimate electron donor sustainability. Performance measures capture the ongoing remedial efforts and should provide adequate information for the site manager to establish ongoing sustainability.

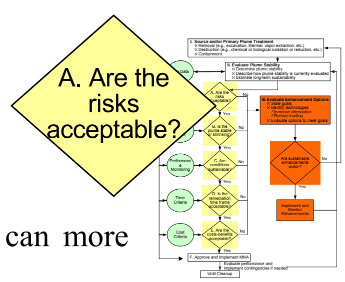
It is important to collect relevant natural attenuation data as early and often as possible, such as during site characterization. Monitoring programs should be designed with the long-term evaluation of plume stability in mind and should include collection of necessary data from the start. Software such as Groundwater Services, Inc.'s Mass Flux Tool Kit (www.afcee.brooks.af.mil/products/techtrans/models.asp), BioBalance (www.gsi-net.com/Software/biobalancetoolkit.asp) and Natural Attenuation Software (NAS, www.nas.cee.vt.edu/index.php) (see Appendix C for additional description of available models) may provide valuable insights during the mass balance/sustainability evaluation. Key factors that should be considered in the mass balance/sustainability evaluation include the following:

- organic substrate
- groundwater flow/replenishment
- sequence of electron acceptors
- geochemistry

See *In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies* (ITRC 2007b) for a more detailed description of the key parameters for evaluating the performance of in situ bioremediation at source zones.

The following paragraphs describe details of each decision point in Section II of the flowchart.

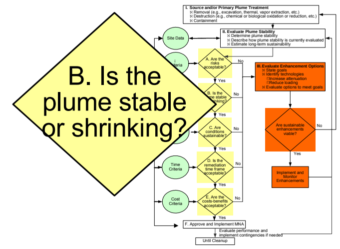
A. Are the Risks Acceptable?



ITRC's *Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices* (ITRC 1999) states, "Natural attenuation should not be considered as the remedy or a portion of the remedy when natural attenuation will not be protective of human health and the environment or alternative remediation technologies can more reliably and cost-effectively treat the contaminants to minimize risk."

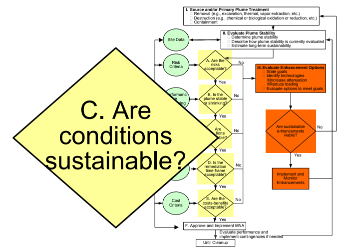
The main concern at this decision point is whether or not the current risk to a receptor requires some additional remediation before MNA can be implemented or whether the risk precludes consideration of an MNA remedy altogether. Even then, MNA may not be acceptable due to public/community pressure or perception or the existence of unacceptable residual risk throughout the plume.

B. Is the Plume Stable or Shrinking?



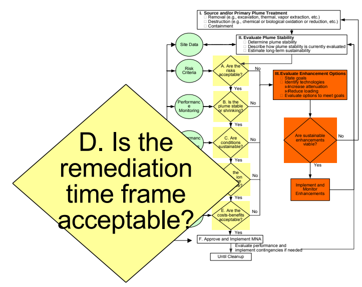
This decision point is a yes/no response based on the actual evaluation of plume stability for the site. Obtaining regulatory agency concurrence is an essential step in documenting plume stability.

C. Are Conditions Sustainable?



This decision point is a yes/no response based on the evaluation of long-term plume stability for the site. Obtaining regulatory agency concurrence is an essential step in documenting long-term plume stability.

D. Is the Remediation Time Frame Acceptable?

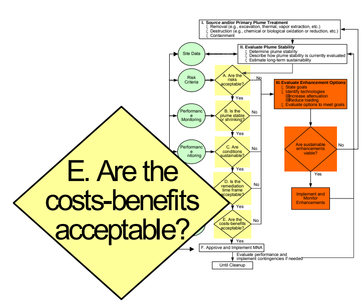


In some cases, remediation time frame may be driven by public/community concerns, political pressure, and/or requirements of the regulatory agencies, irrespective of the cost-benefit analysis. Therefore, for an MNA remedy to be successful, input from key parties such as the following should be carefully considered:

- responsible party(s)
- resource agencies
- local governments
- impacted community/public
- environmental groups/advocates

Many states allow for a “reasonable” time frame for cleanup to reach restorative standards, as long as current risks to human health and the environment are considered acceptable. However, what is considered a reasonable time frame is subjective and varies among state regulators and the public. The key to developing an acceptable time frame is to involve the concerned parties in remedial discussions at an early stage. An important step is to communicate the reality of how long remedial methods are likely to take before contaminant concentrations reach acceptable levels. Once the parties involved understand the realistic time frames, a more productive discussion can occur. Meeting acceptable remediation time frames may require consideration of other risk-reduction strategies either preceding or in tandem with the MNA remedy. More importantly, it may require establishing interim remediation goals to measure MNA remedy success.

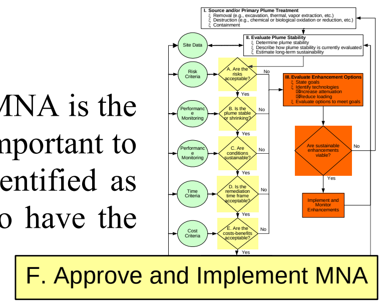
E. Are the Cost-Benefits Acceptable?



Another aspect of evaluating the appropriateness of an MNA remedy is consideration of the cost-benefits. The interplay among remediation time frame, reliability, achieving regulatory standards, performance goals, and cost-effectiveness must be considered when comparing an MNA remedy to other alternatives. Many states have specific requirements aimed at balancing these factors. The desire for faster cleanup, even at greater cost, may be driven by the need to mitigate unacceptable risks or by community/political involvement. In some cases, an alternative may result in faster cleanup at a lower lifetime cost. Specific regulatory requirements and site-specific drivers regarding remediation time frame, reliability, and cost-effectiveness should be thoroughly reviewed and discussed with the regulatory agency. The key questions to address include the following:

- Is an alternative remedy (or combination of remedies) faster, more reliable, or more cost-effective?
- Is faster or more reliable cleanup warranted even if it costs more (i.e., due to unacceptable risks, community/political pressure, etc.)?
- Can enhancements be used to cost-effectively reduce the remediation time frame and support the MNA remedy?

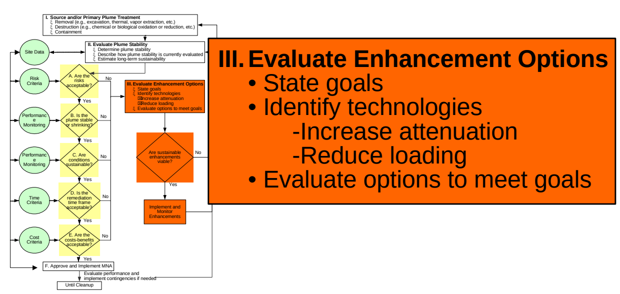
F. Approve and Implement MNA



If the previous five decision steps resulted in "Yes" answers, then MNA is the appropriate remedy. When natural attenuation is the remedy, it is important to monitor the system to ensure that the attenuation mechanisms identified as controlling the system will be sustainable over the time needed to have the plume diminish so that remediation goals are met and will remain below those values over time. The decision to approve and implement MNA should be viewed as part of the total remedy, and it is important to stress that creative approaches to the use of MNA may include using MNA as part of a combination of several treatment technologies and/or enhancements implemented at various times and in various locations of the entire plume. If the attenuation mechanisms cannot be maintained to cause the plume to diminish over time, then contingency plans that will take the responsible parties back into the flow diagram must be enacted.

2.3 Evaluate Enhancement Options

2.3.1 State Goals



Trying to remediate the contaminant mass in the source zone is a primary objective and should never be bypassed. The use of EA builds upon the principle that while working/completing source zone remediation, one may still evaluate, through EA, whether the rates of the attenuation processes are equal to or greater than the rates of the contaminant loading. The use of EA can be applied more than one time and in more than one part of the plume at a site. At any point in time during site remediation, if one can step through the decision process such as risk reduction, expanding plume, etc., use of EA may be appropriate. It becomes obvious that the treatment train will continue to operate until the site can use MNA and/or the site meets regulatory considerations for site closure.

The overall goal of the enhancement(s) is to achieve a mass balance between contaminant loading and natural attenuation processes, such that the plume stabilizes and/or then shrinks over time. To be effective, the enhancement must demonstrate sufficient longevity to ensure that the plume shrinks and the enhancement is no longer required to reduce contaminant concentrations or fluxes.

Specific remedial goals should be identified early in the process. During discussion with regulators, perhaps the goal would be to reduce contaminant concentrations in all monitor wells to an agreed-upon intermediate cleanup goal using an EA technology and then shift the next goal to the use of MNA for the remainder of the plume. The operative words are “scientific” and “innovative.”

When designing enhancements, several fundamental requirements must be met:

- Either plume stability will be achieved followed by plume shrinkage, or plume stability will be maintained (at lower cost or energy consumption), followed by plume shrinkage.
- There is an increased rate of attenuation processes or a decreased loading from the source.
- The enhancements can be monitored and validated.
- The enhancement has sufficient longevity such that when it is “turned off,” the natural attenuation processes within the contaminated zone will be able to maintain a reduction in flux for a period that will achieve regulatory requirements. In other words, the enhancement “works” long enough so that MNA can finish the job and the regulatory requirements are met.

2.3.2 Identify Technologies

An enhanced attenuation technology either reduces loading from the source or increases the attenuation capacity within the plume (e.g., reduce infiltration, source containment, increase biological or abiotic reactions within plume, permeable reactive barriers, etc.). Most of these technologies can also be used for active treatment in the source zone. Detailed information about these technologies can be found in *Enhanced Attenuation: A Reference Guide on Approaches to Increase the Natural Attenuation Capacity of a System* (Early et al. 2006).

2.3.3 Evaluate Options to Meet Goals

After possible EA technologies are identified, each must be evaluated to determine whether it will meet the specific goals for the site. Feasibility study approaches, as outlined in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process, can provide a format; however, the EACO Team believes that site managers should approach regulators early in the process to discuss and identify innovative streamlined approaches for remedial alternative evaluations.. Decision analysis approaches such as the cVOC Decision Tool (Kaback et al. 2007) provide one such alternative format to document the analysis.

2.3.4 Determine Sustainable Enhancements

This decision point is a yes/no response based on the evaluation of the EA options for the site. Obtaining regulatory agency concurrence is an essential step. This process involves subjective as well as objective decisions.

The key elements of the EA evaluation are as follows:

- Ensure the sustainability of the EA remedy.
- Confirm mass concentration and/or flux reductions.
- Confirm protection of human health and the environment through reduced risk.
- Confirm that technology is making progress towards achieving established goals and/or regulatory milestones.
- Allow the opportunity to reconsider the appropriateness of the current remedial response (i.e., ask whether conditions at the site have shifted such that the current site response should be reconsidered).

2.4 Flowchart Summary

The MNA/EA Decision Flowchart provides a process for transitioning sites through the remediation process and encourages the identification and implementation of appropriate remedial alternatives. It reflects the philosophy that, at many sites, remediation is an iterative process using combinations of high-energy, passive, and transition technologies such as EA. No limitations are set on the number of iterations through the flowchart since that will be depend, to a great extent, on the complexity of the contaminated system. Because it is iterative, a user may enter the flowchart at any time and place during the characterization/remediation process.

An example may be a site where MNA was implemented, but a few years into the remediation the plume was growing. The responsible parties would enter the flowchart in block III (Figures 1-2 and 2-1) with an evaluation of whether an enhancement is available that would result in the plume stabilizing and then shrinking.

The flowchart provides a framework for combining remedies or creating "treatment systems" that integrate active and passive remedies to reach remediation goals. In combining remedies, it is possible to move directly from a source zone remedy to MNA. However, in cases where active treatment no longer meets performance standards but conditions do not support complete reliance on MNA, a treatment train can be designed to include a transition technology based on EA concepts that will be implemented before MNA. The combination of source removal, EA, and MNA treatments promotes transfer from high-energy/continuous-input technologies to low-energy/minimal-input technologies to technologies that rely only on natural processes requiring no "human intervention" for the treatment to be sustained. In selecting the transition, or EA, technology, the overarching goal is to modify the subsurface conditions so that they will support MNA. This process is supported by identifying that criteria/conditions that prevent the site from relying on MNA and selecting a low-energy/minimal-input technology that, when implemented, will result in those criteria/conditions being met.

As shown in Figure 2-1, an important component of this entire process is regular monitoring and evaluation to ensure the type of treatment in use is performing as expected and, if not, that a contingency is available that moves the user to a different sector of the flowchart. Regardless of the contaminant and hydrogeologic conditions, all sites being remediated will be somewhere within this framework.

3. EVALUATION OF PLUME STABILITY AND SUSTAINABILITY

Plume stability is a key factor in the regulatory decision process. Generally speaking, plume stability means that the plume is no longer expanding in size, nor is it migrating. Empirically, this condition is often assessed by evaluating the trends of concentrations along a flow line within the plume and along the plume boundary. Sustainability is defined by the DOE TWG as the ability of a system to maintain the important attenuation mechanisms through time (Looney et al. 2006b).

3.1 Plume Stability

It is informative to consider more fundamental definitions of plume stability in terms of contaminant or mass loading (contaminants being added) and attenuation (e.g., contaminants being destroyed or sequestered). For example, plume is stable when the rate of contaminant loading (from all sources) is equal to the rate of attenuation (from all mechanisms), as depicted in Figure 3-1. If the loading rate exceeds the attenuation rate, then the plume is expanding. Chapelle et al. (2004) discuss mass loading and mass balance in the context of remediation and specifically detail the accounting that is part of the tool and how a review of that accounting leads to an excellent understanding of overall site remediation and the relative importance of the site aspects.

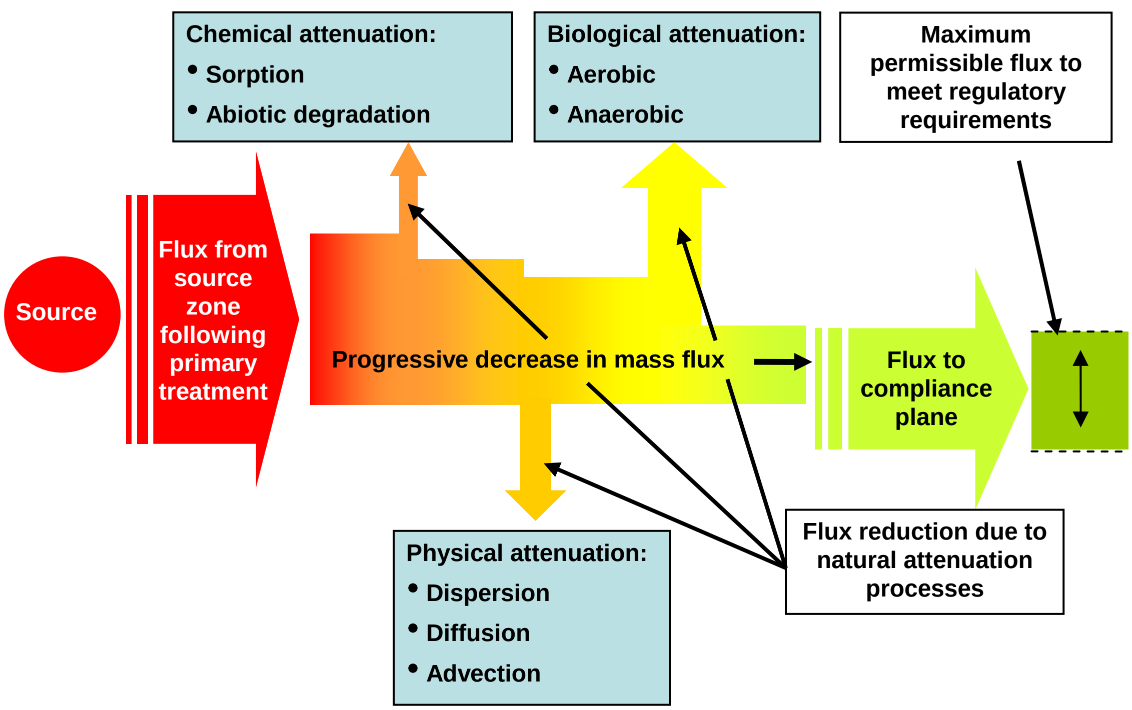


Figure 3-1. Natural attenuation mass balance. (*Source:* Early et al. 2006)

Since the contaminant or mass loading rate is often difficult to quantify, it is useful to consider plume stability in terms of an overall attenuation rate and mass flux at the plume boundaries. DOE 1999 and Looney et al. 2006a discuss the multiple uses of a mass balance approach and ways to implement such an approach.

3.1.1 Mass Loading, Flux, and Attenuation Rates

As contaminant (or mass) loading occurs from a source area into the aquifer, the mechanisms of dispersion, convection, and advection cause the contaminants to spread within the groundwater and aquifer materials. Contaminant mass flux is defined as the amount (mass) of contaminants that flow through a given area over a specific time period. Therefore, the mass flux varies depending on where within the plume the measurement is taken. For a stable plume, the mass flux at the plume boundaries is constant over time as the rate of contaminant loading is in equilibrium (steady state) with the rate of destruction by the existing attenuation mechanisms. However, unless the plume boundary is defined as the line at which the contaminant concentration is zero, contaminant mass per volume of groundwater will be present. Because plume boundaries are typically identified as the contaminant maximum contaminant level (MCL), both a non-zero concentration and flux will be measured.

It is important to evaluate the rate at which contaminants are destroyed or sequestered within the aquifer due to all mechanisms (i.e., overall attenuation rate) to determine whether the rate is sufficient for complete remediation. At a particular location the attenuation rate may be very low or even zero, but it is important to quantify the attenuation rate so that it may be compared with the mass loading rate. It should also be recognized that, just as attenuation mechanisms change throughout the plume, the attenuation rate also changes throughout the plume and through time: the contaminant attenuation rate is location dependent (Figure 3-2, taken from data in Ferry et al. 2004).

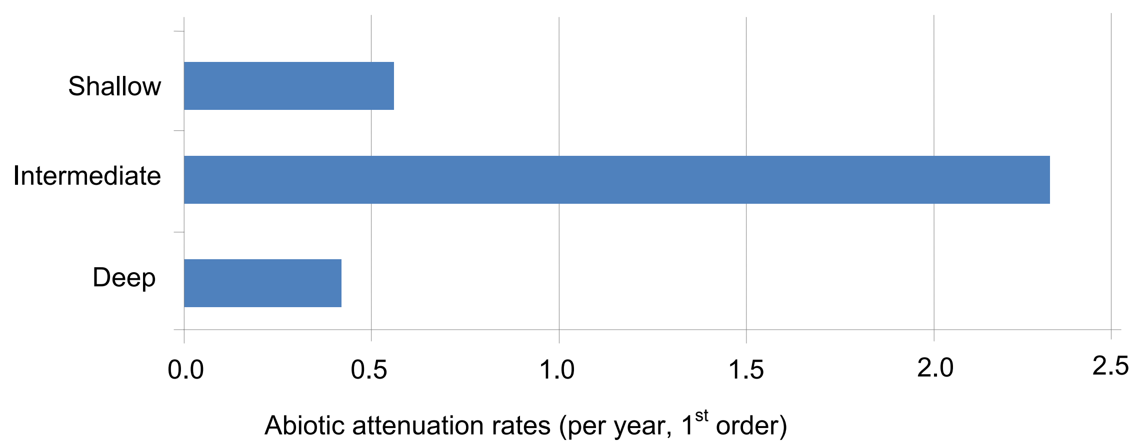


Figure 3-2. Location-specific attenuation rate constants.

One example of this is discussed by Ferrey et al. (2004). A previous investigation at the Twin Cities Army Ammunition Plant found that reductive dechlorination at this site was slow (EPA 2001). However, the investigators realized that, while this finding explained the trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) observations, it did not explain the cis-dichloroethene (DCE) or the 1,1-DCE observations. Ferrey et al. (2004) reported that the observed attenuation of cis-DCE and 1,1-DCE was attributable not to biological reductive dechlorination but to abiotic remediation. Further, it was reported that the attenuation observed was correlated to the magnetite content of the sediment. That magnetite content was found to vary widely across the site, leading to highly location-specific attenuation rates.

Plume stability has most commonly been evaluated using the traditional "lines of evidence" approach (EPA 1998). Application of an EA remedy often requires an evaluation that builds on the traditional approach to evaluate specific attenuation mechanisms, attenuation and loading rates, and long-term sustainability (NRC 2000) of EA rates. Accordingly, the EA evaluation often requires a more rigorous approach to site characterization and monitoring. EPA (1998) cites the following lines of evidence to assess the degree to which natural attenuation is occurring and whether it could be a suitable remedy:

1. a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points (i.e., stable or shrinking plume)
2. presence and distribution of geochemical and biochemical indicators of natural attenuation
3. direct evidence of microbiological activity capable of contaminant degradation

Typically, the first line of evidence (i.e., stable or shrinking plume) is documented by reviewing historical trends in contaminant concentration and distribution in conjunction with site geology and hydrogeology to see whether a reduction in the total mass of contaminants is occurring at the site. This mass loss may be in the source area and/or along the groundwater flow path.

The second line of evidence is documented by examining changes in the concentrations and distributions of geochemical and biochemical indicator parameters that have been shown to be related to specific natural attenuation processes (e.g., oxidation-reduction potential [ORP] should be ≤50 mV or dissolved oxygen [DO] should be <0.5 mg/L for reductive dechlorination).

The third line of evidence (i.e., microbiological evidence) is documented through laboratory microcosm studies and is used to confirm specific chlorinated solvent biodegradation processes that cannot be conclusively demonstrated with field data alone and/or to estimate site-specific biodegradation rates that cannot be conclusively demonstrated with field data alone.

Although geochemical, biochemical, and microbiological evidence may exist, most regulatory agencies consider a stable or shrinking plume to be the critical line of evidence for determining whether natural attenuation alone is an appropriate remedy. In some cases where there are no sensitive receptors in the plume path even though the plume is expanding, a "monitoring only" approach may be followed for a time if there is evidence that attenuation rates are increasing while loading rates are decreasing. However, a "monitoring only" phase is typically only an interim measure to see whether EA is required.

To assess plume stability, it is important to collect relevant attenuation data as early and often as possible, such as during site characterization. Determining plume stability can be difficult, particularly if data resolution is low throughout space and/or time. Assessing plume stability relies on the emplacement of a representative monitoring system to provide the spatial and temporal data necessary to evaluate whether the plume is stable, shrinking, or expanding. EPA (2004) offers the following points regarding monitoring for plume stability:

Trends of increasing contaminant concentrations are often direct evidence of plume expansion. The appropriate number and locations of monitoring points depend on factors such as the size of the plume, groundwater velocity, proximity to receptors, and presence of preferential pathways for contaminant migration.

Monitoring of points throughout the plume, including locations in or near existing or suspected source areas and in the zones of highest contaminant concentrations, generally will be needed to evaluate changes that may lead to plume expansion. Monitoring points of the most immediate concern will often be those points located near the horizontal and vertical plume boundaries and any other compliance boundaries.

At some sites, the geochemical fingerprint of ground water can be established and used to trace water downgradient to distinguish ground water that has never been contaminated from ground water that was previously contaminated [NRC 2000]. Such information may be used to site wells near the current plume boundary in zones where contaminant migration would be expected if plume expansion occurred.

Depletion of electron acceptors and presence of metabolic by-products and nonhazardous daughter products may be used as indicators of appropriate monitoring locations. The most useful parameters for sites with hydrocarbon contamination may include nitrate, sulfate, iron, methane, and dissolved oxygen. The most useful tracers in plumes of chlorinated solvent compounds are often their reduced transformation products, particularly ethane or ethene, but also include the same parameters as for petroleum hydrocarbon plumes. The most appropriate parameters for determining locations for monitoring wells downgradient of a contaminant plume depend on site-specific correlations of contaminants and geochemical indicators.

A word of caution: It is exceedingly difficult to evaluate the potential for natural attenuation mechanisms to remediate a plume when an active treatment is ongoing because the controlling factor in plume attenuation is most likely the active treatment.

3.2 Sustainability

> Enhanced attenuation can be used to "push" plumes toward long-term stability.

Until recently, most evaluations of plume stability focused on the question of current stability, as indicated by spatial and temporal trends in existing monitoring data. Attention is now being turned to the question of a remedy's long-term sustainability in achieving cleanup goals. EA remedies are intended to provide a sustainable bridge between high-energy treatment and MNA by using appropriate technologies at optimal times to prevent further plume migration in a stable manner and/or achieve plume reduction.

3.2.1 Estimating Sustainability

It is important to determine how sustainable the remediation mechanisms will be over the expected life of the plume. Stephen Ritter (2007) points out, "By most written definitions, sustainability means having the ability to meet the needs of a healthy lifestyle for all people in the present without compromising the needs of future generations." The National Research Council does not directly define sustainability but does it operationally:

> When analyzing data from a natural attenuation site, a key question often is whether the mechanisms that destroy or immobilize contaminants are sustainable for as long as the source area releases them to the groundwater. More specifically, whether the rates of the protecting mechanisms will continue to equal the rate at which the contaminants enter the groundwater may be a concern. Sustainability is affected by the rate at which the contaminants are transferred from the source area and whether or not the protecting mechanisms are renewable. (NRC 2000, p. 216)

The words "will continue" differentiate this from a definition of plume stability. In this application, sustainability is the requirement that stability be maintained over time and that the stability be maintained by renewable mechanisms. As with EPA's MNA guidance (1998), NRC dictates that to estimate sustainability, a subset of parameters specific to the active attenuation mechanisms should be determined and their presence and/or concentration monitored and evaluated to document the sustainability of the stable plume.

Sustainability is defined by the DOE TWG (Looney et al. 2006b) as the ability of a system to maintain the important attenuation mechanisms through time. In the case of reductive dechlorination, sustainability might be limited by the amount of electron donor that might be used up before remedial goals are achieved. A "sustainable enhancement" is then defined as an intervention action, the effects of which continue until such time that the attenuation mechanism are no longer required to reduce contaminant concentrations or fluxes.

Prior to the implementation of an enhancement, a monitoring program should be designed to evaluate the long-term effectiveness and availability of the enhancement and optimize the cost. Specific analytes, parameters, analytical methods, and evaluation techniques should be established based on the attenuation mechanisms of interest and their sustainability. For example, if biological processes are important to the attenuation process, then collection of relevant indicator data (e.g., pH, DO, metals, total organic carbon [TOC], etc.) that support the biological treatment mechanism are most important. Furthermore, use of tools that evaluate potential biological activity, substrate use, and contaminant degradation should be monitored. Knowing why an enhancement isn't working can be critical to future success and be a key factor in contingency planning.

A sensitivity analysis of the parameters/assumptions within the mass balance will help determine their relative importance to know which will make the best indicators of attenuation mechanisms and rates. For example, in a system where biodegradation is the dominant mechanism, a sensitivity analysis will reveal that increasing the dispersion rate by 10% will not have a significant effect on the overall attenuation rate.

Although specific enhancements will be discussed in more detail in Chapter 4, the following are some important tools, analyses, and indicator parameters that should be considered where evaluation of biological attenuation mechanisms and rates is important:

- enzyme probes
- bioavailable ferric iron
- volatile fatty acids (VFAs: C2–C4 and C5 + acids)
- solid-phase analyses
- contaminant concentration
- saturation
- flow rate
- bioavailable nutrients
- effects of groundwater recharge on attenuation mechanisms and rates

Total plume remediation strategies may include a combination of several treatment technologies and/or enhancements targeting different parts of the plume. Evaluating different regions of the plume, defined by the key factors above, allows for innovative approaches to be evaluated and applied at the site. If the attenuation mechanisms cannot be sufficiently enhanced (or loading rates sufficiently diminished) to demonstrate a stable or shrinking plume, then contingency plans should be initiated, including reevaluation of the mass balance on contaminant mass loading and attenuation rates.

3.2.2 Indicators of Sustainability

Consideration of an EA remedy increases the demands upon characterization and monitoring because the goal is to understand how much "enhancement" of the rate of natural attenuation is needed to create a stable and shrinking plume. The introduction of the EA concept is a change to the traditional MNA paradigm that previously drove characterization and monitoring efforts. Often evaluation efforts were conducted to see whether natural attenuation could be sufficient to remediate a plume. While this was a complex task, the answer needed to be only semiquantitative—a general sense as to whether natural attenuation could be an appropriate remedy and a rough estimate of the time frame to reach cleanup standards. With the EA concept, however, the goal is to refine these estimates to optimize costs and energy and also the sustainability of enhanced attenuation mechanism to achieve cleanup goals in the long term. As we consider enhancements, it becomes important to explore characterization and monitoring data much more carefully.

The question now is not, "Can MNA remediate this site?" but, "How much can we expect MNA to do?" and, "What are the impedances to complete remediation?" For these reasons it becomes important to look at the following:

- **Ethene and ethane concentrations to 0.5 µg/L**—The presence of ethene and ethane at concentrations <0.5 µg/L was previously considered uninteresting because a reductive chlorination remedy that produced so little ethene or ethane could never be considered an effective remedy. However, now the measured concentrations are being used to answer the question, "Is there any evidence of complete reductive dechlorination, or are microbes lacking?" Evidence of any increase in ethene and ethane concentrations beyond background levels is an important observation in an EA framework. In addition, it is becoming more widely recognized that ethene can be readily oxidized (Coleman et al. 2002, Danko et al.

2004). Since background levels are typically well below 0.5 µg/L levels, reporting limits at or below that limit are very useful.

- **VFA concentrations to 0.1 mg/L**—Past practice was to assess the carbon available as the substrate for reductive dechlorination with a TOC measurement. This led to a discontinuity: when enhancements were used that rely on the addition of a carbon substrate to drive reductive dechlorination, it was often observed that there was substantial reductive dechlorination even in regions where the TOC result was nondetect. Recent experience has shown that not until the analysis is focused just on the extremely bioavailable VFAs (also called "metabolic acids": acetic, propionic, butyric, iso- and n-pentanoic, iso- and n-hexanoic, lactic, and pyruvic acids) and those acids are detected at concentrations <0.1 mg/L that the correlation between added organic substrate (the enhancement) and observed reductive dechlorination becomes apparent (McLoughlin and Pirkle 2006). For this reason a simple TOC analysis of the groundwater or dissolved organic carbon provides neither the specificity nor the sensitivity necessary to assess the organic substrate availability for an EA project.

- **Mechanisms other than biological reductive dechlorination**—This includes two major mechanisms which scientists are rapidly learning more about: co-metabolic oxidation of chlorinated ethenes and abiotic reductive dechlorination of chlorinated ethenes. Because these mechanisms are likely to be active in only portions of the plume, their contribution was previously ignored. However, as the use of enhancements begins to be considered, it becomes more important to consider these contributions, both to account for their effect in the assessment of the attenuation rate and to rule out enhancements which may terminate the contribution of these remedial mechanisms. Accordingly, it may become necessary at some sites to do very specific analyses such as enzyme activity probes or compound-specific analyses to investigate these mechanisms.

To aid in the assessment of plume stability, it may be helpful to interpret the historical data in terms of loading/attenuation rates. If the attenuation mechanism is reductive dechlorination, the kinetics can be complicated by the simultaneous production of lower-chlorinated solvents from higher-chlorinated solvents and the degradation of those less-chlorinated solvents. However, simple mechanisms can often be used to describe loading and the reduction of parent chlorinated solvents. Further, at sites where the remaining contaminants have all been reduced to cis-DCE and vinyl chloride (VC) is not accumulating, a simple model may be applicable to describe the attenuation of that cis-DCE.

As these historical data are reviewed, both the temporal and spatial dependence of the attenuation rates and the contaminant mass flux become apparent. In the purest terms, the plume boundaries are defined as the points where no contamination exists; thus, the contaminant mass flux is zero. In most cleanup actions the plume boundaries, or compliance points, are identified as the points where the MCLs are reached. In this case, the contaminant flux is not zero but should have reached a steady state or be decreasing for the remediation to be considered complete. Indeed, to account for this in an organized and scientific fashion, analytical models, such as Geosyntec's Mass Flux Tool Kit (www.afcee.brooks.af.mil/products/techtrans/models.asp) and BioBalance model (www.gsi-net.com/Software/biobalancetoolkit.asp) and NAS (www.nas.cee.vt.edu/index.php) may provide valuable insights during the assessment of plume stability. For complex sites, sophisticated numerical biogeochemical models such as RT3D (http://bioprocess.pnl.gov/rt3d.htm) and SEAM3D (www.nas.cee.vt.edu/index.php?cat=software&item=version) may be needed to assess plume stability. Key factors that should be considered include the following:

- organic substrate
- groundwater flow/replenishment
- sequence of electron acceptors
- geochemistry (e.g., pH, bioavailable nutrients, sulfate, sulfide, DO, various metals)

It is also essential to periodically reevaluate the mass balance using newly collected data. This can be done as part of periodic performance evaluations and site reviews. Similarly, the advantages of a mass flux approach should also be used (Early et al. 2006)

Most current regulations evaluate remedial effectiveness and risk based on concentration data collected from monitoring wells (i.e., mass of contaminant per volume of collected water). The EA paradigm advocates supplementing this traditional approach with mass flux information (i.e., mass/area/time). Many methods are being developed to estimate mass flux at different places within a contaminant plume. Fluxes measured near the head of the plume provide information about the loading from the source. Fluxes measured downgradient and how they change from one place to another and over time provide information about flow, transport, and attenuation. Some of the flux measurement methods simply manipulate the data from a transect of monitoring well data (Wiedemeier et al. 1999). Other methods employ innovative contaminant collector systems (Annable et al. 2005, Basu et al. 2006, Hatfield et al. 2004), pump testing (Holder et al. 1998), or information about overall plume structure and change over time (Newell et al. 2002). As flux monitoring methods mature, the associated flux estimates should improve along with the quality of the overarching mass balance models. Further, an evaluation by Einarson and MacKay (2001) documented that mass flux can potentially improve risk and exposure estimates in some cases. This improvement was related to the fact that human exposure via a water production well and similar exposures (ecological systems near an outcrop zone) integrate water within the plume and correlate better with flux than with a point concentration. The analysis suggested that flux-based measures may be a useful adjunct to traditional methods when developing environmental remediation goals. The combined approach supports effective operating remediation systems, decision making, and transitioning between technologies while ensuring that compliance with a concentration standard is consistently maintained.

4. ENHANCEMENTS

The goal of this chapter is to define "enhancement," identify where in a contaminant plume an enhancement may be implemented, describe the types of possible enhancements, and discuss what must be considered when implementing these technologies. EA is built on the foundation that the rates of the attenuation processes can be equal to or greater than the rates of the contaminant loading. An enhancement is implemented in response to a "no" in the MNA decision path of Figure 2-1, meaning MNA alone cannot currently remediate the site and a condition must be enhanced to allow attenuation rates to exceed contaminant loading. To be effective, the enhancement must demonstrate sufficient longevity to ensure that the plume shrinks and the enhancement is no longer required to reduce contaminant concentrations or fluxes. Since many of these technologies are presently available, this document assumes the reader has a basic knowledge of them, and detailed descriptions are not provided here.

4.1 Enhancements

Enhancements are specific technologies that fall into two main categories:

- source strength reduction technologies—those that reduce the mass flux of contaminants from the source zone
- attenuation capacity enhancement technologies—those that increase the natural attenuation capacity of the aquifer downgradient from the source (see Figure 4-1)

Because of its unique definition and goals, the design basis and approach for implementing an enhancement differ somewhat from a traditional treatment. Enhancements have several fundamental requirements:

- achieve or maintain the stability of the plume and results in plume shrinkage over time
- result in an increased attenuation capacity and/or reduced mass loading from the source
- can be monitored and validated
- must be sustainable to maintain a reduction in flux for a period that achieves regulatory requirements

As noted in Figure 4-1, source treatment by various methods should always be the initial remedial step in the site remedial treatment action (see ITRC's forthcoming BioDNAPL-3). Some of the technologies noted in Figure 4-1 may be implemented either as an enhancement or as a primary treatment. Examples are (a) the use of in situ bioremediation either as a primary source treatment (see ITRC's forthcoming BioDNAPL-3) or as an enhancement to increase attenuation capacity (bioaugmentation, biostimulation, see ITRC 1998) and (b) soil vapor extraction either as a primary removal method in the source area or as an enhancement to reduce loading of residual source material via passive soil vapor extraction (barometric pumping).

It is important to achieve a lasting balance between source loading (mass flux from the source) and plume attenuation capacity (mass flux due to all natural and enhanced attenuation mechanisms). This is one key element that differentiates enhancements from high-energy or active treatments. For high-energy or active treatments, the design basis is rapid removal of large quantities of contaminants. The sustainability of the attenuating mechanisms that are driving that active treatment is not an important design element.

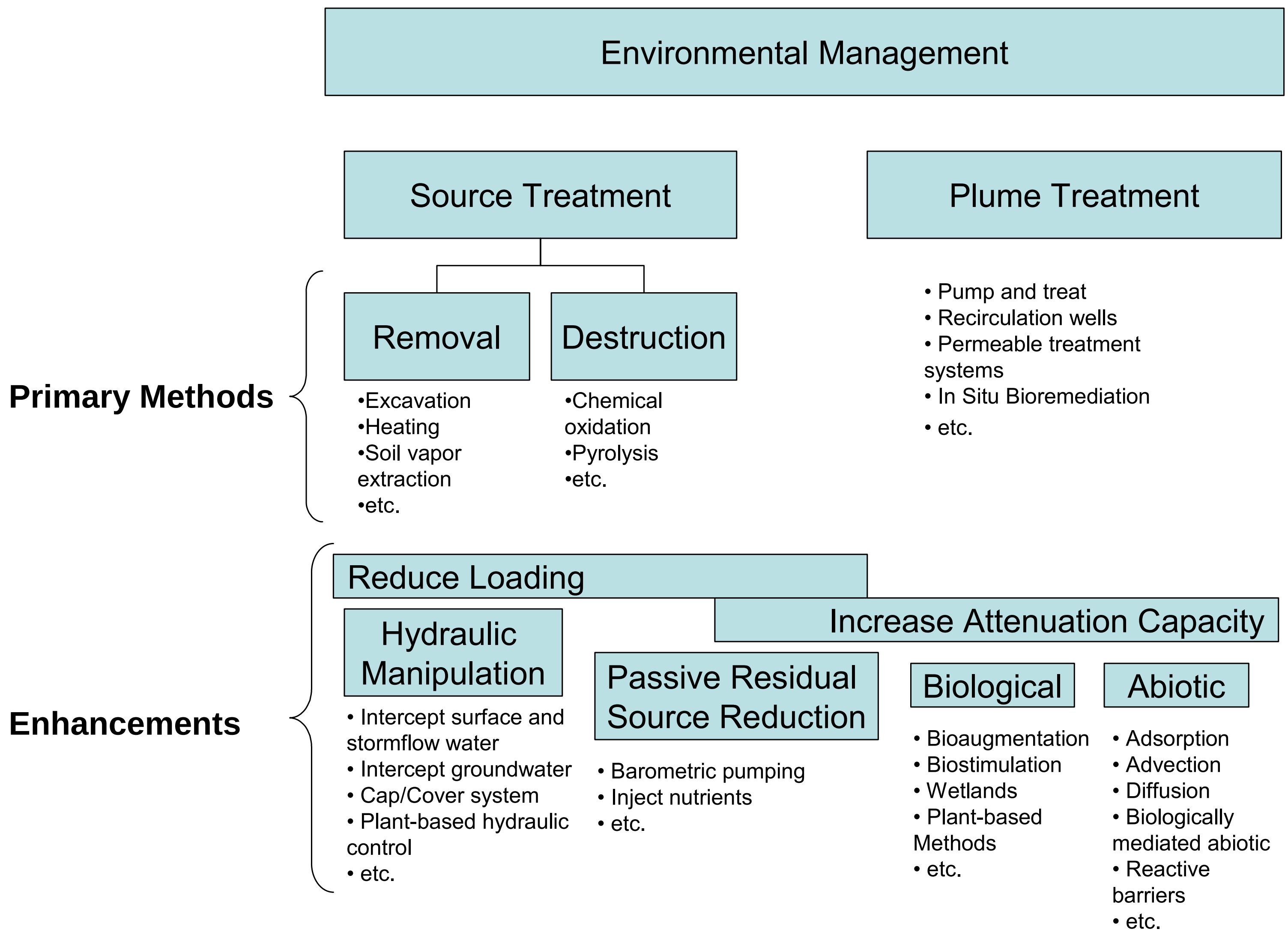


Figure 4-1. Examples of potential "sustainable" enhancements and how they relate to the primary treatment technologies at a waste site.

Sections 4-3 through 4-6 expand on the classes of enhancements. For greater detail on enhancements, the reader should refer to the EACO Team's *Enhanced Attenuation of Chlorinated Organics: Electronic Resource Guide* available at www.itrcweb.org/teamresources_50.asp and to *Enhanced Attenuation: A Reference Guide on Approaches to Increase the Natural Treatment Capacity of a System* (Early et al. 2006). Both references provide additional descriptions of the technologies and references for additional reading. Note that references provided in the two documents identified above do not describe the processes in terms of EA, as this is a new term. These references tend to provide information on the basis of the process and case studies the authors thought were reflective of the concept of transitioning from high- to low-energy treatments.

4.2 Enhancements Options

As indicated by Figure 4-1, enhancements cover a broad range of technologies. Figures 4-2, 4-3, and 4-4 depict enhancements being deployed in contaminated source, plume, and discharge areas. The source zone provides the greatest number of options for enhancements. Some of the source enhancements may be deployed in either the unsaturated or saturated zone.

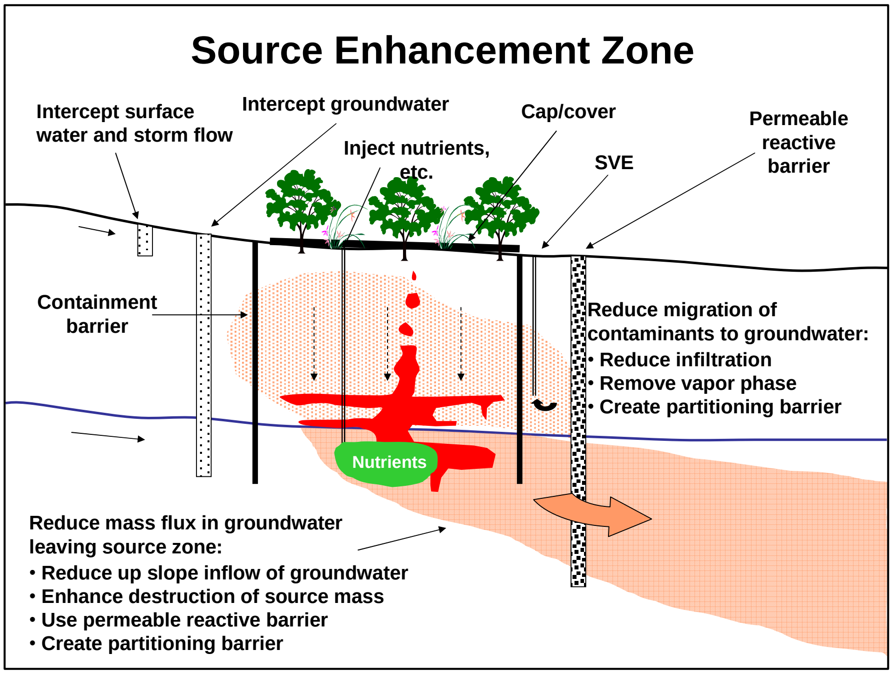


Figure 4-2. Examples of enhancements that may be deployed in contaminant source zones, both saturated and unsaturated. (*Source:* Early et al. 2006)

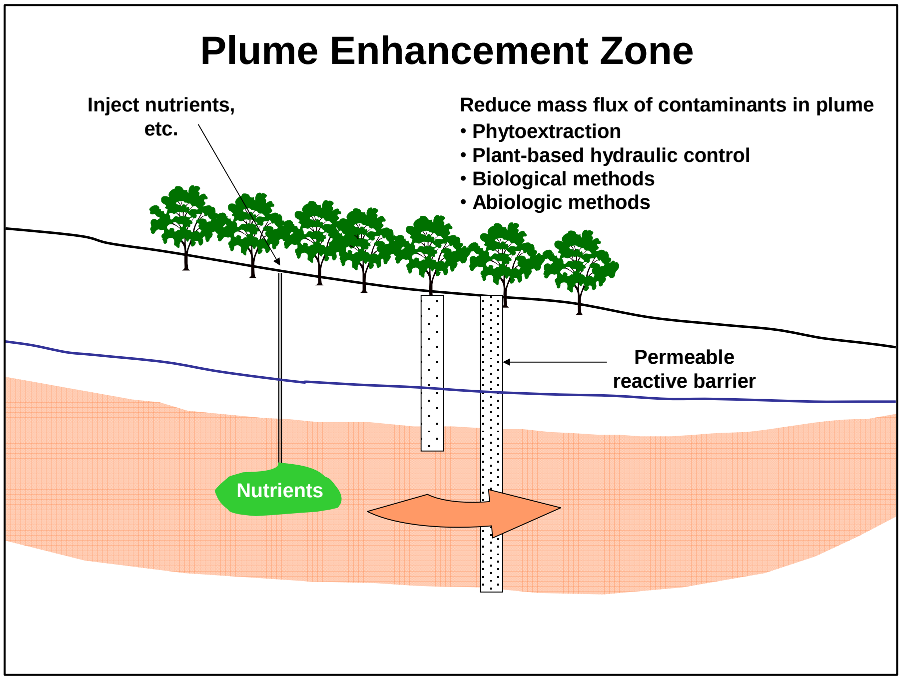


Figure 4-3. Examples of enhancements that may be deployed in the dissolved contaminant plume zone. (*Source:* Early et al. 2006)

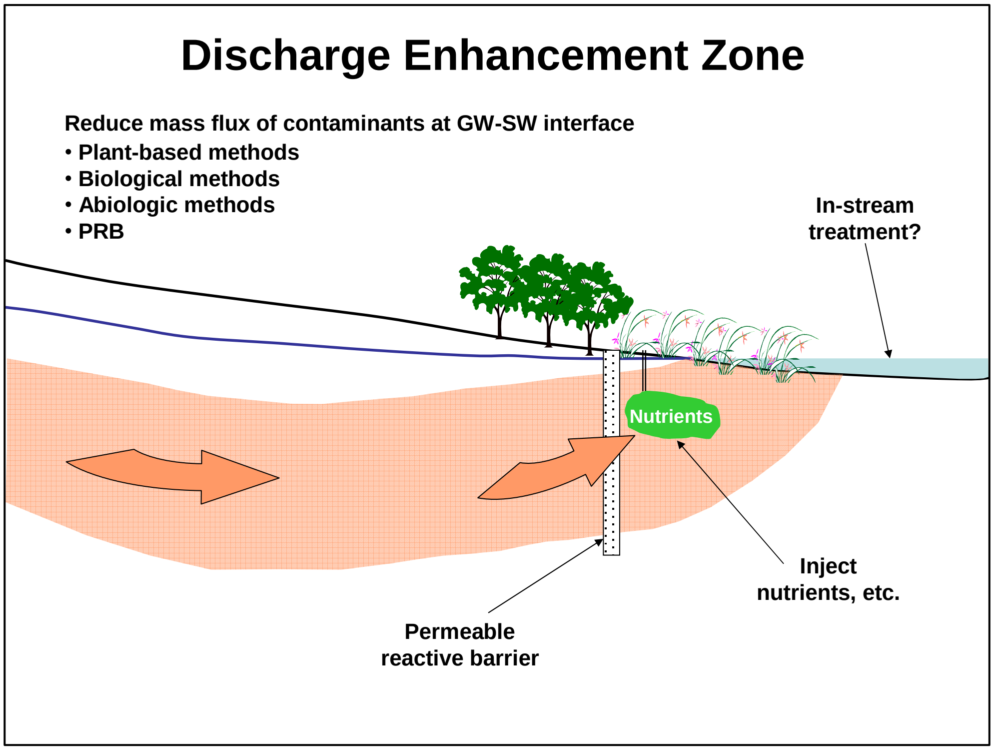


Figure 4-4. Examples of enhancements that may be deployed in the contaminant discharge zone. (*Source:* Early et al. 2006)

In regions where there is a deep (10s to 100s of feet) unsaturated zone, combining high-energy and EA treatments or transitioning from high-energy to EA treatments to reduce the loading of contaminants into the saturated zone may have a measurable effect on stability of the contaminant plume. Such enhancements can come in the form of either reducing loading or increasing attenuation capacity. In many instances an enhancement in the unsaturated zone will be implemented as a transition from an high-energy or active treatment that is no longer performing at an acceptable rate (e.g., mass contaminant removed/volume of groundwater treated is too low or cost of treatment per mass of contaminant removed is too high). Enhancements implemented in the plume and discharge zones may be chosen versus a high-energy treatment because they are low energy and are less infrastructure intensive than high-energy treatments, resulting in a less negative impact (e.g., generation of greenhouse gases and less invasive treatments) to the environment while providing a similar level of treatment.

Enhancements can be deployed in combination. For example, an impermeable barrier can be installed to decrease loading of groundwater through residual contamination, and an electron donor can then be injected in the residual contamination to increase the attenuation rate. Key to combining remedies, whether they are from traditional high-energy treatments to enhancements or multiple enhancements in various portions of the contaminant plume, is to understand the effect of the upgradient action on the plume and that impact on the downgradient treatment.

4.3 Enhancements that Reduce Contaminant Loading from the Source Using Hydraulic Manipulation

The objective of reducing contaminant loading from the source is to reduce or eliminate mass flux from the source. The desired outcome is to create an environment either in that zone and/or downgradient where the rate of the attenuation processes is greater than the loading rate of the contaminants, creating a stable and then decreasing plume. The reduction of contaminant loading may be accomplished using a variety of approaches, with the most common being the modification of the hydraulic properties of the source zone or the surrounding materials.

Most of these concepts rely on reconfiguring the site to permanently modify the large-scale hydrology in the vicinity of the source. Because "loading" is the product of concentration and flow, this term can be reduced by altering the system hydraulics to reduce the flow of water into or through the contaminant source zone. In general, it is important to note that the majority of approaches used to reduce contaminant loading do not destroy or alter the contaminant but increase the time frame for which the contaminant is released. This approach may result in a longer time frame for complete remediation of the source zone due to the reduction of groundwater flow through the source zone. On the other hand, the reduced loading from the source zone may reduce the expansion of the downgradient plume by creating conditions where the attenuation rate is greater than the loading, resulting in degradation of the contaminants of interest at a point closer to the contaminant point of origin. For example, if a sensitive receptor is downgradient of an expanding plume, methods that will result in the plume stabilizing and shrinking before it reaches that receptor become worthy of consideration.

Implementing permanent, sustainable, and easily documented changes in large-scale hydrology is relatively straightforward. Proper design and implementation of these traditional concepts will provide hydrologic control that will be in place as long as the hydraulic controls are in place. Moreover, modification of large-scale hydrology is relatively easy to model, and monitoring is likely to be inexpensive.

4.3.1 Reducing Infiltration through the Source Zone

This section outlines a variety of hydraulic manipulation approaches, some conventional and some innovative, used to reduce contaminant loading from source zones A major way to reduce the mass loading to a plume is by reducing the infiltration of precipitation. Infiltration can be fed by (a) direct precipitation on the surface overlying the source, (b) sheet runoff advancing downslope to the source area, and (c) storm flow traveling downgradient in the top ~1–2 m of the soil column, where permeability is greatest. Not all of these processes are important at every site. Several methods to reduce loading by reducing infiltration are discussed below.

4.3.1.1 Interception and Diversion of Surface Water

Interception and diversion of surface water can have a significant impact on the amount of water that passes through a source zone, the rate of mass transfer of contaminants to groundwater, and the mass flux feeding a plume. The main purpose of this class of enhancements is to maximize runoff and minimize infiltration.

The question to be asked when designing for interception and diversion of surface water as part of an EA approach is, "How much surface water needs to be diverted to reduce contaminant mass loading to the zone of interest so the rate of the attenuation mechanisms will be greater than the loading rate, resulting in a stable and then shrinking plume?" Another way to ask the same question is, "How much surface water can be allowed to infiltrate through the source so the attenuation rate in the zone of interest will be greater than the contaminant loading rate, resulting in a stable and then shrinking plume?"

The answers to these questions impact the chosen size and type of interception/diversion configuration, which ultimately drive cost. Types of configurations may range from minimal recontouring of the topography and/or lining drainage-ways to major recontouring of the surrounding topography and constructing lined drainage-ways.

4.3.1.2 Cover/Cap Systems

Covers/caps either reduce the permeability of soils overlying a source zone or favorably manipulate the soil water balance so as to limit percolation through a source zone. Conventional engineered cover designs are based on guidance developed to comply with the Resource Conservation and Recovery Act of 1976 (RCRA). These designs rely on the low permeability of a compacted soil layer to limit percolation (EPA 1989). Alternative covers meanwhile are designed to *accommodate* and *enhance* beneficial natural processes, such as evapotranspiration and capillary forces (see ITRC 2003a).

The question to be asked when designing a cover/cap system as part of an EA approach is similar to the question asked when designing for interception and diversion of surface water described earlier: "How much surface water per time increment needs to be diverted off the cap to reduce contaminant mass loading through the source to the zone of interest so the rate of the attenuation mechanisms will be greater than the loading rate resulting in a stable and then shrinking plume?" Another way to ask the same question is, "How much surface water per time increment can be allowed to infiltrate through the source so the attenuation rate in the zone of interest will be greater than the contaminant loading rate, resulting in a stable and then shrinking plume?" The answer to this question impacts the type and size of cover/cap system chosen and ultimately the cost. Cover/cap systems range from traditional RCRA-style caps to alternative covers (evapotranspiration or vegetative).

4.3.2 Reducing Mass Transfer of Contaminants to Groundwater in a Source Zone

Hydraulic manipulations implemented below ground surface typically divert water around the contaminant source, either through containing the source with barriers or manipulating the hydraulic gradient. In one case, an increase in attenuation rates is also supported. The technologies discussed in this section may be most appropriate when the source contains DNAPL and more aggressive treatments are not practical, such as a DNAPL source beneath an operating facility where access is not feasible. These technologies can also apply after treatment, when DNAPL residuals are all that remain of the source.

The main objective when installing any of these technologies is to reduce flow through the source, resulting in decreased mass flux of contaminants to downgradient plume zones. Like the technologies in Section 4.3.1, the main question to be answered when designing the treatment is, "How much groundwater needs to be diverted around the source to reduce contaminant mass loading through the source to the zone of interest so the rate of the attenuation mechanisms will be greater than the loading rate, resulting in a stable and then shrinking plume?" Another way to ask the same question is, "How much groundwater can be allowed to pass through the source so the attenuation rate in the zone of interest will be greater than the contaminant loading rate, resulting in a stable and then shrinking plume?"

4.3.2.1 Source Containment Methods

Several methods have been identified that will minimize the release of contaminants from the source. They can be classified as either barriers or encapsulation methods. Barriers are typically deployed upgradient of the contaminant source with the goal of reducing the volume of groundwater flowing through the source. Barrier types span the range from slurry walls (cement/bentonite) and sheet piling to impermeable membranes and biobarriers. The first two types are traditional methods of constructing barriers, while the latter two are innovative approaches. Encapsulation methods involve injection of materials into the source region that fill pore spaces, reduce permeability, and thereby result in partial flow diversion around the source. Depending on subsurface geochemical conditions and contaminants of interest, various materials may be used: colloidal silica, cement, bentonite, clay-based materials (alone or in combination with reactive materials such as zero-valent iron), and edible oils. While most of the materials used for source containment support a reduction of mass loading, the last two mentioned have the added benefit of also supporting increased attenuation at the source. These methods provide both a means to promote microbial-mediated reductive dechlorination and barriers to physically mitigate contaminant transport to downgradient receptors.

4.3.2.2 Methods of Modifying the Hydraulic Gradient

Several methods have been identified to modify the hydraulic gradient upgradient of the contaminant source, thus reducing the rate of groundwater flow through that source. Methods include drainage structures, plant-based methods, and combinations of the two.

A common drainage structure that can support hydraulic gradient modification is a French drain. An innovative method of modifying the hydraulic gradient is the use of a geosiphon, a technique that takes advantage of the natural differences in head to create a siphon. Upgradient water is drawn into the siphon and released downgradient of the contaminated zones of interest. Besides modifying the hydraulic gradient in a system, this technology may be combined with a treatment method that increases attenuation rates (Phifer, Nichols, and Sappington 2000).

In locations where the water table is shallow, plant-based methods of hydraulic control are feasible. These methods are based on high rates of water uptake and evapotranspiration of the plants. Besides hydraulic control through the source, these methods may reduce surface infiltration. The goal of these methods is to remove infiltration or groundwater at a rate that exceeds its replenishment to achieve a locally depressed water table. Techniques to increase the depth at which plant-based methods will be effective have included the patented process of "treemediation" (Early et al. 2006). In this process, boreholes, unlined or lined, are drilled to the water table (for depths to ~30 feet below ground surface) and filled with a porous, permeable material that acts as a wick, drawing the groundwater up within the boreholes to the root zones of deep-rooted plants. As this is the closest source of water, the plant roots grow into this zone.

Early et al. (2006) also describe the combining of a French drain installed in a continuous circle around a source (moat) and planting phreatophytes within the perimeter of the moat. The construction of the moat results in a constant head within the perimeter of the moat. During the growing season the phreatophytes take up the groundwater, creating an inward hydraulic gradient.

Depth is a limiting factor in the use of these enhancements. Though the use of drainage structures can be installed at depth, costs may make these prohibitive over other methods. Treatments that involve plant-based methods are limited to the depth of the root zones or slightly beyond when using creative approaches to bring the groundwater to the roots.

4.3.3 Diverting Electron Acceptors away from Contaminants

This method is based on the fact that the presence of electron acceptors (primarily dissolved oxygen, nitrate, and sulfate) in a source zone will result in biodegradation reactions that *compete* with beneficial dechlorination reactions for the electron donor. This competition occurs in cases where the electron donor is present in the source zone prior to remediation (a Type I or Type II chlorinated solvent site, Wiedemeier et al. 1998) or if the electron donor supply is enhanced by adding fermentation substrates or hydrogen directly. These competing electron acceptors can use up the electron donor required for reductive dechlorination of the chlorinated solvents.

The elimination and/or diversion of completing electron acceptors can be used for an evaluation of mass balance. Many enhancement methods described in this chapter would be considered as viable options to control the movement of electron acceptors into the contaminant plume. The overall goal and effect of these enhancements is to yield a stable and sustainable degradation rate for the contaminant(s) of concerns.

4.4 Enhancements that Reduce Contaminant Loading of Residual Contaminants from the Source Using Passive Methods

Like enhancements to the source that manipulate the groundwater hydraulics, the objective of reducing contaminant loading of residual contaminants from the source using passive methods is to reduce or eliminate mass flux from the source. A difference between these two categories is that in the former, reduction in flow is the basis for mass flux reduction and in the latter, contaminant mass removal is the basis. One technology that has been used successfully is passive soil vapor extraction (SVE), a simple, low-energy, low-cost process that relies on changes in barometric pressure to remove contaminants from the unsaturated zone. The case study on the next page describes one instance where passive SVE in the form of baroballs was used as an enhancement once active SVE was no longer able to sustain a contaminant removal rate agreed to by the responsible parties. Technologies in this category are those that reduce or eliminate mass flux by increasing the removal rate of contaminants from the source using passive methods and can be referred to as source strength reduction technologies.

4.5 Enhancements that Increase the Attenuation Capacity Using Biological Processes

Biological processes that promote an increase in the natural attenuation capacity of chlorinated solvent systems are critically important enhancements. One reason for this is the preference by regulators for processes that degrade the contaminants. In the past decade an enormous amount of research has greatly expanded our knowledge of the processes that control biological degradation of chlorinated solvents and our ability to enhance those processes. For a summary of the processes controlling biological degradation of chlorinated solvents and references for additional reading, see Section 6 of *In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: A Resource Guide* (www.itrcweb.org/Team_Resource_BioDNPLs/BioDNAPL_Resource_Guide_7-30-07.pdf), and Sections 2.2 and 4 of *Overview of In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones* (ITRC 2005a). In addition to biological processes such as biostimulation and bioaugmentation, plant-based methods promote increases in the attenuation capacity. Plant-based methods such as natural or engineered (see ITRC 2003b, 2005b) wetlands provide a stable, sustainable environment where the contaminant attenuation rate is greater than the contaminant loading.

When designing either a biological treatment process or plant-based treatment system, an important question to be answered is, "Will the actions taken result in an attenuation rate greater than the loading rate and will that balance remain so for a time sufficient to meet the remediation goals?" For treatments based on biostimulation, one would want to determine whether the process can be designed to inject sufficient "nutrients" to reach the remediation goals with a limited number of injections, if not just a single injection.

Passive Soil Vapor Extraction:
An EA Technology that Reduces Loading from a Vadose Zone Source

Prior to 1983, solvents TCE and PCE contaminated soils underlying a process sewer line located at the M-Area of the Savannah River Site. Active soil vapor extraction (ASVE) removed ~91,500 lbs. of these solvents from the vadose zone 1995–2002. The vadose zone is ~135 feet thick and consists of sand with interbedded clays deposited in shallow marine, lagoonal, or fluvial environments.

As the rate of solvent removal diminished, engineers transitioned to passive SVE (PSVE), employing baroballs alone and in conjunction with microblowers, small 12 volt DC blowers run solely by solar cells, to enhance removal rates. The criteria for shutting down the ASVE units, as documented in the M-Area HWMF RCRA Part B Renewal Application, Rev. 4, 1996, was removal rates that could not be maintained at a minimum of 40 lbs./week for a two-week period followed by confirmatory sediment and soil gas sampling in the treated area. The 40 lb./week criterion was based on a simple comparison with observed asymptotic removal rates from groundwater recovery wells in the M-Area underlying the vadose zone source areas. Once reached, a series of two rebound tests were conducted that consisted of an approximately 3-month shutdown period followed by a restart to preshutdown operating conditions. The results indicated that 40 lbs./week could not be maintained for longer than two weeks. Characterization efforts in 2000 and 2003 indicate the ASVE was successful in removing the contaminants from the sandy regions where the majority of flow would occur. However, residuals remained in the fine grain (clayey) materials, producing a low-concentration but long-lived source of contamination. In the first 3.5-year period of PSVE operation, more than 600 lbs. of solvents was removed.

PVSE takes advantage of the difference in atmospheric and subsurface pressure, allowing contaminants to be released from the subsurface when the pressure in the subsurface exceeds atmospheric pressure. PSVE systems are low in both operation and maintenance costs.

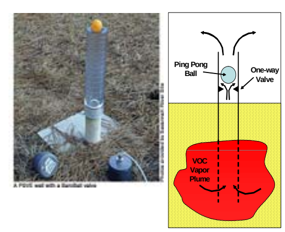
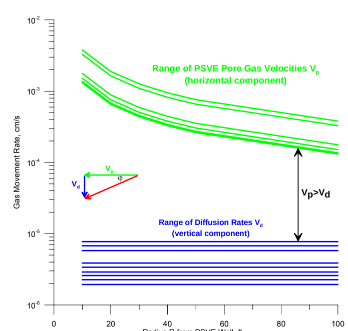


Photo and diagram of deployed baroball.

Important to the transition from ASVE to PSVE was the mass removal estimations versus loading estimate. This was evaluated in terms of mass flux and was based on field gas concentration data. PSVE concentrations were estimated based on concentrations from one of the three ASVE units. This method compares what is being released from the remaining contaminated zones (loading) and what needs to be removed by PSVE (removal), as shown in the table below. This evaluation indicates that the rate of attenuation (removal) is greater than the loading; thus the plume will shrink. A second evaluation evaluated the rate of residual contaminant migration from the vadose zone to the groundwater. PSVE advective flow rates (pore gas velocities, V_p) were compared to diffusion rates, V_d, from the residual source areas to the groundwater. As shown at right, V_p is greater than V_d, indicating that PSVE flow rates are faster than downward diffusion of contaminants and thus the residual contaminants will not contribute to groundwater contamination. Additional, ongoing data collection verifies these estimates.



Graphical comparison of pore gas velocities and diffusion rates.

Calculated and measured concentrations and mass flux based on the mass transfer coefficient and the estimated loading

	Calculated concentration, ppmv (C_{ss})	Measured concentration, ppmv (C_{ss})	**Removal** Calculated well mass flux, lb/day	**Removal** Measured well mass flux, lb/day	**Loading** Mass flux from the fine grain zones, lb/day (*f*)
PCE	17.3	20.4	0.06	0.07	0.053
TCE	26.6	23.5	0.07	0.06	0.048

(*Source of information, figures, and tables:* Riha 2005)

Plant-based treatment methods can support the sustainability of the system by producing environments favorable to degradation of chlorinated solvents. For example, wetland plants not only help to produce an anaerobic zone in the wetland sediment but also provide a steady supply of organic detritus to that sediment. Both of these actions significantly contribute to the sustainability of the wetland. Also, plants can contribute more directly to the treatment of chlorinated solvents through phytovolatilization, rhizodegradation, and phytodegradation. Native wetland plants have been shown to phytovolatilize and phytodegrade (willows) TCE (Punshon, Mills, and Adriano 2003; Nzengung and Jeffers 2001; Casey, Sanford, and Vroblesky 2004). In addition, plant roots stabilize the sediment and protect it against erosion. Plants establish a habitat that is beneficial to wildlife and can create a favorable visual impact, important to nearby communities and responsible parties. Thus, when considering plant-based methods as an enhancement, several mechanisms may be effective (see ITRC's forthcoming PHYTO-2R, Table 1-1, update in progress).

Plant-based treatments are limited to shallow groundwater, rendering them be most applicable for source and discharge zones of a contaminant plume, where root contact with the groundwater is feasible. Also important in evaluating the impact of plant-based treatments on the attenuation capacity of a system is the variability in the attenuation rates based on the growth season(s) for the chosen plants. In other words, attenuation rates will have an annual cycle that should be considered during the mass balance evaluation.

4.6 Enhancements that Increase the Attenuation Capacity Using Abiotic or Biologically Mediated Abiotic Processes

Abiotic processes are those that result in the chemical degradation of contaminants without reliance on bioactivity. Bioactivity may provide or lead to the creation of some of the reactants involved in the degradation, but it is not directly responsible for the ultimate degradation. Within this class of technologies, reactive barriers, such as biowalls and zero-valent iron walls, and biogeochemical reductive dechlorination (BiRD) seem the most promising. With both of these types of treatment, the geochemistry indigenous to the environment of interest has significant influence on the design of the treatment system.

Though not truly an enhancement, microbial benefits of in situ oxidation (MBISO) occur as an outcome of in situ chemical oxidation (ISCO). A remediation can be designed that takes advantage of MBISO in the EA plan. Taking advantage of the subsurface conditions that result from the ISCO may facilitate the transition to either an enhancement or MNA. MBISO involves three benefits to halorespiring bacteria. The first benefit is microbial cycling through abiotic transformation (oxidation) of expired biomass within soil pores, thereby improving aquifer hydraulic conductivity. In this process, trapped nutrients are released for use by viable halorespirative microbes for chloroethene destruction. This first benefit also involves the oxidation of a portion of viable biomass, which also releases nutrients for the subsequent support of other microbes. Over time this reduction in the viable biomass may supply a microbial ecology benefit by facilitating a population change in anaerobic microbial communities toward bacteria that can thrive in the presence of elevated concentrations of chemical oxidants. The second benefit is the oxidation of chloroethene contaminants (especially reductive dechlorination-inhibiting daughter products) and the generation of biologically beneficial effects from that oxidation process. The third benefit is the partial oxidation of natural organic matter that increases substrate surface area for halorespiring bacteria. These benefits are described as a symphony of multiple, complementary, biologically mediated environmental remediation processes. It is now possible to select site-specific, interdisciplinary measurement parameters for the destruction of chloroethene contaminants that had previously been associated with separate (i.e., abiotic and biotic) technologic approaches to the remediation of the environment (Rowland et al. 2001, Rowland and Golden 2003).

4.7 Enhancements Summary

The design basis of an enhancement is to produce either a reduction in source loading or an increase in attenuation rate. The technical team that developed EA attempted to do a thorough evaluation of technologies that would fit these classes, but they do not claim that those technologies should be considered all-inclusive.

For a technology to be an EA technology, it must be able to meet the four criteria identified in Section 4.1:

- The enhancement achieves or maintains the stability of the plume and results in plume shrinkage over time.
- The enhancement results in an increased attenuation capacity and/or source strength reduction from the source.
- The enhancement can be monitored and validated.
- The enhancement has sufficient sustainability to maintain a reduction in flux for a period that achieves regulatory requirements.

Though usually designated by a concentration goal, these criteria are based on the answers to the questions in the diamonds on the left side of Figure 2-1. These questions address acceptability of risk, plume stability and shrinkage, sustainability of conditions, remediation time frame, and cost benefits.

5. ENHANCED ATTENUATION APPLICATION

The goals of this chapter are to present an example of how to implement the EA framework for a hypothetical site and to summarize how EA has been applied to actual sites. The scenario section describes step-by-step how to use the EA framework through the remediation life cycle of a simple example. The second part of this chapter describes the Web-based EACO Case Study Database (www.afcee.brooks.af.mil/products/techtrans/info/default.asp), which contains case studies from throughout the country where the EA site management approach has been used for chlorinated organics remediation.

5.1 Example Implementation of the EA Framework

This section presents an example of how to implement the EA framework for a hypothetical site. The goals of this scenario are to demonstrate the following:

- how the EA framework can be used to optimize remedial solutions
- how a mass balance can be used to evaluate plume stability
- example implementation of the MNA/EA Decision Flowchart

This example scenario demonstrates how the EA framework can be used at the start of a remediation effort for a site. It is possible for the EA framework to be used for remedies that have already been implemented. For example, the EA framework can be adopted to facilitate the transition of a site from high-energy or active remediation to MNA with the option for enhancements as needed. The EA framework can also be used to improve an MNA remedy that may not be working as quickly or as effectively as first anticipated.

The steps associated with the remediation life cycle presented in this example scenario are as follows:

Step 1: Baseline characterization, including a mass balance assessment to characterize plume stability and to provide a baseline for evaluating remedial performance.

Step 2: Aggressive source treatment using high-energy or active remediation technologies and MNA for the downgradient portion of the dissolved plume.

Step 3: Use of the MNA/EA Decision Flowchart to implement MNA for the downgradient plume after the high-energy treatment phase results in substantial reduction of TCE and benzene, toluene, ethylbenzene, xylenes (BTEX) concentrations in the source zone.

Step 4: An enhancement is implemented to increase the rate of mass attenuation of the dissolved plume to accelerate the achievement of compliance with site cleanup criteria.

Step 5: After the enhancement results in a sustained increase in mass attenuation rates for the dissolved plume, MNA is continued as the remedy for the dissolved plume.

Step 6: Site closure is achieved.

A brief description of how the EA framework applies for each of these steps in the remediation life cycle is presented below. Note that this simplified scenario is intended to demonstrate one example of how the EA framework can be applied. The steps cited in this simple scenario do not represent the only pathway that can be followed; these steps are provided as a demonstrative example and are not intended to be prescriptive for any specific site remedy. Section 5.2 cites a number of actual sites where EA technologies have been employed.

5.1.1 Step 1: Baseline Characterization

General characteristics of this example scenario prior to remediation (Figure 5-1) are as follows:

- Confined aquifer with interbedded lenses of finer materials.
- A high-concentration source of TCE and BTEX in the saturated zone with negligible contributions from the vadose zone.

- A dissolved plume with TCE, DCE, VC, and BTEX.
- Anaerobic groundwater conditions.
- Types I and II natural attenuation conditions due to the presence of both anthropogenic electron donors (i.e., BTEX) and native organic matter that also provided a source of electron donors for the biodegradation of the chlorinated organics (Wiedemeier et al. 1999).
- The plume is relatively young, and insufficient time data are available to directly evaluate plume stability.
- There are no potential receptors near the site, although there is public concern about the high concentrations of chlorinated organics leaving the site.

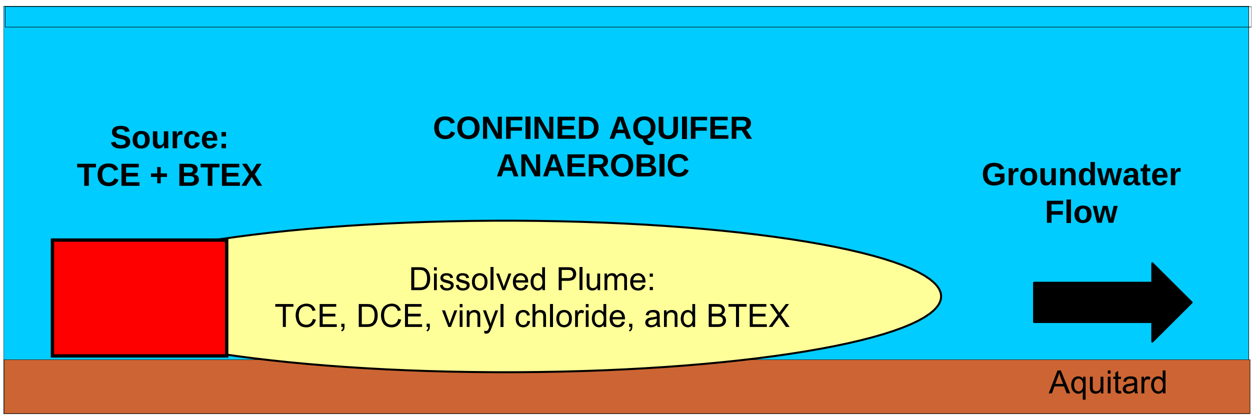


Figure 5-1. General site characteristics.

Prior to implementation of the EA framework, it is necessary to conduct a mass balance assessment to evaluate plume stability and to provide supporting information for making a decision on the site remedy. As previously discussed, a mass balance assessment includes a quantitative estimation of the mass loading to the dissolved plume from various sources, as well as the mass attenuation capacity for the dissolved plume. A description of a mass balance assessment is described by Chapelle et al. (2004). Processes contributing to mass loading can include input from the source to the dissolved plume and can also include desorption (e.g., Imbrigiotta et al. 1997) and infiltration.

Naturally occurring processes that can result in the removal of mass from a dissolved plume include advection, dispersion, biological and abiotic degradation, volatilization, adsorption, and plant uptake. The removal of mass from a plume by advection, dispersion, volatilization, and plant uptake is based on the flux across the plume boundary caused by these four processes. This is distinguished from the degradation and sorption processes, which can occur anywhere in the plume.

Figure 5-2 depicts an example of the components associated with a mass balance for a dissolved plume of chlorinated organics. Figure 5-3 illustrates the concepts associated with the balance between mass loading and mass attenuation capacity that govern whether a plume is stable, expanding, or shrinking. The filled circles represent the relative rate of (a) mass loading and (b) mass attenuation capacity.

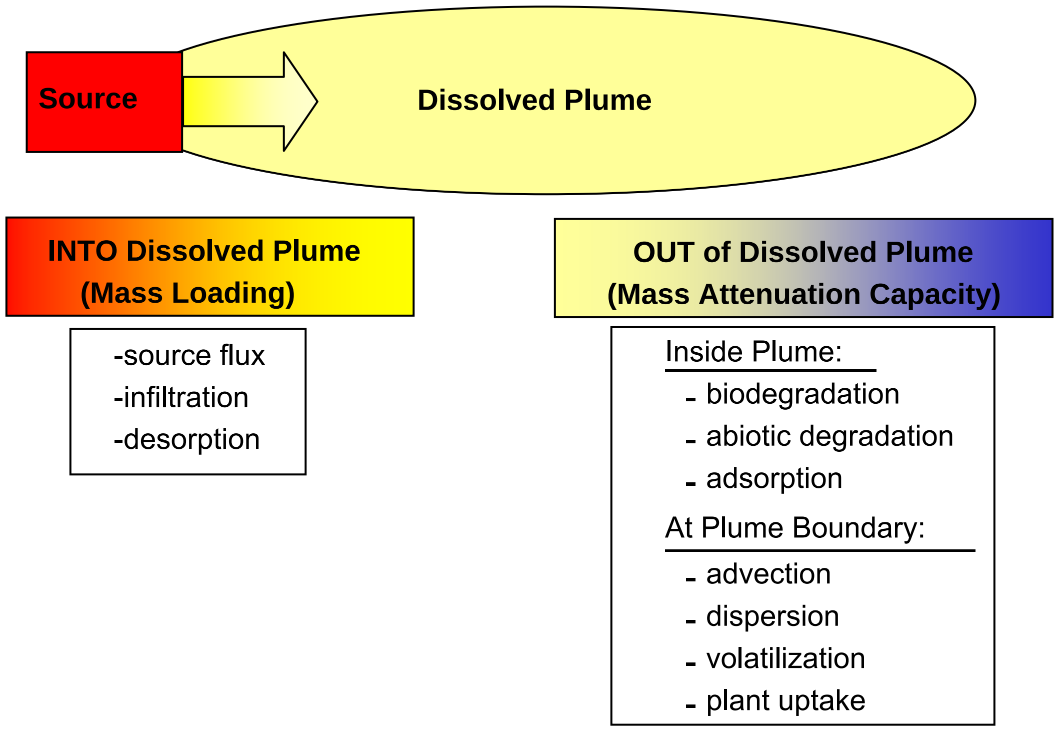


Figure 5-2. Example of a mass balance for a dissolved plume.

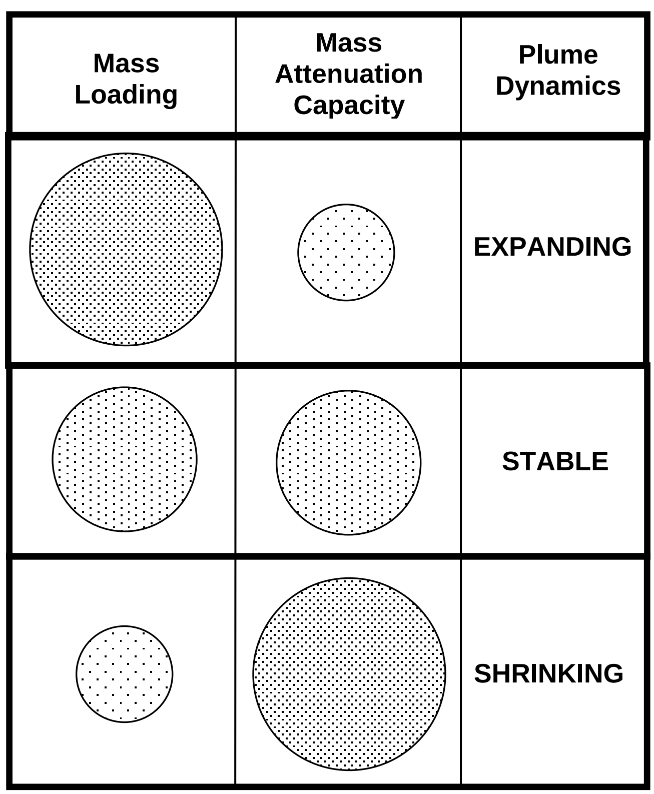


Figure 5-3. Influence of the balance between mass loading and mass attenuation capacity on plume stability. (The filled circles represent the relative rate of (a) mass loading and (b) mass attenuation capacity.)

Figure 5-4 shows the position of the dissolved plume of chlorinated organics (i.e., TCE, DCE, and VC) at the site under baseline conditions prior to remediation. The chlorinated organics plume was defined as the volume of the aquifer where the concentrations exceed site cleanup criteria. The BTEX plume is shorter than the chlorinated organics plume at the site.

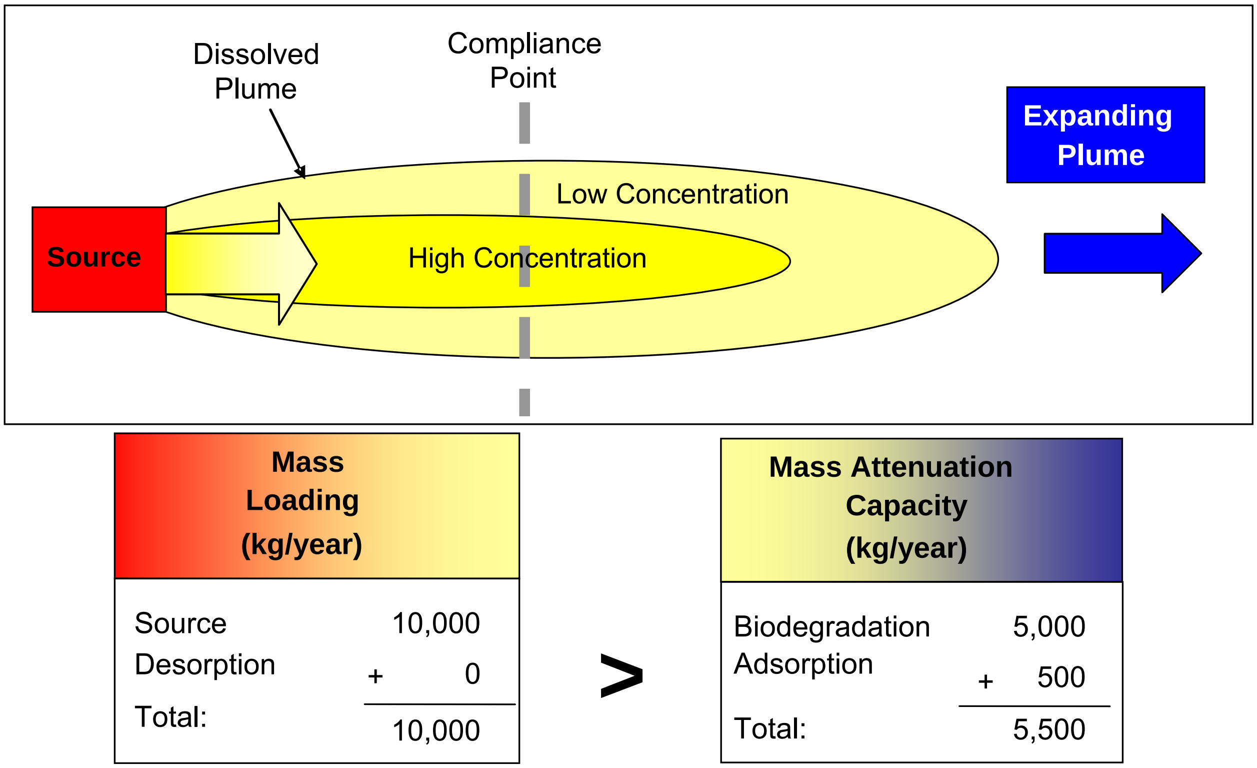


Figure 5-4. Baseline plume conditions before remediation.

Figure 5-4 also shows examples of the processes which were considered in this simplified mass balance assessment. In this example, the mass loading to the dissolved plume from the source zone was estimated to be 10,000 kg/year. Desorption was not occurring prior to remediation at the site. The mass attenuation capacity for the dissolved plume was governed primarily by biodegradation (5,000 kg/year) and adsorption in the leading edge of the plume (500 kg/year). Mass removal at the plume boundaries arising from advection and dispersion are determined to be relatively small because of the low concentrations used to define the plume boundary. The mass loading (10,000 kg/year) to the dissolved plume is greater than the mass attenuation capacity (5,500 kg/year), which indicates that the plume is expanding under baseline conditions.

5.1.2 Step 2: Source Treatment and MNA for Downgradient Plume

The decision was taken to implement an aggressive source treatment remedy to significantly reduce the concentrations of TCE and BTEX loading to the dissolved plume. The relatively fast biodegradation rates measured for TCE, DCE, VC, and BTEX at the site indicated that MNA was an appropriate remedy for the dissolved plume.

It was recognized that aggressive source treatment would significantly reduce the concentration of one of the sources of electron donors: BTEX. Site tests indicated that the native organic matter in the aquifer would continue to provide a sustainable source of electron donors, although there was uncertainty about what changes would occur in the chlorinated organic biodegradation rates when BTEX concentrations were reduced during source treatment activities.

In the EA framework, the contingency for an MNA or enhancement remedy can be increased monitoring, a supplementary enhancement, a high-energy or active remedy, or a staged combination of actions. In this example, the primary contingency for the MNA remedy was an enhancement that would increase the mass attenuation capacity and/or the rate of mass attenuation in the dissolved plume.

The MNA/EA Decision Flowchart (Figure 2-1) was used to develop the combined remedy including source zone treatment and MNA for the downgradient portion of the plume. The decision to use MNA for the downgradient plume was based on the mass balance assessment conducted as part of the baseline characterization. A complete characterization of MNA was conducted in accordance with Section II of the MNA/EA Decision Flowchart.

5.1.3 Step 3: MNA

After a period of source zone treatment, it was evident that continued active source treatment would have significantly diminishing returns based on the slowing decline in source depletion. An evaluation was conducted to demonstrate that the source treatment could be turned off and MNA could become the sole remedy for the site.

Figure 5-5 illustrates the dynamic plume conditions at the end of the source treatment phase. TCE and BTEX concentrations in the source zone had decreased by two orders of magnitude, resulting in a source contribution to mass loading of only 100 kg/year. The change in source conditions had resulted in some desorption in the near-source region of the plume, with a contribution of 20 kg/year to the mass loading. The total mass loading from these sources was thus 120 kg/year.

Figure 5-5 shows that the mass attenuation capacity of the dissolved plume was governed by the biodegradation of chlorinated organics, which resulted in a removal rate of approximately 200 kg/year based on the plume concentrations at the end of the source treatment phase. As the concentrations of the chlorinated organics in the dissolved plume continued to decline with time, the mass attenuation caused by biodegradation also decreased. The shrinking plume dynamics as determined from this initial mass balance assessment indicated that MNA was still an appropriate remedy for the chlorinated organics plume.

As the plume approached a stable position, another mass balance assessment was conducted, as shown in Figure 5-6. The results indicated that the source loading was 100 kg/year because desorption had stopped when the plume reached a stable equilibrium. The plume concentrations had decreased to a point where the mass attenuation capacity was 100 kg/year. The plume reached a stable position when the source loading became equal to the mass attenuation capacity of the dissolved plume.

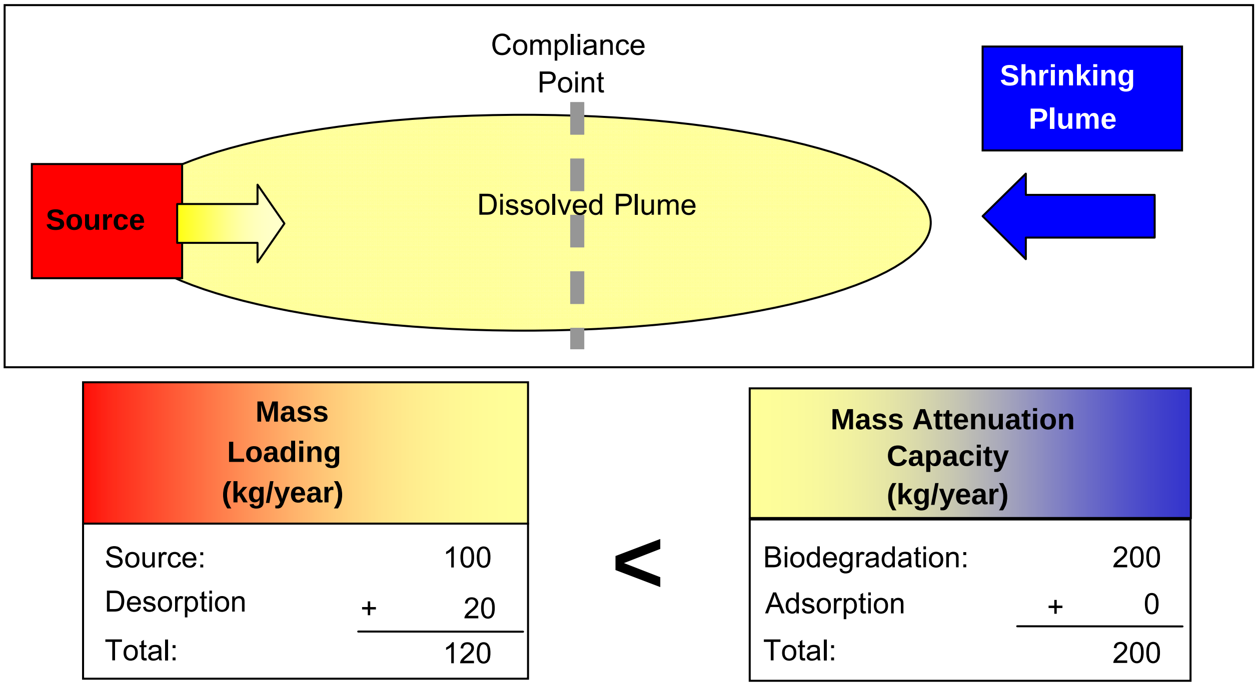


Figure 5-5. Initial plume conditions after source treatment.

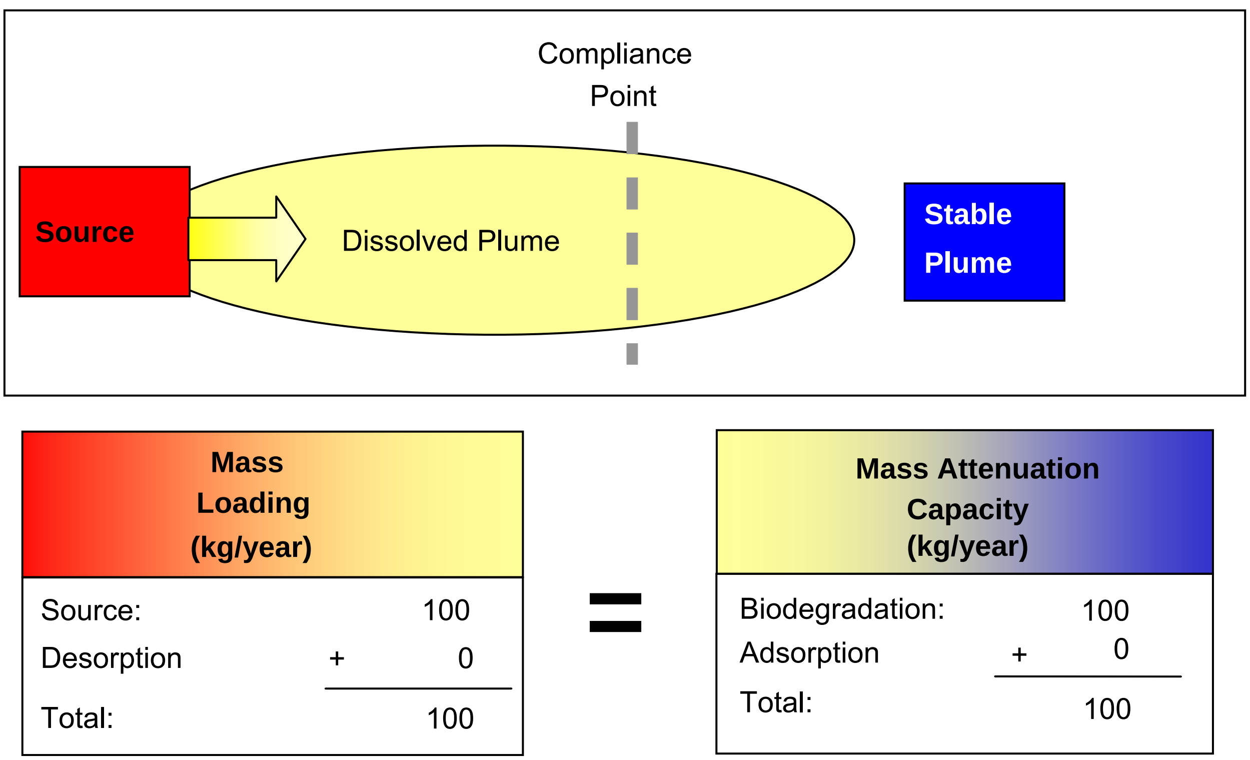


Figure 5-6. Stable plume conditions after source treatment.

As shown in Figure 5-6, the stable plume still extends beyond the compliance point. A site investigation indicated that the rates of DCE and VC biodegradation had slowed somewhat because of the reduced BTEX concentrations. As discussed in the next section, an enhancement was implemented to increase the rate of mass attenuation in the chlorinated organics plume in an attempt to shrink the plume and bring it into compliance. (For this example, it was assumed that public concerns prohibited the establishment of a new point of compliance at a downgradient location and that a risk assessment had already been conducted to develop alternative concentration limits for the chlorinated organics.)

5.1.4 Step 4: Enhancement to Increase Mass Attenuation Capacity

As discussed above, an enhancement was desired to shrink the plume so that it would not extend beyond the point of compliance. In this type of situation, it may also be feasible to implement an alternative or supplementary enhancement that reduces the mass loading from the source zone. Due to the interbedded nature of the soil materials in the source zone, it was decided that the enhancement for increasing the rate of mass attenuation in the plume was more reliable than the enhancement for reducing the mass loading from the source to the plume.

As discussed in Section 5.1, the goals of an enhancement are to (a) increase attenuation capacity or (b) reduce loading of the contaminant (flux) from the source as depicted in the lower half of Figure 5-3. To increase the rate of mass attenuation for DCE and VC, it was decided that bioaugmentation would be implemented because it is a sustainable remedy under site conditions after the initial implementation. Although DCE and VC were undergoing some biodegradation, tests indicated that the rates would accelerate if specific bacteria were injected into portions of the plume.

The proponent developed documented lines of evidence which demonstrated that the increased attenuation rate would result in shrinking of the plume to a level that would bring it into compliance. A supplemental enhancement to reduce mass loading from the source zone was incorporated as a primary contingency measure.

5.1.5 Step 5: Continue with MNA

After the enhancement was implemented, the rates of biodegradation of DCE and VC increased sufficiently that the plume shrank back to a position that was within compliance. Long-term monitoring continued for a period of time to confirm that the plume was stable. Figure 5-7 shows the position of the plume after the enhancement. The mass balance shown in Figure 5-6 indicates that the mass loading and mass attenuation capacity when the plume had reached a stable equilibrium were at the same level as before the enhancement (i.e. 100 kg/year). This demonstrates that the enhancement, which initially increased the mass attenuation capacity of the plume, was successful because it ultimately increased the rate of mass attenuation. Thus, the rates of mass attenuation may also be a consideration when evaluating remedies using the EA framework.

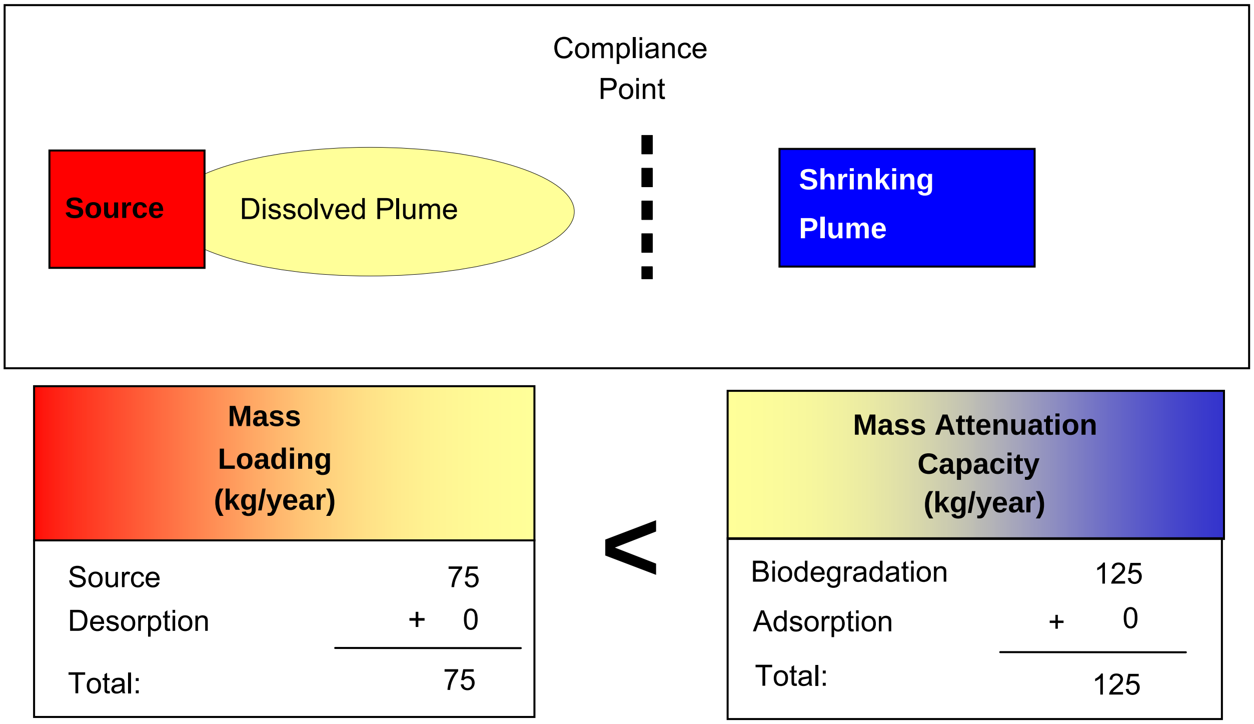


Figure 5-7. Stable plume position after enhancement.

5.1.6 Step 6: Site Closure

After a period of time, the source concentrations declined substantially, indicating that the source had been sufficiently depleted to allow for site closure. If this had not occurred, the proponent could have considered another enhancement to reduce mass loading from the source if remediation time frame was a concern for the MNA remedy.

5.1.7 Summary

In this example, a staged remediation solution was used to optimize site cleanup. The MNA/EA Decision Flowchart provided a clear approach for evaluating remedies and for the periodic reevaluation of the MNA remedy. The mass balance assessment provided an improved understanding of site conditions that ultimately resulted in a more effective remedy for this site.

5.2 Application Summary

The ITRC EACO Team designed a case study database to provide a repository for information on sites throughout the country where EA technologies have been used for chlorinated organics remediation. The decision to employ EA technologies predated the development of the MNA/EA Decision Flowchart and guidance document at several, if not most of the case study sites. However, each decision was undoubtedly based, at least in part, on many of the criteria and site characteristics incorporated into the decision framework and guidance, as those involved sought to maximize the probability project goals would be attained. Therefore, although each case study was not necessarily managed using the formal EA process, the studies as a group document the birth and early development of the EA concept, i.e., when and how to transition from high-energy to less energetic remediation and management technologies.

The Web-based EACO Case Study Database contains case studies of both successful and unsuccessful applications of EA technologies. Launched on July 1, 2006, the database (www.afcee.brooks.af.mil/products/techtrans/info/default.asp) is an ongoing effort. All case studies submitted will be included in the database, provided data presented are sufficient to answer most questions asked in the database. The selection criteria for cases reviewed for this document were as follows:

- The primary treatment type is an EA technology for groundwater.
- The targeted contaminants are primarily chlorinated organics.
- The project is well characterized and has defined cleanup goals.
- A documented basis for selecting EA over alternative strategies is provided.
- The project has well-documented contamination levels to serve as the baseline for MNA/EA.

The creation of the Web-based database involved soliciting the environmental remediation community to identify sites where EA technologies have been used on chlorinated organics. When available, references were reviewed, and site project managers were contacted to confirm and collect additional information. The case studies have and will continue to form the basis for many of the EACO Team's evaluations of EA applications. It is the team's intent to continue to collect case studies; therefore, we encourage their continued submission. If there is a particular remediation strategy that lacks documentation, inclusion in the EACO database is an excellent chance to bring it to the attention of many regulators, remediation professionals, site owners, and other stakeholders.

Table 5-1 is a summary of 24 sites surveyed for this document, listed alphabetically by state. The table includes the site name, city location (unless confidential), state, type of site, primary contaminant of concern (COC), whether nonaqueous-phase liquid (NAPL) is present or indicated by concentration, the maximum initial concentration in groundwater prior to application of EA technology, and the cleanup technology applied. More sites than those listed in Table 5-1 were submitted to the database; however, sufficient data for these sites were not available at the time of publication to include them in this document.

TABLE 5-1. Site summary

Site number and name	Location	Type	Primary COC	NAPL indi-cated	Max. initial conc. (µg/L)	EA cleanup technology
1. Long Beach Navy Base	Long Beach, CA	Dry cleaner	PCE*	No	6,500	Polylactate ester
2. Los Osos Drug Lab	Los Osos, CA	Manufacturer	Freon	No	6,900	Polylactate ester
3. Western Farm Service, Inc.	Vernalis, CA	Commercial distributor	DCP*	No	31,500	Polylactate ester
4. Stratford Drum Storage Site	Stratford, CT	Manufacturer	PCE	Yes	11,700	Polylactate ester
5. Asian Cleaners	Sanford, FL	Dry cleaner	VC	No	1,100	Nutrient-enhanced biosparging
6. Contemporary Cleaners	Orlando, FL	Dry cleaner	TCE	No	4,980	Polylactate ester
7. Former Sta-Brite Cleaners	Sarasota, FL	Dry cleaner	PCE	Yes	33,700	Lactate
8. Test Area North	Idaho Falls, ID	DOE site	TCE	Yes	20,000	Whey powder
9. Manufacturing, Central Illinois	IL	Manufacturer	TCE	No	1,400	Polylactate ester
10. Alliant Techsystems, Inc.	Elkton, MD	Manufacturer	1,1,1-TCA	Yes	17,000	Edible oil
11. Cohasset Dry Cleaners Site	Cohasset, MA	Dry cleaner	PCE	Yes	97,000	Polylactate ester
12. Boeing Fabrication Operations Facility	Hazelwood, MO	Manufacturer	TCE	No	3,800	Polylactate ester
13. Cypress Village Shopping Center	Bridgeton, MO	Dry cleaner	PCE	Yes	65,000	Polylactate ester
14. St. Louis County Brownfield	St. John, MO	Manufacturer	TCE	No	1,800	Polylactate ester
15. Linden Former Electric Motor Site	Linden, NJ	Commercial motor repair	PCE	Yes	45,900	Polylactate ester
16. NJ Printed-Circuit Manufacturer	NJ	Manufacturer	PCE	Yes	60,800	Polylactate ester
17. RCA Facility Nipper Site	Camden, NJ	Manufacturer	PCE	No	5,100	Polylactate ester
18. Tarheel Army Missile Plant	Burlington, NC	Manufacturer	TCE	No	4	Edible oil
19. Charleston Naval Weapons Station	Charleston, SC	DOD	TCE	Yes	18,000	Edible oil
20. Oconee County Manufacturing	West Union, SC	Manufacturer	TCE	Yes	21,000	Polylactate ester
21. Savannah River Site – MetLab Basin	Aiken, SC	DOE	PCE	No	NA	Baro pumping
22. Bellevue Dry Cleaners Site	Bellevue, WA	Dry cleaner	PCE	No	200	Polylactate ester
23. The Cleaners #1 Site	Kent, WA	Dry cleaner	PCE	No	551	Polylactate ester
24. Tosco Manufacturing Facility	Burien, WA	Manufacturer	PCE	Yes	11,400	Polylactate ester

*DCP = dichlorophenol, PCE = perchloroethene.

The sites are distributed in 12 states across the United States and include California, Connecticut, Florida, Idaho, Illinois, Maryland, Massachusetts, Missouri, New Jersey, North Carolina, South Carolina, and Washington (Figure 5-8). Of the 24 sites, 11 are manufacturers, eight are dry cleaners, two are commercial sites, two are DOE sites, and one is a DOD site. The most prevalent primary COC was perchloroethene (PCE) at 12 sites, followed by TCE at eight sites and VC; dichloropropane; 1,1,1-trichloroethane; and Freon 11 at one site each. The presence of NAPL was observed and/or indicated by dissolved concentrations at 11 sites. Of the 24 sites, polylactate ester was applied at 17 sites, edible oils at three sites, and lactate, whey powder, barometric pumping, and nutrient-enhanced biosparging at one site each. Full-scale applications were reported for 16 sites and pilot-scale studies for eight sites.

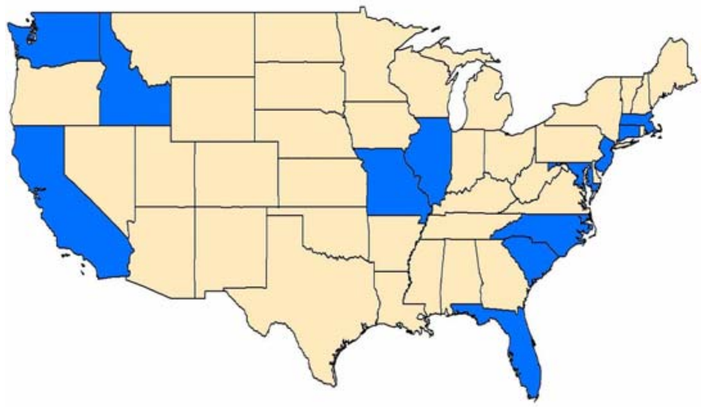


Figure 5-8. States represented in EACO Case Study Database.

6. REGULATORY CONSIDERATIONS

As previously mentioned, EA is a plume remediation strategy that includes three elements: a mass balance evaluation, use of the decision flowchart, and a toolbox of enhancement technologies. The use of EA as a remedial management strategy is consistent with the current regulatory environment and can be accommodated within a broad range of current regulatory programs, such as those that follow CERCLA or state dry cleaner regulations. The new decision process supports environmental cleanup progress on a national scale and can reduce overall costs, while providing protection to human health and the environment.

EA goals and principles include achieving groundwater restoration by evaluating mass loading and attenuation processes and developing an optimized, sustainable remedy. These principles are completely consistent with the current regulatory paradigm, including existing state and federal policy and guidance on the use of MNA.

This chapter discusses some of the results of the team's national regulator survey and explains what's unique about EA and how it fits in with current regulatory framework and policy at the state and federal levels. Regulators need to know what aspects of EA require particular attention and how EA provides a defensible scientific methodology for evaluating and selecting remedial methods and performance goals. Environmental practitioners need to know what concerns regulators are likely to have when EA is proposed in order to effectively address those concerns up-front.

> Enhanced attenuation does not conflict with the established regulatory framework, laws, regulations, or practices.

To that end, the EACO Team has identified, with help of a national regulator survey, several areas where regulators are likely to have concerns about using EA as a remedial strategy or that highlight particularly unique or beneficial aspects of EA. These areas include the following, which are discussed in detail in this chapter:

- EA requires active measurement and monitoring of mass-balance parameters.
- EA complements and supports MNA.
- EA requires good site characterization before remedy implementation.
- EA does not require new regulatory permits.
- EA may require use of institutional controls and other risk-management measures the same as with MNA and other remedies.
- EA may rely on technologies that have the potential for negative affects to aquifers, which should be evaluated the same as with all in situ injection technologies (i.e., depends on material reactivity, longevity, etc.).
- EA provides for the evaluation of risk, remediation time frame, and costs the same as with MNA and other remedies.
- EA emphasizes frequent reevaluation of mass-balance parameters and contingency planning.

6.1 National Regulatory Survey

In 2005, the ITRC EACO Team used a 120-question survey to query regulators from state environmental remediation programs on the use of MNA as a remedial approach for chlorinated organic–contaminated sites. Figure 6-1 depicts the responding states. The team reported results of the national survey in white paper entitled "A National Overview of Monitored Natural Attenuation and Enhanced Attenuation" (see Appendix B).

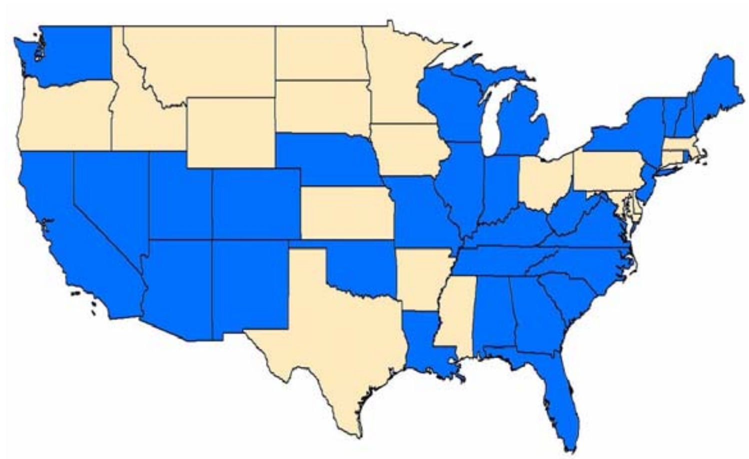


Figure 6-1. Thirty-one states (in blue) responded to the National EA Survey.

The survey was designed to

- understand which programs within the state regulatory agencies are accepting MNA as part of a larger remedy or as a sole remedy for chlorinated organic plumes,
- determine what tools and policies state regulators are using to evaluate the acceptability of MNA for chlorinated organic plumes,
- determine the importance of data and modeling tools,
- introduce the concepts of mass balance and EA.

The EACO Team used the results from the survey to help guide and focus the team in developing products, which can help chlorinated organic sites transition between remedial treatments including source control, plume remediation, and MNA. The responses from the survey reported that, as the number of proposals received by a regulatory program increases, the approval rates for MNA proposals also increase by a certain amount. It is interesting to note that most of the MNA proposals submitted were in combination with high-energy or active treatment systems and that MNA was seldom proposed along with a low-energy treatment technology such as permeable reactive barrier. Figure 6-2 indicates the overall general experience across the nation with regard to the use of MNA in 2005 at sites with chlorinated contaminants.

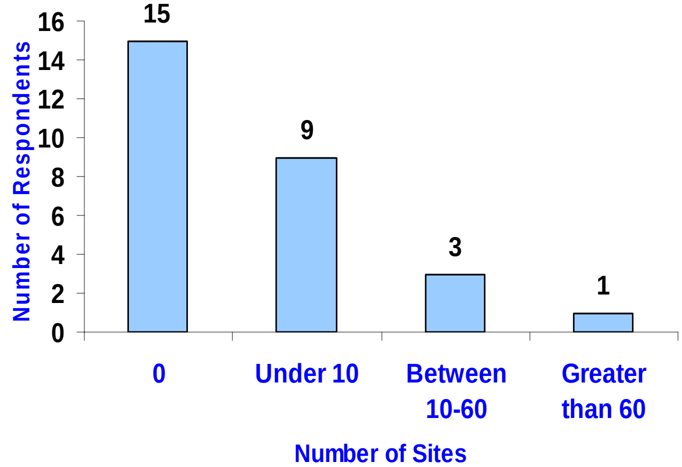


Figure 6-2. General experience with MNA.

While MNA is being approved by some state regulators and used as a contaminated-groundwater remedy on a regular basis, the survey results indicated that MNA still was not being approved for chlorinated sites in some states. Based on responses, 54% (15 of 28 respondents) had no sites using MNA for sites contaminated with chlorinated organics. Reasons reported for not approving MNA include that the site(s) was being effectively treated by other means or that the regulators lacked confidence in the MNA process. Responses to the survey indicate that MNA is being used in combination with more aggressive source remedies. Even though most states seem to be amenable to the use of MNA for chlorinated organics, there did not appear to be many cases available where MNA at a chlorinated organic–contaminated site contributes to full site closure.

One of the survey questions asked, "What was the level of support for developing protocols to encourage a phased MNA/EA decision process?" As noted in Figure 6-3, 86% of responding regulators were very supportive of this effort. As a result, the EACO Team decided to develop a protocol, which evolved into the MNA/EA Decision Flowchart.

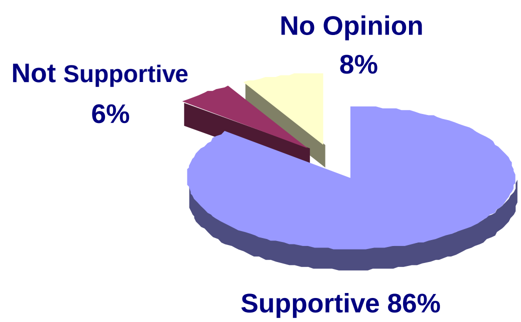


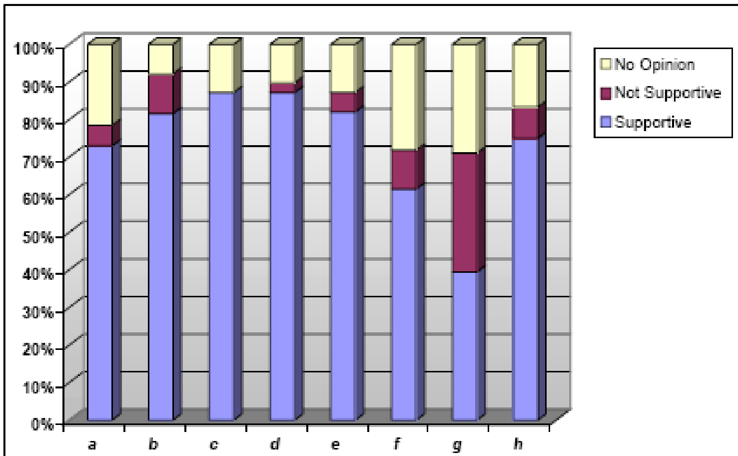
Figure 6-3. Level of support for developing protocols to encourage a phased MNA/EA decision process.

The survey also provided descriptions of new technical concepts and asked the respondents about their acceptance of these concepts, including the following:

- a mass-balance evaluation to assess contaminant mass loading relative to the subsurface system's attenuation capacity, facilitating selection of source treatment technology and treatment duration and determination of when to terminate more aggressive treatment and transition to MNA or EA

- developing EA as transitioning strategy between the initial remedy and MNA that will provide a mechanism for meeting remediation goals in an acceptable time frame

Contaminant levels have traditionally been measured as concentration (mass/volume), and cleanup goals are typically stated as concentrations. One approach to calculating a mass balance is to evaluate the mass loading and attenuation capacity in terms of flux (mass/time). Respondents to the survey were asked to identify their level of support for the use of flux measurements. Approximately two-thirds of the respondents supported the idea of using both flux and concentration measurements, and approximately one-third supported the idea of measuring flux instead of concentration. It is recognized that certain regulatory programs (i.e., CERCLA) require the use of concentration-based standards as a compliance end point. However, this requirement would not preclude the use flux measurements for remedial performance monitoring. Additionally, the survey respondents reported that regulators are supportive of enhancements, and the greatest support is for enhancements to the source and plume areas, as indicated in Figure 6-4. The least supported enhancement was volatilization from wetlands or surface water.



NOTE:
a) Reduce contaminant release rate from source using long-lived sustainable removal treatments
b) Physical modifications to source and/or plume area to reduce water flow
c) Biostimulation in the plume area
d) Bioaugmentation in the plume area
e) Permeable reactive barrier in the plume area
f) Degradation in expanded/constructed wetlands
g) Volatilization from wetlands or surface water
h) Phytoremediation in the plume discharge zone

Figure 6-4. Summary chart of regulatory support for various EA treatment technologies.

6.2 EA Requires Active Measurement and Monitoring of Mass Balance Parameters and Sustainability

EA should be considered for plumes that are not yet stable or shrinking and/or for plumes where natural conditions may not be adequate to sustain a stable or shrinking plume (Figure 6-5). Additionally, EA can be applied to plumes with existing remedies where remedial objectives are not being met. Though some enhancements used in an EA

Contaminants released into the soil and groundwater will spread out into a “plume.” If the contaminants are attenuated by natural processes, the plume will stabilize and then shrink.

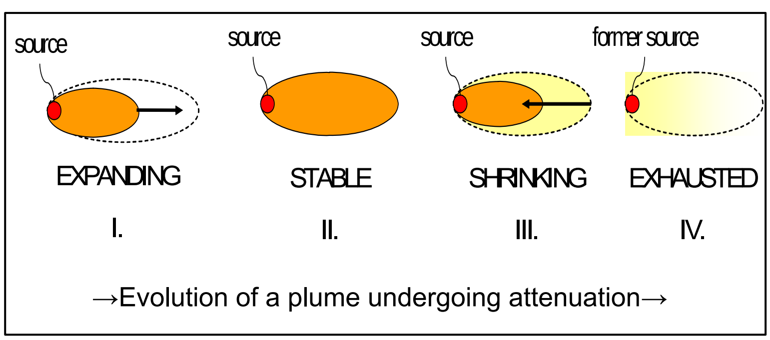


Figure 6-5. Life cycle of a contaminant plume.

remedy may involve high-energy or active treatments, the basis for monitoring remedy performance should include evaluation of mass loading and attenuation processes, rates, and capacity.

Regulators and practitioners should be aware that EA's focus on optimized, sustainable remedies does require frequent, periodic reevaluation of mass loading, attenuation processes, and contingencies to maintain a favorable balance. The focus on mass balance requires evaluation of mass flux to estimate loading and attenuation rates, which in turn requires increased collaboration between regulators and the regulated community to ensure collection of appropriate and defensible data while maintaining concentration-based compliance goals. The EACO Team believes that the use of mass flux is an important performance metric for evaluating the effects of different remedial options. The 2008 ITRC BioDNAPL team will be providing an in-depth evaluation of mass flux (http://www.itrcweb.org/teampublic_BioDNAPLs.asp). Thus EA promotes expansion of the standard plume evaluation "toolbox." As noted in the regulatory survey (Appendix B), some states accept the use of flux measurement at transition intervals; however, the EACO Team believes that compliance points can still rely on contaminant concentration.

Current regulatory frameworks do not typically evaluate the long-term sustainability of a remedy. Enhancements to the geochemistry or biochemistry of a site should consider the groundwater ecology as a whole from a sustainable, long-term perspective. Furthermore, EA considers the remediation life cycle and assists users in making decisions regarding selection of appropriate enhancements and acceptable remediation time frames.

> The concept of sustainability provides the technical basis for assuring that the remedial technology will achieve remedial objectives. Documenting sustainability is a key element that distinguishes EA from a traditional active source or plume remediation.

6.3 EA Complements and Supports MNA

EA complements and supports MNA concepts and in many ways is the next generation of the MNA concept because EA makes the fundamental MNA concept of balancing attenuation mechanisms and mass loading an active priority. In addition, EA requires periodic mass balance evaluation and implementation of contingencies as necessary to adjust the balance. EA further complements MNA by using mass flux evaluation, in addition to concentration, as a tool to measure where and how the remediation strategy should be focused.

The perception that MNA for chlorinated solvents is a "do nothing" approach needs to be overcome. Unless the proper aquifer (e.g., biochemical and geochemical) conditions exist at a site, significant degradation of chlorinated compounds will not occur. Furthermore, unless the proper aquifer conditions are actively demonstrated and controlled to maintain favorable loading and attenuation rates, it will be difficult to know whether MNA is a viable remedy. EA makes the case for active evaluation of mass loading and attenuation rates to demonstrate mass balance through measurement, collection, and modeling of relevant parameters.

6.4 EA Requires Good Site Characterization before Remedy Implementation

The primary goal of site characterization is to develop a conceptual site model (CSM) that provides the basis for appropriate remedy selection and design. However, sometimes there is pressure to implement remedial actions before characterization is complete. This desire is understandable since implementing the remedial action is perceived as cleaning up the site, whereas the connection between further site characterization and site cleanup may seem abstract. In other cases, interim remedial actions and time-critical removal actions are necessary to mitigate unacceptable exposures and risk.

EA seeks to reconnect the site characterization process and CSM development with the selection and design of appropriate remedies because evaluating mass loading and attenuation rates with the accuracy necessary to develop a long-term, sustainable remedy requires a thorough understanding of aquifer characteristics. This is particularly evident with in situ remedies such as enhanced bioremediation because successful deployment relies on accurate, comprehensive biogeochemical characterization or subsurface ecology assessment. Furthermore, development of a strong, dynamic CSM generally provides more regulatory confidence in the selected remedy. Since EA relies on evaluating the mass balance and selecting sustainable technologies, confidence in the site characterization can make or break regulatory acceptance of the proposed remedy. On the other hand, incomplete site characterization can not only result in implementation of an ineffective remedy but also lead to additional and more expensive characterization and remedy implementation in subsequent efforts, not to mention potential litigation and regulatory enforcement.

6.5 Permits

The EACO Team has not identified any permitting hurdles specific to the implementation of an EA remedy. Permitting hurdles may exist for specific "technologies" such as those that rely on injection of materials into the subsurface to enhance attenuation rates. Using the EA concept to design a sustainable remediation strategy based on evaluating and enhancing the mass balance should not require any new permitting or any substantive permitting changes.

As with any other proposed remedial method, one or more permits or permit equivalents may be necessary for the design, construction, monitoring, or closure of an EA remedy to the extent that the activity affects surface water, air, or groundwater quality or involves the management of hazardous waste. A thorough review of all permitting issues and federal, state, and local regulations should be conducted on a site-specific basis.

In addition to regulatory permits, EA remedy approval may occur through different regulatory mechanisms (e.g., CERCLA, applicable or relevant and appropriate requirements [ARARs]). The approval mechanism (approval letter, cleanup order, etc.) often depends on the regulatory program/process under which the site cleanup is managed. Various regulatory programs may require submittal of a work plan, corrective action plan, remedial action plan, feasibility study, etc.

6.6 Institutional Controls

The need for risk management measures such as institutional controls is driven primarily by the level of risk, cleanup time frame, and likelihood of future exposure based on future land or groundwater use scenarios. Therefore, any remedy will likely require the use of institutional controls if the cleanup time frame is long compared to the project future use, long-term evaluation and/or maintenance of the remedy is needed, or cleanup goals are not based on unrestricted use. Because EA remedies typically require longer time frames, long-term monitoring, and periodic evaluation to demonstrate effectiveness, it is important to consider the need for institutional controls as part of the initial EA remedy discussion.

The use of interim institutional controls may vary within each state regulatory program. Even though not specific to EA, states should establish a tracking mechanism of the use of environmentally impacted lands with state and local land-use agencies. A mechanism to return the site to active remediation should be established if institutional controls fail or improper land use creates unreasonable exposure. See *Evaluating, Optimizing, or Ending Post-Closure Care at MSW Landfills Based on Site-Specific Data Evaluation* (ITRC 2006), p. 40, for case studies of states' ability to enforce institutional controls using property covenants.

6.7 Effects of EA Remedy on Aquifer Conditions

There is nothing inherent in the EA remedial strategy concept that will harm aquifer conditions. However, the use of certain remediation technologies (i.e., enhancements) as part of the EA remedial strategy may raise concerns about aquifer effects. This typically includes use of in situ technologies that rely on placement of reactive materials or substances to stimulate biodegradation. This may also include technologies that rely on hydraulic manipulation, which can affect groundwater geochemistry by increasing or decreasing recharge or by inducing flow to or from adjacent aquifers. Furthermore, using multiple or sequenced enhancements can pose similar concerns. Geochemical changes, including the potential formation or liberation of harmful compounds, should be fully assessed as part of the EA remediation proposal. If necessary, pilot and/or field testing should be done to assess potential harmful aquifer effects when new or unusual materials or methods are used. The goals should include evaluation of biogeochemical changes and their longevity and mobility in the aquifer.

Some enhancements can cause geochemical changes brought about by pH adjustments in groundwater that lead to changes in the concentration and mobility of naturally occurring metals and other chemical compounds. Other enhancements, particularly those used to enhance aerobic/anaerobic biological activity or to directly manipulate redox conditions, can affect the prevalence and/or mobility of nitrate and sulfate compounds and/or metals such as iron, manganese, chromium, copper, and arsenic. Furthermore, in biological treatment remedies, it is these changes in nitrate, sulfate, iron, or manganese compounds that provide a line of evidence for the breakdown process. Although these changes in groundwater geochemistry are typically buffered by natural aquifer conditions farther downgradient, this will occur to varying degrees with different enhancements and different site conditions and must be understood in the context of their impact to the entire system.

6.8 Consideration of Risk, Time, and Cost in the Selection of an EA Remedy

The effects of risk, time, and cost considerations often translate into performance objectives, criteria, or goals by which potential remedies are evaluated. Such goals typically are driven by the desire for risk reduction (to acceptable levels), achievement of cleanup standards, cost minimization, accelerated cleanup based on time/liability/public perception constraints, and/or restoration of property values. In this sense, consideration of an EA remedy is the same as any other remedial alternative, with one important difference: EA performance is based on mass balance approach, it must lead to a sustainable remedy, and contingency triggers must be part of the remedial plan. Although other remedies may include rigorous performance evaluations, they typically do not include periodic mass balance or sustainability evaluations and implement contingency plans only as a last resort. Benefits of an EA strategy are the cost and time savings gained through the use of the MNA/EA Decision Flowchart realized by the regulator and regulated community.

6.8.1 Risk Considerations

Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices (ITRC 1999) states, "Natural attenuation should not be considered as the remedy or a portion of the remedy when natural attenuation will not be protective of human health and the environment or alternative remediation technologies can more reliably and cost-effectively treat the contaminants to minimize risk." The main concern is whether the current risk to a receptor requires some additional remediation before MNA/EA can be implemented or whether the risk precludes consideration of such a remedy altogether. If a plume is impacting a receptor such as a surface water body or a drinking water well or causing unacceptable indoor air impacts, then an EA remedy may not be appropriate until other risk mitigation approaches are completed. Even then, EA may not be acceptable due to public/community pressure or perception or the existence of unacceptable residual risk throughout the plume. The goal is to determine the current risk to receptors and evaluate whether any unacceptable risk can be mitigated such that EA could be later implemented for the entire plume or a portion of the plume.

6.8.2 Time Considerations

For an EA remedy to be successful, the time frame for remediation must be acceptable to the regulatory agencies involved. This time frame may be shorter or longer than originally anticipated. Furthermore, when determining acceptable remediation time frames, consideration must be given to input from other key parties:

- responsible party(s)
- resource agencies
- local governments
- impacted community/public
- environmental groups/advocates

Meeting acceptable remediation time frames may require consideration of other risk-reduction strategies either preceding or in tandem with the MNA/EA remedy. Furthermore, it may require establishing interim remediation goals to measure remedy performance.

Many states allow for a reasonable time frame for cleanup to reach remedial goals, as long as current risks to human health and the environment are considered acceptable. However, what is considered a "reasonable" time frame to reach end goals is subjective. The responsible party may favor a longer time frame to minimize current costs, whereas the private landowner whose nearby well or property value is threatened may favor a shorter time frame. Other parties that may have opinions on this issue typically include state/federal regulators, resource agencies, local governments, environmental commissions, environmental advocates, and concerned community members. The key is to involve the concerned parties in remedial discussions at an early stage. To do this, it is important to communicate the reality of how long remedial methods are likely to take before contaminant concentrations reach acceptable levels. Once the parties involved understand the realistic time frames, a more productive discussion can occur.

6.8.3 Cost Considerations

The interplay among remediation time frame, reliability, achieving regulatory standards, performance goals, and cost-effectiveness must be considered when comparing an EA remedy to other alternatives. Many states have specific requirements aimed at balancing these factors. The desire for faster cleanup, even at greater cost, may be driven by the need to mitigate unacceptable risks or by community/political involvement. In some cases, an EA alternative may result in faster cleanup at a lower lifetime cost. Specific regulatory requirements and site-specific drivers regarding remediation time frame, reliability, and cost-effectiveness should be thoroughly reviewed and discussed with the regulatory agency. The key questions to address include the following:

- Is an alternative remedy (or combination of remedies) faster, more reliable, or more cost-effective?
- Is faster or more reliable cleanup warranted even if it costs more (i.e., due to unacceptable risks, community/political pressure, liability concerns, etc.)?
- Can enhancements be used to cost-effectively reduce the remediation time frame?

6.9 Contingency Planning

Like MNA, EA remedies should have contingency plans since the remedy relies on the long-term balance between mass loading and the subsurface attenuation capacity. A contingency action should be initiated in the event that the EA remedy fails to meet the site-specific compliance criteria or interim milestones set for the project. A contingency plan should be available in the event MNA and/or EA fails to achieve necessary cleanup goals in a prescribed amount of time. Contingency plans may range from collecting additional data to understand why attenuation goals are insufficient to modification of the selected remedy and/or selection of different remedial alternatives.

7. STAKEHOLDER INPUT

> In general, the concept of enhanced attenuation, as a part of the overall cleanup strategy of chlorinated organics, was favorably received by stakeholders.

Site managers/responsible parties are required by regulators to clean up contaminated sites through a process that seeks to balance timeliness, cost, and effectiveness. However, unless stakeholders (anyone affected by the contaminated site) are included in this process, vital concerns might not be considered in this process. In most cases, the extent of stakeholder involvement depends on the potential of adverse impact of the planned remediation activities. To have a clear understanding of community interests, early stakeholder involvement and a clear process to develop trust and ensure responsiveness to concerns, are key to the remediation process. Some common concerns are highlighted below.

Will the enhancement do harm to the environment or people? Various enhancement methods may have the potential benefit of cleaning up a contaminated site more quickly and, therefore, be regarded favorably by tribes and stakeholders. However, since some enhancement methods may involve the introduction of chemicals or biological species into the environment, tribes and stakeholders will have the obvious question, "Will it do any harm?" This question must be answered carefully and honestly.

Will an innovative technology be accepted by the stakeholders? In some instances, one can cite examples where the technology has been tried before and report on its success or failure in each situation. In many cases, the technology may have been used on the source zone. In the case of an evolving technology, one may be proposing a solution that is believed to be likely to work but has not been tried previously in a parallel situation. In this situation, accurate and honest information should be given. Explain all the reasons why the technology is likely to work. Give the details of the possible failure scenarios and the consequences of these failures. Have public discussion about the alternatives. The affected tribes and stakeholders must be given the opportunity to weigh the potential risks against the potential benefits since they are often the ones most directly affected by the contamination and by the success or failure of the cleanup technology.

It is important to integrate tribes and stakeholders into decision process for remedial action. In 1997, the Tribal and Stakeholder Working Group, working with DOE, developed a set of principles for the integration of tribes and stakeholders into the process of evaluating and developing new technologies for the treatment of mixed low-level waste. Many of these same principles are applicable for enhanced attenuation technologies for the cleanup of chlorinated organics:

- Minimize effluents.
- Minimize effects on human health and the environment.
- Minimize waste generation.
- Address social, cultural, and spiritual considerations.
- Provide accurate, complete, and understandable information in a time frame that allows stakeholders to have an impact on the remedy selection process.

- Incorporate tribal and stakeholder involvement into the responsible parties' procurement process, the permitting process, and the contractor's performance evaluation.

7.1 General Stakeholder Concerns with Contaminated Sites

First, stakeholders are concerned about the contamination itself and its possible effect on their health and safety. Secondly, they are concerned about the impact of the contamination on the environment and their economic well-being (i.e., impact on land value and business opportunities). To this end, stakeholders want the contamination cleaned up as quickly and as completely as possible. When apprised of possible cleanup solutions, stakeholders want to know whether the proposed solution will get the job done and whether it might result in additional problems (e.g., health risk, environmental impact, economic consequences).

7.2 Specific Concerns with Sites Contaminated with Chlorinated Organics

Plumes from chlorinated organic contamination can spread for long distances to populated areas, increasing the likelihood of an adverse impact on the public. These plumes can connect with drinking water supplies such as wells. In addition, the plumes can flow under occupied spaces such as residences, schools, shopping areas, hospitals, etc. Vapor from the plumes can rise through the soil below these buildings and enter the occupied spaces. People then are exposed to these known carcinogens. Two ITRC documents (ITRC 2007c, d) inform state regulators, site owners, and their contractors the proper method to characterize and mitigate vapor intrusion sites.

7.3 Summary of Actions Taken to Inform Stakeholders about Enhanced Attenuation of Chlorinated Organics

In late 2003 a DOE-sponsored technical working group of federal officials, DOE contractors, and consultants held meetings with operating contractor personnel and stakeholder and tribal representatives associated with the Hanford, Savannah River, and Oak Ridge sites. The meetings focused on providing a summary of the planned activities of the working group on enhanced attenuation and monitored natural attenuation of chlorinated organics.

In 2005, ITRC's EACO Team surveyed regulators from state environmental remediation programs to evaluate factors involved in decisions on the acceptability of MNA and determine interest in new concepts (i.e., enhanced attenuation) to facilitate transition from initial treatment methods to MNA. The survey is described in Section 2.1 and Appendix B.

A decision framework document was developed by the EACO Team that would provide a flowchart to assist decision makers in evaluating the various factors that should be considered before using MNA and EA at sites with chlorinated organic plumes. This document was posted on the EACO Team page of the ITRC Web site and is described in Chapter 3.

Individual stakeholders who attended the follow-up meetings provided by the DOE TWG at the Savannah River, Oak Ridge, and Hanford sites were contacted and provided with a copy of a fact sheet and the decision framework document described above. The fact sheet described the use of EA as part of the remediation process for chlorinated organics. These stakeholders were either members of the local citizen advisory board for the specific site or, in the case of the Hanford site, members of affected Native American tribes.

7.4 Summary of Stakeholder Feedback Concerning Enhanced Attenuation of Chlorinated Organics

The work of the DOE TWG provided an excellent opportunity to convey the concepts of EA to concerned citizens, especially those living near sites. Initial meetings were held to outline planned activities of the team; follow-up meetings were held to summarize the results of the team's activities.

7.4.1 Feedback from Meetings Held in 2003 with the DOE TWG

As a result of this initial series of meetings, several common suggestions were provided by stakeholders present:

- MNA/EA should be coupled with source remediation.
- The linkage of EA with MNA and the high-energy or active remedial options needs to be explained in a clear manner.
- Cost and time need to be considered in evaluating MNA/EA. There is concern that, over the long-term, the monitoring of MNA/EA may be cost-prohibitive.
- EA needs to be well defined.
- EA needs to be sustainable.
- Open communication will be vital to obtain acceptance for using bio-augmentation as an EA option.
- EA should be clearly defined as a response to language in the EPA (MNA) protocol stating that MNA involves "no human intervention."

7.4.2 Feedback from Follow-Up Meetings Held in 2007 by the DOE TWG

After completing the scheduled activities of the DOE TWG, follow-up meetings were again held with site and stakeholder representatives representing the Oak Ridge, Savannah River, and Hanford DOE sites. The issues and concerns from these meetings are as follows:

- There was concern about moving forward on remediation without a clear understanding of site characterization.
- With focus on cleanup of individual contaminated sites, the impact on groundwater of converging plumes from separate sites might not receive adequate attention.
- The standard for remediation of groundwater should be to the highest beneficial use. Drinking water standards for a human receptor at the edge of the plume may not be good enough if fauna closer to the source are impacted by the contamination.
- The entire ecosystem must be considered when addressing questions of risk and performance.
- The assumptions that were made prior to entering the decision flowchart need to be identified.

7.5 Conclusions

In general, the EA concept of as a part of the overall cleanup strategy of chlorinated organics was favorably received by stakeholders. The decision flowchart was especially well received. One stakeholder representative thought she could use the flowchart in monitoring the decision process for remediation of other contaminated sites.

8. CHALLENGES AND SOLUTIONS

This chapter addresses a number of issues, concerns, or perceptions. Based on their experience in the environmental field, the EACO Team offers responses below in the form of solutions to each challenge.

Challenge 1: The detailed requirements of some prescriptive regulations or regulatory programs may conflict with the necessary performance or implementation of an EA technology.
Solution: While EA is a new remediation paradigm, its concepts are not new and the EA decision process does not generally conflict with the established regulatory framework, laws, regulations, or practices. In some cases where existing regulations are detailed and proscriptive (such as RCRA capping rules), reasonable regulatory flexibility should facilitate implementing a technology as part of EA.

Challenge 2: Mass flux is difficult to estimate using current technology approaches, and there are uncertainties in relating mass flux to regulatory goals. There will be a near-term bias to continue to monitor performance based only on contaminant concentration.
Solution: The EACO Team agrees that the actual use of mass flux measurements is still in the early stages, and there are certainly uncertainties. As previously mentioned, ITRC's BioDNAPL Team will be researching the topic of mass flux in 2008. That said, the EACO Team believes that the future use of mass flux will provide a greater understanding of actual plume conditions and therefore improved remedial alternative evaluations. At this time, when used in combination, concentration data and mass flux provide a scientific approach to support decision making and transitioning between technologies and to ensure that compliance is maintained and measured via a concentration standard. There is a large portfolio of currently active research related to the measurement and interpretation of mass flux that will help implement a combination strategy in the future.

Challenge 3: There is a perception that characterization for EA increases costs because of the additional understanding of the subsurface ecology required to engineer appropriate EA technology(s). In addition, there is a tendency, during remediation of the site, to shift funding toward the remedial action and accept a less thorough subsurface ecology assessment.
Solution: Regardless of the chosen remedy, the evaluation of a site contaminated with chlorinated organics typically requires a more thorough characterization because of the unique qualities of chlorinated organics being denser than water and general recalcitrance to degradation. In addition, the characterization required for the determination of an EA remedy is similar to the characterization requirements to evaluate MNA as a remedial alternative.

Challenge 4: EA does not particularly resolve issues such as heterogeneity, co-contaminants, unknown sources, etc., and rather than directly address them, it seems to introduce a particularly open-ended iterative approach.
Solution: While the EA framework faces all of the complexities of any remediation, it provides opportunities for reevaluation and characterization expansion in a structured manner. This is its strength. Rather than proceed on a predetermined pathway despite discovered complications, EA provides opportunities to reevaluate and optimize the site management strategy. This is by no means meant to become a continual loop. Rather, the reiterative nature simply anticipates the occasional remediation failure and provides a direction to be pursued when that failure is recognized.

Challenge 5: Traditional monitoring strategies may or may not be appropriate for EA.
Solution: As part of the implementation of EA, alternative monitoring strategies may be appropriate. Given the amount and type of data typically needed to justify implementation of an EA technology, alternative monitoring strategies may be warranted, which are directed to address the particular "No" responses in the decision flowchart that resulted in the site's being remediated under EA instead of MNA. For example, if PCBs are present in soil at levels exceeding regulatory levels for direct exposure (i.e., MNA is not appropriate given risk concerns associated with direct exposure), an appropriate EA technology may include placement of an impermeable surface atop the contaminated soil to prevent direct exposure. Assuming the appropriate assessment data have been collected and fate and transport conditions are appropriate, an alternative monitoring strategy could be periodic inspection of the impermeable surface in lieu of additional media sampling.

Challenge 6: Remediation technologies fall on a continuum, ranging from very aggressive source destruction and removal methods to less energy-intensive methods, such as phytoremediation. In many cases, it may be difficult to classify a technology as EA.
Solution: It is not productive to focus efforts on the categorization of technology. A more productive focus considers the site-specific information controlling the selection of the appropriate technology. In some cases these technologies could be best applied as a traditional high-energy treatment, and in other cases these might best applied as an EA. A collaborative determination by the regulators and regulated community can identify the best approach.

Challenge 7: There are numerous old, unlined landfills with underlying groundwater plumes that include chlorinated organics. The flux of organic-rich leachate to underlying aquifers can create favorable conditions for the natural attenuation of chlorinated organics below these landfills. Solid waste regulations typically separate the landfill and groundwater plume into different operating units and require independent remedial solutions for these units. How could the MNA/EA Decision Flowchart be applied in this situation?
Solution: As with other types of sites, remediation of any source area (including landfills) can have adverse and/or positive contributions to attenuation processes in the downgradient plume. In some cases where existing regulations are detailed and proscriptive (such as RCRA capping rules), reasonable regulatory flexibility should facilitate implementing a technology as part of an EA.

Challenge 8: Regulators and end users may be reluctant to use the EA concept because it is new and unfamiliar.
Solution: This attitude is common with all new and innovative technologies and processes. The EA concept complies with existing environmental regulations. As potential users consider the possible benefits of using EA over existing processes (see Chapter 1), they will likely become more comfortable with considering it as an alternative.

Challenge 9: Can aggressive treatment result in sustainable EA or MNA?
Solution: Some aggressive remedial strategies in DNAPL source areas, specifically in situ bioremediation, result in a downgradient zone of enhanced biological attenuation of the contaminant. One of the by-products of the implementation of in situ bioremediation (e.g., anaerobic reductive dechlorination) is methane, which can be transported to downgradient regions of the dissolved-phase plume. The excessive availability of methane provides a primary substrate to enhance the aerobic co-metabolic degradation of the contaminant. In this case, EA is an indirect result of aggressive source area treatment as opposed to a direct addition of enhancements for EA.

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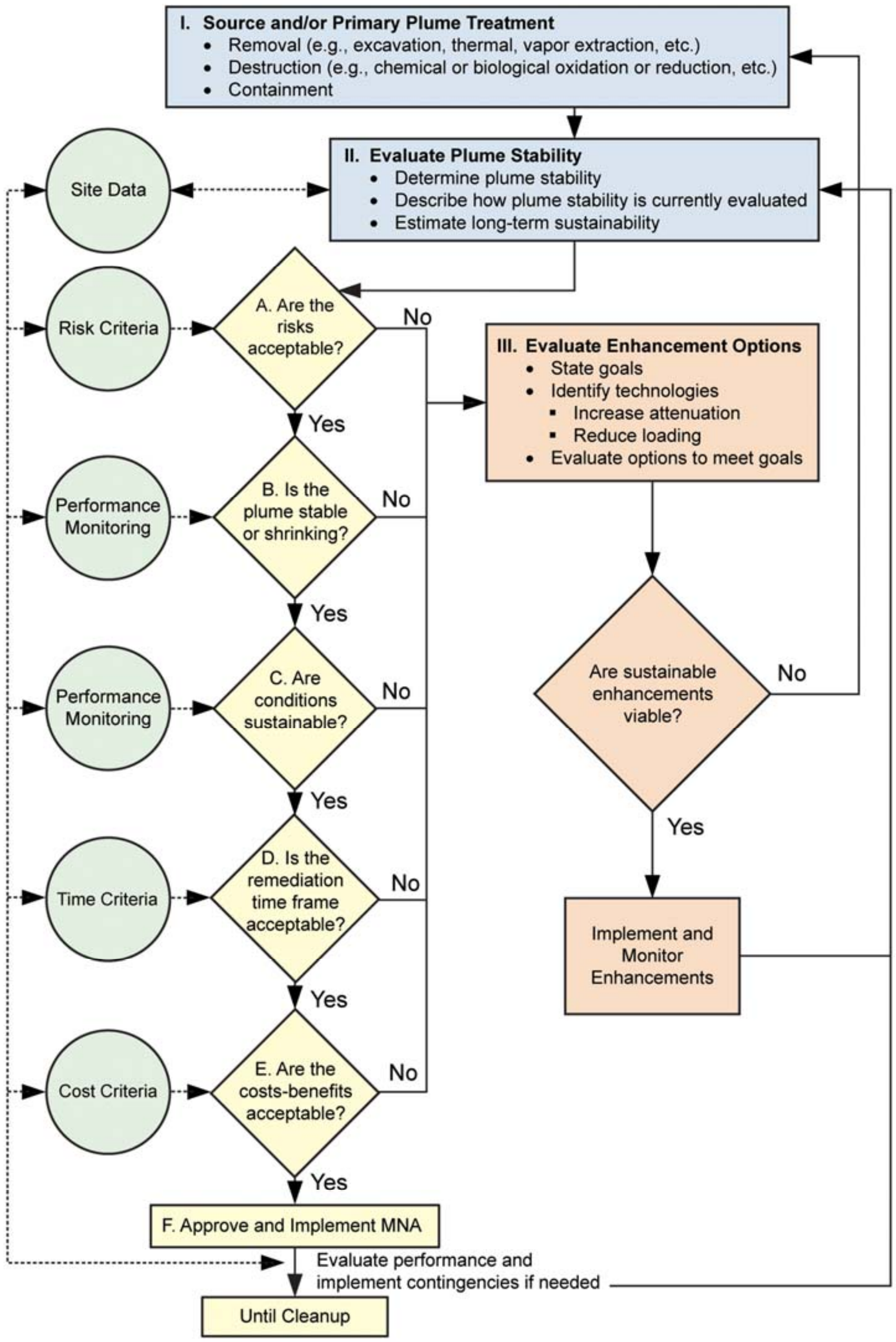
Appendix A

Enhanced Attenuation Decision Flowchart

Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation—Chlorinated Organics



Decision flowchart for the use of monitored natural attenuation (MNA) and enhanced attenuation for chlorinated organic plumes.

Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation—Chlorinated Organics

I. Source and/or Primary Treatment

Many chlorinated organic contaminated sites will require the use of several technologies that combine aggressive and passive technologies to reach cleanup goals.

- Develop a decision process that provides knowledge of when to stop operation of the active remedy in the source zone and transition into other appropriate EA/MNA remedies.
- Provide an evaluation of collateral effects of the technology on the aquifer. Subsurface ecology assessment recognizes the interrelatedness of the living and geochemical components of the subsurface environment.

II. Evaluate Plume Stability

Plume stability indicates that the plume is no longer expanding in size, nor is its footprint moving. "Plume stability occurs when the perimeter of the plume attains sufficient size or location such that attenuative mechanisms equal or exceed the mass flux at that boundary."

- Evaluation of long-term plume stability/reduction can start with the mass balance evaluation on attenuation mechanisms vs. mass loading.
- Key factors: organic substrate, groundwater flow/replenishment, sequence of electron acceptors, geochemistry

A **Risks acceptable?** Current risk to a receptor requires some additional remediation before MNA can be implemented.

B **Plume stable/or shrinking?** Yes/No response based on the actual evaluation.

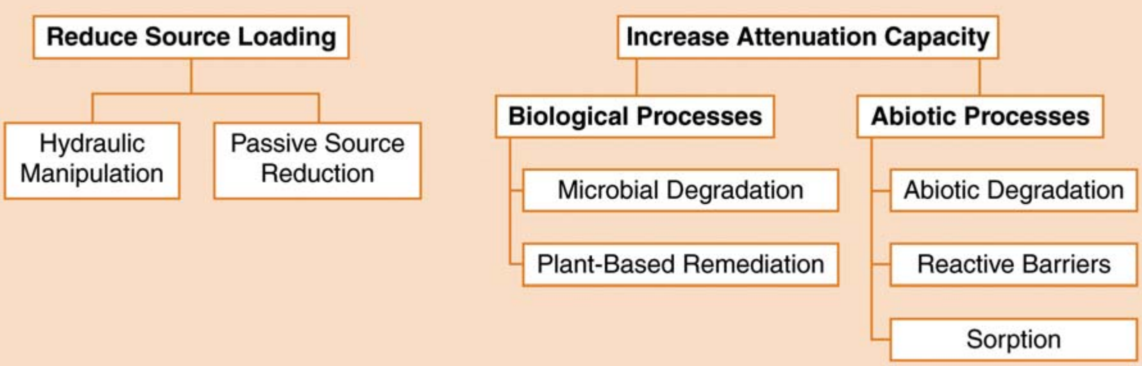
C **Conditions sustainable?** Yes/No response based on the actual evaluation of site conditions.

D **Remediation time frame acceptable?** May be driven by public/community concerns.

E **Cost benefits acceptable?** Desire for faster cleanup, even at a greater cost, may be driven by the need to mitigate.

F **Approve and Implement MNA.** Evaluate performance.

III. Evaluate Enhancement Options—Classes of Enhancements



Appendix B

State Regulatory Survey Report

A NATIONAL OVERVIEW OF MONITORED NATURAL ATTENUATION AND ENHANCED ATTENUATION—RESULTS OF AN INTERSTATE TECHNOLOGY REGULATORY COUNCIL SURVEY

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ABSTRACT: To facilitate an understanding of key issues related to approving monitored natural attenuation (MNA) as a stand-alone remedy or as a component of a larger remedy for a chlorinated solvent site, the Interstate Technology & Regulatory Council (ITRC) Enhanced Attenuation: Chlorinated Organics (EACO) Team conducted a survey of state regulators from state environmental remediation programs. The 2005 survey was designed to evaluate factors involved in decisions on the acceptability of MNA and to determine interest in new concepts to facilitate transition from initial treatment methods to MNA. Respondents included 38 regulators from different environmental programs in 30 states. Data were collected on the respondents' programs, number of sites they had regulated that incorporate MNA, factors contributing to approval/disapproval of MNA, and the protocols/guidance used in making those determinations. Respondents were also queried on their support of and interest in enhanced attenuation (EA) technologies. Survey results indicated that most states dealing with chlorinated solvent sites accept MNA as a viable remediation technology. Generally, state regulators use U.S. Environmental Protection Agency (EPA) protocols or similar state protocols when evaluating MNA proposals. Models are frequently used and considered to be useful, and simple models appear to be more accepted than more complex models. The response was generally positive to the use of EA as a transitional remedial approach and the use of mass balance and flux measurements as tools to scientifically evaluate these alternative remedial approaches.

INTRODUCTION

Although regulators have generally accepted MNA as a viable remediation technology for highly degradable petroleum contamination, the national use and acceptance of MNA for chlorinated solvents is less clear. As in the case with any remedy acceptance, regulatory approval is necessary for MNA to be implemented. The acceptability of MNA by state regulators is typically based on (1) their experience with chlorinated solvent sites, (2) their experience with the use MNA, (3) whether the state has protocols in place for evaluating MNA proposals, and (4) their understanding of these protocols in evaluating the effectiveness of MNA at a particular site.

To obtain a better understanding of the overall experience and acceptance that state regulators have with MNA at sites where chlorinated solvents are impacting groundwater, the EACO Team surveyed state regulators. The survey was constructed to obtain a general idea of regulatory acceptability of MNA for chlorinated solvent sites. Its objective was to secure responses from regulators representing a broad spectrum of regulatory programs that deal with chlorinated solvent sites by querying the regulators on how many chlorinated solvent sites their programs oversee along with the number of MNA proposals submitted and approved for these sites. The survey was also designed to determine which protocols are currently being used by state regulators for the evaluation of MNA proposals, whether models are accepted, and if so, the usefulness and types of models used. The final section of the survey asked about different types of innovative technologies classified as EA technologies and the potential acceptability of these technologies by the regulators.

SURVEY STRUCTURE

The survey comprised 122 questions, either multiple choice or text answers. Questions were categorized by topic and divided into five sections. The first section determined which states and regulatory programs were responding to the survey. The second section aimed to better understand which programs within the state regulatory agencies are accepting MNA as part of a larger remedy or as a sole remedy for chlorinated solvent plumes. The third survey section asked about the tools and policies state regulators are using to evaluate the acceptability of MNA for chlorinated solvent plumes. The fourth section focused on the importance of data and modeling tools. The last section introduced the concepts of mass balance and EA, provided a list of different remedial technologies classified as EA, gauged the general level of support for these concepts, and asked which of these technologies regulators would support as part of a remedial action.

DATA-COLLECTION METHODS

A Web-based survey was published on the ITRC Web site May to September 2005. Requests to complete the survey were submitted to 44 ITRC state point-of-contacts (POCs, i.e., liaisons between state regulatory agencies and ITRC) across the United States. The POCs were asked to have representatives within their regulatory agencies that dealt with the remediation of chlorinated solvent plumes respond to the survey. Respondents were asked to complete the online survey and were told that it would take approximately one hour to complete. All survey responses were compiled in an online database. Not all respondents answered all questions.

EVALUATION OF SURVEY RESULTS

Respondent Demographics and Regulatory Program Jurisdictions. Members of the ITRC EACO Team evaluated the survey results. Thirty-nine responses were received from regulators from 31 different states, as shown in Figure 1. One response and the corresponding state was discounted since the respondent represented a program associated with no chlorinated solvent sites. Of the 38 remaining respondents, 32 worked in programs with statewide jurisdiction, one had jurisdiction over a region within a state, and two performed regulatory oversight of specific U.S. Department of Energy facilities in their states.

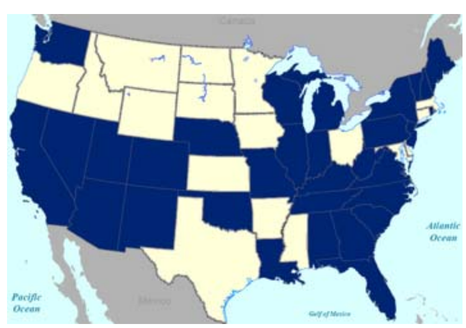


FIGURE 1. States represented in survey response (darkened).

(Four did not respond to this question.) The respondents represented multiple programs within their states, including Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Resource Conservation and Recovery Act (RCRA) programs, dry cleaner, brownfield and voluntary cleanup programs, and other state and federal programs. Figure 2 depicts the number of programs represented.

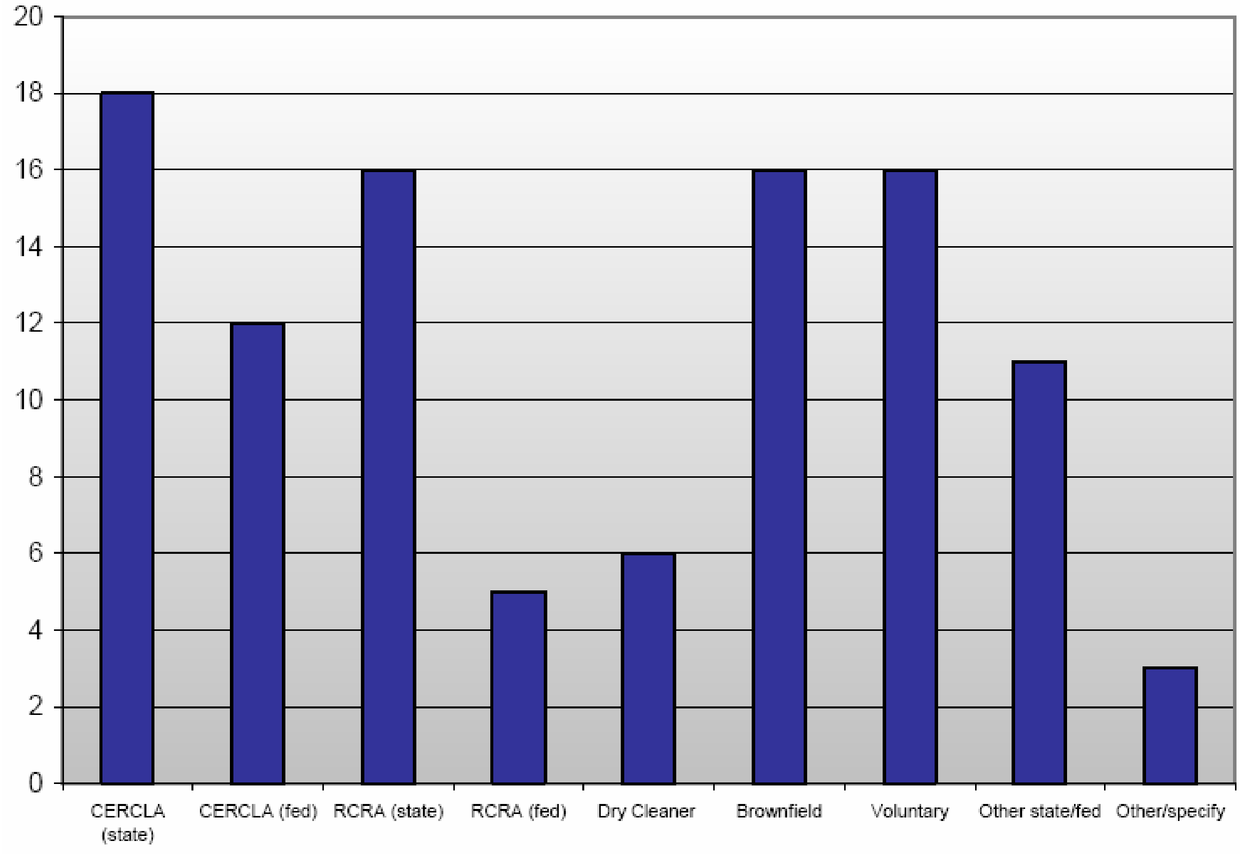


FIGURE 2. Breakdown of regulatory programs represented in the survey.

General Experience with MNA within Each Program Jurisdiction. This section of the survey elicited information related to both experience with and approval/disapproval of MNA for chlorinated solvent plumes. Due to the design of the survey, all programs represented should have had some experience with chlorinated solvent groundwater contamination. Fifteen respondents indicated that their programs had 1–50 chlorinated sites within the programs, 16 indicated that their programs dealt with 51–200 sites, and five respondents replied that their programs had more than 200 sites where chlorinated solvents were present.

Of the 38 respondents, five indicated that the programs they represented have not approved MNA for chlorinated solvent sites. Of these, two indicated that MNA was not a currently accepted remedial technology within their programs, and the other three noted rationales comparable to the responses from the other respondents as reasons for not approving MNA. It is important to note that three of these five respondents had not received any MNA proposals and that the other two had received fewer than five such proposals.

Of the 33 respondents that indicated MNA had been approved for at least one site within their programs, seven respondents had received fewer than five MNA proposals, the majority (16) had received 5–24 MNA proposals, two had received 25–45, and seven had received more than 45 such proposals (one respondent did not answer this question). Evaluation of this data indicates that an increasing approval rate for MNA proposals has a strong correlation with the number of MNA proposals received by a regulatory program. It is interesting to note that most of the MNA proposals submitted were in combination with active treatment systems and that MNA was seldom proposed along with a passive treatment technology such as a permeable reactive barrier, although we did not collect information on how many passive treatments technologies are being proposed.

Of the MNA proposals that had been approved, 15 respondents indicated that none of the sites in their programs had gone through completion. Nine of the respondents replied that fewer than 10% of the sites had gone through to completion, three indicated that 10%–60% had gone through completion, and only one indicated that more than 60% had been completed. This result indicates that, although a significant number of MNA remedies have been implemented, it may be premature to evaluate their success in providing a path to reach remedial goals.

MNA Protocols, Policies, or Guidelines. The EACO Team survey included a series of 12 questions that asked regulators to identify state-specific protocols, policies, or guidelines for using MNA to remediate sites with chlorinated solvent contamination in groundwater. The vast majority of respondents indicated that their states rely on either the EPA protocol for evaluating MNA at chlorinated solvent sites (EPA 1998), the EPA OSWER Directive (EPA 1999), or state protocols, policies, or guidelines that are based primarily on the EPA protocol or OSWER Directive. A majority of the respondents also indicated that site-specific calculations are very important to the approval of MNA at chlorinated solvent sites. Of the 30 states covered in the EACO survey, 15 were reported to have state-specific MNA protocols, policies, or guidelines. In most of these states, MNA policies are generally based on the use of MNA at petroleum hydrocarbon sites, although some states are developing specific documents relating to the use of MNA at chlorinated solvent sites.

Issues Affecting the Approval of MNA. MNA is being approved by regulators and used as a groundwater remedy on a regular basis through out the United States. However, five of the 38 respondents indicated that MNA has not been approved for chlorinated sites within their programs; two of these indicated that MNA is still incompatible with current state policies. Other reasons MNA approvals had not been granted, according to these five respondents, were that sites were being effectively treated by other means or that there was still a lack of confidence in the MNA process. Respondents who indicated that an MNA proposal had been approved within their program were asked a series of questions about the factors important in evaluating a proposal. According to the responses, significant reasons for not approving MNA were (1) the groundwater plume was impacting a receptor, such as a drinking water well; (2) the plume was determined to be expanding; (3) the contaminated sites were already being effectively treated using other methods; (4) site-specific conditions were not favorable; (5) the proposal was incomplete or of poor quality; and (6) the MNA proposal did not contain an appropriate timeframe to reach regulatory goals.

Use and Importance of Data and Modeling Tools in MNA Decision Making. Characterization and monitoring are key components in determining whether natural attenuation processes are contributing to the remediation of a contaminant plume. EPA's technical protocol for evaluating natural attenuation of chlorinated solvents in groundwater (EPA 1998) provides guidance based on the three lines of evidence for characterizing sites: (1) groundwater and/or soil chemistry data that demonstrate clear and meaningful decreasing concentration trends over time, (2) hydrogeologic and geochemical data that can be used to indirectly demonstrate natural attenuation processes active at the site along with reduction rates, and (3) data from field microcosm studies. The survey asked respondents to qualify the relative usefulness of collecting characterization data in accordance with these different lines of evidence in evaluating the approval of an MNA remedy. The results, as shown in Figure 3, indicated that parameters identified as the first line of evidence by EPA are considered the most useful collected data. The collection and usefulness of the second and third line of evidence data is more variable.

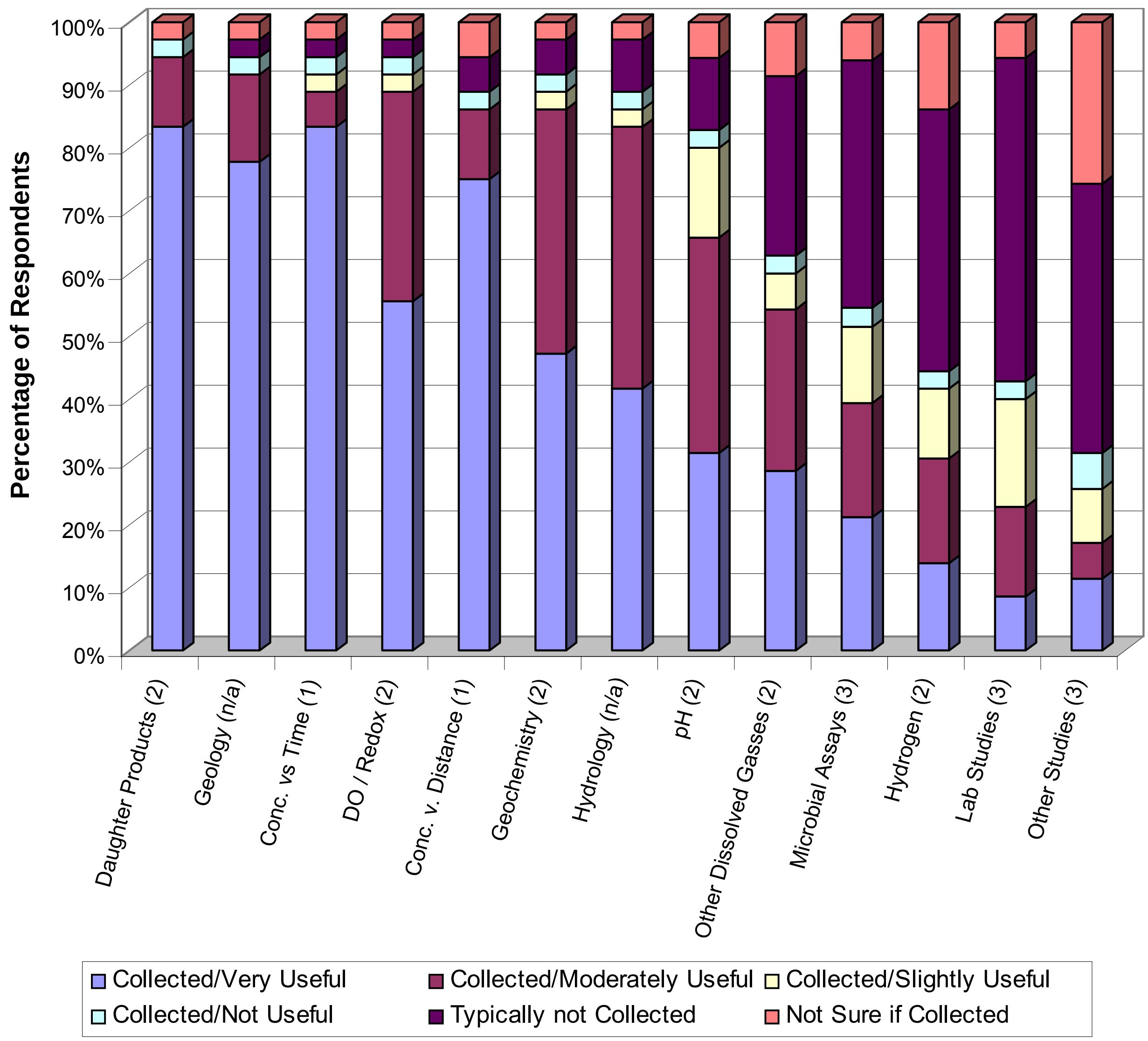


FIGURE 3. Use and importance of data collected for MNA decision making.

Interestingly, only 44% of the respondents characterized geochemical measurements as being very useful when evaluating the efficacy of MNA for chlorinated solvent sites. This is a surprisingly low portion, given the importance of this information in evaluating natural attenuation of chlorinated solvents. Also surprising was the relatively low number of respondents who characterized hydrology (e.g., pumping tests and slug tests) as being very useful, given the importance of groundwater velocity and travel time to the determination of risk to downgradient receptors. It should be noted that all categories of data were identified by at least one respondent as useful.

One possible interpretation of this information is that, for sites where reductive dechlorination is not the predominant attenuation mechanism, it is recognized that other types of data must be collected to evaluate the potential of MNA as a remedy. For example, pH is an important parameter to measure to determine whether hydrolysis of carbon tetrachloride is an attenuation mechanism, as the pH of the groundwater is a controlling factor. Another possible interpretation of this same information, in conjunction with the variability in use of data from the second and third lines of evidence data types, is the lack of user knowledge related to interpreting this data for making decisions on the robustness of various attenuation mechanisms.

Upon collecting and analyzing site-specific data for MNA remedies, models can be generated as part of the evaluation process. These models range from a simple conceptual model to a complex numerical model with degradation reactions. The survey asked, "How often are different model types used and how important are they in supporting the decision to implement MNA as a remedy?" Forty-two percent of the respondents indicated that models are used often, 24% found them to be very useful, and half (50%) believe models are moderately useful. Respondents were asked to evaluate both use and importance of approximately a half-dozen model types. The results, presented in Figure 4, indicate that simpler conceptual models tended to be used more and were of greater importance in supporting decision-making than were analytical or numerical transport models such as BIOCHLOR or RT3D. However, the results indicated that all methods are used and deemed as having importance. One possible interpretation is that regulators perceive models used in decision making that are based on observed data such as chemical concentrations as having more credibility than models based on estimated input parameters (e.g. groundwater velocity, biodegradation rates, dispersion, retardation, etc.).

Interest in Future Research and Policy Development Related to MNA and EA. Research teams continue to develop new tools and processes to improve technical abilities to address characterization and monitoring, as well as remediation, of chlorinated solvent–contaminated sites. From a purely technical perspective, these new developments are viable; however, there may be regulatory and/or nontechnical roadblocks to implementing these new tools and processes. Several questions were asked of the respondents to identify technical concepts related to MNA and EA where development efforts would be supported. Supported areas are as follows:

1. mass balance evaluation for the purposes of
    - evaluating contaminant mass loading versus the system's natural attenuation capacity
    - facilitating selection of source treatment type and duration
    - determining when to terminate active treatment and transition to MNA or EA

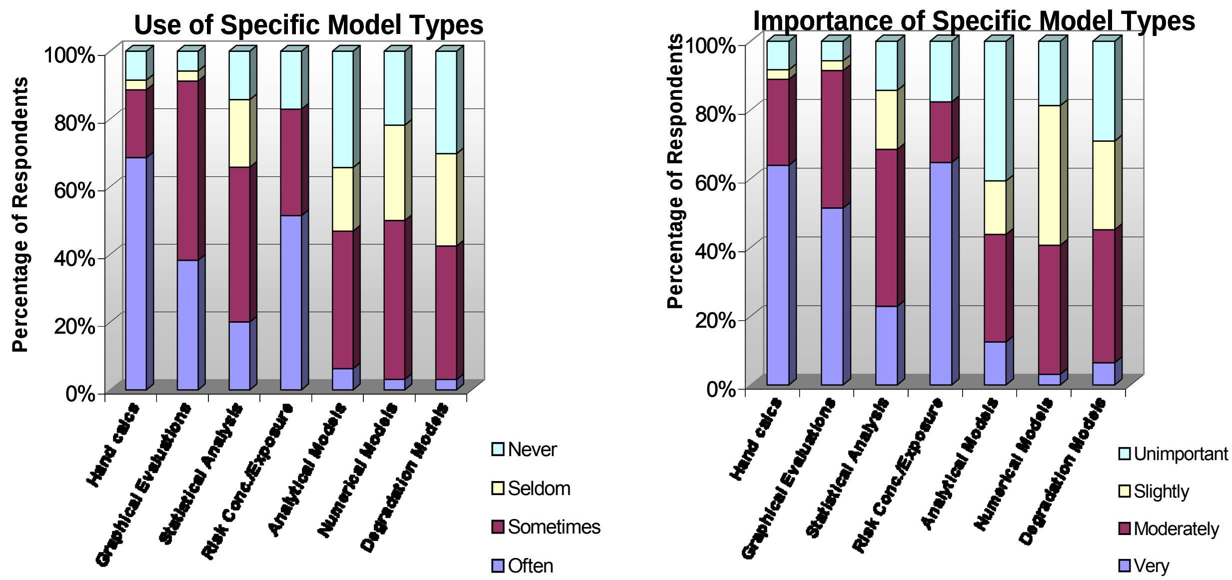
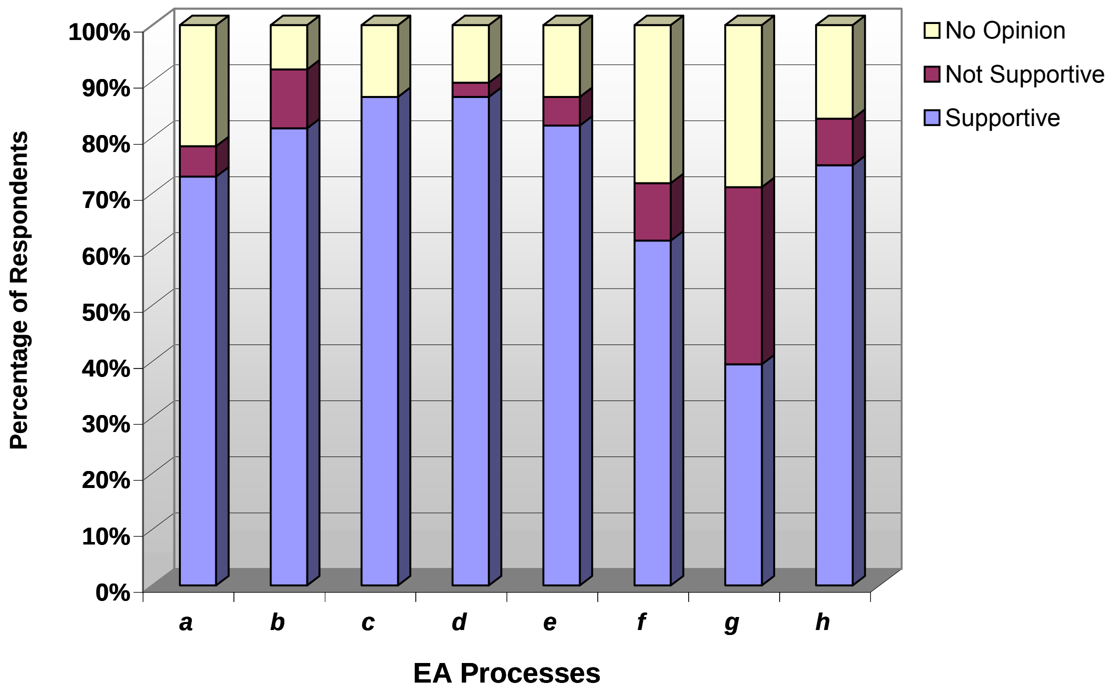


FIGURE 4. The extent to which specific model types are used and their relative importance in the decision-making process to implement MNA.

2. developing EA, a transitioning strategy between the initial remedy and MNA that will provide a mechanism for meeting remediation goals in an acceptable timeframe
3. developing protocols that separate characterization into two stages, with a separate early screening characterization phase
4. developing protocols that separate monitoring into two stages, with a separate long-term monitoring phase

Mass Balance—Contaminant levels have traditionally been measured as concentration, mass/volume. In addition, cleanup goals are typically defined as concentrations. One approach to calculating a mass balance is to evaluate the loading and attenuation capacity in terms of flux, mass/time. Respondents were asked to identify their level of support for the use of flux measurements. Approximately two-thirds of the respondents supported the idea of using both flux and concentration measurements. Interestingly, approximately one-third of the respondents supported the idea of measuring flux instead of concentration.

Enhanced Attenuation—EA is a new strategy that provides a transition between initial remedies and MNA. EA encourages the use of “active” treatments designed to produce sustainable attenuation processes while minimizing the duration of the active component of the remedy. Respondents were asked to identify their level of support for enhancing different processes in either the source, plume or discharge areas of a plume. As shown in Figure 5, the regulators were supportive of enhancements to the majority of the processes. The greatest level of support was for enhancements to the source and plume areas (Figure 5, from left, the first five enhancements on the horizontal axis). Interestingly, one-third of the respondents supported the idea of volatilization of chlorinated solvents from wetlands or surface water. One possible interpretation of this result would be that, while not widely accepted, the inclusion of volatilization as an attenuation process in the remediation of a chlorinated solvent–contaminated site will be on a case-by-case basis.



NOTE: (a) Reduce contaminant release rate from source using long-lived sustainable removal treatments
(b) Physical modifications to source and/or plume area to reduce water flow
(c) Biostimulation in the plume area
(d) Bioaugmentation in the plume area
(e) Permeable reactive barrier in the plume area
(f) Degradation in expanded/constructed wetlands
(g) Volatilization from wetlands or surface water
(h) Phytoremediation in the plume discharge zone

FIGURE 5. Level of support for enhanced attenuation processes that address source, plume, and distal plume areas.

CONCLUSIONS

Several significant points can be concluded from this survey. Protocols generally used by regulatory programs in most states for the evaluation of MNA at chlorinated solvent sites are either the EPA protocols or policies based on those protocols, along with site-specific calculations. The more experience a state program has with chlorinated solvent sites and MNA proposals, the more amenable it is to accepting this technology as a viable remedial alternative. The major reasons for a program's rejecting an MNA proposal were either because either a receptor was impacted or a plume was expanding.

Based on the responses received with regard to the use and usefulness of models, it seems that the regulatory community in general accepts simple conceptual models but is less accepting of the use of analytical or numerical transport models. Though EA is a new concept, the survey respondents were receptive to the development of this concept. Those technologies that support EA in the source and plume areas were most supported; technologies that support EA in plume discharge areas were less supported. This result may tie with the finding that one reason to not approve MNA is impact to receptors. Finally, there appears to be wide support for including flux measurements and a mass balance approach with the more traditional evaluation methodologies.

In general, regulators support the implementation of MNA at chlorinated solvent sites, depending on site-specific information: risk impacts, source zone remediation, etc. However, the success of MNA as a remedial action is undecided, as the majority of sites where it has been implemented have not reached their remedial goals.

ACKNOWLEDGEMENTS

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Appendix C

Mathematical Tools to Calculate Mass Balance

MATHEMATICAL TOOLS TO CALCULATE MASS BALANCE AND SUPPORT NATURAL AND ENHANCED ATTENUATION

(This material is excerpted from Early et al. 2006. References are to those listed in that report.)

Various tools and computer models have been developed, or are in development, to assess mass balance at chlorinated solvent sites. The conceptual basis is the same: a certain mass of contaminant (such as TCE) is “released” to groundwater and a series of mathematical relationships are applied that show what happens to this contaminant mass. Some of the tools are relatively simple, with easy-to-visualize equations entered into the cells of a computer spreadsheet. Other models are more sophisticated numerical approaches that employ a wide variety of simulation processes, and intricate graphical displays of modeling results. Although they differ in complexity, both ends of this modeling spectrum are based on the fundamental concept of mass balance.

These tools/models described above can be divided into the following categories:

- **Flux Calculation Tools.** Some software has been developed to allow the user to convert flow data and monitoring well transect data to a mass flux estimate. Mass flux is an integrated metric of plume strength and a key part of the mass balance approach. This type of software helps users determine the rate that contaminant mass is leaving a source zone or the mass flow rate at some point in the plume.

- **Box Model of Source.** These simple models assume the source is a simple box model, and make *a priori* assumptions about how the mass flux curve will diminish over time (such as an exponentially decaying source). These models are not dependent on simulating actual processes that occur in the source zone over time, but use a simple mathematical function(s) to describe how a source will decay over time. This method accounts for processes such as pool dissolution, ganglia dissolution, matrix diffusion, linear desorption, and dual-equilibrium desorption over the life of the source, but in an indirect, very simplified fashion.

- **Deterministic Source Models.** More sophisticated source models have been developed to simulate the behavior of one or more phases in the life cycle of the source. Several of these models focus on nonaqueous-phase liquid (NAPL) dissolution kinetics and transport over time. Key factors that go into these models include considering NAPL composition and employing Raoult’s Law to assess dissolution kinetics, and considering source architecture (the way that NAPL is distributed in the source zone, such as the relative fraction of NAPL in pools vs. ganglia), to assess NAPL dissolution.

- **Plume Models.** These “traditional” groundwater models simulate the fate and transport of dissolved contaminants once the contaminants have left the source zone. Typically, these plume models include processes such as advection, dispersion, linear sorption and desorption, biodegradation, and sometimes more complex processes (such as nonlinear sorption and preferential flow). The resulting mass balance equations can be solved either analytically (exact mathematical solutions subject to simplifying assumptions) or numerically (where the model domain is divided into grids or elements and solved by stepping through time—this type of model also involves simplifying assumptions but can often be applied to more complicated problems or time varying boundary conditions).

Examples of each type of tool/model are presented in Table 1. Note this table shows only representative tools and models, and many other examples of tools and models are available in the scientific literature. The ability of these tools to help the user address several key questions regarding plume stability and sustainability is summarized in Table 2.

Table 1. Representative chlorinated solvent tools and models

Example tool/model	Does model/tool include these features?			
	Calculates flux from monitoring data	**Uses simple box model of the source**	**Deterministic source model**	**Mass balance after plume leaves source**
Mass Flux Toolkit (Farhat et al. 2006)	Yes			
Farhat et al. 2004		Yes		
BIOCHLOR (Aziz et al. 2000)		Yes		Yes
BIOBALANCE (Kamath et al. 2006)		Yes	Yes*	Yes
BIOPLUME III/IV (Rafai et al. 1998, EPA 2001)				Yes
RT3D (Clement 1997, Clement et al. 1998)				Yes
Natural Attenuation Software (NAS)/SEAM3D (Widdowson et al. 2006)			Yes	Yes

* For donor/acceptor mass balance and competition processes.

Table 2. Key mass balance–related questions addressed by representative chlorinated solvent tools and models

Example tool/model	Can tool/model help user address these questions?				
	How far will plume go before it stabilizes?*	**How long will it take plume to stabilize?***	**How long will this plume persist?***	**What is balance of donors and acceptors?**	**Are attenuation processes sustainable?**
Mass Flux Toolkit	No	No	Not directly—can be used to compare mass flux against source mass estimate	Helpful to analyze relative mass flux of donors/ acceptors leaving source	Can provide supporting information
Farhat et al. 2006	No	No	Yes, with box model	No	No

Example tool/model	Can tool/model help user address these questions?				
	How far will plume go before it stabilizes?*	How long will it take plume to stabilize?*	How long will this plume persist?*	What is balance of donors and acceptors?	Are attenuation processes sustainable?
BIOCHLOR	Yes, with simple analytical model	Yes, with simple analytical model	Yes, with box model	No	No
BIOBALANCE	Yes, with simple analytical model	Yes, with simple analytical model	Yes, with box model	Yes	Yes
BIOPLUME III/IV	Yes, with numerical model	Yes, with numerical model	No	No	No
RT3D	Yes, with sophisticated numerical model	Yes, with sophisticated numerical model	No	No	No
Natural Attenuation Software (NAS)/ SEAM3D	Yes, with simple analytical model	Yes, with simple analytical model	Yes, with numerical model	Not directly	Not directly

*Also referred to as distance of stabilization (DOS), time of stabilization (TOS), and time of NAPL dissolution (TNAD) by Chapelle et al. 2003a.

Recent progress has improved the tools/models in each category. Several researchers have focused on developing better ways to measure mass flux, including new sampling tools and new software tools (such as the Mass Flux Toolkit, Farhat et al. 2006). Box model approaches have been used in groundwater models since 1996 but have recently been applied in new ways in recent software tools (such as BIOBALANCE). The BIOBALANCE software (Kamath et al. 2006) also includes new algorithms for performing a mass balance on electron acceptors/electron donors and for evaluating the effects of competing electron acceptors (such as naturally occurring dissolved oxygen or sulfate), new tools to calculate maximum plume size and timing of plume stabilization, and other features. Plume models have also become much more powerful over the past several years, both for analytical models (such as BIOCHLOR) and numerical models (RT3D). Finally, some research teams have worked on integrating source models more directly with plume models as a single software platform, allowing for a mass balance on the entire system (for example, BIOBALANCE and NAS).

Table 3. Considerations for Selecting Modeling Approach Based on Site Properties

KEY: ◎ better <-------------> ○ <-------------> ● worse

	Sites with supportive geochemical/hydrologic conditions		Sites with hydrologic &/or geochemical complexity/challenges		
Modeling Approach[1]	Simple site with stable or shrinking plume	Plume stability & geochemical footprints uncertain	Documented plume growth or outcrop -- may be stable in the future	Geochemical conditions uncertain and/or complex hydrologic conditions	Attenuation process enhancement evaluation
Conceptual Model - Identify contributing processes and the active zones within a plume	◎	○	● [3]	● [3]	● [3]
Conceptual Model plus Analytical Model or Mass Balance Calculation	○	◎	○	○	○
Conceptual Model, possible analytical model and numerical model	● [2]	○	◎	◎	◎

[1] Underlining indicates the central analysis approach for the table row.

[2] Numerical modeling is not necessarily preferred because costs may not be justifiable for the offsetting benefits in terms of uncertainty reduction, monitoring optimization, etc. However, numerical models may be selected if it is necessary to provide better estimates of time frames and better assurance of meeting certain types of remediation goals (e.g., concentration targets) than can be obtained with analytical modeling.

[3] Conceptual models are good to use for planning and site management but may not be suited as primary support for decision making at complex sites or sites that have high uncertainty because conceptual models do not allow testing of uncertainty and parameter sensitivity and do not strongly support a detailed evaluation of enhancements.

Appendix D

Enhanced Attenuation: Chlorinated Organics Team Contact List

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Appendix E

Acronyms and Symbols

ACRONYMS

AFCEE	Air Force Center for Environmental Excellence
ARAR	applicable or relevant and appropriate requirements
ASVE	active soil vapor extraction
BioDNAPL	Bioremediation of DNAPLs
BiRD	biogeochemical reductive dechlorination
BTEX	benzene, toluene, ethylbenzene, xylenes
CERCLA	Comprehensive Environmental Resource Conservation Liability Act
COC	contaminant of concern
CSM	conceptual site model
DCE	dichloroethene
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
EA	enhanced attenuation
EACO	enhanced attenuation of chlorinated organics
ECOS	Environmental Council of the States
EPA	U.S. Environmental Protection Agency
ERIS	Environmental Research Institute of the States
ISCO	in situ chemical oxidation
ITRC	Interstate Technology & Regulatory Council
MBISO	microbial benefits of in situ oxidation
MCL	maximum contaminant level
MNA	monitored natural attenuation
NAPL	nonaqueous-phase liquid
NAS	Natural Attenuation Software
NRC	National Research Council
ORP	oxidation reduction potential
PAH	polycyclic aromatic hydrocarbon
PCE	perchloroethene
PSVE	passive soil vapor extraction
RCRA	Resource Conservation and Recovery Act

SVE	soil vapor extraction
TCA	trichloroethane
TCE	trichloroethene
TOC	total organic carbon
TWG	technical working group
VC	vinyl chloride
VFA	volatile fatty acid

SYMBOLS

°C	degree Centigrade (Celsius)
°F	degree Fahrenheit
f_{oc}	fraction organic carbon
ρB	sediment bulk density