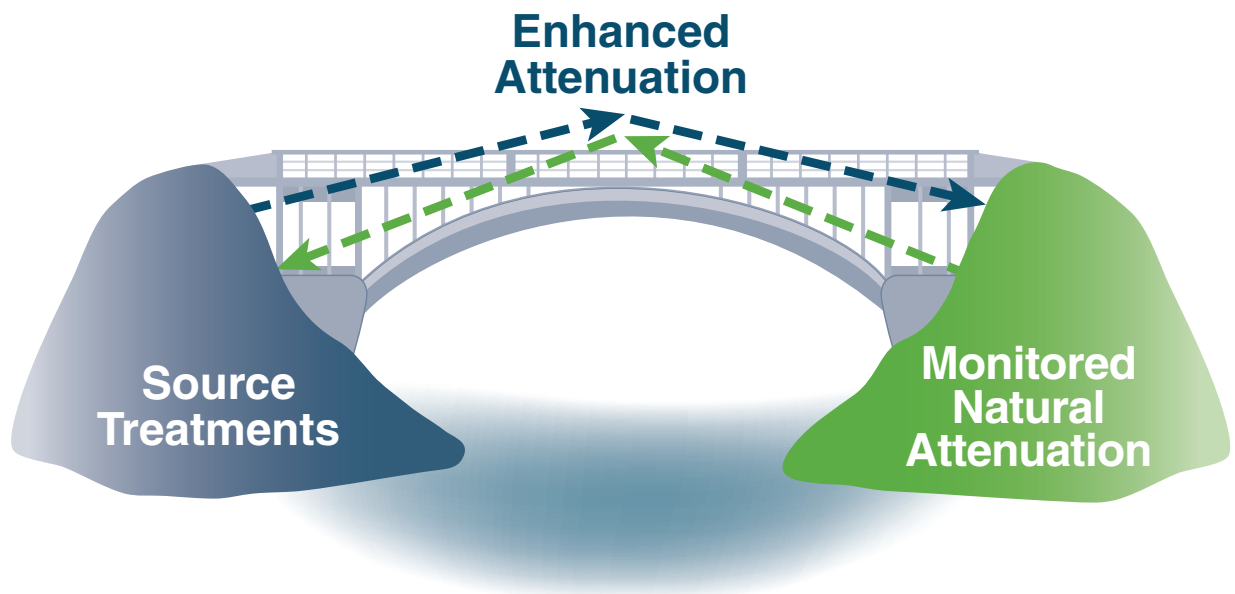




# Technical and Regulatory Guidance

## Enhanced Attenuation: Chlorinated Organics



April 2008

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

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## 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 Response, Compensation, and 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](http://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  $\mu\text{g per L per year}$ .

**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.





































































































































































































