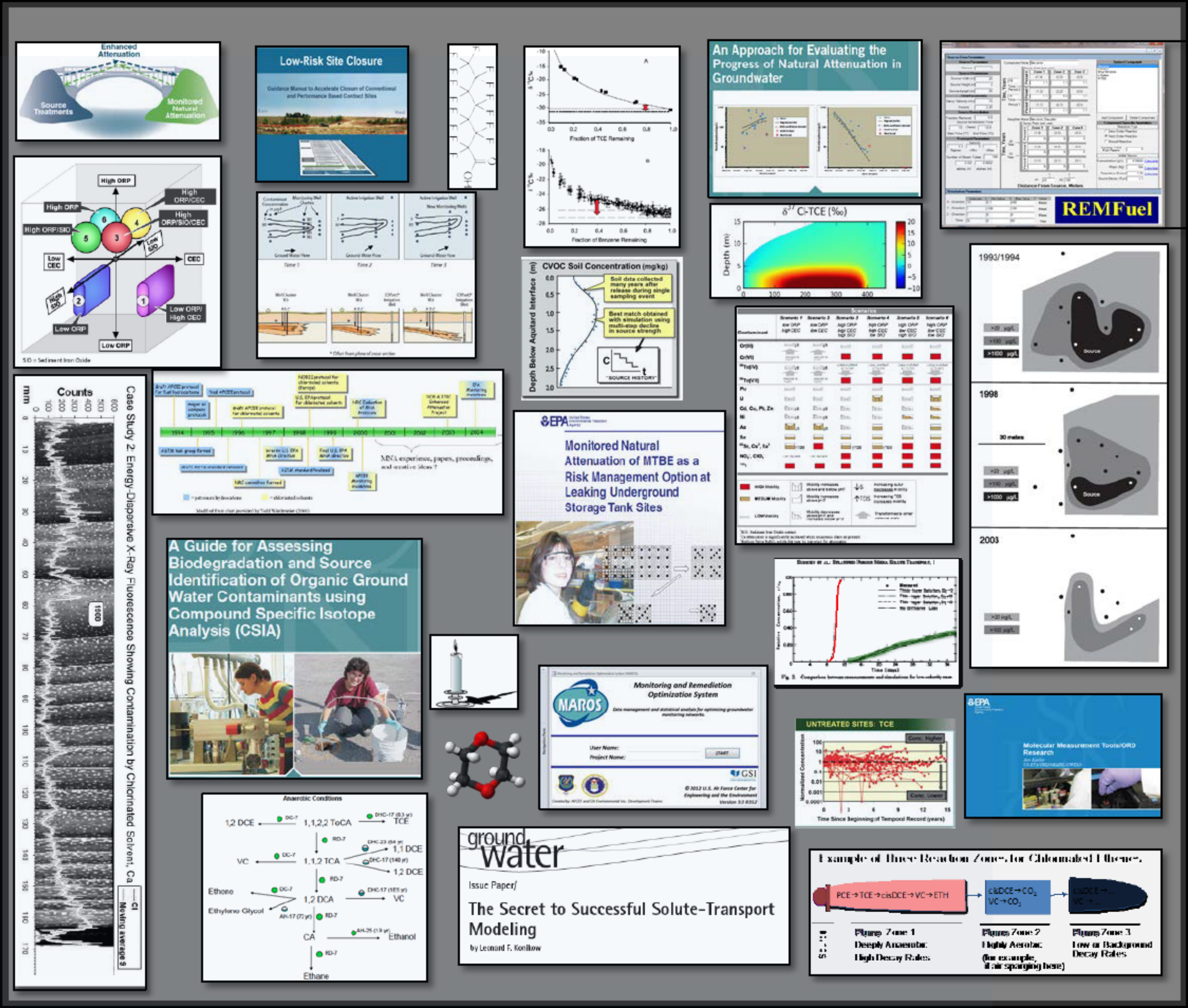

Frequently Asked Questions about Monitored Natural Attenuation in Groundwater

FEBRUARY 2014

David Adamson and Charles Newell

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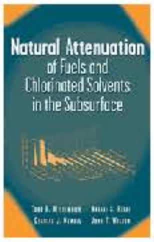
The following Frequently Asked Questions (FAQs) document provides a concise overview of current knowledge regarding management of subsurface contaminant releases using monitored natural attenuation (MNA). The envisioned audience includes state regulators, federal regulators, industry, consultants, DoD staff, and members of the local community involved in selecting remedies for contaminated sites. The intended value of the document is to provide current knowledge in support of sound decisions. In the interest of brevity, the FAQs assume that the reader has a general understanding of hydrogeology, the movement of chemicals in porous media, remediation technologies, and the remedy selection process.



The FAQ for MNA was inspired by the fact that it has been over a decade since publication of *Natural Attenuation of Fuels and Chlorinated Solvents*[15] which was co-authored by one of the FAQ authors. While still useful for certain topics, by 2013 it was missing several important advances in characterization, data interpretation, and regulatory thinking that are now mainstays of MNA. The FAQ for MNA is an attempt to identify and highlight the important advances that have occurred since 1999.

The authors of this document wish to acknowledge the financial support of ESTCP for this project and the important contributions of researchers, scientists, and engineers that have built the knowledge base upon which this document stands. The authors also wish to acknowledge the invaluable contribution of reviewers from government, industry, academia, and the public at large who have supported this project. In particular, the input from four peer reviewers, Dr. John Wilson of the USEPA, Ms. Carmen Lebrón and Mr. Mike Singletary of the Naval Facilities Engineering Service Center, and Dr. Leo Lehmicke of CO_2 & Water, was extremely helpful. In addition to the authors, GSI personnel who contributed to this document include Poonam Kulkarni, Shahla Farhat, Tom McHugh, Mindy Vanderford, Travis McGuire, Tony Daus, John Connor, and Michal Rysz.

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FAQ 1: Do we still need MNA?

Yes.

Monitored Natural Attenuation (MNA) is an important part of today's remediation industry:

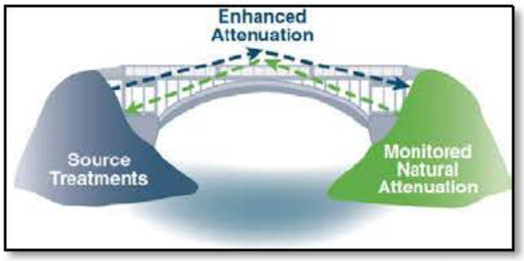
- MNA is used at many sites as the primary or sole remediation technology.
- MNA has been adapted for the purpose of "Enhanced Attenuation"[1] (EA) that provides a bridge between aggressive source zone treatment and MNA alone.
- MNA is typically the final component of the complete remediation process. "In the end almost all sites will rely on MNA" is the implicit theme of several recent remediation guidance documents.

MNA From a Technical - Regulatory Perspective

The Interstate Technology and Regulatory Council (ITRC) is a state-led, national coalition of participants from the environmental regulatory agencies of all 50 states and the District of Columbia, three federal agencies, tribes, and public and industry stakeholders. The ITRC's multidisciplinary, consensus-based teams receive input from states, federal agencies, the private sector, academia, and citizen stakeholders to Technical/Regulatory Guidance documents on multiple subjects. The following are three views from ITRC documents on where MNA may fit into the remediation process for three different situations:

> *Active remediation technologies rarely achieve complete remediation of all contaminant mass; thus, in effect, MNA is typically a component of every chlorinated-solvent site remedy. (ITRC Integrated DNAPL Strategy Guidance, 2011, citing ITRC's Enhanced Attenuation Guidance[1]).*

> *(Natural Source Zone Depletion) is also of significance because engineered remedial actions typically do not always completely remediate soils and NSZD may be useful to address the residual hydrocarbon[2].*



Role of Enhanced Attenuation as a bridge between active source treatment and MNA.

> *Monitored natural attenuation (MNA) may also be a viable remedial alternative for situations in which the potential for adverse impacts to public health or sensitive environmental receptors is very low[3].*

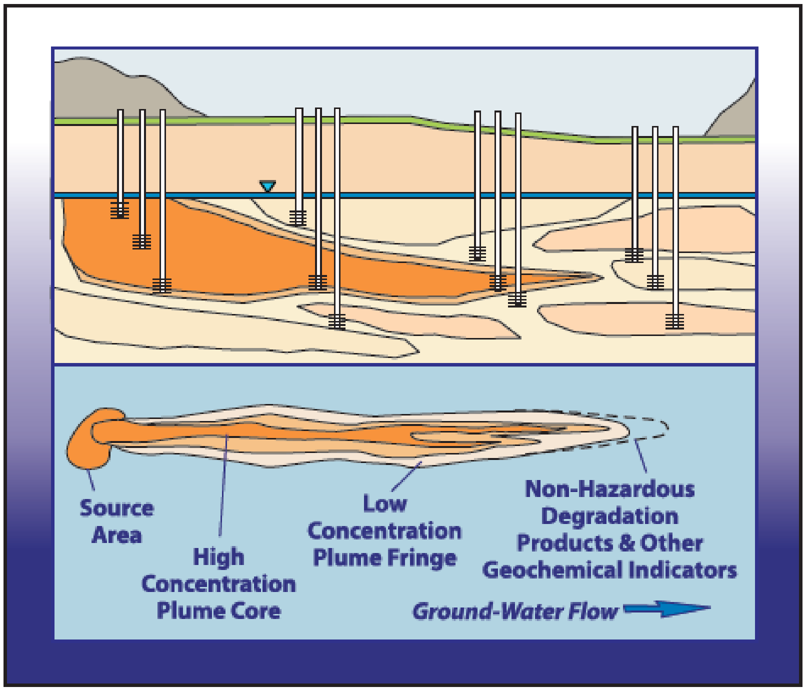
In general, MNA is allowable under CERCLA (Superfund) if it serves as a cleanup technology. Under RCRA, it can be a cleanup technology or risk management technology. Other regulatory agencies have different perspectives on the role of MNA in site cleanup. Overall it appears as sites get older, and more work is performed at a site, that MNA plays a more important role in managing remaining contaminants in groundwater.

Do we still need MNA? (Page 2)

MNA From a Scientific Perspective

There are a number of scientific developments that are making MNA increasingly important at contaminated groundwater sites:

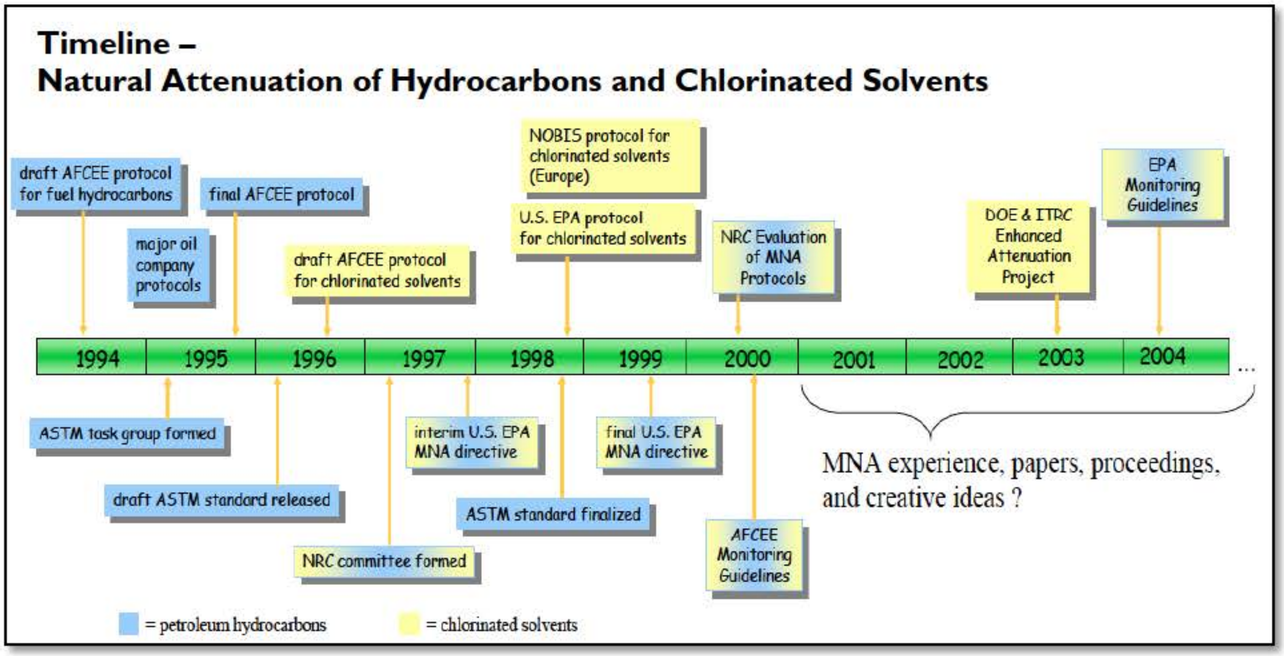
- An increased appreciation that matrix diffusion makes it very difficult at some sites to remove residual contamination and achieve stringent concentration goals (FAQ 22).
- Powerful new diagnostic tools to help understand, quantify and demonstrate MNA, such as stable isotope ratios (FAQ 11), molecular biological tools (MBTs) (FAQ 12), better sampling technologies that reduce variability, and new modeling tools.
- New thinking that some contaminants are more amenable to MNA than was previously thought: metals, radionuclides, perchlorate, explosives, MTBE/TBA, and others (FAQs 8 - 10).
- New implementations of MNA, such as Enhanced Attenuation[1] and source zone attenuation (FAQ 7).[4]
- Several new USEPA MNA and MNA-related guidance documents in the area of isotopes[5]; MBTs[6], MTBE[7], Inorganics[8-10], performance monitoring[11], and evaluating remedial progress[12].



FAQ 2. How has MNA changed over time?

New technologies, concepts, and increasing use. Here is Early MNA…

- 1980s to 1993: A series of scientific articles present new data, models, and ideas about "natural assimilation," "natural biodegradation," "intrinsic remediation," and "natural attenuation."
- 1994-2004: The timeline below presents how MNA developed for petroleum hydrocarbons (in blue) and chlorinated solvents (in yellow)[1]. (Note that some people call these protocols by different names).



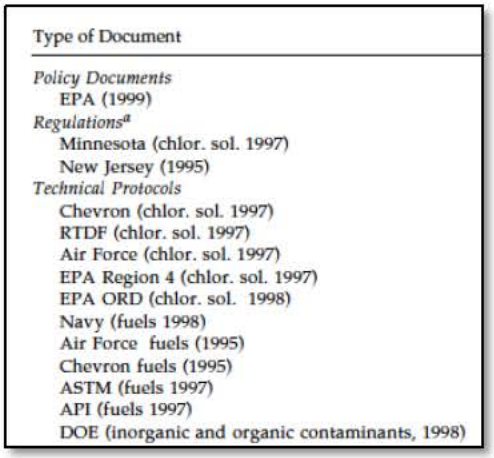
Timeline –
Natural Attenuation of Hydrocarbons and Chlorinated Solvents

How has MNA changed over time? (Page 2)

Through MNA Protocols up to 2000…

The National Research Council (NRC)[13] reviewed 14 natural attenuation protocols through 2000 for whether they addressed community concerns, scientific and technical issues, and implementation issues. Although all played key roles in some part of the MNA domain, the most highly cited documents using the Google Scholar search engine were:

- The USEPA's 1999 Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive that established the Agency's key policies for using MNA[14].
- The 1995 Air Force Fuels Protocol[15] (206 citations) and the USEPA's 1998 Chlorinated Solvent Technical Protocol (240 citations)[16] that emphasized reductive dechlorination natural attenuation processes, site assessment, implementation, and other factors.
- The *Natural Attenuation of Fuels and Chlorinated Solvents* book (600 citations)[17].



Type of Document
Policy Documents
EPA (1999)
Regulations[a]
Minnesota (chlor. sol. 1997)
New Jersey (1995)
Technical Protocols
Chevron (chlor. sol. 1997)
RTDF (chlor. sol. 1997)
Air Force (chlor. sol. 1997)
EPA Region 4 (chlor. sol. 1997)
EPA ORD (chlor. sol. 1998)
Navy (fuels 1998)
Air Force fuels (1995)
Chevron fuels (1995)
ASTM (fuels 1997)
API (fuels 1997)
DOE (inorganic and organic contaminants, 1998)

MNA Since 2000

Although there was tremendous progress in technical and regulatory aspects of MNA, two projects summarize some of the key issues regarding the protocols that were developed prior to 2000. In 2007, the *Scenarios Evaluation Tool for Chlorinated Solvent MNA*[18] noted that historical MNA protocols for chlorinated solvents were often focused on a particular type of site or attenuation process. The Scenarios document tried to broaden the applicability of MNA by providing a framework based on hydrogeology and geochemistry where the MNA methods and decision logic are linked together in one of 13 different "scenarios" or site types. Also in 2007, the USEPA released a three-volume protocol that expanded the types of contaminants where MNA could be applied, in this case for *metals and radionuclides*[8-10]. Extremely detailed, and extending over three volumes and 19 compounds, *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water* was later the focus of a companion *Scenarios* document in 2011[19].

There has been an avalanche of new technologies, approaches, and thinking about MNA. These are presented in more detail in the following FAQs.

FAQ 3. What are the most important new MNA developments?

New Contaminants, Measurements, Processes, and Tools

Our understanding of the subsurface has changed considerably since the first MNA protocols were written in the mid 1990s. A very general chronology of how our understanding of MNA has changed is summarized below.

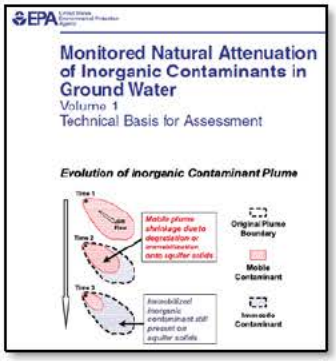
Year	New Contaminant	New Measurement	New Process	New Tools
2000-2005	*MTBE-TBA [7] (FAQ 9)*	*Two types of Rates (FAQ 16)[20]*	*Source attenuation of hydrocarbon sites [21]*	*BIOChlor [22]* *MAROS [23]* *NAS [24]* *SourceDK [21]*
2005-2010	*Metals-Rads [19] (FAQ 8)*	*Compound specific isotopes (FAQ 11) [4]* *Molecular Biological tools (FAQ 12)*	*Biogeochemical/abiotic transformations of solvents [25, 26, 27]* *Matrix diffusion [28]* *Oxidation of chlorinated solvents at low oxygen concentrations [186]*	*REMChlor [29]* *Mass flux toolkit [30]* *BIOBALANCE [31]* *Scenarios for chlorin. Solvents [19]* *MNA Sustainability Framework[32]*
2010-2012	*"Emerging Contaminants" (FAQ 10)*	*CO_2 traps for NSZD [33] (FAQ 15)*	*Natural Source Zone Depletion (NSZD) [2]* *Source attenuation of solvent sites [34]* *Attenuation in low-k zones*	*PREMChlor [29]* *Matrix diffusion toolkit [35]* *Scenarios for metals/rads [19]* *Source history reconstruction*


EPA United States Environmental Protection Agency

Molecular Measurement Tools/ORD Research

Ann Keeley

US EPA/ORD/NRMRL/GWERD

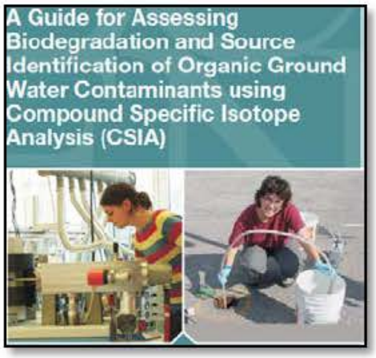

EPA United States Environmental Protection Agency

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1

Technical Basis for Assessment

Evolution of Inorganic Contaminant Plume


A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)

What are the most important new MNA developments? (Page 2)

Most Important?

Of these developments, probably the most important is the development and refinement of Compound Specific Isotope Analysis (CSIA) and Molecular Biological Tools (MBTs). CSIA and some MBTs have now entered the commercial market and have been used for MNA demonstrations for both fuels and chlorinated solvent sites. There are continuing developments on the horizon as well. For example, the 1998 EPA MNA protocol for chlorinated solvent sites is now being expanded to include processes other than reductive dechlorination (see text box below).

Coming Attractions: New Protocol for MNA Now in Development

ESTCP is funding an on-going project (ER-201129) entitled Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches (Monitored Natural Attenuation, Biostimulation and/or Bioaugmentation) at Chlorinated Solvent Sites). The product will be a rigorous guidance document for choosing between potential bioremediation approaches, including MNA. As a scoring-based framework, it represents an extension of the methodology developed in the AFCEE/USEPA protocol (1998). However, it will be able to utilize the increased understanding of biotic and abiotic degradation processes gained during the past 10 to 15 years. By incorporating a combination of established and novel monitoring parameters, the framework will be able to evaluate the applicability of various bioremediation approaches based on site-specific geochemistry and hydrogeologic conditions.

An important aspect of the new protocol is an emphasis on using site-specific data to estimate the attenuation rate, and ensuring that the estimated rate will meet the cleanup objectives. A database compiled from other sites can then be used to assess whether that attenuation rate falls within an acceptable range for specific key parameters (e.g., density of dechlorinating species/genes, concentration of reactive minerals) and thus is technically defensible. Both anaerobic biodegradation (for most chlorinated compounds) and aerobic biodegradation (for vinyl chloride and perhaps dichloroethene) are to be highlighted.

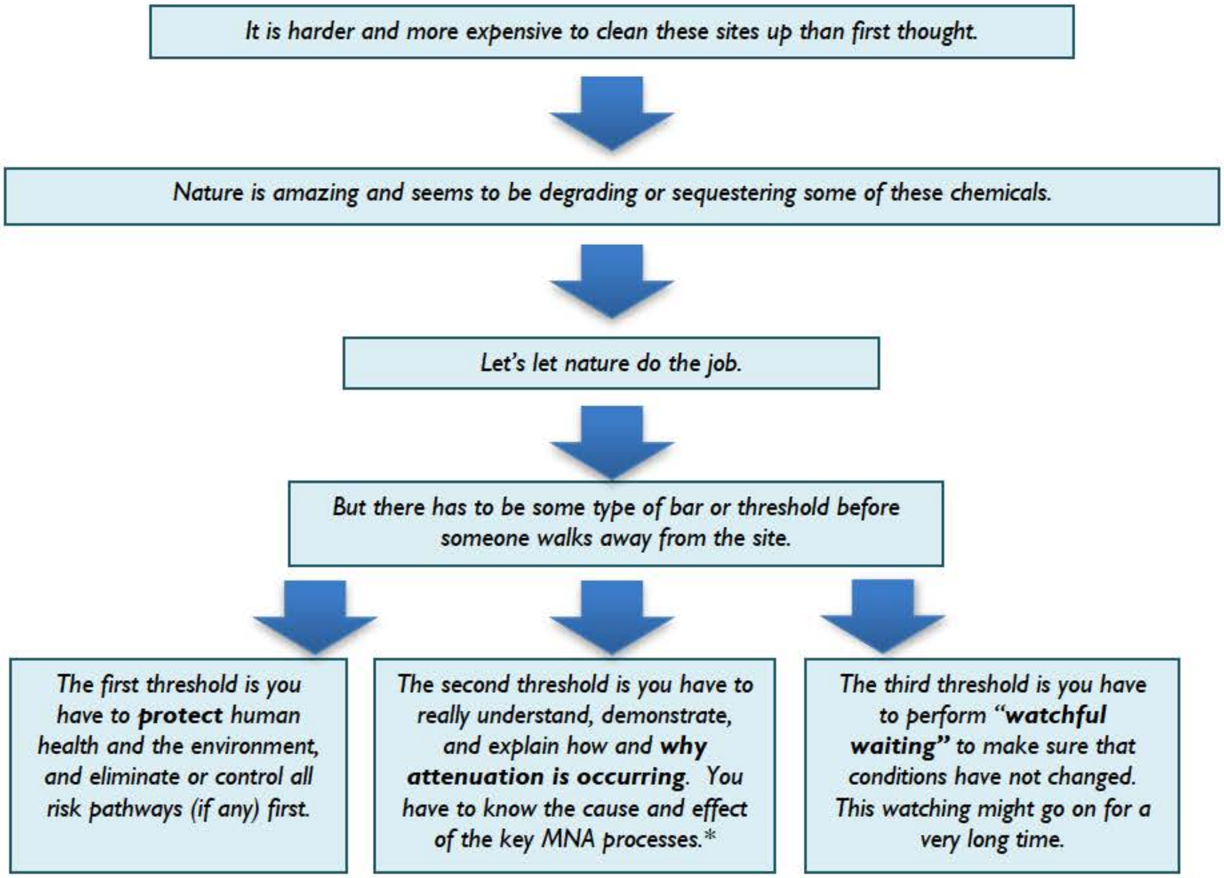
The approach should promote MNA as a remedy: From the proposal: "Application of the management expectation tool will likely increase the number of sites where MNA is determined to be an efficacious approach. This will reduce both capital and O&M expenses, and will also help to minimize detrimental environmental impacts associated with more invasive bioremediation treatment options".

FAQ 4. What is the philosophy behind MNA?

Nature Can Help

While the scientific and regulatory chronologies of MNA in the previous FAQs are helpful in understanding its development, they don't illustrate why and how the concept of MNA became an accepted practice by the groundwater community, stakeholders, and regulators.

One interpretation of an informal, implicit "Philosophy of MNA" is shown below:



It is harder and more expensive to clean these sites up than first thought.

Nature is amazing and seems to be degrading or sequestering some of these chemicals.

Let's let nature do the job.

But there has to be some type of bar or threshold before someone walks away from the site.

*The first threshold is you have to **protect** human health and the environment, and eliminate or control all risk pathways (if any) first.*

*The second threshold is you have to really understand, demonstrate, and explain how and **why attenuation is occurring**. You have to know the cause and effect of the key MNA processes.**

*The third threshold is you have to perform "**watchful waiting**" to make sure that conditions have not changed. This watching might go on for a very long time.*

While this is a very general layman's explanation of what MNA is all about, the USEPA's 1999 MNA Directive[14] formalized parts of this general philosophy and became an important regulatory and technical catalyst for the acceptance of MNA remedies. The Directive was a landmark document stressed that MNA was allowable at certain sites under certain conditions, that source remediation was a likely component of an MNA remedy, and that the USEPA had a preference for destructive attenuation processes.

** Some argue that if attenuation rates are high enough you don't need to know why.*

FAQ 5. What Evidence is Needed for MNA?

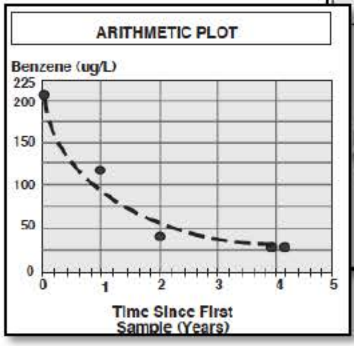
Typically Need Multiple Lines of Evidence

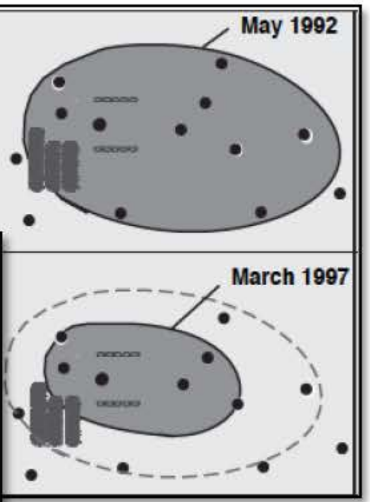
MNA has to be understood, demonstrated, and explained in the context of a complete Conceptual Site Model (CSM). Most of the historical protocols (FAQ 2) have used a Lines of Evidence (LOE) approach to demonstrate and explain attenuation in groundwater. For example, in 1999 the USEPA[14] defined lines of evidence this way:

1999 USEPA HISTORICAL LINES OF EVIDENCE	Why	What	When
LOE 1. *Historical contaminant mass reduction - monitoring data vs. time (temporal data)*	"I shrink therefore I am" (with apologies to Descartes)	Direct method to demonstrate decreasing trend	Always
LOE 2. *Hydrogeologic or geochemical data*	Need to know more than just it is decreasing	Indirect method to demonstrate particular process or rate of degradation	Most of the Time
LOE 3. *Field or microcosm studies*	Need to know more than Lines of Evidence 1 or 2	Direct method to demonstrate particular knowledge	Rarely; used to prove a specific process

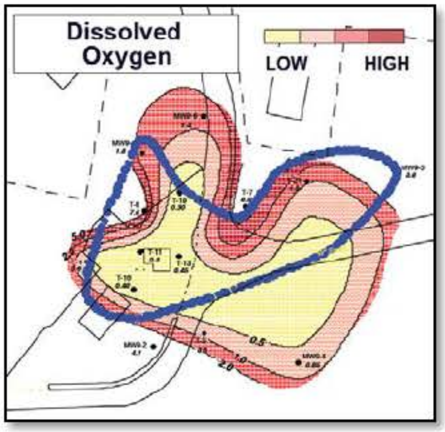
LOE 1. Under this approach, one always needed to demonstrate a loss of contaminant mass or reduction in concentration in groundwater. Typical methods used included:

- Concentration vs. time graphs for individual wells
- A collection of plume maps over time
- Statistical trend analysis, such as
- Mann-Kendall
- Mass loss along a flow line
- Modeling results indicating mass reduction





What Evidence is Needed for MNA? (Page 2)



LOE 2. Most of the time, one needed to show that conditions were conducive to MNA success using geochemical data, such as dissolved oxygen, sulfate, ferrous iron, and methane. The NRC[13] said it was critical to explain *why* MNA is working because:

- Contaminants can bypass sampling locations due to the complex nature of groundwater systems.
- Contaminants that decline at one location may be explained by having the contaminants move to another location or transform to other hazardous constituents;
- The reactions may not be sustainable over the long-term.
- Citizen's groups and others could be skeptical of MNA, and therefore site owners were obligated to ramp up the proof with demonstrated "footprints" of the active degradation processes.

One controversial approach includes the use of MNA scoring systems for preliminary screening to determine if anaerobic biodegradation was occurring. The most common such system was found in the USEPA Chlorinated Solvent Protocol[14]. It consisted of a lookup table where users got to assign from -3 to +3 points for up to 29 different categories. Points were added with appropriate dissolved oxygen and hydrogen concentrations, low levels of competing electron acceptors, having organic carbon in groundwater, and the presence of daughter products. Points were removed for adverse conditions, such as pH outside of the recommended range. After tallying the points from each category, having 20 points or more indicated "Strong Evidence for anaerobic biodegradation of chlorinated solvents"; while 5 or fewer points indicated "Inadequate evidence."

The NRC[13] weighed in with a controversial recommendation to eliminate scoring systems because they were "too simple" and often used "erroneously." Instead, they prescribed that MNA projects include identification of key "footprints" of MNA, generally "*changes in concentrations of reactants or products of the biogeochemical processes that transform or immobilize the contaminants*." These footprints included daughter products (like the presence of *cis*-1,2-DCE for the chlorinated ethenes) and known biogeochemical reactions (benzene can degrade aerobically or anaerobically).

LOE 3 has historically consisted of special microcosm or field studies (such as field push-pull tests) that were to be used infrequently, only when it was important to demonstrate "proof of concept" of a particular process which had not yet been sufficiently documented in the literature (e.g. aerobic vinyl chloride biodegradation in 1995).

A new generation of non-protocol type documents based on "*Scenarios*" rather than lines of evidence are described on the next two pages. As you can see, these documents present a different framework for evaluating MNA at a site.

Scenarios: A New Generation of "Protocols"

The Department of Energy developed two innovative MNA documents based on the Scenarios Approach[18-19]. The authors observed that the historical protocols had several limitations, such as being too focused on a particular reaction or contaminant type (e.g, reductive dechlorination of chlorinated ethenes for the USEPA Chlorinated Solvent MNA protocol) and were sometimes difficult to explain to stakeholders. The new generation of protocols categorizes the wide spectrum of sites that might be amenable to MNA into a limited number of site-types called Scenarios that combined hydrogeologic and different geochemical settings. A summary of the two Department of Energy Scenarios Systems is presented below.

MNA Scenarios for Chlorinated Solvent Sites [18]

Contaminants: Chlorinated ethenes (PCE to VC); Chlorinated ethanes (1,1,1,2-TeCA to CA); Chlorinated methanes (CT to CH_4).

13 different scenarios based on 5 hydrogeologic settings and 3 geochemical environments below:

	Aerobic	*Anoxic*	*Anaerobic*
simple, fast	Scenario 1	Scenario 2	Scenario 3
simple, slow	Scenario 4	Scenario 5	Scenario 6
faster with heterogen.	Scenario 7	Scenario 8	Scenario 8
slower with heterogen.	Scenario 10	Scenario 11	Scenario 12
fractured/ porous rock	Scenario 13		

Other Factors Considered: Source strength, source type, time to receptor, and plume stability.

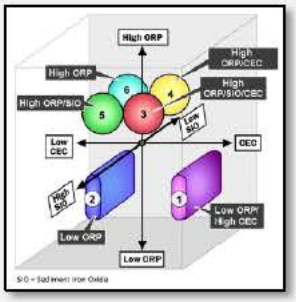
Key Information for Each Specific Scenario:

- Will MNA Work?
- How do I characterize this type of site?
- How do I analyze data?
- What about costs and enhancements?

MNA Scenarios for Inorganic Sites [19] (FAQ 8)

Contaminants: Cr(III), Cr(VI), Tc(IV), Tc(VII), Pu, U, Cd, Cu, Pb, Zn, Ni, As, Se, Sr, Cs, Ra, NO_3, ClO_4, I

Six different scenarios based on oxidation/reduction potential (ORP), cation exchange capacity, and sediment iron oxide, as shown in this 3-dimensional chart mapping the six scenarios as reactive facies. Each reactive facies is associated with a unique combination of ORP conditions (oxic or anoxic), CEC (cation exchange capacity; high or low), and sediment iron oxide content (high or low).

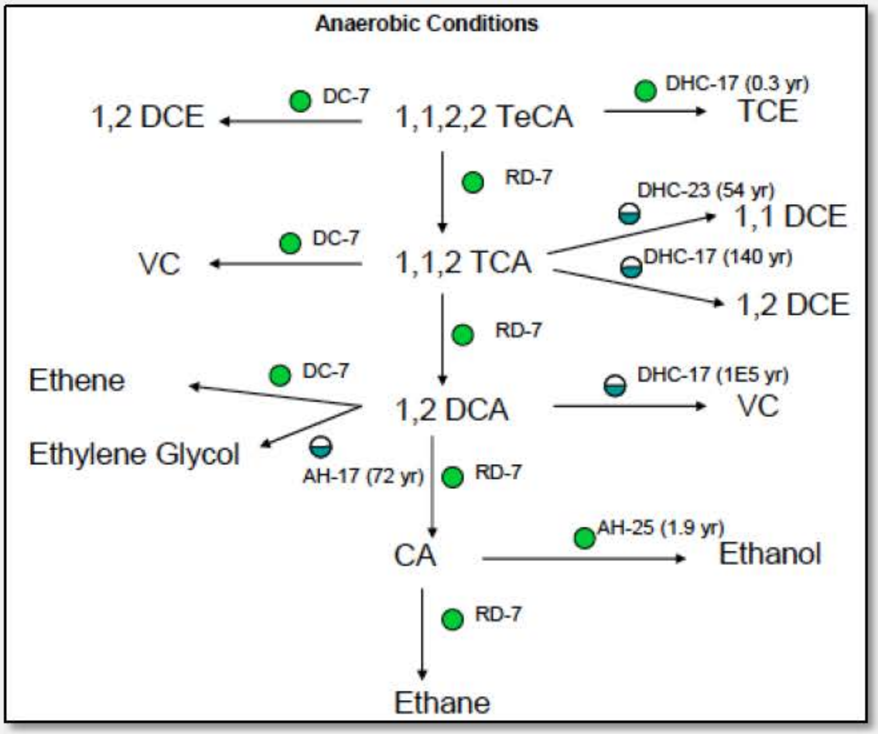


Other Factors Considered: pH, total dissolved solids, sulfur species, facilitated transport, source type, hydrogeology and travel time.

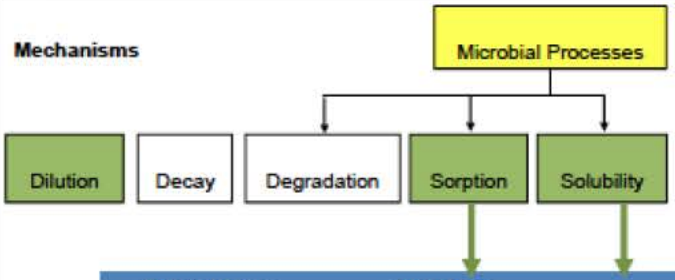
Key Information In Each Specific Scenario:

- Mobility of each of 18 different contaminants
- Explains specific attenuation processes
- Shows how to use the selected scenario to develop a site-specific conceptual model
- Describes how to apply MNA and EA
- Describes how to use EPA's tiered MNA evaluation process at a site

FAQ 5: Example of Key Graphics in Scenarios Documents



Example of Info about Mechanisms for Chlorinated Ethanes[18]



Groundwater Condition	Impact on *Sorption*	Impact on *Solubility*
ORP	*Low:* Dissolution of iron oxides can release arsenic into the groundwater; As(III) (reduced form) sorption is somewhat lower than As(V) sorption	*Low:* Generally no insoluble solids except for arsenic sulfides
CEC	High CEC may increase sorption	
Sediment iron oxide	Iron oxide dissolution may be important (see ORP discussion in this table)	
pH	Sorption may decrease with decreasing pH	Possible increases in solubility with decreasing pH
Sulfur		Under low ORP conditions, sulfide compounds result in low solubility
TDS	Phosphate or silicate can inhibit sorption	

Blank indicates "no major impact"

Key:	🟩 Process is <u>active</u>	☐ Process is <u>usually unimportant</u>

Example of Info about Mechanisms for Aresenic[19]

FAQ 6. MNA Lines of Evidence— How have they changed?

Lines of Evidence (LOE) Are Now More Focused, More Complex

The lines-of-evidence approach remains an important component in any evaluation of the appropriateness of MNA as a site remedy. Using "multiple distinct but converging lines of evidence"[15] to document that attenuation has occurred and will continue to occur, reduces the uncertainty associated with a single piece of evidence and increases confidence that MNA is suitable. This confidence is inherently critical for MNA because it relies on intrinsic processes to eliminate risk and lacks the "visible, active steps to remove contamination"[13]. In some cases, the evidence required for a MNA determination now includes an estimate of the attenuation rate and assurance that the rate is adequate for the remedial action objectives.

As described in FAQ 5, the lines of evidence approach that was presented in many of the protocols and guidance documents developed in the 1990s has typically been a three-tiered process[17]. In the past 10 to 15 years, the lines-of-evidence approach has evolved to incorporate several powerful tools that have achieved technological maturity during that time (see table on next page). In addition, there is increasing evidence of aerobic degradation processes that were given little consideration in early protocols and are often not included in conceptual site models. For example, aerobic oxidation of chlorinated solvents such as *cis*-1,2-DCE and VC can be significant [87, 106] and can even occur in low oxygen environments that were typically thought to be anaerobic. [187]

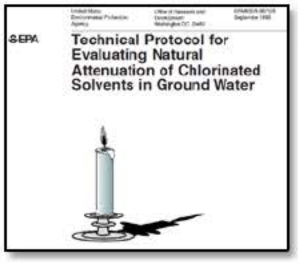
Note that different historical protocols categorized some elements under different lines of evidence. For example, the State of Texas MNA Protocol from 2001 considers attenuation rate calculations using historical data as a "Secondary LOE" and predictive groundwater modeling as an "Other Line of Evidence." [36]

LOE for Metals and Radionuclides

A modified approach was presented by USEPA in their guidance on MNA for metals, inorganics, and radionuclides[8-10]. Their Tiered Analysis Approach has the same objectives, but is organized specifically to optimize data collection efforts since these can be more challenging (and costly) for such compounds than for chlorinated solvents or petroleum hydrocarbons. A DOE-funded Scenarios document[18] provides additional guidance on following USEPA's tiered approach when considering MNA as a potential remedy for these classes of compounds.

The table on the next page compares MNA thinking in the 1990s to commonly used lines of evidence and methodologies today. Note the transition to more colorful covers!

1998


Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

2009


Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water

Line of Evidence	FAQ 6: General Approach to Gathering Evidence	
	1990s PROTOCOLS	**CURRENT**
Historical trends in contaminant data showing decreasing concentration/mass	• Trend analysis to show that contaminant concentrations are decreasing and that plume is shrinking • Mass balance to document concentration reductions are associated with destructive processes • Modeling sometimes used to understand transport processes but not as direct line of evidence	• Improved ability to systematically demonstrate trends using MAROS and other tools (see FAQ 19) • Utilize one of several widely-available analytical and numerical models for better understanding of plume behavior over time • Increased reliance on mass balance and mass flux to establish attenuation capacity • Increased emphasis on matching attenuation rates with objectives • Smarter monitoring programs to document performance [11, 37]
Chemical and geochemical data that support attenuation	• Document that daughter product formation accounts for parent compound concentration decrease • Show that geochemical conditions support the desired attenuation process, such as anaerobic degradation of TCE • Demonstrate that electron acceptors and donors are being depleted ("footprint") for fuels	• Comprehensive suite of biogeochemical parameters still recommended with emphasis on using data to demonstrate reactions are sustainable • Understanding that dissolved oxygen data can be misleading if not carefully measured and cause misidentification of relevant attenuation processes • Analytical protocols for documenting reactive mineral species (to support abiotic degradation) are available [25-27]
Data documenting that degradation is occurring and provides an estimate of the rate	• Recommended only when other lines of evidence are inconclusive • Some included groundwater modeling • Microcosm studies • Emphasis on anaerobic biological reductive dechlorination pathway • Abiotic degradation potential largely ignored	• Degradation rates are now a key part of most MNA projects. Concentration vs. time rates are particularly important to evaluate the timeframes required for MNA • MBTs (FAQ 12) have supplanted some microcosms because they are representative, timely data • CSIA data (FAQ 11) used extensively to provide evidence of degradation; can also be used to estimate rates and differentiate pathways (including abiotic degradation) [5] • Recognition that "degradation chains aren't one-way streets" and that lesser chlorinated solvents (such as *cis*-1,2-DCE and VC) can degrade aerobically at very low DO levels (below typical detection levels) [186]

FAQ 7. MNA for the source zone too?

An Emerging Consensus: *Yes*

MNA was originally developed with the candle and flame metaphor: the source is the candle, and the flame is the solute plume. In the words of Todd Wiedemeier, one of the authors of the chlorinated solvent protocol which had this image on the cover:

> *"You can snuff out the flame with things like ISCO or ORC, etc. but as long as there is a "candle" the "flame" can/will come back and will persist. The solute plume only gets so long because it is attenuated/consumed and converted to CO_2. The effects of the flame can be felt for some distance from the flame."*

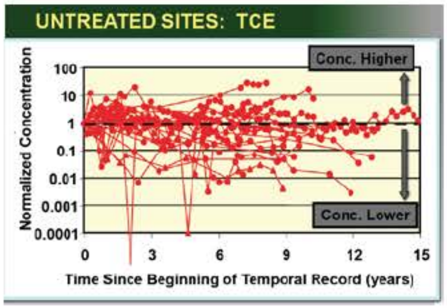
And so in the beginning of MNA, the plume was the primary focus. The USEPA's MNA Directive[14] stated:

> *Sources of contamination are more appropriately addressed by engineered removal, treatment or containment technologies…. Where the sources of contamination have been controlled, dissolved plumes may be amenable to MNA because of the relatively small mass of contaminants present in the plume.*

However, source attenuation was included in the BIOSCREEN Natural Attenuation Model in 1996[38] and its companion model BIOChlor in 1999[22]. In 2000, the National Research Council[13] provided a more nuanced discussion of MNA and source zones in their book *Natural Attenuation for Groundwater Remediation* and suggested that source zone attenuation might be appropriate under some conditions. For example, a 2004 survey of 191 plumes showed that MNA was the sole remedy (no active source remediation) at 21% of sites with CVOC concentrations greater than 10 mg/L[39]. These findings suggested that MNA was being used widely at sites with residual sources.

Source Attenuation Datasets

There have been several long temporal (10 to 20 year) datasets that measure source attenuation rates. A study of 48 benzene sites and 76 MTBE sites in California showed source attenuation concentration half-lives of 3.9 and 2.3 years, respectively[49]. So while the source attenuation rate at some sites may be very low, at other sites it may be considerable. One study of 23 chlorinated solvent MNA sites[41] showed a median source zone concentration half-life of only 3.2 years. The study authors concluded *"If the median point decay rates from these sites are maintained over a 20 year period, the resulting reduction in concentration will be similar to the reported reduction in source zone concentrations achieved by active in situ source remediation technologies (typical project length: 1–2 years)."*



Long-term temporal records from 22 monitoring wells at 13 TCE Sites[41]

MNA for the source zone too? (Page 2)

Source Attenuation Protocols

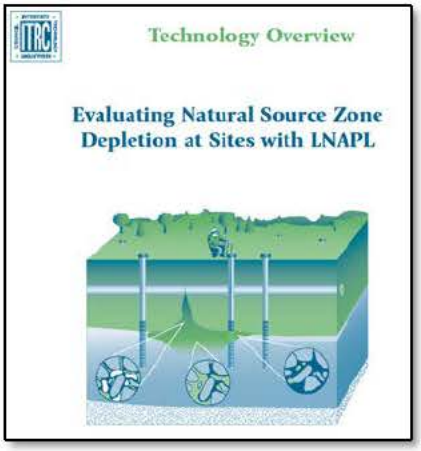
One research group has developed a "Source Zone Natural Attenuation" (SZNA) methodology[42] that requires different techniques and conceptual models than those used for MNA in dissolved plumes. Three data types are defined: *Group 1* data address the question of whether SZNA is occurring; *Group 2* data focus on determining the current rate of SZNA; and *Group 3* data evaluate the long-term implications for residuals, groundwater quality and SZNA rates.

In 2009, the ITRC published guidance on *Natural Source Zone Depletion* (NSZD) for LNAPL source zones[2] that says: *"NSZD is of significance because it occupies a position in the spectrum of remediation options that can be used as a basis for comparing the performance and relative benefit of other remediation options. It is also of significance because engineered remedial actions typically do not always completely remediate soils and NSZD may be useful to address the residual hydrocarbon."*

Finally, the recently-published SERDP/ESTCP Chlorinated Solvent Source Zone Remediation Monograph (2012) includes a separate, stand-alone chapter on *"Natural Attenuation of Chlorinated Solvent Source Zones"*, an inexact but notable sign that source zone MNA has arrived as a viable remediation alternative for chlorinated solvent sites.[4]

Source Attenuation Modeling Tools

Additional tools have joined BIOCHLOR[22] and BIOSCREEN[38] with a focus on source attenuation. The SourceDK model was explicitly developed to help users estimate source attenuation rates and timeframes from either an empirical (data based) or mass balance approach (see graphic on bottom right[17]). More recently, the USEPA's REMChlor model[29] has the ability to simulate source attenuation (either alone, or after remediation removes a portion of the source mass) and then show the resulting plume response. The newly-issued Matrix Diffusion Toolkit[35] allows users to simulate the effects of matrix diffusion processes during source attenuation.

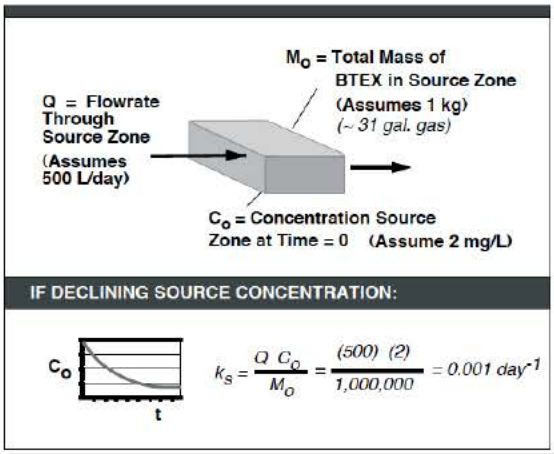


Technology Overview

Evaluating Natural Source Zone Depletion at Sites with LNAPL

ITRC guidance on Natural Source Zone Depletion[2]

Example calculation from SourceDK model[17]



MNA for the source zone too? (Page 3)

SZNA Studies

The research group at Arizona State University is using measurements of contaminant flux as part of an integrated approach to documenting natural attenuation of both LNAPL and DNAPL source zones[43]. Their methodology has been demonstrated at multiple different Department of Defense sites as part of ESTCP project ER-0705. Losses related to vapor transport through the vadose zone (volatilization and diffusion) are measured using shallow monitoring points where vapor-phase concentrations are analyzed using field equipment. These studies have shown that the natural losses from the vadose zone at petroleum hydrocarbon sites can be significantly larger than losses associated with dissolved-phase transport, at least when the source was not submerged (see table below). However, the opposite pattern has been observed at chlorinated solvent sites, where vadose zone transport was much less significant.

Selected Results from Demonstration of Natural Source Zone Attenuation (NZSA) methodology at Several Petroleum Hydrocarbon and Two Solvent Sites. Data compiled from Ekre et al. [43].

Site	Contaminant	Hydrogeology	Loss Rate from Dissolution (kg/year)	Loss Rate from Dissolved Transport Related Biodegradation (kg/year)	Loss Rate Estimate Due to Vadose Transport* (kg/year)
Guadalupe Diluent Tanks	Hydrocarbon	Sand dune	500 - 1600	600 - 1600	140,000 (O_2 Flux)
Guadalupe Compressor	Hydrocarbon	Sand dune	300 - 500	0	16,000 (O_2 Flux)
NAS Jacksonville	Chlorinated Solvent	Silty sand, clay	12 - 32	-	0.27 - 0.79 (Vapor Flux)
Parris Island	Chlorinated Solvent	Silty clay, sand stringers	1.8 - 5	-	0.22 - 0.68 (Vapor Flux)

* *For hydrocarbon sites, loss is from "Oxygen Gas Transport". For chlorinated solvent sites, loss is "Vapor Flux."*

FAQ 8. Can I apply MNA to metals, inorganics, and radionuclides?

Yes, Says USEPA

Much of the focus of MNA has been on sites with chlorinated solvents and petroleum hydrocarbons, but all compounds are subject to natural attenuation to varying degrees. This includes various metals, radionuclides, and other inorganics, many of which are also commonly-encountered at federal and industrial sites. The attenuation mechanisms for these compounds share some similarities with chlorinated solvents and petroleum hydrocarbons, but there are also some important distinctions:

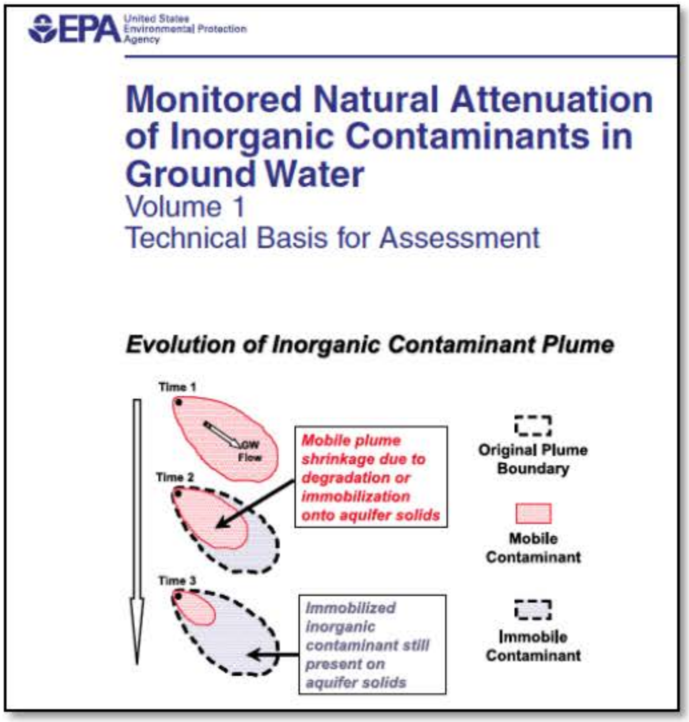
- Reactions are generally more complex, particularly with regards to geochemical conditions
- Many of these compounds—including most metals and radionuclides—are not degraded but transformed to immobile or less mobile forms, typically through co-precipitation or sorption.

As a result, the general goal for MNA of these types of compounds is to document that the existing site conditions promote reactions that generate a stable product with reduced mobility and potential for exposure, such that current and future risk is minimized.

The mechanisms for attenuation of metals, radionuclides, and other inorganics were recognized in the 1999 USEPA directive[14], but a formal protocol for evaluating MNA for these types of compounds was not developed until more recently (between 2007-2010)[8-10, 19, 44]. Other new inorganic candidates for MNA include perchlorate[45]. These are highly useful technical guidance documents that detail the applicability of MNA for these compounds within the context of geochemical site conditions. Highlights include:

The USEPA protocols for inorganics[8-10] accomplish this through the development of a four-tiered lines-of-evidence to support MNA for them:

- Tier 1: Document that the plume is not expanding and that sorption is occurring
- Tier 2: Identify the mechanism and rates of attenuation
- Tier 3: Determine the capacity and sustainability
- Tier 4: Develop monitoring and contingency measures



EPA United States Environmental Protection Agency

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1

Technical Basis for Assessment

Evolution of Inorganic Contaminant Plume

Can I apply MNA to metals, inorganics, and radionuclides? (Page 2)

Biogeochemical Processes Often Control Attenuation of Metals and Radionuclides

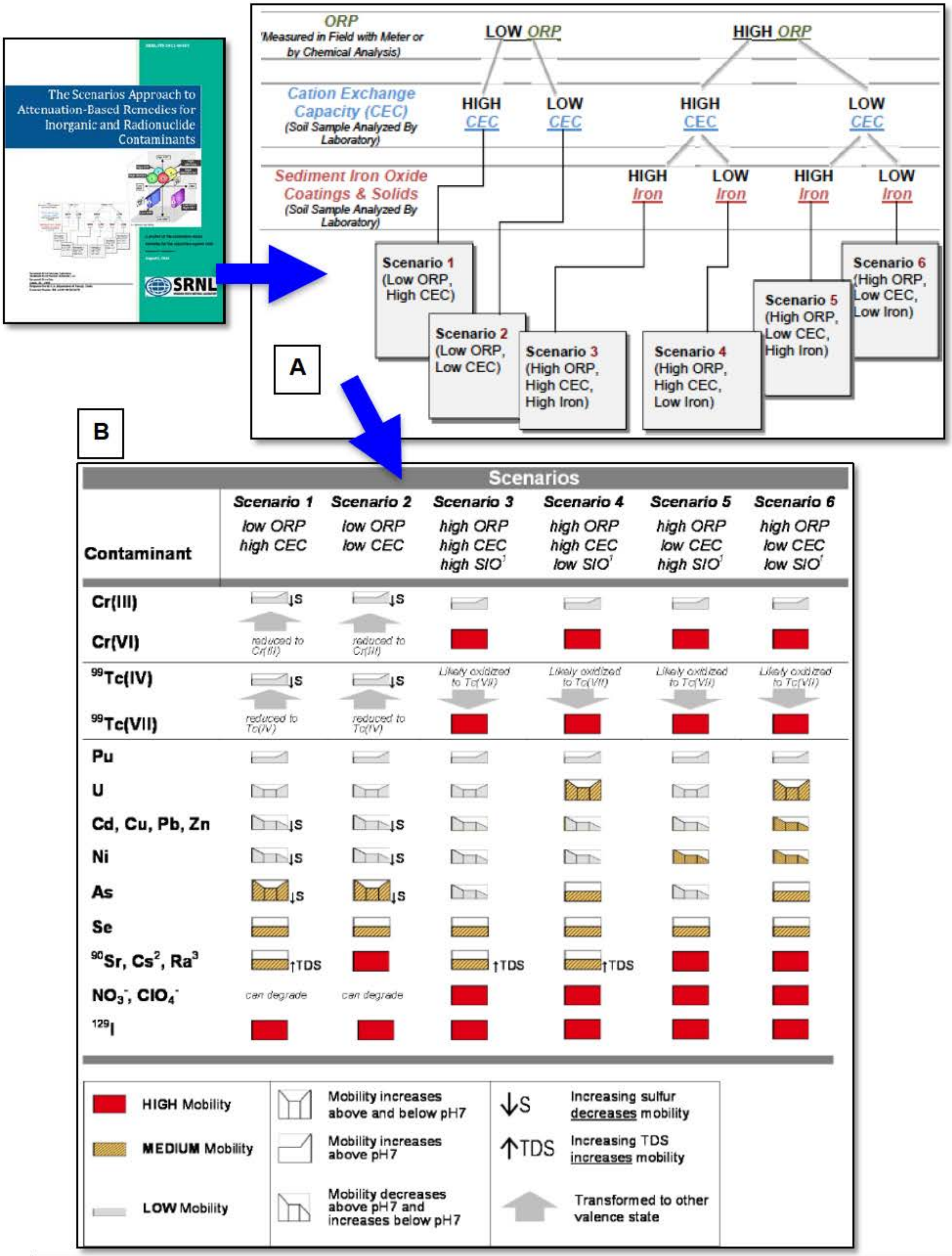
The importance of biogeochemical processes in attenuating these compound classes—specifically biologically-induced formation of reduced iron and sulfur species that abiotically transform or sequester contaminants—was enhanced by the AMIBA protocol[26] and DoD-sponsored investigations[25] for attenuation of organic compounds.

The table below summarizes the relative effectiveness of several different types of in situ attenuation processes for various metals, radionuclides, and other inorganics. These assessments are based on the assumption that there are no limiting factors for a particular attenuation mechanism (e.g., oxygen is readily available for aerobic biological degradation, reactive mineral species are available for abiotic degradation). The list does not include non-destructive physical attenuation processes such as diffusion, dispersion, and advection, and sorption is included as a sequestration process.

Contaminant	Biological Reaction		Abiotic Reaction	Sequestration
	Anaerobic	Aerobic		
Nitrate	Yes, degradation	No	Yes (reactive iron)	No
Perchlorate	Yes, degradation	No	Conflicting Data	No
Chromium (Cr), Selenium (no change) (Se), Copper (Cu), Cadmium (Ca), Lead (Pb), Nickel (Ni), Zinc (Zn), Beryllium (Be), Arsenic (As) (metalloid)	Valence change, generally favorable	Valence change, generally unfavorable	Valence change, generally favorable	Yes (sorption, co-precipitation)
Uranium, Technetium, Strontium, Cesium, Radium, Iodine	Valence change, generally favorable	Valence change, generally unfavorable	Valence change, generally favorable	Yes (sorption, co-precipitation

Scenarios System for Metals and Radionuclides

To apply the Scenarios system that was developed by the DOE[19], one uses the graphic on the next page (A) to select one of six scenarios that best reflect the site conditions based on Oxidation/Reduction Potential (**ORP**), (Cation Exchange Capacity (**CEC**), and Sediment iron oxide content (**SIO**). The bottom figure (B) is then used to provide a qualitative indication of mobility. For MNA to be successful, it is more likely that the contaminants will have low or medium mobility.



	Scenarios					
Contaminant	***Scenario 1*** *low ORP* *high CEC*	***Scenario 2*** *low ORP* *low CEC*	***Scenario 3*** *high ORP* *high CEC* *high SIO*[1]	***Scenario 4*** *high ORP* *high CEC* *low SIO*[1]	***Scenario 5*** *high ORP* *low CEC* *high SIO*[1]	***Scenario 6*** *high ORP* *low CEC* *low SIO*[1]
Cr(III)	▭ ↓S	▭ ↓S	▭	▭	▭	▭
Cr(VI)	⇧ *reduced to Cr(III)*	⇧ *reduced to Cr(III)*	🟥	🟥	🟥	🟥
^{99}Tc(IV)	▭ ↓S	▭ ↓S	*Likely oxidized to Tc(VII)* ⇩	*Likely oxidized to Tc(VII)* ⇩	*Likely oxidized to Tc(VII)* ⇩	*Likely oxidized to Tc(VII)* ⇩
^{99}Tc(VII)	⇧ *reduced to Tc(IV)*	⇧ *reduced to Tc(IV)*	🟥	🟥	🟥	🟥
Pu	▭	▭	▭	▭	▭	▭
U	▭	▭	▭	▨	▭	▨
Cd, Cu, Pb, Zn	▭ ↓S	▭ ↓S	▭	▭	▭	▨
Ni	▭ ↓S	▭ ↓S	▭	▭	▨	▨
As	▨ ↓S	▨ ↓S	▭	▨	▭	▨
Se	▨	▨	▨	▨	▨	▨
^{90}Sr, Cs^2, Ra^3	▨ ↑TDS	🟥	▨ ↑TDS	▨ ↑TDS	🟥	🟥
NO_3^-, ClO_4^-	*can degrade*	*can degrade*	🟥	🟥	🟥	🟥
^{129}I	🟥	🟥	🟥	🟥	🟥	🟥

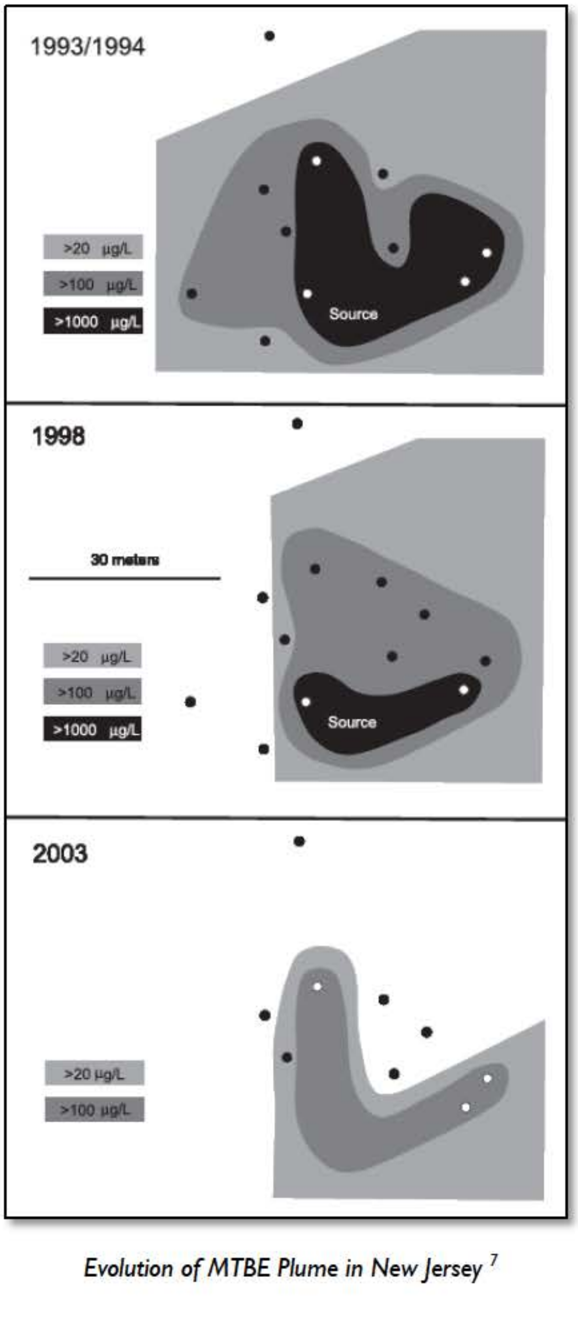
🟥	HIGH Mobility		Mobility increases above and below pH7	↓S	Increasing sulfur decreases mobility
▨	**MEDIUM** Mobility		Mobility increases above pH7	↑TDS	Increasing TDS increases mobility
▭	**LOW** Mobility		Mobility decreases above pH7 and increases below pH7	⇧	Transformed to other valence state

FAQ 9. I can apply MNA to BTEX, but how about oxygenates?

Originally No, But Now Yes

The observation that BTEX and other petroleum hydrocarbons attenuated at fuel sites drove the development of the earliest MNA guidance documents[15] and was key to MNA's initial regulatory acceptance. Just prior to this period, MTBE began to be used extensively as a gasoline additive to boost oxygenate levels. However, the role of MTBE and other fuel additives as groundwater contaminants was not fully appreciated until later. By the time USEPA issued its 1999 MNA directive[14], it noted that MTBE had been found to "*...migrate large distances and threaten downgradient water supplies at the same sites where the BTEX component of a plume has either stabilized or diminished due to natural attenuation*" and included MTBE among compounds "*...that tend not to degrade readily in the subsurface*". However, considerable research was completed in the next decade (while MTBE's use as a fuel oxygenate was phased out in the U.S. and ethanol became the preferred replacement) that demonstrated the viability of MNA for managing some sites contaminated with MTBE and other fuel oxygenates such as TBA (*tert*-butyl alcohol).

Most fuel oxygenates, including MTBE, TBA, and ethanol, are highly soluble, such that they can migrate rapidly in groundwater following dissolution from LNAPL (gasoline) sources. In light of the perceived recalcitrance of MTBE, this led to early concerns that the majority of fuel oxygenate plumes would be long and extend far beyond those associated with co-released BTEX compounds. While there are certainly cases where exceptionally long MTBE plumes have developed, several plume studies have documented that the majority of MTBE plumes are relatively short and/or attenuating (e.g. 46-48). By 2005, the USEPA had issued a guide for MNA for MTBE[7] and the ITRC had evaluated using MNA for MTBE[3].

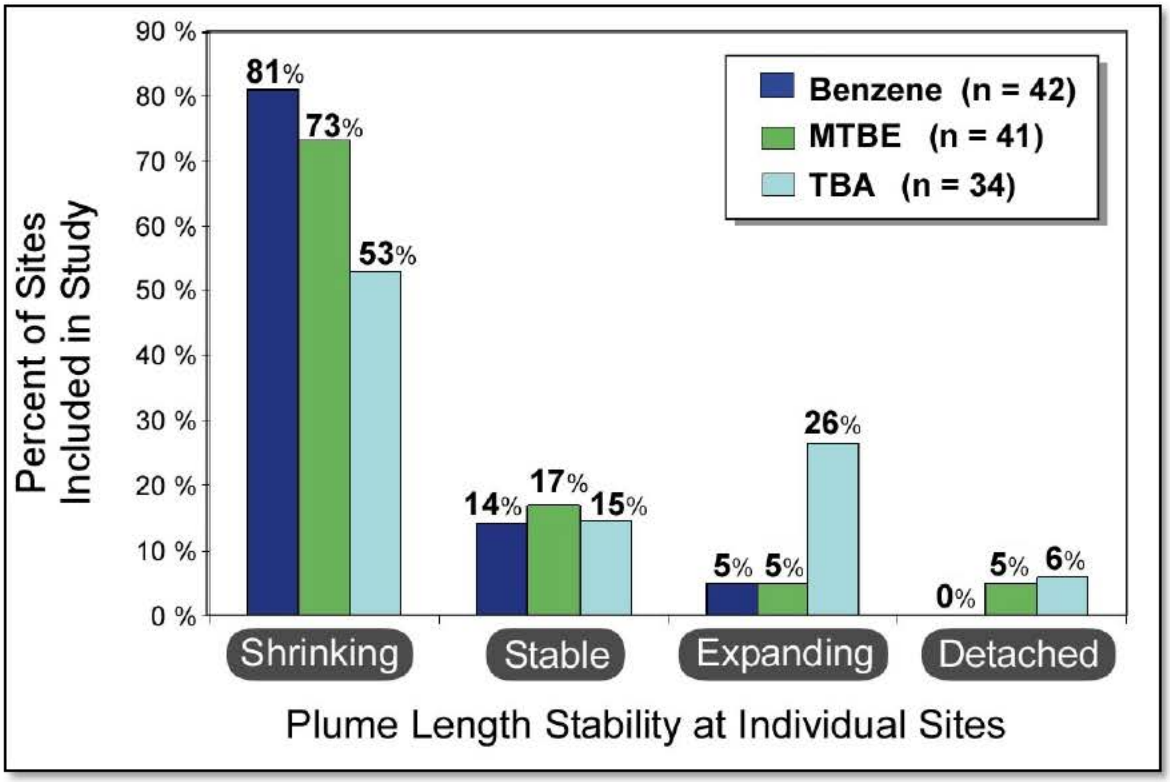


Evolution of MTBE Plume in New Jersey [7]

I can apply MNA to BTEX, but how about oxygenates? (Page 2)

The Data Say...

A comprehensive analysis of MTBE and TBA plume behavior used long-term monitoring records for MTBE, TBA, and benzene from 48 retail gasoline sites[49]. This study confirmed that the majority of MTBE plumes are similar in size (median = 142 ft) to the benzene plumes at these sites, and are stable or shrinking in size and concentration at a rate (median = -0.63 yr^{-1}) comparable to benzene plumes. TBA plumes were shown to be of similar length and attenuating at comparable rates as MTBE and benzene plumes. The primary difference was that the percentage of TBA plumes that were currently stable or shrinking (68%) was less than the percentages of benzene (95%) and MTBE (90%) plumes that were shrinking. The latter observation was attributed to the temporary accumulation of TBA resulting from MTBE biodegradation. For ethanol plumes, there are several studies that document that ethanol can contribute to longer benzene plumes due to preferential utilization and depletion of dissolved oxygen[50-52]. A modeling study demonstrated that this may be partially offset by an increase in biomass growing on the ethanol, such that the lifetime of the BTEX plume may be lower[53].

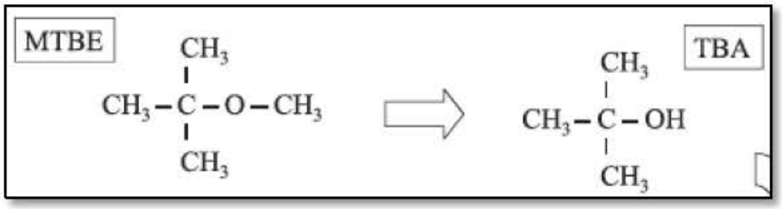


Results of groundwater plume stability analysis for MTBE, TBA, and Benzene at 48 site study[49]

I can apply MNA to BTEX, but how about oxygenates? (Page 3)

Research Summary

Much of the focus of fuel oxygenate attenuation has been on MTBE biodegradation mechanisms, where TBA is a key daughter product. Key research findings are summarized below.



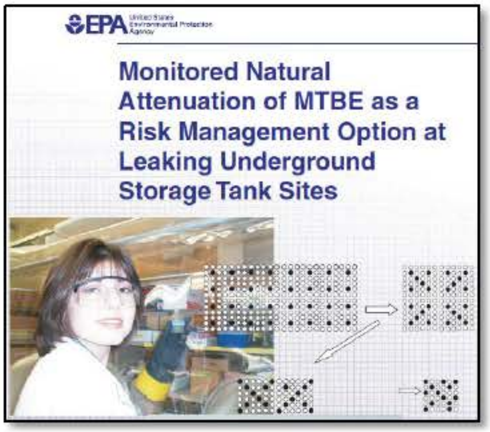
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 \Longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

MTBE Degraders. A large number of native aerobic organisms have been identified that degrade MTBE and TBA either as a sole carbon source or in the presence of co-substrates. Early difficulties in isolating specific degrading organisms have been largely overcome in the past decade, though anaerobic degraders remain elusive[54]. Acclimation to the presence of MTBE (i.e., time elapsed since release) appears to be key in ensuring that a viable population can be developed[3].

TBA can be Parent or a Daughter. MTBE degradation generally proceeds through an oxidative pathway that can generate TBA as an intermediate[55]. However, since TBA was often part of reformulated gasoline, its presence is not a conclusive indicator of MTBE biodegradation. TBA can also be biodegraded under the same conditions as MTBE (though not necessarily by the same organisms), such that a decreasing MTBE to TBA ratio is not always reliable evidence for biodegradation[25].

Aerobic or Anaerobic? Both MTBE and TBA degrade readily aerobically. Anaerobic biodegradation of MTBE and TBA has also been established, an important consideration given that at least part of most MTBE plumes are anaerobic[3]. However, degradation is not always easy to demonstrate at the field level[29]. A readily available pool of electron acceptors (e.g., sulfate, iron, manganese) appears to be one prerequisite for TBA degradation under anaerobic conditions[29], while the initial attack on MTBE can occur under deeply anaerobic (methanogenic) conditions and thus does not require external electron acceptors.

Use Ratios to Demonstrate MNA? Concentration trends (e.g., source attenuation, plume stability) are likely to be better indicators of natural attenuation than MTBE/TBA ratios and should be used to guide expectations for MNA[3, 29]. Because microbial activity can be dependent on spatially variable electron acceptor fluxes, any assessment of plume attenuation should account for the resulting spatial variability in activity (which may require higher-resolution characterization than might otherwise have been performed)[56].



EPA United States Environmental Protection Agency

Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites

I can apply MNA to BTEX, but how about oxygenates? (Page 4)

Molecular Tools. Molecular biological tools (See FAQ 12) have been developed to identify the presence of MTBE/TBA degraders and functional genes in environmental samples. A common focus is on *Methylbium petroleiphilum* PM1 and closely-related aerobic MTBE and TBA degraders [57].

CSIA. Compound-specific isotope analysis (see FAQ 11) to document MTBE and TBA biodegradation and abiotic degradation is well-established[58-61], and field applications of this approach can provide strong supporting evidence for the selection of MNA[62]. Similarly, stable isotope probing (i.e., the introduction of target contaminants that are specifically enriched in ^{13}C) has been used successfully to document that MTBE and TBA have been degraded and incorporated into biomass[63].

Summary of Oxygenate Degradation

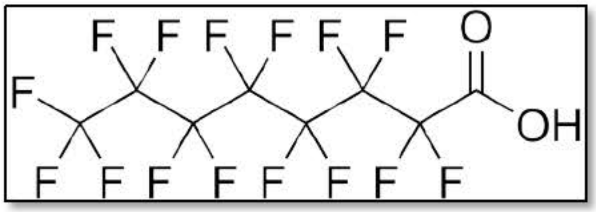
The following table summarizes the relative effectiveness of several different types of *in situ* attenuation processes for fuel oxygenates. The Yes/No assessments are based on the assumption that there are no limiting factors for a particular attenuation mechanism (e.g., oxygen is readily available for aerobic biological degradation). The list does not include non-destructive physical attenuation processes such as diffusion, dispersion, and advection. Sorption is included as a sequestration process.

Contaminant Class	Biological Degradation		Abiotic Degradation	Sequestration
	Anaerobic	Aerobic		
MTBE	**YES** (may require acclimation period)	**YES**	*Limited* (acid hydrolysis, abiotic reduction)	**No**
TBA	**YES** if electron acceptors are readily available(may be limited in methanogenic conditions)	**YES** (generally faster than in anaerobic conditions)	**No** (no available evidence)	**No**
Ethanol	**YES** (tends to be preferentially degraded over BTEX)	**YES** (tends to be preferentially degraded over BTEX)	**No**	**No**
TAME	**YES**	**YES**	**No**	**No**
DIPE	**No**	**No**	**No**	**No**

FAQ 10. Which emerging contaminants are MNA candidates?

Dioxane, TCP, NDMA, Phthalates, and Maybe Others

The Department of Defense (DoD) has an Emerging Contaminants Program to "identify chemicals or materials that either lack human health standards or have an evolving science and regulatory status"[64]. This definition includes largely unregulated compounds whose risks have only recently been recognized, and previously-regulated compounds which will likely have stricter regulatory standards in place due to an improved basis for setting those standards. In addition to this evolving list of compounds on the DoD's list, other compounds that are often placed into the emerging contaminant category include 1,4-dioxane and various perfluorinated compounds (perfluorooctanoic acid (PFOA), perfluorootanesulfonic acid (PFOS). (Note this list is very subjective).



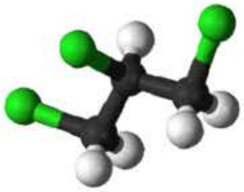
PFOA

MNA and Emerging Contaminants

At some sites with emerging contaminants, MNA has been an important component of the management strategy, for the simple reasons that: i) their prevalence at a particular site has not been well-documented; or ii) any decision about implementing active remedies has been put on hold in the absence of proven and cost-effective treatment technologies. The following table summarizes the potential effectiveness of several different types of *in situ* attenuation processes for selected emerging contaminants. The data gaps illustrated in this list are a focus of intense ongoing research. Next-generation tools (CSIA – see FAQ 11, MBTs – see FAQ 12) are largely undeveloped for these compounds as of 2013.

Note that this table on the next page does not include several other compounds considered emerging contaminants by DoD that were part of categories already described in FAQ 8 and FAQ 9, including perchlorate and various metals. Attenuation processes for most of these compounds have been studied extensively. The real question will be whether or not there is sufficient natural attenuation capacity to achieve the stricter cleanup objectives that are expected to be adopted for these compounds in the near future.

1,4-TCP



1,4-Dioxane

Which emerging contaminants are MNA candidates? (Page 2)

Potentially relevant attenuation processes for selected emerging contaminants

Emerging Contaminant	**Biological Degradation**		Abiotic Degradation	Sequestration
	Anaerobic	Aerobic		
1,4-Dioxane	*Limited* [65, 66]	**YES** (mostly lab studies; can be cometabolic or used as a carbon source)	*Not documented*	**No** (poor sorption)
Perfluorinated Compounds	*Very limited* (incomplete pathway)	*Very limited* (incomplete pathway)	*Limited* (a reliable light+Fe(III) reaction has been established)	*Moderate* (primarily electrostatic sorption to ferric iron minerals; limited organic carbon sorption)[67]
Nanomaterials	Varies	Varies	Varies	Varies
Phthalate Esters	**YES** (generally slower than in aerobic conditions)	**YES**	*Very limited* (hydrolysis)	*Varies* (strong sorption for higher molecular weight compounds)
N-Nitrosodimethylamine (NDMA)	**YES**	**YES** (cometabolic)	**No** *(several ex situ methods, including UV photolysis)*	**No** (poor sorption)
1,2,3-Trichloropropane	**YES** (slow, often incomplete pathway)	**YES** (slow, incomplete pathway)	*Very limited* (reactive iron, base hydrolysis)	*Limited* (moderate sorption)
Beryllium	**No**	**No**	**No**	**YES** (sorption, co-precipitation)
Chlorinated Pesticides (e.g., lindane, DDT, 2,4-D, atrazine, chlorpyrifos)	*Varies* (higher rates generally associated with compounds with poor sorption; some incomplete pathways)	*Varies* (higher rates generally associated with compounds with poor sorption; some incomplete pathways)	Varies (hydrolysis, reactive iron, sulfides)	Varies (some exhibit strong sorption)

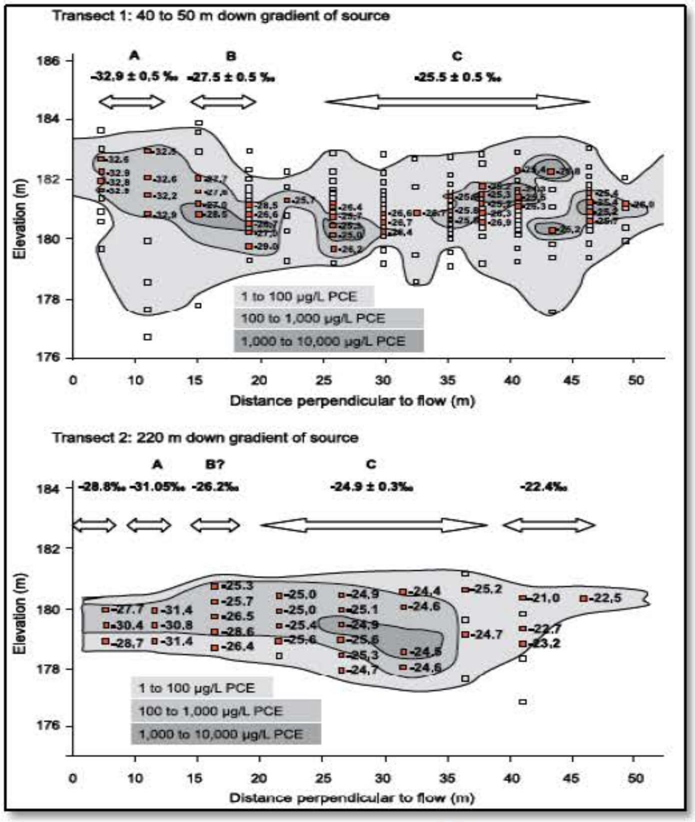
FAQ 11. Can isotopes prove contaminants are being destroyed?

Yes, and More

"Stable isotope analyses can provide unequivocal documentation that biodegradation or abiotic transformation processes actually destroyed the contaminant."[5]. This makes Compound-Specific Isotope Analysis (CSIA) a valuable line of evidence for many MNA projects[68, 69].

CSIA relies on measuring the ratio of stable isotopes of selected elements within a compound. For example, ^{12}C is the most common carbon isotope in naturally-occurring compounds but a small fraction of the heavier ^{13}C will also be present. The ratio between the heavier and lighter isotopes of a newly-synthesized compound can change over time after it is released to the environment and is subjected to attenuation processes. Processes, most notably biotic and, to a lesser extent, abiotic degradation, preferentially degrade compounds containing lighter isotopes (a phenomenon known as the kinetic isotope effect). As a result, the remaining non-degraded compound becomes enriched in the heavier isotope.

Collectively, this enrichment is referred to as isotopic fractionation. One or more isotopic ratios can be analyzed within samples, including carbon ($^{13}C/^{12}C$), oxygen ($^{18}O/^{16}O$), nitrogen ($^{15}N/^{14}N$), chlorine ($^{37}Cl/^{35}Cl$), and hydrogen ($^{2}H/^{1}H$). By convention, the isotopic ratio for an element is expressed relative to a reference standard on a "per mil" (parts per thousand or ‰) basis. This value is referred to as delta (δ) or "del" for a given sample, and increases in del are associated with enrichment in the heavier isotope. Within most environmental samples, a suite of compounds are analyzed to evaluate isotopic ratios in both parent and by-product compounds.



Concentrations and carbon isotope ratios of PCE in two transects downgradient of unidentified PCE sources. All values are given in ‰ relative to the V-PDB standard. Filled squares are depths sampled for determination of both concentration and $\delta^{13}C$. Open squares are depths sampled for concentration only. The figure is modified after[70] *(from* [5]*)*

Can isotopes prove contaminants are being destroyed? (Page 2)

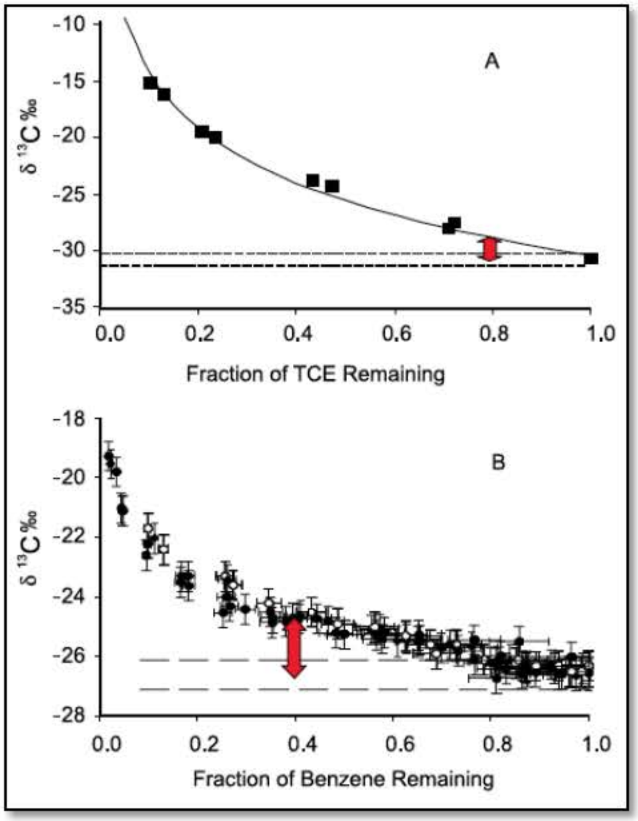
Key Benefits of CSIA

Demonstrating that a parent compound is being degraded. Most subsurface contaminants have initial isotope ratios that fall within a known range, and isotope ratios in environmental samples can be compared to these reported values (or the value for the free product, if available). Observations of fractionation—signified by larger del values in environmental samples relative to the original—are conclusive proof that degradation of the parent compound has occurred. Evidence for fractionation can be demonstrated using both temporal and spatial patterns in isotopic data.

Differentiating between destructive and non-destructive pathways. Non-destructive processes such as dilution, volatilization, and sorption can lead to decreases in contaminant concentrations, but evidence for destructive processes is generally desired to support the selection of MNA[14]. CSIA provides this direct evidence by exploiting the fact that destructive processes such as biotic and abiotic degradation lead to isotopic fractionation while little fractionation is observed as a result of non-destructive processes with some key exceptions[71].

Differentiating between various destructive pathways. Even among destructive attenuation pathways, there are differences between the degree of isotopic fractionation that occurs for various elements. The degree of isotopic fractionation that occurs during degradation is often described using the Rayleigh model. Simply, the change in the isotopic ratio relative to a source compound over time is proportional to the change in concentration, and the proportionality can be expressed as an isotopic enrichment factor (ε). The ε value associated with a particular reaction is relatively distinct from other reactions, and thus can help identify the dominant pathway. This includes distinguishing between:

- *biological and abiotic degradation pathways*[e.g., 83]
- *aerobic vs. anaerobic biological processes*
- *different aerobic processes*

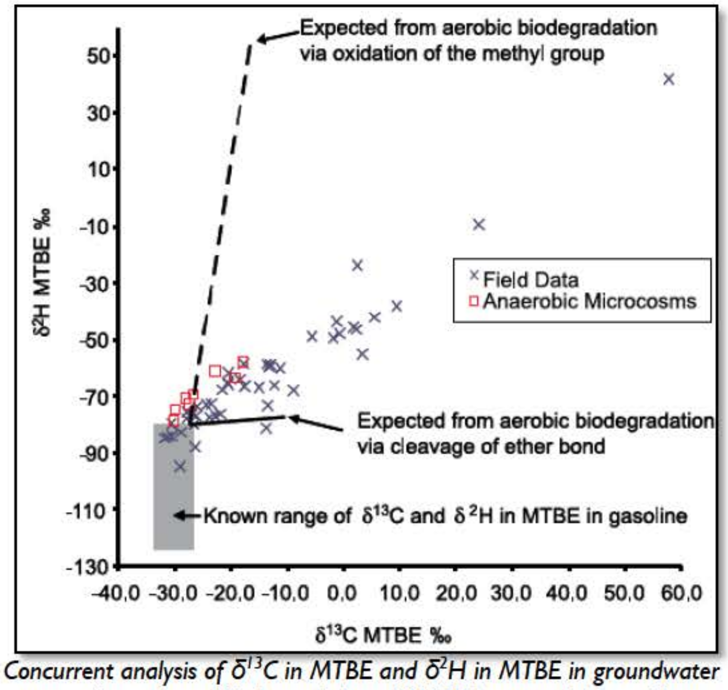


Degradation of (A) TCE and (B) benzene by enrichment cultures. The stable carbon isotope ratios in the substrate that remains after biodegradation are plotted against the fraction of the original concentration remaining. Data for TCE degradation are after Sherwood Lollar et al. [72] *and for benzene after Mancini et al.* [81]. *Dotted lines represent ± 0.5 ‰ around the* $\delta^{13}C0$ *value of TCE and of benzene, respectively. The vertical solid red arrow represents the extent of fractionation necessary to recognize biodegradation in field data (2‰)* [5].

Can isotopes prove contaminants are being destroyed? (Page 3)

Identifying various degradation pathways using CSIA requires that the extent of degradation along a flowpath can be estimated with some confidence. In many cases, there may be insufficient resolution using a single element isotope ratio. Analyzing the isotopic ratios of two different elements (i.e., 2-D CSIA) may be required[74-78]. 2-D CSIA has been done for MTBE ($\delta^{13}C/\delta^{2}H$), benzene ($\delta^{13}C/\delta^{2}H$), explosives ($\delta^{18}O/\delta^{15}N$), and chlorinated solvents ($\delta^{13}C/\delta^{37}Cl$)[59, 60, 73, 75-76, 79-82]. More recently, CSIA is being combined with reactive transport modeling to help discern different degradation pathways and distinguish destructive attenuation and dilution[68]. Pathway identification is an important consideration for MNA because it can be a direct explanation of the key reactions and explain why MNA is working.

Estimating the extent of degradation. As described above, the Rayleigh equation is applied to most reactions that result in fractionation, such that the changes in concentration are related to change in the isotope ratios by a constant known as the enrichment factor. If the dominant reaction pathway is known, then either literature or lab-derived ε values can be used to estimate the fraction of parent compound remaining (f) using the Rayleigh equation. For the purposes of demonstrating natural attenuation potential, these CSIA-based estimates of the extent of degradation are likely to be more conservative than those obtained using concentration changes because the latter includes the influences of non-destructive processes[60].



Concurrent analysis of $\delta^{13}C$ in MTBE and $\delta^{2}H$ in MTBE in groundwater to associate natural biodegradation of MTBE in groundwater with an anaerobic process that allows the selection of an appropriate value for the enrichment factor (ε) used to estimate the extent of biodegradation of MTBE[5]

Demonstrating that complete degradation has occurred. Because molecules containing lighter isotopes are preferentially degraded, by-products start out with isotopic ratios that are more negative than the parent compound. However, fractionation of degradation byproducts is not conclusive evidence that they are also being degraded. If a byproduct is not subject to further degradation, then their delta value will approach the initial isotope ratio of the parent as degradation of the parent proceeds. For a case where *cis*-1,2-DCE is the analyte, this pattern would be evidence of incomplete reductive dechlorination pathway. This would raise concerns about potential *cis*-1,2-DCE "stall" and might push the remedy selection process towards bioaugmentation as opposed to MNA and/or biostimulation alone. On the other hand, if the measured delta value of the byproduct is higher than that of the parent compound, then this is conclusive evidence that the byproduct is degrading (and possibly at a faster rate than the parent compound is being degraded).

Can isotopes prove contaminants are being destroyed? (Page 4)

Estimating the rate of degradation. Because estimating the extent of degradation using CSIA data is based on an understanding of the relationship between fractionation and concentration, the rate of degradation can also be estimated using the same basic principles (i.e., the Rayleigh model). A first-order rate coefficient is estimated as the difference between the del value of the source and the del value at a later time (or travel distance) divided by the product of the isotope enrichment factor (ε) and the elapsed time (or travel distance). This approach has been successfully applied in field studies for compounds such as PCE[84], *cis*-1,2-DCE[85], and MTBE[86]. The latter study found that first-order MTBE degradation rate constants estimated using isotopic data were nearly identical to rate constants estimated using concentration changes.

Well	MTBE (µg/L)	δ^{13}C MTBE (‰)	Fraction MTBE Remaining (C/C_o)	Distance from MW-14 (meters)	Rate of Degradation with Distance (per meter)	Rate of Degradation with Time (per year)
MW-14	28,800	-21.6	0.67	0		
MW-3	174	8.5	0.085	9.6	0.26	9.4
MW-8	21	38.0	0.0113	11.7	0.38	14.1
MW-7	114	-27.3	0.995	23.0	0.00021	0.0077
MW11	334	-28.9	1.11	44.1	0	0
				Distance from Dispenser Island (meters)		
MW-6	612	-1.6	0.171	31.1	0.057	2.1

Rates of natural biodegradation of MTBE in groundwater moving along a flow path to monitoring wells. The rates were calculated from the estimated seepage velocity of ground water and the fraction of MTBE remaining after biodegradation[5]

Source identification and differentiation. The isotopic ratios of two or more different contaminant sources may be sufficiently distinct to differentiate between them. In cases where extensive degradation is suspected or established, the use of a second or third element isotopic ratio can be a useful (and even necessary) complement. When a 2-D plot is created (i.e., del C on the x-axis vs. del H on the y-axis), samples from one source may cluster together in a different area than samples from a second source. While source differentiation may not provide support for implementing MNA, it certainly aids in developing an appropriate conceptual model and site management strategy.

All of the above approaches are consistent with the tiered lines of evidence approach required by the various MNA protocols (e.g., 16). Perhaps most relevant is evidence of actual degradation that is also quantitative in the sense that the data can be used to estimate the rate of degradation. For this reason, CSIA data can replace more time-consuming methods such as microcosm studies for many problems. Alternatively, Stable Isotope Probing (SIP, see FAQ 12)—a permutation of CSIA that

Can isotopes prove contaminants are being destroyed? (Page 5)

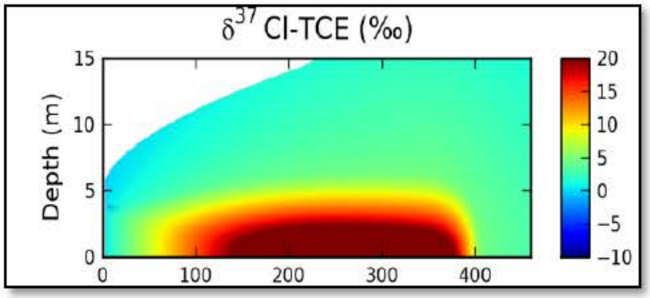
incorporates biomolecular analyses—can be used in an *in situ* microcosm to generate additional degradation data. CSIA is also useful when conventional approaches to establishing plume stabilization/shrinkage are hampered by limited or confusing historical groundwater monitoring data. Finally, CSIA data can be particularly valuable when existing chemical or geochemical data are difficult to integrate into a site conceptual model. For example, the lack of ethene production in conjunction with *cis*-1,2-DCE and VC disappearance could be tied to the predominance of an aerobic oxidation pathway[87] or even to several ethene degradation processes[88], both of which have been established using CSIA techniques.

Commercial laboratory services for CSIA exist but are currently fairly limited; several research laboratories have expertise and may be contracted on a case-specific basis. For this reason, costs can vary widely depending on the number/type of isotopes and compounds being analyzed. While the technology matures, sources for information on sampling and analyses procedures (including QA/QC procedures) are mostly confined to guidance documents such as USEPA's 2008 manual[5]. Note that CSIA is most widely used for organic contaminants but has applicability for many inorganics such as perchlorate[89] and NO_3^-[90] and metals such as chromium[91] and selenium[92]. In theory, chemical transformation should result in some isotopic fractionation regardless of the target compound. The question is whether the extent of fractionation for a particular isotope is significant enough to be measured. This concern is particularly important for high molecular weight compounds, where fractionation of an individual atom at the location of bond breakage may be masked by the presence of multiple copies of that atom at other locations within the molecule.

Modeling and CSIA

There are some factors that can make CSIA data hard to interpret: 1) isotope effects differ between biotic and abiotic processes, as well as among different microbial consortia; 2) for compounds that are reaction intermediates, (e.g., *cis*-1,2-DCE formed in the reductive dechlorination pathway), the observed isotope effect is a function of simultaneous generation and degradation of the compound, not simply of degradation, creating problems in applying the Rayleigh model directly; 3) the Rayleigh equation was written for a closed system, and it does not translate well to complex flow-through hydrogeological settings; and 4) commingling of inputs from multiple sources of the contaminant complicate interpretation of CSIA results.

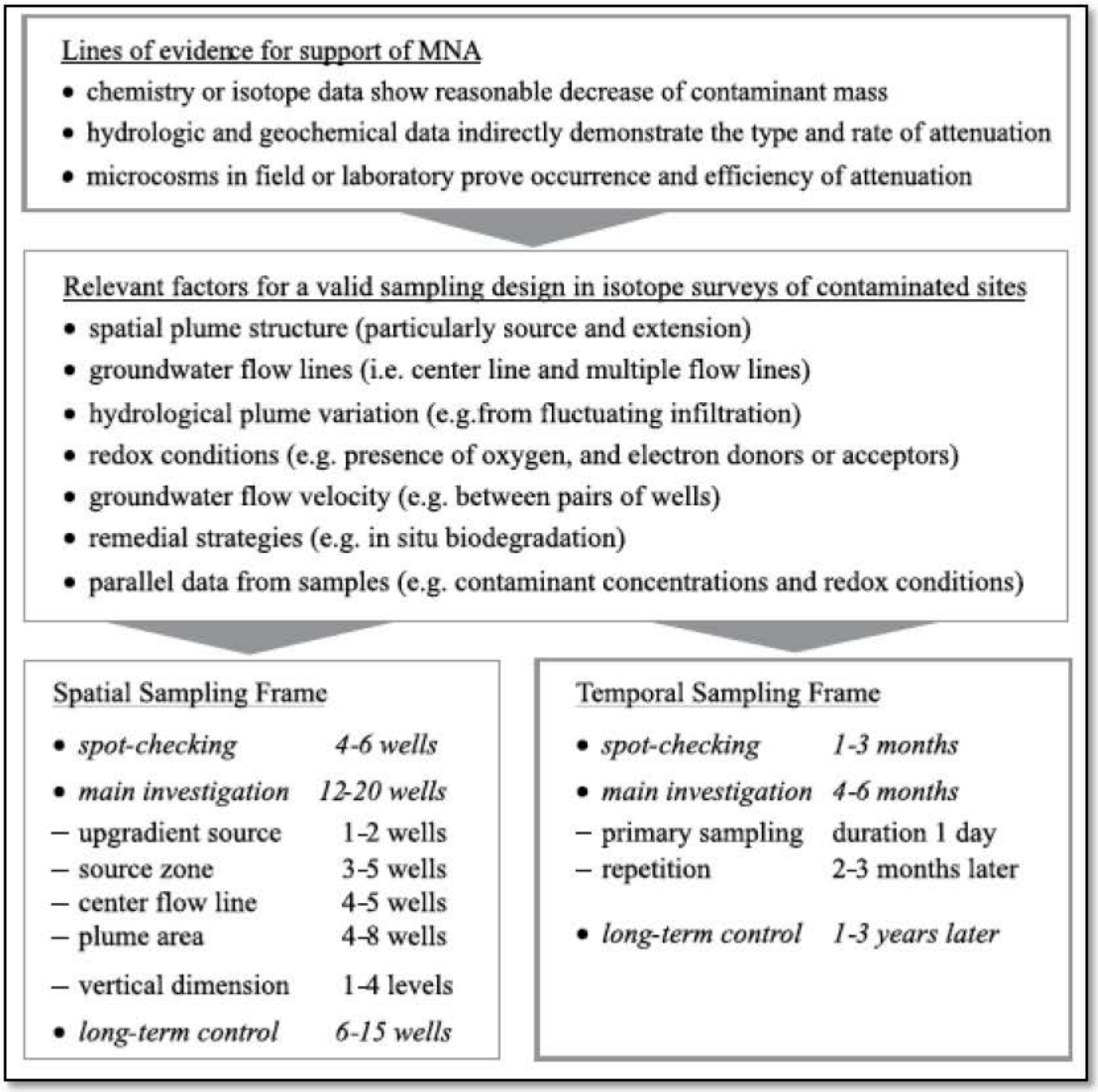
An ongoing ESTCP-funded project is proposing a "Generation 3" approach with two main enhancements[92, 94]. First, instead of focusing solely on carbon isotopes, isotope data from multiple elements (i.e., chlorine and hydrogen) are used together with carbon isotope data. Second, instead of just plotting the data in $\delta^{13}C$ vs. distance-from-source graphs, the data are entered into a Reactive Transport Model (RTM) such as PHREEQC. The inclusion of the reactive model helps isolate processes that result in mass destruction, transport of parent and daughter products and estimates of the timeframe of remediation. This graphic is a preliminary product from this research.



Can isotopes prove contaminants are being destroyed? (Page 6)

Sampling for CSIA

The USEPA recommends the approach shown in the graphic below for developing a spatial and temporal sampling design for CSIA surveys to evaluate MNA[5]. In this case, *"the number of wells are offered as an example for an optimal study of contamination in a single aquifer. The design of a real survey should be adapted to the specific conditions at the site."*



Lines of evidence for support of MNA

- chemistry or isotope data show reasonable decrease of contaminant mass
- hydrologic and geochemical data indirectly demonstrate the type and rate of attenuation
- microcosms in field or laboratory prove occurrence and efficiency of attenuation

Relevant factors for a valid sampling design in isotope surveys of contaminated sites

- spatial plume structure (particularly source and extension)
- groundwater flow lines (i.e. center line and multiple flow lines)
- hydrological plume variation (e.g.from fluctuating infiltration)
- redox conditions (e.g. presence of oxygen, and electron donors or acceptors)
- groundwater flow velocity (e.g. between pairs of wells)
- remedial strategies (e.g. in situ biodegradation)
- parallel data from samples (e.g. contaminant concentrations and redox conditions)

Spatial Sampling Frame

• *spot-checking*	*4-6 wells*
• *main investigation*	*12-20 wells*
– upgradient source	1-2 wells
– source zone	3-5 wells
– center flow line	4-5 wells
– plume area	4-8 wells
– vertical dimension	1-4 levels
• *long-term control*	*6-15 wells*

Temporal Sampling Frame

• *spot-checking*	*1-3 months*
• *main investigation*	*4-6 months*
– primary sampling	duration 1 day
– repetition	2-3 months later
• *long-term control*	*1-3 years later*

FAQ 12. How can molecular biological tools help me with MNA?

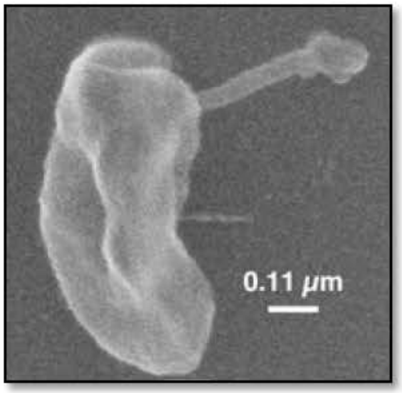
MBTs Provide Strong, But Not Definitive Evidence of MNA

New molecular biological tools (MBTs) provide strong evidence of contaminant biodegradation to support primary lines of evidence (plume trends, geochemical conditions) at a site. This family of methods uses DNA/RNA and isotope-related techniques to:

- Show that key *organisms* are present (like *Dehalococcoides* that dechlorinate PCE to ethene);
- Show that key *enzymes* are present and potentially active (e.g., vinyl chloride reductase)
- Establish *relative abundance* of key microbial populations (e.g. *Dehalococcoides* relative to other bacteria)

MBTs are based on identifying key patterns in nucleic acids (DNA/RNA) and other biomolecules (e.g., phospholipids)[6, 95, 96] and these tools are part of the broader category of techniques referred to as Environmental Molecular Diagnostics[97] that also includes CSIA. Simple MBTs can only establish that a site has the *potential* for a particular attenuation process to occur by identifying organisms and/or microbial populations, while more refined methods attempt to document and measure the activity that is occurring. The table on the next page summarizes the key MBTs being used today for MNA.

Most Widely Used: *Dhc*. The environmental field has benefitted from adapting and refining these methods to address issues related to attenuation of contaminants in the subsurface. The primary driver has been the ongoing maturation of tools that utilize variants of the polymerase chain reaction (PCR) to identify and quantify biomarkers of key microbes and/or enzymes known to mediate desired biodegradation reactions. The use of these techniques to identify *Dehalococcoides* (*Dhc*)—which is still the only group of microbes known to completely dechlorinate PCE and TCE to ethene—is almost certainly the most widely-used. While *Dhc*-containing cultures have occasionally proved finicky to maintain as part of lab-based assays, *Dhc* target genes are readily detectable in soil and groundwater using PCR techniques. For these reasons, nucleic acid-based tools and other tools (CSIA) have largely supplanted the microcosms prescribed in early MNA protocols.



Dehalococcoides SEM images by the late Dr. Robert P. Apkarian and Jeanette Taylor, at the Integrated Microscopy & Microanalytical Facility (IM&MF), Department of Chemistry, Emory University, Atlanta, GA

How can molecular biological tools help me with MNA? (Page 2)

Tool	Description	MNA Application	MNA Limitations
PCR /quantitative PCR (qPCR) /Reverse Transcriptase PCR	DNA or RNA within environmental sample (soil or GW) is extracted and screened for biomarker-specific target sequences during amplification process to determine if those biomarkers are present; qPCR uses fluorescent probes to establish abundance (in gene copies per mL or liter or gram)	• Identify if key organisms / enzymes (including complete degradation for some pathways) are present and in sufficient abundance to support MNA (e.g., > 10^6 *Dehalococcoides* gene copies per L has been cited as associated with high rates of ethene formation)[6]. • Determine if abundance of key biomarkers is increasing/sustainable during monitoring period, particularly after biostimulation is performed	• Many techniques cannot differentiate between live and inactive cells (exception: Reverse Transcriptase-PCR) • Attempts to correlate in situ activity and gene expression still in infancy • Target mostly well-known pathways (others in development)
Microbial Fingerprinting Techniques	Several different methods that provide snapshot of microbial community and diversity through identification of characteristic biomarkers; includes phospholipid fatty acid (PLFA) analyses; denaturing gradient gel electrophoresis (DGGE), and terminal restriction length fragment polymorphism (T-RFLP)	• Establish relative abundance of multiple types of organisms under natural conditions • Can help determine if conditions are favorable for attenuation	• Not necessarily quantitative (DGGE, T-RFLP) • May not identify all organisms present (PLFA) • Interpretive and exploratory in nature
Stable Isotope Probing	Compounds enriched in certain isotopes (^{13}C, ^{18}O, ^{15}N) are used as baits in in-well passive samplers; incorporation of heavy isotope into biomass over time is measured as evidence of growth via compound degradation[98]	• Establish if degradation is occurring without requiring prior knowledge of organisms/enzymes responsible • Provides information on attenuation rates (within the sampler) through incorporation/loss of mass label over time • Potential in situ replacement for microcosms	• Attenuation rates not representative of actual field attenuation rates (e.g., due to preferential growth conditions within in-well passive samplers) • Currently only for compounds that serve as carbon or energy sources (e.g., petroleum hydrocarbons, MTBE) and not chlor. solvents, perchlorate, metals • Extended incubation • High concentrations during deployment may not provide good data for evaluating dilute plume conditions

How can molecular biological tools help me with MNA? (Page 3)

Tool	Description	MNA Application	MNA Limitations
Enzyme Activity Probes	Surrogate substrates are used as reporters to establish that enzymes capable of degrading target contaminant are present	• Direct evidence that target enzyme is present and active • May provide information on attenuation rates	• Little information on whether attenuation rates can be extrapolated to field rates • Limited commercial availability • Current portfolio of EAPs is relatively small • Surrogates may be regulated compounds
Microarrays	Rapid simultaneous screening of large number (>1000) of biomarkers using DNA probes attached to a solid matrix; DNA from environmental sample will bind to complementary DNA probes to establish presence of specific organism/activity	• Comprehensive screening of presence of organisms and key processes under natural conditions (and over time) • Establish if attenuation is occurring (using functional gene array) • Identify competing processes	• Semi-quantitative • Utility is still being established • Not well-developed for chlorinated solvents

See [6] for additional tools

Quantitative Rules for MNA. The use of MBTs to document biological reductive dechlorination has advanced to the point that there are quantitative-based recommendations on how the data can be used to evaluate MNA as a potential stand-alone remedy. One study demonstrated that "generally useful" attenuation rates of *cis*-1,2-DCE and VC (> 0.3/yr based on changes in concentration along groundwater flow path) were associated with sites where DHC was detected, while no attenuation was observed at sites where it was absent.[99]

A recent ESTCP-funded protocol[6] states that

- *Dhc* at 10^4 to 10^6 gene copies/L can support MNA
- *Dhc* at > 10^6 gene copies/L is the target threshold for ensuring ethene production.

The development of MBTs that target functional genes (e.g., vinyl chloride reductase) has overcome uncertainty associated with identity-based methods. As concluded in the protocol[6]:

> *"Although DNA-based tools cannot provide direct evidence for activity, temporal measurements of Dhc target gene abundance can serve as an indirect activity measure because Dhc can only increase in numbers when performing reductive dechlorination reactions".*

This approach represents a bridge as attempts to quantitatively link the expression of dehalogenase genes (through measurement of mRNA or proteins) remains a focus of ongoing research. Use of MBTs providing a more direct measure of activity is particularly important for verifying the performance of bioremediation projects.

How can molecular biological tools help me with MNA? (Page 4)

Other MBTs. Although MBTs focusing on anaerobic degradation of chlorinated solvents remain the most widely-applied, MBTs are available for documenting a variety of attenuation processes for many other contaminants. Methods that focus on petroleum hydrocarbons [100], fuel oxygenates such as MTBE[57, 101], energetics[102, 103], and perchlorate[104, 105] have been established. Identifying and quantifying biomarkers of aerobic degradation of chlorinated solvents has been a goal of several studies (e.g., 106, 107) and the development of these tools has relevance for documenting natural attenuation potential in large dilute plumes that are often dominated by aerobic zones (see on-going ESTCP project [108]).

Getting the Data. Several commercial laboratories offer services related to MBTs, particularly for the PCR-based methods for identifying degradation potential. This availability means that practitioners no longer have to rely exclusively on research laboratories to obtain data. While university and federal labs remain leaders in developing new techniques, the transition to commercialized services has several advantages:

- Analyses are being performed under lab-specific standard operating protocols. There is significant ongoing work on developing standardized QA/QC procedures for MBTs ([109]).
- Data are produced within predictable timeframes and costs. With these techniques, data can be obtained within several weeks. Current costs typically start at the mid $200s per sample for identifying/quantifying a single biomarker. Tests aimed at characterizing microbial communities (e.g., fingerprinting, arrays) are slightly higher. Stable isotope probing is typically more expensive since it requires additional well materials and analyses, while generally providing a higher level of data density per location being characterized.

Regulatory Acceptance. The acceptance of MBTs among the regulatory community has coincided with the establishment of more standardized methods. The data provided by these tools is considered as strong indirect evidence for destructive attenuation processes based on USEPA's MNA protocol[14]. In addition to federal agency support of the use of MBTs, states are beginning to include MBTs in the published guidance on MNA[e.g.,185]. The general recommendation is that MBTs should be considered to complement more traditional lines of evidence (plume trends, geochemical conditions), especially if there is any uncertainty in these primary data.

Much MBT-focused guidance has been published or made available in the past several years that summarize key principles and applications. It is important to note that many practitioners and regulators have little or no training in the underlying fundamentals for MBTs, and understanding how to best use the data requires some technical expertise. Consequently, these MBT guidance documents are particularly valuable for ensuring that data are used appropriately. As next-generation tools are developed—those that focus on gene expression, peptides, proteins, and other biomarkers—continued documentation is critical to ensure technology transfer.

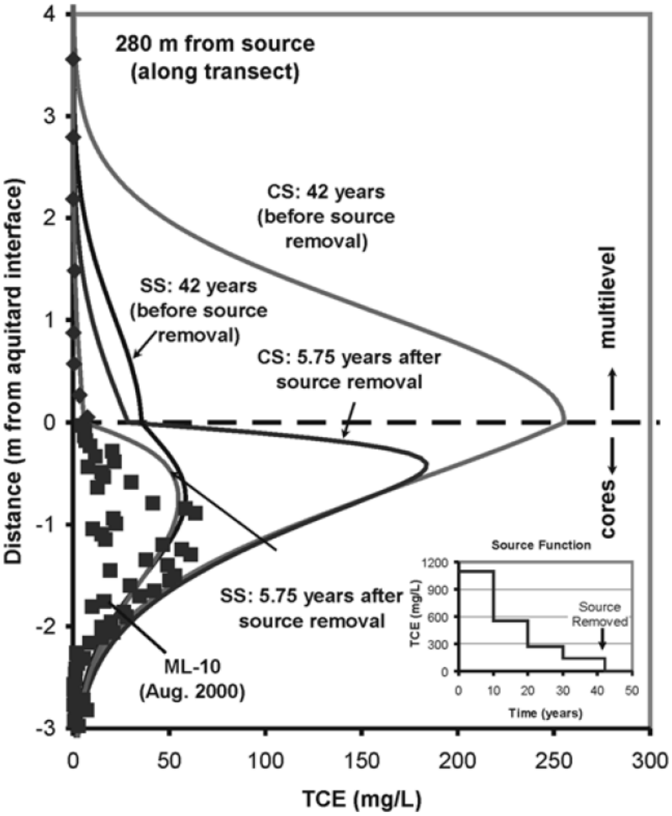
FAQ 13. How can you show attenuation that occurred before the start of your monitoring program?

By Using Clay Diffusion Profiles or Tree Rings

The most common line of evidence used for evaluating MNA is historical trends in contaminant monitoring data, with positive evidence being the loss of contaminant mass and/or plume stabilization. However, the length of these monitoring records may be relatively short at many sites, covering perhaps a few years and only rarely extending to the time when releases occurred. Given the natural variability in groundwater monitoring data (see FAQs 18 and 19), these limited temporal records may be insufficient for establishing decreasing concentration trends that would support use of MNA, or to demonstrate long-term source zone attenuation (FAQ 7).

There are two innovative characterization methods that, in some cases, can look back into time, even before groundwater monitoring started. These methods involve collecting high-resolution data in a diffusion-based medium (either from trees or low permeability zones) to reconstruct a concentration history at that point. Two such methods are:

"Source History" Using Low Permeability Zone Soil Data. This method makes use of the contaminant mass that has migrated (via diffusion and slow advection) into and out of low permeability geologic strata within a source zone or plume (see FAQ 20) during the period following release[110,111]. Detailed, high-resolution soil concentration profiles within the low permeability zones are obtained and serve as "fingerprints" of the source loading (concentration vs. time) extending back to the origin of the source.



Example of source history derived from coring an aquitard.[111] *The soil profile from the silty clay interval (black squares) is used to estimate the concentration vs. time in the overlying aquifer. Four different inputs to a 1-D diffusion model were used to make the four solid lines: CS is "constant source", and SS is a "Stepped Declining Source". The concentration history shown as an inset resulted in the best simulated match to the data, and is labeled "SS: 5.75 Years after source removal." This SS starts out at near solubility concentrations, but declines in half every 10 years* ($t_{1/2}$ *= 10 years).*

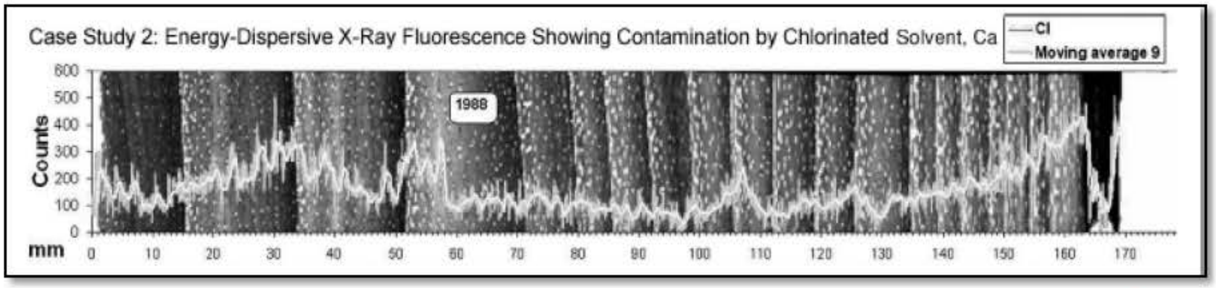
How can you show attenuation that occurred before the start of your monitoring program? (Page 2)

The shape of the soil concentration profile can be used to reconstruct this "source history" using simple analytical or more complex numerical models[112]. These methods are being demonstrated as part of an ongoing project funded by ESTCP[113], and a user-friendly source history software tool and user's guide will be released in early 2014.

"Phytoforensics" Using Tree Core Data

Trees in contact with shallow groundwater can take up contaminants during transpiration, such that accumulation of these contaminants can occur during the year(s) of exposure. As a result, the annual tree ring data can provide a quantitative indicator of changes in contaminant concentration over time[114]. The study of historic impacts on tree ring chemistry, known as dendrochemistry[115-117], is one of several "phytoforensic" methods that can rapidly generate valuable site characterization data at some sites[118]. The depth of the tree roots and depth to groundwater are very site specific, however, and this technique will not be applicable at many sites.

Dendrochemical investigations require collecting deep cores from trees that are scanned using energy diffusive x-ray fluorescence. This means that elements are quantified and used as surrogates of particular contaminants. This includes chlorine for halogenated contaminants (chlorinated solvents) and sulfur for crude oil and petroleum products. While factors such as degradation and naturally occurring variation can confound data interpretation, controls are used to better understand background patterns of targeted elements. The methodology is generally well-developed and has been applied at more than 20 sites[116, 117].



Cl^- patterns (shown on y-axis as x-ray fluorescence counts) over time in tree core (shown on x-axis in mm of core). Pattern identifies potential exposure events (releases) in 1988 and 1993/1994, along with continuing impact at date when core was collected (far right hand side)[117]

FAQ 14. Can DO measurements be a problem for MNA studies?

Yes, If Not Carefully Done

The research team for the ESTCP project entitled "Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites" is evaluating the advantages, disadvantages, and limitations of using dissolved oxygen (DO). At this point in their project, they believe the following about measuring dissolved oxygen in groundwater for MNA studies (or any type of groundwater project):

- *Oxygen partitions rapidly into water.*
- *Great care should be taken to minimize oxygen introduction by measuring at well head using a flow-through cell.*
- *Erroneous dissolved oxygen measurements are often recorded and reported which can cause misinterpretation of subsurface conditions.*
- *Measured concentrations of dissolved oxygen greater than about 1.0 mg/L, in conjunction with the presence of one or more of the following suggests erroneous dissolved oxygen measurements:*
    - *a. CAH degradation products;*
    - *b. elevated TOC/DOC, Fe(II) and/or methane concentrations;*
    - *c. negative ORP;*
    - *d. strictly anaerobic bacteria (e.g., Dehalococcoides).*
- *It is very important to note that measured and actual DO concentrations rarely coincide.*
- *DO measurements must be made by qualified and well-trained field personnel who understand the uses of these data, the potential problems associated with data collection, and how to recognize potentially erroneous measurements. Also, all recommendations made by the probe manufacturer, including calibration procedures, should be followed.*

The FAQ authors provide three additional thoughts about dissolved oxygen data for MNA studies. First, mixed aerobic/anaerobic data (for example, oxygen + methane) from a groundwater sample can be caused by mixing of groundwaters from two separate intervals with very different geochemical environments within a single monitoring well screen. The longer the well screen, the more likely this can happen. Second, one comparison of three field methods concluded that "below 1 ppm, electrodes provide only a qualitative measure of low D.O. level, apparently due to slow electrode response"[119]. Third, not all dissolved oxygen measurements are in error. If the set of wells in a site monitoring program contain a range of measurements above and below 1 mg/L, then we feel useful information can be derived from the DO data.

Dissolved oxygen probes

FAQ 15. What are CO2 traps and how do they help me show attenuation?

A New Tool for Measuring Natural Source Zone Attenuation at LNAPL Sites

Direct methods for documenting contaminant attenuation rates in the field are an important line of evidence for supporting MNA, particularly if MNA is being used to manage an active source. One powerful method that has been recently validated is the use of carbon dioxide (CO_2) traps to measure LNAPL degradation rates at petroleum hydrocarbon sites. These are simple and cheap devices that are installed at grade and specifically designed to measure natural losses of LNAPL over time. Consequently, they are well-suited to support the Natural Source Zone Depletion (NSZD) strategies for LNAPL source zones issued by ITRC[2] (see FAQ 7).

Principles. Following release, hydrocarbon constituents in LNAPL are subject to various natural attenuation mechanisms, including biodegradation. CO_2 is an effective signal of these attenuation processes because essentially all (98%) of the carbon present in LNAPL is converted to CO_2 as an end product during *in situ* degradation[120]. This includes methane generated during anaerobic degradation of petroleum hydrocarbons that is aerobically biodegraded to CO_2 following migration to the O_2-rich vadose zone. By capturing the CO_2 generated from these natural processes in the surface-deployed traps, the time-integrated CO_2 in the traps can be converted to an equivalent LNAPL loss rate (after correcting for background CO_2 flux, or alternatively, using 14C measurements to differentiate between fossil fuel and non-fossil fuel fractions).

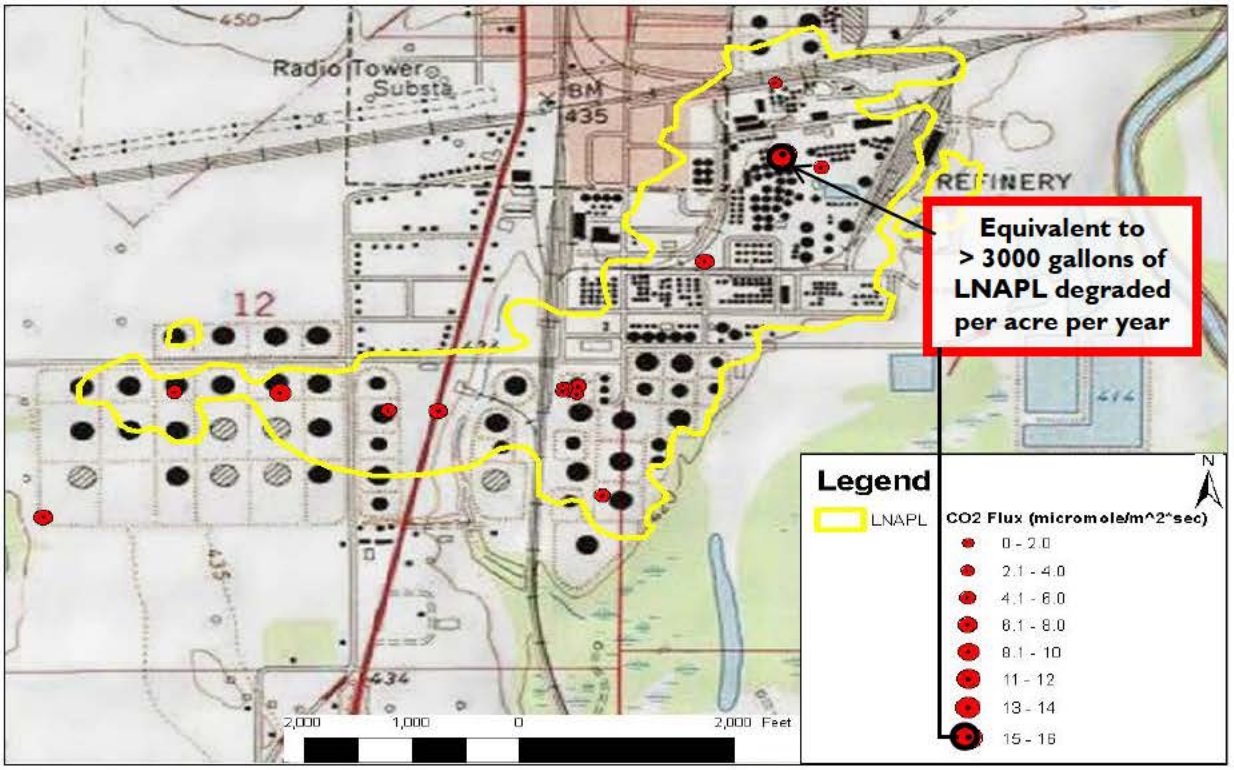
CO_2 trap developed by Colorado State University to measure LNAPL loss rates in the field [121]

How Do They Work? CO_2 traps are passive adsorption devices deployed within shallow monitoring points. They are inexpensive, easily installed (i.e., no special training of personnel), and minimally invasive. Thus, they can be deployed at multiple locations at a site to identify areas of high activity as well as to obtain a site-wide estimate of the LNAPL loss rate (after correcting for background CO_2 generation rates). The photos above show a CO_2 trap developed by Colorado State University (CSU). Similar CO_2 measurement methodologies have been tested successfully by the University of British Columbia (chamber method)[33] and Arizona State University (gradient method)[43].

What are CO_2 traps and how do they show attenuation? (Page 2)

Results from Field Tests

CO_2 traps have been deployed at multiple sites and have documented large CO_2 fluxes equivalent to 100s to 1000s of gallons of LNAPL per acre per year[121]. These loss rates are similar to those observed at sites with active remedies (e.g., hydraulic LNAPL recovery). Mahler et al. [122] have shown that these natural losses contribute significantly to LNAPL stability. Further work by the CSU research group is aimed at confirming that natural losses of LNAPL can be enhanced through self-heating mechanisms that occur during LNAPL biodegradation. Collectively, these results provide important supporting evidence for the viability of MNA as a remedy in place of source removal at LNAPL-impacted sites.



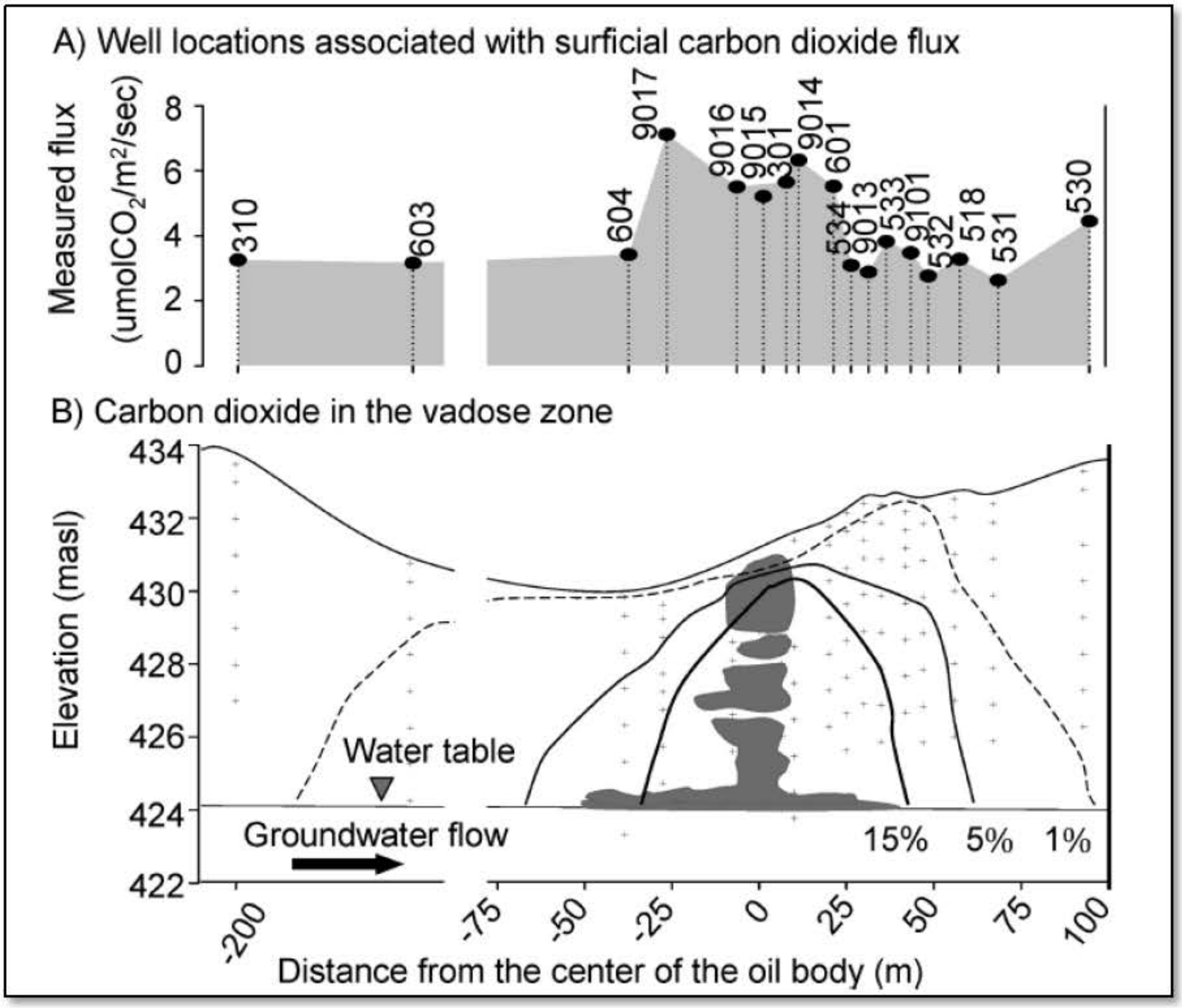
Equivalent to > 3000 gallons of LNAPL degraded per acre per year

Example of field site where CO_2 traps were used to delineate LNAPL natural loss rates. [121]

What are CO_2 traps and how do they show attenuation? (Page 3)

Results from Field Tests (continued)

The University of British Columbia research group has successfully used a dynamic closed chamber (DCC) method to measure CO_2 efflux at the surface of hydrocarbon contaminated sites. The CO_2 measured over time serves as a proxy for hydrocarbon biodegradation rates after correcting for natural soil respiration. Sihota[33] reported average hydrocarbon mineralization rates of 2.6 µmol per m^2 per sec at the Bemidji site, which is very similar to those reported at other field sites where the CSU CO_2 trap was used[121] (see previous page). These data are strong evidence that natural source zone attenuation is occurring, and demonstrate the utility of these methods in delineating hydrocarbon impacts (particularly source zones) and associated loss rates.



Surficial CO_2 efflux from a series of wells located above a crude oil spill measured using the Dynamic Closed Chamber method[33]. Lower panel shows CO_2 contours with depth within the same area.

FAQ 16. How do I estimate rates and timeframes for MNA?

By Understanding There are Different Types of Rates…

While the USEPA MNA Directive[14] prescribes "[a]t a minimum, the monitoring program should be sufficient to enable a determination of the rate(s) of attenuation and how that rate is changing with time", it does not go into detail about how to calculate the rates and what they mean. In 2002, the USEPA issued a Groundwater Issue Paper that described how to apply first-order attenuation rate calculations to MNA studies. The authors emphasized that there are three main types of rate coefficients, each with a different calculation methodology (concentration versus time, concentration vs. distance, model studies), and different uses[20]:

Table Exerted from USEPA Groundwater Issue Paper (2002) Describing First-Order Attenuation Rate Calculations[20]

Rate Constant	Method of Analysis	Significance	Use of Rate Constant		
			Plume Attenuation	Plume Trends?	Plume Duration?
Point Attenuation Rate (k_{point}, time per year)	Concentration vs. Time	Reduction in contaminant concentration over time at a single point	NO*	NO*	YES
Bulk Attenuation Rate (k; time per year)	Concentration vs. Distance	Reduction in dissolved contaminant concentration with distance from source	YES	NO*	NO
Biodegradation Rate (λ, time per year)	Model Calibration, Tracer Studies, Calculations	Biodegradation rate for dissolved contaminants after leaving source, exclusive of advection, dispersion, etc.	YES	NO	NO

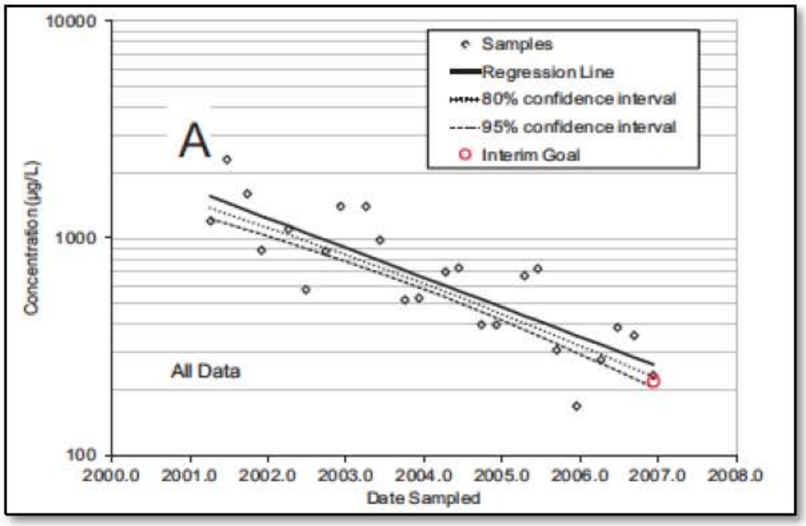
* Note: Although assessment of an attenuation rate constant at a single location does not yield plume attenuation information, or plume trend information, an assessment of general trends of multiple wells over the entire plume is useful to assess overall plume attenuation and plume trends.

Key Points About Remediation Timeframe

Projecting the remediation timeframe (or "cleanup time") was an important part of the USEPA's MNA Directive, where it was specified that MNA be able to meet site remediation objectives within a "reasonable timeframe." To implement this mandate requires two things: 1) stakeholders agreeing on what is a "reasonable timeframe"; and 2) a method to calculate the remediation timeframe. The first requirement has no firm rules or guidelines established. For the second requirement, two broad approaches are often utilized: Extrapolation or a Mass Balance Model.

How do I estimate rates and timeframes for MNA? (Page 2)

Extrapolation. Under extrapolation, a (natural log) concentration vs. time curve is constructed at the point(s) of compliance. The slope is a rate (in units of per year) called a k_{point} that can be used to estimate the duration. A k_{point} in a source zone is called a source attenuation rate or k_{source}. The USEPA has developed a simple, statistically based approach for evaluating the progress of natural attenuation, both before and after MNA is selected as a remedy[12] (FAQ 18).

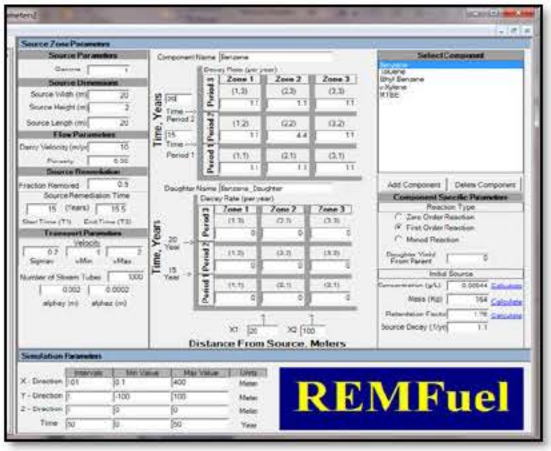


Example of extrapolation method to estimate MNA remediation timeframes with confidence limits.[12]

Use of a Mass Balance Model. Several computer tools and models can be used to estimate remediation timeframe. For example, the SourceDK software[21] is a hybrid tool, allowing the determination of timeframes through either extrapolation of monitoring data, or use of a mass balance model. Both the USEPA's BIOSCREEN and BIOCHLOR models incorporate a first-order source decay feature [22, 38]. BIOSCREEN calculates k_{source} using the relationship[38].

$$k_{source}\text{ (per year)} = \frac{\text{Mass discharge (kg/yr)}}{\text{Mass (kg)}}$$

The NAS software tool[24,123] simulates dissolution from NAPLs, and provides times of remediation. Finally, USEPA's REMChlor and REMFuel models incorporate a more general source attenuation model, allowing users to simulate various types of concentration vs. time relationships, from step functions to "long tails" that are often associated with matrix diffusion sources [124, 125, 129] (see FAQs 22 and 23).

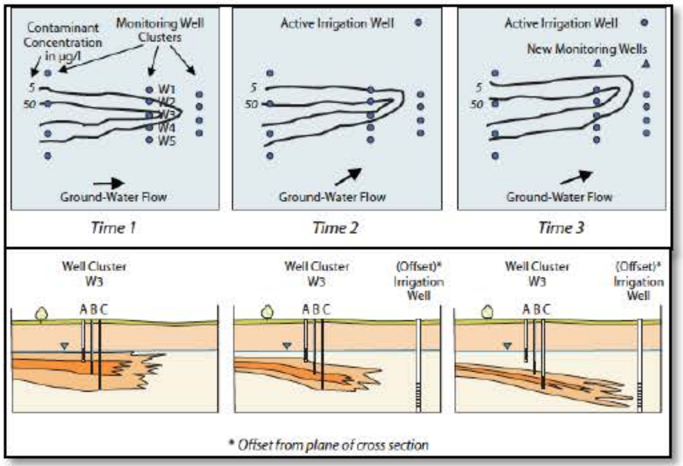


FAQ 17. What is required for MNA Monitoring?

Follow and Understand the USEPA Guidance

In 2004 the USEPA provided their "MNA Performance" guidance that explains how to design MNA monitoring systems[11]. They stress the importance of knowing why you are monitoring, and why site-specific monitoring objectives and performance criteria are needed. Key concepts for designing an MNA monitoring system are presented below, with comments from the FAQ's authors.

From USEPA Performance Monitoring of MNA [11]	*Comments from FAQ Authors*
Use transects across and through the plume, perpendicular to groundwater flow.	*There is a strong movement toward using "high resolution sampling" via transects to understand plumes and sources at all sites, including MNA sites.*
Target zone within and immediately downgradient of remediated source areas.	*The USEPA guidance doesn't address source attenuation directly in their document.*
Target transmissive zones with highest contaminant concentrations or hydraulic conductivity.	*This is one of the goals of high resolution sampling with transects – find areas of high mass flux, as these are the areas that present risk.*
Target the distal or fringe portions of the plume.	*This is important to determine plume stability.*
Monitor plume and compliance boundaries.	*Changing groundwater flow directions can change plume boundaries.*
Sample both contaminated and uncontaminated areas.	*Source zones can change the geochemical conditions, either from contaminants or from co-disposed chemicals.*
Monitor areas supporting site hydrogeology.	*They suggest using piezometers to better understand groundwater flow direction.*
Match screen length to stratigraphic unit or contaminant loading interval. Longer screens may result in artificially lower measured containment concentrations, or even lack of detections, due to mixing of water w/ different compositions.	*New thinking from the application of mass flux techniques suggests a new conceptual model: it is critical to get flow-weighted concentrations from transmissive zones that would be utilized by a receptor. This may mean long well screens.*
Be aware of changing groundwater flow directions.	*The USEPA's graphic illustrating effects of changes in groundwater flow direction is shown below.*



* *Offset from plane of cross section*

What is required for MNA Monitoring? (Page 2)

Recent Developments in MNA Design

Recently there has been more formal discussion about two distinct phases of MNA monitoring:

Site Characterization. During this period, high-resolution sampling techniques are applied that make heavy use of on-site analytical methods, real-time decision making (e.g., the TRIAD approach), mass flux/mass discharge techniques, and transects. The goal is to understand where the high mass flux (mass per area per time) zones are; determine how much mass is in low-k compartments; and define the geochemical conditions across the site. In addition, this phase would identify short term processes, such as seasonal groundwater effects, changes in groundwater flow direction, and the variability of different wells. The USEPA defines this as *Phase I* in their "Evaluation Progress" Guide[12].

Long-term Monitoring. Long-term monitoringhas different goals than characterization, and therefore different approaches are used. Instead of short-screened direct-push monitoring points, wells with longer screens (potentially as long as the screens used in nearby drinking water wells) might be used to get a flow-weighted average concentration for compliance purposes. Integrative sampling (such as passive flux meters) might also be utilized for this task. For most wells quarterly sampling would not be performed. In some cases sampling every five years might be appropriate (FAQ 18).

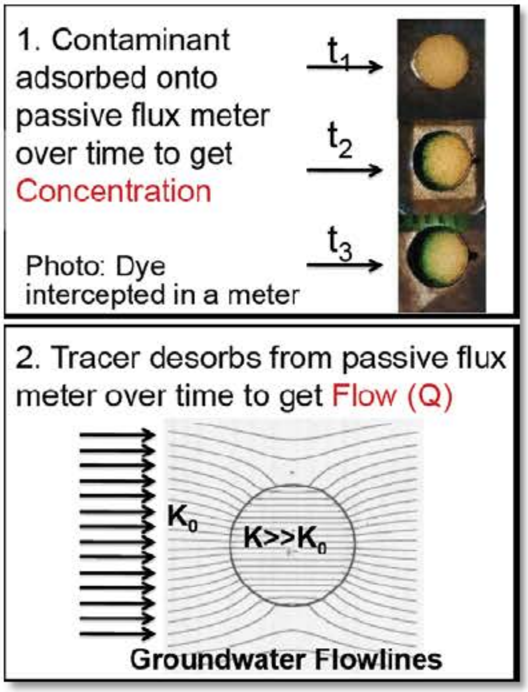


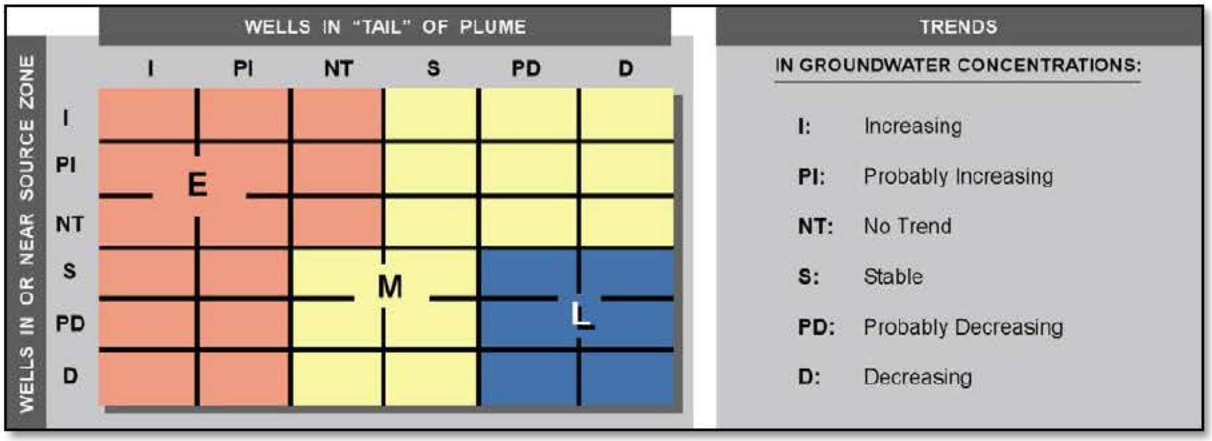
Photo of installation of passive flux meter (above). How flux meter works (right). (Photos courtesy of Enviroflux).

FAQ 18. What is the new thinking about monitoring frequency?

Tailor Monitoring Frequency to the Site, Quarterly Sampling Not That Useful

At many sites, changes in groundwater systems can take several years to become apparent. Groundwater moves relatively slowly, biogeochemical changes can occur over years, and flow conditions and concentrations often vary widely over time and space. The optimal monitoring frequency may be relatively long, and typical quarterly monitoring programs may be inefficient, so it is important to evaluate ongoing long term monitoring results and consider adjusting the frequencies on a regular basis.

One method to determine an appropriate monitoring frequency for any project, including MNA demonstrations, is the Air Force's MAROS tool [23]. The first step is to evaluate the overall trends in the source and plume (using methods summarized in FAQ 19).



	I	PI	NT	S	PD	D
I	E	E	E	M	M	M
PI	E	E	E	M	M	M
NT	E	E	E	M	M	M
S	E	E	M	M	L	L
PD	E	E	M	M	L	L
D	E	E	M	M	L	L

TRENDS

IN GROUNDWATER CONCENTRATIONS:

I:	Increasing
PI:	Probably Increasing
NT:	No Trend
S:	Stable
PD:	Probably Decreasing
D:	Decreasing

By entering the trend in the source zone wells on the rows, and the trend in the plume in the columns, a site is defined as either needing an Extensive (E); Moderate (M), or Limited (L) monitoring system. Almost all MNA projects would likely either be in the M or L categories.

Next, the E, M, or L designation is used to suggest a frequency using this lookup table:

TIME TO RECEPTOR (TTR)	Monitoring System Category		
	Extensive	Moderate	Limited
Close (TTR < 2 yrs)	Quarterly	Biannually (6 months)	Annually
Medium (2 < TTR < 5 yrs)	Biannually (6 months)	Annually	Annually
Far (TTR > 5 yrs)	Annually	Annually	Biennially (2 year interval)

TTR: time to receptor (distance to receptor/seepage velocity)

What is the new thinking about monitoring frequency? (Page 2)

The MAROS system has a companion method "Cost Effective Sampling"[127] based on the rate of change, variability and magnitude of concentrations at a particular point. Stable, low concentration, unchanging wells are sampled less frequently (annually) while unstable, high concentration variable wells are sampled quarterly.

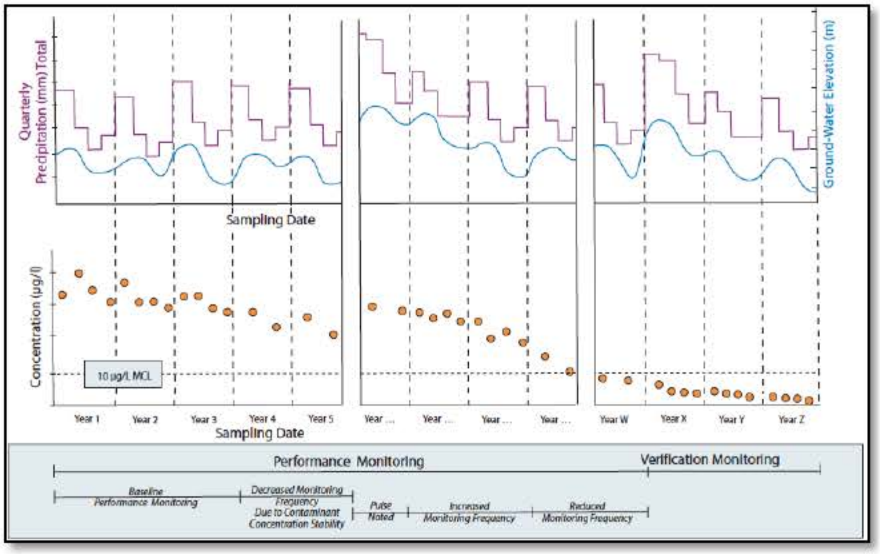
Quarterly or Not Quarterly?

In their 2004 "Performance Monitoring of MNA" guidance[11], the USEPA has a detailed discussion of monitoring frequency. First they cite 1989 research[37] that analyzed data from 12 wells at two sites in Illinois and concluded quarterly sampling is a "good initial starting point":

> *Natural temporal variability and the highly autocorrelated nature of ground-water quality data seriously complicate the selection of optimal sampling frequency and the identification of seasonal trends in ground-water quality variables. Quarterly sampling frequency is a good initial starting point for ground-water quality monitoring network design, though bimonthly frequency may be preferred for chemical constituents.*

The 1989 researchers also concluded that two years of data may be required to determine an optimal frequency. Other guidelines from the USEPA guidance are:

- Sample highly variable locations more frequently.
- More frequent monitoring where groundwater flow is rapid and/or travel time to receptors is short (or less frequent monitoring for slow sites with long travel times to receptors).
- More frequent monitoring of groundwater elevations to understand flow patterns.
- Several years of monitoring data are typically necessary for estimation of the site variability and expected rates of change in ground-water flow, contaminant concentrations, and geochemistry.
- Specifically, monitoring frequency generally should be related to detecting changes in site parameters that indicate ability of the MNA remedy to achieve site-related remedial action objectives, and to provide early warning of possible impact to receptors.
- Account for cyclic or seasonal changes.



Example of changes in monitoring frequency over the life cycle of a plume from the USEPA "Performance Monitoring of MNA" guidance[11]

What is the new thinking about monitoring frequency? (Page 3)

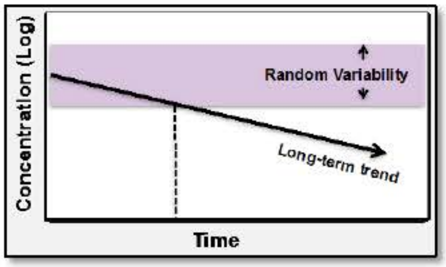
Recent Research Using Large Datasets

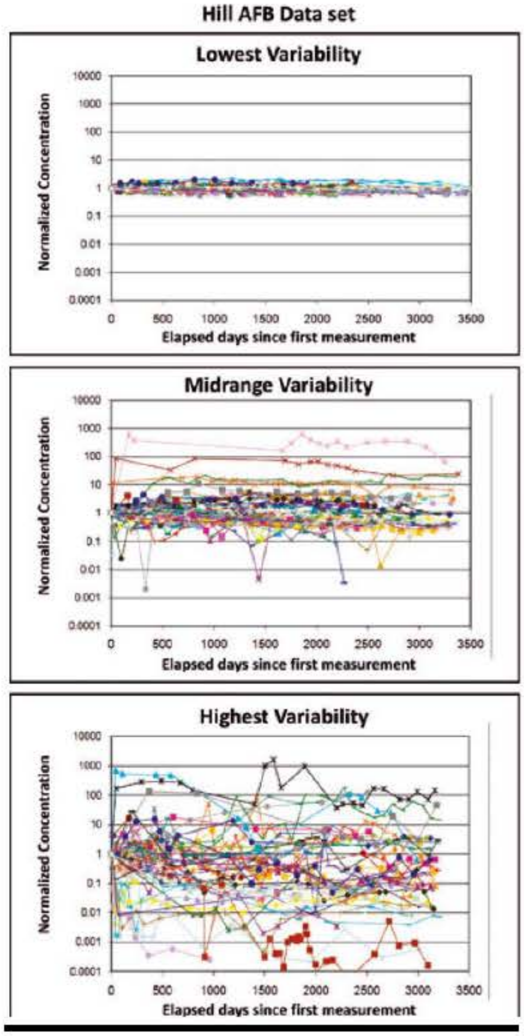
There has been some very recent research (as part of SERDP project ER-1705) on variability in monitoring well data that has implications for the long-term monitoring phase (after baseline sampling has been performed to understand site conditions). Three very large long-term groundwater monitoring datasets with 3090 monitoring wells from both chlorinated solvent sites and hydrocarbon sites, each with an average 10 years of data, were evaluated statistically.[37]

There was a wide difference in the behavior of different wells (see graphic to right that highlights the Hill AFB data from this study), and long-term trends in the data accounted for 30% to 40% of the overall variation in concentrations. Well and aquifer factors were found to be more important contributors to variability than sampling and lab analysis factors.

Regarding sampling frequency, the authors concluded that quarterly sampling for long-term monitoring is inefficient way to characterize trends: [37]

> *"Using current monitoring methods, a monitoring frequency of more than one event per year serves primarily to characterize time independent variability."*





Range of variability between groundwater monitoring wells in 504-well, multiple year monitoring dataset from Hill AFB. Each graph shows 10% of wells with lowest, midrange, or highest variability from each data set. For each well, the contaminant concentration is normalized to the concentration measured during first monitoring event for that well.[37]

The large dataset research team is now developing a spreadsheet tool that defines frequency based on both the short-term variability and the long-term trend. Although counterintuitive, the method specifies that less frequent monitoring is warranted at sites with high short-term variability and slow source attenuation rates; high-frequency sampling is merely sampling the random variability. More frequent monitoring is justified at sites with low short-term variability and faster source attenuation rates.

These results support the USEPA guidance[12] that introduces a five-year statistical analysis strategy where samples are collected in Years 1 and 5 but not in the intervening years (e.g., Years 2, 3, and 4).

FAQ 19. Statistics for two questions: How far and how long?

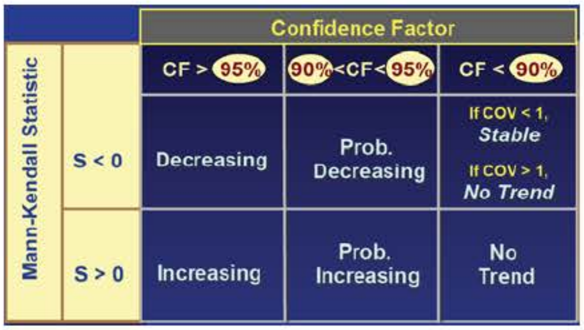
Statistics Can Help

MNA has sometimes been described as a question of "how far" and "how long" to represent plume stability (how far) and timeframe (how long). Statistical tools are available to help evaluate both questions and more.

Has the Plume Gone as Far as it Will Go?

One of the key questions that an MNA study must address is the trend associated with plume length. If the plume is expanding, then MNA is either not feasible or is much more difficult to implement. A shrinking plume, on the other hand, is the result of natural attenuation processes that are overcoming the mass discharge from the source zone. MNA is much easier to implement as a remediation strategy with a shrinking plume.

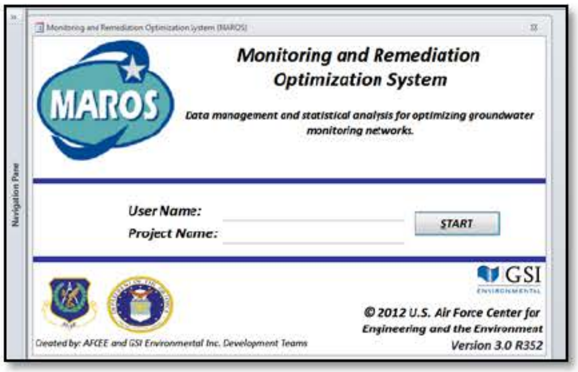
One commonly applied system for evaluating stability from temporal (concentration vs. time) data uses a non-parametric method, the Mann-Kendall method, together with a confidence factor and coefficient of variation to assign temporal data into one of six trend "buckets" [128] (see graphic with "Decreasing" "Increasing" "Stable" "No Trend" etc.). This calculation can either be performed by hand, in a spreadsheet[128] or in the AFCEE Monitoring and Remediation Optimization System (MAROS) system on the Access database platform [126].



		Confidence Factor		
		CF > 95%	90% < CF < 95%	CF < 90%
Mann-Kendall Statistic	S < 0	Decreasing	Prob. Decreasing	If COV < 1, *Stable* If COV > 1, *No Trend*
	S > 0	Increasing	Prob. Increasing	No Trend

Other Applications of Statistics

There are other areas where statistics have been applied to help answer questions indirectly related to MNA. For example, the MAROS System[126, 129] provides utilities to "clean up data" for processing by handling non-detects and duplicate values, and grouping data into time intervals. Besides the trend analysis discussed above, MAROS can also be used to optimize groundwater monitoring networks by helping users identify redundant monitoring wells (wells that are located near other wells, and do not provide much additional information) and identify data gap areas (where additional wells may be required). It also includes a semi-empirical system to define monitoring frequency for wells depending on their variability and other factors, and recommends either bi-annual, annual, semi-annual or quarterly sampling. Other groundwater-focused statistical tools are also available, such as the Geostatistical Temporal-Spatial Tool (GTS)[130].



Monitoring and Remediation Optimization System (MAROS)

Monitoring and Remediation Optimization System

Data management and statistical analysis for optimizing groundwater monitoring networks.

User Name:
Project Name:

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Version 3.0 R352

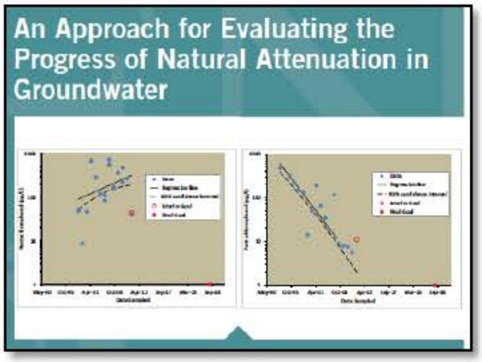
Created by: AFCEE and GSI Environmental Inc. Development Teams

Statistics for two questions: How far and how long? (Page 2)

Will MNA Work? How Long Will It Take for Cleanup?

The USEPA has developed a detailed guidance for using statistics to evaluate remediation timeframe[12]. Based on the concept of first order decay, the guidance breaks up the MNA timeframe question into two parts: when MNA is being considered, and after MNA has been selected.

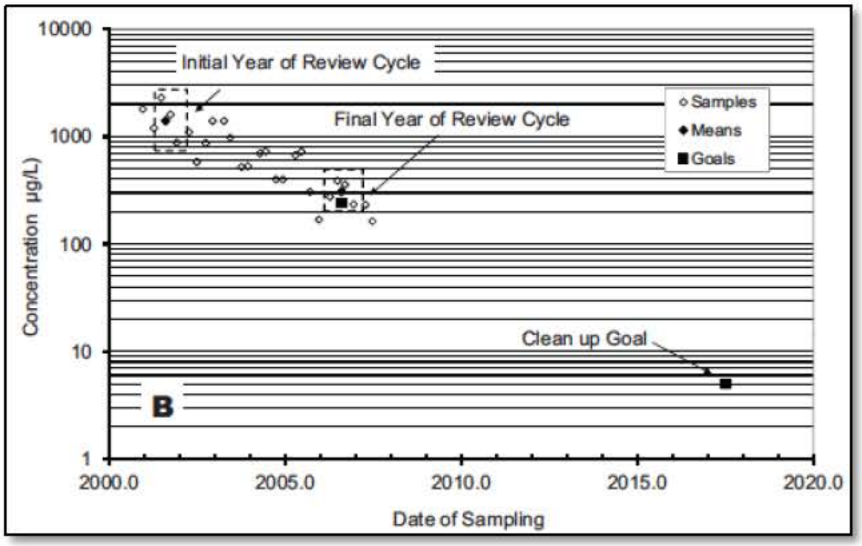
Prior to remedy selection, the guidance describes how to estimate remediation timeframes, and more importantly, estimate the uncertainty in the rate of natural attenuation. These analyses help site managers decide if MNA will work.



An Approach for Evaluating the Progress of Natural Attenuation in Groundwater

For tracking MNA performance after it has been selected as the remedy, procedures are presented for: 1) testing if concentration reductions are statistically significant and 2) testing if the reduction is adequate to reach site goals. Practical information is provided on how to perform the calculations in a spreadsheet environment (see graphic below), and how to tie the statistics into a hydrogeological framework. Simple rules regarding how to deal with variability are given; for example the issue of the "outlier well" (a well with increasing concentration from one five-year review cycle) is treated this way:

> *"If the final concentration in a problematic well at the end of the review cycle is low with respect to the most contaminated wells at the site, then that particular problematic well, alone, does not put the site at risk for not attaining the final goal, at least not in the review cycle under consideration."*

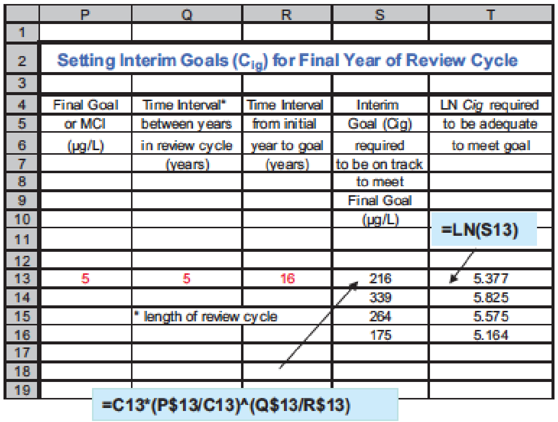


Example of MNA performance monitoring record over the interval of time in a review cycle[12]. At the end of the review cycle, data should be evaluated to determine whether attenuation is adequate to attain the long-term goal by a specified date.

Statistics for two questions: how far and how long? (Page 3)

The USEPA's Approach for Evaluating the Progress of Natural Attenuation guidance[12] is an overall important resource for tracking the performance of MNA in groundwater. Their overall suggestions and recommendations are reproduced below.

> Follow the process outlined in *Performance Monitoring of MNA Remedies* (Pope et al., 2004) to develop site-specific monitoring objectives and performance criteria for MNA. Conduct the performance review with those objectives and criteria in mind.
>
> Prior to a review of the performance of MNA, analyze the monitoring record to reveal:
>
> 1. the attenuation in concentration of each contaminant in each monitoring well over the review cycle (C_i/C_o); and
> 2. determine whether the attenuation is adequate to attain the long term goal by the date specified in the decision documents; or alternatively,
> 3. estimate the probability that attenuation is not adequate to attain the goal.
>
> If the concentrations in a well are not expected to attain the clean-up goal by the specified time, associate a level of statistical confidence and statistical power with that determination. When the confidence in a statistical test and the power of the test are high, the results of the test are more compelling, and provide more justification to initiate active (more aggressive) clean up actions rather than MNA.
>
> Identify those wells that are more likely to prevent a site from attaining the goals for MNA. Then identify and assign priority to those areas of the aquifer that are the best candidates for focused active remediation. Re-evaluate progress toward clean-up and site closure at the end of the next review cycle to determine the impact of the focused active remediation efforts.



Setting Interim Goals (C_{ig}) for Final Year of Review Cycle

Final Goal or MCI (µg/L)	Time Interval* between years in review cycle (years)	Time Interval from initial year to goal (years)	Interim Goal (Cig) required to be on track to meet Final Goal (µg/L)	LN Cig required to be adequate to meet goal
5	5	16	216	5.377
			339	5.825
			264	5.575
			175	5.164

* length of review cycle

=LN(S13)

=C13*(P$13/C13)^(Q$13/R$13)

Using a spreadsheet to set interim clean-up goals for the final year of the review cycle. A separate interim goal is calculated for each sample in the initial year of the review cycle, assuming first order degradation to attain the final clean up goal by the specified date.[12]

FAQ 20. Which computer models work best for MNA?

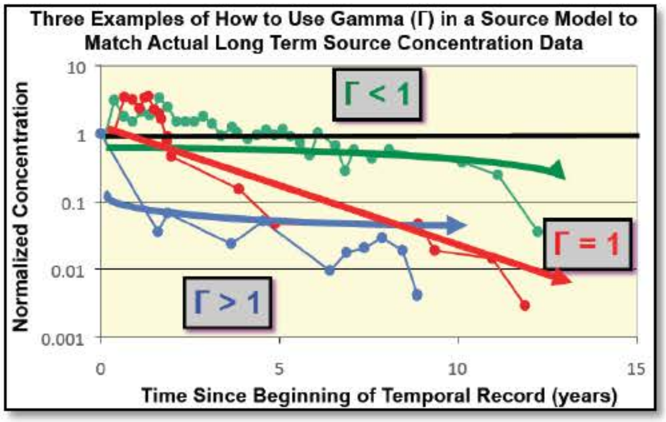
Simple Models are Being Used More Frequently

Models have been used to evaluate MNA for a long time; the Air Force's BIOSCREEN model[38] was first issued in 1996. Since then, new models have been introduced, and existing models have become more powerful. But there are still some potentially striking new developments in the modeling world that may greatly change the types of models that are used for MNA.

Plume Models vs. Source Models

Plume models currently simulate the migration and stability of solute plumes once they leave the source zone using the advection-dispersion equation with additional terms for sorption and degradation. Source models simulate natural attenuation processes affecting source materials, such as dissolution and degradation. Some simpler analytical (equation based) models, such as BIOSCREEN[38]; and BIOCHLOR[22], combine both source and plume models. Users can either assume a constant source, or a source zone with a first order source decay term (FAQ 16).

Simple Source Models. More recently, two new USEPA models developed by Falta et al., REMChlor and REMFuel[29, 124, 125] use the Power Law to simulate source zone attenuation (or remediation), where the relationship between mass remaining in a source zone and the mass discharge (sometimes called mass flux) leaving the source is defined by an input parameter "gamma". Gamma can be used to represent a step function (gamma = 0), a first order decay (gamma = 1.0), or an initial sharp drop followed by a long concentration vs. time tail (gamma > 1). Other models, such as the NAS software, rely on NAPL dissolution relationships. Users of numerical models such as MODFLOW/MT3D have to enter directly their own source concentration vs. time history (and future), as these models do not have a separate source module.


Three Examples of How to Use Gamma (Γ) in a Source Model to Match Actual Long Term Source Concentration Data

New Controversy about Dispersion

For many years the Advection-Dispersion equation (with additional sorption and degradation terms) has been the accepted method for simulating the movement and attenuation of plumes once they have left the source. Although many modelers have accepted the fact that the dispersion concept may have certain theoretical shortcomings, it was accepted as a useful fitting factor for most modeling studies. Since dispersion was not a "first order" process for many modeling simulations (not the primary process), any theoretical inaccuracies were thought to be minor.

Which computer models work best for MNA? (Page 2)

More recently there have been more significant challenges to the advection dispersion model [131-133]. For example, the ITRC presents an "alternative viewpoint" that advises against using advection dispersion models:

> *"The alternative view is that the limited spreading that does occur primarily depends on variations in aquifer permeability along the flow path and on pore-scale diffusion processes (e.g., Gilham et al. 1984[134]), as compared to the assumption that hydrodynamic dispersivity (random-walk dispersion) more strongly influences transport in aquifers. Therefore, any groundwater model that incorporates significant hydrodynamic dispersivity overstates the potential for plume spreading and the resulting dilution. Models that rely on the A-D equation should be used with great caution or not used at all."*

Konikow[133] commented regarding advection dispersion numerical models:

"Well-documented public-domain solute-transport models are readily available and widely used. There are a number of conceptual weaknesses and flaws in the underlying theory and classical governing equation, and the numerical solutions will inevitably contain some numerical errors."

ground water

Issue Paper/

The Secret to Successful Solute-Transport Modeling

by Leonard F. Konikow

This has led to the beginning of a debate about dispersion versus diffusion.[135] An overview of the key issues suggests the following situations where advection-dispersion modeling could lead to inaccurate modeling results:

- Modeling very long plumes (likely miles long) with no degradation where dispersion appears to be the primary attenuation factor
- Models with high estimates of longitudinal dispersivity term (> 20 meters (?))
- Situations where you don't have data to calibrate a model
- Situations where high impact decisions are dependent solely on the modeling results (and not by any other lines of evidence or analysis). McWhorter[136] stated it well: "[w]hile the technical community can do a pretty good job of predicting the first-order features of a solute plume (e.g., the direction of migration, mean velocity, general shape and extent), it is not capable of accurately predicting when a particular well will achieve a concentration of 5 ppb, for example."

Situations where advection-dispersion models can likely provide useful information include:

- Modeling to demonstrate that strong solute degradation will stabilize a plume.
- Simulations of how a plume front can progress due to advection.
- Situations where the goal is to show effects of source attenuation or source remediation, and where stakeholders are cautioned that the time to cleanup the plume is likely to be over optimistic because it doesn't account for matrix diffusion effects (FAQ 22).
- Situations where we have low expectations for modeling[133].

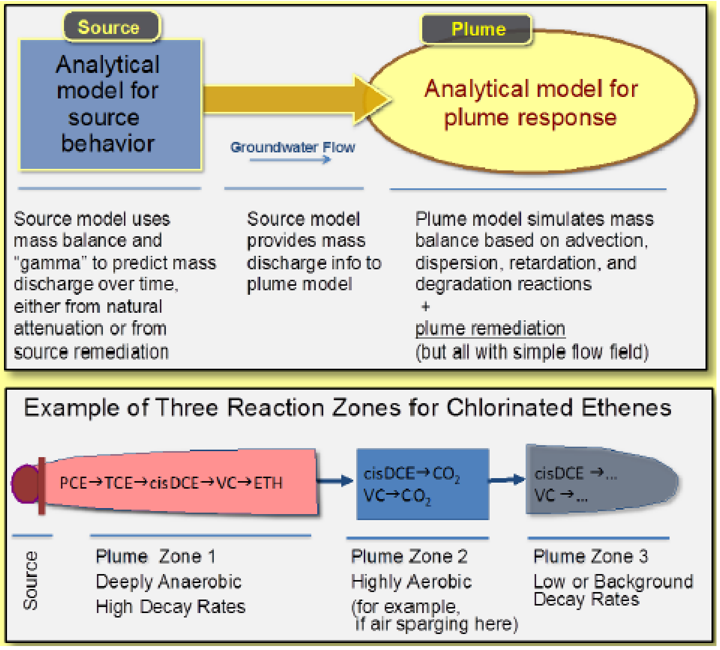
Which computer models work best for MNA? (Page 3)

REMChlor/REMFuel Source Zones. Two new important developments in the MNA modeling world are the introduction of the USEPA's REMChlor and REMFuel models. [19, 29, 124, 125] Both employ an analytical model for the source that is linked to an analytical plume model (see adjacent graphic). Natural attenuation processes can be simulated in both the source (using "gamma" input and for radionuclides an optional source decay term) and in the plume (by adjusting solute first order decay rates).

Plume Degradation Processes in REMChlor and REMFuel. Both models can simulate sequential decay of parent compounds:

REMChlor: PCE to Ethene, TCA to Ethane

REMFuel: MTBE→TBA→"CO_2" (and single step degradation of BTEX)



Overview of REMChlor Model

Strengths of REMChlor/REMFuel Models
Easy to use and understand, simple interface, free
Developed and approved by USEPA
Can simulate source attenuation or source remediation, plume attenuation or plume remediation
Source attenuation can be modeled to achieve matrix diffusion-like effects of long concentration vs. time tails (using a gamma > 1.0)
Plume modeling accounts for decay chains, and can have three separate reaction zones

Weaknesses of REMChlor/REMFuel Models
Have to assume uniform, one directional flow field
Can't directly account for pumping
Simulating remediation is somewhat crude: the user defines the percent mass removal in source, and/or adjust first order decay rates in plume
While source accounts for matrix diffusion, plume model does not, leading to over optimistic plume cleanup times at many sites.
Can be difficult to calibrate if lots of decay chain data

FAQ 21. Are MNA reactions sustainable? Is MNA sustainable?

Depends on Your Meaning

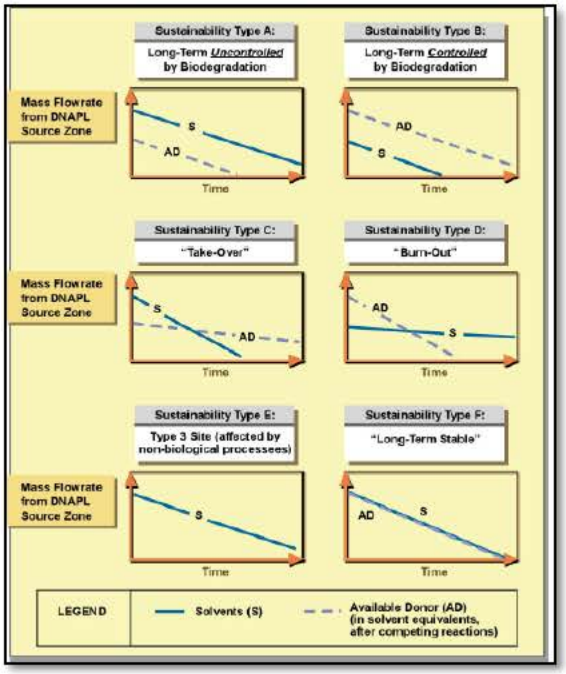
In the case of MNA, "sustainable" has two meanings, one regarding if and how long beneficial MNA reactions will continue, and one regarding how "green" MNA is compared to other technologies. Both are addressed in FAQ 21.

Technical Meaning of MNA Sustainability

The ITRC's Enhanced Attenuation team defined "sustainability" for chlorinated solvent sites as: *"[t]he ability of a system to maintain the important attenuation mechanisms through time."* [1]

Hydrocarbon Sites. For hydrocarbon releases that are sustaining BTEX plumes, the key sustainability mechanism is the continued delivery of electron acceptors (such as dissolved oxygen and sulfate) to the plume over time in clean groundwater that contacts the plume, and the ability for anaerobic conditions to continue (for methanogenesis) under sustainable pH and (less likely) temperature conditions. In general, sustainability of key attenuation reactions into the future is not a high level concern at hydrocarbon sites.

Chlorinated Solvent Sites. In the case of chlorinated solvent sites, several groups have considered the sustainability of chlorinated solvent reactions into the future.[18, 21, 31, 32, 137] A conceptual description of the sustainability of anaerobic reactions at chlorinated solvent sites is presented to the right[18, 137]. The BIOBALANCE model[31] combined a mass balance of electron donors, competing electron acceptors, and chlorinated solvents to assess reaction sustainability.



Sustainability Types For Chlorinated Solvent Sites[18, 137]

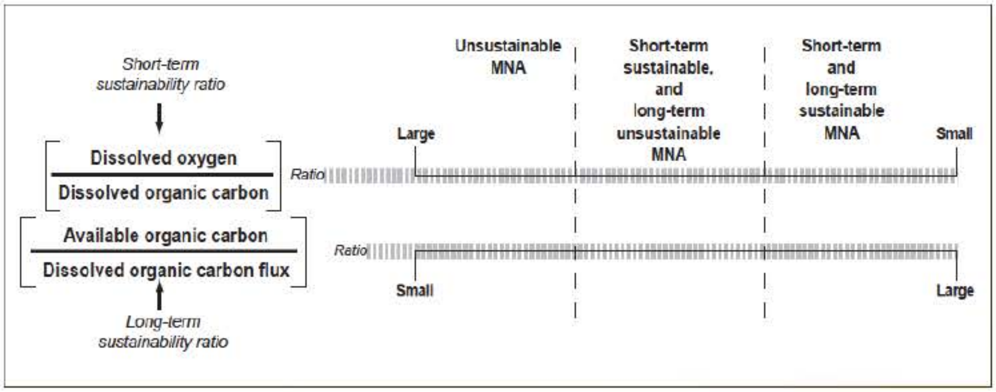
A detailed framework for assessing MNA reaction sustainability was developed by a group of USGS and Virginia Tech researchers that combined two key factors: 1) the presence of chemical/biochemical processes that transform wastes to innocuous byproducts, and 2) the availability of energy to drive these processes to completion.[32] By applying mass balances on contaminant mass loss over time, and tracing the energy in the pool of bioavailable organic carbon that is available, the short-term and long-term sustainability of MNA reactions can be assessed (see conceptual diagram).

Are MNA reactions sustainable? Is MNA sustainable? (Page 2)

This approach was demonstrated at a large research site in Georgia, and the concepts applied using the SEAM3D numerical model. The results suggested that for this site, an estimated 5 mg/L of organic carbon (CH_2O) per day per every 25 meters model grid block is required to support the short-term sustainability of MNA. Because the available carbon source is large ($5x10^7$ mg per model cell; see photo of organic-matter-rich semi-confining bed that is the source of this carbon), the long-term reaction sustainability was considered to be large.[32]

The same group of USGS/Virginia Tech researchers developed the Natural Attenuation Software (NAS), a free tool that is designed for estimating remediation timeframes (see FAQ 16) but is also useful for investigating the sustainability of natural attenuation processes by incorporating SEAM3D. This software was used, along with GMS, in an ESTCP-funded project (ER-200824) to verify methods for assessing MNA sustainability.[187] By collecting and compiling data from a large number of chlorinate solvent sites, this project provided further evidence of the importance of potentially-bioavailable organic carbon (PBOC)[188,189] on sustainability, with a positive correlation established between PBOC concentration and natural attenuation capacity (as well as several other parameters). Quantifying the impact of PBOC, DO, and natural source zone depletion on short-term and long-term sustainability was also achieved at a single site. Important advancements from these studies include the development of analytical techniques for estimating PBOC[190] and an estimate that 200 mg/kg of PBOC is a threshold concentration for supporting reductive dechlorination[191].

Long-Term and Short-Term Components of MNA Sustainability[32]



Inorganics and Rads. In general, the sustainability of inorganics and radionuclide sites will either have sustainability issues similar to the hydrocarbons (typically sustainable) or chlorinated solvents (increased chance of changing conditions). A very general rule is contaminants with low mobility under high ORP conditions (see FAQ 8) will have sustainability qualities similar to hydrocarbon sites, while low mobility under low ORP conditions may be more like chlorinated solvent sites.

Are MNA reactions sustainable? Is MNA sustainable? (Page 3)

Sustainable Remediation

The Sustainable Remediation Forum (SURF) defined "sustainable remediation" as *"a remedy or combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources"* [138]. In their White Paper, the SURF group states that:

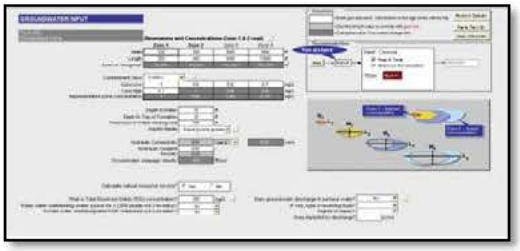
> *"technologies harnessing natural processes (e.g., monitored natural attenuation, enhanced in situ bioremediation, phytoremediation, bioslurping, passive in situ treatment, bioventing, wetlands, bioreactors) are more energy- and resource-efficient. Their incorporation into an environmental restoration program generally results in a reduced or smaller impact."*

But warn that:

> *"However, due to site-specific factors, no single remediation technology can be considered more sustainable than others."*

Tools such as the Air Force Sustainable Remediation Toolkit (SRT)[138] and Battelle's Sitewise[139] can be used to evaluate the sustainability of MNA compared to other technologies (see graphics below). Both tools are based on a spreadsheet platform, but have different architecture. The SRT is built around specific remediation technologies, and has two separate Tiers or levels of complexity. SiteWise is built around more general activities such as Remedial Investigation, Remedial Action Construction, Remedial Action Operations, and Long-Term Monitoring. Metrics that can be computed using these tools include carbon footprint, energy use, air emissions, accident risk, and other factors. An application of the SRT to remediation Feasibility Studies[140] supported the conventional wisdom in some cases, such as a pump and treat system operating for eight years emitting 1500 tons of CO_2 compared to 450 tons for a "green remedy" consisting of a bioreactor, phytoremediation, biobarrier, and MNA. The authors did note "sustainability surprises" in other areas, such as excavation having a much smaller carbon footprint than a 50-well SVE system with activated carbon treatment. A retrospective sustainability analysis of remediation project in Albany Georgia[141] observed that optimization programs performed in 2004 and 2010 that resulted in more focused treatment and optimized long-term monitoring system saved approximately 3700 megawatt-hours of power and reduced the greenhouse emissions by 75%.

When applying sustainability analysis to MNA, the carbon footprint (a common sustainability metric) of an MNA project with limited long-term monitoring program would almost certainly be smaller than an energy-intensive remedy such as thermal remediation. However, the opposite can be true for MNA sites that require an extensive long-term monitoring program involving many decades of monitoring and extensive travel. Over a long period of time the footprint of the truck and planes can exceed the footprint of even a very energy intensive remedy.



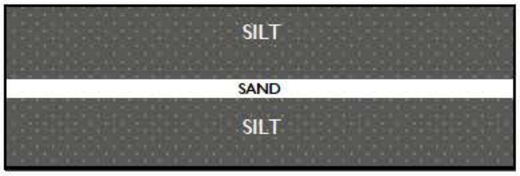
FAQ 22. What is matrix diffusion? How does it affect MNA?

It is a Big Deal, and May Drive Us to MNA

Matrix diffusion is a process where dissolved contaminants can diffuse between "low-k" and "high-k" zones. When contaminants diffuse from higher concentration transmissive zones (such as sands and gravels) to lower concentration "low-k" zones (low permeability, such as silts and clays), this is called the "loading period," and can last for decades.

If the concentration in the transmissive zone becomes small enough (either due to remediation, or natural attenuation), the contaminants will diffuse out of the "low-k" zones back into the transmissive zones. This is called the "release period," and will usually last much longer than the loading period.

Matrix Diffusion as an Attenuation Process. During the loading period, matrix diffusion actually acts as a non-destructive attenuation process, one that reduces concentrations and slows down the plume. In the laboratory tank experiment diagrammed below[142] contaminant transport was monitored in a three-layer system consisting of a thin sand unit that is overlain and underlain by silt. The red line on the concentration vs. time graph is the theoretical breakthrough curve using the *advection-dispersion* equation. The green line shows the actual data from this experiment, and results from several *advection-diffusion* models.



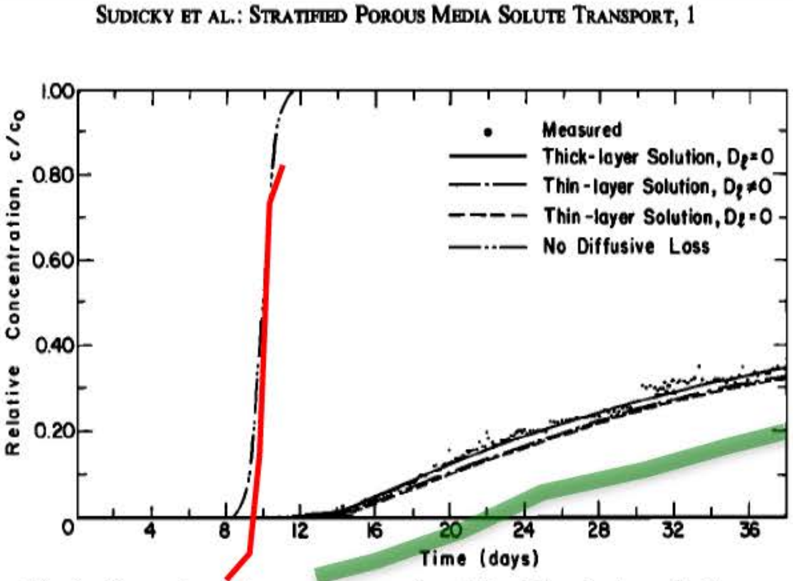
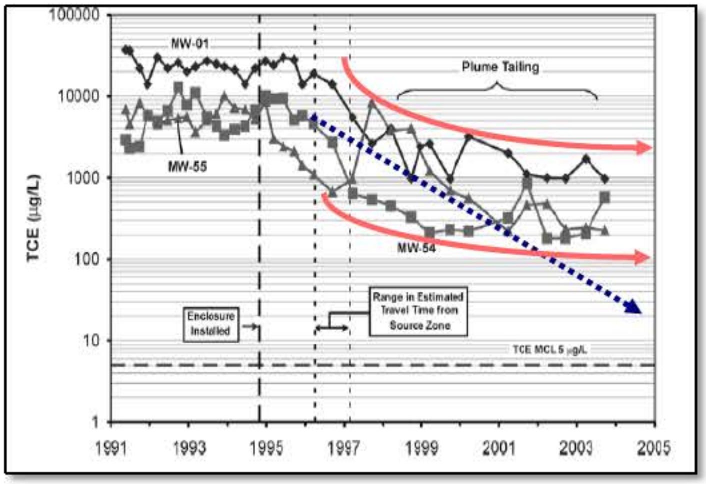


Fig. 2. Comparison between measurements and simulations for low-velocity case.

What is matrix diffusion? How does it affect MNA? (Page 2)

Matrix Diffusion as a Source Process. During the release period, matrix diffusion can serve as a diffuse, low concentration, hard to treat, persistent source of contamination to groundwater.[28, 111, 112] Key implications are:

- Treatment volumes may be large. Matrix diffusion creates secondary sources both within the original source zone and within the plume, and contaminants can diffuse a meter or more into some matrices given 20-30 years or more of exposure. In short, these are similar to non-point sources for surface water quality.
- Amendment-based technologies may be difficult to implement, due to low hydraulic conductivity and large treatment volume.
- Sorption may be high in the low-k zone and further contribute to slow release rates.
- These sources can persist for centuries at some sites. Data from a University of Guelph research[111] site is shown to the right as concentration vs. time profiles. The expectation was "no tailing" (dashed blue line in graph) and cleanup within a few years of source isolation. The data showed significant reductions in concentration (about 1 order of magnitude), before the start of a "long tail" (trend depicted with red lines). University of Guelph modeling suggests the *"aquifer TCE will remain above the MCL for centuries"* because of matrix diffusion.

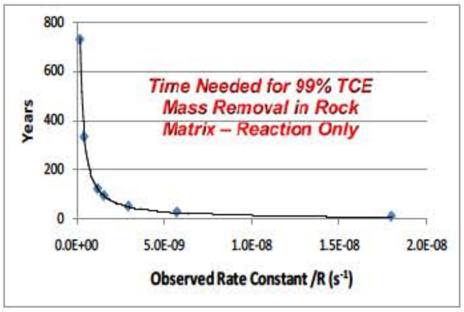


- While the authors are optimistic that new remediation technologies will be developed that can address some matrix diffusion problems, the low strength of most of these sources means that they may be particularly well suited for MNA, for both the source zone and the plume. A key research question is whether attenuation occurs in the low-k zones (FAQ 23).
- Matrix diffusion effects may persist longer than the actual DNAPL sources that load the matrix. A model of a small hypothetical source zone consisting of sand and clay layers and a 675 kilogram TCE DNAPL release showed DNAPL dissolution of the last DNAPL pool would occur in 39 years, while matrix diffusion alone would maintain the source loading above 0.1 grams per day for at least an additional 83 years.[143] A modeling study of fractured rock (sandstone) system observed a similar effect, with the overall remediation timeframe not being "associated with the time that DNAPL sources are present, but rather the time required for back diffusion of aqueous phase contamination from the rock matrix."[144]
- Recently there has been an explosion of guidance and tools that focus on or address matrix diffusion, such as the ITRC's Integrated DNAPL Site Strategy[132], the ESTCP FAQ and Decision Guide[28, 145], and the ESTCP Matrix Diffusion Toolkit[35]. The 14-Compartment model[132, 143] is an important tool for understanding how matrix diffusion fits into a site conceptual model.
- MNA will likely become a more important way to manage low-risk matrix diffusion dominated sites (FAQ 26).

FAQ 23. Do contaminants in low-permeability units attenuate?

Sometimes, We Think

The importance of matrix diffusion processes in influencing remedy selection, including MNA decisions (see FAQ 22), has led to increased interest in understanding how contaminants in low-permeability (k) units attenuate. For MNA to be successful at sites where contaminant mass in low-k zones dominates, it is important to determine if viable attenuation mechanisms are present. While there are several factors that can limit attenuation rates in low-k soils, the good news is that even slow attenuation should: 1) reduce the extent of contaminant penetration during the loading period compared to that expected from diffusion and sorption processes alone, thereby limiting mass storage within deeper, less-accessible intervals and reducing storage in low-k units; and 2) reduce the rate and longevity of mass diffusing out of these low-k zones, thus lessening the impact on sustaining dissolved plumes in the adjacent higher k zones [28]. Modeling completed as part of a recent SERDP study (ER-1740) showed that even slow rates of degradation in low-k zones can result in order-of-magnitude (or greater) reductions in aqueous concentrations in monitoring wells located in transmissive portions of the plume [192]. Further quantification of these impacts has been a focus of SERDP project ER-1685, which has documented significant decreases in contaminant flux due to relatively slow attenuation processes (see graphic to the right) [193].



Impact of Observed Abiotic Degradation Rates in Rock Matrix on Mass Reduction Timeframes. Data obtained in study described in Schaefer et al. [199]

Potentially relevant attenuation mechanisms in low-k units are similar to those for transmissive zones: biotic and abiotic degradation, sequestration, and non-destructive physical processes. However, there are several characteristics of low-k units that may favor or limit degradation capacity, as described below.

Low K Zone Characteristics that Can Influence Attenuation

Characteristics That Favor Attenuation	Characteristics That Hinder Attenuation
Long retention times (little advection/flushing)	Smaller pore throat size restricts migration of microbes, influx of nutrients/carbon sources, and growth density
Reducing conditions are common (little recharge to introduce of competing electron acceptors) and favorable for biological and biogeochemical reductive dechlorination	Salinity can be high and may limit microbial activity
Potentially large reservoir of organic carbon (silts/organo-clays)	Limited bioavailability of organic carbon
Potentially large reservoir of reactive mineral species	Reactivity of mineral species may be limited due to dependence on microbial activity (e.g., iron reduction)

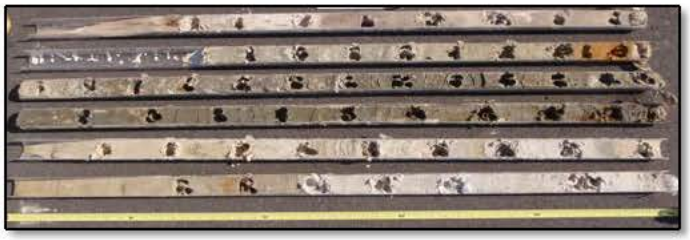
Do contaminants in low-permeability units attenuate? (Page 2)

To-date, research on degradation in lower k matrices has been relatively limited. Biotic processes have been the main focus, though there is evidence that abiotic degradation (e.g., mediated by reactive ferrous iron species) can be significant[196]. There are a few published studies that provide evidence of microbial activity in connection with contaminant degradation within low k zones [40, 146-151, 194]. In reality, our body of knowledge may be limited by the simple fact that there have relatively few attempts at investigating attenuation in these zones. Certainly, size exclusion due to the small pore throat sizes in low-k media (which can be small as 2 nm) represents a challenge to promoting microbial growth and penetration into low-k layers. But the presence of fractures and preferential pathways in many unconsolidated and consolidated units can enhance migration, such that meaningful degradation capacity can be established beyond initial interfaces. A convincing example of this was provided by Lima et al. [151] who used a combination of molecular and isotope analyses at a chlorinated solvent site to demonstrate that a dechlorinating population was present and active in the rock matrices at significant distances (up to 0.63 m) from the nearest fracture surfaces.

Potential lines of evidence for low k zone attenuation to support MNA

1. Molecular biological data confirming presence and/or activity of degraders within low k zone
2. Daughter product distribution suggests greater extent of degradation in low k zone relative to adjacent transmissive zone
3. Favorable geochemical conditions within low k zone
4. CSIA data showing higher fractionation within low k zone
5. Mineralogical analysis of low k zone soil samples that show minerals capable of abiotic degradation of contaminants

Attenuation of contaminants in low k units is closely tied to the concept of sustained treatment, a term used to describe enhanced attenuation capacity after the conclusion of the active treatment period[152] when MNA might be considered for long-term site management. Several mechanisms can contribute to sustained treatment, including slow endogenous decay of newly-grown biomass following enhanced bioremediation, the formation of reactive mineral species following chemical/biological reductive treatments, and the diffusion of remedial amendments in and out of low k zones. These degradation processes are often associated with the interfaces of low k zones, and thus are well-suited to address mass in these matrices. Further, estimated timescales for sustained treatment processes are up to six years (longer than typical active treatment periods), which is compatible with slow diffusion-based release of low-level contaminant mass from low k zones. Enhanced bioremediation is the treatment technology with the strongest evidence for supporting sustained treatment, and thus is the most likely to support long-term attenuation of contaminants associated with low k units during a post-treatment MNA period.

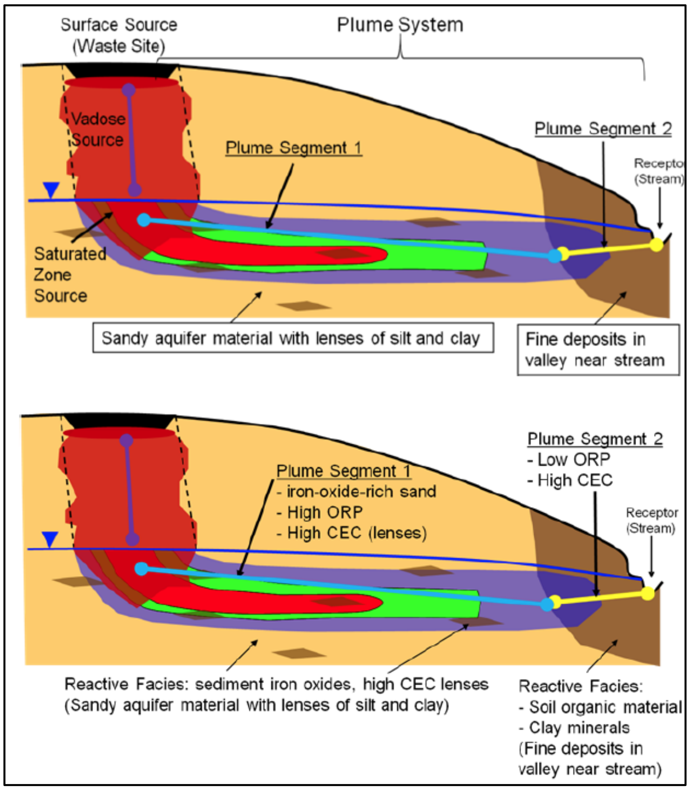


Example of high-resolution sub-sampling of soil cores for assessing attenuation in low-k zones

FAQ 24. Why are interfaces important for MNA?

Interfaces are Where the Action Is At Many Sites

The first generation MNA protocols looked at mass loss over the entire plume. But the focus on explaining mechanisms of attenuation led to sophisticated conceptual models of geochemical zones and reactions at interfaces. Examples of the importance of interfaces for MNA are:

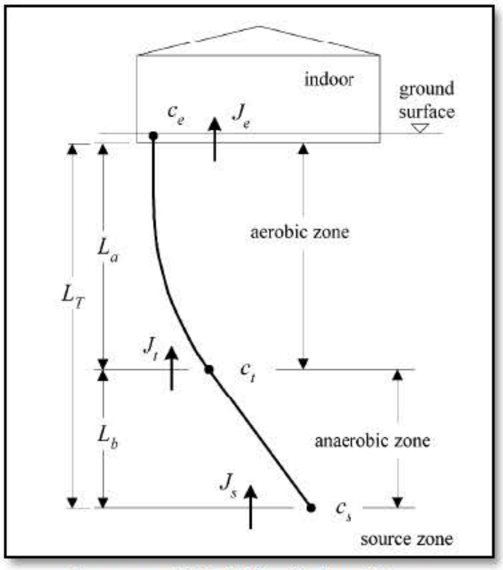


- The division of hydrocarbon plume degradation into methanogenic, sulfate reducing, iron reducing, nitrate reducing, and aerobic zones;[17]
- The architecture of chlorinated solvent MNA computer models that have different reaction zones to account for different biodegradation rates in anaerobic vs. aerobic conditions.[22, 29]
- The introduction of a key concept in the MNA of metals and radionuclides, where "biogeochemical gradients" exist in the interface between different geologic conditions.[19] (see graphic where the interfaces between the plume segments can mark important changes in attenuation capacity).
- The USGS has developed a Draft Technical Protocol for Characterizing Natural Attenuation of Chlorinated Solvent Ground-Water Plumes Discharging into Wetlands.[153] (see photo on the following page)
- More researchers are focusing on geochemical interfaces when they discharge to surface water. In one lab study, a thin (2-3 mm) anaerobic/aerobic interface was found to have a "remarkable capacity" to degrade chlorobenzene (2000 to 4200 milligrams per meter squared per day) and nitrobenzene.[154]
- The UK Environmental Agency has established a *"research programme on the groundwater-surface water interactions, specifically aimed at pollutant attenuation processes at the interface of groundwater and surface waters, sometimes called the hyporheic zone."*[155]

Why are interfaces important for MNA? (Page 2)

Hyporheic Zone. The hyporheic zone has considerable potential for attenuation of a wide variety of groundwater contaminants due to the greater availability of organic matter, nutrients, electron donors/acceptors and steep biogeochemical gradients. But potential downsides include short path-lengths and residence time in the hyporheic zone and the proximity to surface water.[156] For aerobically degradable compounds, one lab study *"..revealed robust biodegradation of toxic compounds migrating across the sediment/water interface and indicate that the biodegradation capacities were sufficient to eliminate transport of the contaminants to the overlying water in the field."* [154] A recent USGS study found that *"MTBE, TBA, and TAME concentrations in groundwater discharge in a 5-foot (1.5-m) thick section of the hyporheic zone were attenuated between 34% and 95%, in contrast to immeasurable attenuation in the shallow aquifer during contaminant transport between 0.1 and 1.5 miles (0.1 to 2.4 km)".*[157] For attenuation of chlorinated solvents, the results can be mixed; the USGS observed complete attenuation of chlorinated solvent plume discharging into one wetland site, but incomplete degradation at a second (see photo of field program to the right).[153] Conant found extensive biodegradation of a PCE plume within the upper 8 feet (2.5 m) of stream bed deposits.[158] In most cases, the mass flux across this interface varied substantially depending on location reflecting the complex physical and geochemical processes within this interface.

Vadose Zone. The vadose zone is another important interface for MNA purposes. It is well established that aerobic processes are active in the vadose zone and can greatly limit the potential for vapor intrusion of petroleum hydrocarbon compounds unless preferential pathways are present.[159, 160] Attenuation of chlorinated solvent vapors in the vadose zone can also occur, but it is not as prevalent or robust as the attenuation of petroleum hydrocarbon vapors.[160] The attenuation potential of the oxic/anoxic interface where a groundwater plume is in contact with the vadose zone has been demonstrated using models[161] and lab studies; one lab study[162] showed degradation rates of 21 mg/m^2 for chlorobenzene at the groundwater/vadose zone interface.



Conceptual Model for Vadose Zone Oxygen-Limited Biodegradation[161]

FAQ 25. How do reactive mineral species contribute to attenuation?

Naturally-occurring minerals can degrade contaminants

Microorganisms have long been known to degrade chlorinated solvents and other contaminants in the environment, but recent research has enhanced our understanding of the contribution of abiotic chemical reactions, particularly those driven by reactive minerals, for the dechlorination of solvents released to the environment. Abiotic reactions have also been explored as a possible means to attenuate metals in aquifers.

Abiotic chemical degradation means that a compound reacts without catalysis by microbes or other life forms. The chlorinated solvents 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane undergo spontaneous abiotic degradation (via hydrolysis) to form 1,1,-DCE and TCE respectively[163]; however, most other chlorinated solvents have been assumed to be fairly resistant to abiotic decay.

Reactive mineral species represent another means for promoting abiotic attenuation. These species include iron (II) sulfides, mackinawite, pyrite, magnetite and so-called 'Green Rusts' have long been theorized to catalyze dechlorination of CVOCs based on their chemical characteristics. Many of these minerals are naturally present in subsurface and anaerobic environments and may be contributing to natural attenuation in groundwater plumes.

Minerals that may contribute to abiotic degradation of CVOCs:

- Iron(II) Sulfide (FeS)
- Mackinawite –($Fe_{1+x}S$)
- Pyrite (FeS_2)
- Magnetite (Fe_3O_4)
- Goethite (α-FeO(OH))
- Hematite (Fe_2O_3)
- Lepidocrocite (γ-FeO(OH))
- Green Rust --(Fe^{2+} and Fe^{3+} cations, O^{2-} and OH^- anions, with loosely bound $[CO_3]^{2-}$ groups and H_2O molecules between the layers)

The successful development and demonstration of Permeable Reactive Barriers (PRB) containing Zero Valent Iron (ZVI) to treat TCE in groundwater ignited more interest in catalytic reactions on mineral surfaces. Several researches have proposed that naturally-occurring, surface-bound ferrous iron can react directly with chlorinated solvents by the same mechanisms as those observed with ZVI amendment.

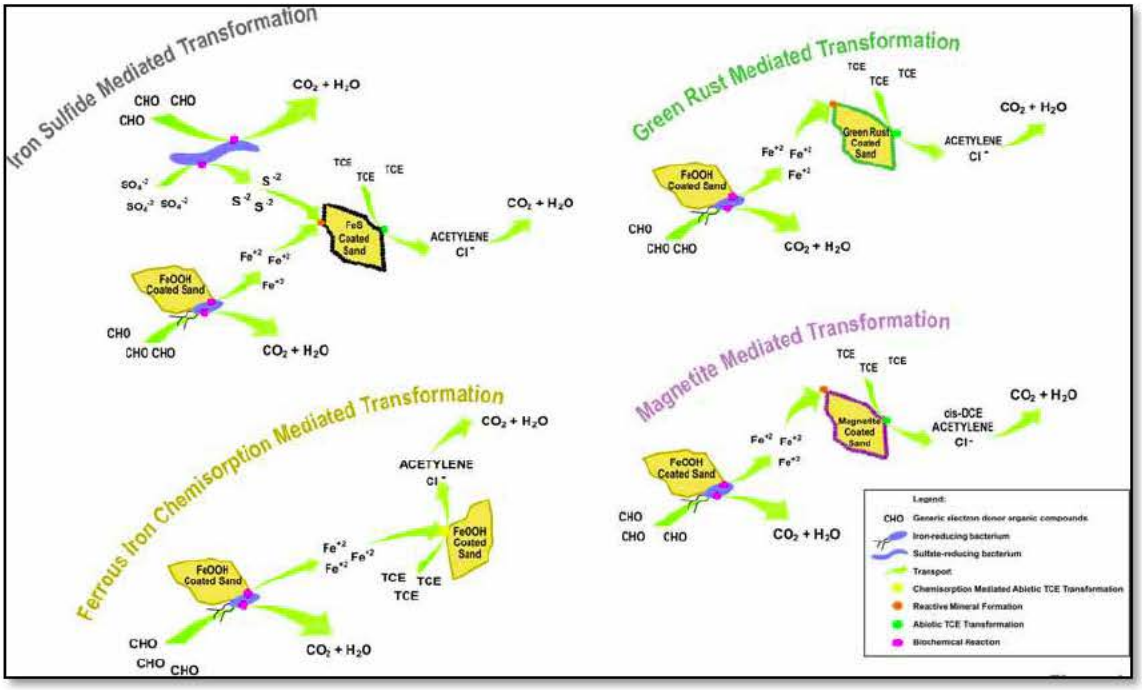
Early laboratory experiments demonstrated that minerals such as iron sulfides[164-166], magnetite and green rusts[167] could transform chlorinated hydrocarbons. Laboratory experiments demonstrated that TCE can be degraded to acetylene, acetate and formate under abiotic conditions[168, 169]. Other research has focused on the precise chemical mechanisms of dechlorination of various solvents by reactive iron species[170-172]. In the laboratory, the extent and sustainability of reactions are often influenced by other conditions such as oxidation/reduction potential, presence of dissolved organic matter, and pH.

How do reactive mineral species contribute to attenuation? (Page 2)

Using both laboratory microcosms and field data, Ferrey et al. demonstrated that the rate of removal of *cis*-1,2-DCE in a groundwater plume was similar to sterile microcosms in the laboratory[173]. These results support the conclusion that naturally-occurring, minerally-mediated reduction of chlorinated solvents *in situ* may be a viable natural attenuation mechanism, particularly under anaerobic conditions. Reactive iron species have also been shown to reduce Cr(VI)[174] and U(VI)[175], indicating that mineral matrix may be important in natural attenuation of metals.

It is important to note that these reactive mineral species are often biogenically formed. For example, iron sulfide may be mediating reductive dechlorination of a contaminant, but the actions of iron-reducing and/or sulfate-reducing bacteria may be responsible for the formation of iron sulfide itself. Consequently, these reactions are often referred to as biogeochemical, or biologically-mediated abiotic degradation (BMAD), to acknowledge the biological component.

In 2007, AFCEE, ESTCP and NAVFAC hosted a workshop to explore the state of the science around abiotic transformations and to identify future research needs.[25] Based on promising early research, the USEPA has developed guidance to facilitate evaluation of the potential contribution of abiotic processes to natural attenuation of chlorinated solvents in groundwater[27]. The guidance includes descriptions of reactive iron species, transformation mechanisms and potential ways to quantify them for MNA evaluations.



Potential in situ biogeochemical transformation mechanisms. Graphic generated from **2007 ESTCP/AFCEE/NAVFAC** *workshop*[25]

FAQ 26. What is a low-risk site? How is MNA involved?

Low Risk Means MNA the Rest of the Way

A relatively new concept is now emerging where certain sites are "low-risk sites" that can be closed or conditionally closed while the site naturally attenuates[176]. This concept is being reflected directly in guidance documents from several regulatory agencies[176-178], and the Air Force [176]. The overall applicability under different regulatory programs is only now being tested.

This concept is based on the recognition that complete cleanup of contaminated groundwater sites is often difficult and consequently, clean closure in the immediate future is unattainable at many sites. At these sites, contaminant concentrations may decrease significantly due to remediation and/or natural attenuation, but persistent low-levels of groundwater contamination above closure criteria can preclude objectives such as reaching background concentrations or drinking water standards. However, this type of contamination can mean that the site actually poses very little risk to human health and the environment in the context of the site characteristics. Consequently, a "low-risk" site may be amenable for complete closure in some regulatory jurisdictions, or a conditional closure where limited monitoring is required while the site attenuates.

Low Risk Site Criteria – Use to determine the case for low risk closure or reduced monitoring (Farhat, 2012)

1 Conceptual Site Model is complete and reflects low-risk site closure concepts

2 All sources are controlled

3 Residual contamination will have no adverse impact on present and future land and water uses

State Regulatory Low Risk Programs. In particular, MNA has applicability to the post-remediation period for "low-risk" sites, where source removal did not achieve all of the site-specific objectives but where residual contamination does not result in risk to any receptors and does adversely affect anticipated uses for the site. This framework has been incorporated into state regulatory guidance for several states, including California and Colorado. On May 1, 2012, the State Water Board for California adopted a statewide policy on closing low-threat sites with underground storage tanks (see grey box)[179].

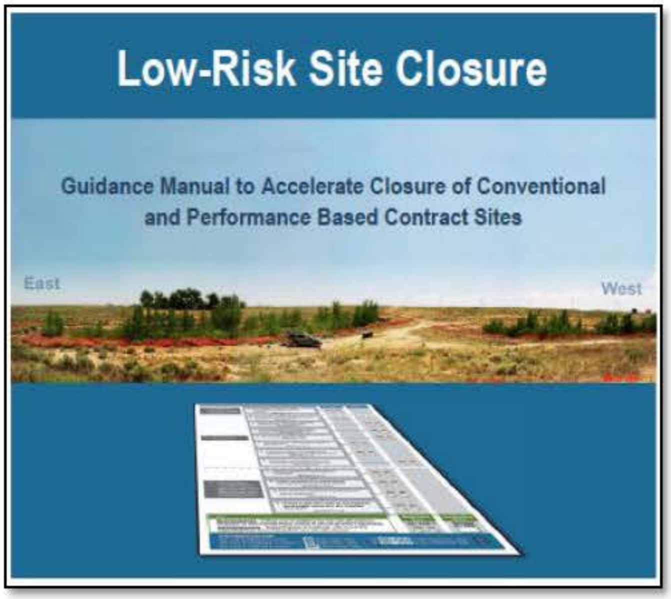
California State Water Resources Control Board Resolution No. 2012-0016

"Program experience has demonstrated the ability of remedial technologies to mitigate a substantial fraction of a petroleum contaminant mass with the investment of a reasonable level of effort. Experience has also shown that residual contaminant mass usually remains after the investment of reasonable effort, and that this mass is difficult to completely remove regardless of the level of additional effort and resources invested. It has been well-documented in the literature and through experience at individual UST release sites that petroleum fuels naturally attenuate in the environment…[and] slows and limits the migration of dissolved petroleum plumes in groundwater…In the absence of unique attributes of a case or site-specific conditions that demonstrably increase the risk associated with residual petroleum constituents, cases that meet the general and media-specific criteria described in this policy pose a low threat to human health, safety or the environment and are appropriate for closure…Cases that meet the criteria in this policy do not require further corrective action

What is a low-risk site? How is MNA involved? (Page 2)

Similar guidance has been issued by the San Francisco Bay Region of the California Regional Water Quality Control office[177] regarding low-threat chlorinated solvent sites. Under this guidance, source zones that have been remediated to the extent feasible, but still exceed cleanup standards, could be closed if "cleanup standards can be met under natural conditions within a reasonable timeframe, following completion of cleanup and monitoring."

Air Force LoRSC Guide. The Air Force has developed a low-risk site closure guidance (LoRSC) manual to help accelerate the closure process for their sites[176]. Consistent with an evaluation of MNA as a management option, this document uses several lines of evidence to evaluate whether a site should be considered low-risk, and to demonstrate that it will not cause a future environmental problem.



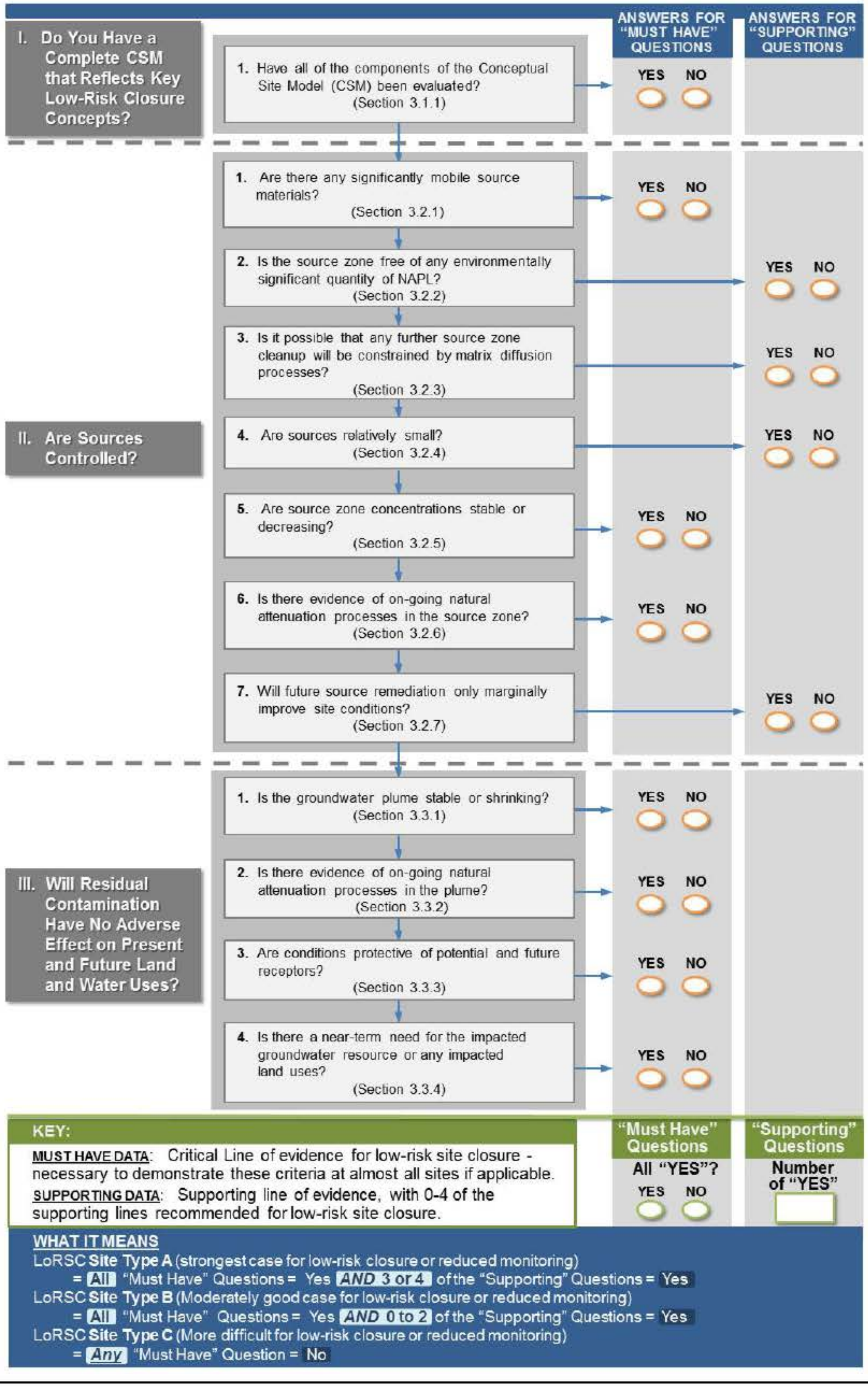
Low-Risk Site Closure

Guidance Manual to Accelerate Closure of Conventional and Performance Based Contract Sites

In the LoRSC manual, "must have" data for prioritizing sites for the low-risk closure process include many of the same data that are used in evaluating MNA (e.g., stable or shrinking source, stable or shrinking plume, evidence of attenuation in source and plume). This is an important link since MNA will be used to manage the site during closure. Other weight of evidence factors in favor of a site being low-risk include:

1) matrix diffusion dominated sources instead of mobile NAPL sources;
2) difficulty in removing the residual contamination; and
3) conditions that are protective of current and future receptors.

The overall LoRSC flowchart is shown on the next page. Overall, the purpose of the LoRSC manual is to open a dialogue on realistic site management by presenting a technically-based framework for evaluating and closing low-risk sites. A related concept proposed by the National Research Council, the Transition Assessment, is described in the next FAQ (FAQ 27).



Air Force LoRSC Manual Methodology to Determine Low Risk Sites[176]

	Question	ANSWERS FOR "MUST HAVE" QUESTIONS	ANSWERS FOR "SUPPORTING" QUESTIONS
I. Do You Have a Complete CSM that Reflects Key Low-Risk Closure Concepts?	1. Have all of the components of the Conceptual Site Model (CSM) been evaluated? (Section 3.1.1)	YES ○ NO ○	
II. Are Sources Controlled?	1. Are there any significantly mobile source materials? (Section 3.2.1)	YES ○ NO ○	
	2. Is the source zone free of any environmentally significant quantity of NAPL? (Section 3.2.2)		YES ○ NO ○
	3. Is it possible that any further source zone cleanup will be constrained by matrix diffusion processes? (Section 3.2.3)		YES ○ NO ○
	4. Are sources relatively small? (Section 3.2.4)		YES ○ NO ○
	5. Are source zone concentrations stable or decreasing? (Section 3.2.5)	YES ○ NO ○	
	6. Is there evidence of on-going natural attenuation processes in the source zone? (Section 3.2.6)	YES ○ NO ○	
	7. Will future source remediation only marginally improve site conditions? (Section 3.2.7)		YES ○ NO ○
III. Will Residual Contamination Have No Adverse Effect on Present and Future Land and Water Uses?	1. Is the groundwater plume stable or shrinking? (Section 3.3.1)	YES ○ NO ○	
	2. Is there evidence of on-going natural attenuation processes in the plume? (Section 3.3.2)	YES ○ NO ○	
	3. Are conditions protective of potential and future receptors? (Section 3.3.3)	YES ○ NO ○	
	4. Is there a near-term need for the impacted groundwater resource or any impacted land uses? (Section 3.3.4)	YES ○ NO ○	

KEY:

MUST HAVE DATA: Critical Line of evidence for low-risk site closure - necessary to demonstrate these criteria at almost all sites if applicable.

SUPPORTING DATA: Supporting line of evidence, with 0-4 of the supporting lines recommended for low-risk site closure.

"Must Have" Questions	"Supporting" Questions
All "YES"? YES ○ NO ○	Number of "YES" ☐

WHAT IT MEANS

LoRSC **Site Type A** (strongest case for low-risk closure or reduced monitoring)
= **All** "Must Have" Questions = Yes ***AND* 3 or 4** of the "Supporting" Questions = Yes
LoRSC **Site Type B** (Moderately good case for low-risk closure or reduced monitoring)
= **All** "Must Have" Questions = Yes ***AND* 0 to 2** of the "Supporting" Questions = Yes
LoRSC **Site Type C** (More difficult for low-risk closure or reduced monitoring)
= ***Any*** "Must Have" Question = No

FAQ 27. Can MNA be a stand-alone remedy? When should you transition to MNA?

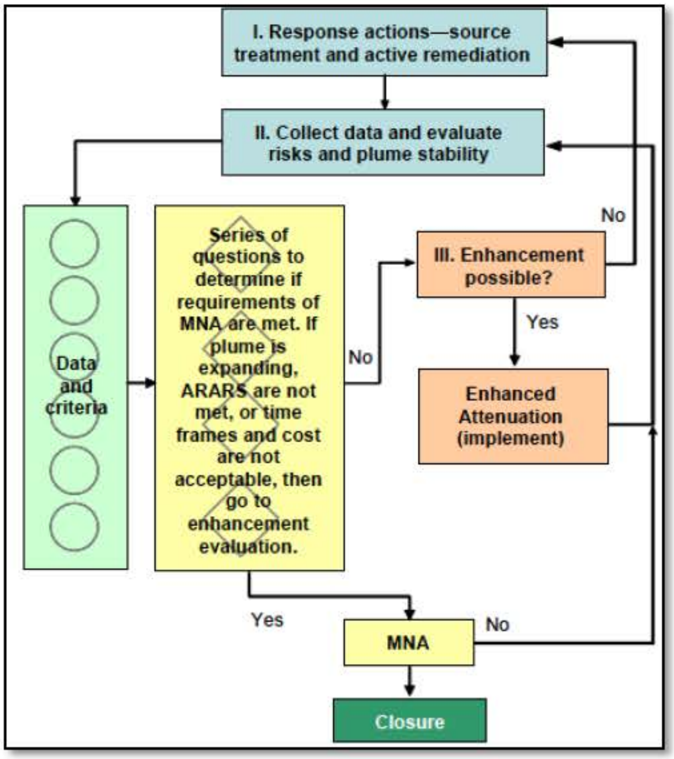
It Depends…

What About MNA as a Stand Alone Remedy?

There are a wide variety of opinions and perspectives about MNA serving as stand-alone remediation approach. The question can be confusing, as some answer this to mean "as the only remedial activity" and others mean "as the sole groundwater remedy." The USEPA MNA Directive[14] said that MNA should not be considered a default or presumptive remedy, and that it should be applied "very cautiously as the sole remedy" and that "source control will be fundamental components of any MNA remedy." But many sites have been managed by MNA alone, and even more with some source treatment and MNA as the sole groundwater remedy.

A 2004 survey of 191 chlorinated solvent MNA sites showed 30% of these sites relied on MNA as the sole remedy and 33% are implementing MNA in conjunction with source zone remediation[39] In 2011, a survey of oilfield groundwater remediation sites showed MNA being used as the sole *groundwater remedy* at 25 of 60 sites in Texas and 85 of 115 in Kansas over a ten year period up to 2011 (this meant that source remediation may have occurred at these sites).[180] An analysis of 3941 underground fuel tank sites using the California Geotracker database[181] indicated that MNA was used as the only remedy at only 2% of the sites (soil vapor extraction and excavation were used at 40% of the sites each).

There is a growing array of technologies, analysis techniques, and regulatory basis for source zone attenuation[4], which would likely increase the application of MNA as the sole remedy at some sites (see FAQs 7 and 24), particularly low-risk sites such as those with stable or shrinking plumes and relatively low concentrations (e.g., <100x the cleanup level). At these low-concentration sites, MNA may not meet typical criteria for remediation timeframe to be considered a traditional clean-up technology, but it can be used as part of a risk management strategy. For example, the Florida Department of Environmental Protection has developed natural attenuation default concentrations (NADCs) that account for this and allow MNA to be used as a default remedy for low concentration sites. [195]



Can MNA be a stand-alone remedy? When should you transition to MNA? (Page 2)

ITRC Perspective for Chlorinated Sites

The ITRC's Enhanced Attenuation Chlorinated Organics Team developed the flowchart to the right to help site managers determine when to transition to MNA[1]. They stated that the basic premise of their document is that "for some sites" source mass flux reductions alone may not be sufficient, and that MNA alone may be unacceptable treatment option.

The ITRC describes their flowchart with:

> *"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)":*
>
> - *Are the risks acceptable?*
> - *Is the plume stable or shrinking?*
> - *Are conditions sustainable?*
> - *Is the remediation timeframe acceptable?*
> - *Are the cost-benefits acceptable?*

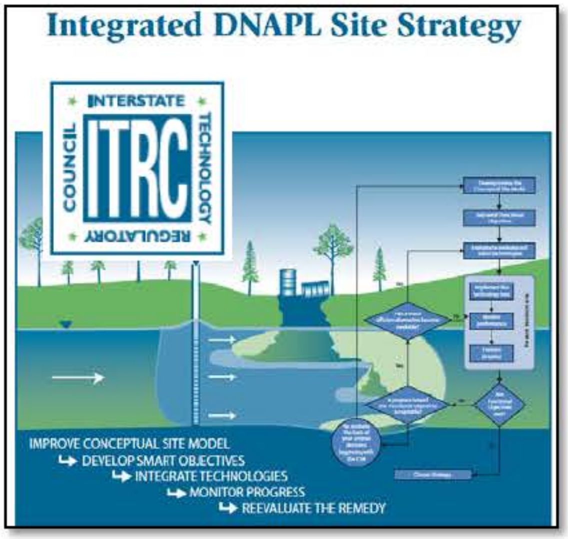
If not, the document stresses that Enhanced Attenuation techniques be considered (see text box for their definition).

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.

Integrated DNAPL Site Strategy (IDSS)

Developed for DNAPL sites by the ITRC, the IDSS states that site managers realize that most sites require coupling of technologies in time or space to make satisfactory progress[132]. MNA was considered to be "generally compatible" as a follow-on technology to all other technologies, and

> *"in most chlorinated solvent remediation sites, MNA is a sequential component of the remedy following source reduction or downgradient of a more aggressive technology."*



Can MNA be a stand-alone remedy? When should you transition to MNA? (Page 3)

National Research Council

The recent National Research Council (NRC) report *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites*[182] suggests a changing perspective about how to manage contamination over the life cycle of a site. They note that despite years of effort and considerable investment, many sites "will require long-term management that could extend for decades or longer." They discuss the need for developments that can aid in "transition from active remediation to more passive strategies and provide more cost-effective and protective long-term management of complex sites," including conducting formal transition assessments. One of their most important conclusions is the need to perform "**Transition Assessments**" which would include MNA at many sites (see text box).

National Research Council's Transition Assessment Concept[182]

At many complex sites, contaminant concentrations in the plume remain stalled at levels above cleanup goals despite continued operation of remedial systems. There is no clear path forward to a final end state embodied in the current cleanup programs, such that money continues to be spent, with no concomitant reduction in risks. If the effectiveness of site remediation reaches a point of diminishing returns prior to reaching cleanup goals and optimization has been exhausted, the transition to monitored natural attenuation or some other active or passive management should be considered using a formal evaluation. This transition assessment would determine whether a new remedy is warranted at the site or whether long-term management is appropriate.

Other Approaches

The question of when to transition to MNA is implicit in the low-risk site movement, which has been applied to hydrocarbon and chlorinated solvent sites (FAQ 26).

Several projects focus on using models to help determine when to transition to MNA. Training by the Department of Energy (DOE) on Practical Tools[183] describe how the REMChlor model can be used to evaluate how much source and plume attenuation is required before transitioning to MNA.

Another DOE publication describes how the RT3D model can be used to evaluate transient plume effects when transitioning from an active remedy to MNA[184].

FAQ 28. How can stakeholders considering MNA make better decisions?

Use SMART Objectives

The ITRC's Integrated DNAPL Site Strategy (IDSS)[132] presents a decision making approach based on the idea of setting realistic objectives. First, the concept of two different classes of objective is introduced:

> *Absolute (objectives based on broad social values, such as protection of public health) or functional (steps or activities taken to achieve absolute objectives, such as supplying bottled water to affected residents). Functional objectives are established to demonstrate attainment of absolute objectives and have often been missing, difficult to measure, or unattainable.*

Second, the IDSS document stresses that the functional objectives should be SMART: Specific, Measureable, Attainable, Relevant, and Time-bound (see text box). They present several important advantages associated with the SMART approach:

> *Selecting objectives that reflect SMART attributes makes subsequent decisions more valid and remedial approaches more successful. It is often necessary to develop SMART functional objectives for different locations, phases, and alternative end points of an overall site cleanup.*

S **Specific—**The objectives should specify what is to be achieved through a remedial action. They should be concrete, detailed, and well defined.
- Diagnostic questions:
    - What exactly are we going to do?
    - Is the objective well understood?
    - Will this objective lead to a desired result?
- *S does not mean "shifting"!*

M **Measurable—**Managers should be able to measure whether or not the objectives are being met. Numbers, quantities, or comparisons should be specified, and the uncertainty in key measurements should be understood.
- Diagnostic questions:
    - How will we know that the change has occurred?
    - Can these measurements be obtained?
- *M does not mean "magical"!*

A **Attainable—**Objectives should be realistic, given the proposed time frame, political climate, and/or the amount of money available.
- Diagnostic questions:
    - Can we get this done in the proposed time frame?
    - Do we understand the limitations and constraints?
    - Can we do this with the resources we have?
    - Is this possible?
    - Has anyone else done this successfully?
- *A does not simply mean "ambitious"!*

R **Relevant—**The objective should have a value and represent a realistic expectation.
- Diagnostic questions:
    - Does the outcome of the objective directly support achievement of the absolute objective?
    - Do we have the resources available to achieve this objective?
- *R does not mean "remarkable"!*

T **Time-bound—**The time allotted for achieving the objective should be clearly defined and short enough to ensure accountability.
- Diagnostic questions:
    - When will this objective be completed?
    - Is someone still going to be accountable for meeting the time frame?
- *T does not mean "timeless"!*

How can stakeholders considering MNA make better decisions? (Page 2)

Smart Objectives, Continued:

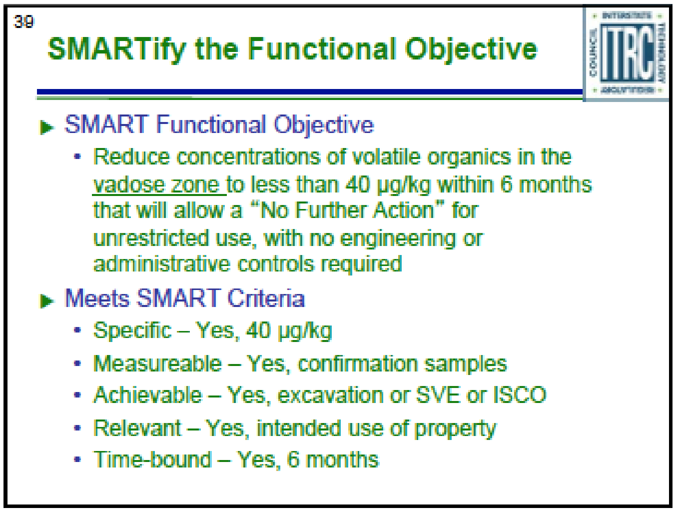
> *Given the unique perspectives of different stakeholders and the practical and economic limitations that exist, defining the SMART functional objectives appropriate for a given site requires cooperation, consensus, and often some compromises. An example site is used in this document to illustrate the potential functional objectives that may apply at a given site and how SMART criteria can be effectively applied when developing the final objectives.*

So while not specific to MNA decision making, this approach has several advantages that can be applied to MNA decision making at any type of site.

20-Year Limit for Functional Objectives

One interesting observation made by the ITRC IDSS team was that typical remediation timeframes for chlorinated solvent sites "may be long (decades to centuries)." However, they stress that the time-bound element for functional objectives should not extend more than 20 years. For example, while the absolute objective for any project (such as a MNA remedy) may take multiple decades, functional objectives such as "MNA should reduce the mass discharge by 99% in 50 years" should be avoided. Rather, the functional objective should have some type of criteria after 20 years, with the realization that new functional objectives based on current site data will then have to be developed.

The rationale for the 20-year duration is *"to encourage accountability for specific actions and to make it easier to measure progress toward the objectives. The consensus of the IDSS Team is that functional objectives that extend beyond ~20 years are generally inappropriate, even though the absolute objectives may well require management and even subsequent active remediation well beyond such durations."*



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SMARTify the Functional Objective

- SMART Functional Objective
  - Reduce concentrations of volatile organics in the vadose zone to less than 40 µg/kg within 6 months that will allow a "No Further Action" for unrestricted use, with no engineering or administrative controls required
- Meets SMART Criteria
  - Specific – Yes, 40 µg/kg
  - Measureable – Yes, confirmation samples
  - Achievable – Yes, excavation or SVE or ISCO
  - Relevant – Yes, intended use of property
  - Time-bound – Yes, 6 months

Example of "SMART" Functional Objective for Remediation[132]

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