Monitored Natural Attenuation

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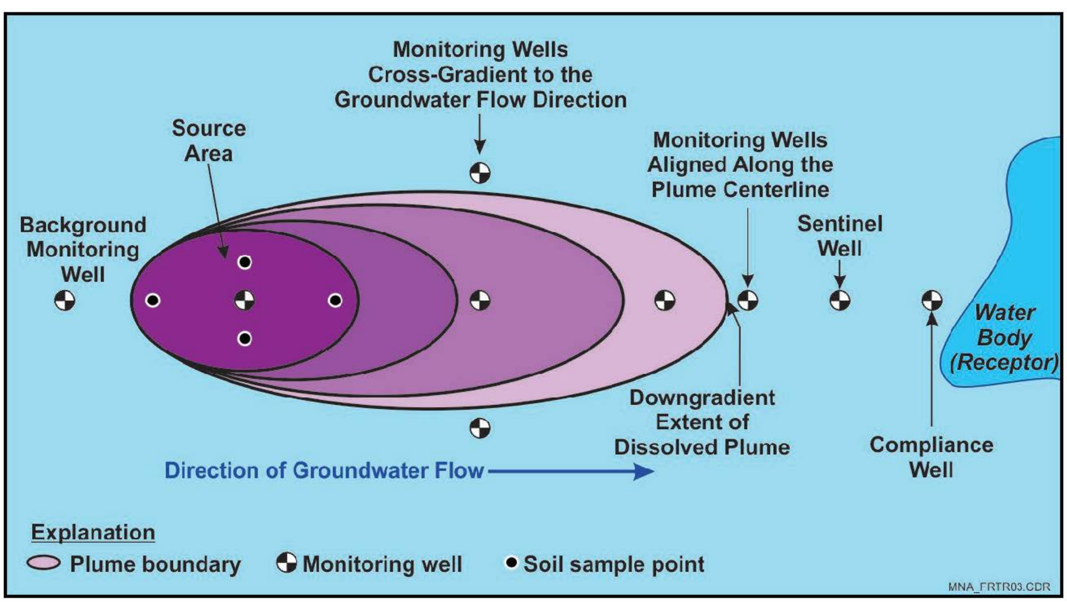
Schematic



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Monitored Natural Attenuation

Introduction

Monitored natural attenuation (MNA) consists of a range of naturally-occurring in situ physical, chemical, and biological processes that attenuate contaminant concentrations in groundwater to achieve remedial goals within a reasonable timeframe, and protect human health and the environment. MNA utilizes groundwater data to develop contaminant trends and to evaluate reductions in contaminant concentrations brought about by naturally-occurring destructive mechanisms (e.g., biodegradation and/or chemical/abiotic degradation) and non-destructive mechanisms (e.g., advection, dispersion, dilution via recharge, sorption, and volatilization). While non-destructive mechanisms decrease contaminant concentrations spatially through redistribution (scattering) of the contaminant mass, destructive mechanisms reduce contaminant concentrations through degradation/alteration of the contaminants' chemical composition. Biodegradation is often the predominant (destructive) mechanism to reduce the mass of the contaminants of concern (COCs) at a site. However, it is noted that the impacts of chemical degradation (or abiotic degradation) mechanisms are becoming better understood and are recognized to contribute more significantly to MNA (under certain site-specific conditions) than previously thought.

Other Technology Names

Natural Attenuation
Intrinsic Remediation
Passive Remediation

Description

MNA is a passive remedial approach where naturally-occurring subsurface processes, such as advection, dispersion, dilution via recharge, sorption, volatilization, and degradation (biological and abiotic), are assessed via an environmental monitoring program to ensure that these processes: 1) allow for sufficient reductions in COC concentrations so that remedial goals will eventually be attained; 2)) minimize further downgradient COC migration at the plume boundaries (i.e., plume is stable); and 3) restore the dissolved-phase plume to levels appropriate for current or future beneficial uses to the extent practicable (EPA, 1998). Appropriate institutional controls or point-of-use treatment may be required until natural attenuation reaches remedial goals. To assess whether MNA is a viable remedy at a site, the following lines of evidence should be demonstrated by site data (NAVFAC, 2008; ITRC, 2008; EPA, 2008; AFCEE, 2007):

- There is a stable to decreasing concentration trend for all COCs observed at the plume boundaries (i.e., plume is stable),
- Analytical results indicate that decreasing trends are statistically significant at a 95% confidence level,
- There is presence of daughter products at statistically significant concentrations
- There is an increase in the $^{13}C/^{12}C$ ratio (EPA, 2008),
- Estimated dissolved mass or mass flux of contaminants onsite, offsite, and within the entire plume continue to remain stable to decreasing, and
- Groundwater chemistry data support geochemical conditions that are suitable for degradation and indicate whether active degradation is occurring.

Three lines of evidence may be evaluated to confirm that site COCs can be remediated via natural attenuation processes:

1. Examine historical contaminant trends to determine if contaminant mass and/or concentrations are decreasing over time or have reached plateau levels due to matrix diffusion or other mass transfer limitations. [Contaminant trends represent the line of evidence to verify ongoing natural attenuation, which is evaluated using the first three bulleted points listed above, which are explicit ways of documenting MNA trends at a site.]
2. Use hydrogeological and geochemical data and/or daughter to parent compound ratios to determine if subsurface conditions are amenable to natural attenuation processes.

   1 [This line of evidence corresponds to the last bullet above which is to determine whether an aquifer's redox condition is amenable to MNA currently as well as into the future.]
3. Site-specific microcosm studies and related indicator parameters are recommended to verify the presence of a specific microbial population and related parameters (e.g., functional genes) necessary to support a particular biodegradation attenuation process and its ability to degrade the COCs. [More recently, advanced microbiological tools, such as metagenomics and

metaproteomics, are being developed and used to provide evidence that biological processes are occurring at a site. Metagenomics can be used to evaluate the abundance of COC-degrading microbial species, which is an indirect line of evidence that natural attenuation (via metabolic or cometabolic biodegradation) is occurring. Metaproteomics, a developing technology, can be used to measure the abundance of proteins known to be expressed during biodegradation of a COC, and may provide another line of evidence that biodegradation of the COC is occurring. Carbon stable isotope analysis involving parent and daughter products can also be used to provide a direct line of evidence of biodegradation versus dispersion as the primary drivers for natural attenuation.]

A variety of guidance documents (see Resource Section) for applying MNA have been produced by the Navy, EPA, Interstate Technology and Regulatory Council (ITRC), and the United States Geological Survey (USGS). These documents describe the application of MNA to treat a wide range of contaminants, including petroleum hydrocarbon constituents, chlorinated solvents, metals, and radionuclides, and the natural attenuation processes that can reduce contaminant mass and/or concentrations over time.

A monitoring program is a critical element of MNA and must be carefully designed to demonstrate that: 1) natural attenuation processes are preventing contaminant migration to potential exposure points; 2) natural attenuation processes are making sufficient progress towards achieving remedial goals within a reasonable timeframe; and 3) other engineered remedial actions will not substantially reduce the cleanup timeframe or eliminate further environmental impact (e.g., carbon footprint). The data obtained must include COC concentration trends, as well as data needed to evaluate the various abiotic, biotic, and physical natural attenuation processes, including but not limited to the parameters listed and discussed in Table 1 (EPA, 1998).

Table 1. Examples of Common Monitored Natural Attenuation Data

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Parameter	Monitoring Purpose	Contaminant
Field Parameters		
Dissolved Oxygen	Determine redox state of	All contaminants

Oxidation-Reduction Potential	aquifer system	
Conductivity	Ensure groundwater samples are collected from the same aquifer system	
pH	Determine preferential biodegradation process (aerobic or anaerobic)	
Temperature	Ensure monitoring well is sufficiently purged for groundwater sampling	
Geochemical Data		
Nitrate	Sufficient Electron acceptor (competing with chlorinated solvents) for microbial respiration under anaerobic conditions	Organic contaminants (petroleum hydrocarbon constituents and chlorinated solvents)
Sulfate		
Dissolved Iron (Fe^{2+})	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese	
Manganese	May determine if anaerobic biodegradation is solubilizing manganese from the aquifer matrix material	
Total Organic Carbon	Determine if reductive dechlorination of chlorinated solvents is possible in the absence of anthropogenic carbon	
Magnetic Susceptibility	Provides indication of level of iron-bearing minerals and potential/likelihood for abiotic degradation to occur	Chlorinated solvents
Iron Sulfides		

Contaminants of Concern and Byproducts		
Parent Compounds	Assess baseline concentrations and remedial progress	Chlorinated solvents, MTBE, 1,4-dioxane
Daughter Products	Evaluate remedial progress, potential for stall (e.g., vinyl chloride), evaluate reaction pathways (e.g., abiotic versus biotic degradation of chlorinated ethenes)	TCE, DCE, VC (chlorinated solvents), tert-butyl alcohol, tert-butyl formate (MTBE)
Reaction End Products	Assess remedial progress and ability to completely mineralize COCs	Ethene, ethane, methane (biotic anaerobic degradation), Acetylene (abiotic degradation)
Biological Parameters		
Quantitative polymerase chain reaction (qPCR)	Assess presence of microbial populations responsible for degradation via multiple potential pathways for different contaminants, as well as functional genes responsible for degradation (e.g., vinyl chloride reductase)	Chlorinated Solvents, MTBE. 1,4-dioxane
Proteomics	Determine degradation activity of microbial population	COCs for which specific degradation enzymes are known
Compound Specific Isotope Analysis (CSIA)	Measurement of isotope ratios provides evidence of degree of degradation of COCs, and can differentiate between biodegradation versus other degradation pathways	Chlorinated solvents, MTBE, 1,4-dioxane
Stable Isotope Probing	Evaluate if biodegradation of	Any biodegradable

	a contaminant is occurring and determine the microorganism responsible for it	contaminant
Green and Sustainable Remediation		
Modifiers, Micronutrients	Amount required to sustain MNA	Carbon footprint[EI]
Monitoring activities	Frequency required to verify performance	Carbon footprint[EI]

EI - Environmental Impact

Evaluation of mass flux and mass discharge also should be included in the monitoring program. Both are useful metrics to understand plume source strength and how it is changing as MNA progresses. Mass flux is defined as the mass of contaminants that flows through an area during a specified time (mass/area/time). Mass discharge is an integration of mass flux values and represents the total mass of contaminants that flows through a plane during a specified time (mass/time) (ITRC, 2010). Because mass flux and mass discharge are functions of contaminant concentration and groundwater velocity, they provide a more accurate depiction of plume behavior than concentration data alone. For instance, results from two sampling depths or locations could exhibit concentrations of 2,000 µg/L of a particular contaminant; however, if groundwater velocity at one location is 10 times that of the other due to differences in stratigraphy, the mass flux would also be 10 times greater

3. Hence, although concentration indicates that it is equally important to remediate both locations, the flux data indicate that it is the more permeable location that could pose greater risk to downgradient receptors and should be evaluated with regard to the ability of MNA to mitigate it.

Mass flux and/or mass discharge at an MNA site are usually determined using the transect method or use of passive flux meters. The transect method uses monitoring data from wells and points to integrate concentration and flow data. Historical site data can be used provided that the data are located along transects perpendicular to groundwater flow, and the groundwater flowrate is known or can be estimated at each location. However, if not available, the passive flux meter method is a simple method to collect such data. It involves placing a tube containing a permeable sorbent material infused with tracers into a well for a known time. Dissolved contaminants in groundwater that pass through the well are sorbed onto the material and the soluble tracer leaches into the groundwater. After the tube is removed from the well, the total mass of contaminants and mass of tracer remaining are calculated and the results can be used to calculate a mass flux. If multiple tubes are placed in a row perpendicular to groundwater flow, results can be integrated to estimate mass discharge (ITRC, 2010).

A typical monitoring well network needed to demonstrate the effectiveness of MNA includes four different types of monitoring wells, each with a distinct purpose:

1. **Background wells** are monitored to confirm areas that are not impacted by COCs. Field parameters/geochemical data are compared to data from impacted wells to assess MNA.
2. **Cross-gradient and downgradient wells** are monitored to ensure that the plume is not expanding or migrating downgradient at concentrations above acceptable risk levels.
3. **Source area and centerline wells** are monitored to demonstrate decreasing COC concentrations in the source area and through the centerline of the plume. Concentration trends along plume centerline wells can also be used to estimate attenuation and mass flux rates with distance.
4. **Compliance and sentinel wells** generally are located at regulator approved points to assure contamination is not migrating towards receptors.

These monitoring wells are vital for establishing that MNA is an option at a site, as well as documenting the progression of a natural attenuation remedy component at a site.

As with all remedial technologies, MNA is considered on a case-by-case basis. At sites where polychlorinated biphenyls (PCBs) are strongly sorbed to deep subsurface soils and are not migrating or where dense, nonaqueous-phase liquid (DNAPL) removal is technically impracticable, MNA may be a viable remediation strategy. However, MNA is seldom used as the sole remediation strategy. It is typically used as a remedy component in combination with an active source area or plume "hot spot" treatment technology to reduce contaminant mass flux over time. Remedial technologies, such as thermal treatment, in situ chemical oxidation (ISCO), air sparging, soil vapor extraction (at source), enhanced in situ bioremediation, and in situ chemical reduction often are employed at select locations at a site (e.g., source zone), while MNA is selected to address the remaining dissolved-phase plume. Active treatment technologies also typically reach a plateau level where continued treatment is no longer cost effective, after which the source area/plume that was undergoing active treatment is then transitioned to MNA until the remedial goals are met. If MNA is to follow active treatment, it is important to recognize the effects the treatment can have on the natural attenuation capacity of the subsurface, such as microorganism population and redox conditions. However, it is noted that at many sites, geochemical conditions usually return to their background values relatively quickly, as has been evaluated and modeled at sites where enhanced in situ bioremediation (EISB) has been applied (Borden et al., 2015).

When assessing the effectiveness of MNA, modeling techniques can be used to determine: 1) if migration of COCs will be controlled to achieve protectiveness of potential receptors; and 2) if remedial goals will be achieved within a projected site-specific "reasonable timeframe". Data collected via the monitoring program are used as input data for a natural attenuation model, which may also serve the purpose of updating the conceptual site model (CSM). Table 2 presents several models that are used in the environmental industry. Additional groundwater software models that can be used for MNA evaluations, as well as fate and transport evaluations, are located on the EPA Web site at https://www.epa.gov/water-research/methods-models-tools-and-databases-water-research.

Table 2. Monitored Natural Attenuation Models

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Model	Capabilities and Access
BioBalance Tool Kit	Evaluate natural attenuation capacity at site. Includes four modules (source, competition, electron donor, and plume) and combines the modules for the final mass balance https://www.gsi-net.com/en/software/free-software/biobalance-toolkit.html
BIOCHLOR	Fate and transport of chlorinated solvents (first-order decay) https://www.epa.gov/water-research/biochlor-natural-attenuation-decision-support-system

BIOPLUME	Fate and transport via inputting site-specific hydraulic and attenuation parameters www.epa.gov/water-research/bioplume-iii
BIOSCREEN	Fate and transport of dissolved phase petroleum hydrocarbon constituents https://www.epa.gov/water-research/bioscreen-natural-attenuation-decision-support-system
Matrix Diffusion Toolkit	Matrix diffusion effects from low permeability zones https://www.serdp-estcp.org/Tools-and-Training/Environmental-Restoration/Groundwater-Plume-Treatment/Matrix-Diffusion-Tool-Kit
MT3D	Fate and transport via inputting site-specific hydraulic and attenuation parameters https://www.usgs.gov/software/mt3d-usgs-groundwater-solute-transport-simulator-modflow (typically used in commercial software package)
NAS	Includes three main interactive modules to provide estimates for distance of stabilization, time of stabilization, and time of remediation https://toxics.usgs.gov/highlights/nas_2.2.0/
REMChlor	Fate and transport of chlorinated solvents (first-order decay). Allows user to remediate source and/or plume at different times and different locations. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=187463
REMChlor-MD	An updated version of the REMChlor (Falta et al., 2007) model with the ability to simulate matrix diffusion processes in the plume (Farhat et al., 2018)
RT3D	Fate and transport via inputting site-specific hydraulic and attenuation parameters https://bioprocess.pnnl.gov/ (typically used in commercial software package)
SEAM3D	Fate and transport via inputting site-specific hydraulic and attenuation parameters
SourceDK	Remedial timeframe decision-support tool that can evaluate data using three tiers. Tier 1 relies on empirical data, Tier 2 uses a box model, and

	Tier 3 uses a process model https://www.gsi-net.com/en/software/free-software/sourcedk.html

Development Status and Availability

The following checklist provides a summary of the development and implementation status of MNA:

☐ At the laboratory/bench scale and shows promise

☐ In pilot studies

☒ At full scale

☒ To remediate an entire site (source and plume) focused on plume

☐ To remediate a source only

☒ As part of a technology train

☒ As the final remedy at multiple sites

☒ To successfully attain cleanup goals in multiple sites

Cometabolic bioremediation is available through the following vendors:

☒ Commercially available nationwide

☐ Commercially available through limited vendors because of licensing or specialized equipment

☒ Research organizations and academia

Applicability

Contaminant Class Applicability Rating for Cometabolic Bioremediation

(Rating codes: ● Demonstrated Effectiveness, ◐ Limited Effectiveness, ○ No Demonstrated Effectiveness,

◊ Level of Effectiveness dependent upon specific contaminant and its application/design, I/D Insufficient Data, N/A Not Applicable)

Nonhalogenated VOC	Halogenated VOC	Nonhalogenated SVOC	Halogenated SVOC	Fuels	Inorganics	Radionuclides	Munitions	Emerging Contaminants
●	●	●	●	N/A	●	●	I/D	I/D

MNA can be used as a remedy component for different portions of a plume or following active treatment to decrease COC concentrations to levels below cleanup goals for a wide range of contaminants, including petroleum hydrocarbon constituents, chlorinated solvents, semi-volatile organic compounds (SVOCs), PCBs, metals, and radionuclides. Even COCs not susceptible to biodegradation can be reduced by other natural attenuation mechanisms such as abiotic degradation or natural groundwater flushing/dispersion. MNA is also feasible at sites contaminated with inorganic constituents if COCs are sorbed to the soil matrix or if there is a change in redox state, which could result from natural groundwater flushing/dispersion or from a gradual return to baseline conditions after application of a technology such as ISCO. Changes in the redox state of inorganics/metals alter their mobility and can either mobilize or immobilize them within the soil matrix. Therefore, the driving factors for redox conditions at the site must be understood. Although MNA is applicable to dissolved-phase petroleum hydrocarbon constituents including those in fuels, it is not directly applicable to free phase product in the form of light non-aqueous phase liquids (LNAPLs). For attenuation of LNAPLs, the reader should refer to the Natural Source Zone Depletion Technology Profile.

For MNA to be a potential remedial approach, there must be limited risk to human health and the environment; the site must be managed such that groundwater monitoring of contaminants can be conducted on a regular basis; and land use controls (LUCs) must be in place as needed to prevent exposure to potential receptors until remedial goals are attained.

Cost

The most critical cost factors for designing and implementing MNA include the nature and extent of contamination and contaminant type as described by the CSM. These factors affect the monitoring well network and analytical suite needed to effectively demonstrate and track the progress of MNA. Major cost drivers include:

Upfront Costs

- Upfront characterization to develop an accurate CSM that may be used to assess progress of the remedy. Nature and extent of contamination, groundwater water geochemistry, and microbiological characteristics must be understood in the contaminated aquifer, as well as in background and downgradient areas. Costs are highly variable depending on the level of site characterization needed to effectively implement MNA.
- Areal extent of contamination.
- Number and design of wells required for groundwater samples. These costs are highly dependent on regulatory requirements and the extent of contamination (i.e., both lateral and vertical extent). These activities and associated costs also include utility locating, permitting, surveying, manifesting, transporting, and disposing of the investigation-derived waste (IDW).

Operation and Maintenance Costs

- Sampling frequency. These activities typically occur on a quarterly, semiannual, annual, or biennial basis, and are influenced by regulatory requirements, quantity of historical data available, and the decision-making purposes of the data. Once a sufficient database has been developed, MNA sampling frequency and parameters can be reduced over time.
- Number of monitoring locations.
- Number/types of analyses required during each monitoring event, which are dependent on the types of COCs, degradation products, and changes to various geochemical properties of the aquifer expected to occur as the remedy progresses.
- Regulatory requirements, which can impact sampling frequency, monitoring locations, and required analyses.
- Modeling and reporting of groundwater monitoring results and progress of MNA. These costs are dependent on the nature and extent of contamination (i.e., modeling approach most appropriate for site conditions) and frequency of required reporting to regulatory agencies.

Costs can range significantly between sites, depending on the size of the site, monitoring frequency, number of monitoring wells within the monitoring network, contaminant type, and modeling and reporting requirements. As a site progresses with MNA, operation and maintenance costs can be reduced through optimization of the monitoring frequency, number of monitoring wells, and number of analytes.

The list above highlights those cost dependencies specific to MNA and does not consider the dependencies that are general to most in situ remediation technologies. Click here for a general discussion on costing which includes definitions and repetitive costs for remediation technologies. A project-specific cost estimate can be obtained using an integrated cost-estimating application such as RACER® or consulting with a subject matter expert.

Duration

The following are key considerations associated with applying MNA:

- Information to develop an adequate CSM, which includes geology, hydrogeology, geochemical, and contaminant data are needed to determine the following: subsurface conditions and plume geometry and behavior; contaminant distribution within site lithology; and primary contaminant and plume migration pathways and rates.
- MNA may not be applicable if the contaminant plume is not stable and is expanding/migrating with concentrations exceeding remedial goals that threaten potential exposure pathways (i.e., indicating that the rate of migration may be greater than the rate of attenuation).
- Natural biodegradation may not be applicable at sites where the appropriate microorganisms are not naturally present, but other attenuation mechanisms may still support use of MNA. Also, toxic substances (e.g., oxygen in the case of TCE) can limit biodegradation.
- For abiotic degradation, catalysts like iron sulfides (FeS) would need to be present in the subsoil.
- A long-term monitoring program is required as a component of MNA.
- LUCs may be required to limit land use/activities and prevent exposure to potential receptors until remedial goals are achieved.
- MNA timeframe estimates and monitoring programs to evaluate progress need to account for all attenuation mechanisms, and should not be based solely on biodegradation. It should be recognized that other attenuation mechanisms

(e.g., abiotic degradation, natural groundwater flushing) become dominant versus biodegradation as COC concentrations decrease to the mid to lower parts per billion levels that no longer support adequate microbial degrader populations.

- If high levels of residual contaminant mass (e.g., LNAPL or DNAPL) exist in the source zone or other portions of the plume, active treatment may be required prior to implementing MNA.
- Some inorganics (e.g., metals) can be mobilized (such as arsenic) or immobilized (such as manganese) by natural attenuation mechanisms, but are not destroyed.
- Intermediate degradation/daughter products (e.g., vinyl chloride) may be more mobile or more toxic than the released parent material.
- The redox state in the subsurface may change over time, which can cease (biotic/organic) or reverse (abiotic/inorganic) MNA processes.
- The uncertainties associated with estimating and/or modeling MNA timeframes to achieve remedial goals must be recognized in the decision-making process throughout the remediation life cycle. Timeframe estimates need to be revisited throughout the remediation life cycle, often using different estimating techniques as more data are generated.
- Endpoint limitations to what can be achieved by active treatment need to be recognized in the remediation decision-making process. It is recommended that technically defensible criteria that allow for transitioning from active treatment to MNA (subject to modification as more data are generated) be developed early on during the remediation life cycle for acceptance by all stakeholders.
- Stakeholder acceptance of MNA as the sole remedy component may require educating the public and be difficult.

Resources

American Petroleum Institute. **Technical Protocol for Evaluating the Natural Attenuation of MTBE (2007) (PDF)** (186 pp, 2.88 MB)
This report describes the natural attenuation mechanisms of MTBE in groundwater.

Borden R.C., J.M. Tillotson, G.-H.C. Ng, B.A. Bekins, and D.B. Kent. **Impacts of Enhanced Reductive Bioremediation on Post-Remediation Groundwater Quality (PDF)** (68 pp, 1.30 MB)
This report presents results from the development of a reactive transport

model, secondary water quality impacts (SWQIs) database, and indicator simulations that were integrated to develop a general conceptual model of the major processes controlling SWQI production and attenuation during enhanced reductive bioremediation (ERB).

Environmental Security Technology Certification Program. **Frequently Asked Questions about Monitored Natural Attenuation in Groundwater (2014) (PDF)** (91 pp, 4.89 MB)
This document provides a concise overview of current knowledge regarding management of subsurface contaminant releases using MNA.

EPA. **Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (1998) (PDF)** (248 pp, 2.46 MB)
This document presents a technical protocol for data collection and analysis to evaluate MNA through biological processes for remediating groundwater contaminated with mixtures of chlorinated aliphatic hydrocarbons and fuel hydrocarbons. Overall, this technical protocol is designed to evaluate the fate of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons in groundwater and includes analytical parameters and weighting for preliminary screening for anaerobic biodegradation processes.

EPA. **Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17P (1999) (PDF)** (41 pp, 278 KB)
This document clarifies EPA's policy with regard to the use of MNA for the remediation of contaminated soil and groundwater at sites regulated under all programs administered by EPA's OSWER.

EPA. **Monitored Natural Attenuation of Petroleum Hydrocarbons Remedial Technology Fact Sheet (1999) (PDF)** (3 pp, 72.7 KB)
This fact sheet describes MNA and the various physical, chemical, and biological processes of natural attenuation that may occur at a site contaminated with petroleum hydrocarbons.

EPA. **Handbook of Groundwater Protection and Cleanup Policies for RCRA Corrective Action (2004 — Updated Version) (PDF)** (102 pp, 422 KB)
This handbook contains EPA's latest interpretation of policies on such topics as cleanup goals, the role of groundwater use, point of compliance, source control, and MNA.

EPA. **In Situ and Ex Situ Biodegradation Technologies for Remediation of Contaminated Sites (2006) (PDF)** (22 pp, 735 KB)

This Engineering Issue paper provides technology descriptions and selection factors for in situ and ex situ biodegradation technologies, including intrinsic bioremediation which may support MNA.

EPA. Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 1 — Technical Basis for Assessment (2007) (PDF) (94 pp, 2.16 MB)

This document is the first in a series of three and addresses the technical basis and requirements for assessing the potential applicability of MNA as part of a groundwater remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants.

EPA. Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 2 — Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium (2007)

This document is the second in a series of three and consists of individual chapters that describe: 1) the natural attenuation processes that may result in the attenuation of the specific contaminant and 2) data requirements to be met during site characterization.

EPA. Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 3 — Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium (2007) (PDF) (147 pp, 5.55 MB)

This document is the third in a series of three and consists of individual chapters that describe: 1) the natural attenuation processes that may result in the attenuation of the specific contaminant and 2) data requirements to be met during site characterization.

EPA. A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA) EPA 600/R-08/148 (2008) (PDF) (82 pp, 3.46 MB)

This guidance document provides recommendations on practice for sampling, measurement, data evaluation and interpretation of CSIA.

EPA. Approach for Evaluating the Progress of Natural Attenuation in Groundwater (2011) (PDF) (84 pp, 1.12 MB)

Monitoring over time ensures that the future behavior of the plume is consistent with past behavior and that the risk of exposure to the contaminants is managed. The trend of contaminant concentrations over time in a particular well can be used to forecast the future concentrations in that well and predict when concentrations will attain a selected concentration level. The purpose of this document is to present a simple, statistically based approach for evaluating the progress of natural attenuation from the data collected during site characterization and long-term monitoring. The intended audience is technical professionals that actually perform the data analyses (i.e., hydrogeologists, engineers) as well as project managers who review those analyses and/or make decisions based on those analyses.

EPA. A Citizen's Guide to Monitored Natural Attenuation (2012) (PDF) (2 pp, 878 KB)
A fact sheet intended for public guidance on natural attenuation to clean up pollution at Superfund and other sites.

EPA. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites, A Guide for Corrective Action Plan Reviewers, Chapter IX — Monitored Natural Attenuation (2017)
This chapter describes the various chemical and environmental factors that influence the rate of natural attenuation processes.

EPA. CLU-IN Technology Focus Web Site on MNA Guidance
This web site serves as a control location for discussion and documents on MNA.

EPA. Office of Underground Storage Tanks, Leaking Underground Storage Tanks Corrective Action Resources, Corrective Action Web Site
This web site provides information on corrective action plans, remediation methodologies (including MNA), LNAPL recovery, performance monitoring, institutional and engineering controls, documentation and reporting, and case studies.

EPA. Ground Water and Ecosystem Restoration Research, Monitored Natural Attenuation
This web site provides an introduction, references and products regarding MNA.

ITRC. Enhanced Attenuation: Chlorinated Organics Technical and Regulatory Guidance (2008) (PDF) (109 pp, 1.91 MB)
This guidance document provides a protocol to assist in the transition between aggressive remedial actions and MNA, including a decision flowchart for successful site characterization, remedy selection and implementation, site closure, and long-term monitoring.

ESTCP. Frequently Asked Questions about Monitored Natural Attenuation in Groundwater (2014) (PDF) (91 pp, 4.89 MB)

This guidance document provides an overview of current knowledge regarding management of subsurface contaminant releases using MNA.

ITRC. **Enhanced Attenuation: Chlorinated Organics (PDF)** (109 pp, 1.91 MB)
This guidance document provides a decision framework that can be applied to identify site-specific areas of concern and identify enhanced attenuation strategies, which include the use of low-energy, long-acting sustainable technologies when MNA is not sufficiently effective or acceptable.

ITRC. **Use and Measurement of Mass Flux and Mass Discharge (2010) (PDF)** (154 pp, 4.85 MB)
This guidance document describes the concepts and practice of mass flux and mass discharge and how to use this information to evaluate progress toward achieving remedial goals.

ITRC. **A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater Technical/Regulatory Guidance (2010) (PDF)** (204 pp, 4.20 MB)
This guidance document facilitates the acceptance of attenuation-based remedies for metals and radionuclides in groundwater at levels above standards and includes recommendations for evaluating attenuation-based remedies in a consistent and technically defensible manner; a decision framework to help determine whether relying on attenuation processes is feasible and can lead to successful implementation; and case study summaries demonstrating application of attenuation-based remedies to real-world scenarios.

ITRC. **Integrated DNAPL Site Strategy Technical/Regulatory Guidance (2011) (PDF)** (209 pp, 4.43 MB)
This guidance document assists site managers in developing an integrated DNAPL site management strategy containing five key features: 1) conceptual site model; 2) remedial objectives; 3) treatment technologies; 4) monitoring strategies; and 5) re-evaluating the strategy. The document describes key concepts and recent developments in each of the areas to help site managers develop successful integrated strategies for DNAPL sites and includes a discussion on several models used in the environmental industry.

NAVFAC. Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Groundwater at Naval and Marine Corps Facilities, DON (1998)
Guidance for Navy Remedial Project Managers on how to assess natural

attenuation as a remedial strategy for groundwater systems contaminated with petroleum hydrocarbons and/or chlorinated solvents.

NAVFAC. **Groundwater Risk Management Handbook (2008) (PDF)** (31 pp, 1.38 MB)
This handbook provides an overview of groundwater risk management strategies that can be used to support optimization concepts addressed in the *Guidance for Optimizing Remedy Evaluation, Selection, and Design* (NAVFAC, 2004; updated 2010).

NAVFAC. **Estimating Cleanup Times Associated with Combining Source Area Remediation with Monitored Natural Attenuation (2008) (PDF)** (89 pp, 1.46 MB)
Natural Attenuation Software v2 (NAS2) is designed to estimate times of remediation to reach remedial action objectives at sites where a treatment train approach of engineered source zone treatment followed by MNA is used. The capability of NAS2 to provide reasonable estimates of MNA cleanup timeframes in a variety of environments and sites throughout the United States was recently validated in an Environmental Security Technology Certification Program (ESTCP) project. This document reports the results of the ESTCP project for the validation of NAS2 used to estimate remediation times whenever MNA is proposed as part of the cleanup strategy.

NAVFAC. **Guidance for Optimizing Remedy Evaluation, Selection, and Design (UG-2087-ENV) (2010) (PDF)** (84 pp, 3.34 MB)
This document provides a general overview and explanation of key optimization concepts as they pertain to the Feasibility Study (FS), Record of Decision (ROD), and Remedial Design (RD) clean-up phases. This document is not intended to provide guidance on determining site-specific risk-based clean-up goals, performing risk assessments, conducting site assessments and background investigations, or other site-specific contaminant characterization activities for which EPA and Navy guidance already exists. Rather, this document complements these important components of the site remediation process by providing recommendations for optimizing remedy selection and design.

NAVFAC. **DON Guidance for Planning and Optimizing Monitoring Strategies (2010) (PDF)** (250 pp, 3.82 MB)
This guidance document provides Navy Remedial Project Managers with comprehensive information for optimizing monitoring programs at remediation sites. Part I of the document provides key concepts such as conceptual site model, data quality objectives, monitoring program goals, and regulatory

framework. This part also describes approaches to optimize monitoring locations, monitoring frequency, list of analytes, data analysis, and reporting. Part II contains specific information on optimizing monitoring strategies for various media and site types including groundwater, sediments, groundwater discharge to surface water, ecological resources, vadose zone, landfills, and land use controls. This guidance document has been updated to include the main elements in designing and optimizing monitoring programs for vapor intrusion sites.

NAVFAC. DON Policy for Optimizing Remedial and Removal Actions at all DON Environmental Restoration Program Navy Sites (2012) (PDF) (12 pp, 0.98 MB)
This updated policy clarifies when optimization reviews are necessary and provides effective remedial strategies to meet remedial action objectives. It also mandates the following actions be performed on DON sites: 1) green and sustainable remediation (GSR) be incorporated into the optimization process, 2) a remedial alternatives analysis (RAA) be performed to ensure sites have been effectively optimized, and 3) ensured use of the SiteWis™ tool in all GSR actions. Finally, in order to facilitate the documentation of effective monitoring efforts during the optimization process, this policy also recommends the use of the Management and Monitoring Approach (MMA) for DON sites.

NAVFAC. Guidance for Optimizing Remedial Action Operation User's Guide (2012) (PDF) (94 pp, 2.76 MB)
This guidance document presents the six general steps for optimizing remedial action operations: 1) review and evaluate remedial action objectives; 2) evaluate remediation effectiveness; 3) evaluate the cost effectiveness and sustainability; 4) identify potential remedy improvements or alternatives; 5) develop and prioritize optimization recommendations and footprint reduction methods; and 6) prepare an optimization report and implement the optimization recommendations. This document also discusses technology-specific optimization considerations.

United States Geological Survey (USGS). Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation (2003) (PDF) (58 pp, 2.93 MB)
This report outlines a method for estimating timeframes required for natural attenuation processes, such as dispersion, sorption, and biodegradation, to lower contaminant concentrations and mass to predetermined regulatory goals in groundwater systems.

USGS. [A Framework for Assessing the Sustainability of Monitored Natural Attenuation (2007) (PDF)] (48 pp, 9.29 MB)
This study illustrates that the short- and long-term susÂ¬tainability of MNA can be assessed by: 1) estimating the time required for contaminants to dissolve/disperse/degrade under ambient hydrologic conditions (time of remediation); 2) quantifying the organic carbon flux to the system needed to consume competing electron acceptors (oxygen) and direct electron flow toward chloroethene degradation (short-term sustainability); and 3) comparing the required flux of organic carbon to the pool of renewable and nonrenewable organic carbon given the estimated time of remediation (long-term sustainability).

Washington State Department of Ecology. [Guidance on Remediation of Petroleum-Contaminated Ground Water by Natural Attenuation (2005) (PDF)] (143 pp, 1.25 MB)
This document provides technical guidance on how to evaluate the feasibility and performance of cleanup action alternatives that use natural attenuation, either alone or in conjunction with other cleanup action components, to clean up petroleum-contaminated groundwater under Washington State regulations.

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1. Oftentimes, microbial studies can provide a more reliable line of evidence than geochemical data for assessing biodegradation. Geochemical monitoring commonly indicates that site conditions are not conducive to biodegradation, but the presence of daughter products indicates that biodegradation is occurring within the aquifer. ↩
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3. Not intended to be a comprehensive list. Techniques are applicable to a wide range of existing and emerging contaminants and new tools and techniques (e.g., molecular biological tools) are continuously being developed that apply to a wide range of compounds. ↩
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5. Assuming similar groundwater gradients. Mass flux is defined as Mass Flux (J) = KiC, where K is the hydraulic conductivity, i is the groundwater gradient, and C is the contaminant concentration. ↩

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7. As presented in the ITRC's Integrated DNAPL Site Strategy Technical/Regulatory Guidance (2011) with the exception that REMChlor-MD has been added. ↩

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