FACT SHEET

Remedy Selection and Optimization Considerations for Monitored Natural Attenuation

Introduction

Monitored natural attenuation (MNA) is a remedial option for monitoring the reduction of concentration, toxicity, and/or mobility of chemicals in groundwater (Figure 1). MNA can serve as a standalone remedy, or it can be implemented as part of a treatment train through a transition from active treatment to a more passive treatment approach over time.

Several lines of evidence are needed to achieve regulatory acceptance when selecting MNA as a primary remedy or transitioning to MNA as part of remedy optimization.

Lessons learned are shared in this fact sheet related to gathering robust lines of evidence to accelerate regulatory acceptance of MNA as a viable remedial approach.

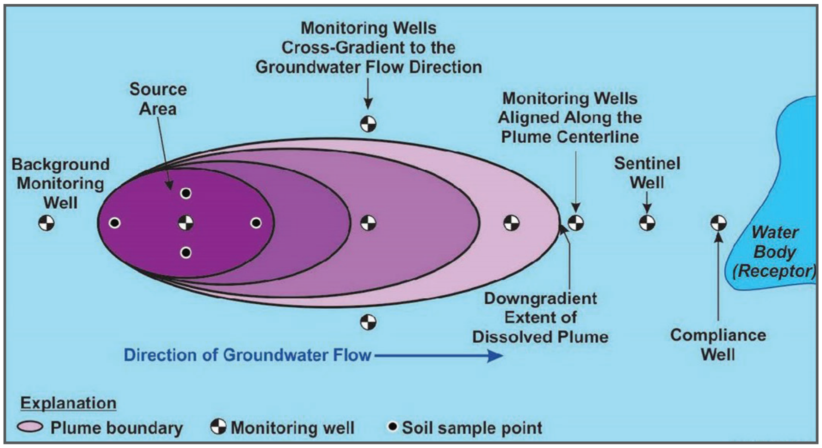

Figure 1. MNA Schematic (Source: Federal Remediation Technologies Roundtable)

How Does It Work?

MNA relies on naturally occurring physical, chemical, and biological processes to mitigate the impact of contamination over time. While biodegradation is often considered the predominant attenuation mechanism, the impacts of chemical and physical attenuation pathways should not be overlooked. Chemical degradation pathways, such as abiotic degradation where iron-based minerals reduce chlorinated solvents, are recognized to contribute significantly to MNA. Physical pathways such as dispersion and mixing at the groundwater to surface water interface (GW-SWI) should also be considered where appropriate. Recent advances in diagnostic tools have also expanded the recognition of biodegradation mechanisms that can occur under a wide range of redox conditions.

How Can It Help?

MNA helps to achieve remedial goals within a reasonable timeframe, minimizes downgradient migration, and restores groundwater quality to levels appropriate for its beneficial use. MNA is considered a viable remedial strategy when:

- Available alternative technologies are less reliable, cost-effective, or sustainable;
- Lines of evidence demonstrate that natural attenuation processes are:
  - Protective of human health and the environment; and
  - Expected to achieve remedial goals in a reasonable timeframe.

MNA Lines of Evidence | Data Challenges and Solutions

MNA Lines of Evidence

What Lines of Evidence Support the Use of MNA?

Several lines of evidence can be used to establish that MNA is ongoing at a sufficient rate and will maintain protectiveness over time. However, practitioners should be aware of potential MNA data collection and/or data interpretation challenges in order to proactively address these issues to better support the selection or transition to MNA. Table 1 summarizes key lines of evidence for documenting MNA processes.

The amount of data required to be collected will be site-specific based on the conditions encountered and discussions with regulators. Defining the intention of data collection and evaluation through data quality objectives (DQOs) is encouraged throughout the CERCLA process to facilitate MNA remedy selection and optimization efforts over time. A conceptual site model (CSM) that supports MNA lines of evidence should be developed as part of the Remedial Investigation (RI) and updated throughout the cleanup process as part of optimization efforts.

Challenges that may be experienced in the collection of adequate data are also summarized in Table 1. Several of these challenges are the subject of ongoing research to advance the state of practice for MNA. This fact sheet focuses specifically on evaluating MNA for organic chemicals (i.e., chlorinated solvents and petroleum compounds).

Table 1. Lines of Evidence for MNA and Challenges with Data Collection and Interpretation

Line of Evidence Description	Data Collection and Interpretation Challenges
Contaminant Mass Loss over Time and/or Space	
Documentation of MNA processes includes: • Plots of concentration over time including plume maps • Statistical analyses • Mass balance calculations • Mass flux calculations • Models that evaluate natural attenuation capacity of an aquifer over time and space. Fate and transport mechanisms include: • Non-aqueous phase liquid (NAPL) dissolution • Dispersion • Advection • Biodegradation • Abiotic degradation • Sorption/desorption of the chemical as it moves through an aquifer • Volatilization to the unsaturated zone (as applicable). Results must establish that a plume is stable or shrinking to remain protective and that cleanup goals will be achieved within a reasonable timeframe.	Incorrect statistical analyses or misinterpreted data may lead to incorrect CSMs and inaccurate degradation rate estimates. Factors contributing to inaccurate data evaluation may include not properly accounting for the impact of active remediation on concentration trends, event-to-event variability, or the effect of seasonal variability on contaminant statistical trends or plume stability analyses. Regulatory acceptance of model inputs and results can also be challenging. Modeling must account for the difference between degradation and dispersion to accurately estimate long-term MNA rates. Model estimates do not always properly account for back diffusion and other mass transfer limitations. Uncertainty in model estimates should also be taken into account and considered as order-of-magnitude results for decision-making purposes. At some sites, there is also insufficient recognition of the natural attenuation occurring at the GW-SWI. Site investigation techniques and models are available to quantify the attenuation occurring at this interface (see the next section of this fact sheet for more information).
Field Parameters and Geochemical Conditions	
Field parameters and geochemical constituents are measured to verify water quality and the prevailing redox conditions. The parameters measured can include pH, temperature, conductivity, dissolved oxygen (DO), oxidation reduction potential (ORP), turbidity, nitrate, sulfate (SO_4), sulfide, dissolved iron, dissolved manganese, total organic carbon (TOC), methane (CH_4), and dissolved hydrogen.	Steps must be taken to ensure field parameters and geochemical data are accurate. DO readings can be inconsistent and other MNA parameters can be more reliable indicators of redox conditions. If DO readings appear to be unreliable, utilize ferrous iron (Fe[II]), SO_4, and CH_4 as more reliable indicators as described in the next section of this fact sheet. Changes in redox conditions do not necessarily indicate that intrinsic degradation will stop; however, the rate may change over time.

Return to Menu

MNA Lines of Evidence

Table 1. Lines of Evidence for MNA and Challenges with Data Collection and Interpretation (Continued)

Line of Evidence Description	Data Collection and Interpretation Challenges
Compound Specific Isotope Analysis (CSIA)	
CSIA is a method for identifying biotic or abiotic degradation processes by measuring the ratio of stable isotopes in site-specific samples. For example, the ratio of carbon isotopes ($^{13}C/^{12}C$) will increase as the parent organic compound biodegrades to the byproducts.	Ongoing or prior remediation activities can complicate the evaluation of CSIA data both on a plume scale or over time at a given location. Minimum contaminant concentrations in the sample must be met to perform isotope analysis. In addition, low rates of biodegradation may be masked by ongoing NAPL dissolution in source areas, making biodegradation rate measurements via CSIA a challenge in some cases. CSIA data is best applied as one line of evidence for MNA, along with the geochemical data and contaminant concentration trend data, including changes in contaminant ratios.
Molecular Biological Tools (MBTs)	
MBTs measure subcellular molecules (e.g., deoxyribonucleic acid [DNA], ribonucleic acid [RNA], enzymes, or lipids) in site samples. The quantitative polymerase chain reaction (qPCR) method is used to quantify the presence of specific microorganisms and functional genes responsible for biodegradation. Evolving MBTs include metagenomics using next generation sequencing to study the diversity of microorganisms present in a sample and proteomics to study the proteins produced as a result of microbial activity. Fluorescent enzyme activity probes can be employed as a way to directly measure enzyme activity.	These tests may not always provide a comprehensive understanding of the diversity of microorganisms present at a site and/or verify their activity. For example, the qPCR method only identifies the presence of known target microorganisms. At times, the targeted microorganism may only be present in small quantities or may be present but not active. Threshold levels suggestive of ongoing biodegradation may not be met. Recent advances show promise as supplemental lines of evidence for biodegradation pathways with metagenomics, proteomics, and enzyme probes as described below.
Microcosm Studies in Field or Laboratory	
Microcosm studies in the laboratory can be used to establish degradation rates using groundwater and soil collected on site. Field-deployed microcosm units are also available. These units contain passive samplers that provide the microbial, chemical, and geochemical data to evaluate the effectiveness of MNA under in situ conditions.	Issues may include representativeness of the data, especially with regard to rates of degradation when measured in the laboratory. These data are best used with a lines-of-evidence approach but may not always be needed. In field microcosms, representativeness can also be an issue as some techniques only consider fixed biomass or specific carbon sources, both of which can be different than the actual in situ conditions for degradation.
Presence of Iron-Bearing Minerals	
Abiotic degradation of chlorinated volatile organic compounds (CVOCs) can occur in the presence of iron-containing minerals in soil and rock. Measurements of these iron-bearing minerals (e.g., magnetite or iron sulfides), or of magnetic susceptibility of soil or bedrock as a surrogate to magnetite abundance can serve as an indicator of a potential abiotic degradation pathway at a site.	Limited studies of magnetic susceptibility have shown that false negatives are possible, but false positives are less likely. The direct measurement of total iron minerals provides definitive information regarding their presence; however, available studies have not observed a good correlation between iron-containing minerals and contaminant degradation rates. Research is ongoing and these data are best used as part of multiple lines of evidence to evaluate the abiotic degradation pathway.

MNA Data Evaluation Challenges and Solutions

How Can Technical and Regulatory Challenges for MNA Selection Be Addressed?

The selection of MNA as a remedy must be supported by site conditions. Technical and regulatory challenges may be encountered as part of the MNA evaluation process. Proposed solutions to address these challenges and to promote more robust MNA lines-of-evidence evaluations are summarized below. Resources for more in-depth information are also provided.

MNA Lines of Evidence: Contaminant Mass Loss over Time and/or Space
Challenge: Variability in Data Affects Trend Analyses
Event-to-event variability and/or the effect of seasonal variability increases the uncertainty of trend analyses and reduces the accuracy of long-term attenuation rates and plume stability evaluations.
Solutions: It sometimes requires three to five years of sampling data to establish statistically significant trends for MNA, particularly for low concentration plumes. This can make selection of MNA at the Feasibility Study (FS) phase difficult. If low risk and/or clear trends are not yet established in the RI/FS phase, some degree of source treatment may be needed and/or MNA may be selected in the Record of Decision (ROD) as a contingency remedy with performance criteria as described in more detail below. Apparent trends characterized using too little data can be misleading and may result in inappropriate management decisions. More monitoring data significantly increases the accuracy of the estimated long-term trend. However, once long-term trends are understood, monitoring optimization is an important tool for managing costs, while ensuring long-term monitoring goals are achieved. Monitoring programs for MNA can be optimized with a monitoring frequency tailored to site needs and remedial action objectives (e.g., less frequent monitoring at sites with low risk and stable or shrinking plumes, and higher frequency at sites with higher risk of exposure or expanding plumes). Data trend evaluations should also account for CSM changes throughout the CERCLA process before, during, and after active remediation as the site transitions to MNA. For information on strategies to minimize event-to-event variability in monitoring data, see NAVFAC Innovative Sampling Methods and Data Analysis for Reduced Long-Term Monitoring Costs (2020).
Challenge: Lack of Consensus on Fate and Transport Modeling
Issues encountered during fate and transport model development include achieving consensus on the input data and performing adequate sensitivity analyses to ensure the model corresponds to site conditions. Poorly developed CSMs and misunderstood degradation mechanisms may lead to greater uncertainties in model results.
Solutions: A well-developed CSM and fate and transport model can support whether or not the timeframe to achieve remedial goals through MNA is reasonable, particularly as compared to active remedial alternatives. Data should be collected to fully develop the CSM and better characterize degradation mechanisms and rates. For example, contaminant attenuation rates should be evaluated relative to tracers or by using contaminant ratios to distinguish between dispersion and degradation. This distinction is important when utilizing an analytical model to predict the long-term effectiveness of MNA. Overestimating the degradation rate will lead to an inaccurate evaluation of MNA effectiveness. Also consider site-specific geology and impacts of back diffusion or slow NAPL dissolution on contaminant transport and remedial timeframes. In some cases, the reasonableness of the timeframe to achieve cleanup goals can be supported through a well-developed CSM and modeling of MNA compared to other active remedial options. In addition, fate and transport modeling can be performed to predict contaminant concentrations throughout the plume and then a sensitivity analysis can be used to bound the expected concentration trends. Regulatory acceptance of MNA may be more achievable if those predictions (with confidence limits) are used as the basis for MNA performance criteria. If trends remain within the predicted interval or lower, then the MNA remedy is on track. If the trends are outside the interval in an upward direction, then the CSM supporting MNA should be reevaluated. These MNA performance criteria can be included in the ROD and/or other key project documents receiving regulatory concurrence. More information on best practices for evaluating remedial timeframes including MNA can be found in NAVFAC Tools for Estimating Contaminant Mass-in-Place, Mass Discharge, and Remediation Timeframes (2018).
Challenge: Lack of Recognition of Attenuation at the Groundwater to Surface Water Interface
At some sites, there is insufficient recognition of the natural attenuation occurring at the GW-SWI.
Solutions: A study can be conducted with specialized instrumentation to evaluate conditions at the GW-SWI. Potential discharge zones can be identified using offshore screening techniques (e.g., a Trident probe, fiber optic sensors, and visual observations). This type of study provides for the characterization of discharge rates and contaminant flux through porewater sampling within the discharge zones. The contaminant discharge rates and contaminant flux measurements can then be incorporated into fate and transport modeling and the calculation of relevant risk endpoints at the site. More information can be found in NAVFAC Groundwater to Surface Water Interface: Summary of Tools and Techniques (2021).

Return to Menu

MNA Data Evaluation Challenges and Solutions

Lines of Evidence: Geochemical Conditions, Presence of Iron-Bearing Minerals
Challenge: Presence of Adverse Geochemical Conditions
Geochemical data can be highly variable; redox conditions can be unfavorable for certain targeted pathways; or adverse geochemical conditions can be present that inhibit bacterial growth (e.g., an unusually low or high pH).
Solutions: Fully Evaluate Geochemical Conditions. If DO readings appear to be unreliable, use Fe(II), SO_4, and CH_4 as more reliable indicators. Measuring dissolved iron using field test kits is recommended to assess redox conditions. SO_4 and CH_4 are also reliably measured; however, changed conditions due to sulfate reduction and methanogenesis can persist long after the biological activity has subsided, subject to transport through the subsurface based on groundwater flow rates. Conversely, dissolved iron quickly precipitates out of solution if it is not being actively produced and is therefore a more reliable indicator of current conditions. Understanding the geochemical conditions will assist with recognizing the relevant attenuation processes at a site. The absence of Fe(II) and CH_4 are good indicators for the presence of oxygen concentrations that support aerobic biodegradation of organic compounds. The representativeness of samples should also be evaluated when determining geochemical conditions in the aquifer. For example, monitoring well screens could potentially intercept multiple vertical intervals with different redox conditions, complicating interpretation of the geochemical data. A well-developed CSM will help ensure that samples are representative of the vertical interval where contaminants are present. Refer to the decision matrix presented in ESTCP Project ER-201129 for more information on geochemical data considerations.
Evaluate Abiotic Processes. Chlorinated solvents can be transformed abiotically through a chemical reaction with reduced Fe(II) minerals that are naturally present as part of the site geology or formed by microbial activity. The minerals typically involved in abiotic transformations include iron sulfides (mackinawite and pyrite), iron oxides (magnetite), green rust, and phyllosilicate clays (vermiculite and biotite). The direct measurement of total iron minerals provides definitive information regarding their presence; however, available studies have not observed a good correlation between iron-containing minerals and contaminant degradation rates. Therefore, these data are best used along with other parameters to evaluate the abiotic degradation pathway. Other lines of evidence include contaminant concentration trends and ratios, specifically the parallel decline of contaminant and daughter product concentrations simultaneously, and the presence of iron sulfides (FeS and FeS_2) which are the primary minerals formed by microbial activity and capable of abiotic contaminant transformations. For more information on abiotic processes, see the NAVFAC Biogeochemical Transformation Handbook (2015).
Continually Assess Geochemical Conditions. Redox conditions may also change over time, which can impact the rate of MNA as the remedy is implemented. A framework has been established to evaluate available organic carbon in the system along with contaminant trends and ratios to better understand if degradation rates are sustainable. For more information, see the United States Geological Survey Framework for Assessing the Sustainability of Monitored Natural Attenuation (2007) and NAVFAC Verification of Methods for Assessing the Sustainability of Monitored Natural Attenuation (2013).

MNA Lines of Evidence: CSIA, Molecular Biological Tools, and Microcosm Studies
Challenge: Findings of Insufficient Microbial Populations
MBT results may indicate there is not a robust population of the desired microbes with known degradation capabilities for the target contaminant. This can increase the challenge in identifying biodegradation pathways.
Solutions: Next generation sequencing can be used to determine the type of microorganisms present; however, it is important to note that the state of the science is such that not all microorganisms potentially responsible for contaminant degradation have been identified and not all degradation pathways are well understood. Focus data collection on other lines of evidence described above to demonstrate that degradation is occurring (e.g., contaminant trends and ratios, geochemical data, redox conditions, CSIA, and the presence of iron-containing minerals). Proteomics is an emerging method that may reveal degradation pathways under specialized circumstances. Another innovative diagnostic tool includes fluorescent enzyme activity probes. These are chemical probes that undergo cometabolic transformation to fluorescent products by the same enzyme systems that can degrade chlorinated ethenes cometabolically, including soluble methane monooxygenase and various toluene mono- and dioxygenases. For more information, see the NAVFAC fact sheets on environmental molecular diagnostics for chemical and biological tools.

MNA Data Evaluation Challenges and Solutions

MNA Lines of Evidence: All
Challenge: Transitioning from Active Treatment to MNA
It may not be cost effective to operate an active treatment system to achieve maximum contaminant levels (MCLs). Achieving regulatory approval to transition from active to passive treatment with MNA can involve significant negotiations. Some sites may not have defined or approved transition metrics in place.
Solutions: MNA may be included in the ROD or ROD amendment as a contingency remedy to be applied once active measures have achieved interim objectives (see example here for an EPA-led Superfund site). Technically defensible metrics should then be established to transition from active treatment to MNA. It is beneficial for the transition criteria to be negotiated and approved by all stakeholders as soon as possible in the cleanup process and ahead of remedy implementation. Establish performance metrics in key deliverables including the ROD and/or remedial design for any active treatment technology. If a project is in a post-ROD phase, the transition criteria from active to passive treatment may be defined in other documents such as monitoring plans or similar deliverables receiving regulatory review and concurrence. Another approach includes implementing a remedy optimization study period for MNA with the temporary shutdown of an active treatment system, while infrastructure remains in place and is properly maintained. Conduct rebound evaluations after active treatment shutdown and collect data to demonstrate that MNA is occurring at a sufficient rate through multiple lines of evidence as described above. Optimized remedial design and implementation, including treatment trains involving MNA, are further addressed in Navy guidance available on the NAVFAC Optimization Web page.
Challenge: Addressing MNA across Dilute, Large-Scale Plumes
It can be challenging to identify remedies for dilute, large-scale plumes with low levels of chemicals above MCLs.
Solutions: Dilute plumes are often the result of matrix diffusion or back diffusion from low permeability lenses or layers in the subsurface. Even sites that are considered relatively homogeneous have variation in hydraulic conductivity with a fraction of the aquifer matrix serving as a reservoir of persistent contaminant storage. Simulating matrix diffusion requires much higher resolution in numerical modeling than is commonly practiced. At a low risk site with monitoring data demonstrating that the plume is stable or receding, MNA can be evaluated for long-term site management. Ensure that the CSM is fully developed and use multiple lines of evidence described above to estimate degradation rates and document that natural attenuation is occurring. Specialized models that account for matrix diffusion can be incorporated. In addition, consider if cometabolic pathways are feasible at sites where initial contaminant concentrations are low. Low threat closure may be an option incorporating land use controls and long-term monitoring to ensure protectiveness. For more information on optimized strategies, see NAVFAC's Webinar on Dealing with Dilute Plumes.
Challenge: Addressing Source Zones
Regulatory acceptance of MNA may be more challenging at sites with NAPL source zones. .
Solutions: Partial source zone treatment may be required prior to the use of MNA as a polishing step. The cost/benefit of partial source zone treatment should be evaluated, as well as resulting reductions in the MNA timeframe. An optimized approach could include establishing interim performance objectives based on contaminant mass flux from the source area, with active treatment transitioning to MNA when the performance objectives are achieved. Tools for modeling partial source zone treatment at dense non-aqueous phase liquid (DNAPL) sites prior to MNA are summarized in NAVFAC Tools for Estimating Contaminant Mass-in-Place, Mass Discharge, and Remediation Timeframes (2018). MNA in the presence of remaining light non-aqueous phase liquid (LNAPL) is termed natural source zone depletion (NSZD). Regulatory acceptance of NSZD is evolving. A complete assessment of the LNAPL body, dissolved-phase plume, vapor plume, potential exposure pathways, and receptors is required to evaluate NSZD. For more information, refer to the Interstate Technology and Regulatory Council (ITRC) Evaluating Natural Source Zone Depletion at Sites with LNAPL (2009) and the NAVFAC Case Study Review of Optimization Practices at Navy Petroleum Sites (2021).

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Key Resources

EPA CLU-IN Technology Focus Web Site on MNA Guidance

ESTCP Frequently Asked Questions about Monitored Natural Attenuation in the 21st Century

Federal Remediation Technologies Roundtable: Monitored Natural Attenuation Technology Profile