Fact Sheet

Performance of Two Technologies to Control Difficult-to-Treat Matrix Diffusion Zones: Post-Bioremediation Sustained Treatment and MNA in Low Permeability Units

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14. ABSTRACT
In-situ bioremediation (ISB) and monitored natural attenuation (MNA) are two widely used approaches to treat and control persistent matrix diffusion sources at chlorinated solvent sites. Such source zones represent a significant liability to the Department of Defense (DoD). Research has suggested that processes may be active at both ISB and MNA sites that could provide additional benefits to their application near or within low-permeability (low-K) matrix diffusion zones. The objectives of the project were: i) to develop new process knowledge on how to measure and demonstrate sustained treatment following application of ISB and ii) to evaluate and quantify MNA processes in low-K matrix diffusion zones. Data from field demonstrations and data mining of other sites indicated the occurrence of these processes and provided useful information on quantifying and assessing these processes. Fact Sheets are provided to allow cost effective application of these concepts at other sites using existing site data.

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Remediation; Chlorinated Solvents; Matrix Diffusion; Bioremediation; Sustained Treatment; MNA

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Assessing Post-bioremedation Sustained Treatment

ESTCP Project ER-201429

Sustained treatment is a term used to describe the enhanced attenuation capacity within an in situ bioremediation (ISB) treatment zone that can prolong the benefits of ISB treatment after the depletion of the primary organic substrate. Results of the field demonstrations conducted for ESTCP Project ER-201429, along with the accompanying data mining study of 34 projects with long-term monitoring data, indicate that sustained treatment of chlorinated volatile organic compound (CVOC) concentrations is observed at approximately three-quarters of sites where ISB was used to treat chlorinated solvents in groundwater.

While site-specific hydrogeologic conditions, design considerations, and implementation effectiveness undoubtedly factor into the remedial outcome for any ISB application, these results suggest that a generally well designed and implemented ISB project more often than not will benefit from sustained treatment, at a minimum in terms of rebound suppression for the parent CVOC, for a period of at least 3 to more than 15 years after the end of treatment.

This fact sheet summarizes findings and methodologies developed under ESTCP Project ER-201429 into simple worksheets that can be used to evaluate sustained treatment at other ISB sites using a lines-of-evidence approach. Worksheets are provided for sites where ISB was applied via an injected organic substrate (e.g., emulsified vegetable oil, molasses, etc.) and via a mulch permeable reactive barrier (i.e., a "Biowall"). It is intended that use of these worksheets will target sites where at least two years of monitoring data are available following the last injection event or following installation of the Biowall.

The box below summarizes the key parameters and lines of evidence used in the assessment, an explanation of how these parameters are assessed along with any associated critical values for assessment, and how to determine whether your site-specific data reflect sustained treatment occurrence. Professional judgement and consideration of the overall site conceptual model should be applied to make an overall determination of the impact of sustained treatment on the efficacy of the technology to meet remedial objectives of the project.

About ESTCP

The Environmental Security Technology Certification Program (ESTCP) is the U.S. Department of Defense's environmental technology demonstration and validation program. The program's goal is to identify and assess innovative technologies that address DoD's high-priority environmental requirements efficiently and cost-effectively.

Key Parameters / Lines of Evidence for Sustained Treatment

The following CVOC concentration metrics should be considered as primary lines of evidence in the sustained treatment assessment:

- **Parent CVOC Concentration Change over Post-Treatment Monitoring Period:** Calculate the concentration reduction for the parent CVOC (typically tetrachoroethene or trichoroethene) over the post-treatment monitoring period to evaluate the occurrence of sustained treatment versus rebound. If two or more years of post-treatment data are available, use the average concentration from the first year of the post-treatment monitoring record and the average concentration from the most recent year. Use only monitoring wells within the ISB treatment footprint. A decrease in parent CVOC concentrations over the post-treatment monitoring period is a strong indicator of sustained treatment, as is maintenance of non-detect concentrations. Relatively small concentration increases that still result in overall "stable" concentrations also suggest sustained treatment, but additional monitoring may be necessary to confirm lack of rebound. McGuire et al. (2006) defined rebound as a 25% increase in parent CVOC concentrationsover the post-treatment monitoring period.

- **CVOC Concentration Trend of Parent and Daughter Products:** Calculate the Mann-Kendall statistical trend for the first 4 to 8 monitoring events immediately following the end of ISB treatment (i.e., the last injection) and the most recent 4 to 8 monitoring events. Note that a minimum of 4 sampling events are required for trend calculation; however, up to an additional 4 events may be needed to establish a trend due to natural variability of groundwater monitoring data. Calculate the trend for parent and daughter products. If insufficient data are available for daughter products, consider using the molar concentration of the sum of the parent and daughter products (i.e., total CVOCs). An improved trend result (e.g., increasing to stable, stable to decreasing, etc.) is a strong indicator of sustained treatment, as is maintaining a decreasing trend. A degradation in the trend from decreasing to stable, or maintaining a stable trend, also indicates sustained treatment occurrence, but additional monitoring or stronger consideration of the other lines of evidence may be needed to support the findings.

The following parameters should be considered as supporting lines of evidence in the sustained treatment assessment:

- **Total Organic Carbon (TOC) in Groundwater:** TOC in groundwater is greatly increased as a result of ISB and is evaluated two ways in the sustained treatment assessment. First, the site-specific concentration is compared to a critical value of 20 mg/L, which is the value established by US EPA (1998) as necessary to support natural attenuation of chlorinated solvents in groundwater. Values exceeding 20 mg/L are indicative of conditions amenable to sustained treatment. Second, TOC is evaluated within the ISB treatment footprint relative to upgradient (naturally-occurring or "background") concentrations. Increased TOC within the treatment zone indicates that geochemistry within the ISB treatment zones continues to be influenced by ISB and may continue to support sustained treatment.

- **Ethene and Methane in Groundwater:** Ethene and methane are dissolved gasses that are generally elevated in groundwater as a result of ISB. For the sustained treatment assessment, these gasses are evaluated within the ISB treatment footprint relative to upgradient (naturally-occurring or "background")

concentrations. Increased ethene and methane within the treatment zone indicates that geochemistry within the ISB treatment zone continues to be influenced by ISB and may continue to support sustained treatment. Similar to TOC, concentration magnitudes of ethene and methane can also be compared to values from US EPA (1998), which are 0.1 mg/L ethene and 0.5 mg/L methane, for supporting evidence.

- ***Dehalococcoides sp.* (Dhc) in Groundwater:** Concentrations of Dhc, the microorganisms most commonly associated with complete reductive dechlorination of chlorinated ethenes in groundwater, are generally stimulated as a result of ISB, particularly at sites where bioaugmentation is part of the remedial strategy. Dhc concentrations are evaluated two ways in the sustained treatment assessment. First, the site-specific concentration is compared to10,000 cells/mL, which is the screening criterion proposed by Lu et al. (2006) to identify sites where biological reductive dechlorination is predicted to proceed at "generally useful" rates. A concentration exceeding 10,000 cells/mL is a strong indicator of sustained treatment potential. Second, Dhc concentrations are evaluated within the ISB treatment footprint relative to upgradient (naturally-occurring or "background") concentrations. Increased Dhc levels within the treatment zone indicates that the treatment zone continues to be influenced by ISB and may continue to support sustained treatment.

- **Sum of Reductive Dechlorinators in Groundwater:** Several microbial species are capable of reductive dechlorination and may be stimulated by ISB, including *Dehalococcoides*, *Dehalobacter*, *Desulfitobacterium*, and *Desulfuromonas spp*. The sum concentration of these species, as measured by the QuantArray-Chlor lab method, can be used as an additional line of evidence for sustained treatment by comparison to the screening criterion discussed above (i.e., 10,000 cells/mL), as well as comparison of concentrations within the treatment zone versus upgradient. Increased concentrations within the treatment zone indicates that the treatment zone continues to be influenced by ISB and may continue to support sustained treatment.

- **Compound-Specific Isotopes (^{13}C) in Groundwater:** Carbon isotope enrichment of the individual CVOCs can be measured and evaluated as part of a sustained treatment assessment. Enrichment of compound-specific isotopes within the treatment zone compared to upgradient concentrations indicate the occurrence of sustained treatment; however, upgradient concentrations may often be below detection limits limiting the effectiveness of this parameter. When considered with the higher cost of isotope sampling, this parameter is not expected to be used at most sites for sustained treatment assessment.

- **Potentially-Bioavailable Organic Carbon (PBOC) in Aquifer Sediments:** PBOC represents the fraction of organic carbon associated with aquifer sediments that may be available to support ongoing biodegradation of contaminants and may be enhanced following an ISB remedy through application of the organic substrate, as well as through microbial carbon cycling. Chapelle et al. (2012) proposed a threshold screening criterion of 200 mg/kg needed to support reductive dechlorination in aquifers. PBOC levels exceeding this threshold are a strong indicator of sustained treatment potential. For the sustained treatment assessment, PBOC can be evaluated within the ISB treatment footprint relative to upgradient (naturally-occurring or "background") concentrations. Increased PBOC within the treatment zone indicates that conditions within the ISB treatment zone continue to be influenced by ISB and may continue to support sustained treatment. A disadvantage of using PBOC as a line of evidence in the sustained treatment assessment is the requirement for collection of soil samples for analysis. An attempt to use biological oxygen demand (BOD) of groundwater samples as a cost-effective surrogate for PBOC proved unsuccessful due elevated detection limits for BOD.

- **Forage Analysis of Mulch Biowall Sediments:** This parameter, applicable to mulch biowall sites only, provides a measure of the bioavailable fraction of mulch remaining. A cellulose plus hemi-cellulose to lignin ratio greater than 1 is indicative of sustained treatment potential (Ahmad et al., 2007).

Worksheet for Sustained Treatment Assessment for Post-ISB Sites

Parameter / Line of Evidence	Critical Value / Relationship	Site-Specific Results	Data Support Evidence of Sustained Treatment?
Parent CVOC Concentration Change over Post-Treatment Monitoring Period	Decrease in parent CVOC conc. from first year of post-treatment monitoring versus last year of post-treatment monitoring		
CVOC Concentration Trend of Parent and Daughter Products	Mann-Kendall trend from the most recent 4-8 monitoring events is same as (or better than) trend from first 4-8 post-treatment monitoring events		
TOC in Groundwater	TOC > 20 mg/L (USEPA, 1998)		
TOC in Groundwater	Treatment Zone (TZ) > Upgradient (UG)		
Ethene in Groundwater	Ethene > 0.1 mg/L (USEPA, 1998)		
Ethene in Groundwater	Treatment Zone (TZ) > Upgradient (UG)		
Methane in Groundwater	Methane > 0.5 mg/L (USEPA, 1998)		
Methane in Groundwater	Treatment Zone (TZ) > Upgradient (UG)		
Dehalococcoides in Groundwater	Treatment Zone (TZ) > Upgradient (UG)		
Dehalococcoides in Groundwater	$> 10^4$ cells/mL (Lu et al., 2006)		
Sum of Reductive Dechlorinators in GW	$> 10^4$ cells/mL		
^{13}C of CVOCs in Groundwater	Enrichment of ^{13}C signature relative to upgradient monitoring locations		
PBOC in Aquifer Sediment	PBOC > 200 mg/kg (Chapelle et al., 2012)		

Worksheet for Sustained Treatment Assessment within a Biowall

Parameter / Line of Evidence	Critical Value / Relationship	Site-Specific Results	Data Support Evidence of Sustained Treatment?
Parent CVOC Concentration Change over Post-Treatment Monitoring Period	Decrease in parent CVOC conc. from first year of post-treatment monitoring versus last year of post-treatment monitoring		
CVOC Concentration Trend of Parent and Daughter Products	Mann-Kendall trend from the most recent 4-8 monitoring events is same as (or better than) trend from first 4-8 post-treatment monitoring events		
TOC in Groundwater	TOC > 20 mg/L (USEPA, 2008)		
TOC in Groundwater	Within Biowall (WB) > Upgradient (UG)		
Ethene in Groundwater	Ethene > 0.1 mg/L (USEPA, 1998)		
Ethene in Groundwater	Within Biowall (WB) > Upgradient (UG)		
Methane in Groundwater	Methane > 0.5 mg/L (USEPA, 1998)		
Methane in Groundwater	Within Biowall (WB) > Upgradient (UG)		
Dehalococcoides in Groundwater	Treatment Zone (TZ) > Upgradient (UG)		
Dehalococcoides in Groundwater	$> 10^4$ cells/mL (Lu et al., 2006)		
Sum of Reductive Dechlorinators in GW	$> 10^4$ cells/mL		
^{13}C of CVOCs in Groundwater	Enrichment of ^{13}C signature relative to upgradient monitoring locations		
PBOC Analysis of Mulch	Cellulose + Hemi-cellulose to Lignin Ratio > 1 (Ahmad et al., 2007)		
Forage Analysis of Mulch	Cellulose + Hemi-cellulose to Lignin Ratio > 1 (Ahmad et al., 2007)		

Worksheet for Sustained Treatment Assessment within a Biowall

Parameter / Line of Evidence	Critical Value / Relationship	Site-Specific Results	Data Support Evidence of Sustained Treatment?
Parent CVOC Concentration Change over Post-Treatment Monitoring Period	Decrease in parent CVOC conc. from first year of post-treatment monitoring versus last year of post-treatment monitoring		
CVOC Concentration Trend of Parent and Daughter Products	Mann-Kendall trend from the most recent 4-8 monitoring events is same as (or better than) trend from first 4-8 post-treatment monitoring events		
TOC in Groundwater	TOC > 20 mg/L (USEPA, 2008)		
TOC in Groundwater	Downgradient (DG) > Upgradient (UG)		
Ethene in Groundwater	Ethene > 0.1 mg/L (USEPA, 1998)		
Ethene in Groundwater	Downgradient (DG) > Upgradient (UG)		
Methane in Groundwater	Methane > 0.5 mg/L (USEPA, 1998)		
Methane in Groundwater	Downgradient (DG) > Upgradient (UG)		
Dehalococcoides in Groundwater	Downgradient (DG) > Upgradient (UG)		
Dehalococcoides in Groundwater	> 10^4 cells/mL (Lu et al., 2006)		
Sum of Reductive Dechlorinators in GW	> 10^4 cells/mL		
^{13}C of CVOCs in Groundwater	Enrichment of ^{13}C relative to upgradient location		
PBOC in Aquifer Sediment	PBOC > 200 mg/kg (Chapelle et al., 2012)		

FOR MORE INFORMATION

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