NAVFAC
Naval Facilities Engineering Command

ENVIRONMENTAL RESTORATION

Using Bioremediation in Dense Non-Aqueous Phase Liquid Source Zones

Introduction

In situ bioremediation (ISB) is the use of biostimulation and/or bioaugmentation to modify existing geochemical conditions in an aquifer to facilitate biodegradation of contaminants. Under the right conditions, ISB has been proven successful as a remedial strategy in chlorinated solvent source zones areas (ITRC, 2008). This fact sheet summarizes initial screening factors that could help you to decide if ISB is right for your dense non-aqueous phase liquid (DNAPL) site. Specifically, the following topics are discussed:

- When is ISB considered for DNAPL source zones?
- Is source zone ISB applied differently than ISB applied in the plume?
- What are the advantages and limitations of using ISB in a DNAPL source zone?
- How is ISB implemented in a DNAPL source zone?
- What lessons have been learned applying ISB in DNAPL source zones?

More detailed information on how to design and implement ISB can be found in the references cited at the end of the fact sheet.

When is ISB considered for DNAPL source zones?

After constructing the conceptual site model (CSM) for a site, the distribution and extent of the contaminants should be understood, as well as the biogeochemistry of the site (e.g., redox state). Thus, the CSM provides the foundation for evaluating the applicability of ISB for the source zone. To facilitate this review, Table 1 summarizes key site parameters and their associated characteristics that support using ISB in a source zone. Table 1 should be considered when developing CSMs for chlorinated solvent sites to direct the collection of key site parameters for this assessment.

Table 1. Summary of Site Characteristics Amenable to ISB Treatment of DNAPL Source Zones

Site Parameters	Characteristics Amenable to ISB
DNAPL Distribution	• DNAPL as residuals • DNAPL with high surface area to mass ratio
Type of Contaminants	• Detection of reductive dechlorination daughter products • Recognition of potential inhibitors (Freon, 1,1,1-TCA, chloroform, PCE >90 mg/L) • Observation of an inhibitor may not preclude ISB, but this should be discussed with a bioremediation expert.
Aquifer Geochemistry	• Circum neutral pH (5.5 to 7.4) • Average temperature range (10°C – 45°C). • Reducing conditions preferred (< -50 mV ORP) • High buffering capacity preferred (>300 mg/L alkalinity)
Aquifer Characteristics	• Unconsolidated media acceptable • Medium to high conductivity and permeability in source area when compared to site-wide aquifer system • Consolidated media (fractured rock) may not be appropriate

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In general, chlorinated solvent sites with active biological degradation already occurring indicate that conditions are amenable for ISB and should be capitalized upon. Evidence of active biological degradation includes the production of daughter products (e.g., cis-1,2-DCE, vinyl chloride, and ethene for TCE degradation). At sites where there is limited evidence of reductive dechlorination, source zones with DNAPL mass predominately residual in nature are prime candidates for ISB. Potential reasons why active dechlorination may not be occurring include lack of appropriate microbes and/or carbon source and inappropriate redox conditions. All three reasons can be engineered to achieve active reductive dechlorination. Most importantly, source zones that have significant DNAPL pools with high saturations are not appropriate for ISB. In such cases, ISB may also be applied as a polishing step after other remedial technologies that address the DNAPL pools (e.g., ISB after thermal treatment has been shown to be effective).

Is source zone ISB applied differently than ISB applied in the plume?

The remedial approach remains the same whether ISB is utilized within the dissolved phase or within the source zone(s). An added benefit for ISB within source zones is an increased rate of source zone mass removal. The primary mechanism responsible for this accelerated removal of source mass is an increase in the DNAPL dissolution rate. Biological degradation occurs only in the aqueous phase and thus the rate of mass removal is limited by the rate of contaminant dissolution. The dissolution rate is greater in the source zone because of a greater concentration gradient at the DNAPL-water interface and an increase in the solubility of the DNAPL constituents caused by cosolvency (i.e., ability of the ISB substrate to enhance solubility of the contaminant in water).

While ISB has been applied traditionally within plumes, ISB for source zone treatment is an emerging technology. Historically, there has been a reluctance to apply ISB in source zones due to the assumption that biodegradation will be limited because of the contaminants' toxicity to the microbial community. However, recent experience (documented in case studies from ITRC's BioDNAPL-2 [2007]) have shown that dechlorinating microbes continue functioning close to the solubility limits for chlorinated solvents.

What are the advantages and limitations of using ISB in a DNAPL source zone?

The advantages of using ISB for DNAPL source zone treatment include: increases DNAPL mass removal; combines well with other technologies for complete site restoration (e.g., downgradient biobarriers or zero valent iron [ZVI] barriers); degrades contamination in situ (no secondary waste to address); and minimizes impact to site infrastructure. Overall, ISB is often more cost-effective and sustainable than aggressive source zone technologies such as excavation, thermal treatment, and in situ chemical oxidation (ISCO).

Conversely, the limitations of using ISB for DNAPL source zone treatment include inhibited microbial activity due to aquifer geochemistry (e.g., low or high pH), slower cleanup timeframes that may not reach objectives as quickly as aggressive technologies, and reduced availability of DNAPL resulting from source age. For example, in older sites, DNAPL residuals may reside predominately in low-permeability materials, which limit dissolution and accessibility to degrading microorganisms. In addition, the impact of co-contaminants on degradation should be considered. For example, while 1,1,1-TCA can inhibit cis-DCE and vinyl chloride degradation, the inhibition can be overcome with the correct dechlorinating microbial communities and recognition that 1,1,1-TCA must degrade prior to the onset of cis-DCE and VC degradation.

How is ISB implemented in a DNAPL source zone?

Enhanced ISB involves the addition of an electron donor and/or a microbial culture to a DNAPL source zone. The electron donors serve as substrates to the fermenting population, which provides the dechlorinating microbial community with their preferred electron donor (e.g., hydrogen). Typical electron donors include soluble substrates (e.g., lactate, whey, and molasses), liquid substrates (e.g., emulsified vegetable oil and neat vegetable oil), solid substrates (e.g., hydrogen releasing compound and chitin), and molecular hydrogen generated in situ. For a complete discussion on types of electron donors, see the *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents Protocol* (ESTCP, 2004). It should be noted that neat vegetable oil can also sequester chlorinated solvents and reduce contaminant flux

from the source zone, as well as serve as a substrate. Bioaugmentation can supply the site with the needed microbial community when sufficient dechlorinators are not present at a site or to overcome DCE and VC stall. There are several commercially available microbial consortia consisting of Dehalococcoides, sulfate reducers, methanogens, and fermentative microbes, which can degrade chlorinated ethene, chlorinated ethane, and mixed plumes.

Approaches for implementing ISB typically fall under two broad categories: active and passive approaches. With active systems, the biostimulant is added to extracted groundwater and re-injected into the aquifer. This re-injection process may be repeated for multi-rounds of aqueous donors and therefore involves the installation of injection and extraction wells at the site. Some designs continue re-injection until a pre-determined pore volume of groundwater has been exchanged in the aquifer. The goal of this approach is to increase distribution of the donor throughout the treatment area and enhance dissolution of the DNAPL. For the passive approach, amendments are injected into the source zone often via direct-push technologies (DPT). Longer-lasting substrates (e.g., chitin or vegetable oil) are often selected for this remedy as the ability to re-inject requires re-mobilization of the DPT rig. Other designs assume that injection of the biostimulant will occur every three to four years and permanent injection wells are installed to reduce mobilization costs. Overall, the passive approach assumes the initial amendment injection achieves the desired radius of influence and relies upon microbial degradation to enhance contaminant dissolution and degradation.

Challenges to implementing ISB in a DNAPL source zone are a result of the technology itself, as well as the subsurface environment. ISB is not an aggressive, fast technology because microbial communities require time to become established in an aquifer. Thus, implementing ISB in conjunction before, during, or after other remedial approaches offers a treatment train approach often selected at a site. In addition, the aquifer's heterogeneity and resulting preferential pathways limit distribution of electron donor and/or the microbial community. As the microbial community grows, biofouling of injection wells may limit distribution of amendments, and degradation byproducts may be formed that impact secondary water quality (e.g., methane and hydrogen sulfide generation). Both reductive dechlorination and fermentation resulting from biostimulation can lower the aquifer pH. Thus, adequate buffering capacity is important to sustain ISB within the source zone. The aquifer should have sufficient buffering capacity to handle the impact of degradation on the system.

What lessons have been learned applying ISB in DNAPL source zones?

As with all remediation technologies, success of ISB in source zones is dependent on adequate site characterization. Specifically, the extent of the source zone must be delineated. If the source zone is not properly understood, the application of ISB may be inefficient and could be deemed a failed remedy. As part of understanding the source zone, it is vital that a CSM is developed and maintained throughout the life of the site. This living document will aid in system design and be the basis for assessing the potential and actual performance of ISB in the source zone.

Realistic expectations for system performance should be included in the remedial approach. To help incorporate performance metrics based on past experiences, the following items should be considered:

- Length of time to establish/stimulate the microbial community can be upwards of a year. Therefore, system expectations and monitoring should reflect this timeframe.
- Hydraulic conductivity and preferential flow paths can limit the effectiveness of ISB in source zones. Pilot testing is recommended to understand and account for these issues.
- On average, ISB applied in DNAPL source zones reduces total contaminant concentrations by 95% (McGuire et al., 2006). McGuire et al. (2006) also provided the range of parent compound concentration reduction (e.g., PCE or TCE) as ranging from 29% to 99.9%. Parent compound concentration reductions were not based on total chlorinated solvent concentrations (i.e., daughter product increases/decreases were not included in the evaluation).
- System monitoring is needed to assess performance and determine if treatment adjustments (i.e., addition of buffering agent) are necessary.
- Sustainability considerations include local procurement of amendments, the frequency and duration of monitoring, and whether a passive ISB approach could be used (vs. active) to reduce pumping and operation and maintenance requirements.

References and Web Links

- NAVFAC T2 Resources
  - RITS Seminars
  - Bio Portal
- Department of Defense ESTCP
  - Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents Protocol (ESTCP, 2004)
- Other Resources
  - BioDNAPL-1 (ITRC, 2005)
  - BioDNAPL-2 (ITRC, 2007)
  - Bio-DNAPL-3 (ITRC, 2008)
  - Mass Flux (ITRC, 2010)
  - Integrated DNAPL Site Strategy (ITRC, 2011)
  - McGuire, T. M., J. M. McDade, and C. J. Newell. 2006. "Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impact Sites," Ground Water Monitoring and Remediation 26(1): 73–84.