ESTCP

EXECUTIVE SUMMARY

Evaluation of a Sustainable and Passive Approach to Treat Large, Dilute Chlorinated VOC Groundwater Plumes

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ESTCP Project ER-201629

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ACRONYMS AND ABBREVIATIONS

cis-DCE	*cis*-1,2-dichloroethene
cVOC	chlorinated volatile organic compound
1,4-D	1,4-dioxane
DO	dissolved oxygen
DoD	United States Department of Defense
ESTCP	Environmental Security Technology Certification Program
MCL	maximum contaminant level
NPV	net present value
O&M	operation and maintenance
P&T	pump and treat
VC	vinyl chloride
ZVI	zero-valent iron

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1.0 INTRODUCTION

Chlorinated volatile organic compounds (cVOC) continue to be primary chemicals of concern for the U.S. Department of Defense (DoD), even though many suitable treatment technologies have been developed and verified. One of the greatest challenges remaining for remediating these chemicals of concern at DoD sites and protecting downgradient receptors is the treatment and/or control of large, dilute plumes. Remedial costs are particularly high at sites where impact is extensive, but concentrations are low. Current approaches to address large, dilute cVOC plumes are typically long-term and have high capital and operation and maintenance (O&M) costs.

Achieving clean-up levels for cVOC and other organic pollutants in plumes that have low part-per-billion [i.e., micrograms per liter (µg/L)] concentrations is a difficult technological challenge. Cometabolism has shown significant promise in this area because organisms grow aerobically on a supplied substrate (e.g., propane or methane) rather than the trace chemical of concern, allowing good degradation kinetics, minimal impacts to aquifer geochemistry, and the ability to achieve nanogram per liter (ng/L) chemical of concern concentrations. However, to meet current DoD needs for large, dilute cVOC plumes, this technology must be efficient, sustainable, and cost effective. The development and field validation of an off-the-grid biosparging system capable of meeting these needs was the key goal of this field demonstration.

2.0 OBJECTIVES

The overall objective of this project was to demonstrate effective *in situ* biological treatment of large, dilute cVOC plumes using an approach that is both sustainable and cost effective. The critical objectives of this demonstration were to determine whether an off-the-grid biosparging system could sustainably and economically deliver gaseous amendments in a biobarrier configuration across a large, dilute plume, stimulating indigenous bacteria to biodegrade target cVOC, and whether consistent *in situ* treatment of these cVOC to target levels (i.e., maximum contaminant levels [MCL]) was feasible.

Specific objectives of this project were as follows:

- Evaluate horizontal and vertical distribution of gaseous amendments within and downgradient of the target treatment zone (e.g., biobarrier) using clustered monitoring wells with short (3 ft) screen intervals installed throughout the vertical treatment zone.
- Monitor oxygen and alkane gas utilization within the biobarrier to optimize gaseous amendment delivery mass and frequencies.
- Quantify changes in concentrations of target cVOC within and downgradient of the treatment zone during the system operational period.
- Estimate degradation rates of target cVOC within the treatment zone during active treatment.
- Determine the efficiency and reliability of a solar-powered passive-delivery system to provide sufficient gaseous amendments for biosparging on a large scale.

3.0 TECHNOLOGY DESCRIPTION

Cometabolic biodegradation typically occurs when one or more broad-specificity oxygenase enzymes are induced in bacteria - enzymes that allow such bacteria to grow on a primary substrate (e.g., methane, propane, butane, isobutene), yet also to biodegrade a range of other non-growth compounds, including many DoD chemicals of concern. The application of this approach for remediation typically entails the addition of a specific growth substrate (often an alkane gas) and oxygen to an aquifer with or without accompanying inorganic nutrients and bioaugmentation cultures. Cometabolic treatment can be applied *in situ* using a number of different configurations based on site conditions, including biosparging, groundwater recirculation with active gas addition, and passive gas addition in groundwater wells. Biosparging was used during this demonstration.

There are multiple reasons that cometabolic treatment should be considered at DoD sites, including the following: (1) the approach is widely applicable for groundwater cVOC (perchloroethene excluded) and anaerobic degradation intermediates (e.g., *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (VC)), as well as a wide range of other DoD chemicals of concern including 1,4-Dioxane, methyl tertiary-butyl ether, *N*-Nitrosodimethylamine, 1,2-Dibromoethane, and 1,2,3-trichloropropane; (2) the technology is very well suited for dilute plumes because the cometabolic organisms are not required to grow on the chemical of concern, but rather utilize the substrate gas that is supplied to the aquifer; (3) very low treatment levels (e.g., low ng/L concentrations) can be achieved for some pollutants; and (4) groundwater remains aerobic, minimizing issues such as mobilization of metals (e.g., iron, arsenic, and manganese), production of hydrogen sulfide, and large shifts in pH, as sometimes observed when high substrate concentrations are added to aquifers for anaerobic treatment of cVOC and other chemicals of concern.

During this *in situ* demonstration, propane, ammonia, and oxygen were added to groundwater via sparging to stimulate native propanotrophs to biodegrade *cis*-DCE and VC *in situ*. The demonstration was performed at the Building 324 plume at former Myrtle Beach Air Force Base. The Building 324 location (Site) had many characteristics that made it ideal for this demonstration, including site accessibility, the presence of a large, dilute cVOC plume (~210 ft wide) with reasonable depth (~35 ft) and thickness (~15 ft) of the target treatment interval, a permeable aquifer that was amenable to sparging, significant historical cVOC concentration data, and existing monitoring wells.

4.0 PERFORMANCE ASSESSMENT

4.1 TREATMENT OF cis-DCE AND VC

The primary objective of this demonstration was to assess the long-term effectiveness of applying aerobic cometabolism to treat low concentrations of *cis*-DCE and VC across the width of the plume. This objective was met. Significant decreases in *cis*-DCE and VC were observed starting approximately 2.5 to 3 months after initiating propane and ammonia biosparging, after sufficient biomass growth had occurred within the aquifer. Decreases in *cis*-DCE concentrations were observed in 20 of the 22 impacted wells located within and downgradient of the biobarrier, with concentrations at all 22 wells consistently below the MCL of 70 μg/L between days 181 and 422 of the demonstration.

The estimated decline in the mass flux of *cis*-DCE was ~ 70-fold due to barrier operation from day 294 to the end of the study. Similarly, VC concentrations were below the MCL of 2 µg/L at 15 of the 18 impacted wells by day 294 and remained low for the remainder of the field demonstration. Much like *cis*-DCE, appreciable decreases in the mass flux of VC were observed starting at day 218 and continuing throughout the course of the field demonstration. VC concentrations remained below the MCL at 16 of the 18 wells during the final performance sampling event conducted on day 422.

The average *cis*-DCE and VC concentrations measured at wells located 25 ft downgradient of the sparge wells during baseline sampling (day -5) and the final performance monitoring event (day 422) showed a 98% and a 92% decrease, respectively. *cis*-DCE and VC generally returned to near baseline concentrations (or in the case of VC, higher than baseline) within 105 days after system shutdown due to the absence of oxygen and cometabolic substrate addition (and possibly nutrient addition), as the degradative activity of the propane oxidizing bacteria (or other bacteria capable of aerobically degrading VC) that were grown within the treatment zone ceased, and impacted groundwater flowing through this area was no longer being treated.

4.2 MAINTAINING AEROBIC CONDITIONS

Achieving and maintaining aerobic conditions within the treatment zone was critical during the demonstration, as cometabolism using an alkane/gas substrate is an aerobic process. This was particularly important at the study site which was anoxic and mildly reducing as the beginning of the study (dissolved oxygen (DO) < 1 mg/L; oxidation-reduction potential (ORP) < -80 mV). DO concentrations above the 3 mg/L target were observed in most of monitoring wells located within the biobarrier throughout the demonstration. Although a few wells (PMW-2I and PMW-3D) were not significantly impacted by oxygen sparging, likely due to aquifer heterogeneity and high oxygen demand (both mineral and biological) in the aquifer, the objective of obtaining and maintaining bulk aerobic conditions in the aquifer was achieved.

4.3 OPTIMIZING PROPANE DELIVERY

Optimization of propane amendment (mass and sparge frequency) was required to supply enough substrate for biological growth, while ensuring that high dissolved propane concentrations did not lead to continuous competitive inhibition and limit cVOC biodegradation rates. Dissolved propane was measured above 100 µg/L consistently at multiple wells within the biobarrier during Phase 2 of the demonstration. The data showed that propane concentrations were generally higher during the first 2.5 months of Phase 2 operation (with concentrations measured more than 2 mg/L in several wells) and decreased significantly thereafter as biodegradation rates increased. Propane fluxes at the site were high early in the study and decreased approximately ten-fold thereafter due to increased biological activity. Propane oxidizing genes were noted to increase by ~1000x between day 50 and day 294 of sparging operations. The data showed that a propane sparging frequency of approximately once every 1 to 2 weeks (with average mass loading of ~1.5 lbs./day) was optimal in maintaining biological growth/activity without leading to continuous competitive inhibition.

4.4 SPARGE SYSTEM RELIABILITY

Reliability of biosparging system operation was an important performance objective, as the regular injection of gaseous amendments is critical to the treatment effectiveness of any cometabolic approach. Additionally, reliable performance minimizes system operating costs. The off-the grid solar power system provided consistent power to the biosparging system throughout the entire 518 days of the demonstration and only required changes to the angles of the solar panel arrays 2 times, with each of these changes accomplished in less than 1 hour. The system operated as designed, and there were no major system or equipment failures during the demonstration.

4.5 EASE OF USE

System O&M requirements, which primarily consisted of regular system checks and changeout of the oxygen cylinders, were not significant during the demonstration. System checks (which entailed collecting manual system pressure and flow data, performing regular system maintenance, and performing leak checks) were generally performed every 2-3 weeks in under 3 hours per visit. Change out of the oxygen 16-packs was conducted approximately every 2-3 months and was typically performed in under 4 hours. The 6 tanks of liquified propane and 4 tanks of liquified ammonia did not require replacement during 12 months of Phase 2 cometabolic biosparging due to the general efficiency of this treatment approach. The ability to communicate remotely with the system (and adjust gas sparging), as well as programmed logging capabilities of the supervisory control and data acquisition system significantly reduced the number of site visits required. Furthermore, other the groundwater sampling purge water, there was no waste generated during application of this *in situ* technology.

5.0 COST ASSESSMENT

The expected cost drivers for installation and operation of a cometabolic biosparging system to treat a full-scale large, dilute cVOC plume, and those that will determine the cost/selection of this technology over other options, included the following:

- Depth of the plume bgs
- Width, length, and thickness of the plume
- Aquifer lithology and hydrogeology
- Passive and sustainable power (solar)
- Length of time for clean-up (e.g., necessity for accelerated clean-up)
- The presence of indigenous bacteria capable of cometabolically degrading cVOC
- Concentrations of chemicals of concern and alternate electron acceptors
- Presence of co-occurring chemicals

A cost analysis of a cometabolic biosparging system and two traditional cVOC groundwater treatment approaches to treat a full-scale large, dilute cVOC plume was performed. Cost estimates for full-scale application were developed for the following technologies:

1. Cometabolic biosparging barrier
2. Passive trench zero valent iron permeable reactive barrier (ZVI PRB)

3. Pump and treat (P&T)

These three technologies were selected for comparison because they are all typically applied as treatment barriers or for cVOC plume capture. The base case presented a situation where a shallow aquifer, consisting of homogeneous silty sands, was impacted with trichloroethene. The impacted groundwater extended from 10 to 50 ft bgs, along the direction of groundwater flow for 800 ft, and was 400 ft in width. The costing for the template site assumed that the source zone had been treated and that there was no continuing source of groundwater impact. The cost analyses comparing the above approaches are presented below based on a 30-year operating scenario.

The estimated total costs for the cometabolic biosparge barrier alternative over 30 years are $3,489,500 with a total net present value (NPV) of lifetime costs of $3,616,221. The capital cost including design, work plan, installation of biosparge and monitoring wells, installation of the solar power system, and fabrication, installation, and start-up of the biosparge system is $445,400. The NPV of the O&M is $2,177,640 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with weekly inspections and battery replacement every five years. The costs for materials and other consumables are negligible with this alternative. The NPV of the 30 years of monitoring and reporting costs is $993,181.

This alternative ranks lowest in estimated total remedy cost and lowest in NPV of lifetime costs. The estimated capital cost for this approach is the lowest of the three alternatives because of the limited infrastructure required and the relative ease of installation. The estimated long-term O&M costs are also the lowest of the three alternatives, which helps make this the least expensive of the alternatives. As with the other alternatives, total remedy costs will increase if the treatment needs to extend beyond 30 years.

6.0 IMPLEMENTATION ISSUES

In summary, the data from this ESTCP field test clearly show that propane, ammonia and oxygen biosparging can be an effective approach to reduce and maintain concentrations of cVOC, such as *cis*-DCE and VC, below relevant MCLs. The off-the-grid solar powered biosparging system proved to be highly reliable, simple to operate and maintain, and economical for dilute plume treatment. For many large, dilute plume applications, this type of biosparging system is expected to be significantly less expensive to install and operate than a conventional P&T system or other *in situ* approaches, such as a ZVI barrier for groundwater treatment.