

Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites

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Abstract

Performance and rebound of intensive source depletion technologies were evaluated at 59 chlorinated solvent sites where remediation targeted dense non-aqueous phase liquid (DNAPL) source zones. The four technologies included in the study are chemical oxidation, enhanced bioremediation, thermal treatment, and surfactant/cosolvent flushing. Performance was evaluated by examining temporal ground water concentration data before and after source remediation was performed. Results indicated that all four technologies have median concentration reductions of 88% or greater for the parent chlorinated volatile organic compound (CVOC). Approximately 75% of the source depletion projects were able to achieve a 70% reduction in parent compound concentrations. A median reduction in total CVOC concentrations (parent plus daughter compounds) of 72% was observed at 12 chemical oxidation sites and 62% at 21 enhanced bioremediation sites. Rebound was assessed at sites having at least 1 year of posttreatment data. Rebound occurrence was most prevalent at sites implementing chemical oxidation. At chemical oxidation sites where rebound was evaluated ($n = 7$), the median parent CVOC concentration reduction was 90% immediately following treatment compared to 78% at the end of posttreatment monitoring (i.e., 1 to 5 years after treatment). For enhanced bioremediation sites where rebound was evaluated ($n = 10$), median parent CVOC concentration reduction changed from 77% to 96% over the posttreatment monitoring period. Minimal concentration change was observed over the posttreatment monitoring period at surfactant/cosolvent sites ($n = 2$) and thermal treatment sites ($n = 1$) evaluated for rebound. Based on current data, none of the 59 source depletion projects was able to meet maximum contaminant levels throughout the treatment zone for all CVOCs.

Introduction

Remediation of sites affected with dense non-aqueous phase liquid (DNAPL) comprising chlorinated volatile organic compounds (CVOCs) presents significant technical and economic challenges (Kavanaugh et al. 2003). While conventional treatment technologies such as pump and treat or containment are often able to control contaminant plumes emanating from DNAPL source zones, they involve extended operating periods (perhaps decades) and potentially high life cycle costs. Therefore, application of more aggressive source depletion technologies, such as chemical oxidation, enhanced bioremediation, thermal treatment, and surfactant/cosolvent flushing, in DNAPL source zones has become more common.

Chemical oxidation and enhanced bioremediation rely on in situ destruction of DNAPL constituents, such as tetrachloroethene (PCE), trichloroethene (TCE), or 1,1,1-trichloroethane, to achieve remediation objectives. For

chemical oxidation, contaminant destruction occurs via addition of an oxidant, such as hydrogen peroxide, permanganate, or ozone, which initiates a chemical reaction whereby the contaminant is oxidized to innocuous reaction products. Enhanced bioremediation, as the name implies, takes advantage of natural microbial processes, such as reductive dechlorination, by supplying a rate-limiting substrate (i.e., electron donor addition), sometimes with the addition of microorganisms (i.e., bioaugmentation) to increase the rate and extent of biodegradation. Enhanced bioremediation, which has primarily been used to treat dissolved-phase contamination, is increasingly being applied within DNAPL source zones to enhance dissolution rates (Parsons Corporation 2004; U.S. DOE 2002).

Thermal treatment and surfactant/cosolvent flushing technologies remediate DNAPL contaminants through non-destructive phase transfer processes and/or by increasing DNAPL mobility for recovery. The most common thermal technologies include steam heating and electrical resistive heating (ERH), both of which heat the saturated zone thereby increasing contaminant volatilization rates. At

higher temperatures (i.e., >100°C), thermal destruction of contaminants may also occur (U.S. EPA 2004a). Addition of surfactants or cosolvents serves to enhance DNAPL recovery through increased solubility of DNAPL constituents and/or increased mobility of the DNAPL. Both thermal and surfactant/cosolvent technologies typically involve ground water recovery and ex situ treatment of recovered contaminants.

There are several potential advantages to implementing aggressive DNAPL treatment technologies (Kavanaugh et al. 2003). From a risk management perspective, source depletion benefits include reduced exposure risk to human and ecological receptors that results from decreasing the mass, volume, toxicity, or mobility of the DNAPL and reducing the concentration and flux of dissolved DNAPL constituents. From an economic standpoint, source depletion may result in reduced life cycle costs by minimizing the remediation time frame and reducing the duration and cost of other control measures (e.g., engineering controls such as hydraulic containment, as well as institutional controls such as restricted land use) that are often implemented at DNAPL sites. While the potential benefits of DNAPL source depletion are apparent, the uncertainties associated with implementing and evaluating such treatments complicate the tasks of quantifying the benefits and translating the results to attainment of remedial goals.

Assessing performance of DNAPL source depletion technologies is necessary in order to determine whether such intensive, costly measures are capable of achieving remedial goals. However, assessing performance is complicated by the variability in remedial goals and metrics used to determine whether those goals are met (ITRC 2004; Kavanaugh et al. 2003). At some sites, measurements of the change in DNAPL mass and/or contaminant flux are used as a performance metric. However, the remedial goals at most sites with impacted ground water are based on reducing ground water concentrations to regulatory standards (e.g., maximum contaminant levels [MCLs] or risk-based values). Since remedial goals are often based on dissolved contaminant concentrations, most sites where source depletion has been applied rely on ground water concentrations to track remediation performance.

As discussed by an expert panel in a recent U.S. EPA document on DNAPL source depletion (Kavanaugh et al. 2003), there have been numerous applications of innovative technologies within DNAPL source zones, but documentation of remediation performance and cost is often inadequate to determine overall treatment effectiveness. Furthermore, comprehensive data sets are rarely made available in the literature to allow for an independent evaluation of remediation performance. The lack of well-documented performance evaluations and accurate cost data led the U.S. EPA panel to conclude that “the degree of uncertainty in the costs and benefits of applying source depletion technologies is currently at levels that discourage widespread use of the available source depletion technologies at DNAPL sites,” and “such documentation would provide important insights on the benefits that could be achieved even with partial DNAPL source depletion” (Kavanaugh et al. 2003). The U.S. EPA panel identified “a thorough and independent

review of a selected number of DNAPL sites where sufficient documentation is available to assess the performance of source depletion using multiple metrics” as a “primary research need.”

A recent study addressed the relative success of chlorinated solvent DNAPL source-zone remediation technologies based on a literature review and survey of DNAPL remediation sites (GeoSyntec Consultants 2004). While this study compiled data from many sites for several technologies, it did not include a rigorous evaluation of remedial success. Rather, remediation success was semiquantitatively evaluated using estimates of mass removal and decrease in mass flux reported by those implementing the remediation. The methods used by respondents to determine mass removal and mass flux decrease were not reported. Another recent study by the U.S. EPA (2004b) reviewed DNAPL remediation at sites where regulatory closure had been attained or was near attainment. The review covered only eight sites, of which seven had achieved closure using risk-based concentration goals and most sites required implementation of institutional controls and/or land-use restrictions.

This study presents results of a rigorous, independent performance evaluation of four DNAPL source depletion technologies (chemical oxidation, enhanced bioremediation, thermal treatment, and surfactant/cosolvent flushing) by comparing actual ground water concentrations of chlorinated compounds before and after treatment. Temporal ground water concentration data were collected from site reports submitted to regulatory agencies, results of a DNAPL remediation survey, and literature reports. Long-term effectiveness of DNAPL source depletion technologies was evaluated by examining the temporal data for occurrence of rebound following treatment. All results reported in this study were calculated from actual concentration vs. time data, and concentration reduction values reported in the literature were not used. A companion study reports costs associated with these treatments (McDade et al. 2005). An electronic decision-support system featuring a customizable database containing data from this project is available for free download at www.gsi-net.com.

Methods

Data Collection Methods

Data from three sources were compiled to evaluate source-zone remediation performance and rebound: (1) published literature; (2) site reports submitted to state regulatory agencies; and (3) a survey of DNAPL source-zone remediation projects. Sites using the following technologies for source depletion were included in the project: enhanced bioremediation, chemical oxidation, thermal treatment, and surfactant/cosolvent treatment. For each site, ground water concentration data for up to four wells within the treatment zone were collected. Data were collected only at sites having a concentration record with data from before treatment (or at start-up of the remediation system) and after treatment. If available, other site data were

Table 1
Summary of Source Depletion Sites

Site No.	Site Name (if available)	Site Location	Hydrogeology	Amendment ¹	Scale	Data Source	Data Record (year)
Enhanced bioremediation sites							
B-01	Dry cleaning facility	Dallas, TX	Fine grained	HRC	Full	TCEQ VCP reports	7.3
B-02	Dry cleaning facility	Houston, TX	Fine grained	Bioaug, ORC	Full	TCEQ VCP reports	5.9
B-03	Dry cleaning facility	Dallas, TX	Fine grained	HRC	Full	TCEQ VCP reports	2.9
B-04	Dry cleaning facility	Massachusetts	Fractured rock	HRC	Full	SERDP survey	1.8
B-05	Industrial facility	Florida	Fine grained	Soybean oil	Full	SERDP survey	3.9
B-06	Industrial facility	New Hampshire	Fine grained	Lactate, yeast	Full	SERDP survey	15.9
B-07	Dry cleaning facility	Jacksonville, FL	Fine grained	HRC	Full	FDEP reports	3.6
B-08	Dry cleaning facility	Orlando, FL	Fine grained	HRC	Full	FDEP reports	5.4
B-09	Industrial facility	Fort Worth, TX	Fine grained	HRC	Pilot	TCEQ VCP reports	0.5
B-10	Dry cleaning facility	Dallas, TX	Fine grained	HRC	Pilot	TCEQ VCP reports	7.3
B-11	Dry cleaning facility	Portland, OR	Fine grained	HRC, HRC-X	Pilot	SERDP survey	5.5
B-12	Industrial facility	New Hampshire	Coarse grained	Lactate, yeast	Pilot	SERDP survey	15.8
B-13	Industrial facility	New Hampshire	Fine grained	Lactate, yeast	Pilot	SERDP survey	1.7
B-14	Dry cleaning facility	Austin, TX	Fine grained	Bioaug, nutrients	Full	TCEQ VCP reports	6.7
B-15	Dry cleaning facility	Houston, TX	Fine grained	HRC, HRC-X	Pilot	TCEQ VCP reports	7.0
B-16	Dry cleaning facility	Dallas, TX	Fine grained	Lactate, ethanol	Pilot	TCEQ VCP reports	5.9
B-17	Industrial facility	Tennessee	Fine grained	HRC	Full	SERDP survey	3.6
B-18	Industrial facility	San Jose, CA	Fine grained	HRC	Full	Literature reports	4.2
B-19	Industrial facility	South Carolina	Coarse grained	Molasses	Full	SERDP survey	1.6
B-20	Industrial facility	Southeast United States	Fine grained	Molasses	Full	SERDP survey	2.3
B-21	Duluth International Airport	Duluth, MN	Fine grained	HRC	Pilot	Literature reports	0.8
B-22	Test Area North	Idaho Falls, ID	Fractured rock	Lactate	Pilot	Literature reports	1.0
B-23	Pinellas STAR Center	Largo, FL	Fine grained	Lactate, methanol	Pilot	Literature reports	0.4
B-24	Manufacturing facility	Houston, TX	Fine grained	Methanol, nutrients	Full	Literature reports	3.5
B-25	Industrial facility	Rochester, NY	Fine grained	HRC	Full	Literature reports	0.3
B-26	Washington Square Mall	Germanstown, WI	Coarse grained	Molasses	Full	Literature reports	1.2
Chemical oxidation sites							
C-01	Dry cleaning facility	Houston, TX	Fine grained	KMnO ₄	Full	TCEQ VCP reports	6.1
C-02	Industrial facility	Pensacola, FL	Coarse grained	H ₂ O ₂	Full	SERDP survey	6.5
C-03	Dry cleaning facility	Jacksonville, FL	Fine grained	H ₂ O ₂	Full	FDEP reports	1.8
C-04	Dry cleaning facility	Florida	Coarse grained	H ₂ O ₂	Full	FDEP reports	3.5
C-05	Dry cleaning facility	Jacksonville, FL	Fine grained	KMnO ₄ , TBA	Pilot	FDEP reports	4.7
C-06	Industrial facility	Dallas, TX	Fine grained	NaMnO ₄	Pilot	TCEQ VCP reports	0.6
C-07	Dry cleaning facility	Dallas, TX	Coarse grained	KMnO ₄	Full	TCEQ VCP reports	5.3
C-08	Dry cleaning facility	Houston, TX	Fine grained	CleanOx [®] , KMnO ₄	Full	TCEQ VCP reports	5.4

Table 1 (Continued)

Site No.	Site Name (if available)	Site Location	Hydrogeology	Amendment ¹	Scale	Data Source	Data Record (year)
C-09	Dry cleaning facility	Dallas, TX	Fine grained	H ₂ O ₂	Full	TCEQ VCP reports	3.1
C-10	Dry cleaning facility	Dallas, TX	Fine grained	KMnO ₄	Full	TCEQ VCP reports	5.8
C-11	Dry cleaning facility	Houston, TX	Fine grained	KMnO ₄	Full	TCEQ VCP reports	5.0
C-12	Broward Co.	Florida	Coarse grained	KMnO ₄	Full	Literature reports	1.1
C-13	Dry cleaning facility	Houston, TX	Fine grained	KMnO ₄	Full	TCEQ VCP reports	8.6
C-14	Dry cleaning facility	Houston, TX	Fine grained	CleanOx [®] , KMnO ₄	Full	TCEQ VCP reports	4.5
C-15	Charleston SWMU 196	Charleston, SC	Fine grained	H ₂ O ₂	Full	Literature reports	2.4
C-16	News publisher facility	Framingham, MA	Fine grained	H ₂ O ₂	Full	Literature reports	0.1
C-17	Savannah River	Aiken, SC	Fine grained	H ₂ O ₂	Full	Literature reports	0.5
C-18	Dry cleaning facility	Hutchinson, KS	Fine grained	Ozone	Pilot	Literature reports	0.4
C-19	Kings Bay Naval Base	Camden Co, GA	Coarse grained	H ₂ O ₂	Full	Literature reports	0.9
C-20	Dry cleaning facility	Rockville, MD	Fractured rock	H ₂ O ₂ , NaMnO ₄	Full	Literature reports	1.1
C-21	Portsmouth Gas Plant	Pikeon, OH	Coarse grained	KMnO ₄	Full	Literature reports	0.3
C-22	Kansas City Plant	Kansas City, MO	Fine grained	KMnO ₄	Full	Literature reports	0.1
C-23	Launch Complex 34	Cape Canaveral, FL	Fine grained	KMnO ₄	Pilot	Literature reports	0.5
Thermal sites							
T-01	Industrial facility	Illinois	Fine grained	Six-phase ERH	Full	SERDP survey	2.1
T-02	Industrial facility	Florida	Fine grained	Steam, 3-phase	Full	SERDP survey	4.4
T-03	Visalia	Visalia, CA	Coarse grained	Steam	Full	Literature reports	5.8
T-04	Charleston Naval Complex	Charleston, SC	Fine grained	Three-phase ERH	Full	Literature reports	2.7
T-05	Manufacturing plant	Not available	Fine grained	Steam	Full	Literature reports	0.5
T-06	Cape Canaveral	Cape Canaveral, FL	Fine grained	Six-phase ERH	Full	Literature reports	1.9
Surfactant/cosolvent sites							
S-01	Dry cleaning facility	Jacksonville, FL	Fine grained	Ethanol	Pilot	FDEP reports	5.3
S-02	Hill Air Force Base	Hill AFB, UT	Coarse grained	Aerosol MA-80I	Full	Literature reports	0.2
S-03	Camp Lejeune Site 88	Jacksonville, NC	Fine grained	Alfoterra 145-4PO	Pilot	Literature reports	1.8
S-04	Bachman Road Site	Oscoda, MI	Coarse grained	Tween 80	Pilot	Literature reports	1.4

¹HRC = hydrogen release compound; HRC-X = HRC extended release formula; Bioaug = bioaugmentation; ORC = oxygen release compound; KMnO₄ = potassium permanganate; H₂O₂ = hydrogen peroxide; TBA = tertiary butyl alcohol; NaMnO₄ = sodium permanganate; ERH = electrical resistance heating; TCEQ VCP = Texas Commission on Environmental Quality Voluntary Cleanup Program; SERDP = Strategic Environmental Research and Development Program; FDEP = Florida Department of Environmental Protection.

collected including distance of monitoring well to treatment point, ground water seepage velocity, predominant lithology of the treatment zone, and treatment cost, volume, and duration.

Performance and Rebound Evaluation Methods

Geometric mean ground water concentrations were calculated for the period before treatment and then for the period after treatment for each well. The percent reduction in concentration observed after treatment relative to before treatment was determined for each well, and the median concentration reduction of all site wells was calculated as the final performance metric for each site. At sites where source treatment is ongoing, concentration data from the most recent year were used to determine the after-treatment concentration. The performance analysis was conducted for the parent CVOCs (e.g., PCE, TCE [at sites with little PCE], chlorobenzene, and pentachlorophenol) and total CVOCs (TCVOCs; e.g., parent CVOC plus degradation daughter products). Only enhanced bioremediation sites and chemical oxidation sites had sufficient data records to evaluate performance in terms of TCVOCs.

Rebound was evaluated at sites having at least 1 year of posttreatment monitoring data. Rebound was calculated as the percent difference between geometric mean concentrations of the first half of the posttreatment data record and geometric mean concentrations of the last half of the posttreatment data record. For sites with two or more years of posttreatment data, geometric mean concentrations from the first year of posttreatment data were compared to geometric mean concentrations from the last year of post-treatment data. Rebound was considered to have occurred

when concentrations increased at least 25% over the post-treatment monitoring period. The rebound analysis was conducted for the parent chlorinated compound only.

Results and Discussion

Concentration vs. time data for 147 wells at 59 source depletion sites were collected. The data included 26 enhanced bioremediation sites, 23 chemical oxidation sites, 6 thermal sites, and 4 surfactant/cosolvent sites. The locations and brief summaries of the sites are given in Table 1. Nearly 40% of the data were collected from reports submitted to either the Texas Commission on Environmental Quality Voluntary Cleanup Program (TCEQ VCP) or the Florida Department of Environmental Protection (FDEP) Drycleaning Solvent Cleanup Program. Data for 20% of the sites were submitted in response to a DNAPL source-zone remediation survey conducted as part of an ongoing Strategic Environmental Research and Development Program (SERDP) project. The remaining data (40%) were collected from literature reports, conference presentations, or conference proceedings. As shown in Table 1, the concentration records for data collected from state agency reports and the SERDP survey were typically longer (median = 5 years) than those reported in the literature (median = 1 year).

Temporal concentration records, normalized to the initial measured concentration, for all monitoring wells are provided in Figure 1. Since only the magnitude in concentration changes is presented in Figure 1, the geometric mean of pretreatment ground water concentrations was calculated for each site to provide insight into the actual

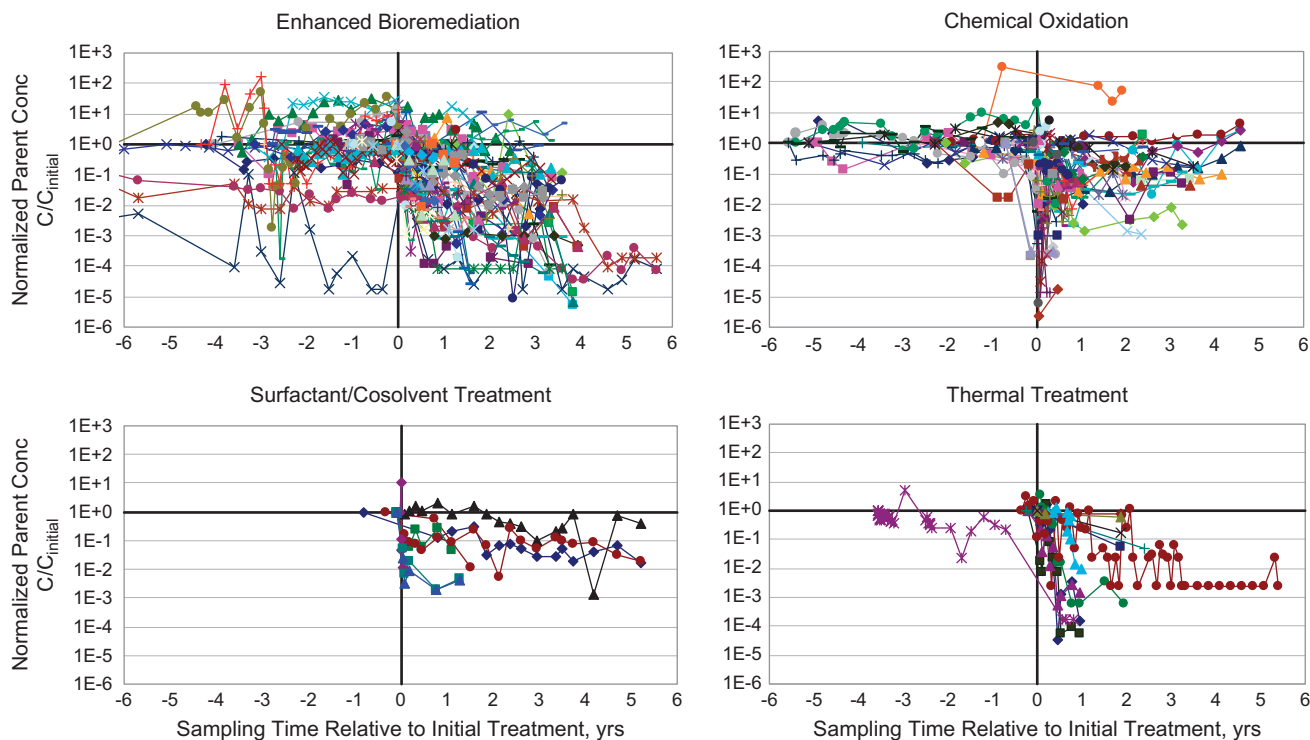


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

concentrations. The median geometric mean pretreatment concentration for all sites, grouped by technology, was as follows: 48 mg/L at surfactant/cosolvent sites, 7.9 mg/L at thermal sites, 5.1 mg/L at enhanced bioremediation sites, and 2.0 mg/L at chemical oxidation sites. Maximum pretreatment concentrations at any well ranged from 4 to 900 mg/L at surfactant/cosolvent sites, 1.3 to 1070 mg/L at thermal sites, 0.4 to 1700 mg/L at enhanced bioremediation sites, and 0.5 to 1110 mg/L at chemical oxidation sites.

Based on maximum pretreatment concentration data, all four technologies have been applied at sites with very high ground water concentrations. But on average, surfactant/cosolvent technology was applied at sites with the highest concentrations, and chemical oxidation was applied at sites with the lowest concentrations.

In addition to pretreatment concentrations, other site characteristics including hydrogeology (e.g., fine grained, coarse grained, or fractured rock) were evaluated to determine if there was a relationship to the technology selected. As shown in Table 1, nearly 75% of the sites reported the treatment zone consisted of fine-grained material (e.g., silts, clays, and silty/clayey sands). Treatment zone stratigraphy was characterized as fine grained at 88% of enhanced bioremediation sites, at 83% of thermal sites, at 73% of chemical oxidation sites, and at 50% of surfactant/cosolvent sites. Chemical oxidation had the most applications (six) in coarse-grained material (e.g., sands, gravels). The treatment zone at only three sites, two implementing enhanced bioremediation and one implementing chemical oxidation, consisted of fractured rock. Seepage velocity and site type (i.e., dry cleaner, industrial, military) also did not correlate to the selected technology (data not shown).

Performance results of source depletion technologies, based on ground water concentration reductions of the parent chlorinated compound within the treatment zone, are illustrated in Figure 2a. All four technologies exhibited median parent reductions of 88% or greater, and enhanced bioremediation, thermal, and surfactant/cosolvent had median parent reductions of 95% or greater. All sites showed some reduction in parent concentrations except for two chemical oxidation sites that had median concentration increases in the parent compound of 27% and 55% (i.e.,

-27% and -55% reduction). Surfactant sites had the least variance in parent concentration reductions, with minimum and maximum reductions ranging from 91% to 99.9%. However, the surfactant/cosolvent treatment had the least representation in the study with only four sites.

Performance, in terms of parent CVOC reduction, did not appear to be related to ground water seepage velocity, treatment volume, or distance from the well to the nearest treatment point. Performance was independent of these parameters as indicated by R^2 values of less than 0.1 for each regression (data not shown). The lack of any relationship between concentration reduction and distance to the nearest treatment point may be a result of the close proximity of most monitoring points to the treatment point. For 97 monitoring points where the distance to the nearest treatment point was available, the median distance from the monitoring point to the nearest treatment point was 7 feet, and 75% were within 13 feet of a treatment point.

Data records for sites implementing enhanced bioremediation and chemical oxidation were sufficient to evaluate performance in terms of reduction in TCVOC concentrations (parent plus daughter products). For TCVOCs, chemical oxidation slightly outperformed enhanced bioremediation, with median concentration reductions of 72% compared to 62% for enhanced bioremediation (Figure 2b). All chemical oxidation sites where TCVOC performance was evaluated had an overall decrease in TCVOC concentrations (the two sites where parent concentrations increased did not have sufficient data to evaluate TCVOCs). On the other hand, over 25% of the enhanced bioremediation sites had an increase in TCVOC concentrations (i.e., 25th percentile = -15%, where a negative number indicates a concentration increase).

Some degree of accumulation of biodegradation daughter products is not unexpected when implementing enhanced bioremediation, as this technology results in the breakdown of more highly chlorinated compounds to lesser chlorinated compounds (Wiedemeier et al. 1999). At some sites, reductive dechlorination of PCE and TCE may lead to an accumulation and persistence of chlorinated intermediates such as *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (Parsons Corporation 2004). However, these

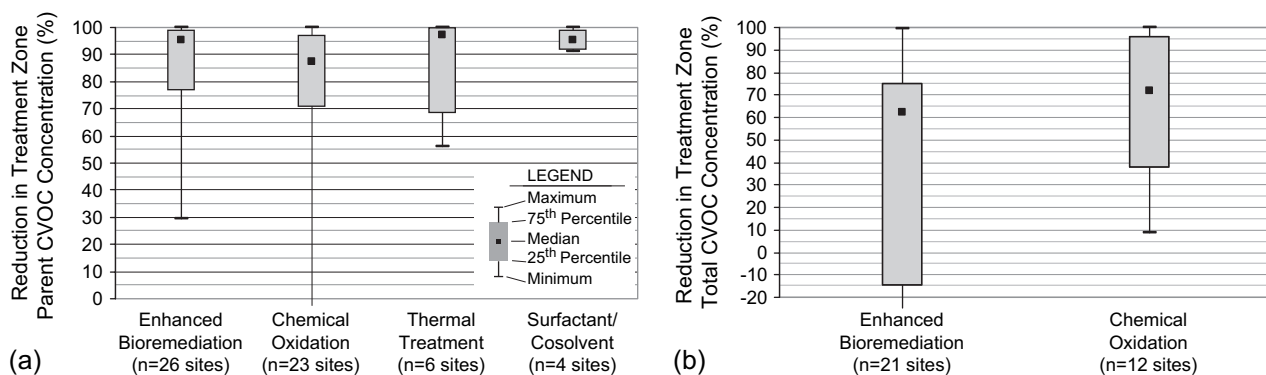


Figure 2. Performance of source depletion technologies: reduction in parent CVOC (a) and total CVOC (b) concentration within the treatment zone. (a) Minimum reduction for chemical oxidation = -55% (value not shown). (b) Minimum reduction for enhanced bioremediation = -150% (value not shown). Only sites implementing enhanced bioremediation and chemical oxidation had sufficient data records to evaluate total CVOCs. Negative value indicates a concentration increase.

less chlorinated compounds may be amenable to additional degradation processes such as biological oxidation (Bradley and Chapelle 1996, 1998). While there are downfalls to production of the lesser chlorinated intermediates, such as greater toxicity and lower regulatory standards for vinyl chloride, there are also potential advantages to their production in DNAPL source zones. In many cases, increasing concentrations of daughter products are a goal of bioremediation as recent studies (Carr et al. 2000; Cope and Hughes 2001; Adamson et al. 2003) have reported enhanced dissolution rates of DNAPL constituents as a result of daughter products within the source zone, which may lead to decreased remediation time frames.

Researchers have suggested that technologies including chemical oxidation, thermal treatment, and surfactant/cosolvent flushing may also enhance natural bioremediation processes (U.S. EPA 2004a; Kavanaugh et al. 2003; Marley et al. 2003). Comparison of concentration reductions for parent CVOC to TCVOCs for chemical oxidation sites suggests that bioremediation was not enhanced as a result of chemical oxidation treatment at many of the sites studied. Since no thermal sites had daughter product concentration data, TCVOC reduction could not be used to evaluate whether thermally enhanced bioremediation occurred at these sites. One cosolvent flushing site (Table 1, Site S-01) did have TCVOC concentration data, and daughter product concentrations exceeded parent CVOC concentrations, indicating bioremediation processes may have been enhanced. Other researchers studying this site (Mravik et al. 2003) concluded that bioremediation was enhanced in the presence of residual cosolvent. Although no surfactant sites had TCVOC data, a recent study on the effects of surfactants on reductive dechlorination of chlorinated ethenes concluded that surfactants are likely to inhibit reductive dechlorination to some degree, particularly reduction beyond *cis*-DCE to vinyl chloride and ethene (McGuire and Hughes 2003).

A notable characteristic of DNAPL source-zone depletion projects is the duration over which the technology is actively applied. For this study, treatment duration was measured as the time period beginning when application of the treatment was initialized until treatment ceased. For enhanced bioremediation and chemical oxidation treatments, which often involve multiple injection events, the treatment duration was the time between the first and last injection events.

As summarized in Table 2, sites implementing enhanced bioremediation had both the longest median duration (427 d) and the greatest variation in treatment duration (1 to 2123 d). Notably, 43% of enhanced bioremediation sites reporting treatment duration ($n = 21$) implemented one-time injections, while 26% of chemical oxidation sites ($n = 19$) used one-time injections. Chemical oxidation and thermal treatment technologies had similar median treatment durations (212 and 228 d, respectively), while surfactant/cosolvent had the lowest median duration (46 d). Duration of surfactant/cosolvent treatments also varied least, with a range of 6 to 58 d. These results are comparable to those reported in a recent DNAPL remediation survey (GeoSyntec Consultants 2004), which had median treatment durations for enhanced bioremediation, chemical oxidation, and thermal treatment sites of 380 d, 183 d, and 167 d, respectively. The GeoSyntec Consultants study did not report treatment duration for surfactant/cosolvent sites.

For some technologies, treatment duration may extend beyond the period of active treatment. Examples include enhanced bioremediation using a slow-release electron donor and thermal treatments where elevated temperatures persist beyond the period of active heating. Extended treatment beyond the active treatment period is evident at many enhanced bioremediation sites included in this study as temporal records (Figure 1) show that concentrations continue to decline several years after treatment. The period of active treatment may also affect costs related to implementing the remedy. In a companion cost analysis of the sites presented in this study, McDade et al. (2005) report that treatment duration is inversely related to treatment cost (in terms of dollars per cubic yard), though at a low correlation ($R^2 = 0.25$).

The occurrence of rebound (i.e., an increase in ground water concentrations following treatment completion) is another important factor in evaluating the success of source depletion technologies. Many case studies and literature reports document decreases in concentrations following source depletion activities. However, the data presented are typically of short duration and do not allow a complete assessment of whether or not the reduction achieved was permanent (Parsons Corporation 2004; U.S. EPA 2004b; U.S. EPA 2001; ESTCP 1999; U.S. EPA 1998). Of the few studies that have monitored concentrations for extended periods beyond completion of source depletion activities, several have observed some level of concentration rebound

Table 2
Treatment Duration Summary Statistics

Treatment Duration (d) Summary Statistics	Enhanced Bioremediation	Chemical Oxidation	Thermal Treatment	Surfactant/Cosolvent
Minimum	1	1	142	6
25th percentile	1	29	174	26
Median	427	212	228	46
75th percentile	639	457	320	52
Maximum	2123	731	1127	58
<i>n</i>	21	19	5	4

(ITRC 2004; ESTCP 1999). In order to more accurately assess the occurrence of rebound, sites with concentration records including at least 1 year of posttreatment data were evaluated.

Results of the rebound analysis are presented in Table 3 and Figures 3 and 4. Rebound was analyzed for 43 wells at 20 sites (10 enhanced bioremediation sites, 7 chemical oxidation sites, 2 surfactant/cosolvent sites, and 1 thermal site). On an individual well basis (Table 3 and Figure 3), rebound was observed in 20% of wells at enhanced bioremediation sites, in 81% of wells at chemical oxidation sites, and was not observed at surfactant/cosolvent and thermal sites. As shown in Figure 3, concentrations in several wells at chemical oxidation sites rebounded by as much as 1 to 2 orders of magnitude throughout the posttreatment monitoring period. In fact, at 30% of the chemical oxidation rebound wells, rebound resulted in concentrations higher than pretreatment conditions. For rebound wells at enhanced bioremediation sites, the increased concentrations observed during the posttreatment period were still below pretreatment concentrations.

Figure 4 presents a comparison of median concentration changes from before treatment began to concentrations immediately following treatment and at the end of the post-monitoring data record (minimum postmonitoring record of 1 year, maximum postmonitoring period of 5.5 years). For most enhanced bioremediation and surfactant/cosolvent flushing sites, concentrations continued to decrease after treatment. At enhanced bioremediation sites, more decrease was observed, with a median reduction in concentration of 77% in parent CVOC immediately following treatment changing to a 96% reduction at the end of the postmonitoring record. Possible explanations of these results are (1) residual electron donor continued to promote bioremediation even after injections ceased, and (2) the treatment created conditions more conducive to support natural bioremediation without the need for enhancement. The continued concentration reduction in the parent CVOC over the posttreatment period at the surfactant/cosolvent sites is interesting since this observation is likely due to biodegradation rather than flushing. Recent studies by Ramsburg et al. (2004) and Mravik et al. (2003) support this conclusion.

Rebound at the seven chemical oxidation sites caused the remediation performance to deteriorate in the period

after the treatment, as the median concentration reduction was 90% immediately after treatment compared to only a 78% reduction at the end of posttreatment monitoring (at least a year later). It is unclear why rebound was most prevalent at chemical oxidation sites. One factor considered was pretreatment ground water concentrations. Results from an analysis of pretreatment ground water concentrations at the wells evaluated for rebound (data not shown) were similar to results obtained from the same analysis for all wells (discussed above). Pretreatment ground water concentrations were typically lower at chemical oxidation sites than at sites implementing other technologies.

Other possible explanations for the occurrence of rebound at chemical oxidation sites are (1) DNAPL diffusion from low-permeability zones following treatment; (2) alteration of naturally occurring organic carbon and other geochemical conditions; and (3) decreased microbial activity following treatment due to toxicity effects of the oxidant. Since diffusion from low-permeability regions would also be expected at bioremediation sites and surfactant sites (where rebound was less prevalent), it is unlikely that diffusion from a low-permeability matrix accounts for the observed rebound at chemical oxidation sites. At the four chemical oxidation sites where rebound was observed in >50% of wells, the treatment zone stratigraphy was characterized as fine grained (e.g., silts, clays, and silty/clayey sands) at two sites and coarse grained (e.g., sands and gravels) at two sites. These limited data support the conclusion that diffusion from low-permeability zones is unlikely to fully account for rebound at chemical oxidation sites.

In aquifers affected with chlorinated solvents, naturally occurring organic carbon may serve as sorption material as well as electron donor for intrinsic biodegradation. As naturally occurring organic carbon is depleted by chemical oxidation, contaminant sorption sites and electron donor available to bacteria are decreased, which may cause contaminant concentrations to increase following treatment. Since organic carbon data were not available for the sites studied, this hypothesis could not be evaluated.

The addition of chemical oxidants may also lead to decreased microbial activity within the treatment zone, thereby limiting the naturally occurring biodegradation of contaminants remaining in the treatment zone, as well as contaminants flushed from untreated areas. Decreased

Table 3
Evaluation of Rebound at Source Depletion Sites

Source Depletion Technology	Percent of Sites with Rebound ¹ at One or More Well	Percent of Sites with Rebound at >50% of Wells	Number of Wells Analyzed for Rebound	Number of Wells with Rebound
Enhanced bioremediation	40	10	20	4
Chemical oxidation	88	57	16	13
Thermal treatment	50	0	1	0
Surfactant/cosolvent	0	0	6	0

¹For this study, rebound occurrence is defined as an increase $\geq 25\%$ in posttreatment ground water concentrations (see Methods section). Rebound was only evaluated at sites having at least 1 year of posttreatment monitoring data.

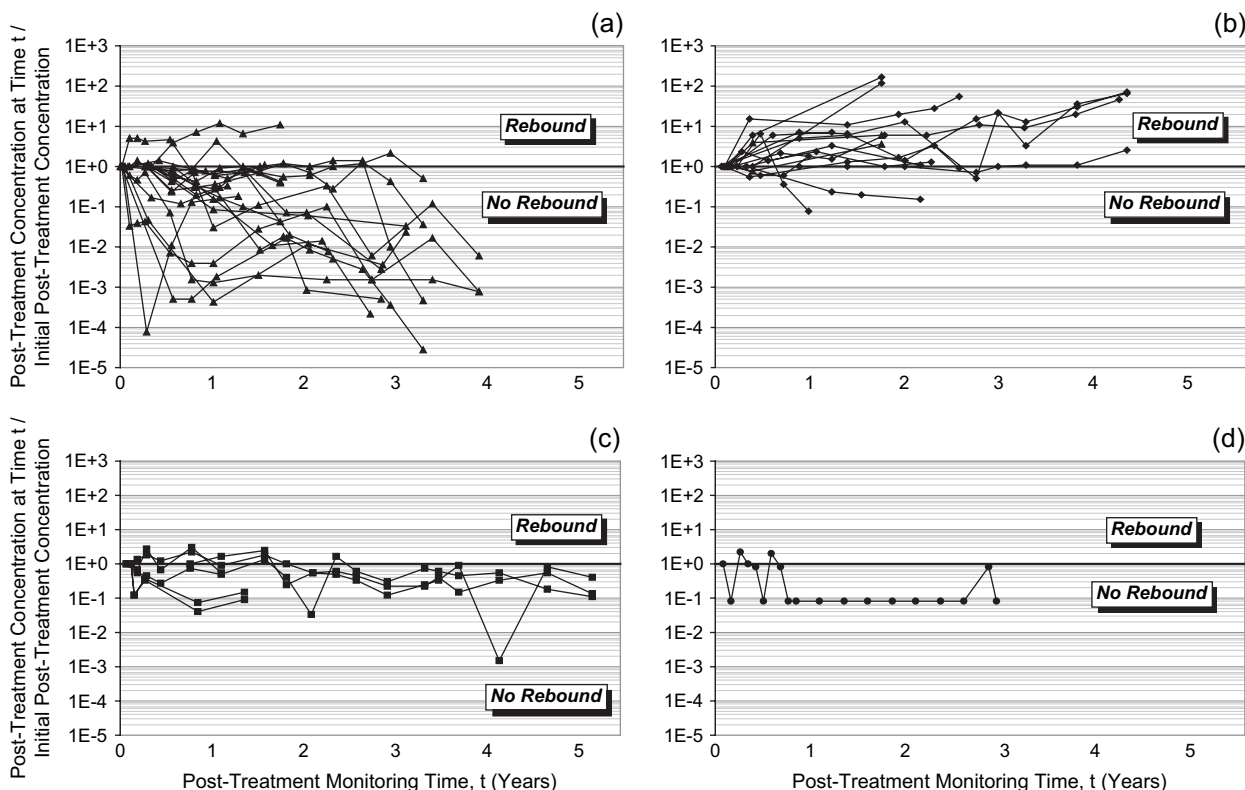


Figure 3. Change in posttreatment ground water concentrations. (a) Enhanced bioremediation sites ($n = 20$ wells); (b) chemical oxidation sites ($n = 16$ wells); (c) surfactant/cosolvent sites ($n = 6$ wells); (d) thermal treatment sites ($n = 1$ well).

microbial activity following chemical oxidation of TCE DNAPL using potassium permanganate was recently observed in laboratory column studies by Hrapovic et al. (2005). In these studies, the authors observed no microbial

activity following permanganate flushing until the influent was changed from distilled water (containing ethanol and acetate as electron donors) to site ground water, which introduced new microorganisms. Researchers have

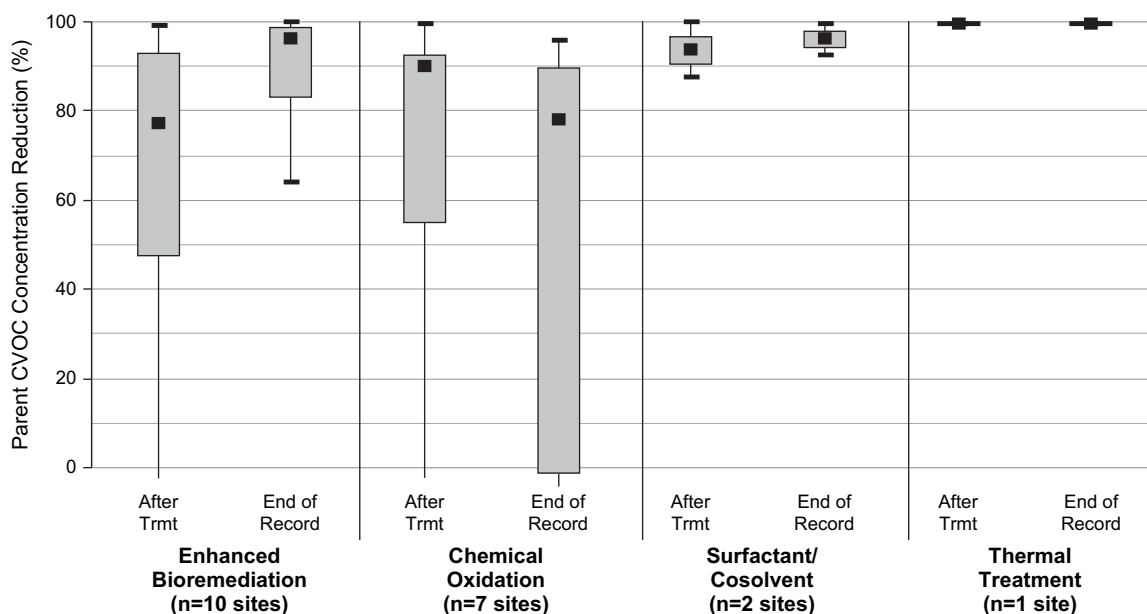


Figure 4. Rebound assessment at source depletion sites: concentration reduction from before treatment to immediately after treatment and at end of data record. Minimum reduction after treatment for enhanced bioremediation = -174% ; minimum reduction after treatment for chemical oxidation = -9% ; 25th percentile and minimum reduction at end of record for chemical oxidation = -45% and -216% , respectively (values not shown). Negative values indicate a concentration increase (see Figure 2 for box-and-whisker diagram legend).

suggested that the presence of residual oxidant, oxygen produced during chemical oxidation, and low pH values are likely to limit intrinsic biodegradation following chemical oxidation of CVOCs (Kastner et al. 2000; Christ et al. 2005).

Data from a DNAPL remediation survey (GeoSyntec Consultants 2004) also found that the occurrence of rebound was more prevalent at chemical oxidation sites compared to sites implementing other technologies. In that study, a total of 21 sites indicated that rebound had been evaluated, and one-third (7 sites) reported that rebound did occur. Of the seven confirmed rebound sites, five (71%) represented chemical oxidation sites. Five additional chemical oxidation sites (50%) reported that rebound did not occur. The other two sites with rebound implemented thermal treatment and excavation as DNAPL removal technologies. Rebound was not observed at any of the three enhanced bioremediation sites evaluated as part of the GeoSyntec Consultants (2004) study. The criteria used by survey respondents to evaluate rebound were not reported.

Results of this study indicate that all four technologies are capable of achieving significant reductions in the dissolved-phase concentration of the parent chlorinated compound within the treatment zone. Approximately 75% of the sites exhibited at least 70% reduction in source-zone parent CVOC concentrations. Enhanced bioremediation was less successful at removing TCVOCs because daughter products were generated, but had the advantage of continued source depletion after treatment. Chemical oxidation had better removal of TCVOCs (parent plus daughter compounds) but had significantly more rebound. Thermal treatment and surfactant treatment showed good performance, but these technologies had more limited data sets. Surfactant/cosolvent treatment has significantly higher costs than those of thermal treatment, enhanced bioremediation, or chemical oxidation (McDade et al. 2005).

The relationship between source concentration reduction and source mass reduction is of interest to assessing the performance of source depletion projects. Falta et al. (2005a, 2005b) recently presented site data and analytical modeling results illustrating source concentration reduction vs. mass reduction relationships. For this study, reductions in source-zone DNAPL mass were reported for 11 sites. Figure 5 contains a plot of source ground water concentration reduction (calculated by the authors) vs. mass reduction (calculated by site personnel) for the 11 sites. As shown in Figure 5, the concentration reduction achieved for a given mass reduction was within 30% of a 1:1 relationship at most sites. As discussed by the U.S. EPA expert panel (Kavanaugh et al. 2003) and others (e.g., Stroo et al. 2003; Sale and McWhorter 2001), reductions in ground water concentrations resulting from mass removal are highly influenced by the source architecture (i.e., DNAPL distribution and geometry within the subsurface). Results from modeling studies and limited site data have suggested that at homogeneous sites with pooled DNAPL, large reductions in source mass (e.g., >90%) may be necessary to achieve significant improvements in ground water quality (Sale and McWhorter 2001; Falta et al. 2005a), while at heterogeneous sites with most DNAPL located in high-

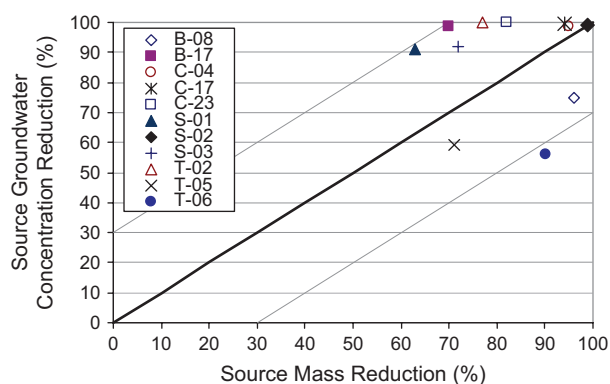


Figure 5. Calculated source zone ground water concentration reductions for reported source zone mass reductions at 11 source depletion sites. The black line represents directly proportional relationship between source mass reduction and ground water concentration reduction, and the gray lines represent $\pm 30\%$ of the directly proportional relationship. See Table 1 for site and technology descriptions of the eleven sites shown using the site numbers indicated in the legend.

permeability zones, significant improvements in ground water quality can occur even for modest reductions (e.g. 50% to 70%) in source mass (Rao and Jawitz 2003; Falta et al. 2005a). The mass reduction data reported for the sites in the current study suggest that at sites where detailed knowledge of source architecture is absent, it is reasonable to approximate the concentration reduction resulting from source depletion as directly proportional to mass reduction (i.e., there are points on either side of the 1:1 line in Figure 5).

It remains unclear how the improvements in ground water quality achieved within the source zone will affect remediation time frames at these sites. Newell and Adamson (2005) have developed a planning-level tool to help evaluate the benefits of partial source depletion in terms of remediation time frame. For a source depletion project that removes 90% of DNAPL mass and has a goal to reduce concentration by a factor of 1000 (e.g., from 5 to 0.005 mg/L), the planning-level tool predicts the reduction in remediation time frame over natural attenuation alone to be ~33%.

Since the source depletion technologies evaluated in this study were applied in DNAPL source zones that had relatively high initial dissolved concentrations, common regulatory standards, such as MCLs, were not achieved in most cases. Though several sites achieved MCLs at some wells, none of the sites attained and sustained MCLs for all chlorinated compounds at all wells. Given the inability of most source depletion technologies to achieve the primary remediation goal of returning ground water to usable conditions, it is likely that some type of site management (e.g., institutional controls, long-term monitoring, monitored natural attenuation, or containment controls) will be necessary at many of these sites.

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