Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

WORK PLAN FOR HYDROGEN RELEASE COMPOUND (HRC) INJECTION

RACER TRUST
Flint West #12990
Flint, Michigan
EPA ID# MIK204011722

Æ Project # 11-4317-102

October 9, 2019

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1. INTRODUCTION AND BACKGROUND

1.1 Introduction

This Work Plan for Hydrogen Release Compound (HRC) Injection has been prepared on behalf of the Revitalizing Auto Communities Environmental Response (RACER) Trust for the property identified as “Flint West Industrial Land,” RACER Site #12990, located in Flint, Michigan (Site) (Figure 1).

The purpose of this Work Plan is to outline implementation of Regenesis HRC injection described in detail in the *Corrective Measures Study* (CMS), which was submitted to the United States Environmental Protection Agency (USEPA) on November 1, 2014. In addition, this Work Plan is submitted to USEPA as an addendum to the CMS in accordance with the request in USEPA’s January 13, 2017 letter approving the now-completed HRC injection pilot study.

The CMS indicated the following proposed corrective actions for the Site to address chlorinated volatile organic compounds (CVOCs) in soil and groundwater:

- Land Use Restrictions
- Groundwater Use Restrictions
- Monitored Stability
- In-Situ Bioremediation (HRC injection)

The objective of proposed HRC injection as outlined in the CMS is to reduce soil contamination to levels that further enhance attenuation of groundwater contamination levels at and downgradient from the Site boundary.

1.2 Background

The Site consists of approximately five acres of land located west of Stevens Street and north of Glenwood Avenue in Flint, Genesee County, Michigan. The Site is developed with a Consumers Energy electrical substation in the central portion. Almost the entire Site consists of concrete pavement, remaining after the demolition of a former manufacturing building. The concrete pavement is supported by a concrete retaining wall that runs east-west and immediately south of the northern property line. A small area on the north portion of the property is unpaved and part of a former railroad. Nearly all of the Site is secured with a locked chain-link fence.

A railroad grade runs along the northern property boundary, beyond which is located the Chevy Commons (formerly known as Chevy-in-the-Hole) property. Former industrial land is located to the east, across Stevens Street and to the west. Current and former commercial uses are located to the southwest and south. A General Motors tool and die facility is located to the southeast.

Subsurface lithology consists of sandy glacial tills consisting primarily of silty sand and clay layers in the upper approximately 20 feet to 30 feet below grade with shallow groundwater perched on a clay layer. (Note that site topography varies approximately 8 feet to 10 feet due to the retaining wall.) The depth to groundwater ranges from approximately eight to 17 feet below grade, the saturated thickness above the clay ranges from about 10 feet to 15 feet, and groundwater flow in this unit is generally to the northwest toward the Flint River. Bedrock was encountered at approximately 20 feet below grade on the north portion of the Site.

The primary constituent of concern is trichloroethene, and it appears to be present from historical releases. No significant trichloroethene source mass was found in unsaturated soils. The highest remaining concentrations of trichloroethene are in the saturated unit and underlying clay in the central portion of the Site and the immediately adjacent abandoned railroad property, currently owned by Genesee County Parks (GCP).

Geochemistry data, collected during low-flow groundwater sampling in July 2019 from monitoring wells near the proposed HRC injection area was used in the HRC injection evaluation an area as follows:

Well ID	pH	Oxidation Reduction Potential (mv)	Dissolved Oxygen (mg/L)	Conductivity (cm/c)	Temperature (C)
MW-109S	7.73	-105.8	1.03	0.779	15.61
MW-111S	6.73	-42.6	1.78	0.838	12.69
MW-113S	6.98	-60.0	0.34	0.923	16.29

Groundwater velocity is estimated to range from approximately 0.0017 ft/day to 0.17 ft/day based on the gradient calculated using the July 2019 gauging data (0.018 ft/ft), the range of hydraulic conductivity values for silty sand (0.0284 ft/day to 2.84 ft/day[1]), and an effective porosity of 0.30.

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[1] Fetter, C.W. 1988, *Applied Hydrogeology, Second Edition*, Merrill Publishing Company

2. TECHNICAL APPROACH

An evaluation of potential electron donors and combinations of donors (i.e., reductive dechlorination options), was conducted to determine which electron donors would be the most effective at the site. It was decided that to achieve a relatively rapid response with long-term residual benefits, Regensis HRC would be the preferred remediation option. HRC is an electron donor material that is designed to produce an extended, controlled release of lactic acid when hydrated. The lactic acid is used for the production of hydrogen, which is the key ingredient in reductive dechlorination. Reductive dechlorination is the mechanism by which chlorinated compounds are biodegraded into less harmful constituents such as ethene, ethane, carbon dioxide, and water. The CMS indicated the following remediation goals:

- A short-term response to generate electron donors in the treatment area within six months, and
- A long-term response lasting up to five years.

Based on information provided by Regenesis, HRC is a simple, passive, low-cost, and long-term option for anaerobic bioremediation of CVOCs through reductive dehalogenation. HRC is a proprietary, food-quality, polylactate ester that, upon being deposited into the subsurface, slowly degrades to lactic acid. Lactic acid is then metabolized to hydrogen, which in turn drives the reductive dechlorination of CVOCs. This has been demonstrated effectively in the laboratory and in the field. Evidence suggests there is competition between reductive dehalogenators and methanogens in which the methanogens compete for the use of hydrogen in the conversion of carbon dioxide to methane. Some researchers believe that a low concentration of hydrogen favors the reductive dehalogenators and starves out the methanogens. The objective, therefore, is to keep hydrogen concentrations low. The time-release feature of HRC, which is based on the hydrolysis rate of lactic acid from the ester and the subsequent lag time to hydrogen conversion, facilitates this objective.

Specific technical information for Regenesis HRC is provided in Appendix B.

Additional technical evaluations conducted that support the use of HRC injection for CVOCs plumes similar to that present on the site were based on the 2006 Groundwater & Remediation Technology publication, *Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites*, Travis M. McGuire, James M. McDade, and Charles J. Newell. A copy of the document is attached as Appendix B.

Note that the CMS indicates that the HRC injection would be completed in the areas of SB-122/133, SB-123/132/133, and areas to the northeast, approaching MW-109S. This approach was designed to focus on soil remediation at the source areas while providing long-term reductions in groundwater contamination. The completed pilot test and additional soil and groundwater data subsequent to the CMS and evaluations conducted during preparation of this Work Plan identified the benefit of completing injections over a broader area upgradient of MW-114S. Based on results of the pilot study, including the TCE concentrations identified in MW-114S (the highest TCE concentrations found in groundwater Site-wide), which was installed as part of the pilot study evaluation, it was determined that MW-114S likely is close to the center line of the dissolved phase TCE plume. Therefore, the proposed HRC injection points were reevaluated, and revised locations were determined in order to provide the likely greatest down-gradient effect on dissolved phase

TCE (See Figure 2). This approach provides for the potential short-term reduction of the elevated CVOCs identified in MW-111 and long-term reduction in other downgradient wells.

2.1 Pilot Test

A pilot test was conducted, starting in July 2018. Injection of HRC was conducted on July 2 and 3, 2018 on the Site and the adjoining GCP property. A Geoprobe® direct-push track-mounted unit was used to complete the injection. An injection point was advanced into the subsurface at each boring location until bedrock was encountered, at approximately 20 feet below grade. The injection point was then retracted while HRC was injected into a five-foot interval, using a grout pump. A total of 1,200 pounds of HRC were injected in equal volumes in 24 injection points at pressures of 600 to 1,000 pounds per square inch (psi). Approximately five gallons of potable water was injected through the drill tooling before and after injection of the HRC. The HRC was also preheated to approximately 140^{o} F prior to injection.

The pilot test was conducted to evaluate the effectiveness of HRC and evaluate implementation details. Results of the pilot test indicate HRC injections could be completed with the field conditions encountered and was effective in reducing the concentrations of CVOCs in soils and groundwater in the pilot study area.

3. IMPLEMENTATION PLAN

HRC will be applied in the north-central portion of the Site. HRC will be applied using a grout pump and direct push methods at a rate of 10 pounds per foot based on the manufacturer's recommendation. Injection will be conducted in 10-foot vertical intervals designed to remediate the CVOC source in the silty clay soils underlying the saturated sand unit. The HRC will be applied in 60 injection points spaced approximately 10 feet apart.

A copy of a Regensis document - *HRC Installation Instructions*, and the Safety Data Sheet for HRC is provided in Appendix B.

This pressurized injection process allows the product to be placed directly into the zone of contamination (saturated soil). The bottom of the injection at each point will vary along with the elevation of the bedrock. At each point, injection rods will be first driven to the bedrock to begin the injection. The rod will be slowly pulled up, while injecting from the bottom up at the prescribed dosing rate, to 10 feet below grade, where the injection will end.

The general locations of the proposed HRC injection are shown on Figure 2. The actual injection locations may vary somewhat from the proposed, as needed, due to the presence of utilities, vegetation, and areas of concrete where direct push may not be feasible due to imbedded concrete layers encountered during previous drilling.

The in-situ bioremediation injection plan is summarized as follows:

Applied By:	Direct push and grout pump
Application Rate:	10 pounds per vertical foot
Application interval (vertical):	10 feet. Approximately 10-20' below grade
Application Interval (horizontal):	10-foot spacing (60 injection points total, divided into two lines)
Application area:	See Figure 2
Number of Application Points:	60
Pounds of HRC	6,000

The proposed injection area is primarily lawn space and concrete pavement. Neither electricity nor water are available at the Site currently. Municipal water will be transported to the Site in portable containers for equipment cleaning purposes.

Equipment will be cleaned to prevent clogging using a gasoline-powered stream pressure washer. All injection equipment will be gasoline powered, so electricity is not needed at this time.

3.1 Contingency Plans

The scope of work was designed to identify logistical, environmental, and other factors that may affect the project. More detailed information is provided below:

- Some proposed injection points may have limited accessibility due to surface conditions and drilling obstructions (such as concrete in the subsurface on the north end of the RACER site). Should this occur, alternative injection locations will be placed as close as possible to the original locations proposed.

- Should fluid be observed daylighting from any nearby monitoring well, injection will immediately stop until the fluid level in the affected monitoring well falls to a few feet below the ground surface. When injection starts back up, the injection pressure will be reduced in order to prevent any fluid from daylighting from nearby wells and the fluid level in the affected well will be monitored to make sure the reduced injection pressure is appropriate and will not result in more daylighting.

- Should complications arise due to equipment limitations, weather and/or ambient lighting, field activities will be rescheduled. Due to the nature of the proposed activities, delays and rescheduling will be easily accommodated.

- If future groundwater monitoring indicates excessive formation of methane, options to address this concern, such as passive venting, will be evaluated for implementation.

4. MONITORING PLAN

Groundwater samples will be collected from wells, MW-109S, MW-111S, MW-112S, MW-113S, and MW-114S within approximately 30 days prior to the injection, three months after the injection, and six months after the injection. Samples will be analyzed for VOCs, turbidity (from field instruments); total organic carbon; iron (total and dissolved); manganese (total and dissolved), methane and oxidation reduction potential (ORP), in order to obtain data to help evaluate the impacts of the injected HRC on CVOCs and the general geochemistry. The third monitoring event will be included in a Site-wide groundwater monitoring event, after which the need and scope of additional monitoring will be evaluated.

Because the Pilot Study demonstrated that HRC was effective in reducing the concentrations of TCE in soils in the primary source areas, follow-up soil sampling is not proposed.

5. SIGNATURES

This report was prepared under the supervision of the following Environmental Professionals.

Michael D. Smith

October 9, 2019

Michael D. Smith, Senior Technical Manager Date

Rodney Abke

October 9, 2019

Rodney Abke, Senior Geologist Date

MICHAEL D. SMITH

SENIOR TECHNICAL SERVICES MANAGER

Mr. Smith is a 1995 graduate of the University of Michigan-Flint. He has over twenty years of experience in environmental consulting. He has completed all phases of underground storage tank (UST) management, Phase I and II Environmental Site Assessments (ESAs), site remediation and closure, asbestos assessments, wetland assessments, industrial storm water compliance evaluations, spill contingency plans, Baseline Environmental Assessments (BEAs), Due Care Evaluations, RCRA Corrective Action, and brownfield redevelopment projects.

Education

- University of Michigan, B.S. Resource Planning
- ASTM Risk-Based Corrective Action Training
- Brownfield Development Training, Michigan Municipal League
- Wetlands Delineation Training, Army Corp of Engineers
- Various due diligence seminars

Registrations, Certifications

- Certified Underground Storage Tank Professional - MI
- Hazardous Waste Operations and Emergency Response, OSHA
- EPA Asbestos Building Inspector
- Industrial Storm Water Operator-MI

Areas of Expertise

- Phase I, II ESAs
- Baseline Assessments (BEAs)
- Due Care Evaluations
- Compliance/Regulatory Reporting
- Transaction Screens
- Subsurface Investigations
- UST Removal and Assessment
- Refueling System Management
- Part 201 evaluation and closures
- Asbestos Assessments
- Wetlands
- Brownfield Redevelopment
- Hazardous materials evaluations for building demolition and renovation

Professional Experience

- Senior Technical Services Manager,
  Applied *Eco*Systems
- Project Manager,
  Applied *Eco*Systems

Project Experience Highlights

- Completed multiple environmental assessment projects for a variety of public and private clients whose facilities include commercial office, retail, and proposed development sites, and various industrial and manufacturing facilities in Michigan, Ohio, Indiana, Illinois, Florida, Maine, Colorado, New Mexico, and Nevada.

- Coordinated numerous UST investigations throughout Michigan, Wyoming, Nebraska, Ohio, Indiana, and Colorado, including obtaining regulatory permits, compliance reporting and site closure.

- Completed UST removal oversight and verification sampling activities at various Michigan and Colorado industrial and manufacturing facilities.

- Completed soil boring and groundwater investigations at numerous leaking underground storage tank (LUST) sites and sites of environmental concern. Field activities have included soil, groundwater and sediment sampling, well installation and sampling, and determination of appropriate investigation areas based on site and area conditions.

- Completed facility determinations, BEAs, and due care evaluations for multiple sites in Michigan, including a former airport/gasoline station; automobile repair facilities, dry cleaners, gasoline stations, former industrial landfills, marinas and manufacturing facilities.

- Conducted a BEA on an expedited schedule for a 20-acre industrial facility formerly operated as a landfill. Investigations included three acres of geophysical assessment and over 70 soil borings. The investigation and reporting was completed within 35 days.

- Implemented a PCB cleanup at a multi-story commercial building. Responsibilities included tracing, cleaning, and replacement of various drain pipes, sewer outlets, cleaning an elevator shaft; confirmatory wipe and concrete core sampling, waste disposal coordination, and preparation and submittal of a Closure Report to the Region V EPA.

- Conducted RCRA Corrective Action activities, including Quality Assurance Project Plans, investigations, and reporting.

- Completed PCB-remediation projects under the Toxic Substances Control Act (TSCA)

RODNEY ABKE — SENIOR GEOLOGIST

Mr. Rodney Abke is a 1988 graduate of Lake Superior State University, with a Bachelor of Science, Geology, and a 1994 graduate of Ball State University with a Master of Science, Geology. He has over 25 years of experience in environmental consulting. He has completed all phases of underground storage tank (UST) management, Phase I and II Environmental Site Assessments (ESAs), site remediation and closure, Baseline Environmental Assessments (BEAs), Due Care Evaluations, and Part 201 assessments and remediation.

Education

- Lake Superior State University
  B.S. Geology
- Ball State University
  M.S. Geology
- ASTM Risk-Based Corrective Action Training

Registrations, Certifications

- Certified Professional Geologist
- Licensed Professional Geologist, Indiana

Areas of Expertise

- Phase I, II ESAs
- BEAs
- Due Care Evaluations
- Compliance/Regulatory Reporting
- Health and Safety
- Transaction Screens
- Subsurface Investigations
- UST Removal and Assessment
- Part 201 evaluation and closures
- Manufactured gas plant site assessments

Professional Experience

- Applied EcoSystems, 2017 to present
- AKT Peerless, 2016 to 2017
- ATC Group Services, 2009 to 2016
- Stantec Consulting, 2001 to 2009

Project Experience Highlights

- Completed multiple environmental assessment projects for a variety of public and private clients whose facilities include commercial office, retail, and proposed development sites, and various industrial and manufacturing facilities in Michigan, Ohio, and Indiana.

- Coordinated numerous UST investigations throughout Michigan, including obtaining regulatory permits, compliance reporting and site closure.

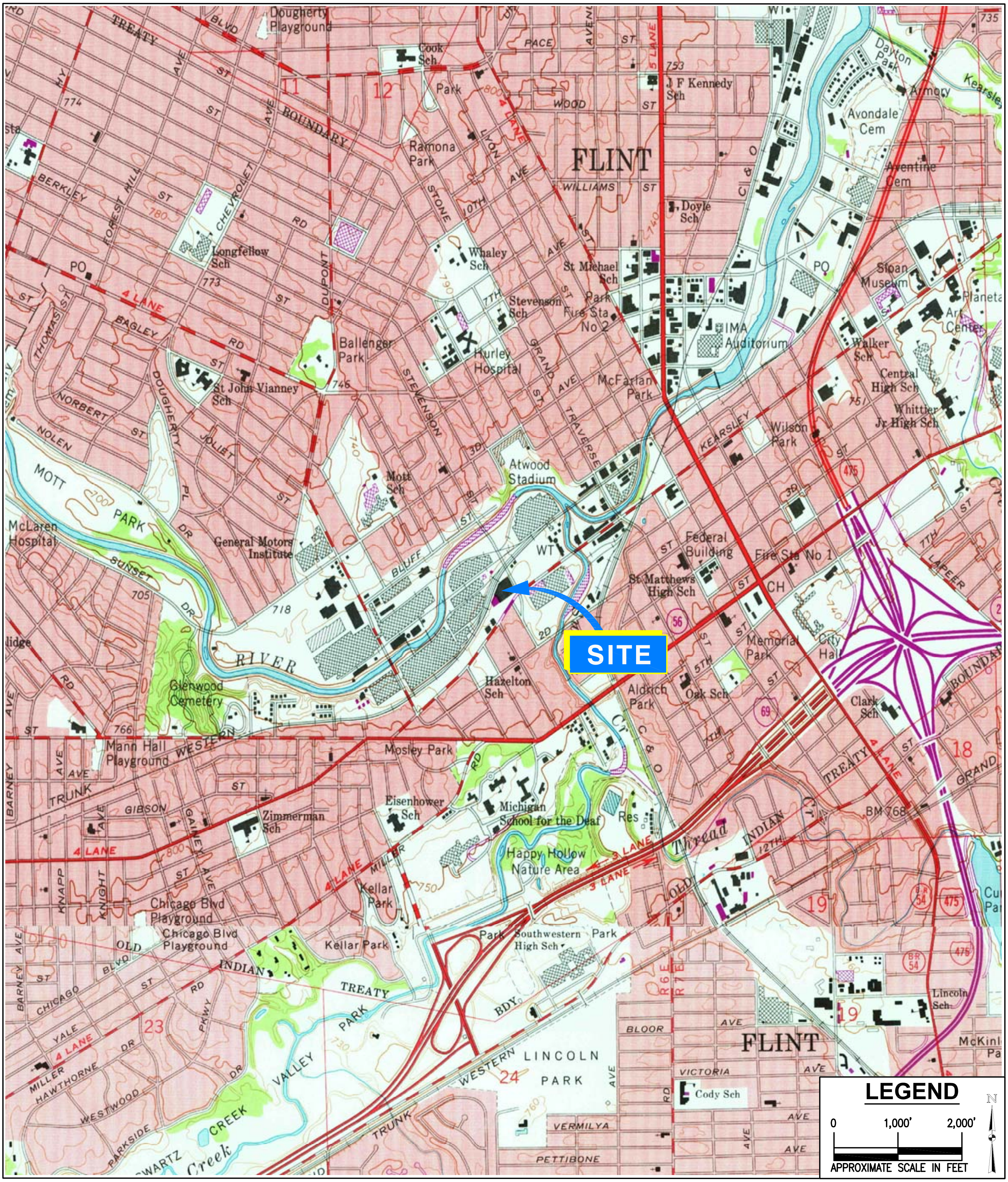
- Completed soil boring and groundwater investigations at numerous leaking underground storage tank (LUST) sites and sites of environmental concern. Field activities have included soil, groundwater and sediment sampling, well installation and sampling, and determination of appropriate investigation areas based on site and area conditions.

- Completed facility determinations, BEAs, and Due Care evaluations for multiple sites in Michigan, including automobile repair facilities, dry cleaners, gasoline stations, former industrial landfills, marinas and manufacturing facilities.

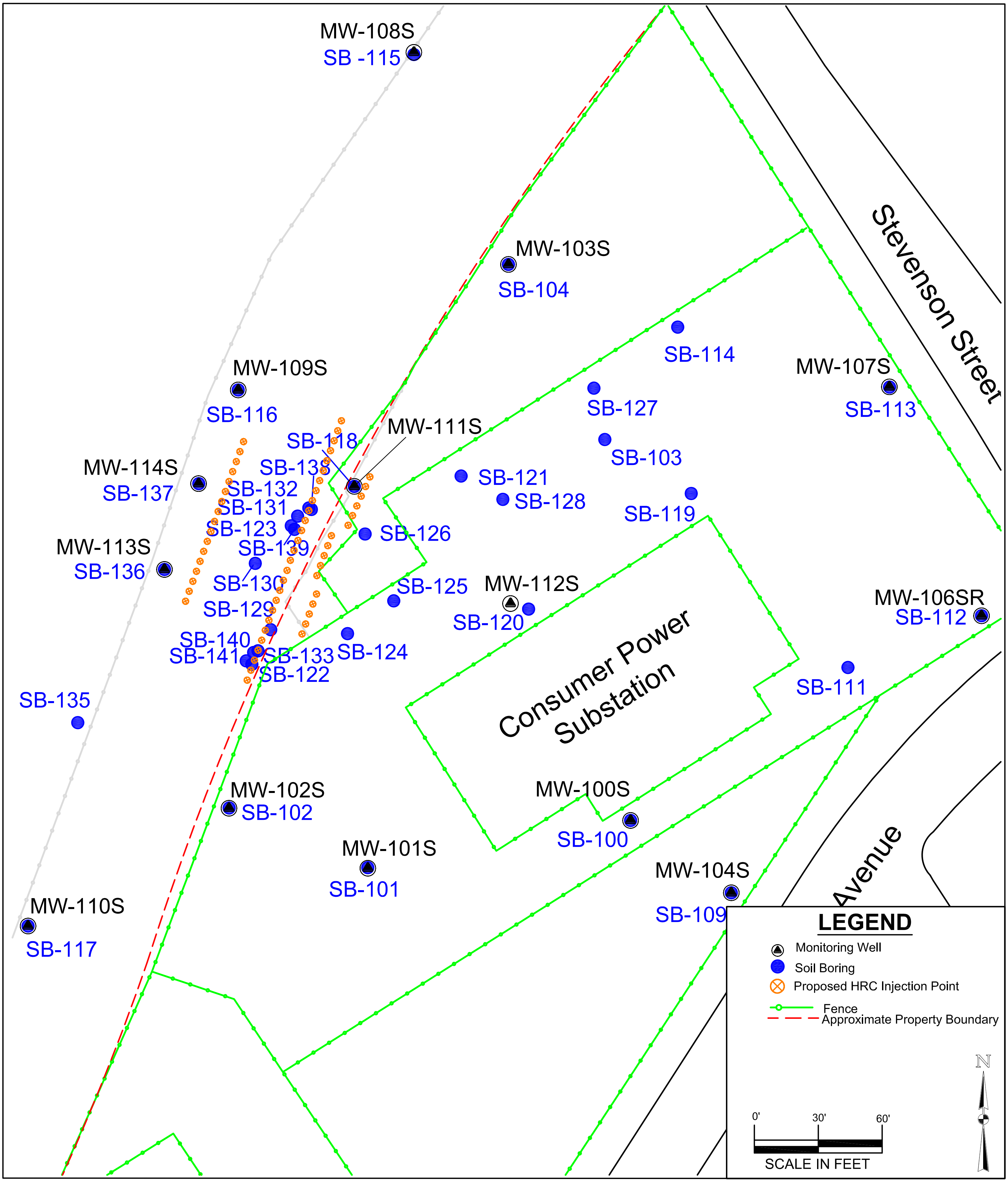
- Coordinated and implemented hydrogeological study of the effects of pumping of municipal groundwater supply system and mobile LNAPL site. Included planning, field work and analysis of aquifer data collected over a one-week period. Coordinated with the local municipality to obtain data from water supply system, which was used to compare with data collected from monitoring well network to determine if the municipal well system was influencing groundwater in the area of impact.

- Coordinated and implemented remedial investigations at several manufactured gas plant (MGP) sites. Work scopes included subsurface investigation, groundwater sampling, and aquifer testing. These sites were regulated under Michigan Part 201 of Act 451 as amended.

APPENDIX A: FIGURES



Applied EcoSystems, Inc. Environmental Management, Consulting & Field Services G-4300 South Saginaw Street, Burton, Michigan 48529 Phone: 810.715.2525; Fax: 810.715.2526	***Site Location Map*** **RACER Flint West #12990** **Glenwood Avenue & Stevenson Street** **Flint, Michigan** **SOURCE: USGS FLINT SOUTH QUADRANGLE** **(PROVISIONAL EDITION 1975)**	**DRAWING DATE:** 09/18/2019	**CHECKED BY:** MDS
		PROJECT: 11-4317-102	**FIGURE:** 1



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Proposed Treatment Area Map

Racer Flint West -12990
Flint West Industrial Land, Flint, Michigan

DATE: 10/08/2019	**CHECKED BY:** MDS
PROJECT: 11-4317-102	**FIGURE:** 2

APPENDIX B

Applied EcoSystems, Inc.

Environmental Management, Consulting & Field Services

HRC® Technical Description

Example of HRC

HRC® is an engineered, hydrogen release compound designed specifically for enhanced, in situ anaerobic bioremediation of chlorinated compounds in groundwater or highly saturated soils. Upon contact with groundwater, this viscous, polylactate ester material becomes hydrated and subject to microbial breakdown producing a controlled-release of hydrogen for periods of up to 18-24 months on a single application.

HRC enables enhanced anaerobic biodegradation by adding hydrogen (an electron donor) to groundwater and/or soil to increase the number and vitality of indigenous microorganisms able to perform the naturally occurring process of enhanced reductive dechlorination. During this process, certain naturally occurring microorganisms replace chlorine atoms on chlorinated contaminants with the newly available hydrogen effectively reducing the contaminant to a less harmful substance with the preferred and innocuous endpoints of ethene or ethane.

For a list of treatable contaminants with the use of HRC, view the Range of Treatable Contaminants Guide.

Chemical Composition

- Glycerol Tripolylactate- CAS #201167-72-8
- Glycerin- CAS #56-81-5
- Lactic acid- CAS #50-21-5

Properties

- pH - 3 (3% solution/water)
- Appearance – Viscous gel/liquid. Amber color
- Odor – Odorless
- Vapor Pressure – None

Storage and Handling Guidelines

Storage
Store away from incompatible materials
Store in original tightly closed container
Store in a cool, dry, well-ventilated place

Handling
Wash thoroughly after handling
Wear appropriate personal protective equipment
Wear eye/face protection
Provide adequate ventilation
Observe good industrial hygiene practices

HYDROGEN
RELEASE
COMPOUND

HRC® Technical Description

Applications

- Permanent injection wells
- Direct-push injection (barriers and grids)
- Recirculating wells
- Soil borings
- Excavation applications into soil or on top of bedrock
- Gravity feed into bedrock wells

Application instructions for this product are contained in the HRC Application Instructions.

Health and Safety

Avoid contact with eyes, skin, and clothing. Provide adequate ventilation. Wear appropriate personal protective equipment. Observe good industrial hygiene practices.

Please review the HRC Material Safety Data Sheet for additional storage, usage, and handling requirements.

Hydrogen Release Compound (HRC®) Installation Instructions

General Guidelines

The best method to deliver HRC® into the subsurface is to inject the material through direct push rods using hydraulic equipment. This approach increases the spreading and mixing of HRC into the aquifer. This set of instructions is specific to direct push equipment.

REGENESIS® has found that very few pumps can adequately deliver HRC to the subsurface. Although other pumps may be capable of injecting HRC, we have developed the following instructions specifically for use with an R.E. RUPE Company Model ORC/HRC 9-1500 mixing and pumping machine. There is also strong evidence that the Geoprobe GS-2000 pump can effectively deliver HRC to the subsurface. In general, REGENESIS strongly recommends using a pump with a minimum pressure rating of 1,500 pounds per square inch (psi) and a minimum delivery rate of 3 gallons per minute.

The installation of HRC should span the entire vertical contaminated saturated thickness. If the vertical extent of HRC application is confined to a limited interval, then the HRC material should be placed across a vertical zone extending a minimum of 2 feet above and below the screened Interval of monitoring wells to be used to evaluate the performance of the bioremediation project.

Material Overview, Handling, and Safety

HRC is shipped in 4.25- gallon buckets and each bucket has a gross weight of approximately 32 pounds (net weight of HRC is 30 pounds). At room temperature, HRC is a sticky gel with a viscosity of approximately 20,000 centipoise (roughly equivalent to cold honey). The HRC material has a nominal density of 1.3 grams/cubic centimeter or approximately 10.8 pounds per gallon. The viscosity of HRC is temperature sensitive. Significant changes in viscosity are observed with large changes in product temperature.

It should be noted that the temperature/viscosity relationship is not linear. For ease of installation, HRC should be stored in a warm, dry place that is protected from direct sunlight. It is common for stored HRC to settle somewhat in a container. Pre-heating HRC makes it easier to work with the material. Although HRC is manufactured as a food-grade material that is safe to ingest, field personnel should take precautions while handling and applying HRC. Field personnel should use appropriate safety equipment, including eye protection. The low pH when dissolved in water and the viscosity of the product make eye protection mandatory. Gloves should be used as appropriate based on the exposure duration and field conditions.

A Material Safety Data Sheet is provided with each shipment. Personnel who operate field equipment during the installation process should have appropriate training, supervision, and experience.

Specific Installation Procedures

1. Prior to the installation of HRC, any surface or overhead impediments should be identified as well as the location of all underground structures. Underground structures include but are not limited to: utility lines, tanks, distribution piping, sewers, drains, and landscape irrigation systems.
2. Planned installation locations should be adjusted to account for all impediments and obstacles.
3. REGENESIS recommends pre-heating HRC in a hot water bath. Place unopened buckets of HRC into an empty water tank. A Rubbermaid fiberglass Farm Trough Stock Tank (Model 4242-00-GRAY) is typically used for this application and can hold up to 16 buckets of HRC. Hot water (approximately 130-170 °F or 54-77 °C) should be added to the tank after the buckets of HRC have been placed inside. When the HRC reaches a minimum temperature of 95 °F or 35 °C (approximately 20-30 minutes) it is ready to be poured into the pump hopper.
4. Pre-mark the installation locations, noting any points that may have different vertical application requirements or total depth.
5. Set up the direct push unit over each specific point and follow the manufacturer standard operating procedures (SOP) for the direct push equipment. Care should be taken to assure that probe holes remain in the vertical.
6. For most applications, REGENESIS suggests using 1.25- inch O.D./0.625-inch I.D Geoprobe brand drive rods. However, some applications may require the use of 2.125- inch O.D./1.5- inch I.D. drive rods.
7. The HRC delivery sub-assemblies that REGENESIS currently uses are designed for 1.25-inch Geoprobe rods. Other brands of drive rods can also be used but require the fabrication of a sub-assembly (see REGENESIS Website).
8. Advance drive rods through the surface pavement, as necessary, following SOP.
9. Push the drive rod assembly with an expendable tip to the desired maximum depth. REGENESIS suggests pre-counting the number of drive rods needed to reach depth prior to starting injection activities.
10. After the drive rods have been pushed to the desired depth, the rod assembly should be withdrawn three to six inches. The expendable tip can be dropped from the drive rods, following SOP.
    a) If an injection tool was used instead of an expendable tip, the application of material can take place without any preliminary withdrawal of the rods.
11. In some cases, introduction of a large column of air may be problematic. This is particularly the case in deep injections (>50 ft) with large diameter rods (>1.5- inch O.D.). To prevent the injection of air into the aquifer during HRC application, fill the drive rods with water.
12. Pour the pre-heated HRC into the pump hopper (up to 40 gallons). Remove the separated HRC from the bucket bottom by tipping the bucket into the hopper and scraping out the smooth residual material. Use the pumps mixing and recirculation features to create a uniform consistency. This typically requires recirculation of approximately one hopper volume.
    NOTE: Do not attempt to mix HRC with water or other liquids to thin or decrease the viscosity of the material. This may adversely affect HRC longevity.
13. A volume check should be performed prior to injecting HRC. Determining the volume displaced per pump stroke can be accomplished in two easy steps.
    a) Determine the number of pump strokes needed to deliver 3 gallons of HRC (use a graduated bucket for this)
    b) Divide 3 gallons by the results from the first step to determine the number of gallons of HRC delivered by each pump stroke.
    c) Level indicators present in the hopper are in 3 gallon increments.

    d) The volume of HRC displaced should be confirmed using the HRC level indicators located inside the pump hopper.

14. Connect the 1.25-inch O.D., 1-inch I.D. delivery hose to the pump outlet and the provided HRC delivery sub-assembly. Circulate HRC though the hose and the delivery sub-assembly to displace air in the hose.
15. Connect the HRC sub-assembly to the drive rod. After confirming that all of the connections are secure, pump the HRC through the delivery system to displace the water/fluid in the rods. NOTE: Prior to pumping HRC into the aquifer, close the pump recirculation valve; failure to do so will allow material to short-circuit into the hopper and change the volume of HRC delivered per pump stroke.
16. The pump engine RPM and hydraulic settings should remain constant throughout the day. However, if the hydraulic system starts to “squeal”, the pump speed should be decreased until the noise is mitigated.
17. Use the pump’s stroke counter and the provided volume/weight conversions to apply the appropriate HRC volume per injection location (and per vertical foot of contaminated saturated zone). Table 1 shows typical HRC delivery information followed by an example calculation.

Table 1: Pump Volume Calculation

Example: For each injection location, install 60 pounds of HRC across 10 vertical feet of aquifer (an application rate of 6 pounds per vertical foot).

Solution:

- 60 pounds/10.8 pounds per gallon + 5.6 gallons for the injection location
- 5.6 gallons/0.2 gallons per stroke + 28 pump strokes for the injection location
- 28 pump strokes/10 vertical feet = 2.8 strokes per vertical foot
- 2.8 strokes per vertical foot = 8.4 strokes per 3 foot drive rod
- 2.8 strokes per vertical foot = 11.2 strokes per 4 foot drive rod

18. Slowly withdraw the drive rods us ing Geoprobe Rod Grip or Pull Plate Assembly (Part AT1222-For 1.25-inch drive rods). While slowly withdrawing single lengths of drive rod (3 or 4 feet), pump the pre-determined volume of HRC into the aquifer across the desired treatment interval (Step 13). Use the stroke counter and pump on/off switch to control volume of injection. See Helpful Hints at the end of this section.
19. Remove one section of the drive rod. The drive rod may contain some residual HRC. Place the HRC-filled rod in a clean, empty bucket and allow the HRC to drain. Eventually, the HRC should be returned to the HRC pump hopper for reuse.
20. Observe any indications of aquifer refusal. This is typically indicated by a high-pitched squeal in the pump’s hydraulic system or (in the case of shallow applications) HRC “surfacing” around the injection rods or previously installed injection points. If aquifer acceptance appears to be low, allow enough time for the aquifer to equilibrate prior to removing the drive rod.
21. Repeat steps 15-20 until treatment of the entire contaminated vertical zone has been achieved.
22. Install an appropriate seal, such as bentonite, above the HRC material through the entire vadose zone. Depending on soil conditions and local regulations, use a bentonite seal via chips or pellets after the probe rods have been removed. This assures that the HRC remains properly placed and prevents contaminant migration from the surface. If HRC continues to “surface” up the direct push borehole, an appropriately sized (oversized) disposable drive tip or wood plug/stake can be used to plug the hole until the aquifer equilibrates and the HRC stops surfacing.

23. Remove and clean the drive rods as necessary.
24. Finish the borehole at the surface as appropriate (concrete or asphalt cap, if necessary).
25. Periodically compare the pre- and post- injection volumes of HRC in the pump hopper using the pre-marked volume levels. Volume level indicators are not on all pump hoppers. In this case, volume level markings can be temporarily added using known amounts of water and a carpenter's grease pencil (Kiel crayon). We suggest marking the water levels in 3-gallon increments.
26. Move to the next probe point, repeating steps 8-25.

Helpful Hints

1) Application in Cold Weather Settings

The viscosity of HRC is directly related to the ambient temperature. As discussed in the Material Overview, Handling, and Safety section, cold weather tends to increase HRC viscosity and decrease ease of pumping. To maintain HRC at a temperature/viscosity at which it is easy to apply:

- Raise and maintain the temperature of the HRC to at least 95 °F (35 °C) prior to pouring it into the pump hopper.
- Insulate the delivery hose and keep the pump and hot water bath inside an enclosed structure such as a cargo van or trailer.
- Periodically check the HRC temperature in the hopper.
- Occasionally re-circulate HRC through the pump and hose to maintain temperature and viscosity.
- The volume of HRC recirculated should not exceed the volume of HRC in the hopper.
- Do not constantly recirculate HRC through the pump and hoses, as this may adversely affect the longevity of HRC.

2) HRC Pump Information

REGENESIS has evaluated a number of pumps that are capable of delivering 20,000 centipoise HRC to the subsurface at a sufficient pressure and volumetric rate. Although a number of pumps may be capable of delivering the HRC to the subsurface at adequate pressures and volume, each pump has a set of practical issues that make it difficult to manage in a field setting.

As a result of this evaluation, REGENESIS has determined that the R.E. RUPE Company Model ORC/HRC 9-1500 meets the pressure and volume requirements needed to successfully inject HRC in the field. In general, REGENESIS strongly recommends using a pump with a minimum pressure rating of 1,500 pounds per square inch (psi) and a minimum delivery rate of 3 gallons per minute. When applying measured volumes of HRC via probe boreholes, it is useful to know the volume of a single pump stroke (Table 1 above) and the associated delivery system lines.

The following additional information is provided for reference:

Table 2: HRC Physical Characteristics

Density	1.3 g/cc or 10.8 lbs/gal
Viscosity	Approx. 20,000 centipoise

Table 3: Equipment Volume and HRC Weight per Length

Equipment	Volume	HRC Weight
1-inch OD; 0.625- inch ID hose (10 feet length)	0.2 gallon	1.8 lbs.
1.25-inch OD; 0.625- inch ID drive rod (3 feet length)	0.05 gallon	0.5 lbs.
1.25-inch OD; 0.625- inch ID drive rod (4 feet length)	0.06 gallon	0.7 lbs.

3) Pump Cleaning

For best results, use a hot water pressure washer (150-170 °F or 66-77 °C) to clean equipment and rods periodically throughout the day. Internal pump mechanisms and hoses can be easily cleaned by circulating hot water and a biodegradable cleaner such as Simple Green through the pump and delivery hose. Further cleaning and decontamination (if necessary due to subsurface conditions) should be performed according to the equipment supplier's standard procedures and local regulatory requirements.

NOTE: The remote control/pump counter should be kept dry at all times. If it gets wet, it will short-circuit and will need to be replaced.

Before Using the Rupe Pump, Check the Following:

- Fuel level prior to engaging in pumping activities (it would be best to start with a full tank)
- Remote control/pump stroke counter LCD display (if no display is present, the electronic counter will need to be replaced (Grainger Stock No. 2A540))
- Monitor pump strokes by observing the proximity switches (located on the top of the piston).

4) HRC Bedrock Applications

When contaminants are present in competent bedrock aquifers, the use of direct push technology as a delivery method is not possible. REGENESIS is in the process of developing methods for applying HRC via boreholes drilled using conventional rotary techniques. To develop the best installation strategy for a particular bedrock site, it is critical that our customers call the technical support department at REGENESIS early in the design process.

HRC can be applied into a bedrock aquifer in cased and uncased boreholes. HRC can be delivered by simply filling the borehole without pressure or by using a single or straddle packer system to inject HRC under pressure. Selection of the appropriate delivery method is predicated on site-specific conditions.

The following issues should be considered in developing an HRC delivery strategy:

- Is the aquifer's transmissivity controlled by fractures?
- Backfilling may be the better delivery method in massive, unfractured bedrock. This is particularly true in an aquifer setting with high permeability and little fracturing (such as that found in massive sandstone).
- Down-hole packer systems may be more advantageous in fractured bedrock aquifers.

  - In this case the fracture type, trends, and interconnections should be evaluated and identified.
- Are the injection wells and monitoring wells connected by the same fractures?
- Determine if it is likely that the HRC injection zone is connected to the proposed monitoring points.
- If pressure injection via straddle packers is desired, consideration should be given to the well construction.

Specific issues to be considered are:

  - Diameter of the uncased borehole (will casing diameter allow a packer system to be used?).
  - Diameter of the casing (same as above).
  - Strength of the casing (can it withstand the delivery pressures?).
  - Length of screened interval (screened intervals greater than 10 feet will require a straddle packer system).

For further assistance or questions please contact REGENESIS Technical Services at 949.366.8000

REGENESIS
Technology-Based Solutions for the Environment

SAFETY DATA SHEET

1. Identification

Product identifier	**Hydrogen Release Compound (HRC®)**
Other means of identification	None.
Recommended use	Remediation of soils and groundwater.
Recommended restrictions	None known.

Manufacturer/Importer/Supplier/Distributor information

Company Name	Regenesis
Address	1011 Calle Sombra San Clemente, CA 92673
Telephone	949-366-8000
E-mail	CustomerService@regenesis.com
Emergency phone number	CHEMTREC® at 1-800-424-9300 (International)

2. Hazard(s) identification

Physical hazards	Not classified.	
Health hazards	Skin corrosion/irritation	Category 2
	Serious eye damage/eye irritation	Category 1
OSHA defined hazards	Not classified.	

Label elements

Signal word	Danger
Hazard statement	Causes skin irritation. Causes serious eye damage.
Precautionary statement	
Prevention	Wash thoroughly after handling. Wear protective gloves. Wear eye/face protection.
Response	If on skin: Wash with plenty of water. If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a poison center/doctor. If skin irritation occurs: Get medical advice/attention. Take off contaminated clothing and wash before reuse.
Storage	Store away from incompatible materials.
Disposal	Dispose of waste and residues in accordance with local authority requirements.
Hazard(s) not otherwise classified (HNOC)	None known.

3. Composition/information on ingredients

Mixtures

Chemical name	CAS number	%
Glycerol Tripolylactate	201167-72-8	62-67
Glycerin	56-81-5	33-38
Lactic acid	50-21-5	<10

Composition comments	All concentrations are in percent by weight unless otherwise indicated.

4. First-aid measures

Inhalation	Move to fresh air. Call a physician if symptoms develop or persist.

Skin contact	Remove contaminated clothing. Wash with plenty of soap and water. If skin irritation occurs: Get medical advice/attention. Wash contaminated clothing before reuse.
Eye contact	Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Get medical attention immediately.
Ingestion	Rinse mouth. Never give anything by mouth to a victim who is unconscious or is having convulsions. Do not induce vomiting without advice from poison control center. Get medical attention if symptoms occur.
Most important symptoms/effects, acute and delayed	Severe eye irritation. Symptoms may include stinging, tearing, redness, swelling, and blurred vision. Permanent eye damage including blindness could result. Skin irritation. May cause redness and pain.
Indication of immediate medical attention and special treatment needed	Provide general supportive measures and treat symptomatically. Keep victim under observation. Symptoms may be delayed.
General information	Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves.

5. Fire-fighting measures

Suitable extinguishing media	Water spray. Carbon dioxide (CO2). Dry chemical powder. Foam.
Unsuitable extinguishing media	Do not use water jet as an extinguisher, as this will spread the fire.
Specific hazards arising from the chemical	During fire, gases hazardous to health may be formed. Combustion products may include: carbon oxides, phosphorus compounds and metal oxides.
Special protective equipment and precautions for firefighters	Self-contained breathing apparatus and full protective clothing must be worn in case of fire.
Fire fighting equipment/instructions	Move containers from fire area if you can do so without risk. Water spray should be used to cool containers.
Specific methods	Use standard firefighting procedures and consider the hazards of other involved materials.
General fire hazards	No unusual fire or explosion hazards noted.

6. Accidental release measures

Personal precautions, protective equipment and emergency procedures	Keep unnecessary personnel away. Keep people away from and upwind of spill/leak. Wear appropriate protective equipment and clothing during clean-up. Do not touch damaged containers or spilled material unless wearing appropriate protective clothing. Ensure adequate ventilation. Local authorities should be advised if significant spillages cannot be contained. For personal protection, see section 8 of the SDS.
Methods and materials for containment and cleaning up	Large Spills: Stop the flow of material, if this is without risk. Use water spray to reduce vapors or divert vapor cloud drift. Dike the spilled material, where this is possible. Cover with plastic sheet to prevent spreading. Absorb in vermiculite, dry sand or earth and place into containers. Following product recovery, flush area with water. Small Spills: Wipe up with absorbent material (e.g. cloth, fleece). Clean surface thoroughly to remove residual contamination. Never return spills to original containers for re-use. For waste disposal, see section 13 of the SDS.
Environmental precautions	Avoid discharge into drains, water courses or onto the ground.

7. Handling and storage

Precautions for safe handling	Do not get this material in contact with eyes. Avoid contact with eyes, skin, and clothing. Provide adequate ventilation. Wear appropriate personal protective equipment. Observe good industrial hygiene practices.
Conditions for safe storage, including any incompatibilities	Store in original tightly closed container. Store in a cool, dry, well-ventilated place. Store away from incompatible materials (see Section 10 of the SDS). Recommended storage containers: plastic lined steel, plastic, glass, aluminum, stainless steel, or reinforced fiberglass.

8. Exposure controls/personal protection

Occupational exposure limits

US. OSHA Table Z-1 Limits for Air Contaminants (29 CFR 1910.1000)

Components	Type	Value	Form
Glycerin (CAS 56-81-5)	PEL	5 mg/m3	Respirable fraction.
		15 mg/m3	Total dust.

Biological limit values	No biological exposure limits noted for the ingredient(s).
Appropriate engineering controls	Good general ventilation (typically 10 air changes per hour) should be used. Ventilation rates should be matched to conditions. If applicable, use process enclosures, local exhaust ventilation, or other engineering controls to maintain airborne levels below recommended exposure limits. If exposure limits have not been established, maintain airborne levels to an acceptable level. Eye wash facilities and emergency shower must be available when handling this product.

Individual protection measures, such as personal protective equipment

Eye/face protection	Wear approved, tight fitting indirect vented or non-vented safety goggles where splashing is probable. Face shield is recommended.
Skin protection	
Hand protection	Wear appropriate chemical resistant gloves. Rubber or vinyl-coated gloves are recommended.
Other	Wear appropriate chemical resistant clothing.
Respiratory protection	If engineering controls do not maintain airborne concentrations below recommended exposure limits (where applicable) or to an acceptable level (in countries where exposure limits have not been established), an approved respirator must be worn.
Thermal hazards	Wear appropriate thermal protective clothing, when necessary.
General hygiene considerations	Always observe good personal hygiene measures, such as washing after handling the material and before eating, drinking, and/or smoking. Routinely wash work clothing and protective equipment to remove contaminants.

9. Physical and chemical properties

Appearance	
Physical state	Liquid.
Form	Viscous gel/liquid.
Color	Amber.
Odor	Odorless.
Odor threshold	Not available.
pH	3 (3% solution/water)
Melting point/freezing point	Not available.
Initial boiling point and boiling range	Not available.
Flash point	Not available.
Evaporation rate	Not available.
Flammability (solid, gas)	Not applicable.
Upper/lower flammability or explosive limits	
Flammability limit - lower (%)	Not available.
Flammability limit - upper (%)	Not available.
Explosive limit - lower (%)	Not available.
Explosive limit - upper (%)	Not available.
Vapor pressure	Not available.
Vapor density	Not available.
Relative density	1.1 - 1.3
Solubility(ies)	
Solubility (water)	Not available.
Solubility (other)	Acetone and DMSO.
Partition coefficient (n-octanol/water)	Not available.
Auto-ignition temperature	Not available.
Decomposition temperature	Not available.
Viscosity	20,000 - 40,000 cP

10. Stability and reactivity

Reactivity	The product is stable and non-reactive under normal conditions of use, storage and transport.

Chemical stability	Undergoes hydrolysis in water to form lactic acid and glycerol.
Possibility of hazardous reactions	No dangerous reaction known under conditions of normal use.
Conditions to avoid	Avoid temperatures exceeding the flash point. Contact with incompatible materials.
Incompatible materials	Strong oxidizing agents. Bases. Acids.
Hazardous decomposition products	Thermal decomposition or combustion may produce: carbon oxides, phosphorus compounds, metal oxides.

11. Toxicological information

Information on likely routes of exposure

Inhalation	May cause irritation to the respiratory system.
Skin contact	Causes skin irritation.
Eye contact	Causes serious eye damage.
Ingestion	Ingestion may cause irritation and malaise.
Symptoms related to the physical, chemical and toxicological characteristics	Severe eye irritation. Symptoms may include stinging, tearing, redness, swelling, and blurred vision. Permanent eye damage including blindness could result. Skin irritation. May cause redness and pain.

Information on toxicological effects

Acute toxicity

Components	Species	Test Results
Glycerin (CAS 56-81-5)		
Acute		
Oral		
LD50	Rat	12600 mg/kg

Skin corrosion/irritation	Causes skin irritation.
Serious eye damage/eye irritation	Causes serious eye damage.
Respiratory or skin sensitization	
Respiratory sensitization	Not a respiratory sensitizer.
Skin sensitization	This product is not expected to cause skin sensitization.
Germ cell mutagenicity	No data available to indicate product or any components present at greater than 0.1% are mutagenic or genotoxic.
Carcinogenicity	This product is not considered to be a carcinogen by IARC, ACGIH, NTP, or OSHA.

OSHA Specifically Regulated Substances (29 CFR 1910.1001-1050)

Not listed.

Reproductive toxicity	This product is not expected to cause reproductive or developmental effects.
Specific target organ toxicity - single exposure	Not classified.
Specific target organ toxicity - repeated exposure	Not classified.
Aspiration hazard	Not an aspiration hazard.

12. Ecological information

Ecotoxicity	The product is not classified as environmentally hazardous. However, this does not exclude the possibility that large or frequent spills can have a harmful or damaging effect on the environment.
Persistence and degradability	Material is readily degradable and undergoes hydrolysis in several hours.
Bioaccumulative potential	No data available.

Partition coefficient n-octanol / water (log Kow)

Glycerin (CAS 56-81-5)	-1.76
Lactic acid (CAS 50-21-5)	-0.72

Mobility in soil	No data available.
Other adverse effects	None known.

13. Disposal considerations

Disposal instructions	Collect and reclaim or dispose in sealed containers at licensed waste disposal site. Dispose of contents/container in accordance with local/regional/national/international regulations.
Local disposal regulations	Dispose in accordance with all applicable regulations.
Hazardous waste code	The waste code should be assigned in discussion between the user, the producer and the waste disposal company.
Waste from residues / unused products	Dispose of in accordance with local regulations. Empty containers or liners may retain some product residues. This material and its container must be disposed of in a safe manner (see: Disposal instructions).
Contaminated packaging	Empty containers should be taken to an approved waste handling site for recycling or disposal. Since emptied containers may retain product residue, follow label warnings even after container is emptied.

14. Transport information

DOT

Not regulated as dangerous goods.

IATA

Not regulated as dangerous goods.

IMDG

Not regulated as dangerous goods.

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code	Not established.

15. Regulatory information

US federal regulations	This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200. One or more components are not listed on TSCA.

TSCA Section 12(b) Export Notification (40 CFR 707, Subpt. D)

Not regulated.

OSHA Specifically Regulated Substances (29 CFR 1910.1001-1050)

Not listed.

CERCLA Hazardous Substance List (40 CFR 302.4)

Not listed.

Superfund Amendments and Reauthorization Act of 1986 (SARA)

Hazard categories	Immediate Hazard - Yes Delayed Hazard - No Fire Hazard - No Pressure Hazard - No Reactivity Hazard - No

SARA 302 Extremely hazardous substance

Not listed.

SARA 311/312 Hazardous chemical	Yes

SARA 313 (TRI reporting)

Not regulated.

Other federal regulations

Clean Air Act (CAA) Section 112 Hazardous Air Pollutants (HAPs) List

Not regulated.

Clean Air Act (CAA) Section 112(r) Accidental Release Prevention (40 CFR 68.130)

Not regulated.

Safe Drinking Water Act (SDWA)	Not regulated.

US state regulations

US. Massachusetts RTK - Substance List

Glycerin (CAS 56-81-5)

US. New Jersey Worker and Community Right-to-Know Act

Glycerin (CAS 56-81-5)

US. Pennsylvania Worker and Community Right-to-Know Law

Glycerin (CAS 56-81-5)

US. Rhode Island RTK

Not regulated.

US. California Proposition 65

California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65): This material is not known to contain any chemicals currently listed as carcinogens or reproductive toxins.

International Inventories

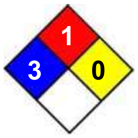
Country(s) or region	Inventory name	On inventory (yes/no)*
Australia	Australian Inventory of Chemical Substances (AICS)	Yes
Canada	Domestic Substances List (DSL)	Yes
Canada	Non-Domestic Substances List (NDSL)	Yes
China	Inventory of Existing Chemical Substances in China (IECSC)	Yes
Europe	European Inventory of Existing Commercial Chemical Substances (EINECS)	Yes
Europe	European List of Notified Chemical Substances (ELINCS)	No
Japan	Inventory of Existing and New Chemical Substances (ENCS)	Yes
Korea	Existing Chemicals List (ECL)	Yes
New Zealand	New Zealand Inventory	Yes
Philippines	Philippine Inventory of Chemicals and Chemical Substances (PICCS)	Yes
United States & Puerto Rico	Toxic Substances Control Act (TSCA) Inventory	Yes

*A "Yes" indicates this product complies with the inventory requirements administered by the governing country(s).
A "No" indicates that one or more components of the product are not listed or exempt from listing on the inventory administered by the governing country(s).

16. Other information, including date of preparation or last revision

Issue date	10-April-2015
Revision date	-
Version #	01
Further information	HMIS® is a registered trade and service mark of the American Coatings Association (ACA).
HMIS® ratings	Health: 3 Flammability: 1 Physical hazard: 0

NFPA ratings



Disclaimer

Regenesis cannot anticipate all conditions under which this information and its product, or the products of other manufacturers in combination with its product, may be used. It is the user's responsibility to ensure safe conditions for handling, storage and disposal of the product, and to assume liability for loss, injury, damage or expense due to improper use. The information in the sheet was written based on the best knowledge and experience currently available.

HYDROGEN
RELEASE
COMPOUND

HRC® Technical Description


Example of HRC

HRC® is an engineered, hydrogen release compound designed specifically for enhanced, in situ anaerobic bioremediation of chlorinated compounds in groundwater or highly saturated soils. Upon contact with groundwater, this viscous, polylactate ester material becomes hydrated and subject to microbial breakdown producing a controlled-release of hydrogen for periods of up to 18-24 months on a single application.

HRC enables enhanced anaerobic biodegradation by adding hydrogen (an electron donor) to groundwater and/or soil to increase the number and vitality of indigenous microorganisms able to perform the naturally occurring process of enhanced reductive dechlorination. During this process, certain naturally occurring microorganisms replace chlorine atoms on chlorinated contaminants with the newly available hydrogen effectively reducing the contaminant to a less harmful substance with the preferred and innocuous endpoints of ethene or ethane.

For a list of treatable contaminants with the use of HRC, view the Range of Treatable Contaminants Guide.

Chemical Composition

- Glycerol Tripolylactate- CAS #201167-72-8
- Glycerin- CAS #56-81-5
- Lactic acid- CAS #50-21-5

Properties

- pH - 3 (3% solution/water)
- Appearance – Viscous gel/liquid. Amber color
- Odor – Odorless
- Vapor Pressure – None

Storage and Handling Guidelines

Storage
Store away from incompatible materials
Store in original tightly closed container
Store in a cool, dry, well-ventilated place

Handling
Wash thoroughly after handling
Wear appropriate personal protective equipment
Wear eye/face protection
Provide adequate ventilation
Observe good industrial hygiene practices

HYDROGEN
RELEASE
COMPOUND

HRC® Technical Description

Applications

- Permanent injection wells
- Direct-push injection (barriers and grids)
- Recirculating wells
- Soil borings
- Excavation applications into soil or on top of bedrock
- Gravity feed into bedrock wells

Application instructions for this product are contained in the HRC Application Instructions.

Health and Safety

Avoid contact with eyes, skin, and clothing. Provide adequate ventilation. Wear appropriate personal protective equipment. Observe good industrial hygiene practices.

Please review the HRC Material Safety Data Sheet for additional storage, usage, and handling requirements.

Hydrogen Release Compound (HRC®) Installation Instructions

General Guidelines

The best method to deliver HRC® into the subsurface is to inject the material through direct push rods using hydraulic equipment. This approach increases the spreading and mixing of HRC into the aquifer. This set of instructions is specific to direct push equipment.

REGENESIS® has found that very few pumps can adequately deliver HRC to the subsurface. Although other pumps may be capable of injecting HRC, we have developed the following instructions specifically for use with an R.E. RUPE Company Model ORC/HRC 9-1500 mixing and pumping machine. There is also strong evidence that the Geoprobe GS-2000 pump can effectively deliver HRC to the subsurface. In general, REGENESIS strongly recommends using a pump with a minimum pressure rating of 1,500 pounds per square inch (psi) and a minimum delivery rate of 3 gallons per minute.

The installation of HRC should span the entire vertical contaminated saturated thickness. If the vertical extent of HRC application is confined to a limited interval, then the HRC material should be placed across a vertical zone extending a minimum of 2 feet above and below the screened Interval of monitoring wells to be used to evaluate the performance of the bioremediation project.

Material Overview, Handling, and Safety

HRC is shipped in 4.25- gallon buckets and each bucket has a gross weight of approximately 32 pounds (net weight of HRC is 30 pounds). At room temperature, HRC is a sticky gel with a viscosity of approximately 20,000 centipoise (roughly equivalent to cold honey). The HRC material has a nominal density of 1.3 grams/cubic centimeter or approximately 10.8 pounds per gallon. The viscosity of HRC is temperature sensitive. Significant changes in viscosity are observed with large changes in product temperature.

It should be noted that the temperature/viscosity relationship is not linear. For ease of installation, HRC should be stored in a warm, dry place that is protected from direct sunlight. It is common for stored HRC to settle somewhat in a container. Pre-heating HRC makes it easier to work with the material. Although HRC is manufactured as a food-grade material that is safe to ingest, field personnel should take precautions while handling and applying HRC. Field personnel should use appropriate safety equipment, including eye protection. The low pH when dissolved in water and the viscosity of the product make eye protection mandatory. Gloves should be used as appropriate based on the exposure duration and field conditions.

A Material Safety Data Sheet is provided with each shipment. Personnel who operate field equipment during the installation process should have appropriate training, supervision, and experience.

Specific Installation Procedures

1. Prior to the installation of HRC, any surface or overhead impediments should be identified as well as the location of all underground structures. Underground structures include but are not limited to: utility lines, tanks, distribution piping, sewers, drains, and landscape irrigation systems.
2. Planned installation locations should be adjusted to account for all impediments and obstacles.
3. REGENESIS recommends pre-heating HRC in a hot water bath. Place unopened buckets of HRC into an empty water tank. A Rubbermaid fiberglass Farm Trough Stock Tank (Model 4242-00-GRAY) is typically used for this application and can hold up to 16 buckets of HRC. Hot water (approximately 130-170 °F or 54-77 °C) should be added to the tank after the buckets of HRC have been placed inside. When the HRC reaches a minimum temperature of 95 °F or 35 °C (approximately 20-30 minutes) it is ready to be poured into the pump hopper.
4. Pre-mark the installation locations, noting any points that may have different vertical application requirements or total depth.
5. Set up the direct push unit over each specific point and follow the manufacturer standard operating procedures (SOP) for the direct push equipment. Care should be taken to assure that probe holes remain in the vertical.
6. For most applications, REGENESIS suggests using 1.25- inch O.D./0.625-inch I.D Geoprobe brand drive rods. However, some applications may require the use of 2.125- inch O.D./1.5- inch I.D. drive rods.
7. The HRC delivery sub-assemblies that REGENESIS currently uses are designed for 1.25-inch Geoprobe rods. Other brands of drive rods can also be used but require the fabrication of a sub-assembly (see REGENESIS Website).
8. Advance drive rods through the surface pavement, as necessary, following SOP.
9. Push the drive rod assembly with an expendable tip to the desired maximum depth. REGENESIS suggests pre-counting the number of drive rods needed to reach depth prior to starting injection activities.
10. After the drive rods have been pushed to the desired depth, the rod assembly should be withdrawn three to six inches. The expendable tip can be dropped from the drive rods, following SOP.
    a) If an injection tool was used instead of an expendable tip, the application of material can take place without any preliminary withdrawal of the rods.
11. In some cases, introduction of a large column of air may be problematic. This is particularly the case in deep injections (>50 ft) with large diameter rods (>1.5- inch O.D.). To prevent the injection of air into the aquifer during HRC application, fill the drive rods with water.
12. Pour the pre-heated HRC into the pump hopper (up to 40 gallons). Remove the separated HRC from the bucket bottom by tipping the bucket into the hopper and scraping out the smooth residual material. Use the pumps mixing and recirculation features to create a uniform consistency. This typically requires recirculation of approximately one hopper volume.
    NOTE: Do not attempt to mix HRC with water or other liquids to thin or decrease the viscosity of the material. This may adversely affect HRC longevity.
13. A volume check should be performed prior to injecting HRC. Determining the volume displaced per pump stroke can be accomplished in two easy steps.
    a) Determine the number of pump strokes needed to deliver 3 gallons of HRC (use a graduated bucket for this)
    b) Divide 3 gallons by the results from the first step to determine the number of gallons of HRC delivered by each pump stroke.
    c) Level indicators present in the hopper are in 3 gallon increments.

d) The volume of HRC displaced should be confirmed using the HRC level indicators located inside the pump hopper.

14. Connect the 1.25-inch O.D., 1-inch I.D. delivery hose to the pump outlet and the provided HRC delivery sub-assembly. Circulate HRC though the hose and the delivery sub-assembly to displace air in the hose.
15. Connect the HRC sub-assembly to the drive rod. After confirming that all of the connections are secure, pump the HRC through the delivery system to displace the water/fluid in the rods. NOTE: Prior to pumping HRC into the aquifer, close the pump recirculation valve; failure to do so will allow material to short-circuit into the hopper and change the volume of HRC delivered per pump stroke.
16. The pump engine RPM and hydraulic settings should remain constant throughout the day. However, if the hydraulic system starts to "squeal", the pump speed should be decreased until the noise is mitigated.
17. Use the pump's stroke counter and the provided volume/weight conversions to apply the appropriate HRC volume per injection location (and per vertical foot of contaminated saturated zone). Table 1 shows typical HRC delivery information followed by an example calculation.

Table 1: Pump Volume Calculation

Example: For each injection location, install 60 pounds of HRC across 10 vertical feet of aquifer (an application rate of 6 pounds per vertical foot).

Solution:

- 60 pounds/10.8 pounds per gallon + 5.6 gallons for the injection location
- 5.6 gallons/0.2 gallons per stroke + 28 pump strokes for the injection location
- 28 pump strokes/10 vertical feet = 2.8 strokes per vertical foot
- 2.8 strokes per vertical foot = 8.4 strokes per 3 foot drive rod
- 2.8 strokes per vertical foot = 11.2 strokes per 4 foot drive rod

18. Slowly withdraw the drive rods us ing Geoprobe Rod Grip or Pull Plate Assembly (Part AT1222-For 1.25-inch drive rods). While slowly withdrawing single lengths of drive rod (3 or 4 feet), pump the pre-determined volume of HRC into the aquifer across the desired treatment interval (Step 13). Use the stroke counter and pump on/off switch to control volume of injection. See Helpful Hints at the end of this section.
19. Remove one section of the drive rod. The drive rod may contain some residual HRC. Place the HRC-filled rod in a clean, empty bucket and allow the HRC to drain. Eventually, the HRC should be returned to the HRC pump hopper for reuse.
20. Observe any indications of aquifer refusal. This is typically indicated by a high-pitched squeal in the pump's hydraulic system or (in the case of shallow applications) HRC "surfacing" around the injection rods or previously installed injection points. If aquifer acceptance appears to be low, allow enough time for the aquifer to equilibrate prior to removing the drive rod.
21. Repeat steps 15-20 until treatment of the entire contaminated vertical zone has been achieved.
22. Install an appropriate seal, such as bentonite, above the HRC material through the entire vadose zone. Depending on soil conditions and local regulations, use a bentonite seal via chips or pellets after the probe rods have been removed. This assures that the HRC remains properly placed and prevents contaminant migration from the surface. If HRC continues to "surface" up the direct push borehole, an appropriately sized (oversized) disposable drive tip or wood plug/stake can be used to plug the hole until the aquifer equilibrates and the HRC stops surfacing.

23. Remove and clean the drive rods as necessary.
24. Finish the borehole at the surface as appropriate (concrete or asphalt cap, if necessary).
25. Periodically compare the pre- and post- injection volumes of HRC in the pump hopper using the pre-marked volume levels. Volume level indicators are not on all pump hoppers. In this case, volume level markings can be temporarily added using known amounts of water and a carpenter's grease pencil (Kiel crayon). We suggest marking the water levels in 3-gallon increments.
26. Move to the next probe point, repeating steps 8-25.

Helpful Hints

1) Application in Cold Weather Settings

The viscosity of HRC is directly related to the ambient temperature. As discussed in the Material Overview, Handling, and Safety section, cold weather tends to increase HRC viscosity and decrease ease of pumping. To maintain HRC at a temperature/viscosity at which it is easy to apply:

- Raise and maintain the temperature of the HRC to at least 95 °F (35 °C) prior to pouring it into the pump hopper.
- Insulate the delivery hose and keep the pump and hot water bath inside an enclosed structure such as a cargo van or trailer.
- Periodically check the HRC temperature in the hopper.
- Occasionally re-circulate HRC through the pump and hose to maintain temperature and viscosity.
- The volume of HRC recirculated should not exceed the volume of HRC in the hopper.
- Do not constantly recirculate HRC through the pump and hoses, as this may adversely affect the longevity of HRC.

2) HRC Pump Information

REGENESIS has evaluated a number of pumps that are capable of delivering 20,000 centipoise HRC to the subsurface at a sufficient pressure and volumetric rate. Although a number of pumps may be capable of delivering the HRC to the subsurface at adequate pressures and volume, each pump has a set of practical issues that make it difficult to manage in a field setting.

As a result of this evaluation, REGENESIS has determined that the R.E. RUPE Company Model ORC/HRC 9-1500 meets the pressure and volume requirements needed to successfully inject HRC in the field. In general, REGENESIS strongly recommends using a pump with a minimum pressure rating of 1,500 pounds per square inch (psi) and a minimum delivery rate of 3 gallons per minute. When applying measured volumes of HRC via probe boreholes, it is useful to know the volume of a single pump stroke (Table 1 above) and the associated delivery system lines.

The following additional information is provided for reference:

Table 2: HRC Physical Characteristics

Density	1.3 g/cc or 10.8 lbs/gal
Viscosity	Approx. 20,000 centipoise

Table 3: Equipment Volume and HRC Weight per Length

Equipment	Volume	HRC Weight
1-inch OD; 0.625- inch ID hose (10 feet length)	0.2 gallon	1.8 lbs.
1.25-inch OD; 0.625- inch ID drive rod (3 feet length)	0.05 gallon	0.5 lbs.
1.25-inch OD; 0.625- inch ID drive rod (4 feet length)	0.06 gallon	0.7 lbs.

3) Pump Cleaning

For best results, use a hot water pressure washer (150-170 °F or 66-77 °C) to clean equipment and rods periodically throughout the day. Internal pump mechanisms and hoses can be easily cleaned by circulating hot water and a biodegradable cleaner such as Simple Green through the pump and delivery hose. Further cleaning and decontamination (if necessary due to subsurface conditions) should be performed according to the equipment supplier's standard procedures and local regulatory requirements.

NOTE: The remote control/pump counter should be kept dry at all times. If it gets wet, it will short-circuit and will need to be replaced.

Before Using the Rupe Pump, Check the Following:

- Fuel level prior to engaging in pumping activities (it would be best to start with a full tank)
- Remote control/pump stroke counter LCD display (if no display is present, the electronic counter will need to be replaced (Grainger Stock No. 2A540))
- Monitor pump strokes by observing the proximity switches (located on the top of the piston).

4) HRC Bedrock Applications

When contaminants are present in competent bedrock aquifers, the use of direct push technology as a delivery method is not possible. REGENESIS is in the process of developing methods for applying HRC via boreholes drilled using conventional rotary techniques. To develop the best installation strategy for a particular bedrock site, it is critical that our customers call the technical support department at REGENESIS early in the design process.

HRC can be applied into a bedrock aquifer in cased and uncased boreholes. HRC can be delivered by simply filling the borehole without pressure or by using a single or straddle packer system to inject HRC under pressure. Selection of the appropriate delivery method is predicated on site-specific conditions.

The following issues should be considered in developing an HRC delivery strategy:

- Is the aquifer's transmissivity controlled by fractures?
- Backfilling may be the better delivery method in massive, unfractured bedrock. This is particularly true in an aquifer setting with high permeability and little fracturing (such as that found in massive sandstone).
- Down-hole packer systems may be more advantageous in fractured bedrock aquifers.

  - In this case the fracture type, trends, and interconnections should be evaluated and identified.
- Are the injection wells and monitoring wells connected by the same fractures?
- Determine if it is likely that the HRC injection zone is connected to the proposed monitoring points.
- If pressure injection via straddle packers is desired, consideration should be given to the well construction.

Specific issues to be considered are:

- Diameter of the uncased borehole (will casing diameter allow a packer system to be used?).
- Diameter of the casing (same as above).
- Strength of the casing (can it withstand the delivery pressures?).
- Length of screened interval (screened intervals greater than 10 feet will require a straddle packer system).

For further assistance or questions please contact REGENESIS Technical Services at 949.366.8000

REGENESIS
Technology-Based Solutions for the Environment

SAFETY DATA SHEET

1. Identification

Product identifier	**Hydrogen Release Compound (HRC®)**
Other means of identification	None.
Recommended use	Remediation of soils and groundwater.
Recommended restrictions	None known.

Manufacturer/Importer/Supplier/Distributor information

Company Name	Regenesis
Address	1011 Calle Sombra San Clemente, CA 92673
Telephone	949-366-8000
E-mail	CustomerService@regenesis.com
Emergency phone number	CHEMTREC® at 1-800-424-9300 (International)

2. Hazard(s) identification

Physical hazards	Not classified.	
Health hazards	Skin corrosion/irritation	Category 2
	Serious eye damage/eye irritation	Category 1
OSHA defined hazards	Not classified.	

Label elements

Signal word	Danger
Hazard statement	Causes skin irritation. Causes serious eye damage.
Precautionary statement	
Prevention	Wash thoroughly after handling. Wear protective gloves. Wear eye/face protection.
Response	If on skin: Wash with plenty of water. If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a poison center/doctor. If skin irritation occurs: Get medical advice/attention. Take off contaminated clothing and wash before reuse.
Storage	Store away from incompatible materials.
Disposal	Dispose of waste and residues in accordance with local authority requirements.
Hazard(s) not otherwise classified (HNOC)	None known.

3. Composition/information on ingredients

Mixtures

Chemical name	CAS number	%
Glycerol Tripolylactate	201167-72-8	62-67
Glycerin	56-81-5	33-38
Lactic acid	50-21-5	<10

Composition comments	All concentrations are in percent by weight unless otherwise indicated.

4. First-aid measures

Inhalation	Move to fresh air. Call a physician if symptoms develop or persist.

Skin contact	Remove contaminated clothing. Wash with plenty of soap and water. If skin irritation occurs: Get medical advice/attention. Wash contaminated clothing before reuse.
Eye contact	Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Get medical attention immediately.
Ingestion	Rinse mouth. Never give anything by mouth to a victim who is unconscious or is having convulsions. Do not induce vomiting without advice from poison control center. Get medical attention if symptoms occur.
Most important symptoms/effects, acute and delayed	Severe eye irritation. Symptoms may include stinging, tearing, redness, swelling, and blurred vision. Permanent eye damage including blindness could result. Skin irritation. May cause redness and pain.
Indication of immediate medical attention and special treatment needed	Provide general supportive measures and treat symptomatically. Keep victim under observation. Symptoms may be delayed.
General information	Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves.

5. Fire-fighting measures

Suitable extinguishing media	Water spray. Carbon dioxide (CO2). Dry chemical powder. Foam.
Unsuitable extinguishing media	Do not use water jet as an extinguisher, as this will spread the fire.
Specific hazards arising from the chemical	During fire, gases hazardous to health may be formed. Combustion products may include: carbon oxides, phosphorus compounds and metal oxides.
Special protective equipment and precautions for firefighters	Self-contained breathing apparatus and full protective clothing must be worn in case of fire.
Fire fighting equipment/instructions	Move containers from fire area if you can do so without risk. Water spray should be used to cool containers.
Specific methods	Use standard firefighting procedures and consider the hazards of other involved materials.
General fire hazards	No unusual fire or explosion hazards noted.

6. Accidental release measures

Personal precautions, protective equipment and emergency procedures	Keep unnecessary personnel away. Keep people away from and upwind of spill/leak. Wear appropriate protective equipment and clothing during clean-up. Do not touch damaged containers or spilled material unless wearing appropriate protective clothing. Ensure adequate ventilation. Local authorities should be advised if significant spillages cannot be contained. For personal protection, see section 8 of the SDS.
Methods and materials for containment and cleaning up	Large Spills: Stop the flow of material, if this is without risk. Use water spray to reduce vapors or divert vapor cloud drift. Dike the spilled material, where this is possible. Cover with plastic sheet to prevent spreading. Absorb in vermiculite, dry sand or earth and place into containers. Following product recovery, flush area with water. Small Spills: Wipe up with absorbent material (e.g. cloth, fleece). Clean surface thoroughly to remove residual contamination. Never return spills to original containers for re-use. For waste disposal, see section 13 of the SDS.
Environmental precautions	Avoid discharge into drains, water courses or onto the ground.

7. Handling and storage

Precautions for safe handling	Do not get this material in contact with eyes. Avoid contact with eyes, skin, and clothing. Provide adequate ventilation. Wear appropriate personal protective equipment. Observe good industrial hygiene practices.
Conditions for safe storage, including any incompatibilities	Store in original tightly closed container. Store in a cool, dry, well-ventilated place. Store away from incompatible materials (see Section 10 of the SDS). Recommended storage containers: plastic lined steel, plastic, glass, aluminum, stainless steel, or reinforced fiberglass.

8. Exposure controls/personal protection

Occupational exposure limits

US. OSHA Table Z-1 Limits for Air Contaminants (29 CFR 1910.1000)

Components	Type	Value	Form
Glycerin (CAS 56-81-5)	PEL	5 mg/m3	Respirable fraction.
		15 mg/m3	Total dust.

Biological limit values	No biological exposure limits noted for the ingredient(s).
Appropriate engineering controls	Good general ventilation (typically 10 air changes per hour) should be used. Ventilation rates should be matched to conditions. If applicable, use process enclosures, local exhaust ventilation, or other engineering controls to maintain airborne levels below recommended exposure limits. If exposure limits have not been established, maintain airborne levels to an acceptable level. Eye wash facilities and emergency shower must be available when handling this product.

Individual protection measures, such as personal protective equipment

Eye/face protection	Wear approved, tight fitting indirect vented or non-vented safety goggles where splashing is probable. Face shield is recommended.
Skin protection	
Hand protection	Wear appropriate chemical resistant gloves. Rubber or vinyl-coated gloves are recommended.
Other	Wear appropriate chemical resistant clothing.
Respiratory protection	If engineering controls do not maintain airborne concentrations below recommended exposure limits (where applicable) or to an acceptable level (in countries where exposure limits have not been established), an approved respirator must be worn.
Thermal hazards	Wear appropriate thermal protective clothing, when necessary.
General hygiene considerations	Always observe good personal hygiene measures, such as washing after handling the material and before eating, drinking, and/or smoking. Routinely wash work clothing and protective equipment to remove contaminants.

9. Physical and chemical properties

Appearance	
Physical state	Liquid.
Form	Viscous gel/liquid.
Color	Amber.
Odor	Odorless.
Odor threshold	Not available.
pH	3 (3% solution/water)
Melting point/freezing point	Not available.
Initial boiling point and boiling range	Not available.
Flash point	Not available.
Evaporation rate	Not available.
Flammability (solid, gas)	Not applicable.
Upper/lower flammability or explosive limits	
Flammability limit - lower (%)	Not available.
Flammability limit - upper (%)	Not available.
Explosive limit - lower (%)	Not available.
Explosive limit - upper (%)	Not available.
Vapor pressure	Not available.
Vapor density	Not available.
Relative density	1.1 - 1.3
Solubility(ies)	
Solubility (water)	Not available.
Solubility (other)	Acetone and DMSO.
Partition coefficient (n-octanol/water)	Not available.
Auto-ignition temperature	Not available.
Decomposition temperature	Not available.
Viscosity	20,000 - 40,000 cP

10. Stability and reactivity

Reactivity	The product is stable and non-reactive under normal conditions of use, storage and transport.

Chemical stability	Undergoes hydrolysis in water to form lactic acid and glycerol.
Possibility of hazardous reactions	No dangerous reaction known under conditions of normal use.
Conditions to avoid	Avoid temperatures exceeding the flash point. Contact with incompatible materials.
Incompatible materials	Strong oxidizing agents. Bases. Acids.
Hazardous decomposition products	Thermal decomposition or combustion may produce: carbon oxides, phosphorus compounds, metal oxides.

11. Toxicological information

Information on likely routes of exposure

Inhalation	May cause irritation to the respiratory system.
Skin contact	Causes skin irritation.
Eye contact	Causes serious eye damage.
Ingestion	Ingestion may cause irritation and malaise.
Symptoms related to the physical, chemical and toxicological characteristics	Severe eye irritation. Symptoms may include stinging, tearing, redness, swelling, and blurred vision. Permanent eye damage including blindness could result. Skin irritation. May cause redness and pain.

Information on toxicological effects

Acute toxicity

Components	Species	Test Results
Glycerin (CAS 56-81-5)		
Acute		
Oral		
LD50	Rat	12600 mg/kg

Skin corrosion/irritation	Causes skin irritation.
Serious eye damage/eye irritation	Causes serious eye damage.
Respiratory or skin sensitization	
Respiratory sensitization	Not a respiratory sensitizer.
Skin sensitization	This product is not expected to cause skin sensitization.
Germ cell mutagenicity	No data available to indicate product or any components present at greater than 0.1% are mutagenic or genotoxic.
Carcinogenicity	This product is not considered to be a carcinogen by IARC, ACGIH, NTP, or OSHA.

OSHA Specifically Regulated Substances (29 CFR 1910.1001-1050)

Not listed.

Reproductive toxicity	This product is not expected to cause reproductive or developmental effects.
Specific target organ toxicity - single exposure	Not classified.
Specific target organ toxicity - repeated exposure	Not classified.
Aspiration hazard	Not an aspiration hazard.

12. Ecological information

Ecotoxicity	The product is not classified as environmentally hazardous. However, this does not exclude the possibility that large or frequent spills can have a harmful or damaging effect on the environment.
Persistence and degradability	Material is readily degradable and undergoes hydrolysis in several hours.
Bioaccumulative potential	No data available.

Partition coefficient n-octanol / water (log Kow)

Glycerin (CAS 56-81-5)	-1.76
Lactic acid (CAS 50-21-5)	-0.72

Mobility in soil	No data available.
Other adverse effects	None known.

13. Disposal considerations

Disposal instructions	Collect and reclaim or dispose in sealed containers at licensed waste disposal site. Dispose of contents/container in accordance with local/regional/national/international regulations.
Local disposal regulations	Dispose in accordance with all applicable regulations.
Hazardous waste code	The waste code should be assigned in discussion between the user, the producer and the waste disposal company.
Waste from residues / unused products	Dispose of in accordance with local regulations. Empty containers or liners may retain some product residues. This material and its container must be disposed of in a safe manner (see: Disposal instructions).
Contaminated packaging	Empty containers should be taken to an approved waste handling site for recycling or disposal. Since emptied containers may retain product residue, follow label warnings even after container is emptied.

14. Transport information

DOT

Not regulated as dangerous goods.

IATA

Not regulated as dangerous goods.

IMDG

Not regulated as dangerous goods.

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code	Not established.

15. Regulatory information

US federal regulations	This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200. One or more components are not listed on TSCA.

TSCA Section 12(b) Export Notification (40 CFR 707, Subpt. D)

Not regulated.

OSHA Specifically Regulated Substances (29 CFR 1910.1001-1050)

Not listed.

CERCLA Hazardous Substance List (40 CFR 302.4)

Not listed.

Superfund Amendments and Reauthorization Act of 1986 (SARA)

Hazard categories	Immediate Hazard - Yes Delayed Hazard - No Fire Hazard - No Pressure Hazard - No Reactivity Hazard - No

SARA 302 Extremely hazardous substance

Not listed.

SARA 311/312 Hazardous chemical	Yes

SARA 313 (TRI reporting)

Not regulated.

Other federal regulations

Clean Air Act (CAA) Section 112 Hazardous Air Pollutants (HAPs) List

Not regulated.

Clean Air Act (CAA) Section 112(r) Accidental Release Prevention (40 CFR 68.130)

Not regulated.

Safe Drinking Water Act (SDWA)	Not regulated.

US state regulations

US. Massachusetts RTK - Substance List

Glycerin (CAS 56-81-5)

US. New Jersey Worker and Community Right-to-Know Act

Glycerin (CAS 56-81-5)

US. Pennsylvania Worker and Community Right-to-Know Law

Glycerin (CAS 56-81-5)

US. Rhode Island RTK

Not regulated.

US. California Proposition 65

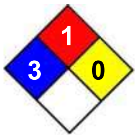
California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65): This material is not known to contain any chemicals currently listed as carcinogens or reproductive toxins.

International Inventories

Country(s) or region	Inventory name	On inventory (yes/no)*
Australia	Australian Inventory of Chemical Substances (AICS)	Yes
Canada	Domestic Substances List (DSL)	Yes
Canada	Non-Domestic Substances List (NDSL)	Yes
China	Inventory of Existing Chemical Substances in China (IECSC)	Yes
Europe	European Inventory of Existing Commercial Chemical Substances (EINECS)	Yes
Europe	European List of Notified Chemical Substances (ELINCS)	No
Japan	Inventory of Existing and New Chemical Substances (ENCS)	Yes
Korea	Existing Chemicals List (ECL)	Yes
New Zealand	New Zealand Inventory	Yes
Philippines	Philippine Inventory of Chemicals and Chemical Substances (PICCS)	Yes
United States & Puerto Rico	Toxic Substances Control Act (TSCA) Inventory	Yes

*A "Yes" indicates this product complies with the inventory requirements administered by the governing country(s).
A "No" indicates that one or more components of the product are not listed or exempt from listing on the inventory administered by the governing country(s).

16. Other information, including date of preparation or last revision

Issue date	10-April-2015
Revision date	-
Version #	01
Further information	HMIS® is a registered trade and service mark of the American Coatings Association (ACA).
HMIS® ratings	Health: 3 Flammability: 1 Physical hazard: 0
NFPA ratings	
Disclaimer	Regenesis cannot anticipate all conditions under which this information and its product, or the products of other manufacturers in combination with its product, may be used. It is the user's responsibility to ensure safe conditions for handling, storage and disposal of the product, and to assume liability for loss, injury, damage or expense due to improper use. The information in the sheet was written based on the best knowledge and experience currently available.

Ground Water Monitoring&Remediation

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

by Travis M. McGuire, James M. McDade, and Charles J. Newell

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 nondestructive 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	Germantown, 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_2O_2	Full	SERDP survey	6.5
C-03	Dry cleaning facility	Jacksonville, FL	Fine grained	H_2O_2	Full	FDEP reports	1.8
C-04	Dry cleaning facility	Florida	Coarse grained	H_2O_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_2O_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_2O_2	Full	Literature reports	2.4
C-16	News publisher facility	Framingham, MA	Fine grained	H_2O_2	Full	Literature reports	0.1
C-17	Savannah River	Aiken, SC	Fine grained	H_2O_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_2O_2	Full	Literature reports	0.9
C-20	Dry cleaning facility	Rockville, MD	Fractured rock	H_2O_2, $NaMnO_4$	Full	Literature reports	1.1
C-21	Portsmouth Gas Plant	Piketon, 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

[1] HRC = hydrogen release compound; HRC-X = HRC extended release formula; Bioaug = bioaugmentation; ORC = oxygen release compound; $KMnO_4$ = potassium permanganate; H_2O_2 = hydrogen peroxide; TBA = tertiary butyl alcohol; $NaMnO_4$ = 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 posttreatment data. Rebound was considered to have occurred when concentrations increased at least 25% over the posttreatment 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

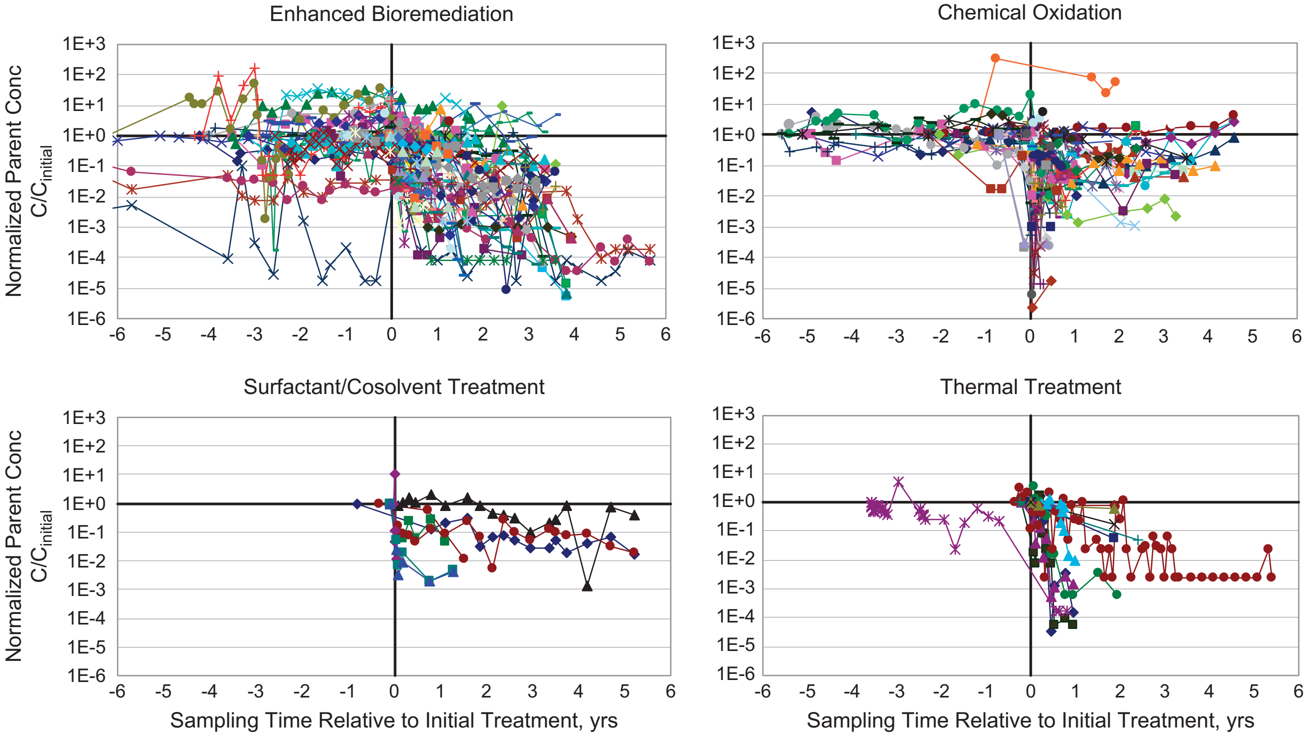


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

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

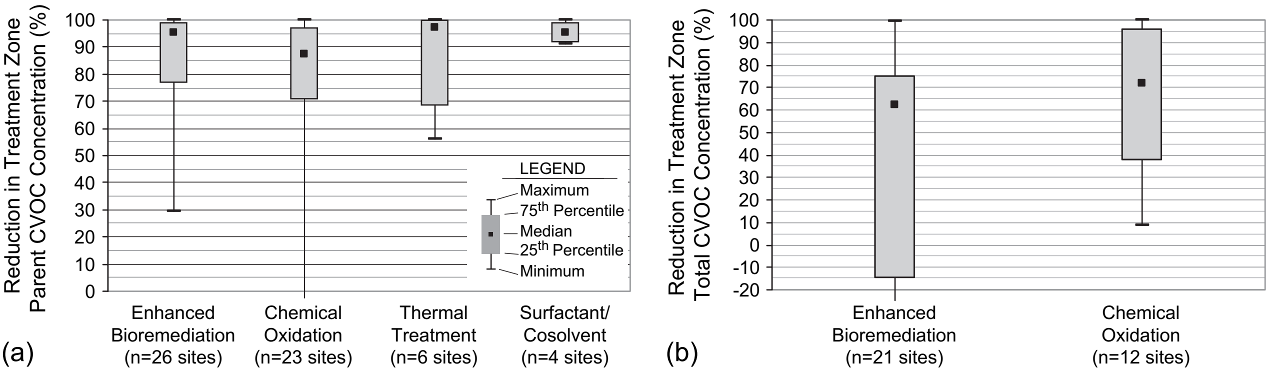


Figure 2. Performance of source depletion technologies: reduction in parent CVOC (a) and total CVOC (b) concentration within the treatment zone. (a) Minimum reduction for chemical oxidation = −55% (value not shown). (b) Minimum reduction for enhanced bioremediation = −150% (value not shown). Only sites 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
n	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 postmonitoring 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

[1] For 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.

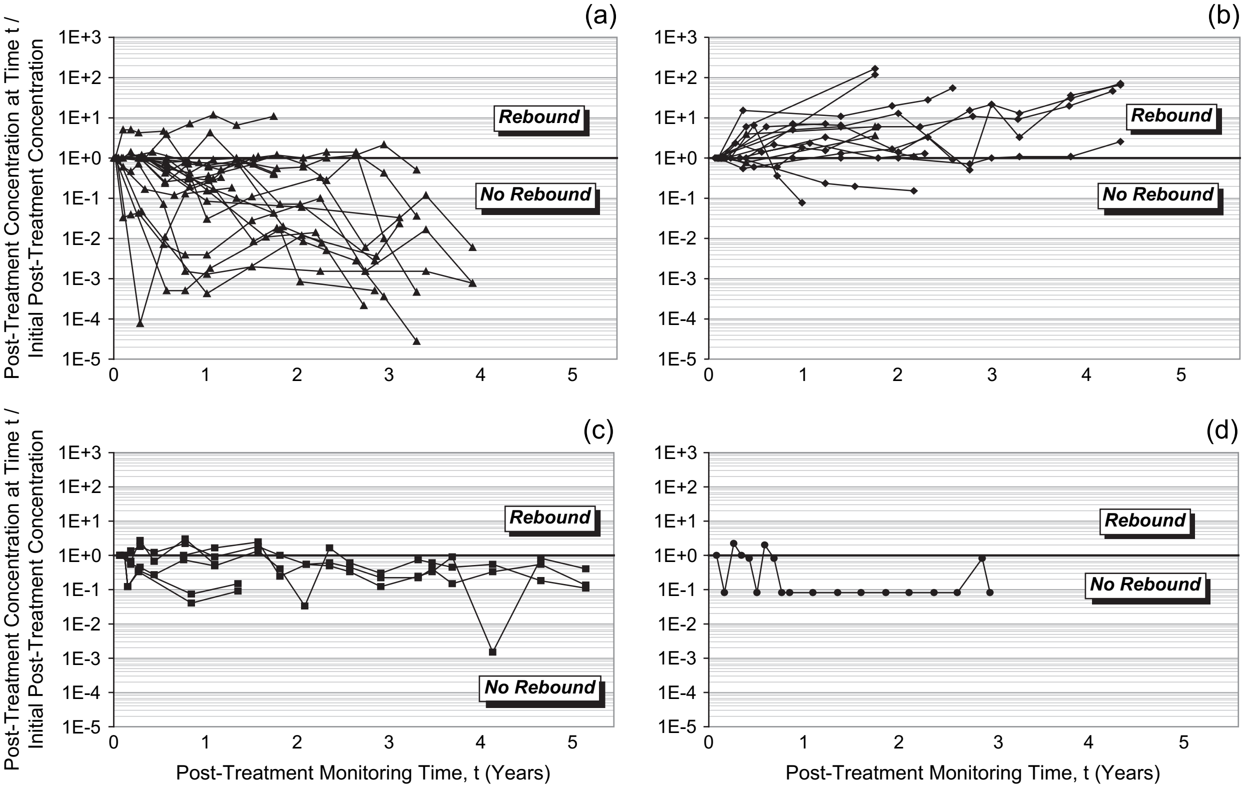


Figure 3. Change in posttreatment ground water concentrations. (a) Enhanced bioremediation sites ($n = 20$ wells); (b) chemical oxidation sites ($n = 16$ wells); (c) surfactant/cosolvent sites ($n = 6$ wells); (d) thermal treatment sites ($n = 1$ well).

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

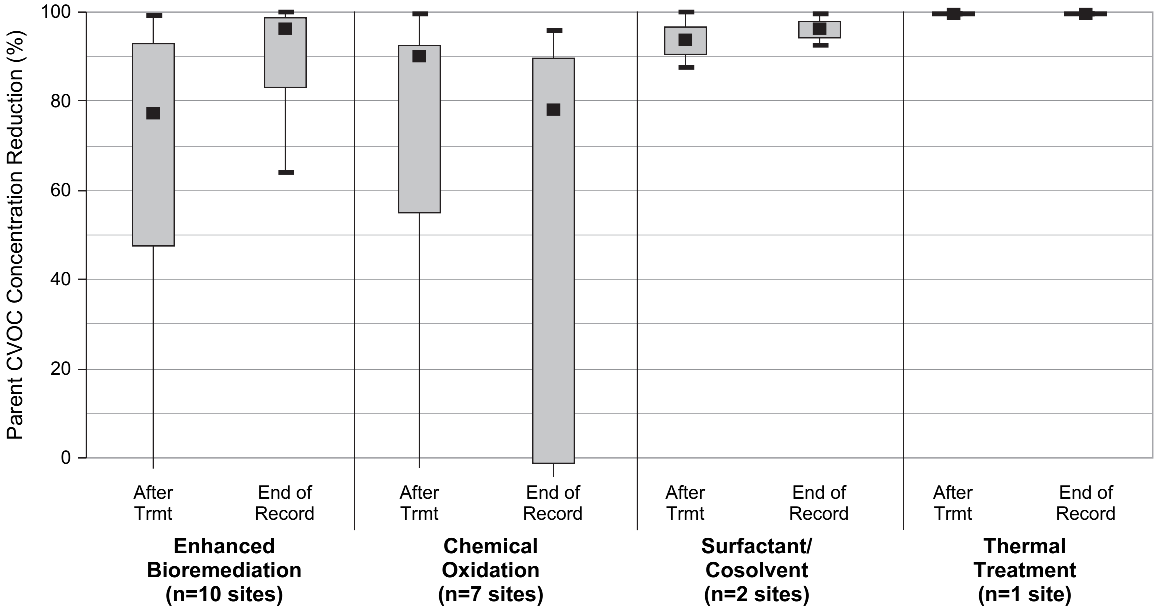


Figure 4. Rebound assessment at source depletion sites: concentration reduction from before treatment to immediately after treatment and at end of data record. Minimum reduction after treatment for enhanced bioremediation = −174%; minimum reduction after treatment for chemical oxidation = −9%; 25th percentile 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-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).

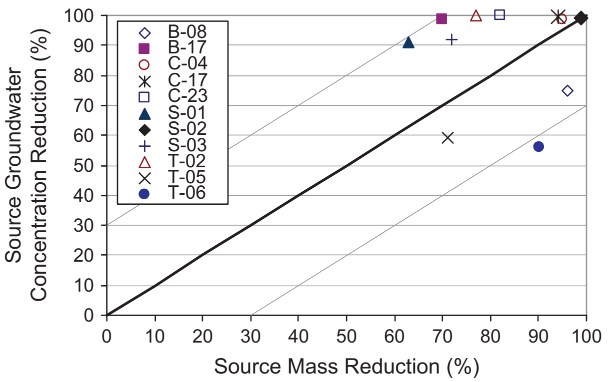


Figure 5. Calculated source zone ground water concentration reductions for reported source zone mass reductions at 11 source depletion sites. The black line represents directly proportional relationship between source mass reduction and ground water concentration reduction, and the gray lines represent ±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.

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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Ground Water Monitoring&Remediation

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

by Travis M. McGuire, James M. McDade, and Charles J. Newell

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 nondestructive 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

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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	Germantown, 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_2O_2	Full	SERDP survey	6.5
C-03	Dry cleaning facility	Jacksonville, FL	Fine grained	H_2O_2	Full	FDEP reports	1.8
C-04	Dry cleaning facility	Florida	Coarse grained	H_2O_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_2O_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_2O_2	Full	Literature reports	2.4
C-16	News publisher facility	Framingham, MA	Fine grained	H_2O_2	Full	Literature reports	0.1
C-17	Savannah River	Aiken, SC	Fine grained	H_2O_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_2O_2	Full	Literature reports	0.9
C-20	Dry cleaning facility	Rockville, MD	Fractured rock	H_2O_2, $NaMnO_4$	Full	Literature reports	1.1
C-21	Portsmouth Gas Plant	Piketon, 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

[1] HRC = hydrogen release compound; HRC-X = HRC extended release formula; Bioaug = bioaugmentation; ORC = oxygen release compound; $KMnO_4$ = potassium permanganate; H_2O_2 = hydrogen peroxide; TBA = tertiary butyl alcohol; $NaMnO_4$ = 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 posttreatment data. Rebound was considered to have occurred when concentrations increased at least 25% over the posttreatment 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

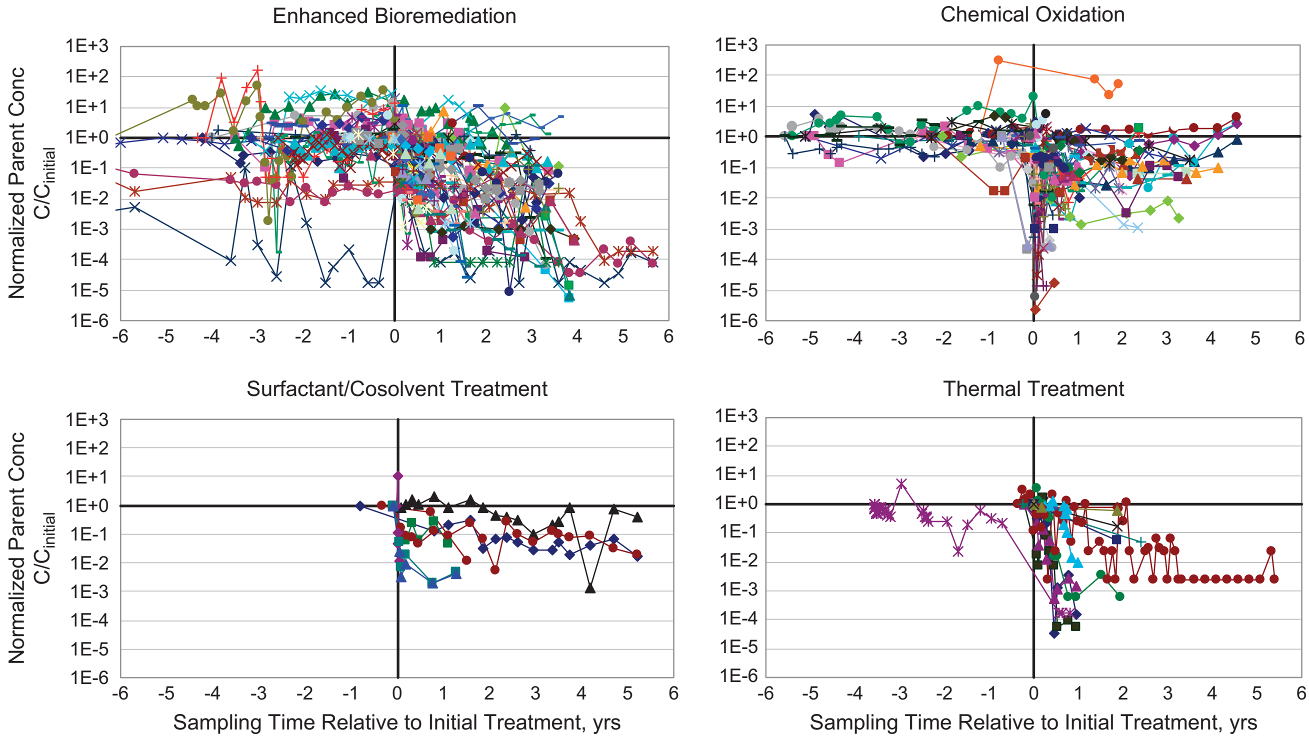

Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

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

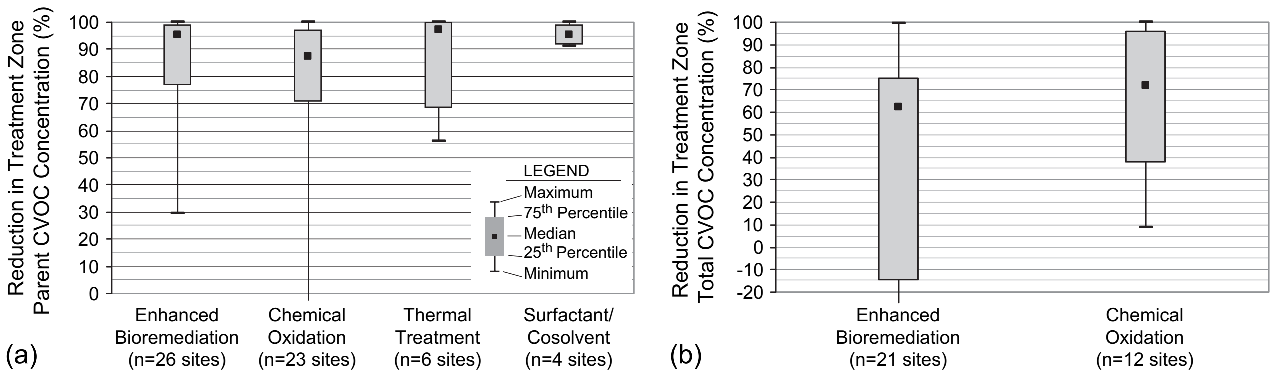

Figure 2. Performance of source depletion technologies: reduction in parent CVOC (a) and total CVOC (b) concentration within the treatment zone. (a) Minimum reduction for chemical oxidation = −55% (value not shown). (b) Minimum reduction for enhanced bioremediation = −150% (value not shown). Only sites 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
n	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 postmonitoring 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

[1] For 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.

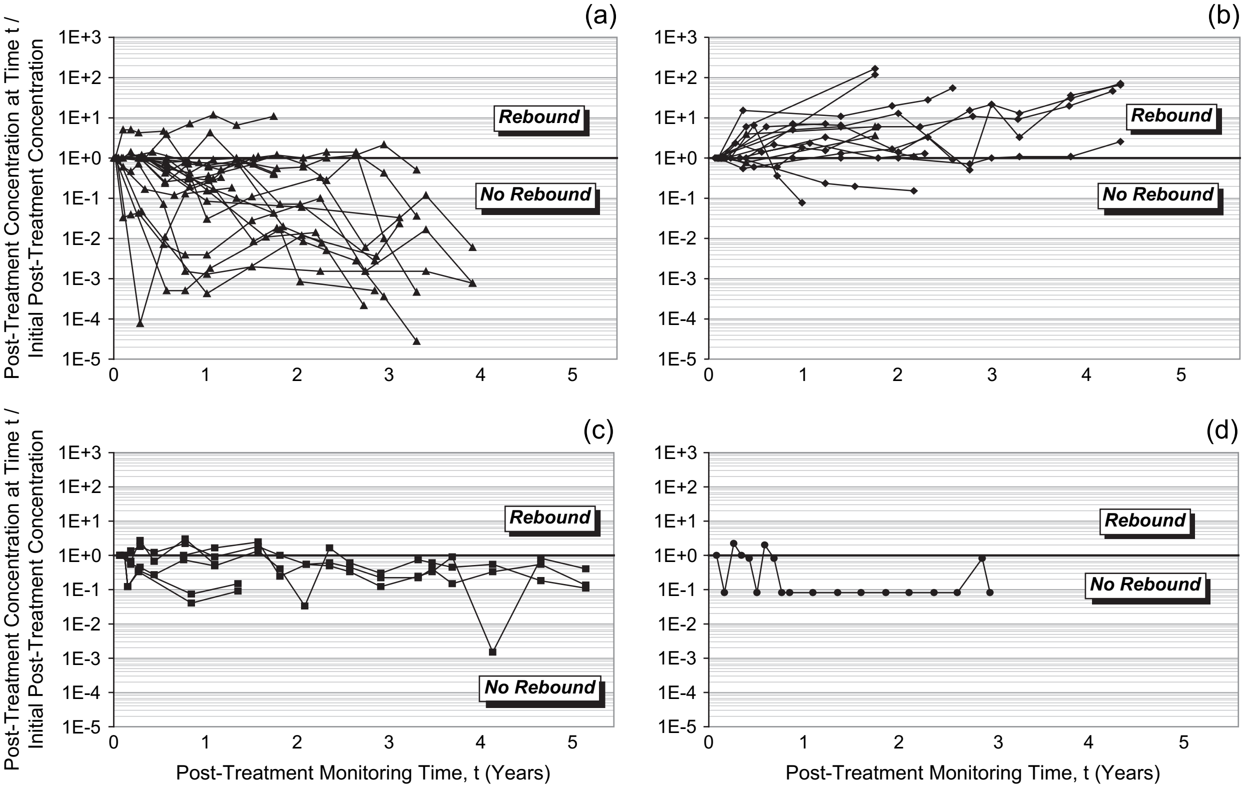

Figure 3. Change in posttreatment ground water concentrations. (a) Enhanced bioremediation sites ($n = 20$ wells); (b) chemical oxidation sites ($n = 16$ wells); (c) surfactant/cosolvent sites ($n = 6$ wells); (d) thermal treatment sites ($n = 1$ well).

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

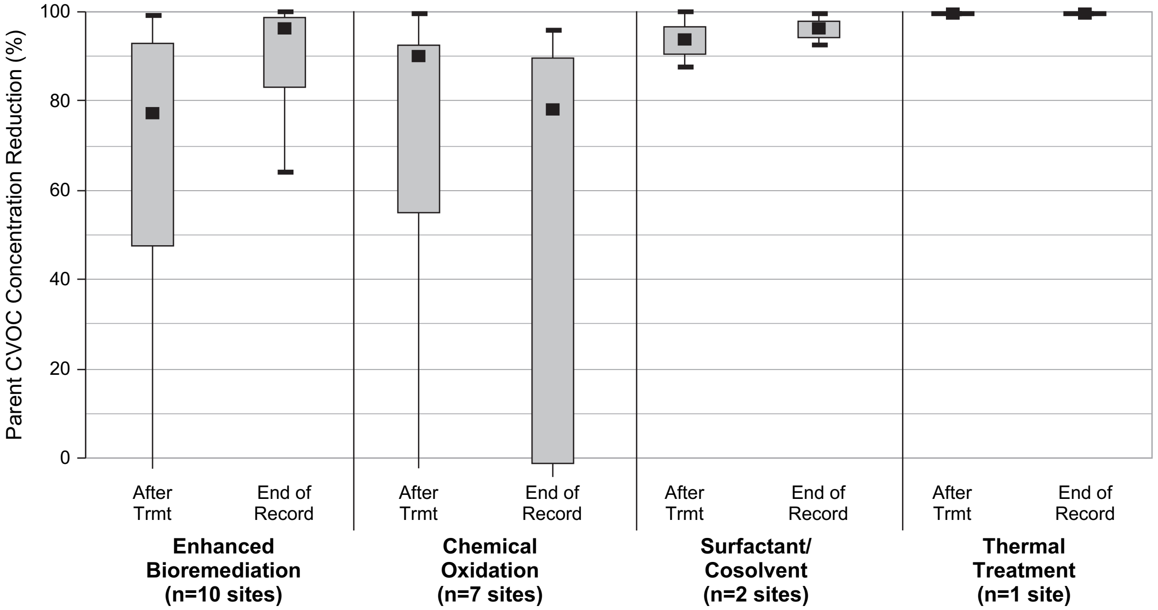

Figure 4. Rebound assessment at source depletion sites: concentration reduction from before treatment to immediately after treatment and at end of data record. Minimum reduction after treatment for enhanced bioremediation = −174%; minimum reduction after treatment for chemical oxidation = −9%; 25th percentile 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-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).

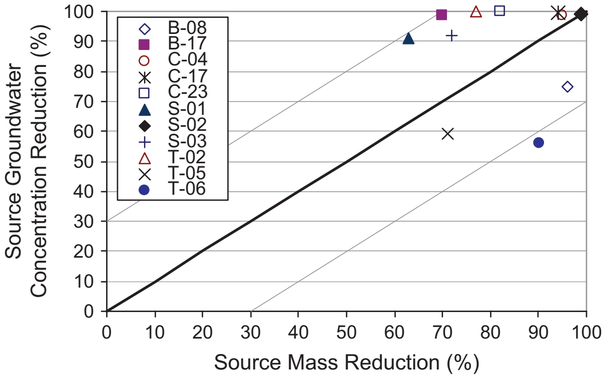

Figure 5. Calculated source zone ground water concentration reductions for reported source zone mass reductions at 11 source depletion sites. The black line represents directly proportional relationship between source mass reduction and ground water concentration reduction, and the gray lines represent ±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.

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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