# MULTIPLE LINES OF EVIDENCE SHOW CVOCs DEGRADING ON PLUMESTOP, LEADING SITE TO NFA STATUS

## CASE STUDY:
## Pilot Study Demonstrates PlumeStop's Longevity and Effectiveness to Treat CVOCs

REGENESIS®


This site was one of the original PlumeStop pilot tests for *in situ* groundwater treatment of CVOCs

Combined remedy approach proves successful in treating chlorinated solvents at former dry cleaner

## Introduction

# Question: Do Contaminants Biodegrade When Treated With PlumeStop?

This site is one of the original PlumeStop® pilot tests for *in situ* groundwater treatment of chlorinated volatile organic compounds (CVOCs or chlorinated solvents) at a former dry cleaner location in Marina, California. REGENESIS treated the CVOCs using a novel, sorption-enhanced reductive dechlorination (ERD) approach. This approach consisted of immediate sorption followed by the sequential elimination of chlorine from the CVOC molecules, transforming them into non-toxic end products such as ethene, carbon dioxide, and chloride. REGENESIS Remediation Services (RRS) applied the following remedial technologies as part of this pilot test demonstration:

PLUME STOP® Liquid Activated Carbon

HRC® HYDROGEN RELEASE COMPOUND

BDI® PLUS BIO-DECHLOR INOCULUM

This site provided ideal challenge conditions to demonstrate complete biodegradation using a sorption-ERD approach

In the early development of PlumeStop, the REGENESIS Research & Development team had demonstrated biodegradation of CVOCs through a battery of tests using a combination of PlumeStop, electron donors, and bioaugmentation substrates. Once proof had been established in the lab, REGENESIS sought to move the biodegradation demonstration to the field. Thus, the primary goal of this study, using field data obtained during the pilot test, was to address the following question:

## Are CVOCs biodegraded after sorbing onto a PlumeStop-treated aquifer matrix?

Periodically, this question arises in the environmental industry, challenging the approach of using colloidal activated carbon while trying to degrade CVOCs via ERD (i.e., the addition of electron donor and bioaugmentation substrates). Some believe that once the contaminants attach to the carbon, they are sequestered and not accessible to biodegrading microbes. In response, REGENESIS completed this pilot test to demonstrate CVOC biodegradation following the initial PlumeStop sorption effects. The pilot test was conducted in an aerobic aquifer, with no biodegradation evident at baseline, providing an ideal challenge condition for the demonstration.

The site was granted NFA status in June 2019 as a result of this pilot study

Through the effort to demonstrate complete biodegradation using a sorption-ERD approach, the impacted groundwater was fully treated, and the site was granted no further action (NFA) status in June 2019 by the State of California, Central Coast Regional Water Quality Control Board (CCRWQCB).


## Background

# REGENESIS Identifies a Chlorinated Solvent Pilot Test Site to Answer the Biodegradation Question

Historical spillage of dry cleaning solvents led to PCE contamination of groundwater.

The project site is a former dry cleaner in the city of Marina, located on the Central Coast of California. The dry cleaner operated from 1965 to 1999, and historical spillage of dry cleaning solvents led to sustained tetrachloroethene (PCE) concentrations in groundwater, observed since 2001. Limited site assessment activities had been conducted with no remediation completed before the PlumeStop pilot test.

In 2014, REGENESIS formally launched PlumeStop as a platform remediation technology. Some of the earliest sites were single-well pilot tests to demonstrate field performance, building on the knowledge gained from years of research and development.

In initial assessments, the Marina site had several attributes that made it an ideal candidate for an early field-scale pilot test to demonstrate that CVOCs are not merely sorbed out of solution but also biodegraded, following a PlumeStop application. These attributes included:

- The CVOC impact to groundwater was confined to a relatively small area, represented by a single monitoring well.
- Monitoring data demonstrated consistent PCE concentrations over several years, between 500 and 600 micrograms per liter (µg/L)
- No PCE degradation products (i.e., daughter products) such as trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), and vinyl chloride (VC) had been detected.
- The treatment area was within a naturally aerobic environment with a baseline dissolved oxygen (DO) concentration above 4 milligrams per liter (mg/L) and an oxidation-reduction potential of 250 millivolts.
- There were no detectable concentrations of *Dehalococcoides sp.* (DHC).
- In the treatment zone, the aquifer soil material was sand with little to no silt and clay, providing optimal conditions for minimizing potential complexities in performance dynamics.

The combination of consistent, non-degrading PCE, an aerobic environment, and no DHC, established that little to no biodegradation had been occurring prior to the pilot test. These conditions presented an optimal, clean starting point to assess CVOC biodegradation under the influence of PlumeStop.

# Treatment

## Pilot Testing One of the First-Ever PlumeStop Sorption-ERD Treatments

### Application Design Summary

**Contaminants of Concern**

PCE 550 µg/L

**Injection Information**

PlumeStop, HRC, BDI Plus

Direct Push Application
Injection Pressure Range:
10-34 psi

**Treatment Interval**

12-22 feet below ground surface

### Application Details

The pilot test area was centered on a single target monitoring well where residual PCE-impacted groundwater remained; the baseline PCE concentration was 550 µg/L. The application design was comprised of a grid array of injection points surrounding the target well. The target vertical injection interval fully encompassed the monitoring well screen, installed at 12 to 22 feet below ground surface (ft bgs), and extended to the top of the water table at approximately 7 ft bgs.

RRS injected PlumeStop, HRC, and BDI Plus in May 2014. A hydraulic percussion rig was used to drive to depth, utilizing 1.5-inch diameter drilling rods and attached retractable screens. The remedial fluids were mixed and applied through the rod-screen assembly at low injection pressures, ranging from 10 to 34 pounds per square inch. The volume of remedial substrates injected was equivalent to approximately 40 percent of the total pore volume in the target treatment zone.

### Treatment Mode of Action and Indicator Parameters

PLUMESTOP® Liquid Activated Carbon

PlumeStop is a colloidal form of activated carbon with a polymeric, biodegradable surface charge treatment that minimizes its interactions with the soil matrix as applied. The patented surface treatment allows it to move through soil pores easily, under low injection pressures, leaving a carbon coating on the soil matrix as it distributes from the injection point. Once in the subsurface, the polymeric coating is biodegraded, typically over a few weeks, allowing the colloidal carbon to attach to the soil surfaces permanently. The one to two-micron particle size creates a large surface area for sorption of contaminants and their removal from the aqueous phase, almost immediately upon contact.

HRC® HYDROGEN RELEASE COMPOUND

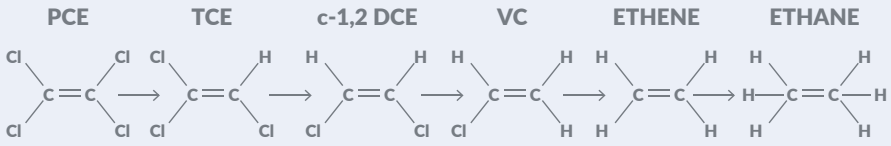
HRC is a low-volume, controlled-release hydrogen substrate that has been applied to ERD treatments of CVOCs in groundwater for over 20 years. BDI Plus is a live culture of *Dehalococcoides, sp.*, widely known to dechlorinate CVOCs completely and accelerate cleanup timeframes. In typical ERD treatments utilizing HRC and BDI Plus to treat dry cleaning solvents in groundwater, PCE is sequentially degraded through the daughter products TCE, cis-1,2-DCE, and VC to non-chlorinated and non-toxic end

BDI® PLUS BIO-DECHLOR INOCULUM

compounds such as dissolved gases, ethene, and carbon dioxide, and ionic species like chloride. These end products are highly mobile in water and non-sorptive; thus, they do not remain attached to the PlumeStop surface. By degrading contaminants to non-sorptive end products, the PlumeStop sorption sites are again made available to sorb more contaminants (i.e., regenerated).

### PCE Biodegradation Pathway

In typical ERD treatments utilizing HRC and BDI Plus to treat dry cleaning solvents in groundwater, PCE is sequentially degraded through the daughter products TCE, cis-1,2-DCE, and VC to non-chlorinated and non-toxic end compounds such as dissolved gases, ethene, and carbon dioxide, and ionic species like chloride.




**If it is true that CVOCs first attach to the PlumeStop, then are biodegraded to non-sorptive compounds, regenerating the PlumeStop, then it must also be true that the contaminants are accessible for the DHC bacteria to exchange chlorine for hydrogen on the individual CVOC molecules. In other words, DHC must be degrading contaminants at the carbon surface.**

However, it can be difficult to document biodegradation in a PlumeStop-treated zone if little or no daughter products are detected in groundwater — a desirable outcome. To observe contaminant biodegradation in these scenarios, one must do it indirectly through sampling and analysis of other parameters that indicate biodegradation.

To learn more about Microbial Insights' QuantArray analyses, visit microbe.com

Of these indicator parameters, microbial population response and activity provide robust lines of evidence of CVOC biodegradation. Only the presence of the dissolved gas ethene provides more potentially substantial evidence. However, ethene is frequently not detected on ERD treated sites when starting PCE concentrations are below 1 mg/L. Therefore, REGENESIS developed a groundwater monitoring plan that included sampling and analyses for dechlorinating microbes (DHC) and functional enzymes, which gauge the microbial activity level. Samples were submitted to Microbial Insights for QuantArray® analyses to obtain this information. Samples included a background collected prior to the application, and then at two weeks post application to establish the baseline population that resulted from the bioaugmentation with BDI Plus. Thereafter, samples were collected at one, two, three, nine, twelve, and fifteen months post application.

## Results

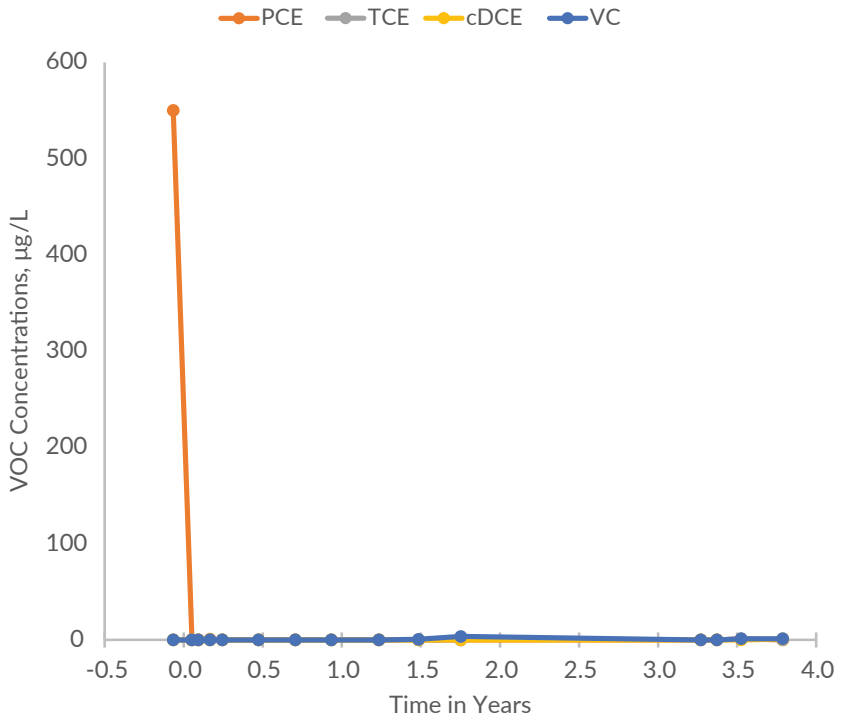
# With Groundwater Concentrations Reduced Immediately, Multiple Lines of Evidence Show CVOCs Degrading on PlumeStop, Leading Site to NFA Status

**99.9% CVOC Reduction**

CVOCs were reduced 99.9% within 19 days and remained below or near detection levels for nearly 4 years.

Following the treatment, total CVOC concentrations in groundwater were reduced by over 99% to non-detect (<5 µg/L) within 19 days, documenting the initial sorption effect from PlumeStop. CVOCs have remained below the US EPA 's drinking water maximum contaminant levels (MCLs) throughout the four-year monitoring period, except for a brief period of very low VC detections, reaching a maximum concentration of 5.6 µg/L, approximately two years following the application. This brief rise of vinyl chloride was only measured after the complete depletion of HRC, a common observation in the ERD process with the system is hydrogen-limited. However, the brief presence of this vinyl chloride was informative as it presented direct evidence that the biotransformation of PCE was occurring. REGENESIS re-applied the remedial reagents at that point to account for the hydrogen depletion and also to incorporate findings from recharacterization work completed after the initial application.

### CVOC Concentrations in Pilot Test Monitoring Well

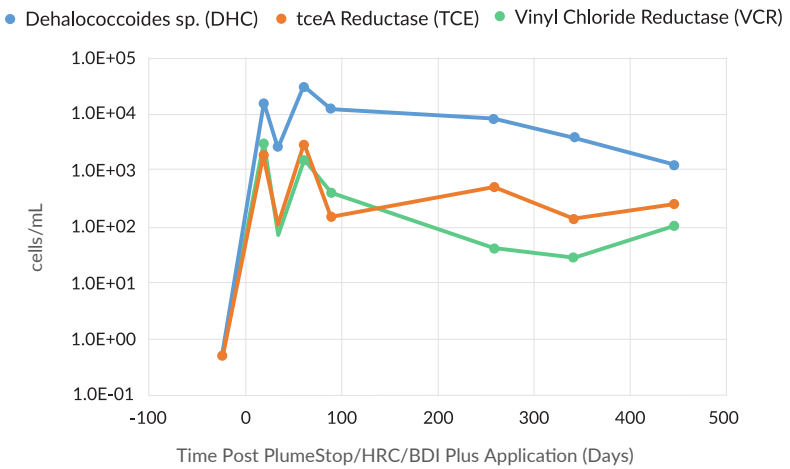


Oxidation-reduction potential (ORP) quickly stabilized at near-ideal conditions (-150 mV +/- 30 mV) post-application. Electron acceptors nitrate and sulfate decreased while dissolved iron increased within the first one to two months. These geochemical shifts indicated an optimal environment to promote ERD treatment of the CVOCs.

Microbial populations were sustained while CVOCs were reduced and remained poised near detection limits in groundwater following injection, indicating CVOC degradation after sorption onto PlumeStop carbon.

The microbial QuantArray data revealed an expected, marked increase in DHC and the functional enzymes from the background after the application of BDI Plus. The populations remained relatively constant over the next nine months followed by a slight decline. This decline correlated with a decrease in total organic carbon as the HRC was being depleted in this aerobic treatment zone. Had the sampling continued after the re-application of HRC, we may have anticipated an increase in the populations, so long as a sufficient food-source was also still fluxing into the treatment area.

DHC, tceA Reductase and Vinyl Chloride Reductase Concentrations Following Application




Populations of active dechlorinating microflora were sustained in the months following injection, even while CVOCs were below or near detection limits in groundwater through the same period. These observations indicate continued degradation of CVOCs after sorption onto PlumeStop carbon.

The site was granted NFA status following the pilot study.

In summary, the CVOC, biogeochemical, and microbial data collected during the pilot test monitoring program provide multiple lines of evidence for post-sorption degradation of the target solvents on the PlumeStop carbon surface. Therefore, based on the pilot test results the question posed earlier is confirmed. Biodegradation of CVOCs does occur once sorbed onto a PlumeStop-treated aquifer matrix. These findings led to the site being granted NFA status by the CCRWQCB.

## Technology Used

# PlumeStop, HRC, and BDI Plus

PlumeStop® Liquid Activated Carbon™ is an innovative groundwater remediation technology designed to address the challenges of excessive time and end-point uncertainty in the *in situ* remediation of groundwater contaminants. PlumeStop is composed of very fine particles of activated carbon (1-2µm) suspended in water through the use of unique organic polymer dispersion chemistry. Once in the subsurface, the material binds to the aquifer matrix, rapidly removing contaminants from groundwater, and expediting permanent contaminant biodegradation.

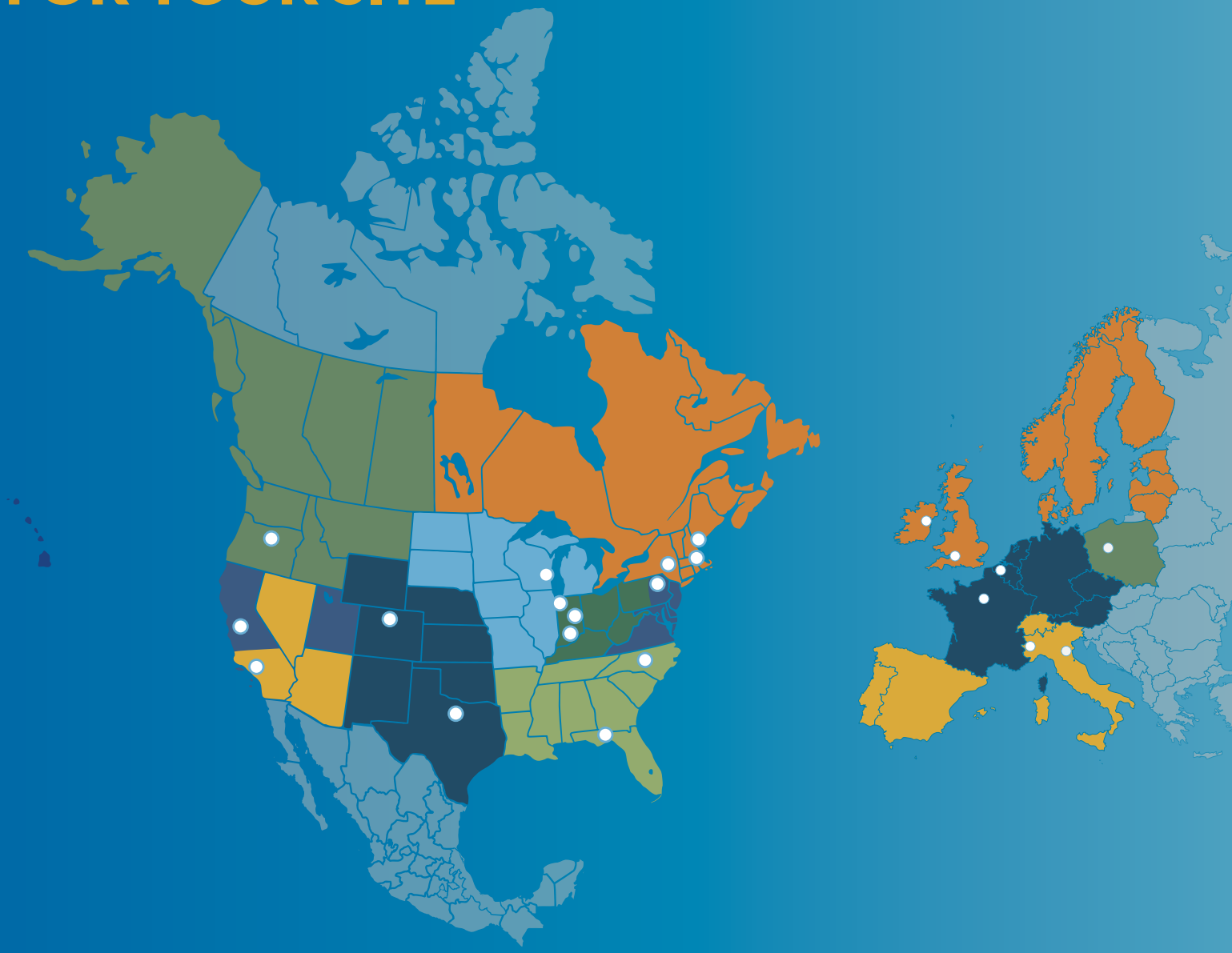
HRC® is an engineered, hydrogen release compound designed specifically for enhanced, *in situ* anaerobic bioremediation of chlorinated compounds in groundwater or highly saturated soils. Upon contact with groundwater, this viscous, poly-lactate ester material becomes hydrated and subject to microbial 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.

Bio-Dechlor INOCULUM Plus (BDI Plus)® is designed for use at sites where chlorinated contaminants are present and unable to be completely biodegraded via the existing microbial communities. BDI Plus is an enriched, natural microbial consortium containing species of *Dehalococcoides sp.* (DHC) which are capable of completely dechlorinating contaminants during *in situ* anaerobic bioremediation processes. BDI Plus has been shown to stimulate the rapid dechlorination of chlorinated compounds such as tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC). It also contains microbes capable of dehalogenating halomethanes (e.g. carbon tetrachloride and chloroform) and haloethanes (e.g. 1,1,1 TCA and 1,1, DCA) as well as mixtures of these halogenated contaminants.

REGENESIS®

# WE'RE READY TO HELP YOU

## FIND THE RIGHT SOLUTION FOR YOUR SITE




### Global Headquarters

1011 Calle Sombra
San Clemente, CA 92673 USA
Ph: (949) 366-8000
Fax: (949) 366-8090

### Europe

Bath, United Kingdom
Ph: +44 (0) 1225 731 447

Dublin, Ireland
Ph: +353 (0) 1 9059 663

Torino, Italia
Ph: +39 (0) 11 19781549

Ieper, België
Ph: +32 (0) 57 35 97 28

www.REGENESIS.com



REGENESIS®