

**LOW COST IN-SITU REDUCTION
OF
SOLVENTS, EXPLOSIVES, AND PERCHLORATE**
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Introduction

Enhanced reductive dechlorination (ERD) has become the remedy of choice for application to many chlorinated solvent releases in ground water when hydrogeologic and microbiological factors are favorable. Successful applications have been made to plumes of trichloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride utilizing vegetable oil, molasses, sodium lactate, and other proprietary solutions for substrate to promote the biological processes associated with reduction of chlorinated compounds. The work reported here sought to test a new, low cost substrate on these and other contaminants frequently encountered at military sites.

The paper begins with a summary of the ERD process and research comparing the value of different substrates relative to their ability to provide the desired hydrogen as an electron donor for subsequent reduction of target compounds. It then describes a source of substrate that is a low or no cost wastewater available throughout the country. Data are provided indicating the performance of that substrate on TCE and its degradates at a field scale, as well as perchloroethylene (PCE) used in dry cleaning and the solid rocket propellant ingredient perchlorate, both at a bench scale. The implication of the results are discussed and projected to other target species such as the military explosives RDX and HMX.

Background

Anaerobic reductive dechlorination is a naturally occurring biodegradation process whereby microbes can degrade contaminants such as chlorinated volatile organic compounds (VOC) in groundwater. The microbes use a primary substrate as a carbon based energy source, producing enzymes and other compounds that degrade organic compounds present in the groundwater. The process name of reductive dechlorination comes from the method by which these reactions strip chlorine atoms from VOC molecules present in the groundwater. To facilitate their respiration while they metabolize available carbon-energy source material, microbes must utilize electron acceptors. As electron acceptors are depleted, the groundwater environment becomes increasingly reduced electrochemically (i.e., lower oxidation-reduction potential [ORP]) and the microbes are forced to use successively less susceptible electron acceptors, ultimately using the chlorinated compounds as the electron acceptor.

Chlorinated solvents undergo a series of reductions through dechlorination reactions. For example, PCE is converted to TCE, then cis-DCE, VC, and finally ethene. More recently, work at private sites has demonstrated that ERD can be effectively used in the reduction of the perchlorate ion, while demonstrations at Pueblo Chemical Depot and Milan Army Ammunition Plant have shown applicability to the explosive compound RDX. In essence, the biochemical reactions would appear to function on oxidized species in solution, whether the oxidation state of the target chemical results from oxygen, nitrates, or halogens.

Reductive dechlorination in particular takes place only when all other redox reactions have been depleted. This means that species such as nitrate, sulfate, carbonate, and perchlorate are reduced through removal of the oxygen atoms before halogenated species are attacked. As a consequence, different suites of contaminants may react differently when subjected to reductive conditions and could result in generation of unacceptable by-products. Hence, there is a need to study the reactions and by-products for unique suites of contaminants prior to full-scale application, both to ensure the utility of the approach and to optimize operations and design.

Existing studies presented in the available literature indicate that the most common rate-limiting factors that result in slow, or minimal compound degradation in groundwater include one or more of the following:

- 1) Lack of sufficient organic carbon in the site groundwater.
- 2) Relatively mild redox conditions (often slightly aerobic).
- 3) Lack of the appropriate bacteria for the specific compounds to be degraded (specifically *Dehalococcoides*, or very similar microbes capable of degrading intermediate products).

Degradation is often slowed due to the depletion of natural organic carbon in the groundwater and less than optimal reducing conditions present in the aquifer (redox above -100 mV).

Enhanced reductive dechlorination (ERD) is achieved by altering the conditions in the subsurface through injection of biostimulation amendments and/or specialized cultures.

The goal of a biostimulation amendment is to provide a carbon source for driving the redox conditions lower and a hydrogen releasing compound that will serve as the electron donor. A wide variety of compounds have been used as biostimulation amendments for ERD applications. Some of the compounds include: sodium acetate, sodium lactate, methanol, ethanol, yeast extract, sodium sulfate, soybean oil, molasses, and HRC (a polylactate ester product sold by Regenesis). These materials have been successfully used in a variety of laboratory microcosm and field applications.

The considerations necessary in selecting a suitable biostimulation amendment include the nature, solubility, and viscosity of the material. Food-grade materials (or equivalent purity) are typically preferred to ease the permitting requirements regarding an injected material. Other considerations include unit costs of the material, the rate of fermentation to generate hydrogen, potential proprietary and/or patent considerations, and the success of other field applications using the specific amendment.

There are a variety of substrates that can be injected to enhance the in-situ biodegradation process. Several design/performance factors that need to be considered include:

- 1) Oxygen demand (chemical oxygen demand [COD] or biochemical oxygen demand [BOD]) of the substrate;
- 2) Theoretical volume of hydrogen that may be produced (based on reaction stoichiometry);
- 3) Actual efficiency of hydrogen generation;
- 4) Cost of the substrate; and
- 5) Rate and longevity of hydrogen generation.

Table 1. Comparison of Substrate Properties

Basic Substrate	Theoretical COD Demand ⁽¹⁾ (mol O/ mg substrate)	Theoretical H ₂ Yield ⁽²⁾ (mol/mol)	Observed H ₂ Yield ⁽³⁾ (mol/mol)	H ₂ Production Efficiency ⁽⁴⁾
Sucrose	0.07	8	1.8	23%
Glucose	0.1	4	0.92	23%
Molasses	0.07	8	1.8	23%
Lactate	0.05	2	0.01	0.50%

(1) Theoretical COD demand is based on 100% conversion of substrate to carbon dioxide (CO₂) and water.

(2) Theoretical hydrogen yield is based on stoichiometric equations and assumes reaction to acetic acid, CO₂ and hydrogen.

(3) Observed hydrogen yield is based on experimental measurements reported by Logan et al, 2002.

(4) Production efficiencies are comparisons of the theoretical yield and actual measured yield.

Approach

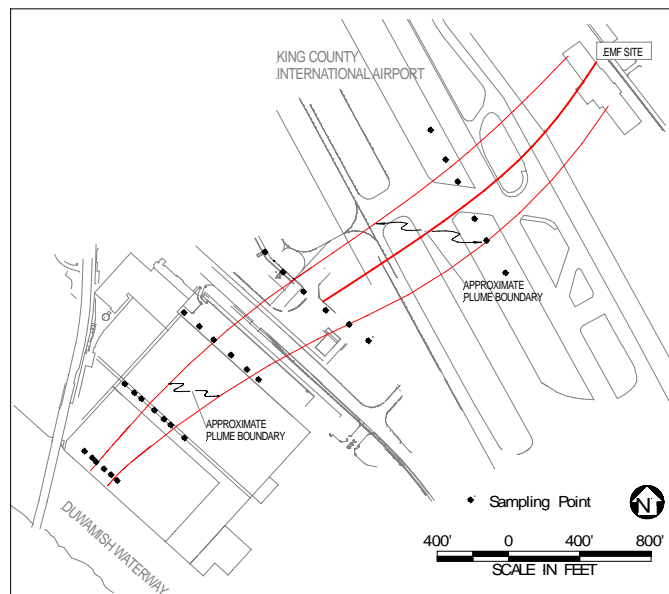
Use of a new, low cost substrate was tested in a groundwater remediation demonstration project for an international aerospace manufacturing corporation. The project site is a former manufacturing facility that used solvents for cleaning/degreasing operations. Inadvertent discharge of solvents resulted in a VOC plume within groundwater that extends 3,600 feet from the plant in a plume that is 150 to 450 feet wide and 15 feet thick, as depicted in Figure 1. After implementation of in-well stripping and in-situ chemical oxidation in the more concentrated source area, ERD was selected for application to the residual plume. Primary constituents in the residual plume are dichloroethylene (DCE) and vinyl chloride (VC).

Initially, ERD was implemented using reagent grade sodium lactate. Solutions in the range of 10 percent sodium lactate in water were mixed on site and pumped into injection wells in the pilot test area. Monitoring wells were then sampled periodically to determine both the rate of removal of the primary constituents and rate of evolution of ethane, the non toxic by-product from degradation of chlorinated ethylenes. After successful completion of the pilot, the decision was made to transition to a low cost alternative substrate for the full-scale project.

The project objective was to evaluate enhanced reductive dechlorination (ERD) of VOCs in groundwater using a food industry wastewater and concentrates that otherwise would cost the producer to dispose in a publicly owned treatment works (POTW). Use of this substrate offered a beneficial re-use of a former waste-product stream and allowed the property owner to realize significant cost savings. The wastewater was available in solutions containing anywhere from several 3 to 12 percent sugar. On occasion, concentrations as high as 30 percent can be obtained. The higher concentrations reduce injection times for achieving any given level of substrate loading and allow for placement of substrate inventories that will support prolonged reducing conditions.

As depicted in Figure 1, the plume extends several thousand feet from the source area under a runway complex and ultimately discharges in to the adjacent waterway. The plume was initially mapped through installation of a series of 31 direct push geoprobes in six transects installed perpendicular to the axis of the flow.

Figure 1. Plume Configuration



Existing site conditions within the VOC plume include ongoing biodegradation processes that remove VOCs. It was therefore important to evaluate any ERD performance data relative to existing baseline degradation rates. The baseline and ERD degradation rates can also be a useful comparison for the FS evaluation of options in regards to the expected time frame for remedial action, the expected mass removal rate for comparison criterion based on reduction in toxicity/mobility, etc., and for evaluating the cost-effectiveness of an ERD application.

All of the calculated degradation rate constants are based on a first-order removal process (i.e., $C = C_0 e^{-kt}$) and use the measured site data to derive an empirical rate constant, k). The site VOC concentration data exhibit variability and the calculated rate constants contain significant uncertainty; however the calculated rate constants are used primarily for relative comparison between options hence the effects of the uncertainty are more limited because of the relative comparison.

The baseline degradation rate is calculated based on the spatial distribution of the VOC plume (concentrations declining over distance assuming a steady state plume shape), and converting to a rate constant using the calculated groundwater velocity. The VOC data from the site to the Waterway are shown in Figure 2 and the rate constant is calculated as 0.0012 (1/days), this corresponds with a half life ($T_{1/2}$) of 19 months. These empirical parameters are derived by a least squares fit of the 1st order degradation model to the measured site data and the calculated site groundwater velocity (derived from an aquifer pumping test).

The measured VOC data also indicate a likely reduction in the rate constant over the last ~ 1,500 ft of the plume from the west side of the airport. This may be due to a variety of factors potentially including changes in geochemistry, substrate availability, and VOC type (such as depletion of natural organic matter present in the groundwater, or elimination of the TCE fraction of the VOC plume which is typically biodegraded more rapidly than the DCE and VC fractions). Based on some group of processes/changes, the degradation rate appears to diminish over the second half of the plume.

The same degradation rate analysis can also be applied to the VOC plume from the west side of airport the Waterway. The data from this area (normalized to the peak total VOC concentration in the area on the west side of airport) are shown in Figure 3 and the rate constant is calculated as 0.0011 (1/days), this corresponds with a half life of 21 months. This second rate constant is considered more representative because it is based solely on the site data directly from the area of interest where the pilot test was conducted.

The analysis of site data to derive a degradation rate under the ERD conditions can also be completed for the data from the pilot test injection wells (IW1, IW2, and IW3) and the down gradient monitoring well (WF-33). The data from the injection wells (presented as average reduction of all 3 wells over each time period) are shown in Figure 4. The rate constant is calculated as 0.0125 (1/days), this corresponds with a half life of 1.8 months. Calculation of rate constants for each well individually provides very similar results but the average of all 3 wells provides some smoothing of the data and a slightly better fit to the process model. This empirical rate constant for the ERD condition also includes expected variability due to the depletion of substrate before subsequent injections occurred (these wells are the upstream edge of the pilot area and the up gradient VOCs migrate into this zone).

The data from the down gradient monitoring well are shown in Figure 5. The rate constant is calculated as 0.031 (1/days), this corresponds with a half life of 0.7 months.

A comparison of the empirically calculated rate constants and half lives are shown in Table 2. A general comparison of the expected effects over the range of rate constants calculated is shown in Figure 6. The

actual field implementation will take significantly longer because of the travel time required (approximately 1 year) for the substrate to travel between injection zones

Table 2 Comparison of Empirically Calculated Degradation Rate Constants

Basis for rate constant	Rate constant k, 1/days	Half-life Months	Calculated time for 99% destruction (~ 7 half lives) Years
Baseline	0.0011	21	12.2
IW- wells data	0.0125	1.8	1
WF-33 data	0.031	0.7	0.4

Figure 2. Site Data Used to Derive Rate Constant; Whole Plume

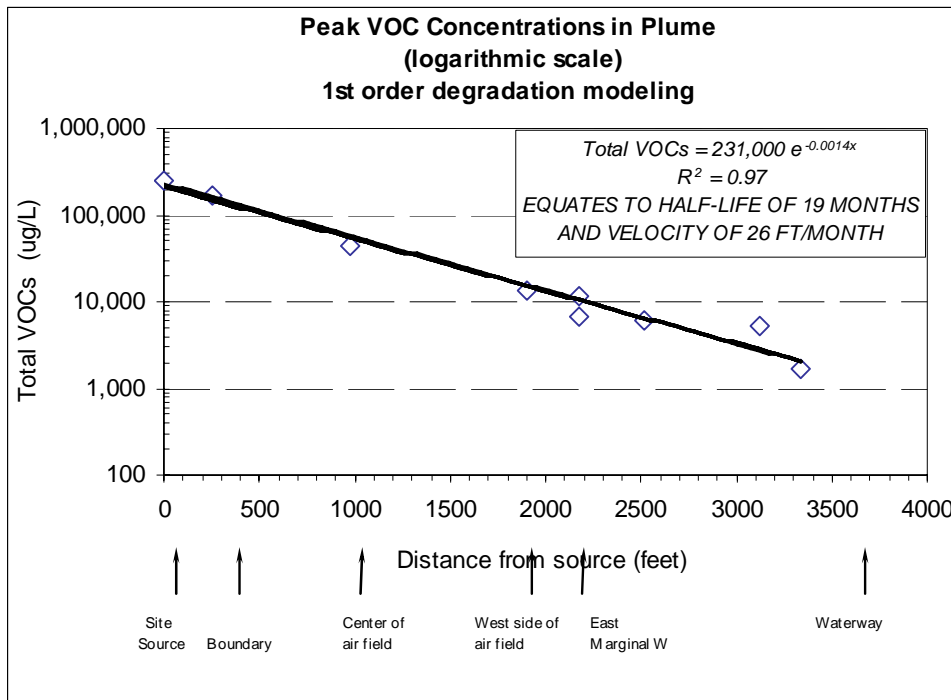


Figure 3. Site Data Used to Derive Rate Constant in Pilot Test Area

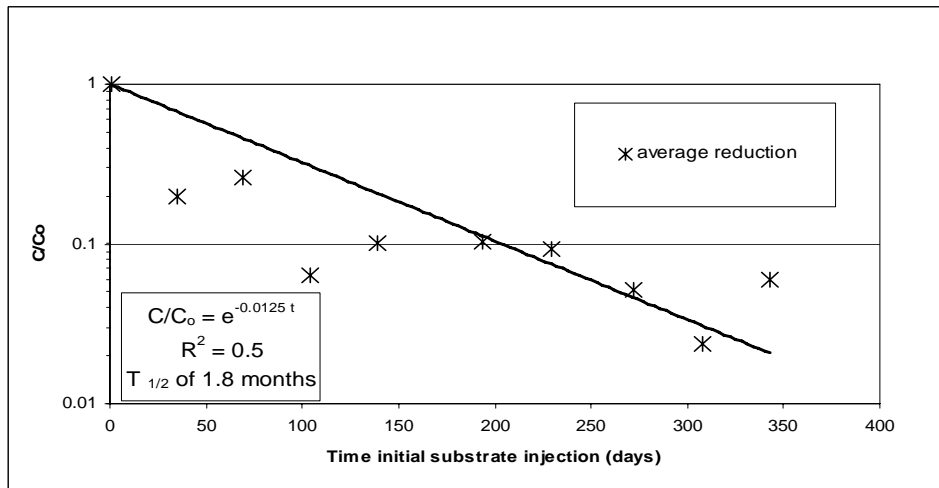


Figure 4. Pilot Test Data from Injection Wells Used to Derive Rate Constant for ERD Condition

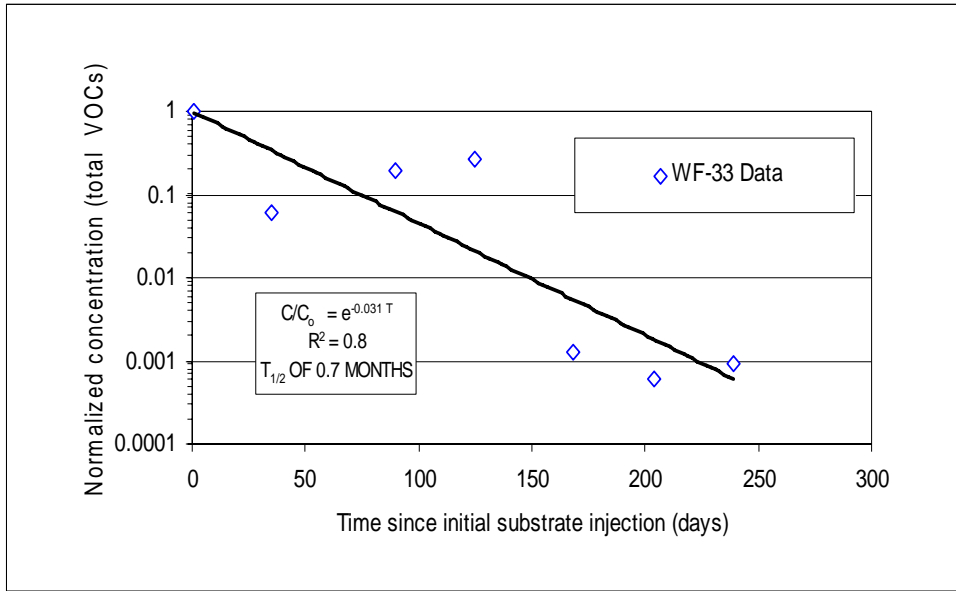


Figure 5. Pilot Test Data from WF-33 used to Derive Rate Constant for ERD Condition

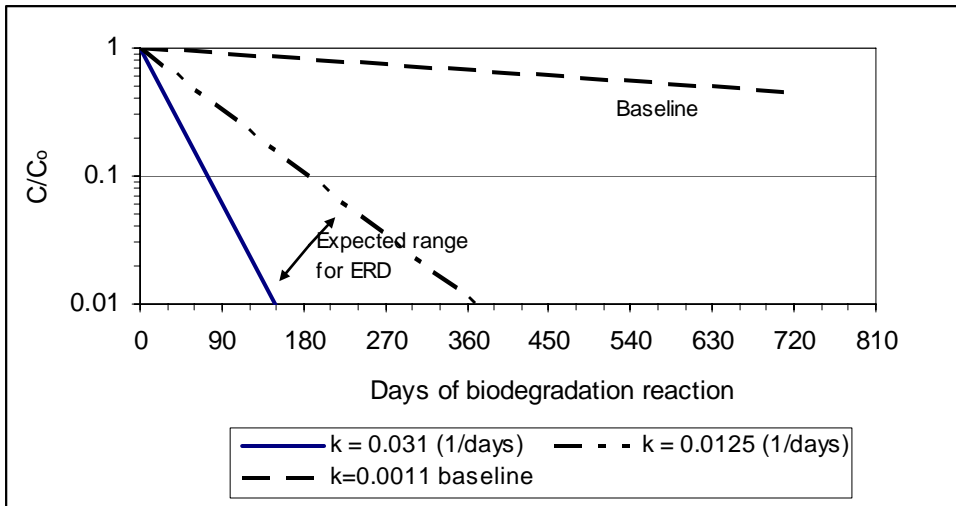


Figure 6a. VOC Monitoring Data Demonstrating Degradation Rates: Well IW-2

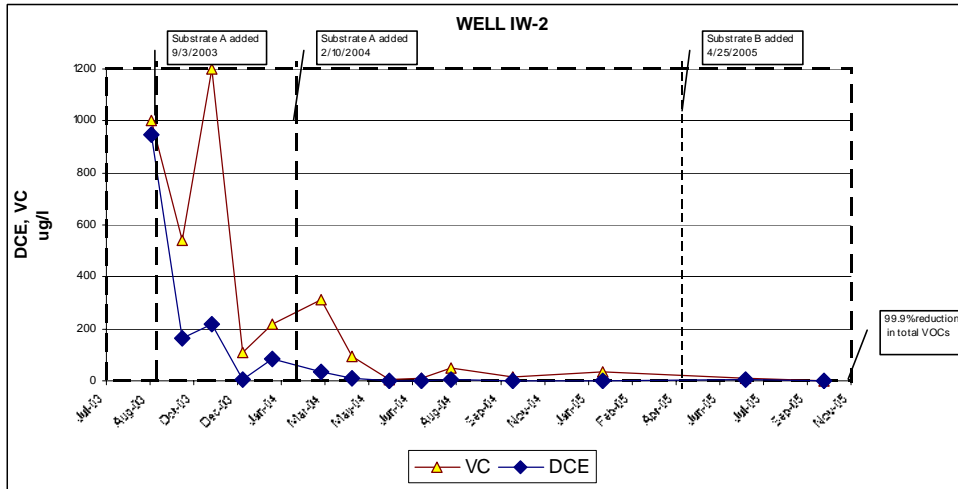
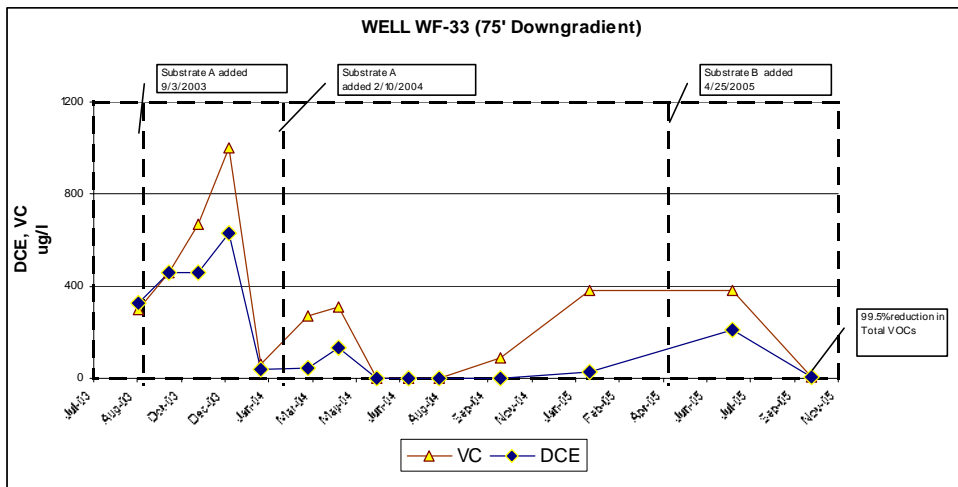


Figure 6b. VOC Monitoring Data Demonstrating Degradation Rates: Well WF-33



Results

Based on the impressive results from this demonstration project, the property owner has proceeded with full scale design and implementation of treatment throughout the VOC plume that extends for over 3,500 ft. Contaminant concentrations have continued to decrease over time. While it is not possible to shut down operations and address the entire plume at once, the migration of the plume allows for treatment at the down-gradient edge of the plume until all of the plume has moved from under the runway. In addition, runway maintenance periods are being reviewed to determine if time periods are available when injections could be made through the tarmac during a hiatus in flight operations.

Summary and Conclusions

The use of the low cost substrate has proven effective and economic when applied at a field scale to TCE-DCE-Vinyl Chloride contamination. In order to determine the breadth of the application potential, bench-scale tests were also conducted on the dry cleaning solvent perchloroethylene (PCE) and the solid rocket propellant oxidizer ammonium perchlorate.

The bench test with PCE contaminated groundwater was collected from a site that was initially in an oxidized state (reductive dechlorination was not occurring) and the test was planned to include both biostimulation and bioaugmentation. All samples spiked to an initial level of 1,000 ug/l PCE and the test included bioaugmentation with bacteria known to be capable of reductive dechlorination. The bench test results are presented in Table 3 which shows a rapid and complete reduction of PCE to ethene for the tests which included bioaugmentation.

Table 3. Microcosm Test Results with PCE

	Start date	NO ₃ Reduced by day 6	SO ₄ Reduced by native bacteria by day 22	Bio-augment day 22	Sulfate Reduced by day 41	PCE → TCE by day 27	PCE → VC by day 61	PCE → Ethene by day 61
Killed control	3/24	n.a.	n.a.	n.a.		0 %	0 %	0 %
Lactate donor	3/24	100 %	0 %	yes	100 %	0 %	3 %	97 %
Whey donor	3/24	100 %	67 %	yes	100 %	18 %	0 %	100 %
Whey donor, no bioaugmentation	4/28	n.a.	n.a.	No	no bioaug	n.a.	n.a.	n.a.

n.a. = not analyzed

Detection Limits, ug/L: VC = 4, cDCE = 20, TCE = 14, PCE = 20 all in ug/L

In a similar bench-scale test, ground water from a former solid rocket production facility containing 300 ppm perchlorate was treated with the wastewater substrate. Within 30 days of application, the perchlorate had been reduced to concentrations below the detection limit. These results appear to match unpublished results from field applications at the facility and suggest ERD may be effective with perchlorate. Similarly, field applications on explosives such as RDX have also been reported to be successful. If the low cost substrate is equally effective, significant cost savings may be possible with introduction at military sites.

The implications of these results are far reaching. In addition to the obvious fact that ERD is applicable to a broad range of contaminants, it is clear that when substrate is free, the entire strategy for injection is changed. In particular, free substrate means there is no penalty for injecting more substrate than is stoichiometrically required. As a consequence, injection should be limited only by the volume of substrate that can be injected in each well. The benefits of the higher substrate dosing include:

1. Costs reduced by 25 to 50 percent because chemicals need not be purchased;
2. Excess reducing power in the event matrix requirements have been underestimated and it takes more substrate to reach the desired lower oxidation state;
3. Lengthened time over which reducing conditions can be maintained, thus reducing the number of re-injections required;
4. Fewer campaigns to inject substrate that reduce labor and mobilization costs; and
5. Increased ease of acceptance due to use of food grade, consumer products with which the public is familiar.

Given these factors, ERD is rapidly becoming the preferred option for remediation of groundwater contamination, as well as a means of reducing life-cycle cost and closure time for ongoing remedies such as pump and treat. With the reduced cost, ERD can be implemented in plumes with active pump and treat systems in order to accelerate reaching a concentration at which the remedy can be transferred to monitored natural attenuation.