IN SITU/EX SITU ACCELERATED ANAEROBIC REDUCTION OF PERCHLORATE

William Smith, P.G., ***Kevin A. Morris, Bioremediation Specialist*** (kmorris@envalliance.com), and Christopher Underwood, P.E.
(Environmental Alliance, Inc., Wilmington, Delaware)

ABSTRACT: The anaerobic reduction of perchlorate via indigenous subsurface bacteria is fast becoming a widely accepted tool for the remediation of perchlorate-impacted soil and groundwater. Pilot tests were initiated in 2001 to determine the applicability and effectiveness of stimulating the anaerobic biological treatment of soils and groundwater. Anaerobic composting was demonstrated as an effective ex situ method for treating heavily perchlorate-impacted soils, reducing perchlorate concentrations in site soils from approximately 40 mg/kg to non-detectable levels (i.e., less than 0.01 mg/kg) within 9 to 12 months. The use of an infiltration gallery in conjunction with a soluble substrate (i.e., calcium magnesium acetate) feed system was demonstrated as an effective technique to flush perchlorate from vadose zone soils and create an in situ anaerobic treatment zone in shallow groundwater. The use of a series of injection points to create a subsurface biobarrier composed of insoluble substrate (i.e., recycled vegetable oil) was also proven to be an effective method of creating an in situ anaerobic treatment zone for perchlorate-impacted groundwater. Reductions in perchlorate concentrations in groundwater of 89% and 44% were observed for the infiltration gallery and biobarrier areas, respectively.

INTRODUCTION

Several pilot tests were initiated to determine the applicability and effectiveness of stimulating the anaerobic biological treatment of soils and groundwater via the introduction of carbon-based electron donor substrates at an industrial site. The pilot study activities were focused within and immediately downgradient of a source area with maximum identified soil and groundwater concentrations in excess 50 mg/kg and 600 mg/L of perchlorate, respectively.

The four main geologic strata identified at the site include: silt/clay, silty sand, gravel with sand, and loose fine sands underlain by a clayey aquitard zone. The confining clay zone beneath the surface aquifer has been identified across the site and appears to be acting as an aquiclude. The in situ pilot testing addressed shallow vadose zone soils (0 to 2.4 meters below ground surface [bgs]), deeper vadose soils (2.4 to 4.6 meters bgs), shallow zone groundwater (4.6 to 6.2 meters bgs), and intermediate zone groundwater (greater than 6.2 and less than 10.7 meters bgs). Low permeability soils encountered at the site presented challenges regarding the development of effective substrate delivery methods.

Based on the results of the pilot tests, three remediation techniques proved to be successful methods for the treatment of perchlorate-impacted soil and groundwater.

Pilot Test - Biocell. Soil containing elevated concentrations of perchlorate was excavated and hauled to an onsite "biocell" for bioremediation via anaerobic composting. The purpose of this pilot test was to determine the applicability of reducing perchlorate concentrations in soil using an aboveground (i.e., ex situ) biocell.

Pilot Test - Infiltration Gallery. The intent of the infiltration gallery is to deliver soluble substrate to the deeper vadose zone soil to promote the biodegradation of perchlorate and to flush perchlorate from the deeper vadose zone soil into the groundwater to enhance perchlorate bioavailability for subsequent treatment via in situ anaerobic reduction.

Pilot Test - Biobarrier. This type of in situ biobarrier system involves the periodic addition of an insoluble substrate into the subsurface via a series of injection points to create an anaerobic treatment zone along the leading edge of the dissolved perchlorate plume.

MATERIALS AND METHODS

Pilot Test - Biocell. Field screening of soil during excavation using the ion selective electrode (ISE) method guided the selection of soil to be placed in the ex situ biocell. A composite sample of 34 field screening soil samples was collected and sent to a laboratory for analysis by ion chromatography (IC) as a confirmatory baseline sample. This analysis, which reflected the average perchlorate concentration for the new biocell, yielded an initial composite perchlorate concentration of 42 mg/kg.

The biocell consists of approximately 76 cubic meters of soil taken from the perchlorate source area excavation. Prior to transportation of the excavated soil to the biocell location, hardwood sawdust was added as a bulking agent at an approximate ratio of 10:1 soil to sawdust. The augmented soil was then transported to the area proposed for biocell construction. The new soil was mixed with actively composting soil from an existing biocell to introduce additional substrate and active perchlorate-reducing bacteria. Calcium magnesium acetate (CMA) was added to the biocell to test the feasibility of using this additional carbon source to promote anaerobic activity in the biocell. Shredded and rotting prairie hay was added as an additional carbon source. The soils added to the biocell were thoroughly mixed and leveled with a backhoe.

Upon completion of biocell construction activities, approximately 60 meters of 1.9 cm (¾-inch) diameter rubber sprinkler hose was placed across the top of the biocell. This hose was used to facilitate the addition of substrate and water (as needed to maintain the moisture content required to support the anaerobic biodegradation process) without uncovering the biocell. Prior to placing the 18-mil plastic cover over the biocell, all groundwater generated during pilot test activities was added to the biocell for treatment and to assist in maintaining moisture levels within the biocell. Water from the existing biocell sumps was also used to thoroughly saturate the new biocell to achieve the desired moisture level. The top cover was placed over the biocell such that at least one meter of the cover overlaid the retention berm. Landscaping timbers were laid end to end to keep the cover in place. Except for periodic sampling and water addition to maintain desired soil moisture levels, the biocell was left covered and undisturbed to promote the establishment and maintenance of anaerobic conditions.

Pilot Test - Infiltration Gallery. The excavation resulting from soil removal activities associated with the biocell was used to construct an infiltration gallery to treat residual soil contamination. During excavation, a sampling grid was established and soil samples were collected from the bottom of the excavation after the removal of each lift to delineate the vertical distribution of perchlorate in the subsurface. The excavation was completed to a depth of 3.7 meters below ground surface (bgs). As stated, the most heavily perchlorate-impacted soil was transported to the biocell for treatment. The remaining soil, which exhibited lower or non-detect concentrations of perchlorate, was eventually returned to the excavation. Groundwater was not encountered during excavation.

Upon completion of the excavation to 3.7 meters bgs, installation of the electron donor delivery system was initiated. First, the excavation was backfilled with approximately 0.3 meters of pea gravel. Three lengths of corrugated black poly perforated pipe were placed on the pea gravel to serve as conduits for substrate delivery. This pipe was connected directly to a Schedule 40 PVC manifold and riser assembly. After installation, the substrate distribution piping system (i.e., the perforated pipe, manifold, and riser) was covered with an additional one meter of pea gravel. Filter fabric and a 15-centimeter layer of hardwood sawdust were placed on top of the pea gravel to prevent fouling of the pea gravel and piping by soil fines down-washed from overlying soil. The remainder of the excavation was backfilled with native soil to approximately 10 centimeters bgs. A layer of 6-mil plastic sheeting was placed over the backfilled excavation, and additional soil was placed over the plastic to allow for reseeding. The substrate distribution piping system in the infiltration gallery was connected to a venturi feed system. The venturi feed system includes a venturi injector with associated valves, pressure gauges, and flow meters required to control and monitor substrate feed rate. A 2,800-liter (750-gallon) tank for storage of substrate solution was located adjacent to the venturi feed system.

The infiltration gallery was designed to facilitate the cyclic addition of extracted groundwater amended with substrate into the subsurface. A monitoring well was installed within the infiltration gallery to approximately 3.7 meters bgs to enable water level measurement. An extraction well was installed approximately 7.6 meters downgradient of the infiltration gallery. The extraction well was fitted with a submersible stainless steel pump and connected to the venturi feed system via a buried black poly line. A high-low water level controller was installed within the monitoring well to control operation of the submersible well pump. Under normal operating conditions, the pump is activated when the water level in the infiltration gallery falls below 3 meters bgs, and deactivated when the water level reached 2.4 meters bgs to maintain water levels within the clay zone and not within the overlying perched zone. A failsafe control was installed in the extraction well to prevent operation of the pump when the groundwater level falls to within 0.2 meters of the top of the pump.

Pilot Test - Biobarrier. The biobarrier was created by injecting an insoluble substrate into the more permeable shallow aquifer zones via one 2.5-cm (one-inch) and three 5.0-cm (two-inch) diameter injection points. The flow rate and backpressure were monitored during injections in an effort to prevent short-circuiting of the substrate

solution through the annular well seal. An improved well seal design was also developed and utilized to minimize the short-circuiting at the injection points. The substrate injection system consisted of a 2,800-liter (750-gallon) storage tank filled with a vegetable oil in water emulsion, an air-driven dual diaphragm pump, a ball valve, a flow meter, a pressure gauge, and the associated tubing, piping, and fittings.

The monitoring system for the biobarrier consisted of a series of shallow and intermediate monitoring wells located upgradient, within and downgradient of the biobarrier created via IP's 1-4 (refer to Figure 1). The shallow monitoring wells were constructed with screens exposed to the water-bearing sands and gravel of the shallow aquifer (3.4 to 6.4 meters bgs). The intermediate monitoring wells were constructed with screens exposed to a deeper interval within the shallow aquifer (7.6 to 10.7 meters bgs).

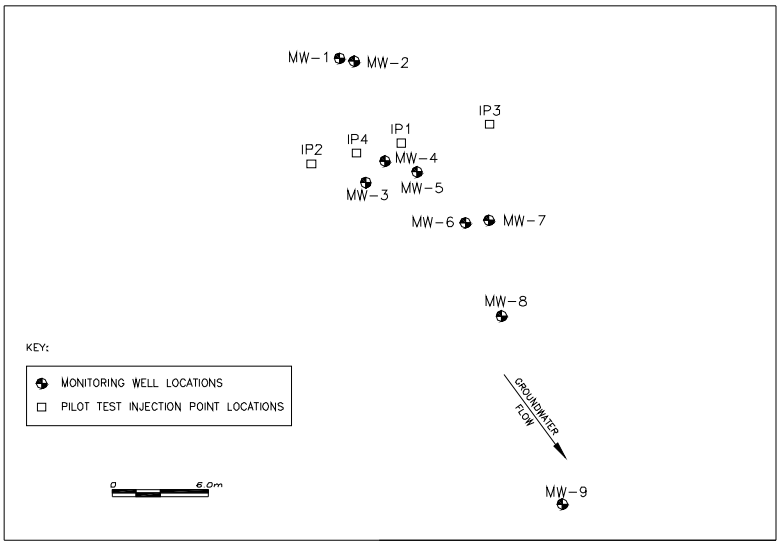


FIGURE 1. Monitoring well system for biobarrier pilot test area

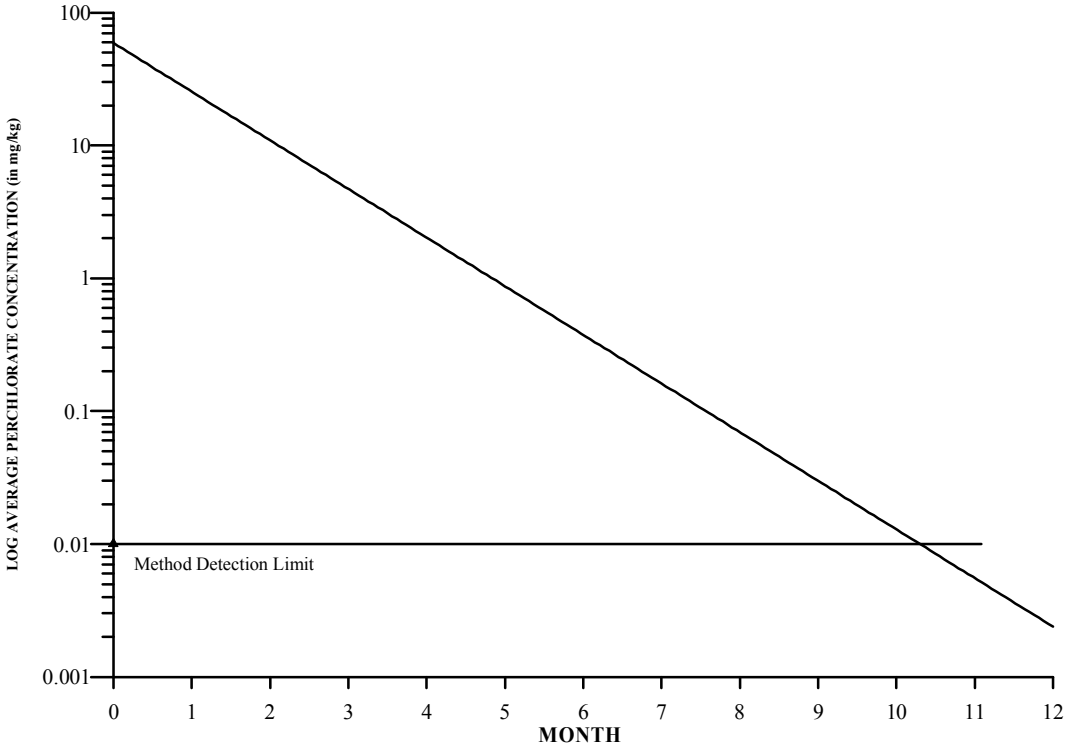
RESULTS AND DISCUSSION

Pilot Test - Biocell. During December 2001, prior to placing the cover over the biocell, soil samples were collected using a hand auger at four locations (i.e., A, B, C, and D) at depths of 15 and 60 centimeters. This sampling event represents the baseline laboratory analysis for the biocell soils. All sampling locations had measurable levels of perchlorate except for location B. The average perchlorate concentration for the samples collected from the other locations (i.e., A, C, and D) was 37.3 mg/kg. The non-detect analyses for both soil intervals at sampling location B for this event may be attributed to an excess of bulking agent/substrate (hay) in the soil samples.

During the spring sampling event, the biocell was observed to be noticeably drier on the exterior. Since bacterial activity requires moist conditions, it was determined that the biocell needed to be rehydrated. The sump water beneath the biocell liner was the most logical source of water containing perchlorate-reducing bacteria, so a sample was collected to determine if any perchlorate remained in this water. The sampling analysis report indicated no detectable concentration of perchlorate, so the sump water was deemed suitable for use on the biocell. The decreases in perchlorate concentrations in the

biocell soil can be attributed to the rehydration of the biocell with approximately 5,700 liters of sump water over a three-month period and the concurrent increase in ambient temperatures, which have stimulated bacterial activity. To improve the distribution of moisture and substrate within the perchlorate-impacted soils and accelerate perchlorate degradation, remixing (turning) of soil in the biocell was conducted.

In the eleven months of operation of the biocell pilot test, all sampling locations have exhibited fluctuations in perchlorate concentrations ranging from a high of 307 mg/kg to non-detect at several locations. These fluctuations are probably due to the initial variation of perchlorate concentrations in the soils. However, when the perchlorate concentration data sets are averaged, a significant decreasing trend is observed, from the initial composite concentration of 42 mg/kg to the most recent sampling event indicating no detectable perchlorate concentrations in the biocell soils (i.e., less than 0.010 mg/kg) (refer to Figure 2). This represents an estimated 100 % decrease in perchlorate concentrations.



Note: 12/03/02 data point denotes one-half the detection limit. Result was non-detect to 10 ug/kg.

FIGURE 2. Average perchlorate concentration in soil over time for biocell

Pilot Test - Infiltration Gallery. During excavation of the infiltration gallery, the presence of perched groundwater was observed in the shallow silt and fill layer that overlies the clay layer in which the infiltration gallery was constructed. The interface between these layers exists at a depth of approximately 1.7 meters. Soil at the interface was moist to wet and some seepage of perched groundwater into the gallery was occurring. After a series of heavy rains, the shallow silt and fill layer was observed to be fully saturated and the water level in the gallery was observed to rise until it reached a relatively shallow depth (i.e., approximately 0.6 meters bgs). Subsequent monitoring

consistently indicated high water levels in the infiltration gallery, precluding operation of the infiltration gallery system as originally intended. However, substrate was added to the infiltration gallery via the venturi feed system by recirculating water directly from the infiltration gallery. For this pilot test, calcium magnesium acetate (CMA) was selected as the substrate, although the layer of sawdust within the gallery acted as an excellent substrate as the sawdust was degraded.

In general, decreases in nitrate and dissolved oxygen concentrations in groundwater were observed concurrently with decreases in perchlorate concentrations and the detection of acetate. These observations were positive indications that perchlorate and substrate were leaching through the clayey vadose zone soil adjacent to and below the infiltration gallery. This mobilization of perchlorate into the shallow groundwater has increased the bioavailability of perchlorate and acetate, and has created an effective treatment zone that is anaerobically reducing the perchlorate as it enters the groundwater. Perchlorate and chlorate concentration trends in groundwater samples collected from a monitoring well located approximately 12 meters downgradient of the infiltration gallery are presented in Figure 3. Overall, an 89% reduction in perchlorate concentration in groundwater was observed at this monitoring well.

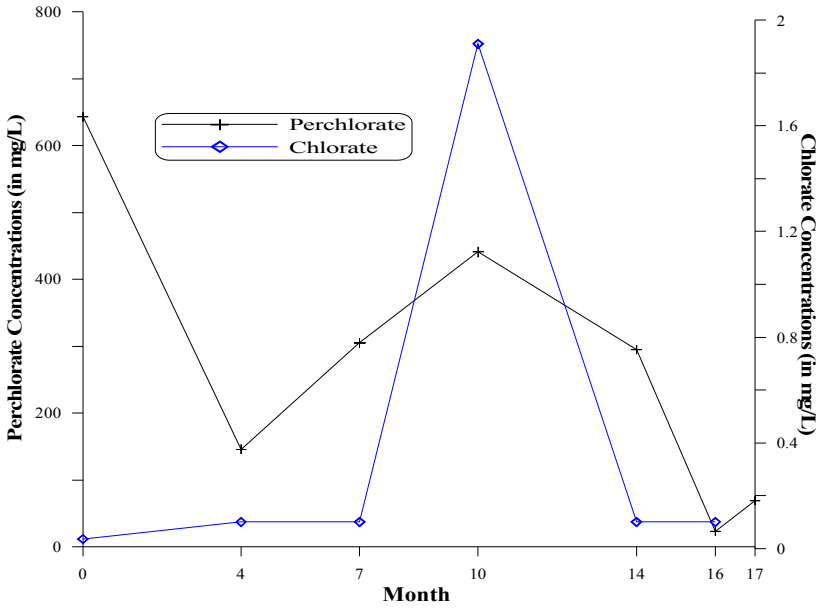


FIGURE 3. Perchlorate and chlorate concentrations in groundwater over time for downgradient monitoring well

Pilot Test - Biobarrier. Overall, the injection of substrate to create an in situ biobarrier was successful. CMA was injected as a buffer for acidic conditions that were detected in the shallow groundwater in the pilot test area. Recycled vegetable oil was injected with water, and various emulsifiers were added to promote dispersion of the vegetable oil in the aqueous phase. A total of approximately 7,800 liters of vegetable oil emulsion was injected into the pilot test area during 2001 and 2002.

Groundwater geochemistry data collected at downgradient monitoring points suggests than an anaerobic system was established in the shallow groundwater.

Decreases in perchlorate, nitrate, and dissolved oxygen levels, as well as the detection of chlorate, are all indications that anaerobic conditions conducive to the reduction of perchlorate were created. A more effective representation of the generation of the biobarrier via the injection of the recycled oil substrate is to recognize the natural dilution and dispersion that occurs in the pilot test area from the most upgradient point to the most downgradient point. Prior to substrate injections, the average upgradient perchlorate concentration was 40 mg/L and the downgradient concentration was 26 mg/L. This represents a naturally occurring reduction in perchlorate concentration via dilution and dispersion effects of 34%. The data from the most recent sampling event indicates average upgradient and downgradient perchlorate concentrations of 18.35 mg/L and 4.02 mg/L, respectively. This represents a decrease of 78%; however, when the assumed natural dilution and dispersion effect is considered, the reduction across the permeable reactive biobarrier due to anaerobic treatment is estimated at 44%. This is a considerable reduction when considering the limited size of the biobarrier created during the pilot test. The average perchlorate concentrations over time for the biobarrier pilot test area are illustrated in Figure 4.

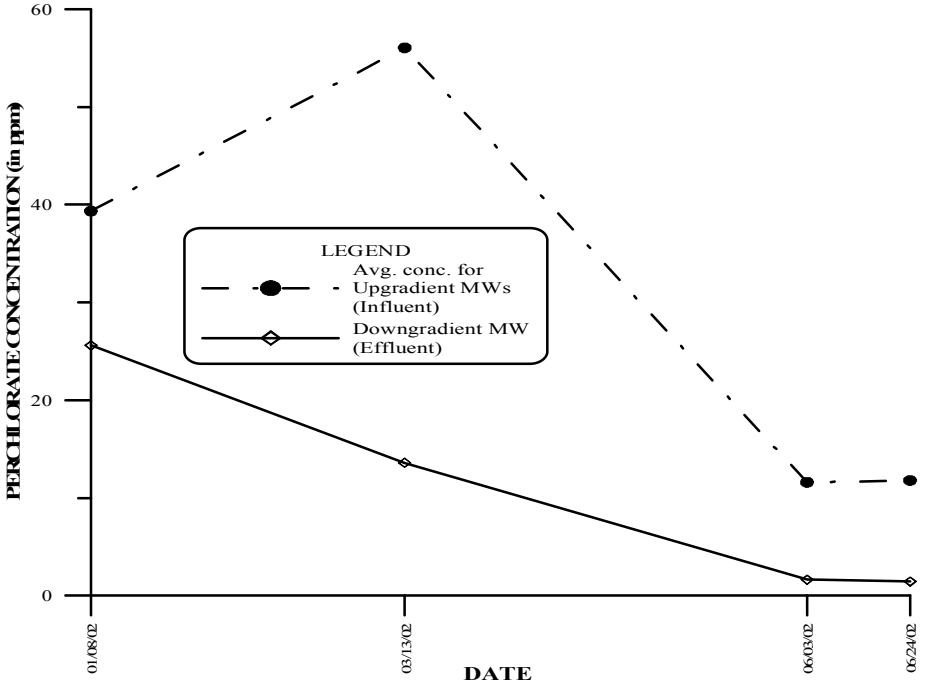


FIGURE 4. Average perchlorate concentration in groundwater over time for biobarrier system

CONCLUSIONS

Pilot Test - Biocell. Based on data collected during this pilot test, ex situ anaerobic composting has proven to be an efficient and cost-effective method for the treatment of perchlorate-impacted soil. This pilot test has demonstrated the possibility of treating heavily perchlorate-impacted soils using a properly maintained ex situ biocell within a timeframe of 9 to 12 months. The treated soil, with regulatory approval, is then available

for use as clean fill and/or as starter substrate for the creation of additional biocells to treat additional perchlorate-impacted soils.

Pilot Test - Infiltration Gallery. Based on the data collected during the pilot test, the infiltration gallery (as operated during the pilot test) represents a slow but effective method of introducing substrate into the shallow groundwater and influencing the groundwater geochemistry. This treatment technique flushes perchlorate from the deeper vadose soils and into the shallow groundwater anaerobic treatment zone generated by the introduction of soluble substrates (CMA and degrading sawdust).

Pilot Test - Biobarrier. Laboratory data collected to date suggests that the biobarrier generated through the injection of insoluble substrate (i.e., recycled cooking oil) is a successful method for the treatment of perchlorate-impacted groundwater and the containment of dissolved perchlorate plumes. Field observations during the pilot test suggest that the improved well seal design prevents short-circuiting of substrate at the injection points, thus allowing a better distribution of substrate in the subsurface.

ACKNOWLEDGEMENTS
The authors would like to recognize the efforts of lead field geologist Robert Kondelin, P.G. and the other participating members of the Environmental Alliance, Inc. field staff. The authors would also like to thank the office support staff at Environmental Alliance, Inc. for their assistance in pilot test documentation and reporting activities. In addition, the authors wish to acknowledge the contributions of GeoSyntec Consultants during the development of the pilot test work plan.

REFERENCES
Coates, J. D., U. Michaelidou, S. M. O'Connor, R. A. Bruce, and L. A. Achenbach. 2000. "The Diverse Microbiology of (Per)chlorate Reduction". Chapter 24 in: Perchlorate in the Environment, E.T Urbansky (Ed.). Kluwer Academic/Plenum Publishers, New York

Cox, E. E., E. Edwards and S. Neville. 2000. "In Situ Bioremediation of Perchlorate in Groundwater," Chapter 21 in: Perchlorate in the Environment, E.T Urbansky (Ed.). Kluwer Academic/Plenum Publishers, New York

Horner, R. R. and M. Brenner. 1992. Environmental evaluation of calcium magnesium acetate for highway deicing applications. *Resour. Conserv. Recycl.* 7:213-37.

Nzengung, V. A., J. Kastner, K. C. Das, and A. G. Browder. 2001. University of Georgia, Athens, Georgia, "Pilot Scale In-Situ Bioremediation of Perchlorate-Contaminated Soil." The Sixth International Symposium on In Situ and On Site Bioremediation, San Diego, CA.

Wiedemeier, T., Henry, B., and Haas, P. 2001. *Technical Protocol for Enhanced Reductive Dechlorination Via Vegetable Oil Injection*, The Sixth International In Situ and On-Site Bioremediation Symposium, Anaerobic Degradation of Chlorinated Solvents 6(7), Battelle Press, pp. 241-248