Paper 4B-01, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2004.* Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2004). ISBN 1-57477-145-0, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

TREATMENT OF PERCHLORATE AND 1,1,1-TRICHLOROETHANE IN GROUNDWATER USING EDIBLE OIL SUBSTRATE (EOS®)

Christie Zawtocki, P.E. (czawtocki@solutions-ies.com) and M. Tony Lieberman, R.S.M.
(Solutions Industrial & Environmental Services, Inc., Raleigh, NC)
Robert C. Borden, Ph.D., P.E. (North Carolina State University, Raleigh, NC)
Gary M. Birk, P.E. (gbirk@eosremediation.com) (EOS Remediation, Inc., Raleigh, NC)

ABSTRACT: Laboratory studies and a pilot-scale field test are being conducted to evaluate the use of edible oil emulsions for biodegradation of perchlorate and 1,1,1-trichloroethane (1,1,1-TCA) in groundwater at a site in Maryland. The patented Edible Oil Substrate (EOS®) process is a cost-effective approach for stimulating in situ anaerobic biodegradation with little or no operation and maintenance. Laboratory microcosms showed rapid and complete removal of perchlorate with slower degradation of 1,1,1-TCA to measurable daughter products. Preliminary results from the pilot-scale permeable reactive biological barrier (PRBB) show complete removal of perchlorate in the injection and downgradient monitor wells as quickly as 5 days after injection. Within 68 days of EOS® injection, 1,1,1-TCA concentrations decreased by 95% in monitor wells located up to 20 feet downgradient of the PRBB. The barrier will continue to be monitored to evaluate the long-term effectiveness and cost associated with the use of EOS® for in situ biodegradation of perchlorate and 1,1,1-TCA.

INTRODUCTION

Groundwater and surface water contaminated with perchlorate (ClO_4^-) has become a major environmental issue for the U.S. Department of Defense (DoD) due to the use, release and/or disposal of solid rocket fuel and munitions containing ammonium perchlorate. Perchlorate is a highly mobile, soluble salt that sorbs poorly to most aquifer material and can persist for decades under aerobic conditions. However, recent research has shown that a very diverse array of bacteria can anaerobically degrade perchlorate to chloride and oxygen. These organisms appear to be widespread in the environment and can use a variety of different organic substrates as electron donors for perchlorate reduction.

Similarly, chlorinated solvents in groundwater are also a frequently encountered problem at DoD facilities. Anaerobic reductive dechlorination has been shown to be an efficient microbial means of transforming more highly chlorinated species to less chlorinated species. Chlorinated solvents amenable to in situ anaerobic bioremediation include tetrachloroethene (PCE), trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-DCE), vinyl chloride (VC), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,2-dichloroethane (1,2-DCA), carbon tetrachloride (CT), and chloroform (CF).

The patented EOS® process (U.S. Patent #6,398,960) provides an innovative, low-cost approach for distributing and immobilizing biodegradable organic substrates in contaminated aquifers to promote in situ anaerobic biodegradation of perchlorate and chlorinated solvents. EOS® consists of food-grade soybean oil, surfactants, macro and micronutrients, and vitamins blended to form a stable micro-emulsion with small, uniformly-sized oil droplets. Once injected, the oil droplets stick to the sediment surfaces providing a residual oil phase. The EOS® then serves as a carbon source for cell growth and an electron donor for energy generation, supporting long-term anaerobic biodegradetion of the target contaminants. This approach provides good contact between the slowly biodegradable organic substrate (oil) and the contaminants and substantially reduces initial capital and long-term operation and maintenance (O&M) costs.

The effectiveness of EOS® is being evaluated under a contract funded by the DoD's Environmental Security Technology Certification Program (ESTCP) at a site in Maryland with a mixed perchlorate and 1,1,1-TCA groundwater plume. The shallow aquifer at the site consists of silty sand and gravel to a depth of approximately 15 feet below ground surface (bgs) and has been impacted by a former lagoon that received ammonium perchlorate and waste solvent. The water table is approximately 5 feet bgs with a groundwater velocity of approximately 100 feet/year. The demonstration activities include both laboratory studies using site soils and a field pilot test involving injection of EOS® to form a permeable reactive biological barrier (PRBB).

LABORATORY STUDIES

A laboratory microcosm study was conducted to evaluate the effectiveness of EOS® for remediating perchlorate and 1,1,1-TCA, and a column study was performed to assess EOS® distribution in site sediments.

Laboratory Microcosm Study. The laboratory microcosms were created in triplicate using site aquifer sediments and groundwater to evaluate the ability of edible oil substrate to support contaminant biodegradation. Treatments included:

#1 – No sediment, no carbon
#2 – Live control, no added carbon
#3 – Killed control, EOS®, NaOH
#4 – EOS®
#5 – EOS® with bioaugmentation culture

Perchlorate degradation was rapid and complete in all microcosms treated with EOS®. In all three replicates in treatment #4, perchlorate concentrations decreased from approximately 50 mg/L to less than 0.008 mg/L within 14 days (Figure 1). Chlorinated solvent degradation results were more variable. In some incubations, 1,1-DCA was produced during biodegradation of 1,1,1-TCA but did not degrade further. However, in other incubations, 1,1-DCA was extensively degraded. There was no correlation between extent of 1,1-DCA degradation and addition of a bioaugmentation culture. 1,1-DCA was completely degraded in some incubations that did not receive the bioaugmentation culture and persisted in some incubations that were bioaugmented. Figure 2 shows results from one microcosm where 1,1,1-TCA degraded from 13.7 µM (1,820 µg/L) to less than 0.5 µM (~50 µg/L). Near stochiometric amounts of 1,1-DCA were produced followed by a decrease in 1,1-DCA to below 1 µg/L. Trace levels of chloroethane (CA) were produced and then declined suggesting further conversion of CA to non-toxic end products.

Overall, the microcosm results demonstrated that EOS® addition was effective in stimulating anaerobic biodegradation of perchlorate and 1,1,1-TCA in site sediments and that bioaugmentation was not required to achieve complete dechlorination of 1,1,1-TCA and other chlorinated compounds to non-toxic end products.

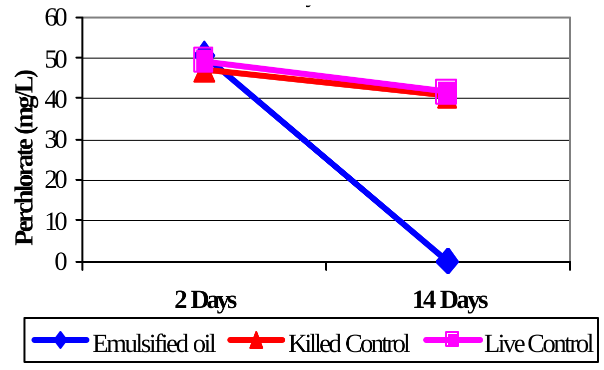

FIGURE 1. Perchlorate vs time in laboratory microcosms.

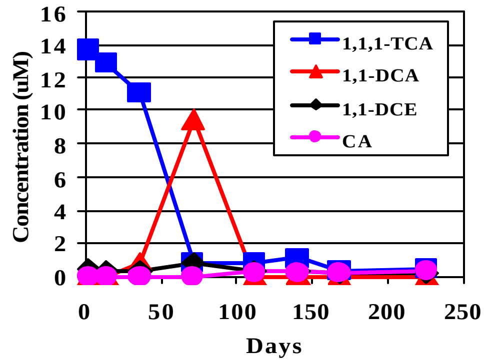

FIGURE 2. TCA biodegradation with EOS® addition.

Laboratory Column Study. Small diameter column experiments (2.5 cm dia. × 80 cm long) were also conducted using aquifer material from the Maryland site to evaluate the transport and distribution of EOS® through the site sediments. A pulse of EOS® was injected into the columns followed by chase water. Measurements of volatile solids in the effluent over time indicated that 97% of the volatile solids were retained in the column. The oil distribution was measured over the length of the column, and the oil was found to be distributed throughout the entire column with higher concentrations near the inlet. These results indicated that EOS® could be readily distributed in sediments from the Maryland site. Data from the column studies were used to develop model parameters to simulate the distribution of EOS® at the site in preparation for the field pilot study. Figure 3 shows the EOS® distribution predicted by the model.

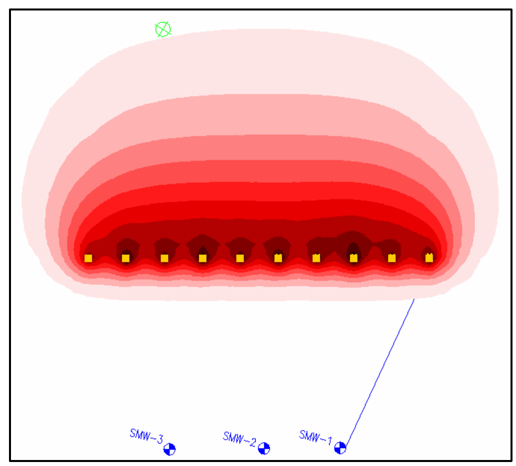

FIGURE 3. Model of EOS® distribution

PILOT STUDY

Based on the results of the laboratory studies, a pilot study was designed to demonstrate the effectiveness of EOS® in the field. The pilot study consisted of installing ten 1-inch diameter direct-push injection wells spaced 5 feet on center perpendicular to groundwater flow to create a PRBB. Monitoring wells were installed upgradient and downgradient of the PRBB to evaluate changes in groundwater concentrations over time. Figure 4 shows the pilot test layout.

In October 2003, approximately 10 gallons of EOS® concentrate (50 gallons of diluted EOS®) were injected into each well followed by approximately 165 gallons of chase water to distribute the EOS® throughout the aquifer. Five wells were injected simultaneously using a manifold injection system. Injection of the EOS® and chase water in all ten injection wells was completed in 2 days by a 2-person field team.

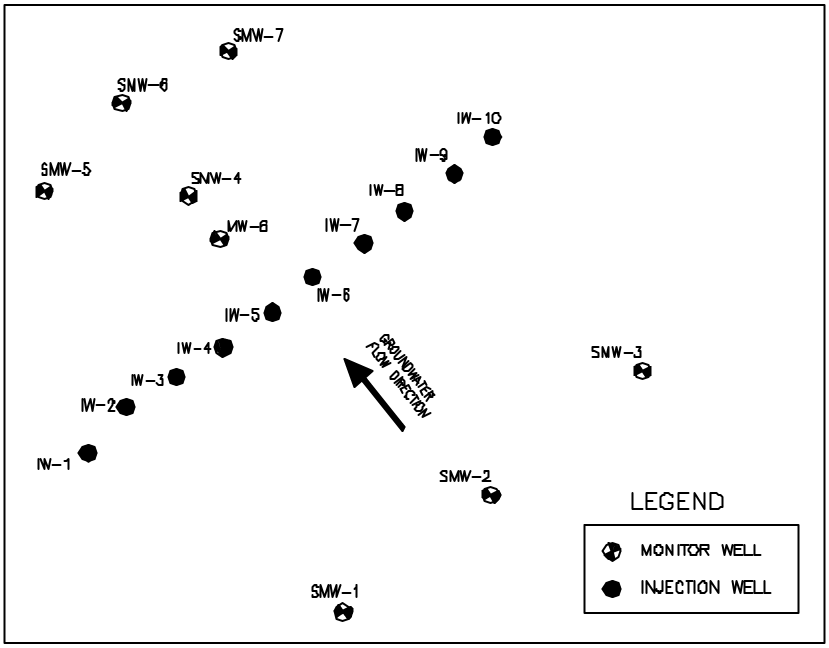

FIGURE 4. Layout of EOS® pilot study

Groundwater monitoring was conducted prior to EOS® injection, 5 days after injection, and at subsequent routine intervals. Performance monitoring is ongoing at the site and will continue for a total of 18 months. Groundwater samples are analyzed for perchlorate, VOCs (including CAHs and trihalomethanes), electron acceptors (oxygen, nitrate, sulfate, phosphate), electron donors (TOC and volatile fatty acids), indicator parameters (pH, Eh), metals (Fe^{+2} and Mn^{+2}), light hydrocarbon gases (ethene, ethane, methane), and chloride.

RESULTS AND DISCUSSION

EOS® injection has resulted in substantial reductions in perchlorate and 1,1,1-TCA concentrations within and downgradient of the PRBB. Geochemical data collected at the site confirm that anaerobic conditions favorable for biodegradation of these compounds have been established in the treatment area. Elevated concentrations of total organic carbon (TOC) within and immediately downgradient of the injection wells indicate good distribution of EOS® throughout the target zone forming a PRBB as simulated by the model.

Figure 5 shows the changes in perchlorate versus time in the pilot test area. Perchlorate concentrations in the injection wells and downgradient wells up to 10 feet from the barrier showed immediate reductions from pre-injection concentrations ranging from 3,100 to 20,000 µg/L to less than the detection limit of 4.0 µg/L within 5 days of EOS® injection. Perchlorate concentrations in monitoring wells 20 feet downgradient decreased from an average pre-injection concentration of 8,700 µg/L to 4,600 µg/L within 5 days and 10 µg/L within 30 days post-injection.

1,1,1-TCA concentrations have also decreased in the pilot test area. Figures 6a and 6b show the 1,1,1-TCA and 1,1-DCA concentrations versus time for the injection wells and monitoring wells located 20 feet downgradient of the PRBB, respectively. The data in the figures are averages of five injection wells (IW-1, -3, -5, -7, and -10) and three

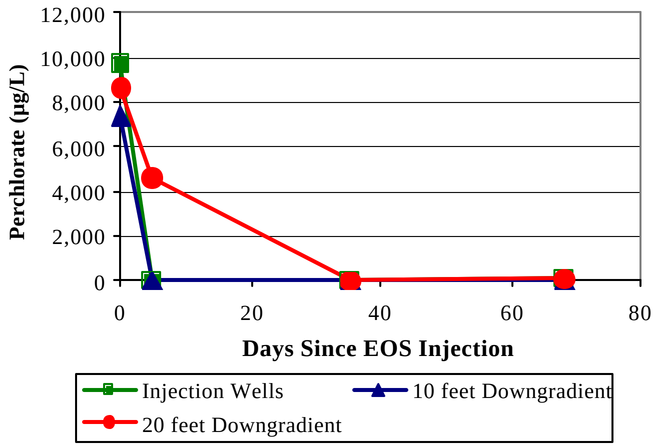

FIGURE 5. Perchlorate vs time in pilot test area.

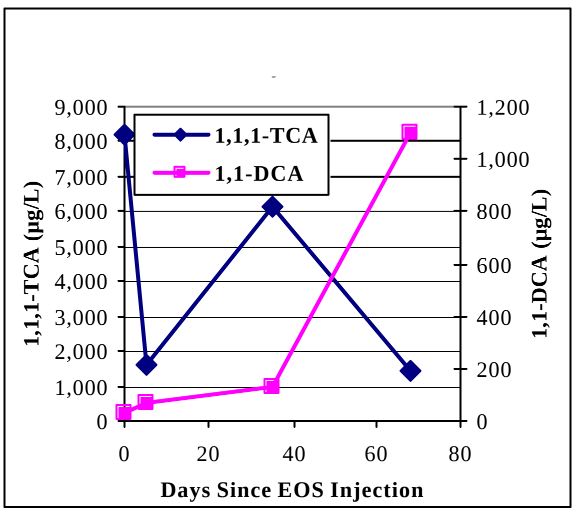

FIGURE 6a. 1,1,1-TCA and 1,1-DCA vs time in EOS® injection wells.

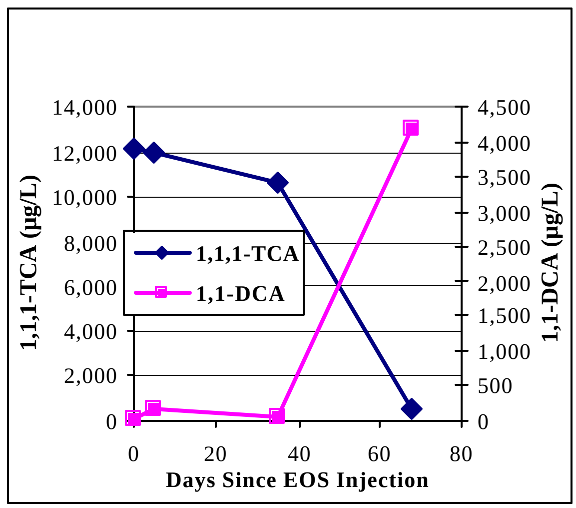

FIGURE 6b. 1,1,1-TCA and 1,1-DCA vs time 20 feet downgradient of EOS® barrier.

downgradient wells (SMW-5, -6, and -7). As shown in Figure 6a, 1,1,1-TCA concentrations initially decreased within 5 days of EOS® injection from 8,220 µg/L to 1,616 µg/L. This decrease is likely attributable to sorption into the oil and/or dilution from the injection. 1,1,1-TCA concentrations rebounded within 35 days to 6,120 µg/L and then decreased again 68 days post-injection to 1,406 µg/L. The decrease in 1,1,1-TCA at 68 days post-injection was accompanied by an increase in 1,1-DCA indicating that biodegradation is occurring. Twenty feet downgradient of the PRBB, a continuous decrease in 1,1,1-TCA concentrations from 12,167 to 559 µg/L is observed over the 68 days since EOS® injection with a corresponding increase in 1,1-DCA from 30 to 4,175 µg/L (Figure 6b).

In addition to monitoring changes in contaminant concentrations over time, several other parameters were evaluated to assess changes in the aquifer geochemistry. In general, these results corroborate the trends seen in perchlorate and 1,1,1-TCA and indicated that conditions favorable for anaerobic biodegradation have been achieved within and downgradient of the EOS® PRBB. Table 1 presents representative geochemical data for an injection well and monitor wells located upgradient and downgradient of the PRBB. In general, nitrate and sulfate concentrations have decreased with time in the injection and downgradient wells indicating nitrate and sulfate reduction, while iron and manganese concentrations have increased with time indicating iron and methane reducing conditions. Methane concentrations have increased in the injection wells suggesting methanogenic conditions within the PRBB. No significant changes have been observed in the upgradient monitor wells.

TABLE 1. Selected geochemical parameters in groundwater (mg/L).

Well	Days Since Injection	Nitrate	Sulfate	Iron	Manganese	Methane
SMW-2	Pre-Injection	7.4	34.4	<0.5	0.36	0.0006
(25' upgradient)	5	8.5	33.6	1.9	0.35	0.0005
	35	9.8	33.4	<0.5	0.28	0.0013
	68	6.7	23.8	<0.5	0.18	0.0010
IW-3	Pre-Injection	12.9	30.1	<0.5	0.052	0.0005
(Injection Well)	5	<0.5	27.6	0.86	3.6	0.0005
	35	<0.5	7.7	69	16	0.0027
	68	<0.5	1.9	24	8.9	0.1418
SMW-4	Pre-Injection	11.7	28.0	<0.5	0.14	0.0002
(10' downgradient))	5	<0.5	43.1	1.2	4.8	NA
	35	<0.5	8.0	22.0	14.0	0.0006
	68	<0.5	<0.5	3.5	19.0	0.0005
SMW-6	Pre-Injection	<0.5	23.3	<0.5	0.11	0.0003
(20' downgradient)	5	<0.5	26.3	<0.5	1.3	<0.0002
	35	<0.5	5.7	2.6	1.4	0.0005
	68	0.9	12.7	4.1	2.4	<0.0002

To evaluate the distribution of the EOS® in the subsurface, TOC and volatile fatty acid (VFA) concentrations have been evaluated over time. Pre-injection data indicated TOC concentrations ranging from <1.0 to 2.0 mg/L and no detectable concentrations of volatile fatty acids throughout the pilot test area. Immediately after EOS® injection, TOC concentrations increased to between 100 and 450 mg/L in the injection wells with corresponding increases in VFAs (oil breakdown products). Sustained TOC concentrations ranging from 25 to 100 mg/L and elevated VFA concentrations have been observed in the injection wells 68 days post-injection.

Downgradient TOC concentrations as high as 190 mg/L were observed in groundwater up to 10 feet away from the injection wells immediately after introduction of EOS®. Sixty-eight days post-injection, TOC concentrations have decreased to less than 15 mg/L in groundwater downgradient of the barrier. Based on these data, the downgradient groundwater was initially impacted during injection of the EOS®. However, the majority of the EOS® droplets became trapped in the soil around the injection wells resulting in a drop in TOC measured in the downgradient groundwater. These results indicate the oil was effectively distributed around the injection wells creating an in situ

PRBB. The oil is entrained in the soil providing a long-term source of carbon to sustain anaerobic biodegradation.

CONCLUSIONS

Based on the laboratory and field pilot testing conducted to date, EOS® can be effectively distributed in the subsurface to stimulate anaerobic biodegradation of perchlorate and 1,1,1-TCA. Perchlorate degradation is rapid and complete. In the field pilot test, 100% perchlorate removal was achieved within and up to 10 feet downgradient of the barrier 5 days after EOS® injection and 99% removal was observed 20 feet downgradient of the barrier within 35 days of injection. Substantial 1,1,1-TCA reductions have also been observed. In the field, 1,1,1-TCA concentrations have been reduced by up to 95% in monitor wells 20 feet downgradient of the PRBB with corresponding increases in 1,1-DCA. Geochemical parameters confirm that EOS® injection has created conditions favorable for anaerobic biodegradation within and downgradient of the barrier. The laboratory column study and field measurements of TOC and VFA demonstrate that EOS® can be effectively distributed to provide a long-term carbon source to stimulate biodegradation of the target contaminants.

The field pilot study will continue to be monitored for up to 18 months to evaluate the longevity of the EOS® and to further assess performance of the PRBB. Data from the pilot study will be used to evaluate scale-up to a full-scale treatment system. Based on data gathered to date, the injection spacing of a full-scale system could be increased to 10 or 15 feet resulting in additional cost savings.

ACKNOWLEDGMENTS

The laboratory and field studies presented in this manuscript were funded by the Environmental Security Technology Certification Program (ESTCP) under project CU-0221. Solutions-IES gratefully acknowledges the financial and technical support provided by this program. We also acknowledge the support provided by Gary Birk, P.E., at EOS Remediation, Inc. (www.eosremediation.com).