Anaerobic Bioremediation of Groundwater Using Edible Oil Substrate EOS® In an Unconfined Groundwater Aquifer

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ABSTRACT: To treat groundwater contaminants *in situ*, enhanced anaerobic bioremediation processes can be stimulated through addition of soluble substrates. At a dry cleaners site located in San Jose, California, the goal was to find a substrate that is long lasting and easily distributed into the saturated soils. After evaluating several alternatives, *in situ* bioremediation using an emulsified edible oil substrate (EOS®) was selected as the preferred alternative for groundwater remediation.

At this site, the impact of injecting substrate into the upper aquifer was observed in an unconfined groundwater aquifer. Tetrachloroethene (PCE) breakdown was monitored at three locations across the site. The highest PCE and trichloroethene (TCE) concentrations in the January 2005 pre-EOS injection-sampling event were detected in well MW-1A at concentrations of 8,500 µg/L and 200 g/L, respectively. The highest *cis*-1,2-dichloroethene (*cis*-DCE) was detected in well MW-1A at concentration of 160 µg/L. *Trans*-1,2-DCE (*trans*-DCE) was also detected and only small amounts of VC were detected in the groundwater prior to treatment.

After 2.5 months post-injection (July 2005), the PCE concentration in MW-1A was reduced to 18 µg/L and the TCE concentration was reported to be 100 µg/L. The concentration of *cis*-DCE had increased in MW-1A to 1,200 µg/L, suggesting the presence of enhanced bioremediation. No PCE, TCE, or 1,1-DCE was detected in the shallow wells during the October 2005 sampling event (6-months post-injection). Conversely, the concentration *cis*-DCE continued to increase and was detected in well MW-1A at 2,300 µg/L. By six months after treatment, VC was readily detected in each of the monitor wells at concentrations of 39, 200, and 35 µg/L in MW-1A, MW-2, and MW-3, respectively.

Sub-reportable levels of PCE, TCE, and 1,1-DCE were detected again in the shallow wells during the January 2006 sampling event (9-months post-injection) The concentration of *cis*-DCE also began to decrease and was detected in well MW-1A at 630 µg/L. By nine months after treatment, VC was readily detected in each of the monitor wells at concentrations of 300, 40, and 88 µg/L in MW-1A, MW-2, and MW-3, respectively.

The results of the pre- and post-injection sampling of three wells in the treatment zone showed the rapid conversion of the aquifer to anaerobic reducing conditions favorable for reductive dechlorination to occur. The enhanced conditions resulted in rapid disappearance of PCE from 8,500 µg/L to below the MDL, reductions in TCE, and a measurable increase of *cis*-DCE and VC at all the shallow zone wells. Some methane is being produced, but ethane or ethene production has yet to be detected. The emulsified oil substrate (EOS®) is expected to continue to sustain favorable conditions for an extended duration. Continued monitoring is expected to eventually document to complete remediation of the site.

INTRODUCTION: To treat groundwater contaminants *in situ*, enhanced anaerobic bioremediation is a cost-effective alternative. Contaminants amenable to *in situ* anaerobic bioremediation include certain heavy metals, nitrate, perchlorate, acid mine drainage and chlorinated organics, such as 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).

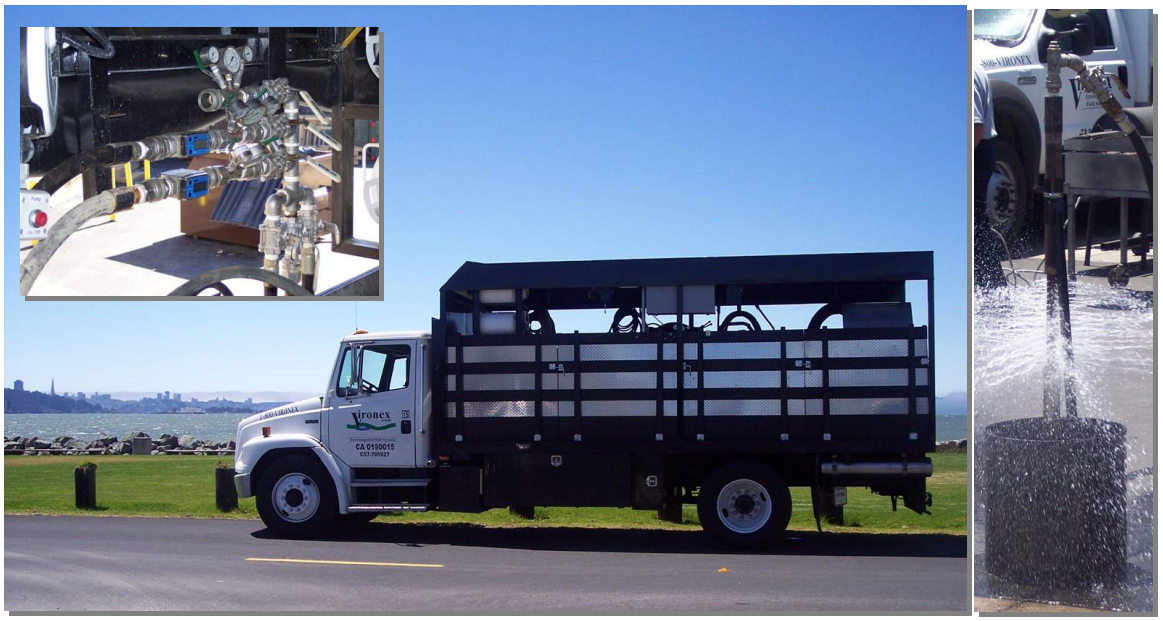
Anaerobic bioremediation processes can be stimulated through addition of soluble substrates (e.g., lactate, butyrate, propionate, acetate, molasses, and refined sugars), solid substrates (e.g., bark mulch, compost, chitin and peat), and slowly soluble substrates such as vegetable oil. For some sites, the goal is to find a substrate that is long lasting and easily distributed into the saturated soils. After evaluating several alternatives, *in situ* bioremediation using an emulsified edible oil substrate (EOS®) was selected as the preferred alternative for groundwater remediation.

EOS® TECHNOLOGY: Remediation Sciences, Inc. (RSI) purchased EOS® from EOS Remediation of Raleigh, NC. The concentrated emulsified soybean oil product is manufactured with uniform oil droplets approximately 1 micron in diameter. It is primarily composed of food-grade vegetable oil and emulsifiers with additional vitamins to support bacterial growth. The emulsion is injected into the saturated zone. The soybean oil ferments, provides hydrogen, and donates its electrons to the chlorinated contaminants resulting in a microbial-mediated sequential removal of chlorine atoms from the target chlorinated volatile organic compounds (CVOCs). Sequential anaerobic reductive dechlorination of TCE results in the formation of intermediate, less-chlorinated daughter products including *cis*-DCE and VC, and non-toxic metabolic non-chlorinated end products, ethane and/or ethane.

DIRECT PUSH INJECTION OF EOS®: Vironex, Inc., a national environmental field service company, was contracted to inject the EOS®. They utilized Geoprobe® direct push technology systems (truck, track, or limited access mounted) to advance a Vironex custom-designed bottom-up injection tool at each of the injection boreholes. This injection tooling promotes lateral distribution of reagents to enhance contact with contaminants throughout the target injection interval. To ensure that the site remains safe, clean and professional throughout the process, Vironex integrated a one-way check valve assembly to eliminate any backpressure that may occur while retracting the injection tooling out of the borehole.

While the injection tooling was advanced, Vironex utilized its custom built, self-contained remediation delivery systems to prepare the EOS® to the desired concentration. The injection system integrated a single motor control center to operate their mixing systems and pumps, which was integrated within a stainless steel secondary containment.

Vironex targeted 1 feet to 5 feet (0.3 to 1.5 m) injection intervals with their customized injection tooling to provide for uniform vertical and horizontal distribution of EOS® throughout the target injection zone.



During injection flow, total flow and pressure are continuously monitored to ensure adherence to injection design parameters. Over the duration of the project, Vironex injected 4,400 gallons of EOS mix and 22,700 gallons of flush water over a period of 6 days.

Once the injection tooling was retracted through the injection zone, it was removed from the borehole and sealed with an appropriate backfill material.

INJECTION DESIGN: Injecting the oil as an oil-in-water emulsion can enhance distribution of edible oils in the subsurface. The emulsion is prepared to: (1) be stable for extended time periods (e.g., non-coalescing); (2) have small, uniform droplets to allow transport in most aquifers; and (3) have a negative surface charge to optimize oil droplet sorption to soil. At other project sites, emulsified oils have been effectively distributed over 20 ft (6.1 m) away from the injection point and were demonstrated to provide a long-lasting carbon source to support reductive dechlorination (Borden et al., 2001) for over 3 years.

Oil emulsions have been used to treat contaminated groundwater in a permeable reactive barrier (PRB) configuration by injecting the emulsion through a series of injection points or permanent wells installed in a line perpendicular to groundwater flow. The oil breaks down to shorter-chain fatty acids and eventually to hydrogen, and donates its electrons to the chlorinated contaminants in the groundwater that pass through the emulsion treated zone. Typical injection well layouts for a permeable reactive barrier and source zone grid approach are shown in Diagram 1.

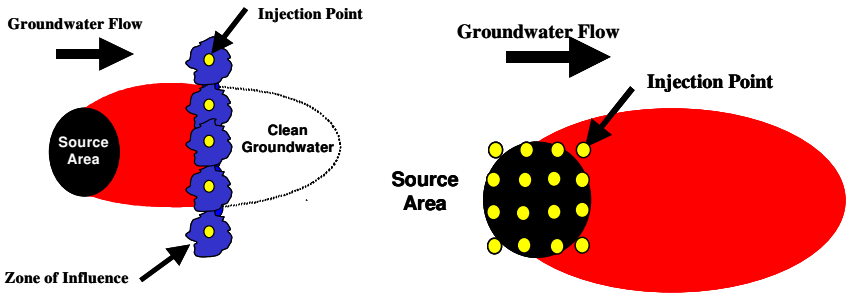


DIAGRAM 1. Typical Layouts for Injecting EOS®

RSI injected the emulsified oil substrate (EOS®), into the groundwater at a dry cleaners site in the proximity of San Jose area between April 20 and April 28, 2005. The injections were the initial steps in a bioremediation process to break down PCE in groundwater at the site, by applying the substrate in a 10-foot (3.1 m) center grid in three areas. Part of the application was in a small grid layout into the source area with PCE concentration of over 5,000 µg/L. Additional substrate was injected in barrier formations up gradient of the source area just north of the north wall of the dry cleaners, and also down gradient of the source area just south of the south wall.

RSI applied vegetable oil substrate in a barrier line parallel to the alley in the source area and a second barrier line just east of the cleaners by introducing the emulsified oil using six borings 10 feet (3.1 m) apart just west of the cleaners and also in a second line in front of the cleaners. Based on a model RSI ran using the substrate calculation spreadsheet furnished by EOS Remediation, approximately 1,100 gallons (4,164 liters) of EOS® concentrate were required for the shallow zone groundwater remediation. Following the vendor recommendations, the emulsified concentrate was diluted to a ratio of 3 portions of water to 1 portion of concentrate and then injected. Therefore, approximately 4,400 gallons (16,655 liters) of the diluted emulsion was injected into the groundwater zones.

Following the application of the vegetable oil, approximately 22,700 gallons (85,928 liters) of dechlorinated tap water were injected, and dispersed through the aquifer via the 12 injection points, to distribute the vegetable oil into zone of contamination beneath the cleaners. The water was mixed with vitamin B-12 to nourish and enhance the bacteria already present. Pre-injection samples collected from the contaminated aquifer indicated the presence of a viable population of Dehalococcoides ethenogenes, the microorganisms necessary for the complete biotransformation of the PCE to ethene to occur.

RESULTS: The impact of injecting substrate into the aquifer beneath the dry cleaners site on PCE breakdown was monitored at three locations across the site. MW-1A is located up gradient, just north of the plume, in close proximity to the source area of contamination. MW-2 is located northwest of the source toward the edge of the plume. MW-3 is located down gradient of the source, in the center of the original contamination plume. Of the three wells, MW-1A was the most heavily impacted at the beginning of the project. Well locations are indicated in the Figures 1 thru 4 (See Appendix 1).

The highest PCE and TCE concentrations in the January 2005, pre-EOS injection, sampling event were detected in well MW-1A at a concentrations of 8,500 µg/L and 200

g/L, respectively. The highest *cis*-DCE was detected in well MW-1A at concentration of 160 µg/L. *Trans*-DCE was also detected and only small amounts of VC were detected in the groundwater prior to treatment. Analytical data are summarized in Table 1 and plotted in charts 1 through 3 corresponding to each well. The extent of the plume of the major contaminants is given in Figure 1 (See Appendix 1).

After just 2.5 months post-injection (July 2005), the PCE concentration in MW-1A was reduced to 18 µg/L and the TCE concentration was reported to be 100 µg/L. The concentration of *cis*-DCE had increased in MW-1A to 1,200 µg/L, suggesting the presence of enhanced bioremediation. The analytical data are provided in Table 1 and plotted in charts 1 through 3 corresponding to each well. The extent of the plume of the major contaminants is given in Figure 2 (See Appendix 1).

No PCE, TCE, or 1, 1-DCE was detected in the shallow wells during the October 2005 sampling event (6-months post-injection). Conversely, the concentration *cis*-DCE continued to increase and was detected in well MW-1A at 2,300 µg/L. By six months after treatment, VC was readily detected in each of the monitor wells at concentrations of 39, 200, and 35 µg/L in MW-1A, MW-2, and MW-3, respectively. Tabulated data are provided in Table 1 and plotted in charts 1 through 3 corresponding to each well. The extent of the plume of the major contaminants is given in Figure 3 (See Appendix 1).

Sub-reportable levels of PCE, TCE, and 1, 1-DCE were detected again in the shallow wells during the January 2006 sampling event (9-months post-injection) The concentration of *cis*-DCE also began to decrease and was detected in well MW-1A at 630 µg/L. By nine months after treatment, VC was readily detected in each of the monitor wells at concentrations of 300, 40, and 88 µg/L in MW-1A, MW-2, and MW-3, respectively. The data in Table 1 are plotted in charts 1 through 3 corresponding to each well. The extent of the plume of the major contaminants is given in Figure 4 (See Appendix 1).

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REFERENCES

Robert C. Borden and Christie Zawtocki, Michael D. Lee, Erica S Becvar, Patrick E. Haas, Bruce M. Henry, AFCEE Protocol For Enhanced Anaerobic Bioremediation Using Edible Oils

APPENDIX 1

TABLE 1 ANALYTICAL AND FIELD MEASUREMENT PARAMETER DATA

Well ID	Analyte / Units	PCE[1] µg/L[2]	TCE[3] µg/L	Cis-1,2-DCE[4] µg/L	Trans-1,2-DCE[5] µg/L	Vinyl Chloride µg/L	Methane mg/L	Ethane mg/L	Ethene mg/L	TOC[6] mg/L[7]	DO[8] mg/L	ORP[9] mV[10]	pH --	SEC[11] mS/cm[12]	Sulfate mg/L	Chloride mg/L
	DATE SAMPLED															
Shallow Zone:																
MW-1A	5/21/2002	11,000	ND(250)/212(J)[7]	ND(250)/80(J)	ND(250)/36(J)	ND(250)	--	--	--	--	0.14	104	6.31	0.233	--	--
	1/27/2005	8,500	200	160	30J	79	--	--	--	2.4	--	--	--	--	--	--
	7/14/2005	18	100	1,200	26	23	0.80	ND(0.12)	ND(0.0050)	830	0.90	-114	5.77	0.247	24	37
	10/26/2005	ND(14)	ND(14)	2,300	32	39	3.60	ND(0.00030)	ND(0.00040)	326	0.00	-164	6.09	0.207	ND(2)[2]	46
	1/18/2006	ND(1.3)	ND(1.2)	630	19	300	3.50	ND(0.00030)	ND(0.00040)	202	0.00	-160	6.31	0.233	0.79J	57
MW-2	5/21/2002	470	30	34	ND(0.5)/3.5(J)	ND(0.5)	--	--	--	--	--	--	--	--	--	--
	1/27/2005	540	32	37	5.6	1.8J	--	--	--	1.9	--	--	--	--	--	--
	7/14/2005	4.4J[8]	5.6J	520	19	12	0.59	ND(0.12)	ND(0.0050)	87	0.00	-229	6.04	0.253	13	87
	10/26/2005	ND(1.7)	ND(1.8)	15	3.8	200	3.60	ND(0.00030)	ND(0.00040)	84	0.00	-114	6.01	0.265	ND(2)	84
	1/18/2006	ND(0.13)	0.16J	5.5	1.1	40	2.60	ND(0.00030)	ND(0.00040)	85.1	0.00	-155	6.22	0.265	3.4	84
MW-3	5/21/2002	860	44	23	ND(100)/3.4(J)	ND(100)	--	--	--	--	0.02	135	6.42	0.328	--	--
	1/27/2005	340	15	7.7	1.3J	ND(1.2)	--	--	--	1.9	--	--	--	--	--	--
	7/14/2005	1.7J	3.5J	270	8.6	4.6J	1.20	ND(0.12)	ND(0.0050)	88	0.00	-134	6.13	0.283	5.8	88
	10/26/2005	ND(1.4)	ND(1.4)	130	4.2	35	4.60	ND(0.00030)	ND(0.00040)	85	0.00	-98	6.09	0.261	ND(2)	85
	1/18/2006	0.2J	0.37J	2.2	5.8	88	4.60	ND(0.00030)	ND(0.00040)	114	0.00	-89	6.26	0.233	ND(0.33)	82
	MCLs[24]	5	5	6	10											

Notes:

1. PCE = tetrachloroethene
2. µg/L = microgram per liter
3. TCE = trichloroethene
4. Cis-1,2-DCE = cis-1,2-dichloroethene
5. Trans-1,2-DCE = trans dichloroethene
6. TOC = Total organic carbon
7. mg/L = milligram per liter
8. DO = Dissolved oxygen
9. ORP= Oxidation Reduction Potential
10. mV = millivolt
11. SEC = Specific Electric Conductance
12. mS/cm = milliSiemens per centimeter
13. Mn = Manganese
14. Fe = Ferrous iron
15. COD = Chemical oxygen demand
16. BOD = Biochemical oxygen demand

-- = Not Analyzed

J = Below the reporting limits, but above the minimum detection limits (MDL)

FIGURES 1 THRU 4 EXTENT OF THE PLUME OF THE MAJOR CONTAMINANTS


TETRACHLOROETHENE
CIS- 1,2- DCE
VINYL CHLORIDE
ETHENE
5-50 µg/L
5-500 µg/L
500-5000 µg/L
> 5000 µg/L
5-50 µg/L
5-500 µg/L
> 500 µg/L
5-50 µg/L
50-500 µg/L
> 500 µg/L
EXPLANATION
MONITORING WELL LOCATION
µg/L = MICROGRAMS PER LITER
ND = NOT DETECTED ABOVE ITS LABORATORY DETECTION LIMIT
REMEDIATION SCIENCES, INC.
4500 CAMPUS DRIVE, SUITE 380
NEWPORT BEACH, CALIFORNIA
TEL. (949) 660-9292
FAX (949) 660-9295
OCTOBER 2005
VOLATILE ORGANIC COMPOUND CONCENTRATIONS
SAN JOSE, CALIFORNIA
Figure
3
INJECT_ZONE_A_OCT_05


TETRACHLOROETHENE
CIS- 1,2- DCE
VINYL CHLORIDE
ETHENE
5-50 µg/L
5-500 µg/L
500-5000 µg/L
> 5000 µg/L
5-50 µg/L
5-500 µg/L
> 500 µg/L
5-50 µg/L
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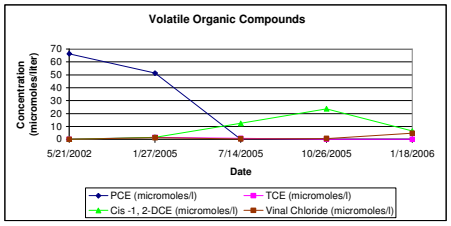
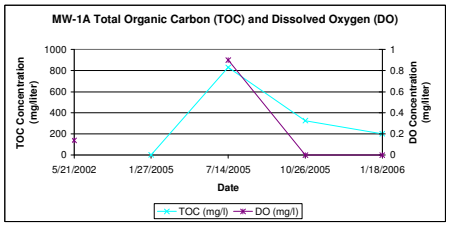
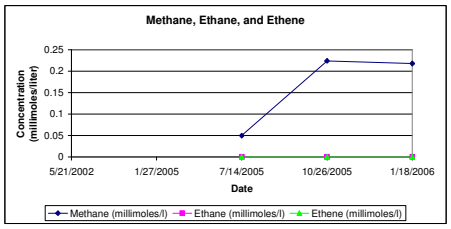
JANUARY 2006 INJECTION
VOLATILE ORGANIC COMPOUND CONCENTRATIONS
SAN JOSE, CALIFORNIA
Figure
4
INJECT_ZONE_A_JAN06

CHART 1: MW-1A ANALYTICAL RESULTS VERSES TIME







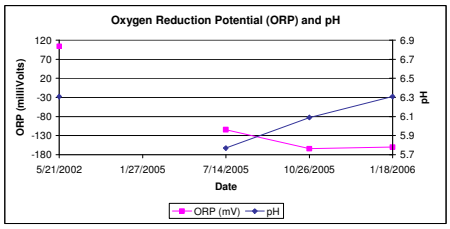
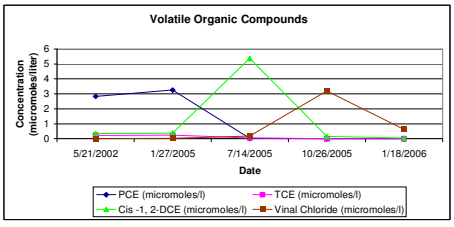
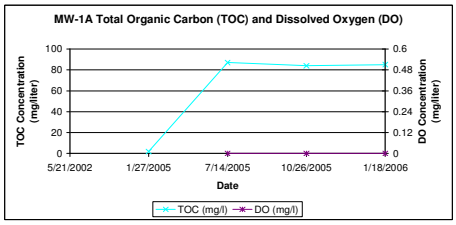
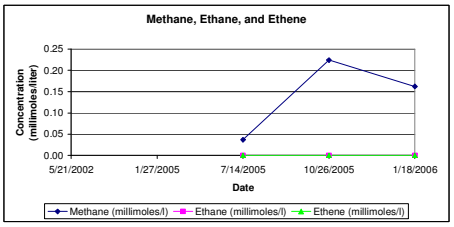


CHART 2: MW-2 ANALYTICAL RESULTS VERSES TIME







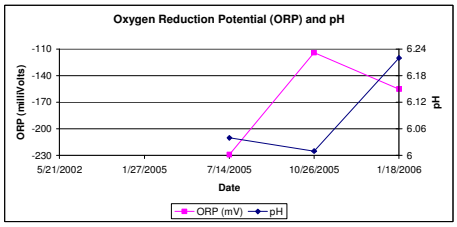


CHART 3: MW-3 ANALYTICAL RESULTS VERSES TIME