TCE PLUME MANAGEMENT THROUGH EDIBLE OIL INJECTION AND NATURAL ATTENUATION

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ABSTRACT: Two pilot-scale edible oil barriers were constructed in the upper portion of a 1,500 m long chlorinated solvent plume at Dover Air Force Base (AFB), DE.
Edible soybean oil was injected into two 6.1 m-long barriers with monitoring wells spaced up to 4.6 m downgradient. Barrier 1 was treated by low pressure, direct injection of soybean oil into ten wells spaced 0.6 m apart. After eight months, a coarse emulsion was injected to increase the vertical and horizontal distribution of soybean oil. In Barrier 2, an emulsion of soybean oil and lecithin was injected under low pressure into four wells spaced 1.5 m apart. In both barriers, the injected edible oils have continued to release dissolved organic carbon (DOC) thirty-nine months after the initial injection with between 280 and 1,600 mg/L DOC found in injection wells of the two barriers. Before injection of the soybean oil, daughter products made up on average 34% of the total chlorinated ethenes and ethanes on a micromolar basis in Barrier 1. The daughter compounds increased to as much as 86.3% of total chlorinated ethenes and ethanes after 22 months. After 39 months, the daughter products represented an average of 78%. In Barrier 2, parent compounds initially represented an average of 55% of the chlorinated ethenes and ethanes. A maximum average of 77% percent daughter compounds was achieved after 9 months. Although little of the chlorinated ethenes and ethanes have been completely degraded, the edible oil in both barriers has been effective in supporting partial dechlorination of the parent compounds to daughter products are then being degraded in the downgradient aerobic zone. Thus Dover AFB will be able to overall effectively remediate the site to target levels, without the need of reaching complete end products in the active treatment area. The emulsion barrier has recently been expanded.

BACKGROUND: Laboratory studies and limited field evaluations had suggested the potential that introduction of "insoluble" vegetable oil into the aquifer via one or more injection wells could stimulate anaerobic reductive dechlorination while reducing operation and maintenance (Lee et al 2000, Borden et al. 2004). To better understand and evaluate the potential for remediating chlorinated solvents in groundwater using edible oils, injection of soybean oil directly and emulsions of soybean oil and water were conducted at DAFB. As part of the Air Force Center for Environmental Excellence (AFCEE) Enhanced In Situ Bioremediation (EISB) Initiative, two pilot-scale edible oil barriers were constructed in an upgradient area of a chlorinated solvent plume at Dover Air Force Base (AFB), DE.

The site is underlain by approximately 12.2 m of fine to coarse sand with discontinuous lenses of silt overlying a clay aquitard (Dames and Moore 1999). The average depth to groundwater is 3.4 m below grade, but varies seasonally. The saturated thickness ranges from 7.3 to 11.6 m with an average of 9.8 m. An aquifer pump test in the area showed a hydraulic conductivity of 5 X 10^{-2} cm/sec. Using the average regional hydraulic gradient of 0.001 and assuming 30 percent porosity, the groundwater flow velocity within the shallow zone has ranged from 11.9 to 40.5 m per year with an average of 27.4 m/yr. Groundwater flow velocities in the deeper ranged from 13.7 m to 46.6 m/yr. with an average of 29.9 m/yr.

The source area of the plume is anaerobic (Advanced Infrastructure Management Technologies and URS Group, Inc. 2002). An aerobic zone is found downgradient. Daughter products such as cDCE and VC are degraded in the aerobic zone. However, any of the parent compounds PCE and TCE which reach the aerobic zone are not degraded. 1TCA and its daughter products 1DCA, 1DCE, and CA are degraded in the anaerobic source zone.

SUBSTRATE INJECTION: In Barrier 1, ten substrate injection points (IW-004 to IW-013) were installed 0.61 m apart in a row generally perpendicular to groundwater flow (Figure 1). The Geoprobe® equipment advanced 5.4 cm-diameter OD steel casing through the vadose zone and into the groundwater to between 12.2 and 15.2 m bgs. In Barrier 2, four substrate injection points (IW-014 to IW-017) were installed in a line 1.5 m apart generally perpendicular to groundwater flow (Figure 1).

Six direct push 1-inch diameter PVC monitor wells were constructed to monitor each of the two test barriers from 1.5 m upgradient of the barrier to 4.3 m downgradient. The 1-inch diameter monitoring wells were installed to a depth of 12.2 m with 4.6 m of screen.

Two different barrier approaches were evaluated by injecting insoluble substrate into the contaminated aquifer through lines of Geoprobe® points. Each of the ten injection wells in Barrier 1 received 83 L liquid soybean oil in April 2000 at 3.8 to 7.6 L/min with no significant backpressure. The soybean oil in each injection well was then “chased” with approximately 871 L of groundwater to provide a column of substrate approximately 0.73 m in diameter by 9.1 m long assuming equal and radial distribution with an effective porosity of 25%. Monitoring performed after the initial injections in April 2000 revealed that soybean oil had only been delivered to the top of the aquifer, presumably due to the low injection pressure used to deliver the oil. To provide more uniform distribution of oil throughout the vertical interval, a second oil injection was conducted in Barrier 1 in December 2000 to January 2001. During this second injection, a coarse emulsion of soybean oil and lecithin was prepared with a static in-line mixer and the emulsion injected under pressure of 12 to 23 pounds per square inch followed by 312 to 620 L of groundwater.

Barrier 2 received a soybean oil-lecithin emulsion in water. A total of 833 L of soybean oil, 83 L of lecithin, and 30,280 L of groundwater were injected into the four injection wells. Assuming that the emulsion was distributed equally and radially along the entire depth of the 9.1 m well screen, and the effective porosity in the subsurface was 25%; this was designed to provide a column of emulsion approximately 2.1 m in diameter around each injection point.

RESULTS: Table 1 presents the results of the two barriers through 39 months after the first substrate injections in April 2000. The results for the well AA-106 1.8 m downgradient of the barrier and the average in Barrier 1 and well AA-113 1.8 m downgradient of Barrier 2 and the average in Barrier 2 are shown. Wells AA-106 and AA-113 are representative of the degradation patterns observed in the other wells.

As shown in figure 1, dissolved organic carbon (DOC) remained elevated in the injection wells and the downgradient monitoring wells for 39 months after the initial substrate injection. Barrier 1 had a peak concentration of 540 mg/L DOC in downgradient monitoring well AA-105 located 0.61 m from the barrier four months after the coarse emulsion injection. Thirty-nine months after the initial injection, injection well IW-005 in Barrier 1 contained 1,900 mg/L of DOC, and the monitoring wells had an average of 6.5 mg/L DOC with greater than 10 mg/L of DOC found in wells AA-105 and AA-106. The DOC in the Barrier 2 monitoring wells reached a maximum of 630 mg/L DOC three months after injection in well AA-112 located 1.8 m from the barrier. After 39 months, injection well IW-015 contained 280 mg/L of DOC, and the monitoring wells contained an average of 15 mg/L DOC.

In Barrier 1, average PCE, TCE, and cDCE concentrations have declined by 83, 91, and 70%, respectively since the beginning of the pilot. Before injection of the soybean oil, cDCE and VC made up on average 33% of the total chlorinated ethenes on a micromolar basis and 1TCA represented 52% of the chlorinated ethanes. The daughter products increased to as much as 86% of chlorinated ethenes and ethanes after 22 months. After 39 months, the daughter compounds cDCE and VC represented an average of 74% of the chlorinated ethenes. Well AA-106 shown in Table 1 illustrates the results seen in the other monitoring wells. Overall the percent of daughter products of the chlorinated ethenes and ethanes increased from 34% to 78%.

In Barrier 2, cDCE and VC initially represented an average of 53% of the chlorinated ethenes. A high of 84% percent daughter chlorinated ethenes was achieved after 22 months. After 39 months, the edible oil emulsion still supported extensive reductive dechlorination with 83% of the total chlorinated ethenes being cDCE, VC, and ethene. Daughter products of 1TCA initially made up an average of 56% of the chlorinated ethanes in Barrier 2. After 39 months, the daughter products CA, 1DCE, 1DCA, and 2DCA constituted an average of 50% of the chlorinated ethanes. Together the chlorinated ethene and chlorinated ethene daughter products increased from an average of 55% to a maximum of 77% after 9 months, but then declined to 56% after 39 months.

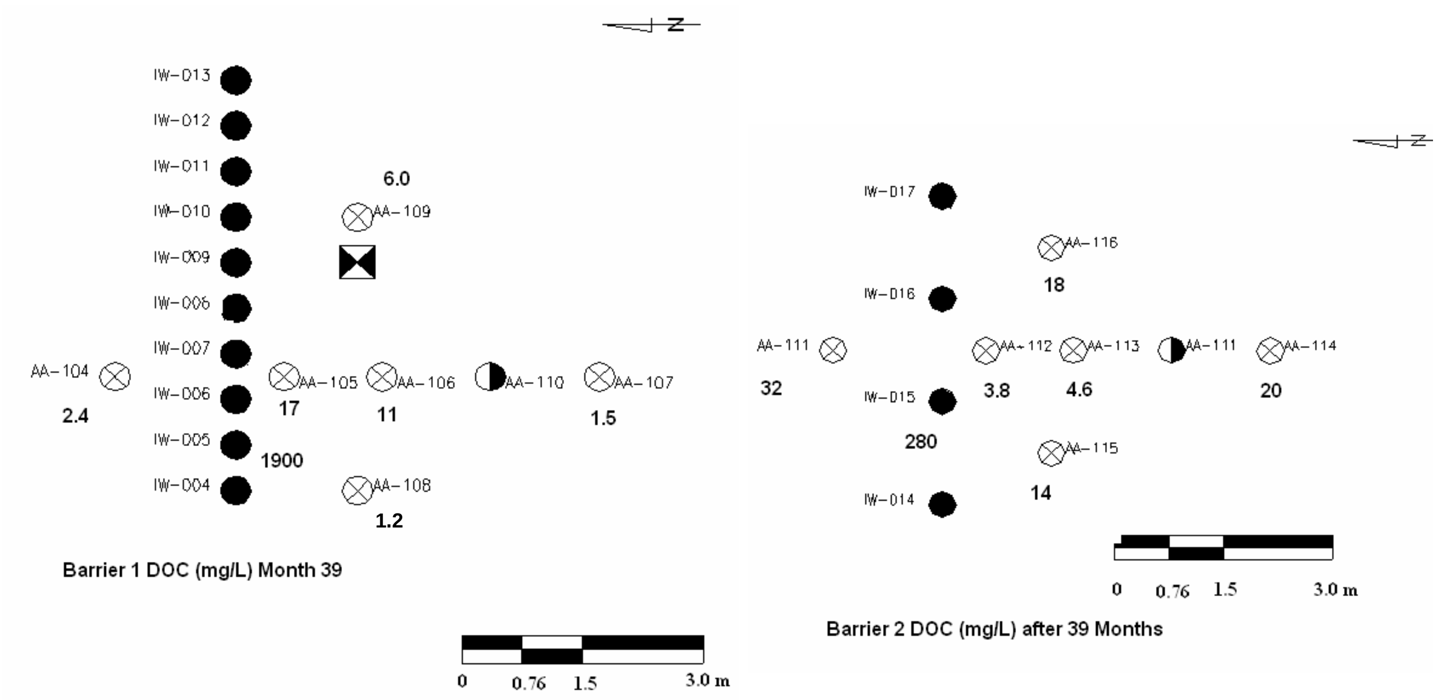

Figure 1. DOC Concentrations in Barriers June 2003 (Month 39)

Table 1. Concentrations of Chlorinated Ethenes and Chlorinated Ethanes (μM), Methane, and DOC (mg/L) in Wells AA-106 and AA-113 and Average for All Six Monitoring Wells in Each Barrier

Well ID Distance	Date	Methane mg/L	Ethene μM	Ethane μM	VC μM	cDCE μM	TCE μM	PCE μM	CA μM	1DCE μM	1DCA μM	2DCA μM	1TCA μM	TVOCs μM	% Daugh-ter	DOC mg/L
Barrier 1. Direct Injection of Soybean Oil and Coarse Emulsion																
AA-106 1.8 m	3/30/2000	0.020	<0.21	<0.20	<0.096	2.3	5.7	1.03	<0.093	1.1	0.12	<0.061	1.3	11.5	30.6	2.2
	5/11/2000	0.014	<0.21	<0.20	<0.096	1.7	3.1	0.53	<0.093	1.1	0.13	<0.061	1.2	7.8	37.6	1.2
	7/12/2000	<0.006	<0.21	<0.20	<0.096	1.1	2.6	0.60	<0.093	<0.062	0.131	<0.061	1.0	5.5	23.0	1.2
	10/12/2000	0.008	<0.21	<0.20	<0.096	0.43	1.1	0.26	<0.093	0.40	0.364	<0.061	0.44	3.0	40.4	1.8
	1/26/2001	0.029	<0.21	<0.20	<0.096	1.0	2.5	0.42	<0.093	1.3	0.31	<0.061	0.90	6.5	40.9	31
	5/3/2001	2.4	<0.21	<0.20	<0.096	0.79	1.1	0.39	<0.093	0.73	<0.061	<0.061	0.42	3.5	44.0	16
	10/2/2001	8.4	<0.21	<0.20	<0.096	1.0	0.91	0.16	<0.093	0.31	<0.061	<0.061	0.30	2.7	49.4	77
	2/5/2002	21.2	<0.043	<0.043	0.069	9.2	2.6	0.35	0.11	1.55	0.15	<0.061	0.73	14.7	75.1	57
	7/8/2003	14.1	0.75	<0.043	0.090	1.5	0.15	0.054	0.086	0.43	0.27	<0.057	0.30	3.6	87.3	11
Average	3/30/2000	0.023	0.000	0.000	0.000	5.3	5.0	0.69	0.000	2.8	0.50	0.014	3.1	17.4	34.3	2.2
	5/11/2000	0.019	0.000	0.000	0.000	2.2	2.7	0.48	0.000	1.1	0.22	0.000	1.4	8.1	34.7	1.9
	7/12/2000	0.000	0.000	0.000	0.12	2.1	2.4	0.68	0.067	0.96	0.26	0.027	1.5	8.1	33.5	12
	10/12/2000	0.043	0.000	0.000	0.000	2.3	1.8	0.45	0.000	1.5	0.43	0.096	2.4	8.9	40.3	17
	1/26/2001	0.26	0.000	0.000	0.000	3.7	2.4	0.62	0.000	2.3	0.63	0.034	2.0	11.8	50.1	90
	5/3/2001	2.2	0.000	0.000	0.038	2.1	0.93	0.32	0.000	1.5	0.17	0.13	1.0	6.2	59.6	106
	10/2/2001	12.6	0.065	0.000	0.045	3.8	0.62	0.16	0.062	1.0	0.07	0.033	0.87	6.8	74.6	53
	2/5/2002	14.2	0.079	0.063	0.055	6.6	0.52	0.13	0.079	1.1	0.11	0.000	0.56	9.3	86.3	91
	7/8/2003	12.9	0.54	0.000	0.083	1.6	0.46	0.12	0.014	0.48	0.26	0.000	0.26	3.8	77.8	6.5
Barrier 2. Soybean Oil Emulsion																
AA-113 1.8 m	3/30/2000	0.013	<0.21	<0.20	<0.096	10.2	8.7	0.72	<0.093	9.3	4.3	0.12	10.0	43.3	55.3	3.7
	5/11/2000	0.020	<0.21	<0.20	<0.096	1.8	0.65	<0.036	<0.093	0.80	0.36	<0.061	0.82	4.4	66.5	60
	7/12/2000	<0.006	<0.21	<0.20	0.82	2.2	<0.046	0.17	<0.093	1.1	0.89	<0.061	0.82	6.0	83.4	630
	10/12/2000	3.8	0.68	<0.20	<0.096	10.7	0.18	0.15	1.0	5.6	4.3	0.46	6.2	29.3	77.7	110
	1/26/2001	9.2	<0.21	<0.20	0.62	13.8	0.20	0.10	2.2	8.0	4.8	0.35	4.5	34.7	86.2	220
	5/3/2001	6.6	<0.21	<0.20	0.13	6.1	0.18	0.17	1.0	2.6	1.8	0.41	1.6	14.1	85.8	65
	10/2/2001	36.0	<0.21	<0.20	0.22	11.6	0.048	0.044	2.3	4.4	2.0	0.11	2.7	23.5	88.1	60
	2/5/2002	8.6	0.075	0.047	<0.096	7.8	0.71	0.21	0.17	3.2	2.0	<0.061	4.3	18.6	71.7	15
	7/8/2003	2.8	0.50	<0.043	0.045	13.8	2.9	2.6	0.13	15.9	4.7	0.19	12.9	53.8	65.7	4.6
Average	3/30/2000	0.014	0.000	0.000	0.00	9.0	7.2	0.79	0.00	8.0	3.5	0.020	8.9	37.5	54.7	2.9
	5/11/2000	0.015	0.000	0.000	0.00	6.9	3.7	0.37	0.00	5.2	2.9	0.061	6.7	25.8	57.7	28
	7/12/2000	0.005	0.000	0.000	0.39	7.6	2.3	0.60	0.25	6.8	3.5	0.23	7.3	28.9	70.9	137
	10/12/2000	1.4	0.65	0.000	0.00	11.4	1.3	0.33	0.98	6.9	4.9	0.45	10.5	37.3	68.9	49
	1/26/2001	5.1	0.000	0.000	0.41	12.6	0.9	0.29	0.95	8.7	4.5	0.42	7.4	36.2	76.9	122
	5/3/2001	2.3	0.000	0.000	0.057	3.5	0.36	0.19	0.23	2.5	1.3	0.41	2.1	10.7	75.1	28.2
	10/2/2001	14.9	0.000	0.000	0.11	7.7	0.85	0.28	0.72	3.3	1.8	0.13	3.7	18.7	73.7	25
	2/5/2002	10.8	0.077	0.064	0.050	13.9	0.73	0.19	0.46	5.0	3.2	0.00	7.3	31.0	75.4	21
	7/8/2003	4.4	0.18	0.000	0.062	13.0	1.2	1.5	0.31	9.4	4.0	0.12	13.7	45.7	55.6	15

SUMMARY AND CONCLUSIONS

Oil Injection and Distribution. In Barrier 1, 83 L of food-grade liquid soybean oil were added to each of ten injection wells followed by 833 L of water per well to distribute and immobilize the oil. The large majority of the oil appeared to be distributed in the upper portions of the aquifer with less than 1% of the added oil remaining in the injection wells. Results from cone penetrometer testing with a Laser Induced Fluorescence (LIF) probe and hexane extractions of soil cores indicate that the large majority of the oil was distributed between 3.0 and 7.0 m bgs with oil detected up to 3.0 m from the injection wells. However these results also indicate that very little oil was distributed throughout the lower two-thirds of the aquifer (7 to 12.2 m bgs). As a consequence of the limited vertical distribution of oil, there was little or no increase in TOC concentrations in monitor wells screened in the lower portion of the aquifer.

The limited vertical distribution of oil in Barrier 1 may have been due to the low pressure used for oil and water injection. Oil and water were injected into each of the ten wells at a flowrate of approximately 3.8 to 7.6 Lpm per well at less than 5 psi. This low flowrate was selected to prevent fracturing of the formation due to excessive pressure. However the flowrate was so low that there was no observed pressure buildup during injection.

A second oil injection was conducted in December 2000 – January 2001 to overcome the problems with the initial oil injection in Barrier 1. First, 2,080 L of coarse soybean oil-in-water emulsion was prepared containing 10% lecithin, 30% soybean oil and 60% water using a centrifugal pump and static in-line mixer. Approximately 208 L of this coarse emulsion was then injected into each well at a pressure of 12 to 23 psi followed by 300 to 530 L of groundwater at 11 to 19 psi. While the cold temperatures complicated the emulsion preparation, this second injection was effective in increasing TOC levels in the lower portion of the aquifer. With the exception of the most downgradient well (AA-114), TOC concentrations were above 50 mg/L in all monitor wells, thirteen months after the coarse emulsion injection.

In Barrier 2, approximately 8,330 L of emulsion and 22,700 L of chase water were injected though four wells over a 3 day period. The emulsion was prepared by blending 833 L of soybean oil, 83 L of lecithin and approximately 7,570 L of water through a high shear mixer. Assuming the emulsion was uniformly distributed over the 9.1 m injection interval, the injection process was designed to provide a 2.1 m diameter column of emulsion treated aquifer material surrounding each injection point. The injection points were spaced 1.5-m on-center to provide some overlap between injections. While time consuming, this injection process appeared to provide effective distribution of oil throughout the vertical extent of the aquifer. Cone penetrometer testing and soil sampling indicated that emulsion was distributed over 9.8 m below ground surface. TOC concentrations in monitor wells screened in the lower portion of the aquifer (7.6 to 12.2 m BGS) show a clear response with TOC concentrations in the closest monitor wells increasing to over 600 mg/L shortly after emulsion injection.

Effectiveness. Following the soybean oil injections, both barriers became more anaerobic with low dissolved oxygen levels, negative oxidation-reduction potentials, reduced nitrate and sulfate concentrations, and elevated ferrous iron and methane levels.

In both barriers, PCE and TCE concentrations generally decreased with increases in cDCE. Relatively little VC or ethene was formed. Similarly, 1TCA concentrations generally declined, but concentrations of 1DCE appeared to increase. Concentrations of 1DCA fluctuated but overall did not change appreciably. CA was detected in several wells, but constituted a maximum of 56% of the total chlorinated ethanes. Ethane was a minor product.

Adsorption of the contaminants into the oil played a role in the early reductions in contaminant concentrations (particularly in wells AA-105 and AA-107 in the direct oil barrier and wells AA-113 and AA-115 in the emulsion barrier), but the contaminant concentrations have largely increased as contaminants partitioned out of the oil. However, there was a larger proportion of daughter products.

There is clear evidence of the biological transformation of TCE and 1TCA to cDCE and 1DCA with lesser production of VC, CA, ethene, and ethane. As groundwater migrates further downgradient, the remaining contaminants will be further oxidized to carbon dioxide. However, it appears that microbes capable of complete dechlorination to ethene and ethane are either not present in the immediate vicinity of the edible oil barrier or were not stimulated by the creation of a carbon-rich anaerobic environment.

Although little of the chlorinated ethenes have been completely degraded to ethene or ethane within the treatment areas, the edible oil in both barriers has been effective in supporting partial dechlorination of the parent compounds to daughter products are then being degraded in the downgradient aerobic zone.

Thus, through EISB of the “source zone”, the base will be able to overall effectively remediate the site to target levels, without the need of reaching complete EISB end products in the active treatment area. The emulsion barrier was expanded in July 2003.

Hydraulic Conductivity. Injection of the soybean oil alone or as emulsion impacted the hydraulic conductivity of the injection wells. In Barrier 1, the two injection wells tested showed a variable response. In Barrier 2, a two order of magnitude reduction in the hydraulic conductivity was noted in the two injection wells tested (data not shown). The loss in hydraulic conductivity may be a result of oil clogging the soil pores, growth of microbes resulting in biofouling, or trapping of methane bubbles. Neither direct soybean oil nor oil emulsion injection affected the hydraulic conductivity of the downgradient wells. Although the permeability in the area immediately surrounding the injection wells was reduced, there was still evidence that groundwater moved through the barrier.

Methane Accumulation. A significant portion of the injected soybean oil was biodegraded to methane. High levels of methane were found in all of the monitoring wells surrounding both barriers. Methane accumulation in excess of the lower explosive limit was found in the deep soil gas monitoring points. However, methane was not detected in the shallow monitoring points 6.1 m downgradient of either barrier indicating that methane is being degraded in the vadose zone.

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