PERMEABLE MULCH BIOWALL FOR ENHANCED BIOREMEDIATION OF CHLORINATED ETHENES

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ABSTRACT: A permeable mulch biowall was installed at Altus Air Force Base (AFB), Oklahoma in June 2002 to stimulate reductive dechlorination of chlorinated aliphatic hydrocarbons (CAHs) in groundwater at Landfill 3 (LF-3). The objective of the biowall application is to contain and attenuate a shallow groundwater plume contaminated with trichloroethene (TCE) and *cis*-1,2-dichloroethene (cDCE), in order to prevent surface water discharge or off-base migration. The biowall is composed of shredded tree mulch, cotton gin compost, and sand (to maintain permeability). These substrates are intended to be used as solid-phase, long-term carbon sources to stimulate reductive dechlorination of CAHs over periods of 5 years or more. In June 2003, a 455 feet long by 24 feet deep by 1.5 feet wide biowall was installed in 4 days using a continuous trenching machine, . Depth to water varies from 6 to 8 feet below grade, and the permeable biowall is intended to intercept over 80 percent of the groundwater plume contaminant flux (subject to depth limitations of the trencher). Two different monitoring wells arrays consisting of upgradient, biowall, and downgradient monitoring well locations were utilized for remedial performance monitoring. Initial sampling at 4 weeks following installation indicated that sulfate reduction and methanogenesis had been stimulated within the biowall, with over 90 percent reduction in concentrations of TCE. Significant changes in TCE to daughter compound ratios combined with measured changes in ground water geochemistry directly within the biowall and five feet downgradient provided a clear indication that contaminated ground water was flowing through the biowall and that TCE reductions were primarily due to biodegradation effects. Concentrations of TCE within the biowall at 3 months following installation had declined an average of 98 percent. The total molar concentration of chlorinated ethenes in September 2002 for the biowall locations was 90 percent less than that measured in the upgradient locations. Total organic carbon (TOC) and metabolic acids decreased between 4 weeks and 3 months after installation, suggesting readily soluble organic carbon in the mulch and compost was being depleted, and that levels of organic carbon within the biowall had declined to more sustainable levels. The resultant concentrations of TCE breakdown products, to include increasing concentrations of ethene over time, suggest that the biowall is facilitating the complete mineralization of site chlorinated solvent contaminants. Future monitoring is planned to determine the ability of the biowall to sustain degradation.

INTRODUCTION

Solid-phase organic substrates used to stimulate reductive dechlorination of CAHs include plant mulch and compost. Mulch and compost are byproducts of the landscaping and agricultural industries, and can often be obtained for little cost or for the cost of handling alone. Mulch may be composted prior to emplacement, or the mulch may be mixed with another source of compost, to provide active microbial populations for further degradation of the substrate in the subsurface. Mulch is primarily composed of cellulose, but "green" plant material is typically incorporated to provide a source of nitrogen for microbial growth. Typically, these substrates are emplaced in a trench or excavation in a permeable reactive barrier configuration. This treatment method relies on the flow of groundwater under a natural hydraulic gradient through the biowall to promote contact with slowly-soluble organic matter. Degradation of the substrate by microbial processes in the subsurface provides a number of breakdown products, including metabolic acids. While the nature of the breakdown products and metabolic acids produced by degradation of mulch in a saturated subsurface environment are as yet not well known, they likely provide secondary electron donors or fermentable substrates for hydrogen generation. Thus, a mulch biowall has the potential to stimulate reductive dechlorination of CAHs for periods of many years. In addition to the application at Altus AFB discussed in this paper, mulch biowalls for degradation of chlorinated compounds have also been installed at Offutt AFB, Nebraska (Haas *et al*., 2000 and Aziz *et al*., 2001) and Naval Weapons Industrial Reserve Plant, McGregor, Texas (Cowan, 2000).

Objectives

A permeable reactive mulch biowall was installed across the path of groundwater flow along the downgradient (eastern) edge of LF-3 to assess the applicability and feasibility of promoting the *in-situ* bioremediation of CAHs in groundwater, primarily TCE and cDCE. The biowall trench is intended to intercept and degrade sufficient contaminant mass flux to attenuate and contain the groundwater plume and in order to prevent surface water discharge or potential off-base migration.

Site Description

Landfill Number 4 (LF-04), located in the northeastern portion of Altus AFB (Figure 1), operated from 1956 through 1983. LF-04 includes several disposal features, including LF-3 and a Petroleum, Oil, and Lubricant (POL) Tank Sludge Burial area. LF-3 is located at the eastern portion of the site, and is bordered by the Ozark lateral irrigation canal on the west and south, Stinking Creek on the northeast, an unnamed drainage canal on the north, and the Base boundary and Taxiway "M" on the east. From 1956 to 1965, the LF-3 portion of LF-04 received waste materials including garbage, wood, paper, metal, and shop wastes. After 1965, LF-3 received construction debris, concrete, brush, and several drums of paint waste. Waste at LF-3 was buried in trenches at depths ranging from 6 to 8 feet below ground surface (bgs). Historical waste management activities at LF-3 have resulted in low concentrations of CAHs in groundwater beneath, and immediately to the east-southeast of the landfill.

Surface soils at the site consist of approximately 5 feet of clayey silt and a weathered and fractured stiff silty clay that extends to depth of approximately 25 to 30 feet bgs. These sediments are underlain by well-cemented silt and dense shale of the Hennessey Group of Permian age. Shallow groundwater occurs under unconfined conditions and generally flows towards the east-southeast and Stinking Creek. Shallow groundwater at the site occurs at a seasonally variable depth of approximately 6 to 12 feet bgs. The groundwater surface slopes toward the southeast with an average horizontal hydraulic gradient of approximately 0.003 foot per foot (ft/ft). Hydraulic conductivity ranges from 8.4 to 20 feet per day (ft/day) in the overburden clay. Using a calculated hydraulic conductivity of 8.4 to 20 ft/day, a horizontal hydraulic gradient of 0.003 ft/ft, and an estimated effective porosity of 5 percent, the advective groundwater flow velocity in the overburden clay is calculated to range from 0.50 to 1.2 ft/day [183 to 438 feet per year (ft/yr)]. Visual examination of sediments from borehole cores indicates the presence of secondary permeability due to dissolution features and soil fractures.

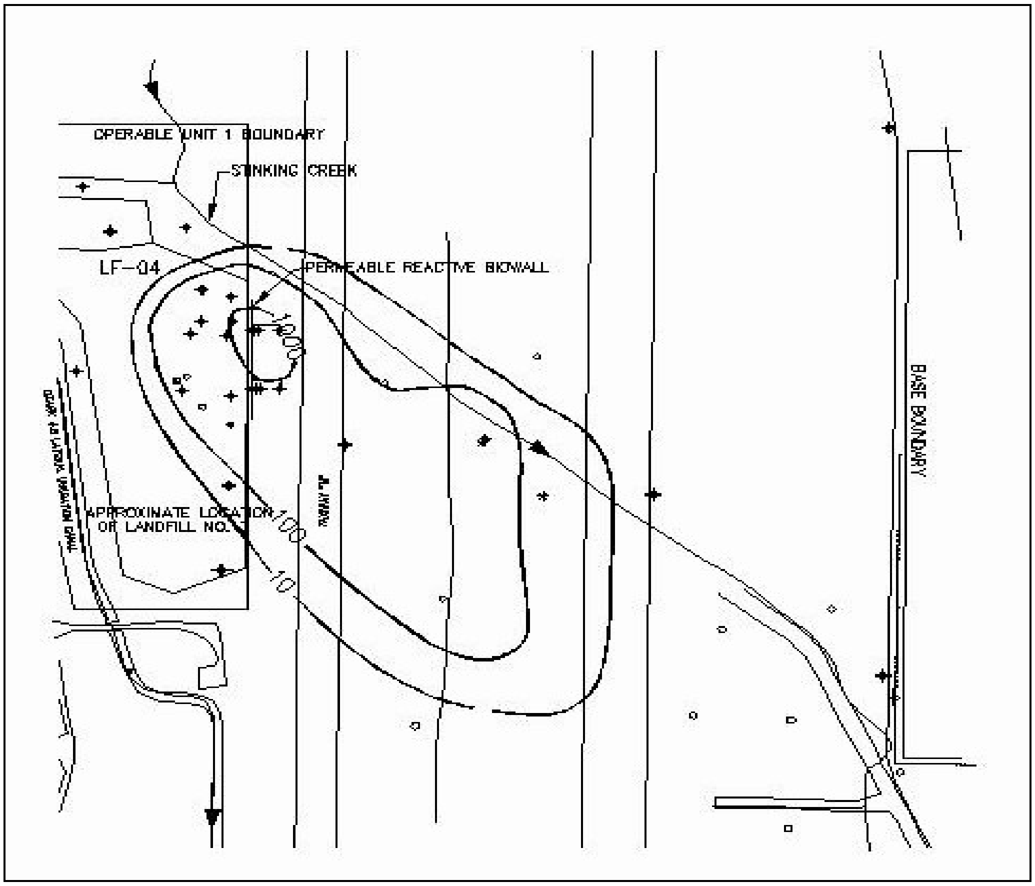

Figure 1. Location of Biowall relative to TCE Plume (isoconcentration contours in micrograms per liter of TCE)

TCE and the dichloroethene isomer cDCE are the most prevalent CAHs in both extent and concentration in groundwater at LF-3. The areal extent of TCE based on groundwater samples collected in April 1999 is illustrated in Figure 1. The TCE plume originates from LF-3 and extends southeastward approximately 4,000 feet to the Base's eastern boundary. Concentrations of TCE in April 1999 ranged up to 6,110 micrograms per liter (μg/L). Migration of the TCE plume to the east appears to be limited by Stinking Creek. Groundwater samples collected from monitoring locations northeast of Stinking Creek during previous investigations did not contain detectable levels of TCE or other CAHs. Stinking Creek may be exerting hydraulic control, resulting in no further TCE plume migration northeast of the creek. Hydraulic control could occur under both gaining- and losing-stream scenarios and could vary seasonally. Under a losing-stream scenario, groundwater recharge could create a barrier to flow in the form of a groundwater divide. Under a gaining-stream scenario, a significant percentage of under-flow could be captured by the creek.

METHODS AND MATERIALS

System Design and Installation

The biowall was constructed across the path of groundwater flow on the downgradient edge (eastern boundary) of LF-3 (Figure 1). The biowall is intended to capture over 80 percent of the mass flux originating from the landfill. A 455 foot-long, by 24 foot-deep, by 1.5 foot-wide mulch biowall was installed from June 19 to 23, 2002 by DeWind Environmental of Zeeland, Michigan. Final biowall composition consisted of approximately 300 cubic yards of shredded mulch, 60 cubic yards of cotton gin compost, and 265 cubic yards of sand. The mulch consisted of shredded plant material generated by the City of Altus after a winter storm event and during seasonal landscaping operations throughout the surrounding community. This material was provided to the Air Force at no cost other than minimal transportation costs.

A continuous trenching machine was employed to excavate the trench for the biowall and simultaneously place the mulch, compost, and sand mixture into the trench. Given the buoyant nature of nature of the organic mulch and the dense nature of the sand, the method of emplacement must avoid the inadvertent separation of the "lighter" and "heavier" fractions of this mixture. Site soil and aquifer characteristics were considered to be compatible with a continuous trencher mode of construction. The trencher is a track-mounted vehicle that has a cutting boom resembling a large chain saw (i.e., linked chain belt with cutting teeth). A steel box with a hopper assembly is fitted atop the cutting boom. The cutting boom excavates a trench by simultaneously rotating the cutting chain and advancing the boom until the desired depth of excavation relative to the ground surface has been achieved. The steel box and hopper assembly provide for stabilization of the trench sidewalls during excavation and subsequent placement of the sand and mulch mixture, which is introduced through the feed hopper. Simultaneous excavation and placement of backfill materials eliminates concerns associated with open excavations and eliminates the need to conduct dewatering operations.

Following construction of the biowall, ten groundwater monitoring wells and four soil vapor monitoring points were installed. Groundwater monitoring wells were installed along two lines perpendicular to the biowall. Wells were installed within the footprint of the biowall, and at distances of 5, 10, 30, and 100 feet downgradient (to the east) of the biowall. These points are be used to monitor groundwater geochemical indicators and contaminant concentrations within and immediately downgradient of the biowall. Two existing groundwater monitoring wells (OU-1-01 and WL019) located approximately 25 feet upgradient of the biowall are also being monitored. Two soil vapor monitoring points were installed within the footprint of the biowall, and two vapor points were installed at a distance of 5 feet downgradient of the biowall. These points are used to monitor volatilization or accumulation of vapors in the vadose zone that may be indicative of the biochemical processes within and immediately downgradient of the biowall.

Performance Monitoring

Post-installation sampling of groundwater at the newly installed monitoring wells and existing monitoring wells OU-1-01 and WL019 was conducted in July and September 2002. Groundwater samples were analyzed for chlorinated solvents and their degradation products, dissolved oxygen (DO), nitrate, ferrous iron, manganese, sulfate, hydrogen sulfide, carbon dioxide, methane, ethane, ethane, oxidation-reduction potential (ORP), alkalinity, pH, temperature, specific conductance, TOC, volatile fatty (metabolic) acids, and chloride.

RESULTS AND DISCUSSION

Groundwater Geochemistry

Biodegradation causes measurable changes in groundwater geochemistry that can be used to evaluate the effectiveness of substrate addition in stimulating biodegradation. For reductive dechlorination to be an efficient process, the groundwater typically must be sulfate-reducing or methanogenic. Thus, groundwater in which reductive dechlorination is occurring should have the following geochemical signature:

- Depleted concentrations of DO, nitrate, and sulfate;
- Elevated concentrations of ferrous iron, manganese, methane, ethene, ethane, hydrogen, carbon dioxide, chloride, and alkalinity; and
- Reduced ORP.

Selected geochemical parameters are shown on Table 1. Comparison of geochemical parameters for biowall locations PES-MP01 and PES-MP06 to locations outside the biowall can be summarized as follows:

- With the exception of the furthest downgradient well locations, dissolved oxygen levels were already depleted (less than 2 milligrams per liter [mg/L]) in the study area.
- Oxidation-reduction potential in the biowall has been lowered to –212 millivolts (mV) to –325 mV as measured in September 2002.
- Sulfate levels in the biowall have been depleted to 17 to 300 mg/L in September 2002, compared to background levels of 1,400 mg/L to 2,200 mg/L. Meanwhile, hydrogen sulfide levels are elevated in the biowall at concentrations of 15 mg/L to 32 mg/L (data not shown).
- Methane levels in the biowall are elevated at concentrations of 7.0 to 8.8 mg/L.
- TOC (unfiltered samples) within the biowall was measured at 2,800 mg/L for location PES-MP01 in July 2002 (4 weeks after installation), but dropped to concentrations of 380 to 390 mg/L in September 2002 (3 months after installation). Elevated levels of TOC (greater than 20 mg/L) were observed as far downgradient as wells PES-MP04 and PES-MP09, located 30 feet from the biowall.

- Total metabolic acids (comprised primarily of acetic, propionic, and butyric acids) are elevated in the biowall.

Degradation of Chlorinated Ethenes

Table 2 summarizes chlorinated ethenes detected in groundwater during monitoring in July and September 2002. Well installation and the first round of groundwater sampling was performed approximately 4 weeks after installation of the biowall, based in part on availability of the drilling contractor. While true “baseline” conditions for the wells located in the trench (PES-MP01 and PES-MP06) were not obtained, data from upgradient wells can be used to infer “baseline” conditions across the site.

Table 1. Groundwater Geochemistry

Sample Location (feet from trench)	Sample Date	Dissolved Oxygen (mg/L)[a/]	Redox Potential (mV)[b/]	Total Organic Carbon (mg/L)	Total Metabolic Acids (mg/L)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Methane (mg/L)[c/]
Monitoring Flowpath No. 1								
OU-1-01	17-Jul-02	<0.1	88	<5.0	--	<0.01	1,600	2.4
(upgradient)	18-Sep-02	<0.1	9	5.6	--	<0.01	1,700	5.2
PES-MP01	18-Jul-02	0.1	-365	2,800	959	3.5	410	8,800
(biowall)	18-Sep-02	<0.1	-212	380	8.4	1.2	17	7,000
PES-MP02	18-Jul-02	0.2	-94	19	--	0.7	1,900	150
(5’)	18-Sep-02	<0.1	-179	43	--	2.3	1,700	3,500
PES-MP03	18-Jul-02	1.9	20	5.2	--	0.2	1,900	200
(10’)	18-Sep-02	<0.1	-68	16	--	0.2	1,900	1,400
PES-MP04	18-Jul-02	<0.1	-204	130	--	1.0	1,800	1,900
(30’)	18-Sep-02	<0.1	-169	30	--	1.6	1,700	4,100
PES-MP05	18-Jul-02	4.6	63	<5.0	--	<0.01	1,900	4.8
(100’)	19-Sep-02	<0.1	26	5.4	--	<0.01	1,800	14
Monitoring Flowpath No. 2								
WL019	17-Jul-02	<0.1	107	<5.0	--	<0.01	2,000	4.2
(upgradient)	19-Sep-02	<0.1	150	<5.0	--	<0.01	1,600	3.6
PES-MP06	18-Jul-02	<0.1	-266	NA	1,367	4.1	--	7,900
(biowall)	17-Sep-02	<0.1	-325	390	244	0.3	300	7,900
PES-MP07	19-Jul-02	<0.1	-227	710	--	1.7	1,100	2,500
(5’)	17-Sep-02	<0.1	-201	80	--	0.9	700	6,400
PES-MW8	19-Jul-02	<0.1	-235	520	--	0.8	1,400	1,700
(10’)	19-Sep-02	<0.1	-237	77	--	1.1	800	6,200
PES-MP09	17-Jul-02	0.2	-6	17	--	1.3	1,800	47
(30’)	19-Sep-02	<0.1	-161	25	--	0.9	1,100	3,300
PES-MW10	19-Jul-02	--	45	<5.0	--	<0.01	2,200	5.2
(100’)	19-Sep-02	4.2	72	<5.0	--	<0.01	2,100	0.99

[a/] mg/L = milligrams per liter. [b/] mV = millivolts. [c/] μg/L = micrograms per liter.

The primary contaminants detected at the site include TCE and cDCE. Concentrations of TCE ranged up to 8,000 micrograms per liter (μg/L) at upgradient location OU-1-01. Concentrations of cDCE ranged up to 1,100 μg/L at upgradient location OU-1-01 as well. Lesser concentrations (less than 25 μg/L) of tetrachloroethene (PCE), *trans*-1,2-DCE (data not shown), 1,1-DCE (data not shown), and vinyl chloride (VC) also were detected at the site. During the 4 week sampling event in July 2002, the ratio of TCE to *cis*-1,2-DCE ranged from 25:1 to 1.5:1, with the notable exception of biowall location PES-MP01. For location PES-MP01, the ratio of TCE to *cis*-1,2-DCE was less than 0.1:1, indicating that degradation of TCE to cDCE was stimulated within the biowall within 4 weeks of installation. As of the 3 month monitoring event, the trend of decreasing TCE and increasing cDCE was observed at all locations located within 30 feet downgradient of the biowall.

Table 2. Concentrations of Select Chlorinated Ethenes

Sample Identification	Location Relative to Biowall	Sample Date	PCE (µg/L)[a/]	TCE (µg/L)	cDCE (µg/L)	VC (µg/L)	Ethene (µg/L)
Monitoring Flowpath No. 1							
OU-1-01	25' Upgradient	19-Jul-02	<9.3	6,200	850	<7.3	0.077
		18-Sep-02	<31	8,000	1100	<24	0.170
PES-MP01 (0')	Within Biowall	18-Jul-02	<5.6	48	680	<4.4	0.065
		18-Sep-02	<2.8	0.12J	480	3	0.010
PES-MP02 (5')	5' Downgradient	18-Jul-02	0.10J	290	49	<1.1	0.062
		18-Sep-02	<3.5	55	770	0.64J	0.220
PES-MP03 (10')	10' Downgradient	18-Jul-02	0.18J	350	22	<1.1	0.036
		18-Sep-02	<5.6	150	1,200	0.27J	0.100
PES-MP04 (30')	30' Downgradient	18-Jul-02	0.20J	430	260	0.055J	0.360
		18-Sep-02	<5.6	120	1,100	0.35J	0.130
PES-MP05 (100')	100' Downgradient	18-Jul-02	0.37J	2,500	240	<5.5	0.032
		19-Sep-02	<16	3,000	590	<12	0.110
Monitoring Flowpath No. 2							
WL019	25' Upgradient	19-Jul-02	0.28J	1,500	130	<4.4	<0.005
		19-Sep-02	0.19J	1,200	140	<3.7	0.045
PES-MP06 (0')	Within Biowall	18-Jul-02	<2.8	170	80	<2.2	0.220
		17-Sep-02	<2.8	5.2	310	1.5J	0.063
PES-MP07 (5')	5' Downgradient	19-Jul-02	0.051J	190	130	<1.1	0.790
		17-Sep-02	<2.8	10	300	0.88J	0.210
PES-MP08 (10')	10' Downgradient	19-Jul-02	0.063J	250	130	0.16J	0.970
		19-Sep-02	<1.4	4.5	330	0.90J	0.240
PES-MP09 (30')	30' Downgradient	17-Jul-02	<1.4	220	150	0.19J	0.290
		19-Sep-02	<1.4	69	200	0.38J	0.530
PES-MP10 (100')	100' Downgradient	19-Jul-02	0.47J	670	27	<2.2	0.870
		19-Sep-02	0.28J	460	32	<2.2	0.340

[a/] µg/L = micrograms per liter.

The average decrease in TCE concentrations from July to September 2002 within the biowall was 98 percent. For all locations downgradient of the biowall, the average decrease in TCE was 60 percent. While concentrations of cDCE increased in many locations over the same period, the concentration of cDCE declined from 680 µg/L to 480 µg/L at location PES-MP01, the first location to show evidence of degradation of TCE to cDCE in July 2002. This hints at the potential for significant degradation of cDCE to occur, without an accumulation of VC. A more important observation is that the total molar concentration of chlorinated ethenes for the biowall locations in September 2002 was 90 percent less than that measured in the upgradient locations. Therefore, the apparent accumulation of cDCE should be taken in the context of a significant reduction in overall contaminant mass.

Capitol and Monitoring Costs

Approximate costs to install and monitor the biowall include $10,000 for design and work plan development; $169,000 for procurement, mobilization, trench installation, and monitoring well installation; $57,000 for three rounds of process monitoring; and $34,000 for reporting and meetings. Total cost for design, installation, one year of semi-annual monitoring and reporting is approximately $270,000. Capitol cost ($169,000) for installation of the biowall is approximately $370 per linear foot, including all materials, labor, and installation of the monitoring network. Future operations and maintenance (O&M) costs are anticipated to be approximately $25,000 per year for semi-annual monitoring and reporting.

SUMMARY

Geochemical data indicate that levels of organic carbon within the biowall are sufficient to induce sulfate reduction and methanogenesis, oxidation-reduction conditions that are highly conducive to reductive dechlorination of chlorinated compounds. Elevated levels of TOC and metabolic acids (primarily acetic, propionic, and butyric) were observed. Fermentation of these low-molecular weight fatty acids is known to produce molecular hydrogen and to stimulate reductive dechlorination. An average decrease of 98 percent in concentrations of TCE was observed within the biowall at 3 months following installation. It is not yet known the extent to which the system is capable of degrading cDCE. However, a 90 percent differential in total molar concentration of chlorinated ethenes has been observed between the upgradient and biowall monitoring locations. Additional monitoring is planned to document the ability of the biowall to sustain biological activity and contaminant mass degradation. In addition, AFCEE will be conducting solid phase soil mineral profiling to evaluate whether reactive iron sulfide minerals are formed which have been shown to promote abiotic reductive dechlorination.

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