

Lee, Michael D, M. Tony Lieberman, Walt Beckwith, Robert C. Borden, Jess Everett, Lonnie Kennedy, and Jim R. Gonzales. In Press. Pilots to enhance trichloroethene reductive dechlorination and ferrous sulfide abiotic transformation. To be presented at the In Situ and On-Site Bioremediation Seventh International Symposium, Orlando, FL, June 2-5, 2003.

PILOTS TO ENHANCE TRICHLOROETHENE REDUCTIVE DECHLORINATION AND FERROUS SULFIDE ABIOTIC TRANSFORMATION

Michael D. Lee, Ph.D. mlee@terrasystems.net (Terra Systems, Inc., Wilmington, DE, USA), M. Tony Lieberman, Walt Beckwith, and Robert C. Borden, Ph.D. (Solutions Industrial & Environmental Services, Raleigh, NC, USA)

Jess Everett, Ph.D. and Lonnie Kennedy, Ph.D. (Rowan University, Glassboro, NJ, USA) and Jim R. Gonzales (Air Force Center for Environmental Excellence, Brooks AFB, TX)

ABSTRACT: Two field pilots are being conducted at Altus Air Force Base (AFB), Oklahoma in areas with high levels of sulfate and iron. An edible oil emulsion was injected into these pilots to promote biological reductive dechlorination of trichloroethene (TCE) and to stimulate ferric sulfide and ferric disulfide production and the abiotic reaction with TCE. Within the injection zone of the larger SS-17 pilot, TCE declined from 9.9 μM to $<0.043 \mu\text{M}$ after 13 months with decreases in cis-1,2-dichloroethene (cDCE) [26%] and sulfate (99%), and increases in vinyl chloride (VC) to 0.75 μM and methane to 16.3 mg/L. In a well 7.6 m downgradient, TCE declined from 12.6 μM to $<0.043 \mu\text{M}$ with decreases in cDCE (92%), and sulfate (42% to 247 mg/L). Increases in VC to 28 μM , ethene to 18.2 μM , and methane to 15.2 mg/L were observed at 13 months in this well. Although ferric sulfide and ferric disulfide were produced in the treatment zone by microbial activity, acetylene (an abiotic reaction product from ferric sulfide and ferric disulfide) was not detected at appreciable concentrations. Biological reductive dechlorination processes appeared to predominate in this area. A second smaller pilot was conducted in the OU1 plume with 1,700 mg/L of sulfate, but with no evidence for the presence of dechlorinators. In one injection well, TCE decreased from 43 μM to 0.33 μM after 13 months, cDCE increased to 7.1 μM , and little VC was detected. Both ethene and ethane were detected at high concentrations after 5 months, but then declined to trace levels at 13 months. Although acetylene was not detected, the abiotic pathway for TCE removal appeared to be favored because of the low levels of cDCE and VC that were produced. The results from these field pilots demonstrate that dechlorination of TCE can be stimulated by biological and abiotic process in areas with high sulfate and iron levels.

INTRODUCTION: Biological reductive dechlorination of TCE to cDCE, VC, and ethene or ethane has been demonstrated at a number of sites (Ellis et al. 2000, Lee et al. 1998). The activity of dehalorespiring organisms such as *Dehalococcoides ethenogenes* is promoted by the addition of an electron donor to generate anaerobic conditions and provide electrons for the reductive dechlorination process (Maymo²-Gattell et al. 1999). *Dehalococcoides ethenogenes* have been found at many sites where ethene was detected (Hendrickson et al. 2002). However, it was not found at sites where cDCE was the final degradation product. The dehalorespirers typically operate under methanogenic conditions and are inhibited by high levels of sulfate (Harkness et al. 1999). In contrast, Drzyga et al. (2002) conducted column studies under sulfate-reducing conditions fed

methanol, lactate, and sulfate. Ethene and ethane were detected in each column effluent along with sulfate levels in excess of 200 mg/L.

When a biodegradable organic substrate is present in an aquifer with ferric iron and sulfate, sulfate and iron reduction occurs (Kennedy and Everett 2001). Bacteria generate several forms of ferrous sulfide including amorphous iron sulfide, mackinawite ($\text{Fe}_{0.995-1.023}\text{S}$), greigite (Fe_3S_4), and pyrrhotite ($\text{FeS}_{1.1}$). Upon further reaction with elemental sulfur, pyrite (FeS_2) can be formed.

Butler and Hayes (2000 and 2001) have demonstrated that ferric sulfides and ferric disulfides such as mackinawite and pyrite can promote the abiotic dechlorination of TCE. In one lab study with 10 g/L freshly synthesized mackinawite, TCE was transformed to 11% cDCE, 76% acetylene, and 12% residual TCE at pH 7.3 with an observed half-life of 1,690 days. Lee and Batchelor (2002) reported a transformation rate of 1.59 day^{-1} for TCE with pyrite yielding 3.3% cDCE, 43 % acetylene, 2.2% ethene, and 50% TCE after 32 days. VC was not produced from TCE, but was generated when cDCE was treated with pyrite. Gander et al. (2002) reported enhanced degradation of 1,1,1-trichloroethane in a system containing ferric sulfide and a methanogenic culture over that achieved by the ferric sulfide or methanogenic culture alone.

Two pilots were initiated at Altus AFB to evaluate the potential for an emulsion of soybean oil to promote reductive dechlorination and abiotic transformation of the TCE found in the groundwater. The edible oil substrate or EOSTM was developed as inexpensive, long-lasting carbon source that can be easily distributed from the point of injection (Borden and Lee 2002).

SITE DESCRIPTION: Historical solvent releases of degreasing agents at Altus AFB resulted in a 1,520 m-long chlorinated solvent plume with TCE concentrations reaching 78,000 $\mu\text{g/L}$ in the source area. The geology at the site consists of reddish-brown, moderately plastic, sandy clay to a depth of roughly 4.6 m, underlain by fractured clayey shale with occasional gypsum layers. The depth to ground water is 2.4-3.1 m below ground surface (bgs). Most ground-water flow and contaminant transport appears to occur through a series of weathered shale fractures located immediately beneath the surficial clay and within a thick gypsum layer approximately 10.7 m below grade. The soil and groundwater contain high levels of ferrous iron and sulfate.

SS-17 PILOT: Groundwater at the SS-17 site was impacted by TCE and a fuel release which had led to the development of a microbial population capable of partial dechlorination of TCE to cDCE, trans-1,2-dichloroethene (tDCE), VC, ethene, and ethane, and removal of some of the sulfate. Sulfate levels prior to the addition of the emulsified substrate ranged from 107 to 2,000 mg/L with lower levels in wells impacted by the fuel release.

An emulsion of soybean oil, surfactant, yeast extract, and lactate was prepared and injected into six injection wells spaced 1.5 m apart in a barrier configuration to intercept the groundwater plume at the SS-17 site approximately 76 m downgradient from the source area (Figure 1). The wells were screened from 2.4 to 5.5 m below ground surface to achieve maximum distribution of the treatment mixture in the upper weathered fracture zone.

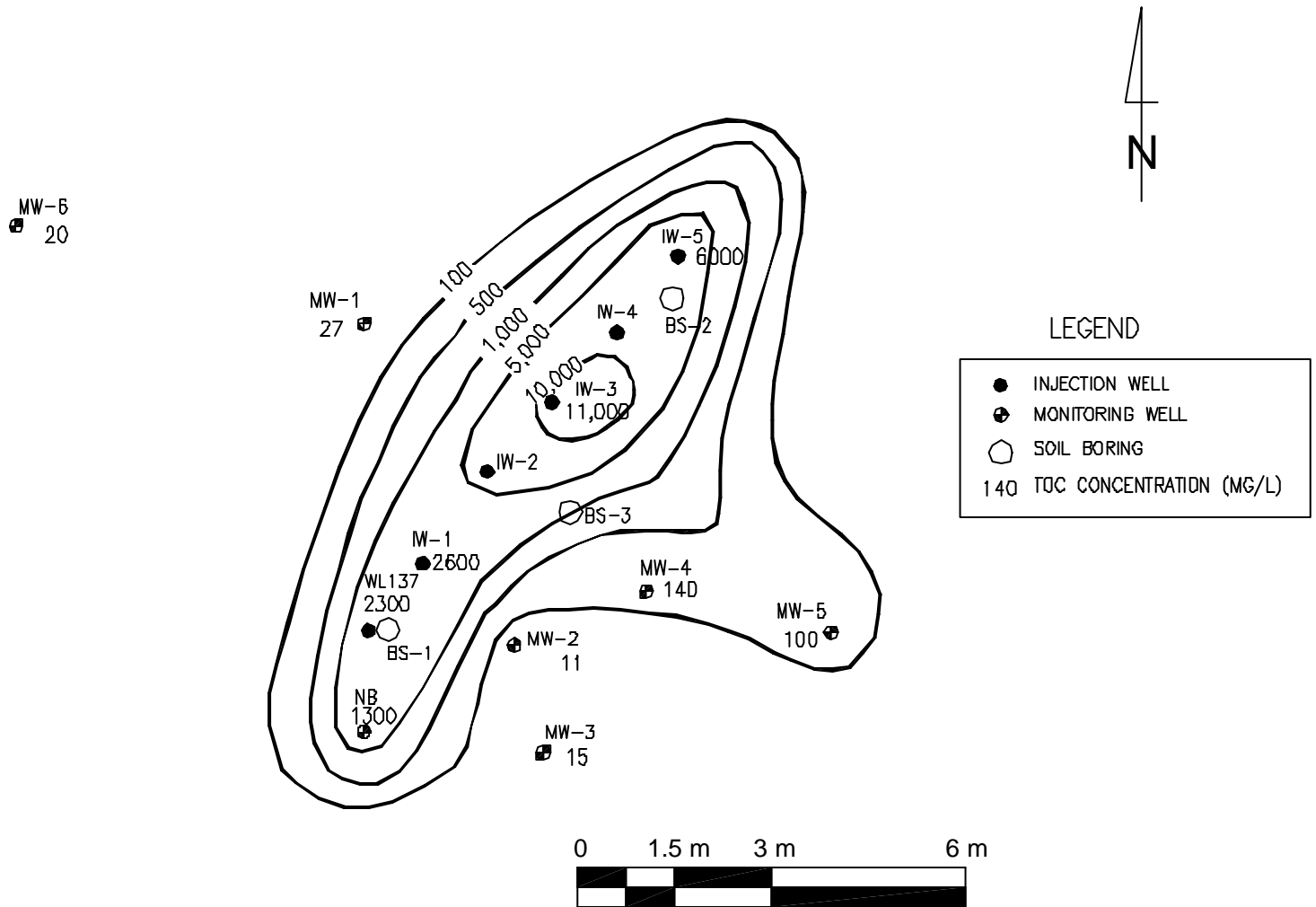


FIGURE 1. SS-17 test plot and TOC distribution (mg/L) on 4/2/02.

Table 1. Volatile contaminants, sulfate, methane, and TOC for SS-17 pilot wells IW-3 and MW-5

IW-3	Units	11/14/01	12/18/01	4/24/02	7/31/02	1/16/03
Ethene	μM	<0.046	<0.046	0.43	1.9	<0.046
Ethane	μM	<0.043	0.43	0.83	5.3	<0.043
Acetylene	μM	<0.046	<0.046	<0.046	<0.046	<0.046
VC	μM	<0.090	<0.090	0.12	0.77	0.75
cDCE	μM	1.0	<0.058	0.096	1.6	0.76
tDCE	μM	0.25	<0.058	<0.058	0.15	<0.056
TCE	μM	9.9	0.43	0.26	0.75	<0.043
Total CE	μM	11.2	0.86	1.7	10.4	1.5
Sulfate	mg/L	1623		100		1.6
Methane	mg/L	0.24	0.023	0.83	7.5	16.3
TOC	mg/L	5.1	33000	11000	7300	2900

MW-5	Units	11/15/01	12/17/01	4/23/02	7/30/02	1/17/03
Ethene	μM	0.25	0.43	3.9	3.3	18.2
Ethane	μM	0.083	0.37	0.14	0.11	0.070
Acetylene	μM	<0.046	<0.046	<0.046	<0.046	<0.046
VC	μM	7.0	13.3	12.6	19.0	28.3
cDCE	μM	9.3	10.8	0.071	1.0	0.75
tDCE	μM	0.46	0.25	<0.058	0.42	0.14
TCE	μM	12.6	4.0	<0.043	0.15	<0.043
Total CE	μM	29.8	29.2	16.8	24.0	47.5
Sulfate	mg/L	424		558	103	247
Methane	mg/L	1.5	5.4	3.4	4.5	15.2
TOC	mg/L	5.5	2200	100	74	15

Monitoring of adjoining wells during the injection process showed that EOSTM reached monitoring well MW-5 located 7.6 m from the injection wells, but several closer wells in less permeable zones received little substrate as measured by Total Organic Carbon or TOC (Figure 1). TOC levels four months after EOSTM injection ranged from 11 to 11,000 mg/L. In injection well IW-3, TCE concentrations dropped immediately after injection due to sorption to the oil (Table 1). However by August 2002 (7.5 months after injection), total ethenes (molar concentration) in this well had recovered to over 90% of the pre-injection concentration indicating that sorption to the oil was no longer significant. After 13 months, TCE declined from 9.9 μM to <0.043 μM with decreases in cDCE (26%) and sulfate (99%), and increases in vinyl chloride (VC) to 0.75 μM and methane to 16.3 mg/L. In well MW-5, 7.6 m downgradient, TCE declined from 12.6 μM to <0.043 μM after 13 months with decreases in cDCE (92%), and sulfate (42% to 247 mg/L). Increases in VC to 28 μM, ethene to 18.2 μM, and methane to 15.2 mg/L were observed after 13 months. Acetylene (an abiotic reaction product from ferric sulfide and ferric disulfide) was not detected.

Biological reductive dechlorination processes resulting in the production of VC, ethene, and ethane appeared to predominate in the SS-17 area in zones impacted by the injection of the edible oil substrate. In addition to biological mechanisms, the contribution of abiotic transformation mechanisms was evaluated. Samples were taken from three cores near the injection zone (BS-1, BS-2, and BS-3 on Figure 1) with a fourth core from a background location. Samples were analyzed for bioavailable ferrous iron (Fe^{II}), bioavailable total iron, completely extracted ferrous iron, completely extracted total iron, sulfide from ferrous sulfide, and sulfide from ferrous disulfide (Kennedy and Everett 2001). The bioavailable ferrous and total iron were extracted with a mild acid, 0.5 N HCl. Completely extracted ferrous and total iron were extracted with 6N HCl.

Table 2 shows the results on analysis of soil samples collected from six different depths in three soil cores installed within the SS-17 pilot barrier and one background location in July 2002, approximately eight months after injection of the edible oil substrate. Samples collected from below 2.4 m below ground surface were in the saturated zone. Bioavailable ferrous and completely extracted ferrous iron were elevated beneath the water table in the three borings near the injection wells compared to the background locations and the shallow samples which were not impacted by the emulsion injection. While some samples from the beneath the water table in the injection zone showed elevated bioavailable and completely extracted total iron, there was no clear pattern. Both forms of sulfide (FeS and FeS_2) were elevated in the saturated zone and were generally higher than those seen in the background location. The vegetable oil has stimulated both iron and sulfate reduction and the production of ferric sulfide and ferric disulfide.

TABLE 2. Bioavailable and total extractable iron and sulfide with depth for cores from SS-17 Pilot in July 2002.

Well	Depth (m)	6N Fe II (mg/Kg)	6N Fe T (mg/Kg)	S-FeS (mg/Kg)	S-FeS ₂ (mg/Kg)	0.5 N Fe II (mg/Kg)	0.5N Fe T (mg/Kg)
BS1	0.8	364	19735	0.00	2.24	15	3095
BS1	1.5	265	20359	0.47	1.01	60	2738
BS1	2.4	562	21168	0.97	48.11	941	2917
BS1	3.0	392	23504	15.94	54.84	950	2935
BS1	3.8	987	41492	9.72	38.56	1044	3806
BS1	4.6	1253	29044	1.51	19.39	424	5796
BS2	0.8	282	18315	0.28	0.78	167	3607
BS2	1.5	295	28469	0.21	1.28	79	4849
BS2	2.3	512	19635	2.35	154.86	719	2386
BS2	3.0	718	39607	0.51	35.31	428	2681
BS2	3.0	828	29532			566	3620
BS2	3.0	923	38502	2.18	25.39	507	3718
BS2	3.8	1667	29749	5.65	11.59	909	4260
BS2	4.6	630	15573	0.26	1.91	229	1454
BS3	0.8	103	21317	0.23	1.89	79	3814
BS3	1.5	444	25562	0.41	1.29	67	4159
BS3	2.0	387	19180	24.77	39.15	1097	3344
BS3	2.3	637	21100	9.17	36.68	1107	3705
BS3	3.0	761	50373	0.43	49.44	764	3157
BS3	3.8	762	49339	1.01	41.31	1040	5711
BS3	4.6	833	25344	0.87	35.61	613	2380
Background	0.8	176	19425	0.36	2.07	54	3443
Background	0.8	166	22352	0.14	8.54	62	3881
Background	1.5	89	9563	0.91	4.30	144	4786
Background	2.3	92	9691	0.91	4.10	47	3142
Background	3.0	116	13894	0.64	3.61	38	2583
Background	3.7	225	18208	0.73	3.41	75	2862

6N Fe^{II} = ferrous iron extracted with strong acid (6N HCl). 6N Fe T = total iron extracted with strong acid (6N HCl). S-FeS – Sulfide in the form of ferrous sulfide. S-FeS₂ – sulfide in the form of ferrous disulfide. 0.5 N Fe^{II} – bioavailable ferrous iron extracted with weak acid (0.5 N HCl). 0.5 N Fe T = bioavailable total iron extracted with weak acid (0.5N HCl).

OU-1 PILOT: A second, smaller pilot was conducted near a landfill in the OU-1 plume at Altus AFB. TCE levels of up to 10,400 µg/L were found in a high sulfate groundwater with between 1,560 and 2,110 mg/L sulfate. The emulsified soybean oil was injected into two wells. As shown in Table 3, TCE levels have fallen in injection well IW-6 from 43 µM to 0.33 µM, cDCE increased from 4.4 to 6.1 µM, and VC has increased from <2 µM to 0.12 µM after 13 months. Maximum ethene and ethane levels of 28.2 µM and 24.7 µM were found after four months. Sulfate fell from 1,717 mg/L to 26 mg/L while methane increased from non-detect to 10 mg/L. Although acetylene was not detected, the

low levels of cDCE and VC that were produced, suggest that the abiotic pathway for TCE removal appeared to be favored at this location.

TABLE 3. Volatile contaminants, sulfate, methane, and TOC in OU-1 pilot well IW-6

IW-6	Units	11/14/01	12/18/01	4/24/02	7/31/02	1/17/03
Ethene	μM	<1.1	0.15	28.2	0.50	<0.046
Ethane	μM	<1.0	0.32	24.7	0.37	0.057
Acetylene	μM	<1.0	<0.42	<0.42	<0.046	<0.046
VC	μM	<2.0	<0.090	<0.80	0.50	0.12
cDCE	μM	4.4	9.7	4.4	7.5	6.1
tDCE	μM	<1.3	<0.058	<0.52	<0.058	<0.058
TCE	μM	43.0	45.7	3.8	4.3	0.33
Total CE	μM	47.4	55.8	61.1	13.2	6.6
Methane	mg/L	<0.016	<0.066	0.89	3.9	10.0
Sulfate	mg/L	1717		100	518	26
TOC	mg/L	3.2	19000	11000	3400	2400

SUMMARY: Field pilot-scale projects were conducted at two locations at Altus AFB. At SS-17, the injection of EOSTM into the shallow aquifer resulted in the rapid establishment of conditions to support and promote anaerobic reductive dechlorination. After only nine months, significant decreases in TCE were observed with concomitant increases in cDCE, VC, and ethene observed in several monitoring wells downgradient of the permeable reactive barrier production. Although biological reduction of iron and sulfate resulted in the accumulation of ferric sulfide and ferric disulfide within the treatment zone compared to an untreated location, the abiotic transformation mechanism appeared to be a minor contributor to the removal of TCE within this area of the aquifer. At the OU-1 pilot site, there was a substantial decrease in the concentration of TCE without substantial increases in cDCE and VC that would be expected from biological reductive dechlorination. Although the abiotic by-product acetylene was not detected at appreciable levels, the loss of TCE and sulfate suggest that the transformation at this location was primarily due to abiotic processes with the biological component providing a measurable, but minor contribution.

Degradation of TCE can be stimulated by biological and abiotic process in areas with high sulfate and iron levels. Injection of a soluble or long-lasting substrate can promote reductive dechlorination of TCE and stimulate the reduction of sulfate and iron that can then abiotically react with TCE.

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