

## CHLORINATED SOLVENT BIOREMEDIATION: 3 CASE STUDIES

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**ABSTRACT:** Three field-scale studies were conducted to evaluate in situ bioremediation of chlorinated solvent-contaminated groundwater at Naval Base Ventura County, Point Mugu, California. The three sites have a number of similarities, although the approaches taken to implement in situ bioremediation differed. The geology of the sites is similar with sand/gravel fill material (not present at Site C) over a 1-3 ft thick layer of clay, under which exists a relatively homogeneous and transmissive sand zone. The water table lies a foot or two above or within the clay layer. The sediments and associated groundwater geochemistry at each site are consistent with a hypersaline lagoon depositional environment. The groundwater has a relatively high TDS/sodium chloride content as well as considerable levels of sulfate. All three sites were contaminated by chlorinated ethenes, although the waste source for Site C differs and contained heavy metals as well. Anaerobic in situ bioremediation was initiated under sulfate reducing (and/or methanogenic) conditions at all three sites, but differed in the implementation. Sites A and B used groundwater recirculation cells to distribute lactic acid as the electron donor for stimulation of biological activity, while citric acid was the electron donor distributed under electrokinetically induced flow at Site C. Although each site initially had similar elevated sulfate concentrations, the sulfate concentrations during the anaerobic dechlorination process differed substantially at the three sites (0-20 mg/L, 100-200 mg/L, and 500-1500 mg/L for Sites A, B, and C, respectively). All sites showed relatively rapid anaerobic biodegradation of the parent solvent compounds to vinyl chloride (VC), which was degraded to various extents. At Site A only, a polishing step based on aerobic cometabolism by methanotrophic bacteria was applied to more quickly treat the remaining VC. Similar aerobic cometabolic treatment of residual VC is planned for Site B. At site C, the data showed that VC rapidly disappeared by a mechanism other than anaerobic biodegradation to ethene.

## INTRODUCTION

Three field-scale studies were conducted to evaluate in situ bioremediation of chlorinated solvent-contaminated groundwater at Naval Base Ventura County, Point Mugu, California. The three sites have a number of similarities, although the approaches taken to implement in situ bioremediation differed. All three sites are located within the historical boundary of the 4 square miles (10.4 square km) encompassed by the Mugu Lagoon estuary. Sites A and B are located on filled estuarial wetlands. Site C is within the current day estuary boundary. Mugu Lagoon is the largest remaining tidal marsh located between San Francisco, California and the border with Mexico.

Sites A and B exhibit similar geology with intermixed fill, sand, and clay in roughly the first 15 feet below ground surface (bgs). Underlying this material, and often separated by a continuous clay layer, is a relatively homogeneous and transmissive sand

zone. The water table is nominally at 5 ft bgs, with the clay layer at 8-10 ft bgs and the sand zone below to at least a depth of 80 ft.

At Site C, the continuous clay layer is found in the first 1-3 ft bgs and underlying this layer is the same relatively homogeneous and transmissive sand zone. The water table is nominally at 1 ft bgs with the sand zone extending to at least a depth of 80 ft.

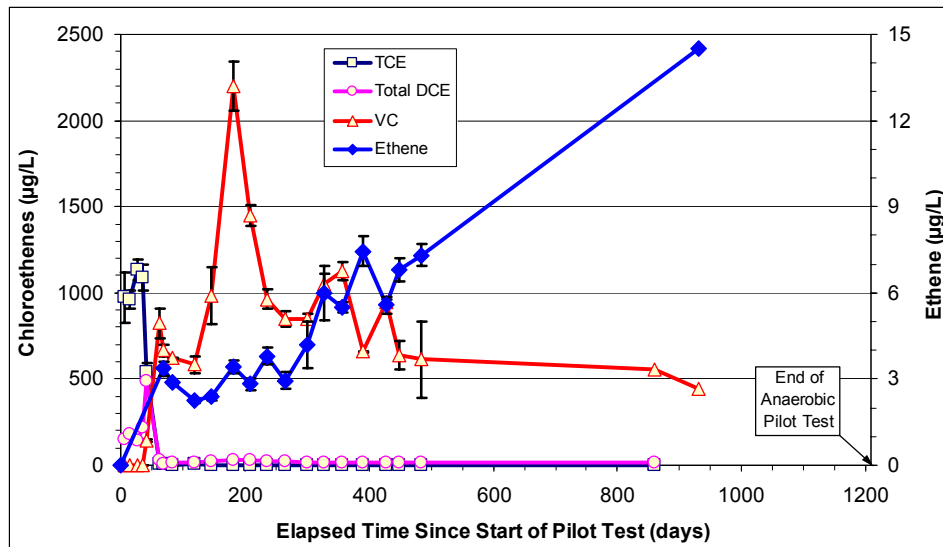
The sediments and associated groundwater geochemistry at each site are consistent with a hypersaline lagoon depositional environment. The groundwater has a relatively high TDS/sodium chloride content as well as considerable levels of sulfate. All three sites were contaminated by chlorinated ethenes. Sites A and B both had trichloroethene (TCE) releases to groundwater from underground oil/water separators that were used as part of paint stripping operations. Site C was a settling pond that received plating shop liquid waste, including heavy metals and tetrachloroethene (PCE) that subsequently contaminated the groundwater.

Anaerobic in situ bioremediation was initiated under sulfate reducing conditions at all three sites, but differed in the implementation. Sites A and B used groundwater recirculation cells to distribute lactic acid as the electron donor for stimulation of biological activity. Site A subsequently injected methane and oxygen to stimulate in situ aerobic cometabolism for degradation of vinyl chloride (VC), an intermediate degradation product, as a final polishing phase. Site C used citric acid as the electron donor, which was distributed under electrokinetically induced flow.

## TEST OPERATIONS AND RESULTS

**Site A.** The pilot test at Site A was started in December 1998 and continued through November 2002. Groundwater at the site had been affected by a discharge of chloroethenes, predominantly trichloroethene (TCE) and dichloroethene (DCE). Initial concentrations of TCE and DCE were 972 µg/L and 149 µg/L, respectively. In the first phase of the test, lactic acid was circulated throughout the portion of the contaminated aquifer with the highest concentration of TCE using a single cell (2-well) recirculation system to stimulate anaerobic biotransformation of the contaminants. It was thought (based on laboratory microcosm results and literature information) that dechlorination would occur mainly under methanogenic conditions; hence the sulfate would need to be removed from the system before methanogenic conditions would be established. Initial sulfate levels were approximately 700 mg/L. The lactic acid was distributed in periodic, high concentration pulses to stimulate sulfate reduction. A final large pulse of lactic acid was injected after 57 days of groundwater recirculation (when sulfate in the flow field had been reduced to less than 20 mg/L) to promote chloroethene biodegradation. Recirculation was halted at day 64. Long-term monitoring began after recirculation ceased and continued through April 2002 for a total of 1208 days of treatment. Figure 1 presents the chloroethene data from the anaerobic portion of this pilot test for a well located in the middle of the treatment zone. Complete reduction of the sulfate in the treatment area occurred within the first 60 days. As the sulfate was reduced, the dissolved methane concentration began to increase up to nominally 12 mg/L. Upon removal of the sulfate, TCE and DCE were rapidly dechlorinated to vinyl chloride (VC), which peaked at 2200 µg/L by day 181 (although the mass balance is inconsistent, with significantly more VC being produced than expected based on the initial TCE concentrations). VC concentrations slowly declined over the next 2½ years, with until

reaching a concentration of 441  $\mu\text{g/L}$  on day 930 (July 2001). Concentrations of ethene increased to 14.5  $\mu\text{g/L}$  during the same period. The rate of VC dechlorination in the field is slower than the rate measured in lactate-fed laboratory microcosm tests with site sediments and groundwater. Field data were analyzed using the change in ethene concentration as an indication of the VC transformation rate. From these calculations, the estimated VC transformation rate is  $5.6 \cdot 10^{-4} \mu\text{M/day}$  (i.e., a half-life of about 3.4 years) in the field. This rate is two orders of magnitude lower than expected from the microcosms.



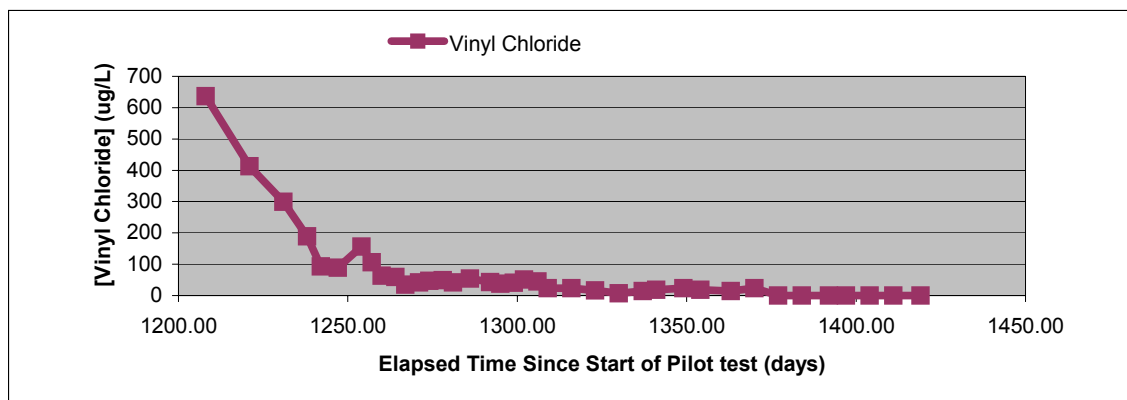
**FIGURE 1. Chloroethene concentrations in well MW-3 at Site A.**

Given the slow rate of anaerobic VC transformation, in situ cometabolic aerobic biodegradation was proposed as a method to accelerate destruction of the remaining VC. The process was based on applying aerobic cometabolic bioremediation within an in situ biofilter configuration [Truex et al., 2002]. The biofilter approach used a recirculation cell to move groundwater through a treatment zone that is established in situ in the area surrounding the injection well. Multiple extraction wells “feed” this injection well. Operation of the in situ aerobic biofilter required injection of dissolved methane and oxygen to stimulate the methanotrophic bacteria that are used for destroying VC. After a period of injection with excess stoichiometric oxygen, recirculation was halted to allow the bacteria to consume the methane and subsequently for VC to be destroyed by available methane monooxygenase enzyme. The aerobic pilot test was operated through day 1421.

VC degradation began within 13 days of starting the aerobic system. The initial VC concentration average from the four extraction wells for the aerobic process was 691  $\mu\text{g/L}$  on day 1208. VC continued to degrade until the conclusion of the test. VC concentrations declined to non-detectable at a well inside the aerobic cell. Complete VC results are shown in Figure 2.

In summary, TCE and DCE at Site A were reduced from 972  $\mu\text{g/L}$  and 142  $\mu\text{g/L}$  to non detect levels by use of lactic acid injection to support in situ anaerobic bioremediation under methanogenic conditions. The VC reaction intermediate was degraded slowly to

ethene from peak levels of 2,200  $\mu\text{g/L}$  to 441  $\mu\text{g/L}$ . Subsequently, VC concentrations were reduced to non-detectable levels by use of methane and oxygen injection to support an in situ aerobic biofilter. DCE levels increased to 30  $\mu\text{g/L}$  during the aerobic phase due to mixing of water from outside of the test cell coupled with the low one-pass efficiency of the biofilter for DCE degradation. A full-scale sequential anaerobic/aerobic bioremediation cleanup is currently planned for the site.



**FIGURE 2. Average VC concentrations from the aerobic recirculation cell extraction wells at Site A.**

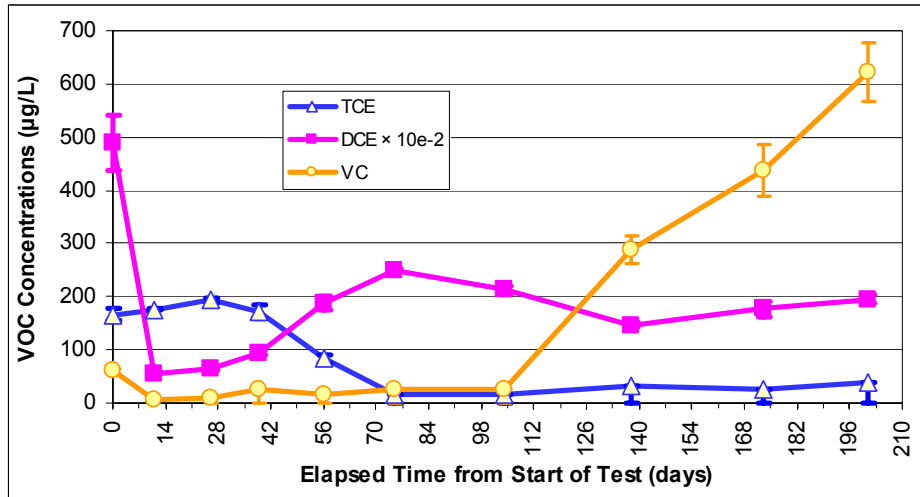
**Site B.** The pilot test at Site B was started in June 2001 and continued through December 2001. Groundwater at the site had been affected by a discharge of chloroethenes, predominantly TCE (0.838  $\text{mg/L}$ ), cis-1,2-DCE (26.5  $\text{mg/L}$ ), trans-1,2-DCE (3.7  $\text{mg/L}$ ), and VC (0.039  $\text{mg/L}$ ). Initial sulfate levels were approximately 1,400  $\text{mg/L}$ . In June 2001, lactic acid was distributed in the subsurface using a single cell (2-well) recirculation system similar to that used at Site A. The lactic acid was distributed continuously at high concentrations over a period of about 4 days.

The test at Site B differed from that at Site A with respect to the amount of sulfate removal that was achieved. Sulfate levels declined to concentrations between approximately 100-600  $\text{mg/L}$  after injection of the lactic acid. Dissolved methane concentrations increased to 10  $\text{mg/L}$ , indicating that methanogenesis was occurring as well. Declining TCE concentrations and the subsequent increase of VC and ethene concentrations showed evidence of sequential dechlorination of chloroethenes. DCE concentrations fluctuated throughout the test and did not correlate well with TCE and VC concentration changes. Changes in conservative tracer (injected concurrently with the lactic acid) indicate that movement of water at the site was responsible for the DCE concentration changes. Changes in the DCE concentration as a result of reductive dechlorination may have also been obscured by the fact that the DCE concentration was so high.

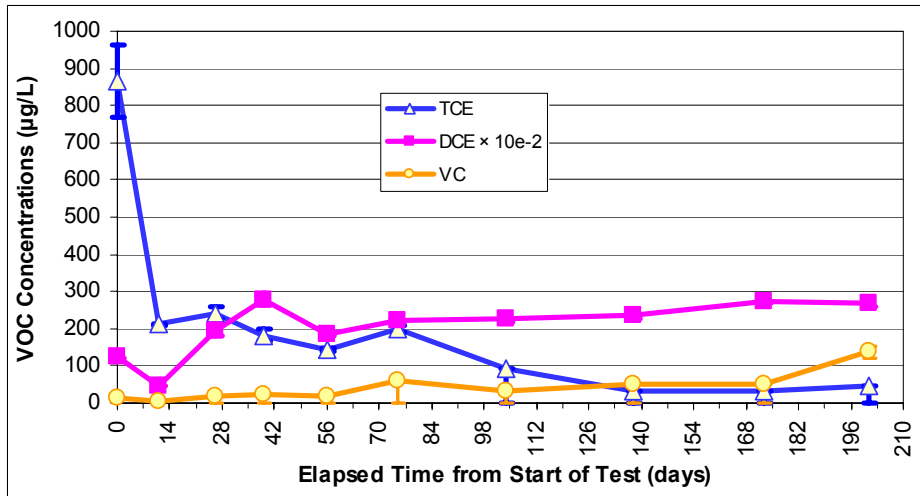
During the test, TCE concentrations decreased from as high as 838  $\mu\text{g/L}$  to near non detect levels. This corresponded to a rise in VC levels from 39  $\mu\text{g/L}$  to as high as 630  $\mu\text{g/L}$ , which is about 15 times the highest historical concentration of VC seen across Site B. Complete data for chlorinated ethenes are presented in Figures 3 and 4. In addition, ethene was detected at several monitoring sites during the test at 2-3  $\mu\text{g/L}$ .

In summary, the pilot test at Site B produced evidence supporting the occurrence of in situ anaerobic bioremediation of chloroethenes under combined sulfate reducing and

methanogenic conditions. TCE degraded from near mg/L levels down to near non-detect levels. VC increased from 39  $\mu\text{g/L}$  to over 600  $\mu\text{g/L}$ . Ethene was detected at the site. Overall the VC formation was the most compelling evidence that in situ anaerobic bioremediation under sulfate reducing conditions was a viable remediation option. Subsequently, a larger cleanup system has been installed at this site to use the same sequential anaerobic/aerobic bioremediation cleanup process developed at Site A.



**FIGURE 3. Chlorinated ethene concentrations for a monitoring well in the middle of the Site B treatment zone, but nearer the injection well.**



**FIGURE 4. Chlorinated ethene concentrations for a monitoring well in the middle of the Site B treatment zone, but nearer to the extraction well.**

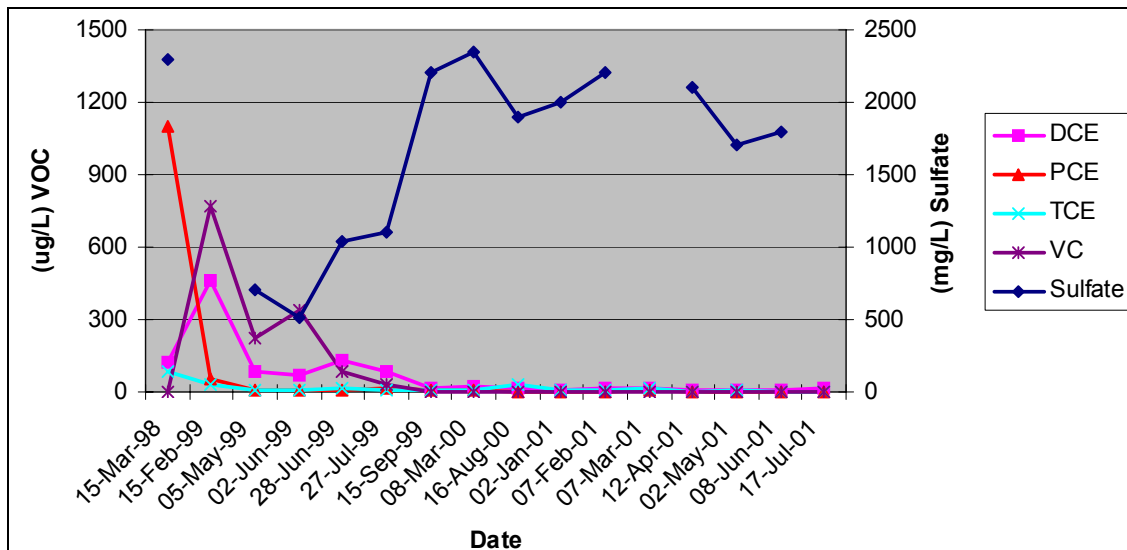
**Site C.** The pilot test at Site C was very different in design than Sites A and B. Site C was originally designed as an electrokinetic remediation system to remediate cadmium and chromium subsurface soil contamination. The pilot test system contained 3 rows of anode wells (24 total wells) and 2 rows of cathode wells (14 total wells) laid out in an array pattern over the two waste lagoons. The anode and cathode wells were spaced 6

feet apart along each row. The anode and cathode rows were spaced approximately 14 feet apart. The entire electrode array was surrounded by an 80-mil, high-density polyethylene sheet pile wall that extended from ground surface to a depth of 20 feet. The sheet pile wall was designed to isolate the pilot system from the surrounding marsh. It also reduced the hydraulic gradient within the electrode array to nearly zero. Electrokinetic remediation is a process in which an electrical field is applied within a sediment or soil matrix by applying a low-voltage direct current (DC) between electrodes placed in the soil. When DC current is applied to the electrodes, an electrical field develops between the anodes and cathodes. The application of the electric field has several effects on the sediment, water, and contaminants. These effects include electromigration, electroosmosis, changes in pH, and electrophoresis. Of the electrokinetic phenomena discussed, electromigration is the transport mechanism for electron donor delivery to support anaerobic dechlorination of chlorinated solvents in the groundwater. An organic acid, citric acid, is added at the cathodes to neutralize the cathodic electrolysis reaction and to maintain a constant pH of 4. The citric acid also acts as an electron donor supporting anaerobic dechlorination of chlorinated solvents.

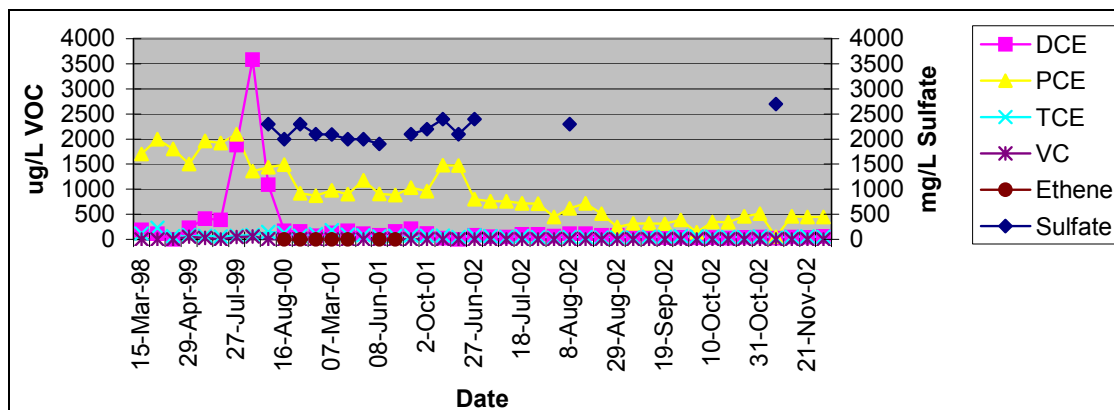
The pilot test to remediate metals contamination at Site C began in March 1998. The realization that anaerobic dechlorination was also occurring was not made until February 1999 when an outlying monitoring well (PW16) showed a decline of PCE from 1100 to 51  $\mu\text{g/L}$  and TCE from 86 to 32  $\mu\text{g/L}$ . At the same time cis-DCE increased from 120 to 460  $\mu\text{g/L}$  and VC increased from non-detect to 770  $\mu\text{g/L}$ . This occurred while sulfate levels were between 2,300 and 710  $\text{mg/L}$ . By June of 2001, PCE, TCE, and VC concentrations had declined to non-detect while cis-DCE had declined to 11  $\mu\text{g/L}$ . Sulfate levels increased during this time back to roughly 2,000  $\text{mg/L}$ . The sulfate levels are much higher than those typically found to support anaerobic dechlorination of chlorinated ethenes. Another anomalous feature of this site is that ethene, the reductive byproduct of VC, has never been detected. Complete chloroethene data for this well is presented in Figure 5.

Enhanced monitoring of a second well at the site was started in February 1999. This well (PW8) was located in the source area of the site and had higher levels of chloroethenes. PW8 had concentrations of PCE at 1,800  $\mu\text{g/L}$  and TCE at 66  $\mu\text{g/L}$  while DCE and VC were not detectable. By September 1999, the PCE concentration had declined to 1,360  $\mu\text{g/L}$  while a large spike of cis-DCE occurred at 3,580  $\mu\text{g/L}$  and VC was detected at a level of 60  $\mu\text{g/L}$ .

The amount of cis-DCE was almost 20 times the amount expected from PCE degradation. This confirmed that we were treating a PCE DNAPL source area. By August 2000, the cis-DCE had declined to 170  $\mu\text{g/L}$  and VC had declined to non-detect. PCE and TCE levels stayed static during this period as did sulfate at concentrations greater than 2,000  $\text{mg/L}$ . Ethene was not detected. By November 2002 the PCE concentration in PW8 had declined to 450  $\mu\text{g/L}$ . Only trace amounts of TCE and cis-DCE were detected while VC and ethene remained non detectable. Complete chloroethene data for well PW8 is presented in Figure 6. It was concluded that an unidentified mechanism was degrading VC to an end point other than ethene. Microcosm tests were initiated to try and identify the unknown mechanism. The field test is scheduled to continue until July 2003.



**FIGURE 5. Chlorinated ethene and sulfate data for well PW16 at Site C.**



**FIGURE 6. Chlorinated ethene and sulfate data for well PW8 at Site C.**

The results of the microcosm tests for Site C became available in August 2002 [Battelle, 2002]. The results confirmed that anaerobic reductive dechlorination could be stimulated in Site C sediments. There were some unusual findings in the microcosm tests. PCE, TCE, and cis-DCE degraded at approximately the same rate. Consequently, cis-DCE did not accumulate during the tests. Ethene was not detected in any of the tests, confirming the findings from the field tests. Sulfate concentrations typically remained greater than 2,000 mg/L, confirming field results. VC degradation was seen to occur in some microcosms, even though PCE, TCE, sulfate, and citric acid were still present. This confirmed the field finding that VC degradation was not linked to reductive dechlorination. The microcosm test attempted to determine the fate of VC using radioisotope tagged VC. Unfortunately, no degradation of VC occurred in these microcosms. A possible explanation for this result is that the use of VC as a parent compound did not create enough selective advantage for a significant population of dechlorinating organisms to develop. So, the endpoint of VC degradation remains unanswered at Site C.

## CONCLUSIONS

Reductive dechlorination was determined to be successful in degrading chloroethenes at three separate sites at Point Mugu, California. Although subsurface and aquifer conditions were similar at the three sites, there were substantial differences in the mechanisms used to achieve reductive dechlorination. Table 1 summarizes the similarities and differences between the sites. Reductive dechlorination worked with sulfate levels varying from non-detect to greater than 2,000 mg/L. The use of either citric acid or lactic acid as the electron donor was shown to be equally effective. The use of pumping and electrokinetics were shown to be effective in distributing electron donor into the contaminated aquifers. Site A fully reduced TCE to ethene anaerobically, although the VC to ethene step is slow, requiring the use of an aerobic polishing phase to degrade VC to carbon dioxide. Site B reduced TCE to VC and ethene anaerobically. PCE at Site C was transformed to VC and the VC at the site degrades to a (currently) unidentified end product.

**TABLE 1. Summary of similarities and differences between the three case study sites.**

Parameter	Units/Scale	Site A	Site B	Site C
Lithology	Elevation (ft relative to Mean Sea Level, NGVD) 10 ft 5 ft MSL -5 ft -10 ft -15 ft -20 ft -25 ft			
Initial Sulfate	mg/L	700	1400	2200
Initial VOC	µg/L	TCE = 972 DCE = 149	TCE = 838 DCE = 30200 VC = 39	PCE = 1100 (1800) TCE = 86 (66) DCE = 120 (ND)
Electron Donor	--	Lactic Acid	Lactic Acid	Citric Acid
Delivery Method	--	Groundwater Recirculation Cell	Groundwater Recirculation Cell	Electrokinetics (electromigration)
Sulfate End Point	mg/L	Below Detection Limit (< 5)	~ 100-600 mg/L	2000 mg/L
Methane Generation	mg/L	~ 12	~ 10	~3
Ethene Generation	µg/L	~ 15	~ 3	None
VOC end point	µg/L	TCE = ND DCE < 30 VC = 441	TCE = ND DCE = 20000 VC = 630	PCE = ND (450) TCE = ND (ND) DCE = 11 (ND) VC = ND (ND)
Aerobic Step	--	Yes. Reduced VC to VC = ND	No	No

## REFERENCES

- Battelle. 2002. *Draft Report. Microcosm Investigation, Point Mugu Installation Restoration Site 5, Naval Base Ventura County*. Prepared for Naval Facilities Engineering Command, Southwest Division. August 30.
- Truex, M.J., C.D. Johnson, D.P. Leigh, and S. Granade. 2002. "Pulsed Injection Flow Strategy for Aerobic Co-Metabolism of Vinyl Chloride." In: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002*. Battelle Press, Columbus, Ohio.