EFFECTS OF POTASSIUM PERMANGANATE OXIDATION ON SUBSURFACE MICROBIAL ACTIVITY

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Abstract

In situ chemical oxidation has the potential for degrading large quantities of organic contaminants and can be more effective and timely than traditional *ex situ* treatment methods. However, there is a need to better characterize the potential effects of this treatment on natural processes. This study focuses on potential inhibition to anaerobic dechlorination of trichloroethene (TCE) in soils from a large manufacturing facility as a result of *in situ* oxidation using potassium permanganate ($KMnO_4$). Previous microcosm studies established that natural attenuation occurs on-site and that it is enhanced by the addition of ethanol to the system. A potential remediation scheme for the site involves the use of potassium permanganate to reduce levels of TCE in heavily contaminated areas, then to inject ethanol into the system to "neutralize" excess oxidant and enhance microbial degradation. However, it is currently unknown whether the exposure of indigenous microbial populations to potassium permanganate may adversely affect biological reductive dechlorination by these microorganisms. Consequently, additional microcosm studies were conducted to evaluate this remediation scheme and assess the effect of potassium permanganate addition on biological reductive dechlorination of TCE.

Samples of subsurface soil and groundwater were collected from a TCE-impacted area of the site. A portion of the soil was pretreated with nutrients and ethanol to stimulate microbial activity, while the remainder of the soil was left unamended. Soil/groundwater microcosms were prepared in sealed vials using the nutrient-amended and unamended soils, and the effects of potassium permanganate addition were evaluated using two permanganate concentrations (0.8 and 2.4 percent) and two contact times (1 and 3 weeks). TCE was then re-added to each microcosm and TCE and dichloroethene (DCE) concentrations were monitored to determine the degree to which microbial dechlorination occurred following chemical oxidation.

Evidence of microbial degradation was generally detected within four weeks after TCE addition. Increases in DCE concentrations were consistent with decreases in TCE. The concentration of TCE in the nutrient-amended samples exposed to 2.4% $KMnO_4$ for one week degraded somewhat more slowly than the samples exposed to the 0.8% $KMnO_4$. The rates of degradation did not correlate with the length of $KMnO_4$ exposure for the nutrient-amended microcosms.

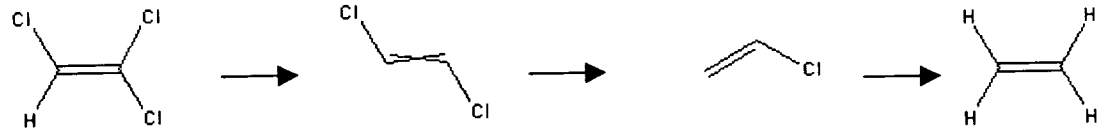
Microbial degradation of TCE in the unamended microcosms was generally similar to that observed in the nutrient-amended microcosms. One treatment condition (unamended, one week exposure, 2.4% $KMnO_4$) was exposed to elevated levels of ethanol and showed little evidence of degradation. It is suspected that the high levels of ethanol were toxic to the microorganisms.

The results of the study indicate that exposure of indigenous soil and groundwater microbial populations to $KMnO_4$ at concentrations of 0.8 to 2.4% do not impair the ability of the microbial populations to dechlorinate TCE. Consequently, the combination of chemical oxidation followed by enhanced biological reductive dechlorination appears to be a viable remedial strategy for highly-impacted subsurface areas of the site.

INTRODUCTION

Biological Reductive Dechlorination

Under anaerobic conditions, chlorinated ethylenes can be biologically remediated through the process of reductive dechlorination. In this process, chlorine atoms are replaced by hydrogen atoms through nucleophilic substitution. For example, trichloroethylene (TCE) can degrade into 1,2-dichloroethylene (DCE), and vinyl chloride (VC), then ethylene.



TCE → cis-1,2-DCE / trans-1,2-DCE → VC → ethylene

The rate at which this reaction takes place decreases as the number of chlorine substituents decreases. Therefore, the biological reductive dechlorination of TCE to cis-1,2-DCE (the predominant isomer resulting from anaerobic biodegradation) occurs much more rapidly than the biotransformation of cis-1,2-DCE to VC, and VC to ethylene. Consequently, cis-1,2-DCE and VC often tend to accumulate at sites where historical releases of TCE to the subsurface have occurred (1-3). Conversely, the rate of chloroethene biodegradation under aerobic conditions typically increases as the number of chlorine substituents decreases. As a result, the complete biodegradation of chlorinated solvents can require the combined activity of both anaerobic and aerobic microorganisms.

The study site, referred to as the Building 190 Tank Farm area, is located at the NASA Michoud Assembly Facility (MAF), 16 miles east of New Orleans, Louisiana. In 1966, a spill of TCE estimated at 16,000 gallons occurred at the facility due to the failure of a piping connector, although additional undocumented releases from chemical sewers, drains and sumps may have also occurred at various times. Impacts to subsurface soils and groundwater were first discovered in 1982. Since that time, extensive subsurface investigations have been performed and groundwater corrective action, consisting of groundwater recovery and above-ground treatment, was initiated in 1984. Despite aggressive remedial efforts, residual dense non-aqueous phase liquids (DNAPL) and dissolved-phase concentrations of TCE, DCE and VC in excess of 10 mg/L still persist in some areas of the site. As a result, additional remedial technologies are being evaluated to enhance the overall effectiveness of the site remediation program.

The documented presence of TCE and its breakdown products, including ethylene and ethane, in groundwater provide strong evidence that biological reductive dechlorination is occurring at the site. In addition, subsurface environmental conditions are especially conducive to microbial degradation of TCE, including:

- High concentrations (up to 100 mg/L) of naturally-occurring organic carbon in the site groundwater
- Highly reducing groundwater conditions, as indicated by low oxidation/reduction potentials (ORP), generally non-detectable levels of nitrate, and high concentrations of dissolved methane

- Neutral pH values and high alkalinity levels (>1,000 mg/L)
- Relatively high groundwater temperature (>20° C) (4)

The site data strongly indicate that natural biodegradation of TCE is occurring in the Building 190 Tank Farm area, and therefore suggest that it may be possible to enhance this natural attenuation process to improve the effectiveness of the overall site remediation program. The process of reductive dechlorination involves the utilization of the chlorinated solvents as electron acceptors by the anaerobic microbial populations, with molecular hydrogen serving as the electron donor. However, these microorganisms compete for available hydrogen with other anaerobes, such as methanogens. The literature indicates that the efficiency of chloroethene dechlorination may be related to the rate of hydrogen production and its steady-state concentration (5). Studies have also shown that a variety of simple organic substrates can stimulate reductive dechlorination by producing relatively low steady-state concentrations of hydrogen when these substrates are metabolized anaerobically. The low steady-state hydrogen concentrations appear to provide dechlorinating microbial populations with a competitive advantage compared to the methanogens.

Previous microcosm studies, conducted with TCE-impacted aquifer material from the Building 190 Tank Farm area, evaluated ethanol, propionic acid, and a proprietary poly-lactate ester (HRC®) for their ability to enhance microbial dechlorination of TCE (6). Degradation of TCE and daughter products was optimized in the ethanol and propionic acid treated microcosms. Figures 1 and 2 show the results of the ethanol-amended study for aquifer material collected from the surficial aquifer and the upper shallow aquifer, respectively.

Figure 1 Concentrations of TCE and Dechlorination Products in Ethanol Amended Surficial Aquifer Soils

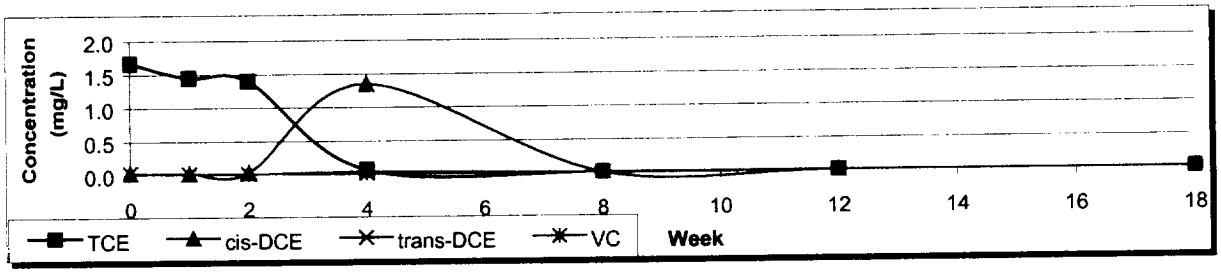
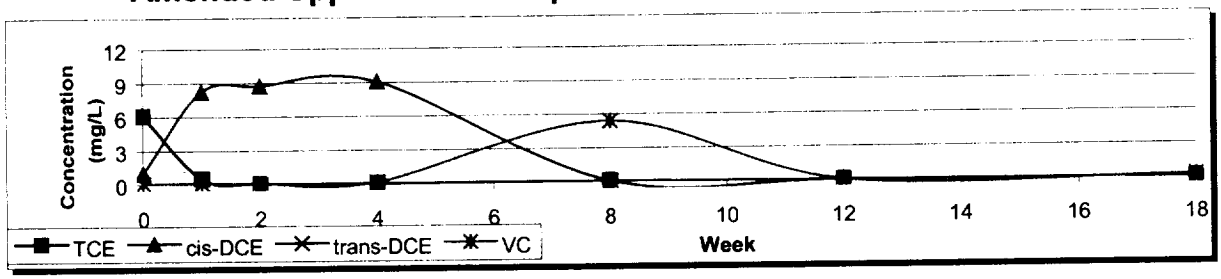


Figure 2 Concentrations of TCE and Dechlorination Products in Ethanol Amended Upper Shallow Aquifer Soils



The results of this microcosm study indicated that ethanol can be an effective and economical amendment for enhancing the anaerobic biodegradation of chloroethenes at the Building 190 Tank Farm site. Additionally, the study demonstrated biological dechlorination activity at initial TCE concentrations of up to 55 mg/L. The literature suggests that TCE can be toxic to

microbes at concentrations ranging from 10 to 100 mg/L (7). Concentrations in some parts of the Building 190 Tank Farm area exceed 100 mg/L, and DNAPL TCE is known to occur in some of these areas. Therefore, a more aggressive remediation scheme may be necessary to reduce the mass of contaminants in highly-impacted areas within a relatively short time period, which might then be followed with enhanced natural attenuation to manage residual levels of contamination.

In-Situ Chemical Oxidation

A number of field and laboratory studies have exhibited that potassium permanganate ($KMnO_4$) is capable of significantly reducing levels of chlorinated solvents in contaminated soils (8-12). The general reaction between TCE and $KMnO_4$ is:

$$C_2Cl_3H + 2MnO_4^- \longrightarrow 2CO_2 + 2MnO_2(s) + 3Cl^- + H^+$$

(Adapted from 10)

These studies have shown that $KMnO_4$ has the potential to be an effective chemical for *in situ* oxidation; however, the effectiveness of this remediation approach is primarily related to the ability to achieve transport of the oxidant through the contaminated regions of the subsurface. Consequently, the application of *in situ* oxidation at sites with low permeability and geologic heterogeneity is likely to meet with limited success. Since these conditions are found at the Building 190 Tank Farm area, it is not expected that *in situ* chemical oxidation alone will be capable of achieving complete removal of TCE in highly contaminated subsurface soils. However, it is conceivable that *in situ* chemical oxidation using $KMnO_4$ could rapidly remove a substantial portion of the chlorinated solvent contamination and thereby improve the long-term effectiveness of enhanced microbial degradation.

Based upon the completed studies, a conceptual remediation strategy for the site is to use $KMnO_4$ to rapidly reduce high concentrations of TCE in highly contaminated areas, then inject ethanol into the treatment area to "neutralize" excess oxidant and act as a substrate to enhance biological reductive dechlorination by indigenous soil and groundwater microbial populations. However, it is not known whether exposure to $KMnO_4$ will adversely affect the metabolic activity of the microbial populations and inhibit their ability to reductively dechlorinate the chlorinated ethene contamination at the site. Therefore, the purpose of the study described in this paper is to evaluate the effects of $KMnO_4$ concentrations and exposure duration on microbial declorination in aquifer material from the Building 190 Tank Farm area.

MATERIALS AND METHODS

The treatablity study consisted of initial screening tests to determine the oxidative "demand" of the site soil, and a microcosm study which evaluated chemical oxidation of chlorinated ethenes using $KMnO_4$ and subsequent biological reductive dechlorination. The study was designed to both demonstrate whether $KMnO_4$ oxidation is capable of effectively reducing concentrations of chlorinated ethenes in the site soils and groundwater, and determine whether the indigenous microbial populations would retain the ability to reductively dechlorinate the chlorinated ethenes following $KMnO_4$ treatment.

Screening Studies to Determine Appropriate $KMnO_4$ Concentrations

A series of preliminary screening tests were conducted to determine the concentration of $KMnO_4$ required to completely oxidize site soils. Screening tests were established in 160-ml

serum bottles with 75-ml of site groundwater and 15g dry weight site soil. Amended tests including nutrients and ethanol and unamended tests were established at each $KMnO_4$ concentration. Selected concentrations of $KMnO_4$ were 0.001%, 0.005%, 0.01%, 0.05%, 0.1%, and 0.5% of the dry soil weight. Following a seven-day exposure period, visual inspection of the microcosms showed that complete destruction of $KMnO_4$ had occurred (i.e., absence of purple color).

Because the soil had not been completely oxidized, a second series of screening tests at higher $KMnO_4$ concentrations was conducted. Microcosms in the second screening test were treated with 0.5, 1.0, 1.5, 2.0, and 2.5% $KMnO_4$ based on dry weight of soil in each microcosm. Results of the study showed that complete oxidation of the soil occurred between 1.5 and 2.0%. Based upon these results, $KMnO_4$ concentrations 0.8% and 2.4% were selected for the study. The 0.8% $KMnO_4$ concentration was expected to be sufficient to oxidize TCE and some natural soil organics. The 2.4% $KMnO_4$ concentration was selected to provide an excess of $KMnO_4$ throughout the exposure period.

Treatablilty Study

The treatability tests were established in 160-ml Wheaton bottles containing 15 grams soil (dry weight) and 75-ml of site groundwater. Microcosms were spiked with 2-ml of a TCE stock solution to increase the final TCE water concentration by 5 ppm. This was expected to achieve a final TCE concentration of approximately 20 ppm in the water phase of the microcosms given the initial concentration of TCE present in the soil.

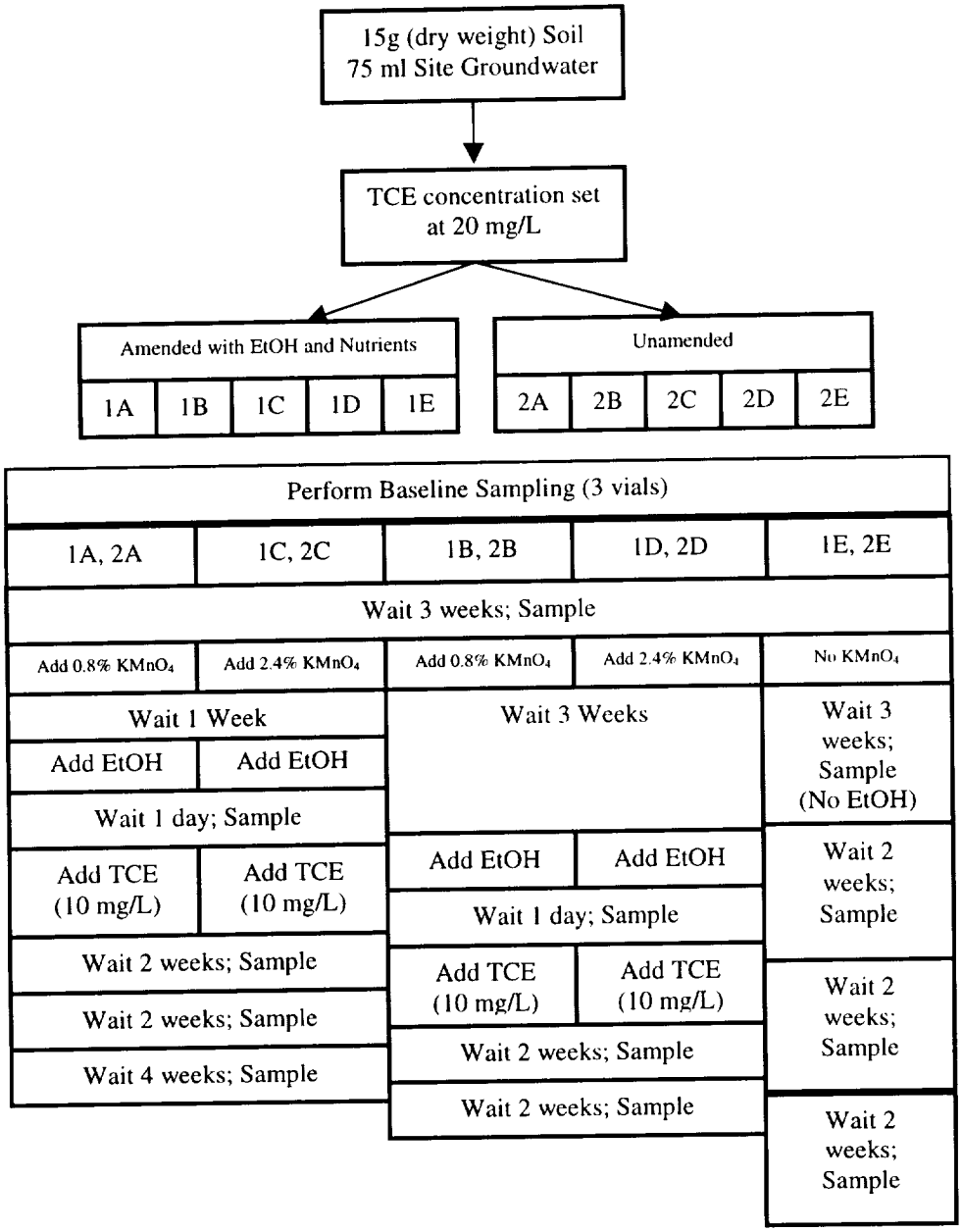
The test matrix consisted of two parallel sets of experiments each with five treatments. Treatments consisted of four combinations of $KMnO_4$ exposure times and concentrations (designated Treatments A, B, C, and D), and one set of vials that was not treated with $KMnO_4$ (Treatment E). The first of the two parallel experiments (Set 1) contained soils and groundwater that had been amended with ethanol and nutrients prior to KMnO4 addition to enhance the native population of organisms. Nutrient concentrations were established in a previous microbial degradation study (6). The other set of vials (Set 2) contained unamended soil and groundwater. Table 1 outlines the composition of the two sets of microcosms. Figure 3 provides a flow-chart illustrating the treatability study design.

Table 1 Composition of $KMnO_4$ Oxidation Study Microcosms

Contents	Set 1 Amended	Set 2 Unamended
Soil	15 grams dry wt.	15 grams dry wt.
Water	75 ml groundwater	75 ml groundwater
TCE	20 ppm microcosm liquid-phase	20 ppm microcosm liquid-phase
Ethanol[1]	100 ppm	None
Nutrients[2]	200 ppm nitrogen 100 ppm phosphorous	None

Note:
1 – Ethanol was added to site groundwater immediately prior to placement in microcosms by mixing 0.1g ethanol per liter of groundwater.
2 – Inorganic nutrients included 200 ppm nitrogen as (NH_4Cl) and 100 ppm phosphorus as an equal molar mixture KH_2PO_4 and K_2HPO_4. These nutrients were added to the amended treatments by dissolving 0.76g NH_4Cl, 0.22g KH_2PO_4, and 0.28g K_2HPO_4 per liter of site groundwater.

Figure 3 Summary of Experimental Program



Individual microcosms were sacrificed at appropriate time points for analysis of VOCs. Analytical samples consisted of the liquid-phase of each test bottle, which was cooled to 4°C and centrifuged prior to being poured into two 20-ml vials. VOC analyses were performed by Analytical Resources Inc., Seattle, Washington, using EPA Method 8260. The initial dissolved VOC concentrations were determined from three random vials to establish baseline concentrations. VOC analyses were repeated after 3 weeks to identify any changes in the VOC concentrations and distributions prior to the addition of $KMnO_4$.

Immediately following the week 3 VOC analysis, vials in Set 1A, 1B, 2A, and 2B were treated with 0.8% $KMnO_4$. Vials 1C, 1D, 2C and 2D were treated with 2.4% $KMnO_4$. After 1 week of exposure to $KMnO_4$ (week 4), ethanol was added to react with any residual $KMnO_4$ and re-establish conditions suitable for anaerobic biodegradation in the each of the two sets of A and C vials. A 0.01 ml aliquot of ethanol was added to each of the A vials (treated with 0.8% $KMnO_4$) and a 2 ml aliquot was added to the C vials (treated with 2.4% $KMnO_4$). The spike amount was determined using screening studies in which various aliquots of ethanol were added to microcosms until all $KMnO_4$ was destroyed. The reaction was shown to proceed slowly requiring a full 24-hour period to reach completion. Consequently, the C vials received an excessive addition of ethanol, which apparently resulted in toxicity to the microbial populations in these vials. The procedure was modified for the B and D vials after 3 weeks of $KMnO_4$ exposure (week 6 of the study). A 0.01 ml aliquot of ethanol was added to each of the B vials (treated with 0.8% $KMnO_4$) and a 0.175 ml aliquot of ethanol was added to each of the D vials (treated with 2.4% $KMnO_4$). This ethanol addition was successful in removing residual $KMnO_4$ from the higher concentration treatment, but did not adversely affect the viability of the microbial populations.

Following quenching of the residual $KMnO_4$ with the ethanol addition, additional TCE was added to the vials to establish a TCE concentration of approximately 10 mg/L. VOC analysis was conducted on duplicate vials from each treatment prior to and following TCE addition. Concentrations of VOCs were then determined at various time periods to monitor biological TCE degradation and the appearance of daughter products. The A and C treatments were sampled and analyzed for VOCs at weeks 6, 8, and 12 of the study. The B and D treatments were analyzed at weeks 8 and 10 of the study. The control vials (E treatments) were analyzed also analyzed for VOC during this period at weeks 6, 8 10, and 12 to monitor biological activity in microcosms which did not receive the KMnO4 treatment.

RESULTS

Effects of $KMnO_4$ Addition on Chloroethene Concentrations

The results of the VOC analyses at each time point are summarized in Table 2 below. The results show little evidence of TCE degradation during the initial three weeks of the treatability study. Initial TCE concentrations for the nutrient-amended and unamended treatments were 9,133 µg/L and 15,000 µg/L, respectively. At the end of the initial three week period, TCE concentrations exhibited a slight increase to 9,233 µg/L in the nutrient-amended condition and 16,333 µg/L in the unamended condition. Likewise, there was essentially no change in concentrations of cis-DCE or VC during this period. However, TCE concentrations in both treatments were reduced by an average of 99% following $KMnO_4$ addition. The reduction of chlorinated ethenes was as effective at the 0.8% addition concentration of $KMnO_4$ as it was at the 2.4% concentration, suggesting that a considerable excess of $KMnO_4$ was present following oxidation of the chlorinated ethenes when the 2.4% concentration was used. In contrast,

relatively little change in TCE concentrations occurred during the course of the study in both the nutrient-amended and unamended microcosms that were not treated with $KMnO_4$, although a slight increase in cis-DCE was observed by the conclusion of the study. These data demonstrate that $KMnO_4$ is highly effective in reducing concentrations of chlorinated ethenes in soils and groundwater from the Building 190 Tank Farm site, under controlled laboratory conditions.

Table 2 Average Concentrations of Chloroethenes in Nutrient-Amended and Unamended Microcosms Resulting from $KMnO_4$ Treatment

Treatment	Time point (weeks)	Nutrient-Amended					Unamended				
		PCE	TCE	cis-DCE	trans-DCE	VC	PCE	TCE	cis-DCE	trans-DCE	VC
A	0.00	225.0	**9133.3**	**983.3**	225.0	**403.3**	225.0	**15000.0**	**1333.3**	225.0	225.0
	3.00	75.0	**9233.3**	**736.7**	75.0	**226.7**	75.0	**16333.3**	**2600.0**	75.0	**218.3**
	3.99	0.5	**74.0**	**5.1**	0.5	**1.6**	1.5	**230.0**	**35.2**	1.5	**3.6**
	4.01	75.0	**9900.0**	75.0	75.0	75.0	75.0	**9250.0**	**132.5**	75.0	75.0
	6.00	50.0	50.0	**8950.0**	50.0	50.0	100.0	**4550.0**	**4292.5**	100.0	100.0
	8.00	31.3	27.3	**4780.0**	31.3	**1100.0**	50.0	**52.5**	**6050.0**	50.0	**840.0**
	12.00	50.0	50.0	**8750.0**	50.0	**100.0**	**25.3**	**30.5**	**3324.0**	**26.2**	**1040.0**
B	0.00	225.0	**9133.3**	**983.3**	225.0	**403.3**	225.0	**15000.0**	**1333.3**	225.0	225.0
	3.00	75.0	**9233.3**	**736.7**	75.0	**226.7**	75.0	**16333.3**	**2600.0**	75.0	**218.3**
	5.99	2.5	**320.0**	**238.0**	**2.9**	**3.8**	1.5	**335.0**	**128.0**	**1.6**	**2.6**
	6.01	50.0	**10000.0**	**130.0**	50.0	50.0	75.0	**10150.0**	**150.0**	75.0	75.0
	8.00	50.0	**575.0**	**9500.0**	50.0	50.0	50.0	**2040.5**	**8050.0**	50.0	50.0
	10.00	37.5	**2025.0**	**6950.0**	37.5	**137.5**	50.0	**87.0**	**8850.0**	50.0	50.0
C	0.00	225.0	**9133.3**	**983.3**	225.0	**403.3**	225.0	**15000.0**	**1333.3**	225.0	225.0
	3.00	75.0	**9233.3**	**736.7**	75.0	**226.7**	75.0	**16333.3**	**2600.0**	75.0	**218.3**
	3.99	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	4.01	75.0	9900.0	75.0	75.0	75.0	75.0	**10450.0**	75.0	75.0	75.0
	6.00	37.5	**6400.0**	**665.0**	37.5	**71.0**	100.0	**9500.0**	100.0	100.0	100.0
	8.00	50.0	**2450.0**	**6200.0**	50.0	50.0	50.0	**11000.0**	**95.0**	50.0	50.0
	12.00	**50.0**	**150.0**	**7900.0**	**50.0**	**50.0**	**50.0**	**9700.0**	**1655.0**	**50.0**	**50.0**
D	0.00	225.0	**9133.3**	**983.3**	225.0	**403.3**	225.0	**15000.0**	**1333.3**	225.0	225.0
	3.00	75.0	**9233.3**	**736.7**	75.0	**226.7**	75.0	**16333.3**	**2600.0**	75.0	**218.3**
	5.99	1.5	**154.5**	**51.2**	1.5	**1.8**	1.3	**45.0**	**42.0**	1.3	1.3
	6.01	50.0	**9650.0**	50.0	50.0	50.0	50.0	**9950.0**	50.0	50.0	50.0
	8.00	50.0	**3385.0**	**5900.0**	50.0	50.0	50.0	**2045.0**	**8150.0**	50.0	50.0
	10.00	50.0	**175.0**	**8050.0**	50.0	**215.0**	37.5	**408.0**	**6500.0**	37.5	37.5
E	0.00	225.0	**9133.3**	**983.3**	225.0	**403.3**	225.0	**15000.0**	**1333.3**	225.0	225.0
	3.00	75.0	**9233.3**	**736.7**	75.0	**226.7**	75.0	**16333.3**	**2600.0**	75.0	**218.3**
	6.00	32.5	**5800.0**	**1025.0**	32.5	**110.0**	50.0	**11500.0**	**3350.0**	50.0	50.0
	8.00	50.0	**6600.0**	**2150.0**	50.0	**78.0**	50.0	**17000.0**	**2650.0**	50.0	50.0
	10.00	50.0	**11700.0**	**2500.0**	50.0	85.0	50.0	**13350.0**	**3150.0**	50.0	50.0
	14.00	**50.0**	**9800.0**	**4500.0**	**50.0**	**50.5**	**50.0**	**7650.0**	**3660.0**	**50.0**	**55.5**

Notes:
The first 2 time points are the average of triplicate microcosms, all other time points are the average of duplicates.
Bold Values - Concentrations above the analytical reporting limit.
Shaded values are obtained from Treatment A. Due to laboratory error, Treatment C was not analyzed following the TCE re-spike.
Treatments -

A - One week exposure to 0.8% $KMnO_4$

B - Three week exposure to 0.8% $KMnO_4$

C - One week exposure to 2.4% $KMnO_4$

D - Three week exposure to 2.4% $KMnO_4$

E - No $KMnO_4$

Effects of $KMnO_4$ Concentrations on Microbial Dechlorination Capacity

Figures 4 and 5 show the concentrations of chlorinated ethenes following a one-week exposure to 0.8% and 2.4% $KMnO_4$, respectively, for the nutrient-amended study group. It should be

noted that, since there was very little difference in the results obtained for the nutrient-amended group, compared to the unamended group, only the data from the nutrient-amended treatment are summarized in these graphs. The shaded area on the graphs represent the period during which the microcosms were exposed to $KMnO_4$. Following the exposure period, ethanol was added to "quench" any residual $KMnO_4$, after which TCE was added to achieve an aqueous phase concentration of about 10 mg/L.

Figure 4 Nutrient-Amended Study, One-Week Exposure to 0.8% $KMnO_4$ (Treatment A)

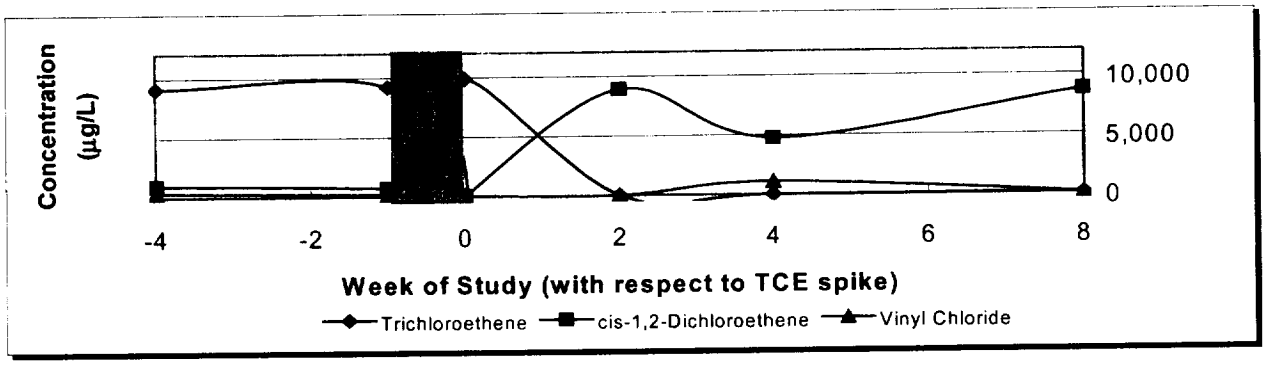
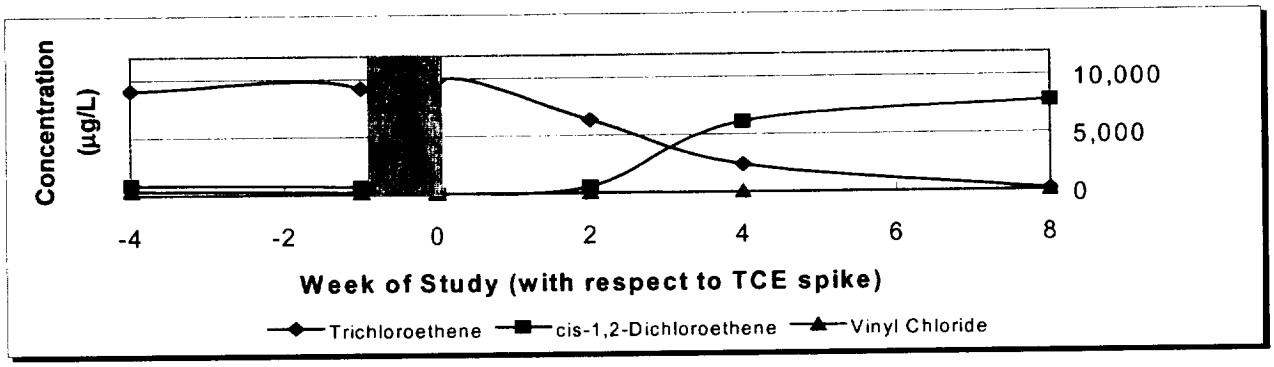


Figure 5 Nutrient-Amended Study, One-Week Exposure to 2.4% $KMnO_4$ (Treatment C)



The figures show that, following the TCE spike, reductions in TCE concentrations occurred rapidly, with a simultaneous production of cis-DCE. The apparent rates of TCE degradation and cis-DCE production were somewhat lower in the microcosms that were exposed to 2.4% $KMnO_4$, which may indicate that the microbial populations were stressed by the exposure to the higher $KMnO_4$ concentrations. However, similar levels of TCE and cis-DCE concentrations of these compounds were achieved by the end of the study under both $KMnO_4$ treatments.

It is noted that, unlike the previous microcosm study described by Figures 1 and 2, significant reduction of cis-DCE and production of VC was not observed in either the microcosms treated with $KMnO_4$, or in the control microcosms that were not treated with $KMnO_4$. It is not clear why dechlorination did not progress beyond cis-DCE. The most likely explanation is that the duration of the study was too short to allow observation of cis-DCE dechlorination. A slight increase in VC and decrease in cis-DCE concentrations is evident for the final data point for the nutrient-amended condition that received the 3-week exposure to 0.8% $KMnO_4$ (Treatment B). However, it is also possible that the oxidation/reduction potential (Eh) within the

microcosm vials was not sufficiently low to permit reductive dechlorination of cis-DCE., or that the levels of available electron donors (organic substrates and/or hydrogen) were insufficient to allow dechlorination to proceed. Nevertheless, the data indicate that the ability of the indigenous microbial populations to dechlorinate TCE was not impaired by additions of $KMnO_4$.

Effects of $KMnO_4$ Exposure Duration on Microbial Dechlorination Capacity

Figures 6 and 7 show the concentrations of chlorinated ethenes in the nutrient-amended microcosms following a three-week exposure to 0.8% and 2.4% $KMnO_4$, respectively. These figures show decreases in TCE concentrations and concomitant increases in cis-DCE concentrations that are very similar to those observed for the one-week exposures to comparable $KMnO_4$ concentrations shown in Figures 4 and 5. Once again, apparent rates of TCE degradation and cis-DCE production were somewhat slower following treatment with the higher $KMnO_4$ concentration. In addition, Figure 6 and the data in Table 2 suggest that reduction of cis-DCE and production of VC may be starting by the final sampling point. However, the data show no evidence that microbial dechlorination activity is adversely affected by the duration of exposure to $KMnO_4$.

Figure 6 Nutrient-Amended Study, Three-Week Exposure to 0.8% $KMnO_4$ (Treatment B)

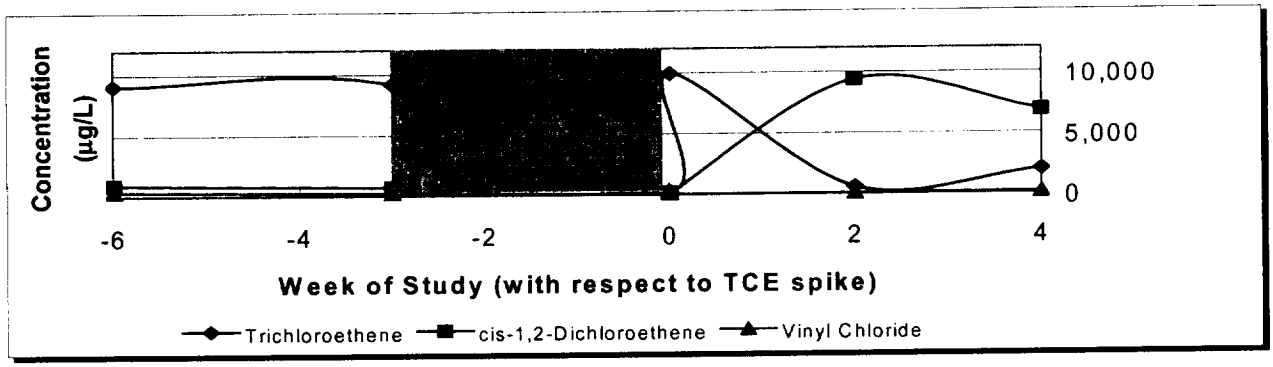
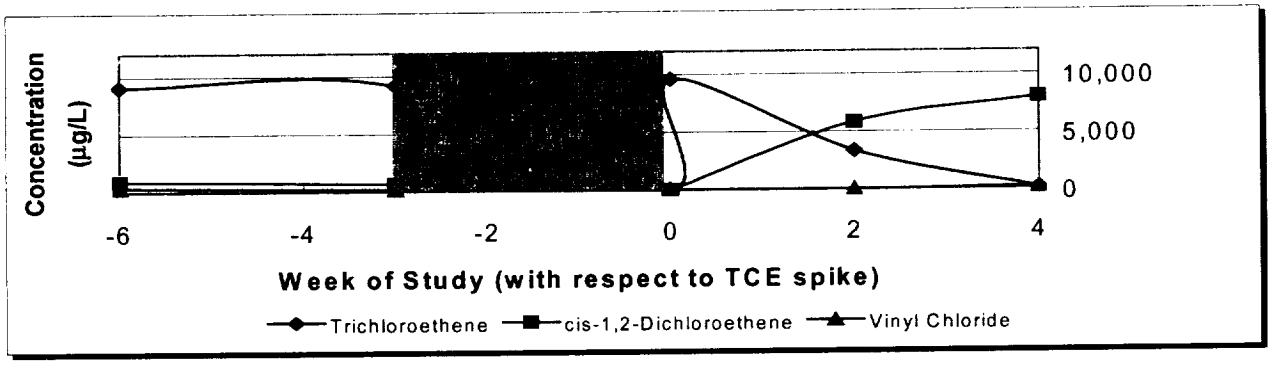


Figure 7 Nutrient-Amended Study, Three-Week Exposure to 2.4% $KMnO_4$ (Treatment D)

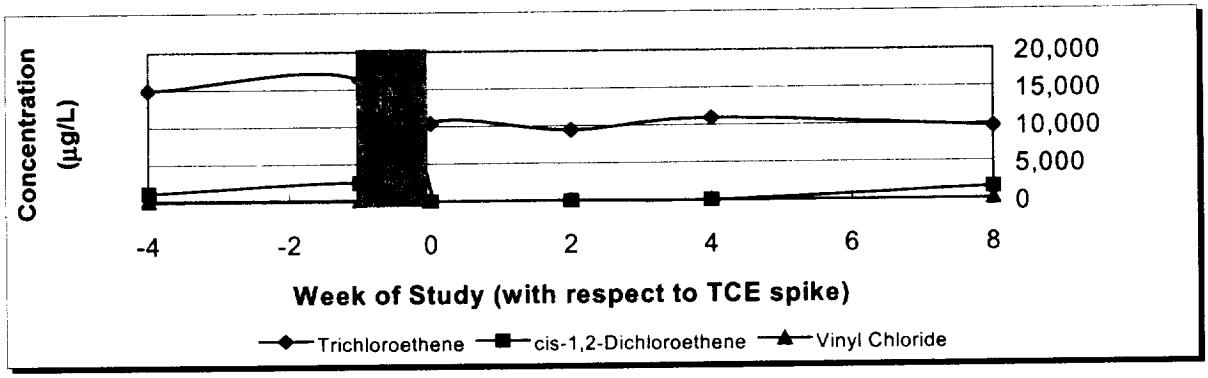


Apparent Ethanol Toxicity in the Unamended Treatment C Microcosms

Of the eight sets of nutrient-amended and unamended microcosms that were treated with $KMnO_4$, only the unamended set that received the one-week exposure to 2.4% $KMnO_4$ (Treatment C) failed to exhibit significant reduction of TCE following treatment with $KMnO_4$ (Figure 8). It is believed that the absence of TCE reduction in these microcosms was due to the

inadvertent addition of an excessive amount of ethanol to quench residual $KMnO_4$ at the end of the one-week exposure period. This set of microcosms was the first that was treated with ethanol. It was initially expected that the reaction of ethanol with $KMnO_4$ would occur rapidly and would be evident by a quick purple-to-clear change in the color of the water within the microcosms. However, the purple color persisted in the unamended Treatment C microcosms in spite of repeated additions of ethanol. When the vials were inspected approximately eight hours later, no purple color was detected, indicating that the reaction of ethanol and $KMnO_4$ was considerably slower than anticipated. Subsequent analysis of the microcosms following re-spiking with TCE showed ethanol concentrations of approximately 13,000 mg/L. Consequently, a period of 24-hours was allowed for the complete reaction of ethanol and $KMnO_4$ for all other treatments, all of which subsequently exhibited TCE degradation and cis-DCE production. Therefore, it is likely that the high concentration of ethanol in the unamended Treatment C microcosms was responsible for the absence of reductive dechlorination in that treatment condition.

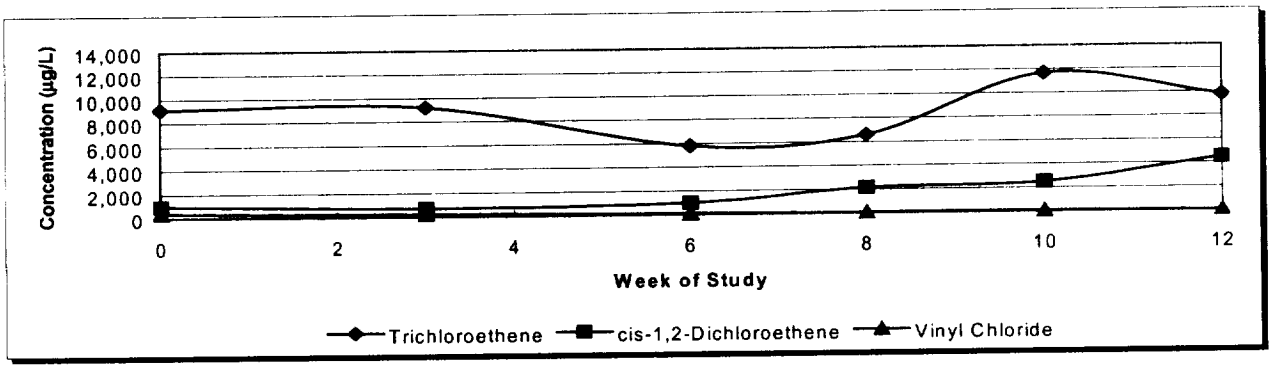
Figure 8 Unamended Study, One-Week Exposure to 2.4% $KMnO_4$ (Treatment C) - Apparent Ethanol Toxicity



DISCUSSION AND CONCLUSIONS

This study has provided a thorough evaluation of the compatibility of combined *in situ* remediation of chlorinated ethene contamination using chemical oxidation with $KMnO_4$ and biological reductive dechlorination. The results of the study demonstrate that microbial dechlorination activity in aquifer material from the Building 190 Tank Farm site is not impaired at $KMnO_4$ concentrations of up to 2.4% and exposure durations of up to three weeks. In fact, the data indicate that TCE dechlorination did not occur to a significant degree until after the microcosms had been treated with $KMnO_4$. During the first three weeks of the study (prior to $KMnO_4$ addition), the concentrations of TCE, cis-DCE and VC in both the nutrient-amended and unamended conditions were essentially unchanged. The relative lack of dechlorination activity in the absence of $KMnO_4$ treatment is further indicated by the control microcosms which did not receive $KMnO_4$. Figure 9 shows the results of the nutrient-amended condition that was not treated with $KMnO_4$ (Treatment E). The data from the unamended Treatment E microcosms is similar.

Figure 9 Nutrient-Amended Study with No Exposure to $KMnO_4$ (Treatment E)



The pattern illustrated by the Treatment E microcosms during the study, and by the other treatment conditions prior to the addition of $KMnO_4$, differs from the previous microcosm study illustrated in Figures 1 and 2, in which dechlorination was occurred rapidly at the outset of the study. The initial absence of TCE dechlorination in the current study may have been due to the presence of a pool of relatively easily-degraded organic substrate in the aquifer material at the beginning of the study. If this is the case, it is likely that degradation of TCE would not commence until the easily-degraded substrate is consumed. Consequently, when $KMnO_4$ was added, the easily-degraded substrate, as well as the chlorinated ethenes, were oxidized. When new TCE was then added following the period of exposure to $KMnO_4$, the easily-degraded substrate would have been depleted, allowing microbial reductive dechlorination of the TCE to proceed. Since $KMnO_4$ was not added to the Treatment E microcosms, the persistent presence of the easily-degraded substrate would suppress dechlorination throughout the duration of the study, or until the pool of substrate was depleted. The increase in the concentration of cis-DCE by the end of the study suggests that the availability of the competing substrate had been reduced, and that TCE dechlorination was commencing.

On the basis of this study, an integrated *in situ* remediation strategy for highly-impacted areas, consisting of initial chemical oxidation using $KMnO_4$, followed by enhanced anaerobic biodegradation using ethanol amendments, is technically feasible and has the potential for effective application at the MAF site. The data indicate that $KMnO_4$ concentrations on the order of 1-2% are not likely to result in microbial toxicity or inhibition of biological reductive dechlorination. It appears appropriate, therefore, to initiate pilot studies to evaluate this remediation approach under actual field conditions.

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