

WRI 09-R020

**USE OF ADVANCED OXIDATION AND AEROBIC
DEGRADATION FOR REMEDIATION OF VARIOUS
HYDROCARBON CONTAMINANTS**

TOPICAL REPORT

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DISCLAIMER

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ABSTRACT

Western Research Institute in conjunction with Sierra West Consultants, Inc., Tetra Tech, Inc., and the U.S. Department of Energy conducted laboratory and field studies to test different approaches to enhance degradation of hydrocarbons and associated contaminants. WRI in conjunction with Sierra West Consultants, Inc., conducted a laboratory and field study for using ozone to treat a site contaminated with MTBE and other hydrocarbons. Results from this study demonstrate that a TOD test can be used to resolve the O₃ dosage problem by establishing a site-specific benchmark dosage for field ozone applications. The follow-up testing of the laboratory samples provided indications that intrinsic biodegradation could be stimulated by adding oxygen. Laboratory studies also suggests that O₃ dosage in the full-scale field implementation could be dialed lower than stoichiometrically designed to eliminate the formation of Cr(VI). WRI conducted a study involving a series of different ISCO oxidant applications to diesel-contaminated soil and determined the effects on enhancing biodegradation to degrade the residual hydrocarbons. Soils treated with permanganate followed by nutrients and with persulfate followed by nutrients resulted in the largest decrease in TPH. The possible intermediates and conditions formed from NOM and TPH oxidation by permanganate and activated persulfate favors microbial TPH degrading activity. A “passive-oxidation” method using microbial fuel cell (MFC) technology was conducted by WRI in conjunction with Tetra Tech, Inc., to degrade MTBE in groundwater. These experiments have demonstrated that a working MFC (i.e., one generating power) could be established in the laboratory using contaminated site water or buffered media inoculated with site water and spiked with MTBE, benzene, or toluene. Electrochemical methods were studied by WRI with goal of utilizing low voltage and amperage electrical sources for “geo-oxidation” of organic contaminants. The results from a study with TCE contaminated-clay indicate that electrochemically inducing reductive dechlorination of TCE in a saturated matrix may offer an effective and viable alternative to remediation TCE and other contaminants with potential of being reduced. Another study focused on steel wool oxidation to electrochemically increase population of hydrocarbon-degrading denitrifying bacteria. Significantly larger denitrifying activity was observed in the cathode chamber of a treatment unit setup like an MFC with steel wool as the anode. This enhanced nitrate reduction could be due to direct electron utilization by denitrifying bacteria on the cathode, thereby stimulating microbial denitrification or a combination of electron transfer directly to NO₃⁻ and electron transfer to nitrate reducing bacteria, which may serve as a type of bio-catalyst on the cathode for nitrate reduction. Overall, the studies conducted under Task 72 demonstrated different innovative methods to enhance petroleum hydrocarbon degradation and associated contaminants.

EXECUTIVE SUMMARY

Conventional treatment methods for hydrocarbon-contaminated soils and groundwater include soil washing, thermal treatment, vapor extraction, land farming and bio-venting. These methods tend to require high operational costs, and are not effective to recalcitrant contaminants or compounds with low volatility. Common groundwater method extracts the contaminated water, treats it above ground, and re-injects the treated water to the subsurface, while disposing of the contaminants separately. This “pump-and-treat” method is expensive and sometimes ineffective due to hydro-geological limitations. There are growing interests in alternative, innovative remediation technologies that can be applied in-situ, which rapidly break down petroleum hydrocarbons in soils and groundwater.

In-situ chemical oxidation (ISCO) has recently shown potentials in destroying various hydrocarbons in groundwater, sediments, and soils. ISCO technologies are based on chemical oxidants that aggressively oxidize free phase, high concentrations of contaminants and recalcitrant constituents to the harmless end products or less harmful intermediates. The duration of a ISCO treatment is typically short. Dissolved oxygen concentration in the post-treatment soils and groundwater can facilitate aerobic bioremediation for a period of time.

Western Research Institute in conjunction with Sierra West Consultants, Inc., Tetra Tech, Inc., and the U.S. Department of Energy conducted laboratory and field studies to test different approaches to enhance degradation of hydrocarbons and associated contaminants. The results and conclusions of these studies are summarized as follows:

- WRI in conjunction with Sierra West Consultants, Inc., conducted a laboratory and field study for using ozone to treat a site contaminated with MTBE and other hydrocarbons. Results from this study demonstrate that a TOD test can be used to resolve the O₃ dosage problem by establishing a site-specific benchmark dosage for field ozone applications. In addition, soluble Cr(III) and Cr(VI) in groundwater and total Cr in soil should be tested to understand the potential for Cr(VI) formation. Prudent field applications of the design dosage can be used to reduce the risk of creating Cr(VI). The follow-up testing of the laboratory samples provided indications that intrinsic biodegradation could be stimulated by adding oxygen. The soil/groundwater slurries that were exposed to the atmosphere and those with applied O₃ demonstrated decreasing MTBE concentrations during period beyond the ozonation. This suggests that O₃ dosage in the full-scale field implementation could be dialed lower than stoichiometrically designed to eliminate the formation of Cr(VI).
- WRI conducted a study involving a series of different ISCO oxidant applications to diesel-contaminated soil and determined the effects on enhancing biodegradation to degrade the residual hydrocarbons. Soils treated with permanganate followed by nutrients

and with persulfate followed by nutrients resulted in the largest decrease in TPH. In other treatments, the high NOM concentration in the soil may have consumed the oxidants, which negatively affects the TPH oxidation. However, the possible intermediates and conditions formed from NOM and TPH oxidation by permanganate and activated persulfate favors microbial TPH degrading activity. Nutrient concentrations at end of study were inconclusive. Further tests are required to determine the effects of NOM on integrating ISCO oxidants and enhancing biodegradation.

- A “passive-oxidation” method using microbial fuel cell (MFC) technology was conducted by WRI in conjunction with Tetra Tech, Inc., to degrade MTBE in groundwater. These experiments have demonstrated that a working MFC (i.e., one generating power) could be established in the laboratory using contaminated site water or buffered media inoculated with site water and spiked with MTBE, benzene, or toluene. The appearance of co-eluting compounds that may be microbial breakdown products from MTBE as well as the power generation in each MFC containing MTBE, benzene, or toluene indicates that microbial activity and possible contaminant degradation was taking place.
- Electrochemical methods were studied by WRI with goal of utilizing low voltage and amperage electrical sources for “geo-oxidation” of organic contaminants. The results from a study with TCE contaminated-clay indicate that electrochemically inducing reductive dechlorination of TCE in a saturated matrix may offer an effective and viable alternative to remediation TCE and other contaminants with potential of being reduced. These reactions can occur within an electric field between electrodes as low as 6 V/m.
- Another study focused on steel wool oxidation to electrochemically increase population of hydrocarbon-degrading denitrifying bacteria. Denitrifying bacteria exist in waters with sufficient nitrate concentrations and can degrade a wide range of petroleum hydrocarbons. Significantly larger denitrifying activity was observed in the cathode chamber of a treatment unit setup like an MFC with steel wool as the anode. This enhanced nitrate reduction could be due to direct electron utilization by denitrifying bacteria on the cathode, thereby stimulating microbial denitrification or a combination of electron transfer directly to NO_3^- and electron transfer to nitrate reducing bacteria, which may serve as a type of bio-catalyst on the cathode for nitrate reduction.

Overall, the studies conducted under Task 72 demonstrated different innovative methods to enhance petroleum hydrocarbon degradation and associated contaminants. This was accomplished by using oxidation processes to directly degrade and indirectly degrade (through microbial enhancement) the organic contaminants.

INTRODUCTION

In known hydrocarbon-contaminated sites in the United States, approximately 80% contain free products in the soils and groundwater. Although bioremediation has been proven to be the cost-effective technique in hydrocarbon cleanup, free phase and very high concentrations of petroleum compounds may be prohibitive to microbial activities, resulting in longer treatment period. In addition, recalcitrant compounds that are closely associated with petroleum industry, such as methyl tert-butyl ether (MTBE) and poly-aromatic hydrocarbons (PAH) consist of a group of contaminants challenging to the sole application of bioremediation. A more aggressive approach is warranted to rapidly eliminate the high concentrations of petroleum contaminants, especially the free phase products and recalcitrant constituents.

Conventional soil treatment methods include soil washing, thermal treatment, vapor extraction, land farming and bio-venting, etc. These methods tend to require high operational costs, and are not effective to recalcitrant contaminants or compounds with low volatility. Common groundwater method extracts the contaminated water, treats it above ground, and re-injects the treated water to the subsurface, while disposing of the contaminants separately. This “pump-and-treat” method is expensive and sometimes ineffective due to hydro-geological limitations. There are growing interests in alternative, innovative remediation technologies that can be applied in-situ, which rapidly break down petroleum hydrocarbons in soils and groundwater.

In-situ chemical oxidation (ISCO) has recently shown potentials in destroying various hydrocarbons in groundwater, sediments, and soils. ISCO technologies are based on chemical oxidants that aggressively oxidize free phase, high concentrations of contaminants and recalcitrant constituents to the harmless end products or less harmful intermediates. The duration of a ISCO treatment is typically short. Dissolved oxygen concentration in the post-treatment soils and groundwater can facilitate aerobic bioremediation for a period of time.

Typical oxidants currently in use include hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), and ozone. All of these technologies are site-specific and the performances vary in different case studies. The instantaneous and aggressive nature of the oxidation makes the ISCO process dosage sensitive, largely varying on contaminants of interests. Additionally, inaccessibility to the plume located in certain geological settings requires a slower transfer of oxidants to the contaminants.

Western Research Institute (WRI) in conjunction with the U.S. Department of Energy (DoE) conducted a series of studies with the goal of using advanced contaminant oxidation methods to degrade organic contaminants in soil and groundwater. WRI in conjunction with Sierra West Consultants, Inc., conducted a laboratory and field study for using ozone to treat a site contaminated with MTBE and other hydrocarbons. Post-ozonation biodegradation of MTBE

was monitored. WRI conducted a study involving a series of different ISCO oxidant applications to diesel-contaminated soil and determined the effects on enhancing biodegradation to degrade the residual hydrocarbons. A “passive-oxidation” method using microbial fuel cell (MFC) technology was conducted by WRI in conjunction with Tetra Tech, Inc., to degrade MTBE in groundwater. Other electrochemical methods were studied by WRI with goal of utilizing low voltage and amperage electrical sources for “geo-oxidation” of organic contaminants.

RESULTS

Ozonation and Biodegradation of MTBE while Minimizing Cr(VI) Mobilization

This study originated from a field pilot work conducted by Sierra West Consultants, Inc., at a leaking underground storage tank (LUST) site impacted by MTBE located in Sacramento, California. In the field pilot study, ozone was injected into the MTBE impacted groundwater at approximately 24.4 m below ground surface (bgs). Monitoring wells were located 4.6 m (15 ft) down-gradient (MW-4B) and 6.1 m (20 ft) cross-gradient (MW-13B) from injection well OZ-2, as shown in Figure 1. An existing shallow interval monitoring well (MW-4A), screened from 10.7 to 15.2 m bgs and located 6.1 m down-gradient, was also included in the test.

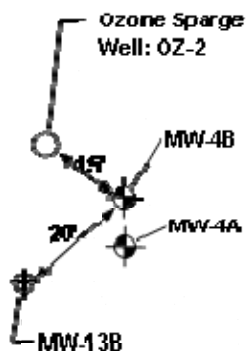


Figure 1. Ozone field pilot layout.

Ozone injection was successful in reducing MTBE from approximately 10,000 µg/L to approximately 300 µg/L after 2 weeks and non-detect after 7 weeks. These results were complicated by Cr(VI) increasing from non-detect after 3 weeks to nearly 400 µg/L after 10 weeks. Field monitoring indicated that MTBE was oxidized prior to Cr(VI) formation. It was assumed that over dosing of O₃ might have caused the elevated Cr(VI). This study was conducted to understand whether O₃ would oxidize Cr(III) to Cr(VI) during or after oxidation of

MTBE in groundwater, and if so, at what ozone dosage would such co-oxidation occur. As series of ozone dosages were tested to determine the optimal concentration that oxidizes MTBE without substantial co-oxidation of Cr III. The obtained optimal dosage was then applied in a field remediation of MTBE-impacted groundwater.

Groundwater and soil samples were collected from the field site in Sacramento, California. Groundwater samples (18.9 L) were collected from monitoring well (MW-4B). Water samples were also taken from a well up-gradient (MW-3) and well (MW-4A) near MW-4B to establish a site baseline and assist in determining site heterogeneity. Field parameters of pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and conductivity (EC) were measured at these locations during the sampling. During this sampling event, a new well (EW-1B) was completed using a sonic drill rig. Core samples taken during drilling were characterized in the field and a well log was produced. Samples were taken from the drilling core above the impacted interval, in the interval, and just below the interval. Soil and water were analyzed to establish baseline characteristics. Analytes included: pH, conductivity (EC), dissolved oxygen (DO), oxidizing-reducing potential (ORP), anions (Fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-})), dissolved organic carbon (DOC), total and dissolved metals (Cr), iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), zinc (Zn), lead (Pb)), Cr(III), Cr(VI), and MTBE.

Field measurements from the three monitoring wells are shown in Table 1. The groundwater is in a low DO to oxygen-depleting state, as evidenced by the DO measurements and verified by the negative ORP measurements. The neutral pH and presence of organic carbon (possibly from the contaminants) suggest that biological activities may be responsible for the depletion of oxygen. However, DO was detected at 1.22 mg/L in groundwater collected from monitoring well MW-4. This was probably attributed to the residual from previous ozone injection and low organic concentrations in the vicinity of this well. Results of other analytes are summarized in Tables 2 and 3. The similar concentrations of anions were found in each well, and the lower concentrations of common electron acceptors such as nitrate and sulfate, indicate that the groundwater onsite is relatively homogeneous and under reduced conditions, which also possess the potential of consuming oxidant during chemical oxidation. Nitrate data from samples collected from MW-4B was not reported due to system error during the analysis. An elevated concentration of dissolved Mn (2602 mg/L) was detected in groundwater collected from well MW-3. This may be attributed to the reduced conditions in the vicinity that results in the solubilization of Mn. No Cr(VI) ($<1.7 \mu\text{g/L}$) was detected in groundwater samples collected from all three wells. Total Cr was detected at an average concentration of $16.3 \mu\text{g/L}$ in the groundwater/soil slurry reactors used in this study, indicating the source of Cr is dominantly in the soil. The presence of total Cr indicates an indigenous presence and the potential of Cr(III) to be oxidized into Cr(VI).

Table 1. Field measurements.

Well ID	pH	DO (mg/L)	ORP(mV)	EC (μS)
MW-3	6.85	0.89	-5.8	556
MW-4	7.17	1.22	29.5	643
MW-4B	7.09	0.57	-66.6	802

Table 2. Baseline anions, cations, and metals concentrations.

Anion (mg/L)	MW-3	MW-4	MW-4B
Flouride (F ⁻)	<1.5	<1.5	<1.5
Chloride (Cl ⁻)	36.9	31.5	35.1
Bromide (Br ⁻)	<3.0	<3.0	<3.0
Nitrate (NO ₃ ⁻)	<0.1	<0.1	N/A
Phosphate (PO ₄ ³⁻)	<3.0	<3.0	<3.0
Sulfate (SO ₄ ²⁻)	30.9	36.2	30.7
Na (mg/L)	21.7	23.0	24.9
Mg (mg/L)	29.0	34.4	38.8
K (mg/L)	1.2	3.2	3.3
Ca (mg/L)	61.8	63.3	80.0
Cr (μg/L)	2.2	2.6	3.5
Mn (μg/L)	2602.2	936.4	152.4
Fe (mg/L)	0.7	0.8	1.1
Ni (μg/L)	6.7	10.9	1.3
Cu (μg/L)	0.8	1.2	0.4
Zn (μg/L)	9.8	227.7	3.8
Pb (μg/L)	0.0	0.1	0.0

Table 3. Baseline organic compound concentrations.

Well ID	TOC (mg/L)	DOC (mg/L)	MTBE (μg/L)
MW-3	1.339	0.382	1.2
MW-4	0.324	0.324	4.6
MW-4B	6.505	6.221	110

Total oxidation demand (TOD) was measured to estimate a design based ozone dosage. A direct TOD test with O_3 is difficult due to the hardship of quantifying residual ozone during the reaction. A TOD protocol was established by using sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) as an oxidant equivalent because it is relatively stable and measurable at intervals during the oxidation reactions. The TOD of the site groundwater and soil samples (10% w/v of soil) was determined by using $2Na_2CO_3 \cdot 3H_2O_2$ (10,000 mg/L) as the surrogate equivalent. Sodium percarbonate concentration was analyzed indirectly by quantifying residual H_2O_2 . The molar O_3 equivalent was calculated from the TOD data for $2Na_2CO_3 \cdot 3H_2O_2$. The $2Na_2CO_3 \cdot 3H_2O_2$ TOD was determined to be 558 mg/L based on the results shown in Figure 2. This concentration was converted to obtain the minimal ozone dosage for complete oxidation of the soil/water slurry as described in the methods and materials section. The design dosage of O_3 (100% dosage) was determined to be 28.33 mg/L, from which all dosages were based from in the bench-scale test. A true O_3 demand would be calculated from the $2Na_2CO_3 \cdot 3H_2O_2$ TOD concentration based on oxidizing potential of the O_3 (2.1 V) and the H_2O_2 (1.8 V) from $2Na_2CO_3 \cdot 3H_2O_2$. The O_3 demand would be determined by the relationship where 0.85 mol O_3 is equivalent to 1.0 mol H_2O_2 (0.28 mol O_3 /mol $2Na_2CO_3 \cdot 3H_2O_2$).

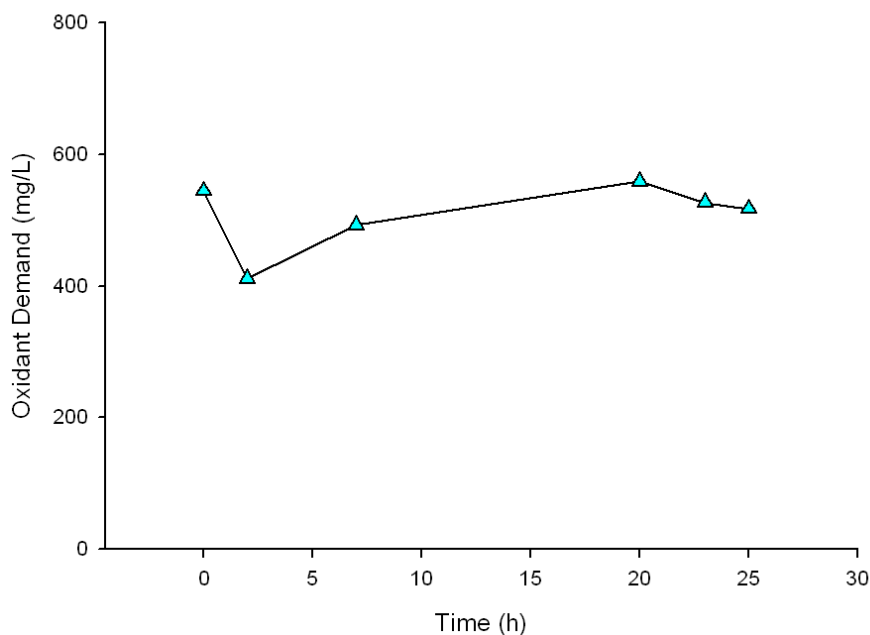


Figure 2. Oxidant demand of MTBE-contaminated groundwater.

Microcosm reactors were established in 500-ml amber glass bottles using site groundwater and soil samples collected from the same depth interval. Soil was set at 10% (wt/v) of the total volume in the reactors. Ozone was applied at dosages based on the design based dosage determined from the TOD test. A range of testing dosages was used to be corresponding

to 0, 25, 50, 100, 200, and 400% of the design based dosage. Ozone was delivered at a steady rate by an Absolute Ozone AE15MC ozone generator (Edmonton, AB, Canada) with emitters placed at the bottom of the reactors. The testing flow rates and system specifications are summarized in Table 4. The reactors were set up in triplicates and oxidation was performed at field-measured temperature. Based on the flow rate, a sampling schedule was established to collect samples when a set dosage was obtained, as recorded in Table 5. Samples were collected periodically after the appropriate test dosages were applied. Temperature, ORP, and pH were measured during the samplings. Samples were analyzed for MTBE and Cr(VI). Anions and total and dissolved metals were also monitored after the ozone application to determine if other substances were oxidized, released and/or precipitated during the O₃ test.

Table 4. Ozone generator parameters.

Ozone Flow Rate	0.13 S L/min
Ozone Production	1440.00 mg/h
Ozone Dosage Rate/Bottle	2.00 mg/h
Flow To Manifold	0.0013 L/min
Flow To Manifold	0.0015 L/min
Or	1.49 mL/min @ 2195 m elevation
N ₂ Mix Flow For 72%	1.87 mL/min @ 2195 m elevation

S L: standard liter, volume adjusted to pressure and temperature.

Table 5. Dosage schedule

Dosage (% of TOP)	Design Dosage (mg ozone)	Treatment Time (min)
0%	0.00	0
25%	4.00	90
50%	7.00	180
100%	14.00	360
200%	28.00	720
400%	57.00	1440

The detectable concentrations (>1.7 µg/L) of Cr(VI) occurred only after 56 mg O₃/L (2 times the design dosage) had been applied to 500 ml samples (Figure 3). At this point, an average of 17.3 µg/L of Cr(VI) was measured. Sparging additional O₃ did not increase the amount of oxidized Cr, and levels of Cr(VI) remained stable. It appeared that total Cr was dissolved from the soil matrix at an O₃ dosage of 56 mg/L and simultaneously most of this Cr was oxidized to Cr(VI). As such, it appeared the formation of Cr(VI) was related to the total Cr

in the soil and the quantity of applied O_3 . The MTBE concentration substantially decreased with increasing O_3 application. After a 28 mg O_3 /L dosage, the depletion of MTBE was approximately 60%, and at 56 mg O_3 /L the MTBE depletion was greater than 90%. However, no decrease in MTBE concentration was observed when O_3 dosage increased above 56 mg/L, and the final average MTBE concentration was approximately 18 $\mu\text{g/L}$ in the reactors. Changes in pH, ORP, and temperature were insignificant during the tests. Similarly, anions and total metals remained stable throughout the tests, except that manganese decreased at an O_3 dosage of 114 mg/L. This may be attributed to the oxidation of Mn at elevated O_3 dosages.

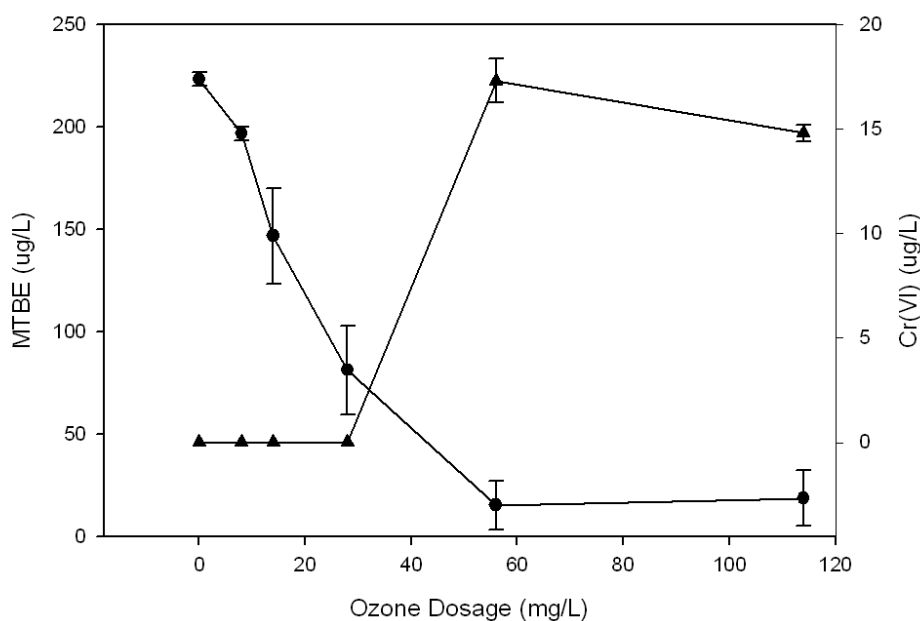


Figure 3. MTBE degradation vs. Cr(VI) production.

Four O_3 injection wells were established and designated as AS-1, OZ-2B, and OZ-3A/B, as shown in Figure 4. Wells AS-1 and OZ-2B were located on the down-gradient side of the source area in the shallow and deep groundwater intervals, respectively. Wells OZ-3A and OZ-3B were located in the former UST area on the up-gradient side of the site. A groundwater extraction and treatment system was installed on the down-gradient edge to capture groundwater from both groundwater intervals. The GET system is intended to capture Cr(VI) that may form and enhance in-situ biodegradation by accelerating groundwater flow and distributing the O_3 -oxygenated water across the site. The O_3 generator used in the field is capable of injecting 0.68 kg/day of O_3 in an air/ozone mixture at a flow rate of approximately 85.0 L/min a pressure of less than 276 kPa. The generator has variable capacity based on a percent of total capacity. Ozone was injected into each well sequentially, allowing an off time after injection into a particular well. As such, the amount of applied ozone was controlled by the generator output and

by the ON/OFF cycle times. The O₃ application was monitored at nearby groundwater monitoring wells. MTBE, TBA, Cr(VI), and DO were monitored to evaluate ozone application and MTBE treatment and potential formation of Cr(VI).

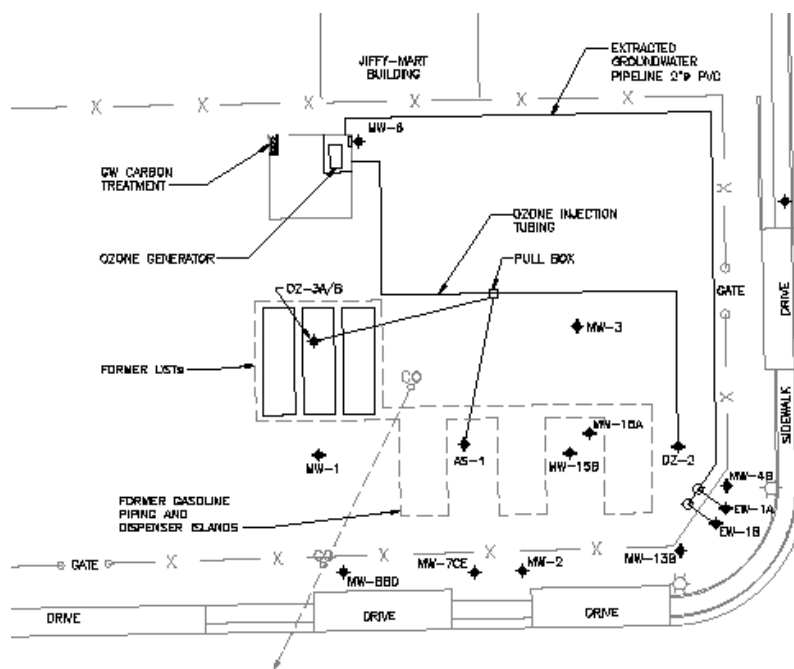


Figure 4. Site plan for field implementation

Based on the laboratory results, a 28 mg O₃/L dosage was used for the full-scale design. Using a modeled groundwater flow velocity and an expected treatment interval, the design application rates were calculated to be 113 g/day in Interval A and 209 g/day in Interval B. The ozone application was divided further with 75% of the dosage applied to the up-gradient injection wells (OZ-3A and OZ-3B) and 25% applied to the down-gradient injection wells (AS-1 and OZ-2B). Ozone generator settings and cycle times were determined based on having an average injection period of 15 to 20 minutes, followed by approximately 60 minutes of off time for each well while ozone injection is cycled through the other wells. The ozone injection was successful based on field monitoring results. Data from monitoring well MW-4B illustrate rapid reduction in MTBE and TBA concentrations with limited formation of Cr(VI), as shown in Table 6. Based on the 11/20/07 data, the ozone injection dosage at OZ-2B was reduced in mid-December 2007. It was unnecessary to maintain higher ozone dosages because site constituent concentrations remained below detection levels. The Cr(VI) concentrations increased, but not to designated trigger levels and well below the significant concentrations observed during the pilot tests.

Table 6. Summary of monitoring data from MW-4B.

Date	MTBE (ug/L)	TBA (ug/L)	Cr(VI) (ug/L)
8/20/07	73	53	4
11/20/07	<0.5	<5	9.6
2/19/08	<0.5	<5	6.4
5/20/08	<0.5	<5	4.5

Results from this study demonstrate that a TOD test can be used to resolve the O₃ dosage problem by establishing a site-specific benchmark dosage for field ozone applications. In addition, soluble Cr(III) and Cr(VI) in groundwater and total Cr in soil should be tested to understand the potential for Cr(VI) formation. Prudent field applications of the design dosage can be used to reduce the risk of creating Cr(VI). The follow-up testing of the laboratory samples provided indications that intrinsic biodegradation could be stimulated by adding oxygen. The soil/groundwater slurries that were exposed to the atmosphere and those with applied O₃ demonstrated decreasing MTBE concentrations during period beyond the ozonation. This suggests that O₃ dosage in the full-scale field implementation could be dialed lower than stoichiometrically designed to eliminate the formation of Cr(VI). Although this practice may not completely deplete non-Cr contaminants during the ozonation period, the follow-up in situ biodegradation is likely adequate to achieve the remediation goal.

Integration of ISCO with Bioremediation of Hydrocarbon-Contaminated Soil

This study investigated ISCO degradation of petroleum contaminants in soil and enhancing follow-up biodegradation. Contaminated sandy clay (diesel) with high natural organic matter was collected from a contaminated site in central area of England. The bench-scale reactors used in this study contained 50 g soil and 23 mL of oxidant and/nutrient solution. The treatments were set up as follows:

- Control
- Nutrients (NH₄Cl, K₂HPO₄)
- Persulfate
- Persulfate + Fe²⁺
- Permanganate
- Persulfate + Nutrients (added 7 days after oxidant)
- Persulfate + Fe²⁺ + Nutrients (added 7 days after oxidant)
- Permanganate + Nutrients (added 7 days after oxidant)

No substantial pH changes observed (even in persulfate-amended soils) and remained in the pH range of 6 to 8 which favors microbial activity. This lack of change in pH is evidence of high buffering capacity of the soil. Soils treated with permanganate followed by nutrients and

with persulfate followed by nutrients resulted in the largest decrease in TPH. In other treatments the higher NOM concentration in the soil may have consumed the oxidants, which negatively affects the TPH oxidation. However, the possible intermediates and conditions formed from NOM and TPH oxidation by permanganate and activated persulfate favors microbial TPH degrading activity. Nutrient concentrations at end of study were inconclusive. Further tests are required to determine the effects of NOM on integrating ISCO oxidants and enhancing biodegradation. Tests also would include determining different intermediates (both organic and inorganic) formation based on the oxidant and direct effects of oxidant on microbial activity.

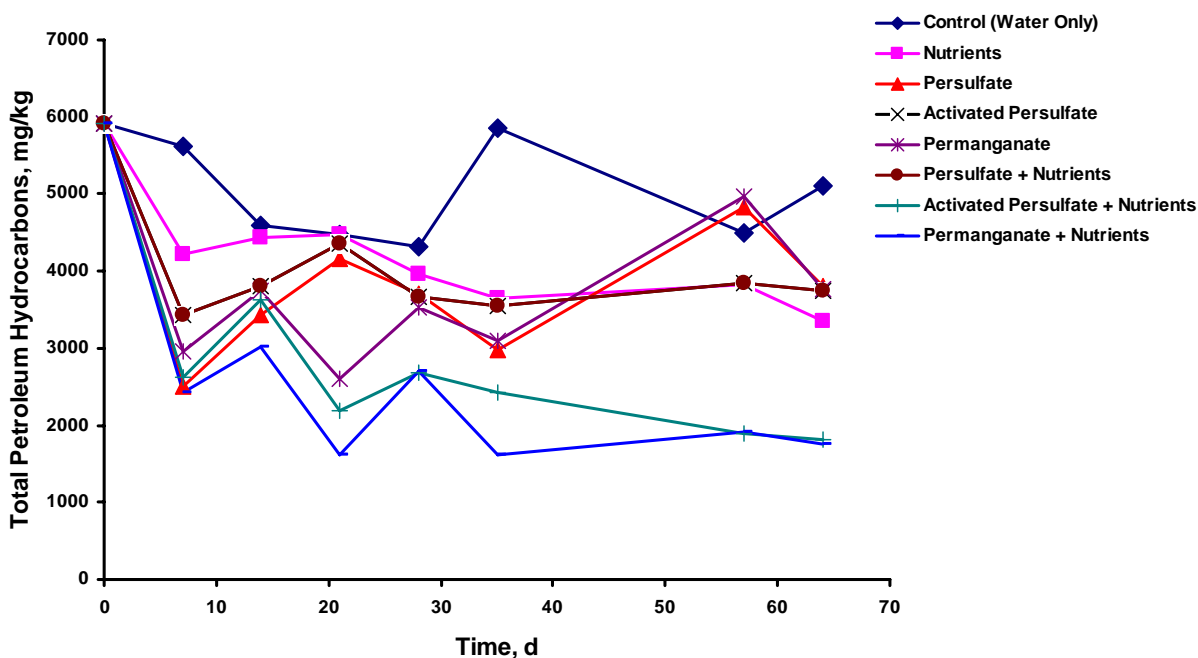


Figure 5. TPH concentrations in soil treated with oxidants and/or nutrients.

Enhancement of MTBE Biodegradation by Electrode Oxidation in Microbial Fuel Cell

Western Research Institute in conjunction with Tetra Tech, Inc. conducted a bench scale feasibility study to determine if a viable microbial fuel cell (MFC) can be established in an existing monitoring well at a fueling station in California. Water samples from the site were shipped by Tetra Tech, Inc. to WRI and used to construct various MFC designs to determine appropriate inoculum and mineral amendments needed (if any) and suitable electrode materials and catalysts for the MFC during feasibility tests. An MFC is a device that provides anaerobic bacteria with an alternative terminal electron acceptor (TEA) in the form of a solid-state anode that is connected through an electrical circuit to a cathode that is in contact with oxygen (Figure 6). This design allows anaerobic bacteria to pass electrons on to the anode while oxidizing various substrates (organic material including contaminants) in the absence of TEAs such as

oxygen, nitrate, or sulfate. The presence of TEAs in solution is necessary for bioremediation of hydrocarbon contaminants that serve as substrate for bacteria. Therefore, if contaminated groundwater is depleted in oxygen or nitrate (as is often the case) bacteria may rely on TEAs that are less thermodynamically favorable such as ferrous iron (Fe^{2+} ; if present) or sulfate, which can result in a decreased rate of bioremediation or no degradation at all. The purpose of this feasibility study was to determine if a microbial fuel design could enhance the natural degradation rate of MTBE, benzene, and toluene in contaminated groundwater.

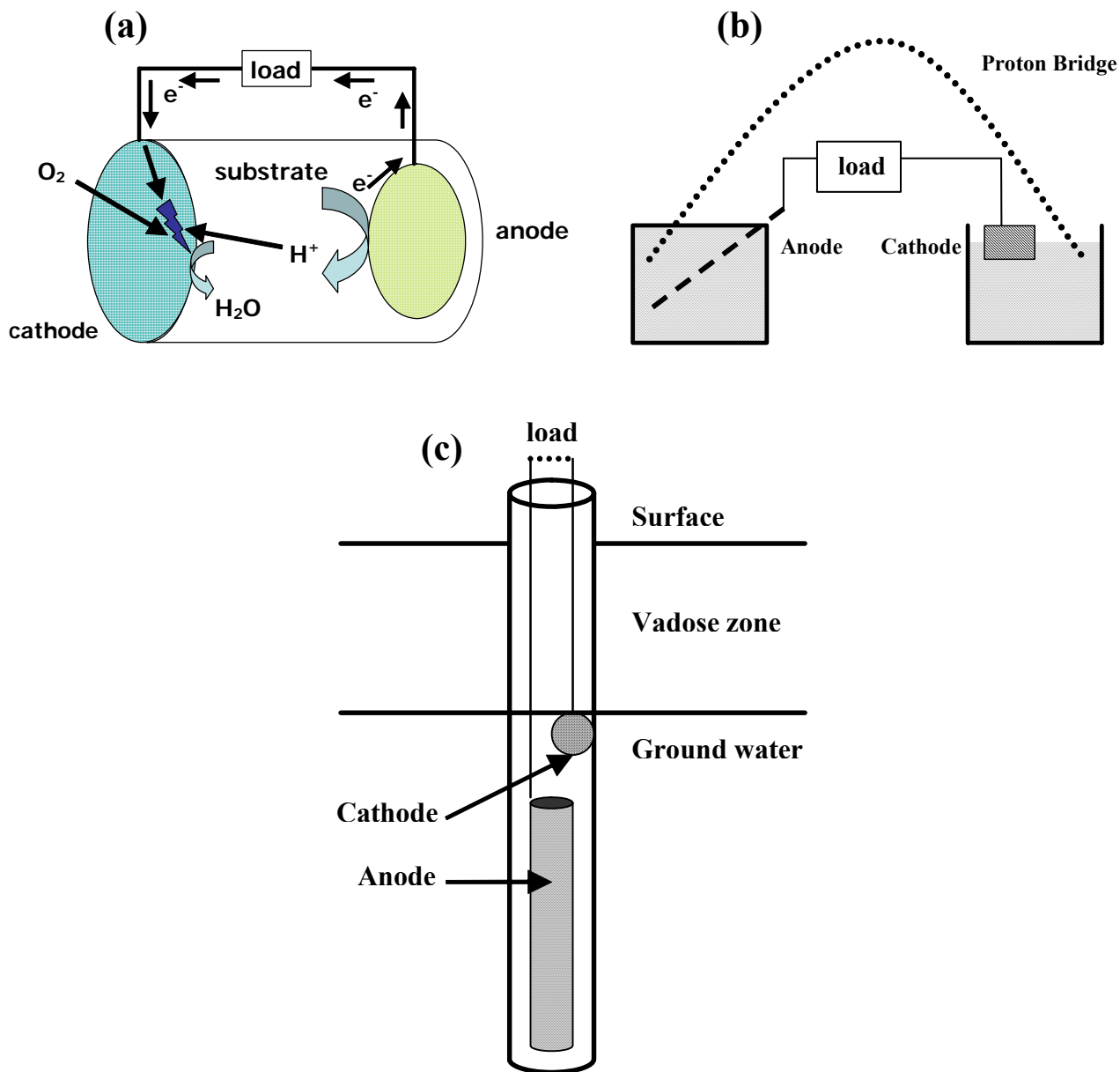


Figure 6. Schematic drawings of (a) a single-cell microbial fuel cell (MFC), (b) a double-cell MFC, and (c) a conceptual design for applying MFC technology in the field.

Several experiments were conducted using double- and single-cell MFCs constructed using plastic pipe, bottles, and fittings and equipped with carbon anodes and carbon/platinum cathodes. Depending on the treatment/experiment, the MFCs were filled with anaerobic buffered growth media (nutrients), groundwater collected from the contaminated site or a combination of these. MFCs not containing site water were inoculated with a small volume of site water. All double-cell MFCs were held at 30°C throughout the experiments and the single-cell MFCs fluctuated slightly (~20-25°C) based on daily changes in room temperature. All MFCs other than the double-cell MFC containing only site water were replicated 3 times and spiked with benzene, toluene, or MTBE for a total of 18 MFCs. The site-water only treatment received spikes of toluene or MTBE at various times. Glucose (200 mg/L) was added to each MFC along with the spiked contaminants and inoculum when they were initially established to boost the microbial population. Experiments did not begin until 3 to 4 weeks after the MFCs were established, during which time the MFCs were refilled with their respective groundwater and contaminants weekly. All MFCs were sampled periodically and analyzed for benzene, toluene, or MTBE by GC-FID, and cell potential (mV) was recorded across a 1K Ω resistor every 10 minutes using a data logger connected to a computer.

Spiked concentrations of benzene, toluene, and MTBE decreased rapidly during the first set of experiments using double-cell MFCs in both the MFCs and disconnected controls from about 200 mg/L to <50 mg/L in 48 hours. In a separate test it was determined that the proton bridge absorbed 75 to 80% of the contaminant and therefore it was not possible to accurately quantify and compare the degradation rates in the MFCs versus the controls. However, samples collected from working MFCs yielded unidentified peaks that co-eluted with MTBE in some of the MTBE chromatograms (Figure 7), which could possibly be breakdown products of MTBE degradation. This suggests that microbial breakdown may have occurred in conjunction with absorption into the proton bridge in the MFCs. Breakdown products of MTBE microbial degradation include TBA, TBF, formaldehyde, MHP, HIBA, 2-propanol, and acetone. At this point, it was ruled out TBA as a possible match for our unidentified co-eluting compound. Given the possibility that microbial degradation of MTBE was occurring in the MFCs, double-cell experiments were conducted using MTBE and we also established single-cell MFCs to test MTBE breakdown in a system that did not utilize a proton bridge. Single-cell MFCs were not used initially because past experience studying diesel degradation in MFC systems indicated that some of the oxygen diffusing across the cathode may not be reduced at the cathode and can be utilized by an aerobic biofilm growing on the inside of the cathode and, therefore, contribute to aerobic degradation of the contaminant. As a result, no difference in degradation was observed for the rates between the controls and single-cell MFCs during this diesel degradation experiment. However, in a subsequent experiment using double-cell MFCs, enhanced degradation of diesel in the MFC was observed at a rate that was 2.6 fold higher than the controls.

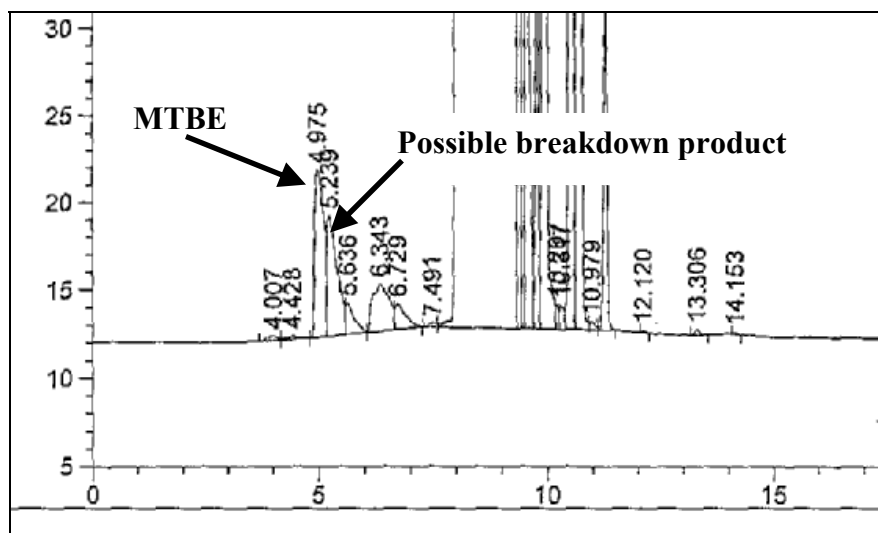


Figure 7. Chromatogram from GC-FID analysis of water sampled from a double-cell MFC utilizing MTBE.

WRI conducted a follow-up experiment using double-cell MFCs with MTBE and collected 6 samples over a 10-hour period and continued to collect samples every few days for about 2.5 weeks. During this experiment the concentration of MTBE once again decreased in all treatments (Figure 8) but at a much slower rate than the previous experiments. However, a significant electrical current (in terms of MFCs) was generated in MFCs with MTBE as a sole substrate as well as in the MFC established in site water that was spiked with MTBE (Figures 9 and 10) indicating that bacteria in these systems were utilizing the anode as a TEA and surviving by degrading the contaminants.

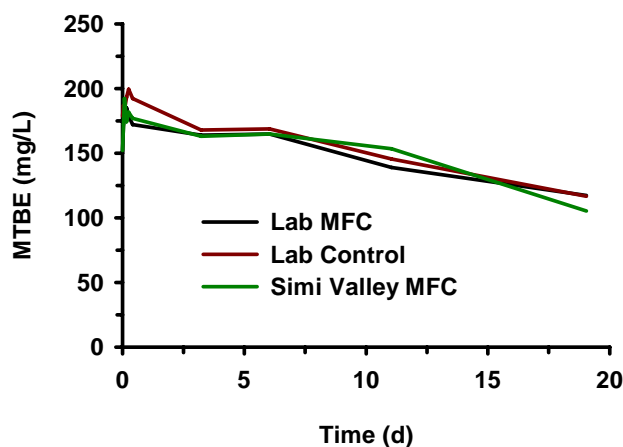


Figure 8. Decreasing MTBE concentrations in double-cell MFCs.

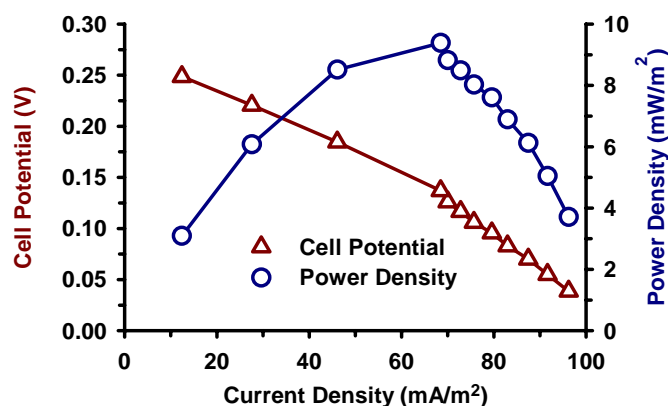


Figure 9. Power density (mW/m^2 cathode) and polarization (V) curves of a double-cell MFC.

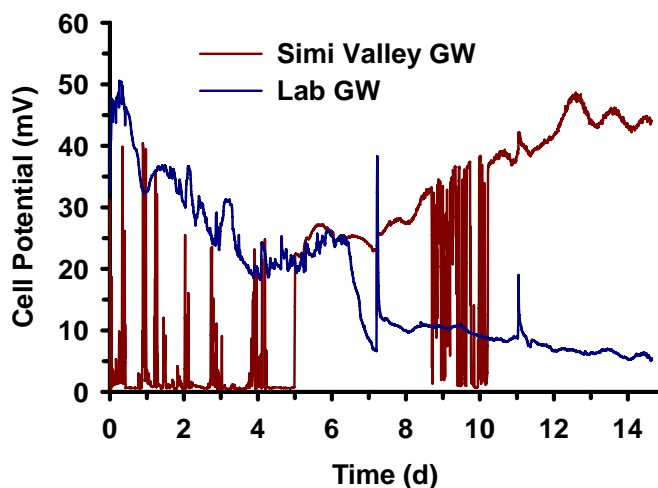


Figure 10. Cell potential (mV) measured in a double-cell MFC filled with site water or buffered media inoculated with site water.

It was observed that similar power generation in MFCs spiked with benzene and toluene and single-cell MFCs spiked with MTBE as in double-cell MFCs spiked with MTBE (Figure 9). Preliminary results from single-cell MFCs spiked with MTBE indicate MTBE concentrations are also decreasing in the MFCs and controls, which may be due to oxygen diffusion across the cathode and a subsequent aerobic degradation or loss of the contaminant across the cathode.

These experiments have demonstrated that a working MFC (i.e., one generating power) could be established in the laboratory using contaminated site water or buffered media inoculated with site water and spiked with MTBE, benzene, or toluene. Although the quantification of the rate of microbial degradation in an MFC due to issues with MFC design components (e.g., possible absorption of the contaminant into the proton bridge or oxygen diffusion across the cathode contributing to aerobic degradation) was not conducted, the appearance of co-eluting compounds that may be microbial breakdown products from MTBE as well as the power generation in each MFC containing MTBE, benzene, or toluene indicates that microbial activity and possible contaminant degradation is taking place.

Electrochemical Treatment of Waters with Compounds Associated with Petroleum Hydrocarbons

Electrochemically induced oxidation-reduction (redox) reactions (also known as “geooxidation”) involve feeding an electrical current through electrodes, creating favorable conditions for redox reactions to occur in the medium between the electrodes. Van Cauwenberghe (1997) performed a field test to immobilize inorganic contaminants and reduce organic contaminant concentrations in soils. Unlike electrokinetic processes, induced redox reactions does not involve the migration of contaminants toward the electrodes. Also, the electric field requirements for induced redox reactions are lower ($<35 \text{ V m}^{-1}$) than other electrical methods (Ho et al., 1999; Rahner et al., 2002; Rohrs et al. 2002). The electrochemically induced redox reaction occurs when a low voltage and amperage DC field is imposed in the saturated soil between electrodes. The induced electric field is created with soil particles acting as capacitors and discharging and recharging electricity.

Chlorinated solvents such as trichloroethene (TCE) are a common group organic contaminants that tend to accumulate in subsurface soils, groundwater, and sediments, and can be associated with petroleum hydrocarbon contamination. Due to the elevated oxidizing status, reductive reactions are usually applied in treating chlorinated solvents. Applying electrochemically induced redox reaction in soils to reduce chlorinated organic contaminants has been performed in laboratory bench-scale tests (Rohrs et al., 2002; Shimomura and Sanford, 2005; Jin et al., 2008). These studies suggest reductive dechlorination of TCE would be feasible in LPM such as clay; however, since clays have high surface area and may contain more iron, the rate of dechlorination was expected to be substantially higher than in sandy media.

Two sets of columns (internal diameter 9 cm) with lengths of 20, 50, 100, and 150 cm were constructed and positioned horizontally. Electrodes were installed at each end of the columns. The electrodes were made from graphite and connected to an AC-DC transformer with adjustable DC voltage outputs of 6, 9, and 12 V. Graphite electrodes were used due to its high efficiency in reduction of TCE in water (Jin et al., 2008). Also, graphite electrodes do not corrode like stainless steel as observed by Rohrs et al. (2002). The clay soil was saturated with RO water containing TCE to reach a target concentration of approximately 100 mg kg^{-1} . Each

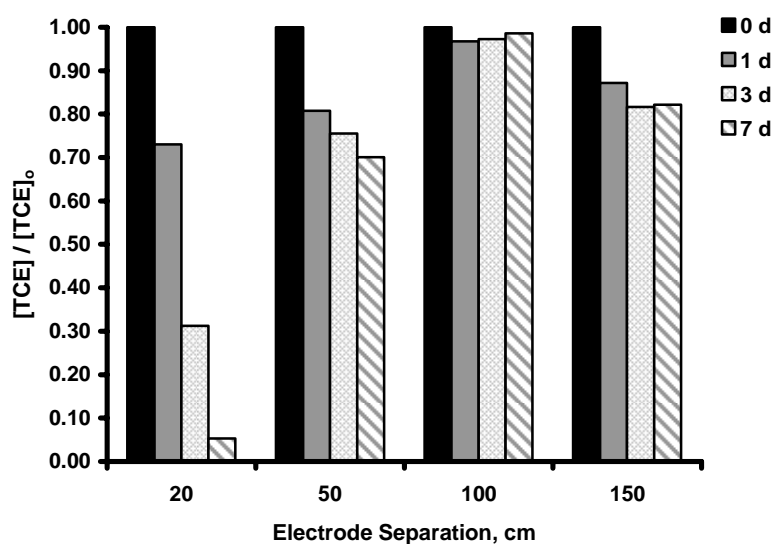
column was filled with the saturated clay and sealed. One set of columns were connected to the DC source set at 6 V, and the other set of columns were not connected to serve as the control. Trichloroethene samples were extracted by n-hexane extractions and analyzed by using a gas chromatograph with an electron capture detector. Potential and current across the column were measured by a multimeter. Chloride and pH were monitored throughout the experiments. Sampling/monitoring events were performed at 0, 1, 3, and 7 days. Experimental runs using the DC source set at 9 and 12 V were performed by using the same procedure described above.

When an electric field (E) of 6 V m^{-1} was applied to saturated clay columns of lengths 20, 50, 100, and 150 cm for 7 days. The concentration fraction of TCE ($[\text{TCE}]/[\text{TCE}]_0$; $[\text{TCE}]_0 = 125.43 \text{ mg kg}^{-1}$) in the 20-cm column decreased to 0.05 (from 125.43 to 6.27 mg kg^{-1}), while a decrease of 0.30 was observed in the 50-cm column (from 125.43 to 87.80 mg kg^{-1}) (Figure 11a). Slight decrease in TCE concentration was observed in the 100-cm column; however, the concentration fraction decreased by 0.17 more in the 150-cm column than that in the 100-cm column. Increased chloride concentrations in the 150-cm columns also confirms that more TCE was being reduced than in the 100-cm (Figure 11b), while the highest chloride concentration in the 20-cm column corresponded with the highest rate of TCE reduction occurred within that electrode separation. The chloride concentrations in the unconnected columns did not have any substantial increase (chloride concentrations ranged from 9.08 to 10.13 mg L^{-1}). No daughter products, such as dichloroethenes (DCEs) and vinyl chloride (VC) were detected throughout the tests.

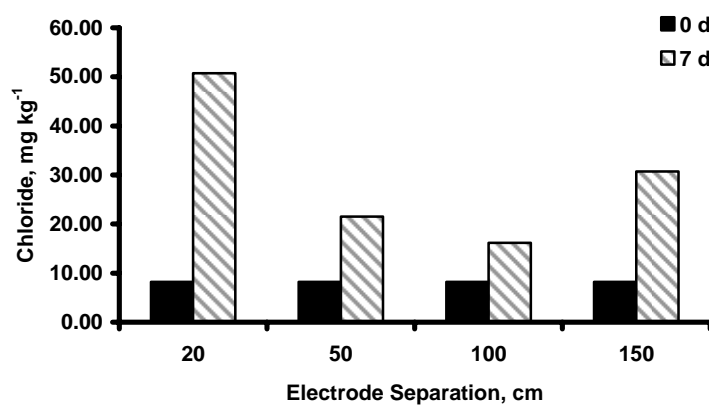
The concentration fraction of TCE ($[\text{TCE}]_0 = 122.77 \text{ mg kg}^{-1}$) in the 20-cm column decreased to 0.03 (from 122.77 to 3.68 mg kg^{-1}) within 7 d when an E of 9 V m^{-1} was applied to the saturated clay (Figure 12a). The concentration fraction of TCE in the 50-cm columns decreased to 0.16, which is substantially less than what was observed when an E of 6 V m^{-1} was applied to the saturated clay. The increase in TCE dechlorination correlated with increases in chloride concentration (Figure 12b). The $[\text{TCE}]/[\text{TCE}]_0$ for the 100 and 150-cm columns decreased by less than 0.30, indicating such electrode spacing lowers reactivity at an E of 9 V m^{-1} . Chloride concentrations in the unconnected columns were between 8.91 to 9.38 mg L^{-1} , indicating little, if any, reductive dechlorination without an E applied to the clay. The concentration fraction of TCE ($[\text{TCE}]_0 = 122.49 \text{ mg kg}^{-1}$) in the 20-cm and 50-cm columns decreased to 0.05 to 0.32, respectively, within 7 d when an E of 12 V m^{-1} was applied to the saturated clay (Figure 13a). The concentration fraction of TCE in the 100-cm columns decreased to 0.49, but this E appeared to have little effect on TCE in the 150-cm column. The increase in TCE dechlorination in the 100-cm column correlated with increases in chloride concentration, as shown in Figure 13b.

Conventional or alternative sources of DC power can be used for the field applications of this technique. Sustainable energy sources such as solar or wind can provide a continuous E in the contaminated matrix. Overall, the results from this study indicate that electrochemically

inducing reductive dechlorination of TCE in a saturated matrix may offer an effective and viable alternative to remediation TCE and other contaminants with potential of being reduced.

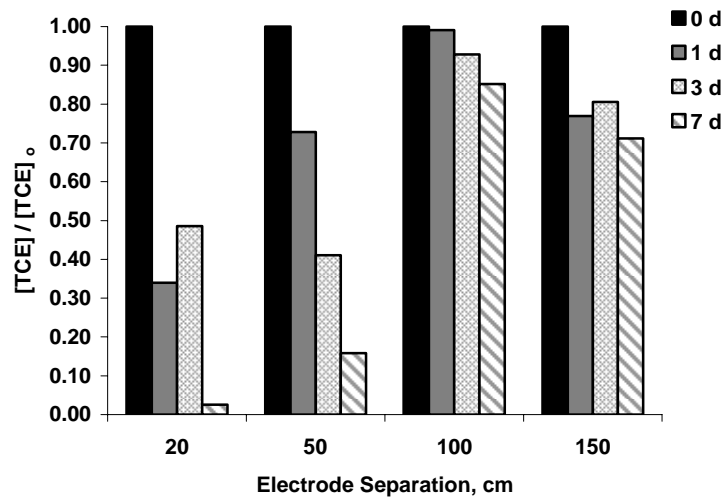


(a)

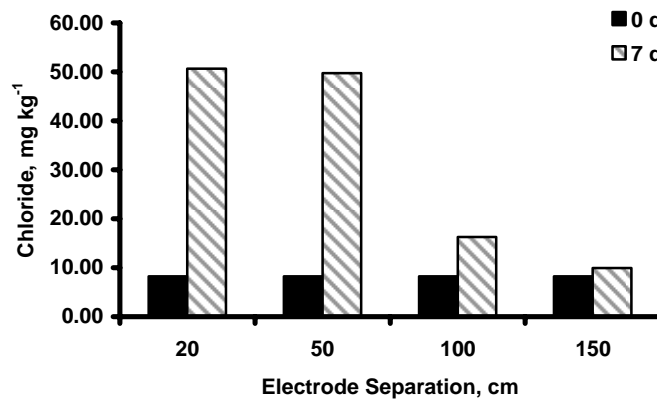


(b)

Figure 11. Normalized TCE concentration fractions (a) and chloride concentrations (b) in saturated clay within an electric field of 6 V m^{-1} .

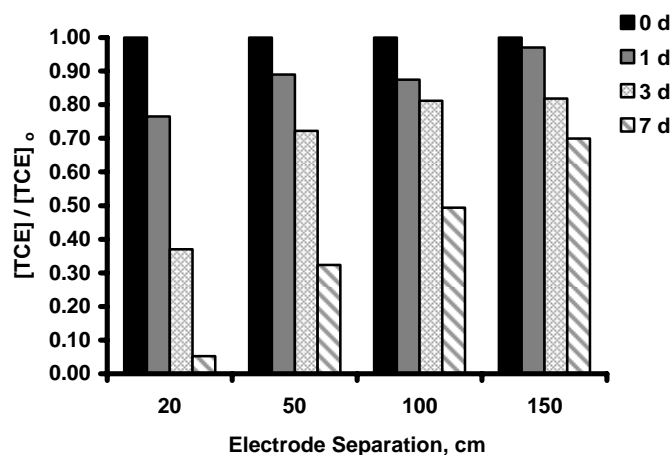


(a)

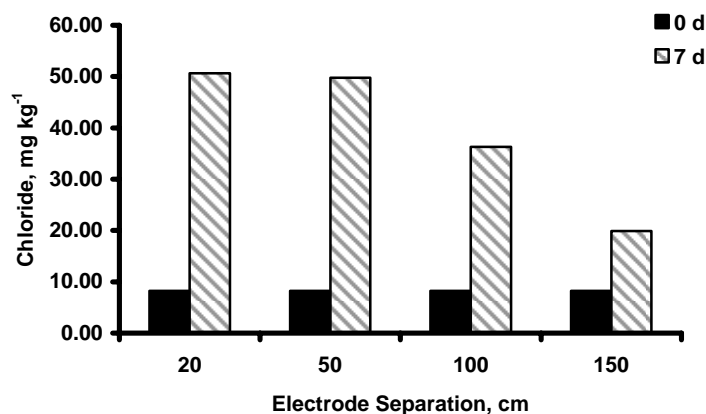


(b)

Figure 12. Normalized TCE concentration fractions (a) and chloride concentrations (b) in saturated clay within an electric field of 9 V m^{-1} .



(a)



(b)

Figure 13. Normalized TCE concentration fractions (a) and chloride concentrations (b) in saturated clay within an electric field of 12 V m^{-1} .

Another study focused on using iron oxidation to increase population of hydrocarbon-degrading denitrifying bacteria. Denitrifying bacteria exist in waters with sufficient nitrate concentrations and can degrade a wide range of petroleum hydrocarbons. Electrostimulation of microorganisms is an alternative means to increase microorganism numbers. This study focused on introducing electrons into denitrifying bacteria to stimulate their growth. This was accomplished by setting up a double-cell MFC with a sacrificial steel wool anode which in a sterile anode chamber. This steel fuel cell (SFC) provided a fairly constant source of electrons from the oxidation of the steel wool anode, which generated electron transfer to the cathode where nitrate was reduced.

The anode chamber was filled with sterilized growth media and the cathode chamber was filled with 160 ml of groundwater, sterilized groundwater, or reverse osmosis (RO) water. The cathode chambers also received 130 g of fine sand that was washed with 0.1M hydrochloric acid (HCl) and 0.1M nitric acid (HNO₃), rinsed with RO water, and dried. The purpose of adding this sand to the cells was to simulate the subsurface matrix. The cathodes in each chamber were pushed into the sand and the dimensions of the proton bridges on each SFC were 30.5 cm long with an inner diameter of 1.3 cm.

Four SFC treatments were established in triplicate under anaerobic conditions as follows: (1) a control treatment that contained N₂-purged groundwater with no proton bridge or electrodes (no power production), (2) a groundwater (GW) treatment that contained N₂-purged groundwater, (3) a sterilized groundwater treatment (SGW) that contained groundwater that was N₂-purged and autoclaved for 2 h, and (4) a reverse osmosis water treatment (ROW) that contained N₂-purged RO water. The control chamber and all cathode chambers received KNO₃ at a nominal target concentration of 1,000 mg NO₃⁻/L. The pH was measured and samples were collected for nitrate and NH₄⁺ analysis from the control and cathode chambers in an N₂ glove box to maintain anaerobic conditions. The voltage across all resistors was monitored periodically using a handheld multimeter throughout the 30-d experiment. Anaerobic conditions in the SFCs were verified by using resazurin. The groundwater used in the control and cathode chambers of the SFCs had a circum-neutral pH (6.94), concentration of NO₃⁻ was less than the MCL (9.7 mg/L), and NH₄⁺ concentrations were below detection limit (0.04 mg/L; Table 1).

During the initial 5 to 7 d of the 30-d SFC experiments, the systems underwent a flux period where the voltage dropped considerably and NO₃⁻ concentrations fluctuated as the system stabilized. Therefore, although the NO₃⁻ values for the entire 30-day experiment are shown in Figures 14 and 15, the starting values used for all calculations were measured on day 7. The GW, SGW, and ROW treatments all produced relatively low voltages throughout the experiment, starting from about 100 to 200 mV and then declining steadily to about 15 mV. However, after the initial decrease in potential, as the system stabilized prior to d 7, the voltage in the GW treatment increased from 28 to 45 mV from days 5 to 15 and a similar increase was not observed in the SGW or ROW treatments (Figure 14).

Table 7. Baseline characterization of groundwater used in the cathode chambers of the groundwater (GW) and sterile groundwater (SGW) treatments.

Parameter	Groundwater
pH	6.94
Conductivity ($\mu\text{S}/\text{cm}$)	713
Total bacteria (cells/ml)	65,593
	<i>mg/L</i>
Dissolved organic carbon	3.96
Chloride	9.81
Nitrate	9.68
Sulfate	13.01
Ammonia	<0.04 ^a
Calcium	45.2
Iron	0.2
Magnesium	7.3
Potassium	2.6
Sodium	9.6
	<i>$\mu\text{g}/\text{L}$</i>
Aluminum	8.8
Copper	0.7
Nickel	1.2
Zinc	3.8
^a below detection limit	

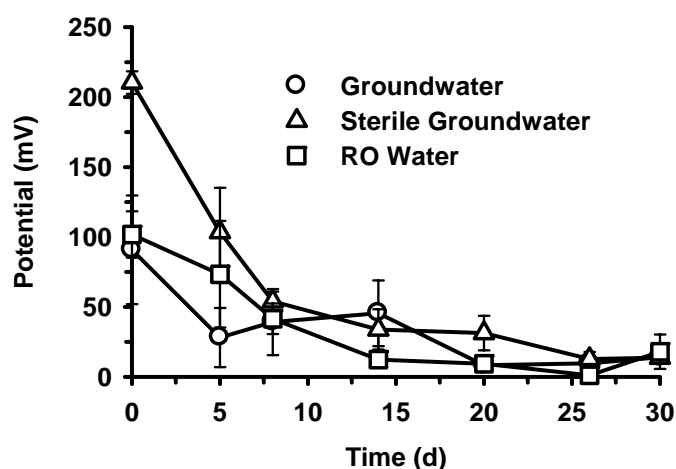


Figure 14. Electrical potential (1K Ω) measured in SFCs.

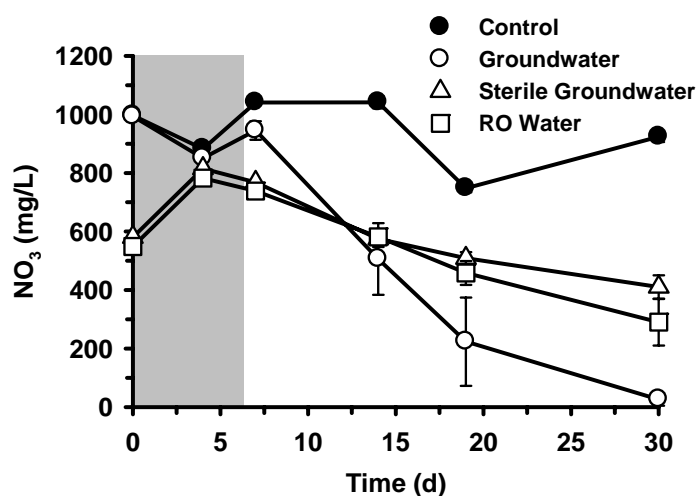


Figure 15. Nitrate (NO₃) concentrations in the cathode chamber of each SFC treatment.

Nitrate concentrations (mg/L) decreased slightly (11%) in the control treatments from $1,040 \pm 3$ (standard error of the mean, $n = 3$) to 923 ± 18 ($5.1 \text{ mg NO}_3^-/\text{L/d}$) over a 23-d period. Nitrate concentrations decreased in the GW, SGW, and ROW treatments by 97, 47, and 61%, from 945 ± 32 to 26 ± 21 ($40.0 \text{ mg nitrate}/\text{L/d}$), 768 ± 4 to 410 ± 40 ($15.6 \text{ mg NO}_3^-/\text{L/d}$), and 738 ± 13 to 290 ± 79 ($19.5 \text{ mg NO}_3^-/\text{L/d}$), respectively (Figure 15). At the end of the 30-d experiment, the percent of initial NO₃⁻ remaining in the cathode chambers of the GW treatment ($3\% \pm 2$) was significantly ($P < 0.001$) lower than in all other treatments and the percent of initial nitrate remaining in the SGW and ROW treatments was significantly ($P < 0.001$) lower than in the

control (Figure 16). The GW treatment resulted in the most favorable overall conversion of NO_3^- to desirable N_2 gas ($76.2 \pm 7.4\%$) and less desirable NH_4^+ ($21.2 \pm 9.9\%$; Figure 16). Ammonium concentrations were below detection limit in the groundwater or RO water added to each treatment and the NH_4^+ concentrations in the C, GW, SGW, and ROW treatments increased to 13.2 ± 0.5 , 56.2 ± 21.0 , 70.1 ± 10.8 , and 31.2 ± 15.0 mg/L by d 30, respectively. Nitrite was not detected in any cathode chambers or the control chambers during this study.

The total bacteria count in the cathode chambers of the control and GW treatments increased from 65,593 cells/ml (baseline in groundwater collected from the field) to $421,425 \pm 141,099$ and $4,702,985 \pm 1,565,598$ cells/ml, respectively; however, due to high variability, these concentrations were not significantly different. As expected, no bacteria were found in the cathode chambers of the SGW or ROW treatments.

The SFC experiments indicate the flow of electrons from the anode enhances nitrate reduction in the cathode chamber; however, the rate of nitrate reduction in the SFC is much higher ($40.0 \text{ mg NO}_3^-/\text{L/d}$). Additionally, the population of microorganisms in the cathode chamber increases with electron flow and the presence of these microbes correlate to a significantly larger reduction in nitrate than in sterile systems. Interestingly, the voltage in these SFCs is influenced by the NO_3^- concentration in the cathode chamber but not by the presence of microbes in the cathode chamber. It appears that electrons flowing to the cathode are capable of directly reducing NO_3^- and stimulating microbial activity and growth, thereby, also indirectly enhancing microbial denitrification. It has been shown that electrodes can serve as direct electron donors for anaerobic microbes involved in nitrate reduction (Gregory et al., 2004) and this process might have enhanced the metabolism and growth of denitrifying bacteria in our system. The relatively low concentration of DOC in the groundwater was apparently insufficient to sustain denitrification in the control treatments, which supports our conclusion that microbes in the GW treatment were utilizing electrons generated from steel wool oxidation as an electron source.

It appears that two possible mechanisms of nitrate reduction may have caused the decrease in NO_3^- concentrations in the SFCs. First, the decrease of NO_3^- in the treatments with sterile cathode chambers (SGW and ROW) but not in the disconnected control suggests that electrons are passed directly to NO_3^- with no microbial intermediary. Second, the significantly larger decrease in NO_3^- in the treatment with a robust microbial population in the cathode chamber (GW) compared to all other treatments indicates that the presence of bacteria enhances nitrate reduction over sterile conditions in the presence of an electrical current and that this flow of electrons to a non-sterile system stimulates bacterial growth. This enhanced nitrate reduction could be due to direct electron utilization by nitrate reducing bacteria on the cathode, thereby stimulating microbial denitrification or a combination of electron transfer directly to NO_3^- and electron transfer to nitrate reducing bacteria, which may serve as a type of bio-catalyst on the cathode for nitrate reduction.

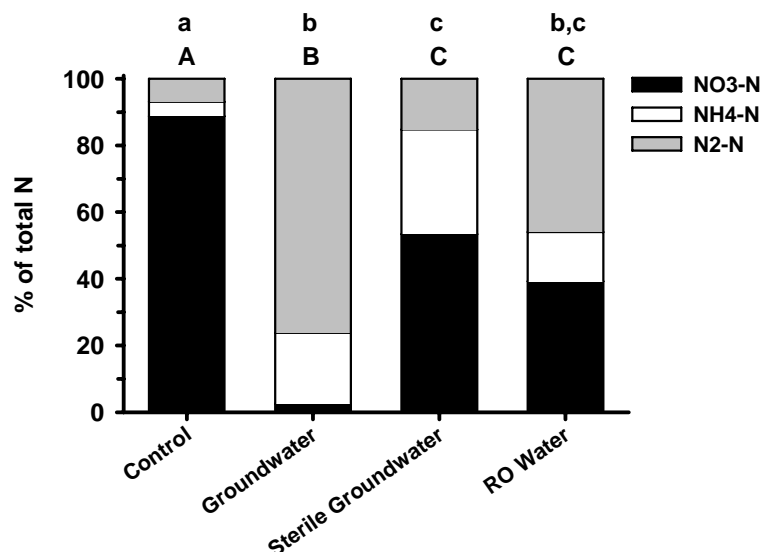


Figure 16. Conversion of nitrate in the catholyte solution in each SFC treatment from day 7 to day 30.

SUMMARY

Western Research Institute in conjunction with Sierra West Consultants, Inc., Tetra Tech, Inc., and the U.S. Department of Energy conducted laboratory and field studies to test different approaches to enhance degradation of hydrocarbons and associated contaminants. WRI in conjunction with Sierra West Consultants, Inc., conducted a laboratory and field study for using ozone to treat a site contaminated with MTBE and other hydrocarbons. Results from this study demonstrate that a TOD test can be used to resolve the O₃ dosage problem by establishing a site-specific benchmark dosage for field ozone applications. In addition, soluble Cr(III) and Cr(VI) in groundwater and total Cr in soil should be tested to understand the potential for Cr(VI) formation. Prudent field applications of the design dosage can be used to reduce the risk of creating Cr(VI). The follow-up testing of the laboratory samples provided indications that intrinsic biodegradation could be stimulated by adding oxygen. The soil/groundwater slurries that were exposed to the atmosphere and those with applied O₃ demonstrated decreasing MTBE concentrations during period beyond the ozonation. This suggests that O₃ dosage in the full-scale field implementation could be dialed lower than stoichiometrically designed to eliminate the formation of Cr(VI).

WRI conducted a study involving a series of different ISCO oxidant applications to diesel-contaminated soil and determined the effects on enhancing biodegradation to degrade the residual hydrocarbons. Soils treated with permanganate followed by nutrients and with persulfate followed by nutrients resulted in the largest decrease in TPH. In other treatments the higher NOM concentration in the soil may have consumed the oxidants, which negatively affects the

TPH oxidation. However, the possible intermediates and conditions formed from NOM and TPH oxidation by permanganate and activated persulfate favors microbial TPH degrading activity. Nutrient concentrations at end of study were inconclusive. Further tests are required to determine the effects of NOM on integrating ISCO oxidants and enhancing biodegradation.

A “passive-oxidation” method using microbial fuel cell (MFC) technology was conducted by WRI in conjunction with Tetra Tech, Inc., to degrade MTBE in groundwater. These experiments have demonstrated that a working MFC (i.e., one generating power) could be established in the laboratory using contaminated site water or buffered media inoculated with site water and spiked with MTBE, benzene, or toluene. The appearance of co-eluting compounds that may be microbial breakdown products from MTBE as well as the power generation in each MFC containing MTBE, benzene, or toluene indicates that microbial activity and possible contaminant degradation was taking place.

Electrochemical methods were studied by WRI with goal of utilizing low voltage and amperage electrical sources for “geo-oxidation” of organic contaminants. The results from a study with TCE contaminated-clay indicate that electrochemically inducing reductive dechlorination of TCE in a saturated matrix may offer an effective and viable alternative to remediation TCE and other contaminants with potential of being reduced. These reactions can occur within an electric field between electrodes as low as 6 V/m.

Another study focused on steel wool oxidation to electrochemically increase population of hydrocarbon-degrading denitrifying bacteria. Denitrifying bacteria exist in waters with sufficient nitrate concentrations and can degrade a wide range of petroleum hydrocarbons. Significantly larger denitrifying activity was observed in the cathode chamber of a treatment unit setup like an MFC with steel wool as the anode. This enhanced nitrate reduction could be due to direct electron utilization by denitrifying bacteria on the cathode, thereby stimulating microbial denitrification or a combination of electron transfer directly to NO_3^- and electron transfer to nitrate reducing bacteria, which may serve as a type of bio-catalyst on the cathode for nitrate reduction.

Overall, the studies conducted under Task 72 demonstrated different innovative methods to enhance petroleum hydrocarbon degradation and associated contaminants. This was accomplished by using oxidation processes to directly degrade and indirectly degrade (through microbial enhancement) the organic contaminants.

REFERENCES

- Gregory, K.B., Bond, D.R. and Lovley, D.R. 2004. Graphite electrodes as electron donors for anaerobic respiration. *Environ. Microbiol.* 6:596-604.
- Ho, S.V., Athmer, C., Sheridan, P.W., Hughes, B.M., Orth, R., McKenzie, D., Brodsky, P.H., Shapiro, A., Thornton, R., Salvo, J., Schultz, D., Landis, R., Griffith, R., Shoemaker, S. 1999. The lasagna technology for in situ soil remediation: small field test. *Environ. Sci. Technol.* 33:1086-1091.
- Jin, S., Fallgren, P.H., Morris, J.M., Edgar, E.S. 2008. Degradation of trichloroethene in water by electron supplementation. *Chem. Eng. J.* 140:642-645.
- Rahner, D., Ludwig, G., Rohrs, J. 2002. Electrochemically induced reactions in soils—a new approach to the in-situ remediation of contaminated soils? Part 1: The microconductor principle. *Electrochim. Acta* 47:1405-1414.
- Rohrs, J., Ludwig, G., Rahner, D. 2002. Electrochemically induced reactions in soils—a new approach to the in-situ remediation of contaminated soils? Part 2: Remediation experiments with natural soil containing highly chlorinated hydrocarbons. *Electrochim. Acta* 47:1405-1414.
- Shimomura, T., Sanford, R.A. 2005. Reductive dechlorination of tetrachloroethene in a sand reactor using a potentiostat. *J. Environ. Qual.* 34:1435-1438.
- Van Cauwenberghe, L. 1997. *Electrokinetics: Technology Overview Report*. Groundwater Remediation Technologies Analysis Centre, 1-17.