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Abbreviations, Acronyms, and Initialisms

bgs	below ground surface
BSM	basal salts media
cfm	cubic feet per minute
CFU	colony forming unit
DAS	data acquisition system
1,2-DCA	1,2-dichloroethane
1,1-DCE	1,1-dichloroethene
1,2-DCE	1,2-dichloroethene
U.S. DOE	U.S. Department of Energy
DSM	Deep Soil Mixing
ft	feet
FID	flame ionization detector
g	gram
gal	gallon
GC	gas chromatograph
h	hour(s)
ID	inside diameter
in.	inch
KCP	Kansas City Plant
kg	kilogram
KMnO ₄	potassium permanganate
L	liter
lb	pound
MDNR	Missouri Department of Natural Resources
μg	microgram
mg	milligram
min	minute
mL	milliliter
mM	millimolar
Mn	manganese
MRVS	mixed region vapor stripping
NEA	Northeast area
NH ₄	sodium hydroxide
nm	nanometers
OD	optical density
ORNL	Oak Ridge National Laboratory
PCBs	polychlorinated biphenyls
PID	photoionization detector
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch

PTYG	peptone-tryptone-yeast extract-glucose
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
SOM	soil organic matter
TC	total carbon
TCE	trichloroethene
TFHA	7,7,7-trifluoro-2-hydroxy-6-oxo-2,4-heptadienoic acid
TFMP	trifluoromethylphenol
TOC	total organic carbon
TPH	total petroleum hydrocarbon compound
VOCs	volatile organic compounds
vs	versus
wt%	weight percent
yd	yard

Executive Summary

In July 1996, the U.S. Department of Energy (DOE) Kansas City Plant (KCP), AlliedSignal Federal Manufacturing & Technologies, and Oak Ridge National Laboratory conducted field-scale tests of in situ soil mixing and treatment technologies within the Northeast Area (NEA) of the KCP. The KCP, in general, and the NEA specifically have abundant chlorinated solvent contamination located below the water table for which no viable cost effective treatment technology has been identified. While the KCP is pursuing alternate concentration limits for this and other identified contamination, this project was conceived because of the success of a soil mixing project performed to a depth of 15 ft in low permeable clay at DOE's Portsmouth Gaseous Diffusion Plant, Piketon, Ohio. Additionally, the project was performed to obtain a benchmark for comparing cost and efficiency of other innovative technologies.

Specific performance objectives were established for the project even though it was recognized that many of the specific tasks had never before been attempted. Untried tasks included the following: drilling with air and an 8-ft diameter auger to 47 ft in stiff clay, dry powder injection with an 8-ft diameter auger, and the introduction and mixing of liquid treatment reagents (KMnO_4 and bacteria solutions) to 47 ft in stiff clay. This combination of untried methods and the project's overall ambitious goals resulted in some inevitable shortfalls. Nevertheless, the overall purpose of the project was satisfied by providing both a benchmark for future comparisons and a clear path forward for additional technology development.

This technology demonstration, therefore, was successful in providing answers to questions regarding the efficiency, costs, and equipment limitations of delivering three in situ treatment reagents in stiff clay soils. As a result of the demonstration the following information was obtained:

- It is possible to drill to 47 ft in stiff clay soils and mix such soils efficiently using an 8 ft diameter mixing tool.
- The biggest limitation for drilling and mixing to 47 ft in KCP soils is fluid control when using water for initial drilling and liquid reagent injection during mixing. In either case, the fluids must be introduced at lower pumping rates to prevent their return to the surface and flooding of the work site.
- The most serious equipment limitation regarding dry powder injection was overcoming system and geostatic back pressure which clogged the distribution lines. With additional testing and development, this limitation could be overcome and provide a cost effective in situ treatment technology.

- Trichloroethene (TCE) mass reductions of 70% or more were achieved by coupling deep soil mixing (DSM) with chemical oxidation using KMnO_4 . During the demonstration, up to 69% TCE removal occurred in the saturated soil and 83% TCE removal occurred in the unsaturated soil.
- TCE mass reductions of 65% were achieved by coupling DSM with mixed region vapor stripping in unsaturated soil. Had the injection of powdered lime been achieved, treatability studies indicated that the mass reduction of TCE could be as high as 90% in saturated soil and greater in unsaturated soil.
- TCE mass reductions of 38% were achieved by coupling DSM with bioaugmentation in soil which had TCE concentrations that are toxic to the injected bacterial population. Had the bioaugmentation been performed in soil with lower TCE concentrations, the mass removal rate may have reached the 70% objective.
- The DSM/Bioaugmentation demonstration concluded that the chemical, physical and biological properties of the soil were not altered.
- Viable TCE degrading bacteria were recoverable from the upper treatment depths (0 to 13 ft bgs) for at least 10 days post-treatment suggesting that TCE degradation could be continued if other limiting factors such as oxygen were augmented.
- Post-treatment microbiological studies determined that survivability of *Burkholderia cepacia* G4 PR1₃₀₁ (injected bacteria) below 13.5 ft was minimal, probably due to the high TCE concentrations (up to 527 mg/kg) encountered at these depths. However, laboratory testing of surviving bacteria demonstrated successful degradation of TCE confirming that the bacteria could be mixed into the subsurface and would survive the DSM process where the TCE concentrations were not toxic.
- Reagent migration was limited to areas with inherent preferential flow net-works such as fractures and the more permeable gravelly zones which are exploited and magnified by the high pressure/high volume flow of air used during initial drilling of the soil columns.
- The results of the DSM/ KMnO_4 demonstration show that the physical and biological properties of the soil remain essentially intact. For example, microbial sampling and analysis suggest that the KMnO_4 treatment could be amended with a microbial remediation treatment. Soil moisture was also affected during DSM, the average background soil moisture of 28% increased to 34% and 41% for the shallow and deep treatment cells, respectively. Increases in soil pH were also

observed, due to addition of KMnO_4 , and these increases were not greater than the pH of the oxidant which was added.

- The results of the DSM/ KMnO_4 demonstrate that the treatment reagent was well distributed in the soil and that treatment levels predicted from laboratory treatability studies can be achieved in the field.
- Although treatment costs using KMnO_4 are estimated to be \$128/yd³ of soil which is roughly twice the cost of the other treatments (bioaugmentation was \$77/yd³ and mixed region vapor stripping was \$62 yd³), it should be noted that this oxidation treatment was also applied in both saturated and unsaturated conditions and had the highest removal efficiency.

1. INTRODUCTION

1.1 Project Description

In July 1996, the U.S. Department of Energy (DOE) Kansas City Plant (KCP), AlliedSignal Federal Manufacturing & Technologies, and Oak Ridge National Laboratory (ORNL), conducted field-scale tests of in situ soil mixing and treatment technologies within the Northeast Area (NEA) of the KCP at the Former Ponds site (Fig. 1.1). The drilling contractor for the project was Geo-Con (Monroeville, Pennsylvania). This demonstration, testing, and evaluation effort was conducted as part of the implementation of a deep soil mixing (DSM) innovative remedial technology demonstration project designed to test DSM in the low-permeability clay soils at the KCP.

The clay soils and groundwater beneath this area are contaminated by volatile organic compounds (VOCs), primarily trichloroethene (TCE) and 1,2-dichloroethene (1,2-DCE). The demonstration project was originally designed to evaluate TCE and 1,2-DCE removal efficiency using soil mixing coupled with vapor stripping. Treatability study results, however, indicated that mixed region vapor stripping (MRVS) coupled with calcium oxide (dry lime powder) injection would improve TCE and 1,2-DCE removal efficiency in saturated soils.

This project was primarily funded by the KCP's Environmental Restoration Program (EM-40) as a result of program cost savings from process improvements. However, the existence of the project stimulated the testing of two EM-50 sponsored projects: chemical oxidation with KMnO_4 and bacteria/bionutrient addition (bioaugmentation). Thus, the scope of the KCP DSM demonstration evolved to implement DSM with the following in situ treatment methodologies for contaminant source reduction in soil and groundwater:

- DSM/MRVS coupled with calcium oxide injection
- DSM/bioaugmentation
- DSM/chemical oxidation using potassium permanganate (KMnO_4)

Laboratory treatability studies were started in 1995 following collection of undisturbed soil cores from the KCP. These studies were conducted at ORNL, and the results provided information on optimum reagent concentrations and mixing ratios for the three in situ treatment agents to be implemented in the field demonstration.

The field demonstration, testing, and evaluation activities involved a crane-mounted vertical rotating blade system designed to mix the subsurface using 8 to 10-ft-dia-

Fig. 1.1. Location of Deep Soil Mixing demonstration.

meter blades (Fig. 1.2). During the in situ mixing process, treatment agents were injected through a vertical, hollow shaft and into the soil through orifices at the rear of the horizontal soil mixing blades.

The DSM test site, approximately 60 ft wide by 140 ft long, was located just north of the former North Lagoon. Here, 15 soil columns (each 8 ft in diameter) grouped three to a treatment cell, were treated in situ to depths of approximately 25 and 47 ft. Two cells, a shallow (25 ft) and a deep (47 ft), were used for in situ mixing with KMnO_4 . One cell was used for in situ mixing with bioaugmentation to a depth of 25 ft. The remaining two cells, a shallow (25 ft) and a deep (47 ft) were intended for the testing of DSM/MRVS coupled with dry powdered calcium oxide injection. However, limitations in the design and application of the dry powder injection system prevented successful testing of this approach. Therefore, the shallow cell was used for DSM/MRVS demonstration to 25 ft. A shakedown column was drilled to 33 ft using a 10 ft diameter mixing tool and served as a process shakedown to test the mixing equipment.

Monitoring and measurement activities focused on evaluation of the VOC treatment effectiveness of each process and included pre- and post-treatment soil samples, water samples, and off-gas monitoring. Pre treatment soil and water samples were analyzed in the field for target VOCs [TCE, *cis*- & *trans*-1,2-DCE, 1,1-dichloroethene (1,1-DCE), and 1,2-dichloroethane (1,2-DCA)] utilizing a Hewlett Packard 5890 Series II gas chromatograph (GC) equipped with an auto-sampler (Fig. 1.3). The post-treatment soil, water, and gas samples were analyzed with the same GC but the target compounds had been limited to TCE and *cis*-1,2-DCE because the pre-treatment sample results did not contain detectable levels of the other previously-targeted compounds.

It was anticipated that the stiff clay soils would challenge the successful applications of all the techniques attempted. Nevertheless, such operations under such challenging conditions had not been attempted previously and laboratory results indicated that some measure of success was likely. Consequently, the results of the laboratory experiments, and field testing should be applicable to many DOE and private sites. Specifically, the DSM demonstration was performed to answer the following questions relative to the stiff clay soils at the KCP:

- Is it possible to drill to a 47-ft depth in such soil and mix such soils efficiently?
- What are the equipment limitations for drilling and mixing to 47-ft depths in the KCP soils?
- What are the equipment limitations for delivery of dry powdered calcium oxide to the subsurface?

(Note: treatment agents are delivered through the mixing blade with emissions captured in the shroud covering the mixing region)
Not to Scale, Conceptual Only.

Fig. 1.2. Conceptual view of a crane-mounted vertical rotating blade system.

Fig. 1.3. Hewlett Packard 5890 Series II with auto sampler.

- Is it possible to degrade TCE and *cis*-1,2-DCE in situ to achieve a mass reduction of 70% or more in saturated and unsaturated soils by coupling DSM with bioaugmentation, chemical oxidation (KMnO_4), or MRVS/calcium oxide injection?
- Can treatment levels achieved in the field be predicted from results obtained in the laboratory treatability studies (specifically KMnO_4)? How well are the treatment reagents distributed in the soil?
- What effect do the treatment reagents have on the chemical, physical, and biological properties of the soil?
- Do the treatment reagents migrate beyond the boundary of the soil column(s) being treated?
- Are contaminants forced out of the treatment zone as a result of the addition of the treatment reagents?

1.2 Site Background Information

1.2.1 Stratigraphy

In the NEA, an alluvial aquifer approximately 40 ft thick comprised of continuous and discontinuous zones of silty clay, sand, and gravel overlies Pennsylvanian age bedrock (Fig. 1.4). Within the DSM demonstration site, which is located at the western edge of the NEA (Fig. 1.5), approximately 48 ft of alluvium overlies interbedded sand and shale of the Pleasanton Group. The alluvium is comprised of approximately 40 ft of predominantly dark-gray, silty clay which overlies an erratic greenish-gray, silty clay up to 5 ft thick. The lowermost member of the alluvium consists of up to 5 ft of basal gravel. It should be noted that the extent of the greenish gray silty clay denoted in the fence diagram (Fig. 1.5) is based on color variation alone. The extent and consistency of the greenish gray silty clay unit has been found to vary widely across the NEA. Its characteristics are summarized in the NEA Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) (U.S. DOE 1994). The basal gravel zone consists of angular limestone and sandstone gravel in a sand-silt-clay matrix, is continuous throughout the site and ranges in thickness from a few inches to 5 ft.

The interbedded sand and shale bedrock underlying the DSM demonstration site is representative of the transitional sequence demarking the lower part of the Knobtown Sandstone and the underlying shale of the Pleasanton Group (Fig. 1.4). Generally, the Knobtown Sandstone is a well-sorted, fine- to very fine-grained, lithic arkose, having a thickness of approximately 10 ft and is comprised of monocrystalline quartz, sedimentary rock fragments, authigenic clay, potassium feldspar, plagioclase, chlorite from altered biotite, muscovite, and carbonaceous material. Results of thin-section

Fig. 1.4. Geologic cross section of Kansas City Plant.

Fig. 1.5. Fence diagram of Northeast Area.

analyses indicate approximately 12% intergranular pore space (Korte et al. 1985).

1.2.2 Description of Contamination

The groundwater from the alluvial aquifer in the NEA has been sampled and analyzed for total metals, VOCs, semivolatile organic compounds, total petroleum hydrocarbon compounds (TPH), and polychlorinated biphenyls (PCBs) as outlined in the *Northeast Area Groundwater Assessment Plan* (U.S. DOE 1990). High concentrations of TCE, 1,2-DCE (over 15,000 $\mu\text{g/L}$), and chloroethene (over 1500 $\mu\text{g/L}$) were detected in groundwater samples. Most of the high concentrations of VOCs were found in the vicinity (within 300 ft) northwest of the former North Lagoon.

Results of previous soil investigations in the NEA are presented in the NEA RFI (U.S. DOE 1994) summarized below. Elevated levels of TPH ranging up to 6,961 mg/kg have been documented. The highest PCB concentration reported was 9.8 mg/kg. The highest concentrations of chlorinated solvents reported in the soil were found below the water table; TCE, 81 mg/kg and 1,2-DCE, 15 mg/kg. Chloroethene and chlorobenzene were reported less frequently, but at concentrations up to 0.770 mg/kg.

1.3 Process Operations

1.3.1 Site Preparation

As stated above, the DSM demonstration site is located just north of the north lagoon. The area was originally grassy with a make-shift gravel road encircling the area formerly inscribed by the now closed and capped north and south lagoons. The demonstration site was laid out with a gravel base and contoured to promote drainage away from the test cells within the demonstration site. Additionally, the demonstration area was encircled with an earthen/gravel dike and adjacent storm drains were protected by a series of earthen dikes covered with an impermeable fabric material. Electrical power requirements for the demonstration were arranged and provided by KCP personnel.

1.3.2 Permitting Requirements

A Missouri Department of Natural Resources (MDNR) Underground Injection Control permit was required for the DSM project at the KCP. Though the demonstration did not utilize "wells" to inject wastes into the subsurface as is typical with permits of this type, state statute required the permit as injection of materials into "waters of the state" (in this case groundwater) occurred. The type and amount of reagents to be injected as a part of the demonstration were required. In addition,

reagents to be injected as a part of the demonstration were required. In addition, analysis of groundwater from an existing groundwater monitoring well was required upon completion of the demonstration. This information was collected and forwarded to MDNR as required by the permit.

1.3.3 DSM Equipment Description

A schematic of the DSM equipment is presented in Fig. 1.6. In situ mixing was performed using an 8-ft diameter mixing tool connected to a 12.75-in. square, hollow, kelly bar. This assembly was powered by a crane-mounted rotary drill table mounted from the crane boom. A photograph of the crane and mixing assembly is provided in Fig. 1.7. The mixing tool, illustrated in Fig. 1.8, was composed of three individual auger flights, spiral-wound around the shaft with three beater bars or mixer paddles attached above the auger flights. The leading edge of each auger flight was equipped with eight teeth and the shaft had a pilot bit with three teeth. Mounted behind and parallel to the cutting edge of each auger flight was an air box fitted with threaded ports or nozzles along its length and end (Fig. 1.8). The nozzles were threaded to permit the installation of reducers to accommodate the different soil treatment media. A 13-ft diameter cylindrical steel hood was mounted over the mixing location to capture and contain off-gas vapors generated during drilling and mixing. A flexible rotating seal in the center of the hood allowed the kelly bar to pass through the hood and minimized venting of off-gas to the atmosphere. Mounted on top of the hood, two 6-in. vacuum lines connected to three vacuum extraction units which routed the off-gas through granular activated carbon before release to the atmosphere. Leaking around the base of the hood was minimized by maintaining it on the ground surface during all drilling and mixing operations. Mixing and drilling were completed using air supplied from two modified compressors. For the oxidation and bionutrient mixing operations, the air was turned off upon reaching the pre-determined depth (25 or 47 ft) and the respective treatment agents were then injected into the column. Initial drilling and ensuing downward mixing were completed using clockwise rotation to the mixing tool and kelly bar. Liquid reagents were delivered at a constant pumping rate (with a Moyno L12 pump) while rotating the mixing tool out from the bottom of the column to the top in a counter-clockwise direction.

1.3.4 Shakedown/DSM Operational Limitations

As noted in Sect. 1.1, this project was initiated with full knowledge that equipment limitations would be encountered as a result of the stiff clay soils found at the KCP. This section details some of the limitations that were identified.

Fig. 1.6. Schematic of DSM and support equipment.

Fig. 1.7. Photograph of DSM equipment illustrating crane, Kelly bar, rotary table, shroud, and mixing tool.

514965 cdr

Fig. 1.8. Photograph of the 8-ft diameter mixing tool used at KCP.

The field project began with drilling subcontractor mobilization in April 1996 with a planned start in mid-May. This was Geo-Con's (drilling subcontractor) first attempt to work with a newly manufactured 10-ft diameter mixing tool and a remanufactured and untested kelly bar. When the first column (shakedown) was attempted, the mixing tool did not penetrate more than a few feet. Moreover, the kelly bar was damaged because it wobbled and banged against the rotary table. Following a two-week delay to complete welding repairs to the kelly bar, a second shakedown using an 8-ft diameter mixing tool was performed in an adjacent but unapproved location was attempted. This time the mixing tool penetrated to a depth of about 8 ft where subsurface conditions caused one of the blades on the tool to break off. Additional damage was also sustained by the kelly bar. Following an eight week-delay needed to modify another kelly bar, the project was reinitiated on July 8, 1996. During the delay, Geo-Con surmised that the original kelly bar, which had been purchased from a third party, failed due to problems with the quality and temper (hardness) of the steel used by the manufacturer. The cause for the breakage of the 8-ft mixing tool was attributed to subsurface debris.

On July 9, prior to any shakedown, Geo-Con suggested a deviation from the original plan of performing the wet and dry shakedowns before proceeding with the actual demonstrations. The suggestion was based on their concern that time would be best served by performing the wet shakedown and the two wet injection demonstrations (bioaugmentation and chemical oxidation) first and then switching over to the dry injection (powdered lime). By doing this, it was believed that time could be saved by avoiding switching the wet and dry injection systems. Additionally, Geo-Con was eager to demonstrate that their modified equipment could succeed in drilling/mixing the KCP soils and had more confidence in the use of water versus air for the initial shakedown. This decision had two significant consequences which are addressed in the following paragraphs.

On July 10, prior to treatment reagent testing, a wet shakedown soil column was drilled near the western edge of the demonstration area (Fig. 1.9). The original location for the shakedown (X1B1 in Fig. 1.9) had been eliminated due to difficult drilling conditions documented during pre-treatment characterization efforts (these findings are discussed in Sect. 2.5.1.) Using the pretreatment characterization boring data, it was evident that the T1 and T2 cells contained varying amounts of concrete debris in the first 10 to 12 ft of soil. Therefore, the location of the shakedown column was centered between borings T2B4 and T2B5 in Fig. 1.9. Although other borings in the T2 cell had encountered debris, the T2B4 and T2B5 borings had encountered no obstructions. The shakedown column was drilled with water to a depth of 22 ft where the mixing tool encountered resistance and the penetration rate stopped. Consequently, the drilling assembly was pulled to the surface and approximately 20 ft of 1-in. diameter steel cable was found tangled up in the teeth of the pilot bit. The

Fig. 1.9. Location of wet shakedown and pre-treatment soil borings, and soil boring NEBH17.

cable was removed and drilling resumed to 33 ft. This event was significant because it confirmed that the usefulness of the T1 and T2 cells for additional shakedown or reagent demonstrations would be thwarted by debris.

Due to the large volume of water needed to successfully drill with the 10-ft diameter mixing blade and the fact that its capability of reaching 45-ft depths was doubtful based on the observed decrease in the rate of penetration below 30 ft, a mutual decision was made to use the 8-ft diameter mixing tool for all of the subsequent reagent demonstrations.

The wet shakedown test, which was successful in proving the DSM equipment would work in the stiff clay soils, unfortunately used a large volume of water (41,640 L), much of which returned to the surface as a sediment slurry. This water leaked out from under the shroud and pooled across the bermed area. Most of the water/sediment slurry eventually flowed to the north east corner of the bermed area (T7 cell) resulting in 3 to 4 ft of water/sediment slurry which was too thick to pump with the equipment provided by the subcontractor. The presence of the pooled water/sediment slurry over the T7 cell influenced the DSM/bioaugmentation demonstration for various reasons addressed in the next paragraph.

Because the T7 cell had an average of 20 parts per million (ppm) TCE in the soil and bioremediation is most effective at contaminant concentrations up to 10 ppm, the T7 cell had been the planned location for the DSM/bioaugmentation demonstration. Unfortunately, the bacteria culture had already been prepared and would degrade in effectiveness with time. Due to the flooded condition of the T7 cell, a decision was made to relocate the DSM/bioaugmentation demonstration to a cell (T3 cell) with significantly higher average TCE concentrations of 126 mg/kg. The presence of the aforementioned obstructions in the T1 and T2 cells in conjunction with relatively low levels of contamination in these cells ruled them out as potential candidates for the DSM/bioaugmentation demonstration.

The intent of the DSM/MRVS coupled with calcium oxide injection was not satisfied because of the inability of the equipment to deliver calcium oxide below the ground surface. Because a dry shakedown had not been performed as originally planned, this problem was not discovered until late in the demonstration program and options to correct the problem were limited by contractual and budget limitations. Although Geo-Con could convey calcium oxide to the nozzles on the mixing blades with the mixing tool above the ground surface, below ground the back pressure created was insurmountable. It should be noted that calcium oxide injection has been achieved on smaller scale using 18 to 24-in. diameter mixing tools where compressed air forced the lime powder from an elevated container into the auger shaft and out through holes in the lower end of the auger shaft (Booms 1991). The technique used by Geo-Con at KCP, however, which involved a dry conveyor to force the lime powder from

the ground surface to the top of the kelly bar and eventually through the nozzles located on the air boxes under the mixing blades, had not been previously attempted. The net result was a condition of insurmountable backpressure after repeated attempts to deliver lime, it was determined that the scope of the demonstration would be limited to DSM using MRVS in one cell to 25 ft (T7). Therefore, the T6 cell which had been planned to demonstrate the same treatment to a depth of 47 ft was not used for any of the demonstrations. In retrospect, had the limitations with the dry conveyor system been identified earlier in the field program, more steps could have been taken to correct the problem.

Another significant and recurring problem was the collapse of one or both vacuum lines during mixing operations. The collapse in the line(s) resulted from too much slack in the thin-walled tubing which was not properly adjusted each time the shroud position changed. Therefore, a great deal of the data collected to measure the volume and pressure of the off-gas is of questionable value.

During the initial drilling of the bioaugmentation cell (T3) several blowouts were observed where, as a result of too much air pressure and volume, the ground surface mounded and then receded after the air escaped via a fracture. This was subsequently controlled by reducing the air volume and pressure.

Another operational problem was related to the repeated failure of the flexible seal located at the top of the shroud. The seal needed to remain intact or the off-gas vacuum system was ineffective. The stiff clayey nature of the KCP sediments, however, were instrumental in the seal failure. As the kelly bar and mixing tool were rotated out of the hole (upward), it was noted that the kelly bar was coated with sticky clay. It was surmised that the clay was repeatedly wearing against the tight-fitting seal and eventually would cause its failure. To thwart the problem, the subcontractor began using a stream of high pressure water to remove some the clay from the kelly bar after it had traveled up through the seal to prevent it from causing more damage during downward movement. The seal was the subject of various repair efforts throughout the field demonstration. In particular, there were persistent problems with seal during the bioaugmentation demonstration, when the seal failed twice during the mixing of three columns. Each time the seal broke, approximately 1 to 2 hrs were required for repair. The time loss prevented additional mixing passes. Thus, although the reagent was successfully added and mixed with soil at a controlled rate, the thoroughness of the mixing was less than anticipated.

Some of the previously noted limitations created additional data collection problems for the data acquisition system (DAS). For example, as a result of the high pressure washing of the kelly bar previously noted, the off-gas temperature and pressure sensors which were located on top of the shroud consistently short-circuited as their installation and design had not anticipated the volume or pressure of water used to

clean the kelly bar. Similarly, the recurring problem with the collapse of the off gas tubing limited the reliability of the flow sensor data collected in the tubing run between the shroud and the vacuum units. Consequently, the mass of VOCs in the off gas could not be calculated.

In conclusion, it is not surprising that some of the previously presented DSM operational problems and limitations were encountered. After all, much of what was being tried had never been attempted before. However, much of the delay and equipment problems could have been avoided or reduced with better preparatory efforts on the part of the drilling contractor.

2. INVESTIGATIVE METHODS

The following sections present the discussion of investigative methods used to assess VOC content in pre- and post-treatment soil and groundwater samples.

2.1 Soil Sampling

Pre-treatment characterization soil sampling was performed with a truck mounted Mobile B-61 rig equipped with 6.25 in. outer diameter, hollow stem augers. A 5-ft long continuous soil sampler was advanced with the hollow stem augers to collect soil samples. Post-treatment characterization soil sampling was accomplished using a direct push rig and Geoprobe Megabore samplers (1.75 by 48 in.) equipped with acetate liners. The depth objectives of the pre- and post-treatment soil sampling correspond with the planned treatment depths for each of test cells discussed in Sect. 1.1.

Upon extraction from the boring, the continuous sampler/acetate liner was opened and samples from the intervals designated in the work plan were collected immediately. These intervals were generally every 5 ft beginning at 1-ft below ground level. A soil sample was always collected at the bottom of the last sampler, representing the bottom of the boring.

Soil samples from the designated intervals were collected by breaking the soil core open and immediately pushing a small coring device (microcore) into the freshly exposed surface. The microcore collected approximately 5 g of soil which was immediately extruded into a tared 40 mL VOC vial containing 5 mL of hexane and 5 mL of deionized water. The vial was labeled and placed in a cooler with Blue Ice. The hole in the soil core created by the microcore was immediately monitored with the photoionization detector (PID). These measurements provided a qualitative measure of the contamination present in the samples.

After the interval samples were collected, the soil core was split lengthwise with a knife. The tip of a PID was then drawn along the split soil to monitor for elevated VOC levels in the core. If elevated levels were discovered, the field team decided whether to collect a biased sample at that location. This decision was based on the relative magnitude of the elevated PID reading compared to other PID measurements from previous soil samples in the boring and the appearance of the core. If a sample was collected, the previously described microcore sampling method was used.

In addition to the soil samples for VOC analysis, several soil samples were collected for various laboratory experiments (treatability studies for MRVS and chemical oxidation) related to the soil mixing process and treatment agents. These were

collected in acetate or brass sleeves or liners, tightly sealed in the collection sleeves, preserved with Blue Ice, and shipped to the laboratory for further use.

2.2 Groundwater Sampling

Pre-treatment groundwater samples were collected by lowering a Teflon bailer into the hollow stem augers. Post-treatment groundwater samples were collected with a stainless steel bailer from temporary 3/4-in. inside diameter (ID) piezometers installed in selected post-treatment borings. The bailer was recovered and the groundwater was decanted into an empty 40 mL VOC vial until the vial was full. Upon arrival at the analytical laboratory, the analyst opened the vial and withdrew 5 mL of the water and injected it into 5 mL of hexane.

2.3 Equipment Decontamination

All sampling equipment was decontaminated between each use. Drilling equipment (i.e., augers, bits, "A" rods, and Geoprobe tools) was decontaminated between each boring. Decontamination was accomplished using a high-pressure hot water washer. Syringes used for groundwater sample transfer and microcore tools were purchased pre-sterilized, used once, and discarded.

Duplicate soil and groundwater samples were collected at a frequency of 10%. Equipment rinse samples were collected daily by pouring deionized water through decontaminated sampling equipment into a 40 mL vial. Field blanks were collected from the deionized water used for equipment rinse samples and from every tank of potable water used by the high-pressure, hot water washer.

All field quality assurance samples were analyzed in the field laboratory using the same techniques and analytical equipment that were used for environmental samples.

2.4 Field Laboratory Methods

Before collection of pre- and post-treatment soil samples, each 40 mL vial was prepared as follows: a sample label was attached, 5 mL of hexane and 5 mL of deionized water were placed in each vial, the vial was weighed, and this tare weight was written on the vial's label. The vials were placed in a clean cooler with Blue Ice and taken to the field for sample collection.

Upon return to the field laboratory, each vial was weighed in order to obtain an accurate weight of the soil in the vial.

Initially, the sample extractant was diluted based on the PID measurement of the soil sample in the field. However, the PID measurements proved to be of limited value. Additional dilution of samples was often required because the field GC was calibrated to be linear within a range of 5.0 parts per billion (ppb) to 1000 ppb and many samples were outside of that range.

Dilutions were accomplished by extracting 0.5 mL of hexane from the sample vial and placing this in 4.5 mL of hexane to create a 1:10 dilution. Dilutions of 1:100 were accomplished by placing 0.05 mL of extractant in 4.95 mL of hexane. Further dilutions, when required, were accomplished using the same methods and starting with the 1:100 dilution created previously. All bottles were labeled with the sample number and dilution. All transfers and dilutions used new bottles and pipette tips. The original sample and all dilutions were stored until the GC runs were complete and the results were within the linear range of the GC.

One (1) mL of hexane from the required dilution was placed in a 2 mL septa top vial and loaded into the autosampler for GC analysis. The first sample loaded in the autosampler was a blank, consisting of 1 mL of hexane in a sample vial.

All samples were analyzed on a Hewlett-Packard 5890 Series II GC equipped with a HP-624 capillary column and an electron capture detector. For the pre-treatment characterization, the GC was calibrated for TCE, *cis*- & *trans*-1,2-DCE, 1,1-DCE and 1,2-DCA. Because the only detectable compounds in the pre-treatment samples were TCE and *cis*-1,2-DCE, the post-treatment characterization limited the GC calibration to the latter two compounds. A calibration curve for TCE was generated from standards at concentrations of 50, 100, 250, 500, 750, and 1000 ppb. The calibration curve for the other compounds was generated from standards at concentrations of 200, 500, 1000, and 2000 ppb. Standards were prepared from custom mix standards diluted to create the range of concentrations. Following initial calibration, standards were run at least every two days to check retention times and concentration determination.

One (1) μ L of extractant liquid was injected directly on the column using a HP7673A autosampler, the autosampler was controlled with a HP3396 Series II integrator. Chromatograms were collected, stored, and reported using Chrom-Perfect, Version 5.05/6.07. Dilution information was entered into ChromPerfect and the concentration of contaminant in each sample were calculated automatically. The analyst calculated the concentration of contaminant per gram of sample and entered that value in the logbook. Following the GC runs, sample reports were studied to determine if any samples were outside the calibration range or if any of the blanks contained

contamination. No blanks were contaminated. Several samples were out of range; these samples were further diluted, as needed, and reanalyzed usually within a holding time of less than 2 to 3 days.

2.5 Pre-Treatment Characterization Results

2.5.1 Physical Characteristics

Pre-treatment characterization began at location X1B1 to a depth of 51 ft (Fig. 2.1). The X is the test cell designator and B1 identifies the location as borehole 1. X1B1 is located outside of the actual treatment area. X1 was planned as "shakedown" area where the DSM process would be tested prior to treating contaminated soil. Following X1B1, all five borings in the T1 cell were drilled to 25 ft. The low level of contaminants in T1 and some riprap encountered at depths of 6 to 10 ft caused the field team to change the strategy slightly. Instead of drilling all five borings in one test cell, one boring was drilled in each test cell to determine if unexpected problems would be encountered. Borings T2B3, T3B3, T4B3, and T5B3 followed in that order. No significant problems were encountered in these borings. Therefore, all borings were completed in T2 to bedrock, T3 to 25 ft, T4 to bedrock, and T5 to 25 ft.

In T2, borings T2B1 and T2B2 encountered large gravels and obstructions at depths from 3 to 10 ft. In addition, the contaminant concentrations in this test cell were very low compared to concentrations in other test cells. Based on the problems drilling in T1 and T2 and the low level of contaminants present, other test cells were added (T6 and T7 in Fig. 2.1). T6 was located between T3 and T4, T7 was located east of T5. These locations were chosen based on logistics of reaching the cells with the mixer, the likelihood of encountering contamination, and the apparent lack of drilling obstacles in the eastern portion of the test area.

A detailed lithologic log was prepared for one boring in each of the test cells, except test cell 6. A lithologic log from test cell 6 was not prepared because T6B3 was drilled approximately 18 in. from NEA Borehole 17 (NEBH17), a borehole drilled as part of a RCRA facility investigation previously performed in the NEA. Detailed lithologic logs from the test cells and NEBH17 are provided in Appendix A. A brief lithologic description of each test cell follows.

Shakedown X1B1: The soil consisted of predominantly silty clay fill to a depth of approximately 15 ft. An obstruction, probably a cobble or other riprap, was encountered at 10 ft. The continuous sampler was removed in order to drill through the obstruction (10 to 12 ft). Sample recovery from 12 to 15 ft was low as debris

● Pre-Characterization Borehole

DSM013

Fig. 2.1. Location of pre-treatment characterization soil borings.

from the obstruction plugged the sampler. The material remaining in the sampler indicated that fill (cap material) graded to native soil in this interval. No further difficulties were encountered in the boring. Silty clay dominates the interval from 15 to 47 ft. However, the interval from 17.5 to 18.2 ft contains a notable amount of very fine grained sand. This interval also showed an oily sheen on the grains and had a strong hydrocarbon odor. The odor was not noticed in other intervals of the boring. The silty clay was very sandy just above a silty gravel at 47 ft. The silty gravels are limestone, sandstone, and chert. The bedrock was encountered at 51 ft.

Test cell 1: Soils in T1B3 consisted of humus to 1 ft; followed by fill, consisting of silty clay with scattered sand and gravels to 6 ft. The continuous sampler had to be removed from 6 to 8 ft because of a layer of gravel or riprap. Silty clay fill continued from 8-13 ft, this interval also contained coarse sand, wood fragments, and other carbonaceous debris. The interval also exhibited an oily sheen, had a strong hydrocarbon odor from 8 to 10 ft, and a sulphurous organic odor from 10 to 13 ft. From 13 ft to a total depth of 25 ft, the soil consisted of dark gray silty clay. No odors were detected below 13 ft.

All the additional boreholes matched T1B3 closely. All had fill to approximately 12 to 14 ft. T1B2 and T1B4 had the same gravel layer present from 6 to 8 ft as T1B3. Drilling was difficult and the samplers had to be pulled in order to auger through this zone. Borings T1B1 and T1B5 were drilled with some difficulty from 6 to 8 ft, however, the samplers did not have to be removed. All the holes had a very strong hydrocarbon odor with some visible staining from 8 to 10 ft. The hydrocarbon odor and staining decreased below 10 ft and was absent for the most part below 13 ft. All the borings encountered water at a depth of 23 to 24 ft. Borings T1B1 and T1B2 encountered an oily sludge and perched water from approximately 9 to 10 ft. There was enough water and oil present to follow the augers and samplers down to at least 25 ft making the water sample results from 25 ft questionable. There were also some large cobbles or other debris at 10 ft in borings T1B1 and T1B2.

Test cell 2: Soils in T2B3 consisted of humus to 1 ft followed by a brown silty clay to 6 ft. An obstruction was encountered at 6 ft, probably cobbles or other riprap. The continuous sampling and drilling continued through the obstruction to a depth of 7 ft. The fill material continued from 7 to 10 ft. A large obstruction was encountered at 10 ft and the sampler was removed; however, the auger would not penetrate the obstruction. The augers were removed from the boring and the rig was moved 1 ft to the west. The new boring was drilled to 12 ft and drilling was very difficult from 10 to 12 ft. The continuous sampler was inserted at 12 ft, but sample recovery was low from 12 to 15 ft. The fill material appeared to stop at approximately 14 ft. Lithology consisted primarily of silty clay from 14 to 47 ft, interrupted by a 1-ft zone of peat (wood fragments and decayed organic material) at 23 ft. An oily sheen was

noted in the upper portions of the silt and a slight hydrocarbon odor was present in the peat. Gravelly silt was encountered at 46 ft, the bedrock was evident at 48.5 ft and the total depth of the boring was 49 ft.

Drilling was very difficult in T2B1 and T2B2 because of gravel layers at 3 ft in both borings. In boring T2B2, the sampler was removed at 4 ft and the soil was gravelly to 10 ft then became softer. The augers were removed from the boring at 11 ft to clean an obstruction from the bit. The obstruction was a portion of a cobble which had obviously been larger than 3 in. A hydrocarbon odor was noted from 8 to 10 ft, and the fill extended to approximately 12 ft.

Borings T2B4 and T2B5 were drilled without major difficulties. Approximately 5 to 6 ft of cap material was drilled before encountering the dark gray fill as seen in other borings. There was a slight increase in moisture at 10 ft accompanied by a strong hydrocarbon and solvent odor. From 20 to 23 ft, visible product was present in T2B4 and the amount of product present had changed the normally cohesive soils to a crumbly mass. There was also a very strong hydrocarbon and solvent odor in T2B4. Boring T2B5 had a moderate hydrocarbon and solvent odor from 20 to 23 ft but there was no visible product and the soil has not been altered as in T2B4. The soil became homogeneous and sticky at approximately 34 to 36 ft in all of the borings. The gravel zone above the sandstone bedrock ranged from 1.5 to 2 ft thick in this cell.

Test cell 3: The soil in T3B3 consisted of humus to 1 ft followed by brown silty clay fill to a depth of 12 ft. A slight solvent odor was noted in the lower portion of the fill. From 12 ft to the total depth of 25 ft, the lithology was dark gray silty clay with occasional fine grained sands. The solvent odor persisted through these depths and became very strong from 20 to 23 ft. Fresh soil faces appeared wet but were actually saturated with product. The soil became wet at 23 ft, and the soil was noncohesive below 20 ft, probably because the product altered the soil structure. No large gravels, riprap, or other obstructions were encountered.

The fill thickness ranged from 11 to 12 ft in all the boreholes. No odors were present in the fill. The first hint of contamination appeared at approximately 15 ft and borings T3B4 and T3B5 became quite contaminated by 20 ft below ground surface (bgs). There was an oily sheen present from 20 to 25 ft with most of the free product concentrated from 20 to 23 ft. The bailer used for collecting the 30 ft water sample was coated in oil upon removal from the augers in boreholes T3B4 and T3B5.

The free product visible in the silty clay was not as prevalent in borings T3B1 and T3B2 as it was in T3B3, T3B4, and T3B5. A slight oily sheen was visible from 20 to 25 ft but not to the extent observed in the other three boreholes. Soil in all of the borings became saturated between 23 and 24 ft bgs.

Results of laboratory analyses performed on soil samples collected from the T3 cell as part of the MRVS treatability study (West et al. 1995) revealed the following characteristics:

<u>Soil Property</u>	<u>Range</u>
Unified Soil Classification	CL to CH
Moisture content	19% (above the water table), 33% (below the water table)
Plastic limit	18 to 20%
Liquid limit	33 to 50%
Dry bulk density	1.33 to 1.48 g/cc
Total organic content	0.4 to 0.7%

Test cell 4: The soil in T4B2 consisted of humus to 1 ft followed by dark brown to dark gray silty clay fill to 12 ft bgs. A slight hydrocarbon odor was noted at 10 ft. The lithology consisted of silty clay from 12 ft to 45 ft and silty gravel from 45 ft to the sandstone bedrock at 47.5 ft. Visible product was noted at 15 ft and the soil was noncohesive and saturated with product from 20 to 34 ft. Some pore spaces and fracture faces were discernable from 34 to 40 ft bgs. Below 40 ft, scattered lenses of sand and silt were visible. A strong hydrocarbon and solvent odor was present from 20 to ~40 ft, and the odor decreases below 40 ft. All of the samplers removed from below the 20 ft interval were coated with a brown, oily substance.

Based on field observations, test cell 4 was the most contaminated cell encountered. Test cell 3 is probably as contaminated as T4, especially in boreholes T3B3, T3B4, and T3B5 but since they were only drilled to 25 ft it was difficult to tell. All the holes in T4 had fill to approximately 11 ft with possible re-worked native soil to 15 ft. Below 15 ft visible product was present in all borings and a strong hydrocarbon and solvent odor were always noted. By 18 ft bgs, the soil generally became noncohesive and crumbly from the product induced alteration. It was difficult to distinguish the actual water table in all 5 boreholes due to abundant free product. The bailer used to collect the water samples at 30 ft was covered with oil upon removal from the augers. There was definite free product floating on top of the water in the bailer. The product resembled weathered kerosene or jet fuel based on the odor. The soil in all of the boreholes was altered to some degree even below 30 ft. Product was visible in all distinguishable fractures or pore spaces above the gravel. A solvent odor was detected in the gravel zone with occasional small pinpoint beads of oil present. Depth

to bedrock was between 47 and 48 ft in test cell 4.

Test cell 5: Soil in T5B3 consisted of humus to 1 ft, followed by brown to dark-gray, silty clay fill to 8 ft bgs. No gravels larger than 3/4 in. were encountered. Dark-gray, silty clay was encountered to a total depth of 25 ft, the interval from 8 to 10 ft had a reworked appearance. A moderate hydrocarbon odor was noted at 12 ft which became a strong odor at 15 ft and the soil became noncohesive at that depth. The odor and the noncohesive soil was prevalent to 25 ft. Free product was present in pore spaces and a brown oily sheen covered all sampling equipment.

Boreholes T5B1, T5B2, T5B4, and T5B5 did not deviate to any great degree from the lithology or contamination that was noted on the log for T5B3. All of the boreholes in test cell 5 had fill to approximately 7 to 8 ft. The native soil beneath the fill had a reworked appearance to a depth of 10 to 11 ft. No contamination was readily identifiable until about 15 ft bgs. From 15 to 20 ft a slight oily sheen was visible accompanied by a very strong hydrocarbon and solvent odor. The amount of contamination increased rapidly below 20 ft to a level where the soil was saturated with product. The soil structure was highly altered from 20 to 25 ft with most of the product concentrated from 20 to 23 ft. The soil was crumbly and little native structure was identifiable in the soil. All of the boreholes were wet at approximately 23 ft, however abundant product remained below 23 ft. Oil was present in and on the bailer used for water sampling on every borehole except T5B4 and T5B5. Even though no oil was present in or on the bailer there was a strong hydrocarbon and solvent odor in the water.

Of the boreholes in test cell 5, T5B4 and T5B5 were the least contaminated. In reviewing the data from a previous investigation it appears the contamination might be more prevalent in a north to northeast direction from this test cell.

Test cell 6: Boring T6B3 was drilled approximately 18 in. from borehole NEBH-17; therefore, the boring log from NEBH-17 was used to describe the lithology in this test cell. Soil in NEBH-17 consisted of dark-brown silty clay fill to 14 ft, dark-gray, silty clay to 47 ft, and a 1 ft layer of gravelly silt to the sandstone bedrock at 48 ft. Bedrock was encountered in test cell 6 at depths between 47.5 and 48.5 ft. The summary for test cells 3 and 4 also describe the conditions present in test cell 6.

Test cell 7: Soil in T7B3 consisted of humus to 1-ft followed by dark gray silty clay fill to 10 ft. Cobbles up to 2 in. were recovered in the sampler and drilling was difficult through the gravels, but the sampler did not have to be removed. Dark gray silty clay was encountered from 10 ft to the total depth of 25 ft. A moderate hydrocarbon odor was noted at 12 ft becoming a strong odor by 15 ft. The soil was altered and noncohesive below 15 with discernable free product. There was an oily sheen on sampling equipment.

Minor drilling problems were also noted in the remaining four borings in test cell 7. There were a couple of instances where large cobbles kicked the augers off to one side causing some minor deviation problems.

As in test cell 6 there was a concern that the contamination was greater further to the north. Thus, T7B3 was drilled first, then T7B2, and finally T7B4. The rationale was that, if there was a significant change in the amount of contamination in T7B4, that being less contamination, then T7B5 would be moved north of T7B1. As in previous borings, no contamination was detected in the fill. The first visible signs of contamination were again at 15 ft. There was visible product in the pore spaces and freshly broken sample faces from 15 to 20 ft were accompanied by a strong hydrocarbon odor. Abundant free product was visible from 20 to 25 ft with the greatest concentrations present from 20 to 23 ft. All the borings were wet at approximately 22 to 23 ft bgs. Soil in all the boreholes was noncohesive from 20 to 23 ft due to product related alteration.

2.5.2 Contaminant Concentrations

Levels of TCE and *cis*-1,2-DCE in individual samples from the pre-treatment characterization are provided in Appendix B. Because no *trans*-1,2-DCE, 1,1-DCE, or 1,2-DCA were detected in any of the samples, results for these analytes have been omitted from Appendix B. Results of the TCE and *cis*-1,2-DCE analyses are discussed below.

Shakedown: No contamination above detection limits was discovered in the shakedown test cell.

Test cell 1: Very low levels of TCE were detected in the test cell 1 soil samples. One sample from 6 ft in boring 3 contained 48 ppb of TCE. Some samples contained 2 ppb. No *cis*-1,2-DCE was detected in the soil in this test cell. No detectable contaminants were discovered in the groundwater.

Test cell 2: Levels of TCE up to 133 ppm (9 ft in B5) were discovered in the shallow soil samples. Most of these shallow soil samples contained concentrations between 100 ppb and 40 ppm. No significant contamination was discovered below a depth of 16 ft. No *cis*-1,2-DCE was detected in the soil in this test cell.

However, the groundwater samples collected at all depths in all five borings contain at least some TCE.

Test cell 3: Levels of TCE up to 527 ppm (25 ft in B4) were discovered in test cell 3. Contamination in this test cell is at a lower depth than in test cell 2 and is more widespread. Boring 1 has lower levels of TCE in the deeper samples. Only one sample (from boring T3B1 at 21 ft) had *cis*-1,2-DCE at a concentration of 59 ppm. The groundwater samples collected at 25 ft contain TCE but no *cis*-1,2-DCE.

Test cell 4: Levels of TCE in test cell 4 range up to 1,666 ppm at 30 ft in B4. Soil contamination is highest between about 20 and 40 ft. The contamination levels tend to be higher in the shallow soils at the north end and higher in the deeper portion of the south end of the test cell. However, all samples below about 10 ft in all borings contain detectable levels of TCE. The presence of *cis*-1,2-DCE in soil was limited to a handful of samples ranging up to 80 ppm in concentration. Groundwater samples from all depths in all borings contain high levels of TCE.

Test cell 5: Although these borings were only drilled to 25 ft, the highest levels of contamination are above that total depth. Levels of TCE in soil range up to 501 ppm (15 ft in B1) with the highest levels of contamination between 15 and 20 ft. However, samples from boring 5 at those depths ranged from nondetectable to only 238 ppb. The contamination at those depths does not appear to extend south of the test cell. The presence of *cis*-1,2-DCE in soil was limited to two samples ranging up to 242 ppm in concentration. Groundwater samples collected at 25 ft indicated TCE contamination in all borings. The sample from boring 5 was the lowest.

Test cell 6: The highest level of TCE in a soil sample was discovered in this cell, 3,800 ppm at 31 ft in T6B5. Soil contamination is highest from about 20 to 40 ft in the southern portion of the cell. Although contamination exists in all five borings at depths from below 12 to total depth, no *cis*-1,2-DCE was detected in this test cell. Groundwater samples from all levels in all borings contained high levels of TCE.

Test cell 7: Levels of TCE contamination in soil samples ranged from 10 to 219 ppm. This level of contamination was concentrated in the 15 to 20 ft depths in all borings. Levels of contamination below and above this interval were much lower. No *cis*-1,2-DCE was detected in this test cell. Groundwater samples collected at 25 ft indicated TCE contamination in all borings.

3. MONITORING AND MEASUREMENT ACTIVITIES

Monitoring and measurement of specific performance parameters were performed with a DAS. The parameters collected by the DAS are presented in Table 3.1.

Table 3.1. DAS parameters

Data Parameter	Unit of Measurement
Auger depth	Ft per unit time
Off-gas VOC	Total VOCs in ppm with a flame ionization detector (FID)
Source temperature (air)	Centigrade
Off-gas temperature	Centigrade
Off-gas pressure	Pounds per square in. (psi)
Off-gas volume	Cubic ft/min (cfm)
Soil temperature	Centigrade

3.1 Gas Analyses for Target VOCs

During mixing operations off-gas vapor was continuously monitored with a Baseline™ 1015A total gas analyzer equipped with a FID. The FID readings, which represent total VOC concentrations in the off gas, were recorded by the DAS and are presented as graphic plots in Appendix C. Subsamples of the vapor stream were collected in septa-equipped glass sampling bulbs for analysis by direct injection into the GC. Results of the off-gas VOC analyses are presented in Table 3.2.

The finding that TCE was the only compound detected in the off-gas was not unexpected considering its predominance over the other target compounds *cis*- & *trans*-1,2-DCE in the pre-treatment soil and groundwater data presented in Appendix B. Another point of interest is the relationship between the total VOCs measured with the FID and the TCE concentration from GC analysis. Consistently higher total VOC concentrations are attributed to the presence of significant amounts of petroleum hydrocarbons and semivolatile compounds (U.S. DOE 1994) which were not targeted for GC analysis. Due to the relatively unknown composition of the off-gas, previously discussed problems with the off gas tubing and a limited number of off gas samples, the value of the total VOC readings for the evaluation of effectiveness of the various reagents' ability to reduce VOC mass is limited. However, in a more qualitative sense, the off gas FID data is useful in attributing the degree of volatilization associated with the mixing operations and indicate that the initial drilling of each column consistently produced the highest total VOCs in the off gas.

Table 3.2. Off-gas sample results

Sample location	Depth, ft	Date	Time	Total VOC, ppm	TCE, ppm
T3C1	10.0	7-11-96	14:55	4,500	906
T3C1	19.0	7-11-96	15:10	8,000	520
T3C1	14.0	7-11-96	15:32	1,400	64
T3C1	8.0	7-11-96	17:04	1,600	194
T3C2	24.0	7-11-96	18:00	6,700	401
T3C2	14.0	7-11-96	18:23	1,300	148
T3C2	8.0	7-11-96	18:31	2,000	29
T3C3	12.0	7-11-96	11:06	7,500	ND
T3C3	16.0	7-11-96	11:11	15,000	784
T3C3	16.0	7-11-96	14:03	2,000	478
T4C1	12.0	7-15-96	15:09	12,000	1,112
T4C1	35.0	7-15-96	15:25	12,000	656
T4C2	21.0	7-16-96	16:24	22,000	1,416
T4C2	24.0	7-16-96	16:26	13,000	1,093
T4C2	42.0	7-16-96	16:38	2,200	215
T5C1	14.0	7-13-96	11:26	13,000	963
T5C1	21.0	7-13-96	11:31	15,000	620
T5C2	13.0	7-13-96	14:39	6,400	539
T5C2	11.0	7-13-96	14:42	15,000	286
T5C3	23.0	7-12-96	17:10	8,000	52
T5C3	5.0	7-12-96	17:26	1,200	11
T7C1	20.0	7-20-96	10:11	1,700	12
T7C2	20.0	7-20-96	14:56	600	12

ND= non detect

4. RESULTS AND DISCUSSION

Figure 4.1 shows the locations of the bioaugmentation cell (T3), two KMnO_4 cells (T4 and T5), and the MRVS cell (T7) that were treated as part of the DSM demonstration. Columns in the T3, T5 and T7 cells were mixed to a depth of 25 ft bgs while the columns in the T4 cell were mixed to a depth of 47 ft bgs. The following sections present the operational information and post-treatment sampling results in chronological fashion.

4.1 DSM/Bioaugmentation Demonstration Results

4.1.1 Bacteria/Bionutrient Background Information

A treatability study examining the biodegradation of TCE in KCP soil using *Burkholderia cepacia* G4 PR1₃₀₁, (referred to as G4 in the following) was completed in 1995. The results of the treatability study, presented in Appendix D, indicated that in 48 hrs a 10% inoculum of G4 could degrade 99.8 % of the TCE present in the 1 and 5 ppm samples. Similarly, the same G4 could degrade 87.4% of the TCE present in the 10 ppm sample in the same time frame.

Bioremediation, with the technique being applied in this project, is most effective at in TCE concentrations up to 10 ppm. As previously discussed, the planned location (T7 cell) for demonstrating DSM and bioaugmentation contained an average of 20 mg/kg TCE. However, the initial shakedown activities at the site flooded the T7 cell with approximately 4 ft of water and sediment. Because the bacteria culture had been inoculated and was time-sensitive, the bioaugmentation location had to be relocated to the T3 cell (Fig. 4.2), a site with significantly higher average TCE concentrations (126 mg/kg). As previously discussed, the lack of contamination and suggested concrete debris material identified in the T1 and T2 cells during pre-treatment characterization, prevented their use for the bioaugmentation demonstration.

The decision to relocate the bioaugmentation demo to the T3 cell resulted from a combination of factors. While the toxic effects on the bacteria from the higher TCE levels were predictable, the risk of creating a slurry with liquid to soil ratio >1, however was considered potentially more damaging by the principal investigator due to relatively low enzyme activity of the bacteria solution—adding more water would dilute it further. Moreover, the lack of a dry shake down added uncertainty to the drilling equipment's ability to reach 25 ft with air alone. Thus, the suggestion that additional water might be needed to complete the drilling and the inability to control

DSM012

- Deep Soil Mixing Location
- Background Soil Boring Location

Fig. 4.1. Test cell locations within the Deep Soil Mixing area.

Fig. 4.2. T3 cell layout with soil boring locations.

the volume of pooled water that would seep in under the vacuum hood if drilling were performed at the T7 cell, precipitated the decision to use the T3 cell.

G4 was initially grown at ORNL in two large reactors (5 gal) using a basal salts media (BSM) (Hareland et al. 1975) with 20 mM glucose as the sole carbon source. On July 7, five gal of active culture (enzyme specific activity >3) were transferred to large sterilized jugs, put on ice and shipped to KCP to be used as an inoculum. Two 500-gal reactors (front, F, and back, B) equipped with a stirring/air delivery mechanism (BioSystems Technology, Blacksburg, Virginia) were filled with municipal drinking water on July 8. Nutrients were slowly added until dissolved. Nutrients included glucose at 20 mM and the BSM. Finally, the G4 inoculum was mixed in. Each reactor contained 450 gal of bacteria/nutrient solution.

G4 growth, enzyme specific activity, and glucose concentrations were monitored daily and at the time of addition into the subsurface. G4 growth, measured by an increase in optical density (OD) of the solution, was determined using a spectrophotometer (Spectronic 20D, Milton Roy Co.) operating at a wavelength of 600 nm. Expression of toluene ortho-monooxygenase, the enzyme responsible for TCE degradation, was measured using a TFMP (trifluoromethylphenol or m-hydroxy benzotrifluoride) oxidation assay. The rate of production of TFHA (7,7,7-trifluoro-2-hydroxy-6-oxo-2,4-heptadienoic acid), a yellow product, from TFMP oxidation correlates to the potential rate of TCE degradation by the enzyme (Shields et al. 1991, Shields and Reagin 1992). Glucose concentrations were determined using a glucose assay kit (Sigma Diagnostics, St. Louis, Missouri).

On July 9, the OD was calculated to be 0.11 for both reactors with no enzyme activity detected and a glucose concentrations of 10 - 11 mM. It is important to note that treatability studies have indicated that enzyme activity cannot be detected for an OD less than 2 using currently available colormetric methods. Although the OD is representative of bacterial density, non detectable enzyme activity does not mean the enzyme is not present, it is simply below very crude colormetric detection limits. Therefore, the lack of detectable enzyme activity does not affect the bacteria's viability to degrade TCE. The ODs for both reactors continued to be low (less than 0.1) on July 10 with no enzyme activity detected and a glucose concentration of 12 and 15 mM. Based on this information, both bioreactors were inoculated with an additional G4 stock that was brought to KCP by BioSystems Technology. On July 11, the day of the demonstration, both reactors revealed denser microbial cultures with a significant amount of foaming. The ODs were 0.17 (F) and 0.30 (B) and the glucose concentrations were 0.7 to 0.85 mM, suggesting that G4 was growing. However, because the ODs were still below 2, the colorimetric assay was not able to measure the enzyme activity (below detection limits).

4.1.2 Bioaugmentation Operational Information

DSM/Bioaugmentation was conducted July 11 in three overlapping test columns (T3C1, T3C2, and T3C3) with 8-ft diameters and 25-ft depths (Fig. 4.2). Column T3C3 was treated first and served as the shake-down test column for drilling with air. This was followed by column T3C1, and finally column T3C2. Following are brief summaries of process operations at each column presented in chronological order.

T3C3 Column

Elapsed time	Process description
0 to 55 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft; off gas tubing is collapsed throughout demonstration.
55 to 66 min	Prepare for mixing.
66 to 86 min	344 gal of bacteria solution mixed in between 24 ft and 3 ft.
86 to 174 min	Repair torn shroud seal.
174 to 197 min	Mix column with air (800 to 1100 cfm) from surface to 24 ft.
197 to 205 min	Mix column with air (800 to 1100 cfm) from 24 ft to surface.
205 to 219 min	Mix column with air (800 to 1100 cfm) from surface to 24 ft.
219 to 224 min	Mix column with air (800 to 1100 cfm) from 24 ft to surface, end of mix.

Following the mixing of column T3C3, the mixing apparatus was moved and located over column T3C1 at the northern end of the T3 cell.

T3C1 Column

Elapsed time	Process description
0 to 47 min	An 8-ft diameter hole drilled with air (800 to 1100 cfm) to a depth of 25 ft, off gas tubing collapses immediately and remains that way.
47 to 64 min	266 gal bacteria solution mixed in between 23 and 2.5 ft.
64 to 140 min	Rig repair (shroud seal replaced).
140 to 165 min	Mix column with air (800 to 1100 cfm) from 1.5 to 23 ft.

165 to 173 min Mix column with air (800 to 1100 cfm) from 23 to 1.5 ft, end mix.

Following the mixing of column T3C1, the mixing apparatus was moved and located over column T3C2 in the center of the T3 cell.

T3C2 Column

Elapsed time	Process description
0 to 20 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft, off gas tubing remains collapsed for entire demonstration.
20 to 31 min	Prepare for mixing.
31 to 38 min	279 gal of bacteria solution mixed in between 24 ft to surface.
38 to 51 min	Mix column with air (800 to 1100 cfm) from surface to 24 ft.
51 to 57 min	Mix column with air (800 to 1100 cfm) from 24 ft to surface.
57 to 59 min	Clear ports on auger blade, end mix.

The most significant consequence of the previously discussed problems with tearing of the shroud seal during the mixing of the T3C3 and T3C1 columns is the time lost which would have been used for additional mixing. Additionally, the collapsed off gas tubing prevented the calculation of the air volume being removed from the shroud as well as the ensuing estimation of contaminant mass in the off gas.

Table 4.1 lists the key operational data from the bioaugmentation treatment cells.

Table 4.1. Bioaugmentation operational data

Treatment column	Mix date	Bacteria added, L (gal)	No. of Passes	Bacteria solution to soil ratio	G4 bacteria OD	Glucose, mM
T3C1	7-11-96	1007 (266 gal)	2	0.028	0.17/0.30	0.7/0.85
T3C2	7-11-96	1056 (279 gal)	2	0.032	0.17/0.30	0.7/0.85
T3C3	7-11-96	1302 (344 gal)	3	0.037	0.17/0.30	0.7/0.85

OD: optical density

The bacteria/bionutrient solution liquid to soil volume ratios presented in Table 4.1 were purposely kept low to prevent the creation of slurry-like conditions in the T3 cell. Although a liquid to soil volume ratio of 1 had been used in the treatability study presented in Appendix D, it was apparent from the lesson learned during the wet

shakedown that this ratio could not be achieved in the field without surface flooding. The respective bacteria solution to soil ratios for each column were calculated by dividing the volume of bacteria solution added to each column by the volume of soil in each column including void space (35,612,649 cm³). To account for the overlap region in the C2 column, the ratios for the C1 and C3 columns were weighted by 30% each and added to that of the C2 column.

Due to the close proximity of the columns in the bioaugmentation cell, post-treatment sampling could not safely be conducted until all three columns had been mixed. This resulted in a minimum delay of two days between mixing and sampling. Post-treatment sampling information for each soil boring in the T3 cell is presented in Table 4.2.

Table 4.2. Bioaugmentation sampling information

Soil boring	Associated column	Sampling date	Days after mixing
T3B1	T3C1	7/13/96	2
T3B2	T3C1/T3C2	7/13/96	1.8
T3B3	T3C2	7/13/96	2.0
T3B4	T3C2/T3C3	7/14/96	2.5
T3B5	T3C3	7/14/96	2.6
T3B6	NA	7/14/96	2.7
T3B7	NA	7/14/96	2.7
T3B1A	T3C1	7/20/96	9.0
T3B3A	T3C2	7/20/96	9.0
T3B5A	T3C3	7/20/96	9.0
T3B8A	NA	7/22/96	11.0
T3B9A	NA	7/22/96	11.0

NA = not applicable

The following sections present the result of the various analyses performed on the post-treatment soil samples collected from the bioaugmentation treatment cell T3.

4.1.3 Post-Treatment VOC Results from Bioaugmentation Cell

It should be noted that the post-treatment boring locations were not intended to replicate the pre-treatment borings due to the redistributing effects of the mixing action. The post-treatment samples were, however, collected in similar fashion and locations as the pre-treatment samples. Furthermore, the inherent heterogeneity in the pre-treatment soil sample data combined with the redistribution of soil characteristics in the post-treatment soil sample data resulting from the mixing effects, required that the data sets be averaged to provide useful interpretation of the treatment effectiveness. The pre- and post-treatment soil boring locations for the T3 cell are presented in Fig. 4.2. The pre- and post-treatment VOC results for the T3 cell are presented in Appendices B and E respectively. Using these data, pre- and post-treatment average TCE concentrations in soil for the T3 cell have been averaged and are presented in Table 4.3. It should be noted that the only pre-treatment sample from the T3 cell with detectable levels of *cis*-1,2-DCE was outside the zone mixed during the DSM. No *cis*-1,2-DCE was detected in any of the post-treatment samples from the T3 cell. Thus, the VOC mass removal efficiency discussion is limited to TCE only.

The average TCE concentration for each soil boring was calculated by summing the depth-specific TCE values and dividing by the number of depth intervals in each boring.

Table 4.3. Pre- and post-treatment average TCE concentrations in T3 Cell borings

T3C1 Column				T3C2 Column				T3C3 Column			
Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg
T3B3	146.3	T3B1	75.3	T3B4	150.7	T3B2	64.0	T3B5	80.3	T3B4	74.8
		T3B2	64.0			T3B3	57.7			T3B5	122.0
		T3B1A	41.7			T3B4	74.8			T3B5A	121.3
						T3B3A	63.3				

The average TCE concentrations for each pre-treatment boring in each of the T3 columns shown in Table 4.3 were then averaged to arrive at an average pre-treatment TCE concentration for each column. The respective average pre-treatment TCE concentrations for the C1, C2 and C3 columns are 146, 151, and 80 mg/kg - which yield an average pre-treatment TCE concentration of 126 mg/kg for the T3 cell. The mass of soil for the T3 cell was calculated using three 25-ft deep columns with 8 ft

diameters, a 60% overlap for the center column, a particle density of 2.65 g/cm^3 and an estimated porosity of 30%. The resulting mass of soil in the T3 cell is 158,548 kg which when multiplied by the average TCE concentration of 126 mg/kg yields a total pre-treatment TCE mass of 20 kg in the T3 cell.

The average TCE concentrations from each of the post-treatment soil borings in the T3 columns shown in Table 4.3 were treated in the same fashion and yield respective average post-treatment TCE concentrations for the C1, C2 and C3 columns of 60, 65 and 106 mg/kg which yield an average post-treatment TCE concentration of 77 mg/kg for the T3 cell. The estimated total mass of post-treatment TCE in the T3 cell is calculated to be 12.2 kg using the same column dimensions and previously mentioned parameters. Comparing the pre- and post-treatment values of 20 and 12.2 kg TCE indicates an overall removal rate of 39% or 7.8 kg of TCE from the T3 cell.

While the 39% reduction in TCE mass falls below the overall treatment objective of 70%, it is useful to note that TCE concentrations verify that VOC reductions did occur. Considering that toxic effects on the bacteria from the high TCE concentrations were expected, the reported reduction in mass of TCE is significant. It is also useful to note that different TCE mass reductions could be represented with the same data set. For example, the values could be calculated on a per column basis rather than a per cell basis and show that one column (T3C3) where the post-treatment TCE exceeds the pre-treatment TCE mass. However, due to the previously discussed aspects associated with inherent heterogeneity in soil sampling and the redistribution of soil characteristics introduced by the soil mixing process, it is difficult to draw any significant conclusion from this approach. Moreover, the bulk of the pre-and post-treatment data from the T3 cell suggests that treatment did occur and, thus, indicate that treatment of the data on a per-cell basis is appropriate.

Post-treatment groundwater samples collected after installing piezometers in the boreholes at locations T3B1, T3B3, and T3B5, yielded TCE concentrations of 26, 48, and $<0.005 \text{ mg/L}$ respectively. These results produce an average post-treatment TCE concentration of 37 mg/L for the T3 cell groundwater which can be compared to an average pre-treatment groundwater TCE concentration of 231 mg/L. However, it should be noted that the groundwater sample from the C3 column (T3B5) had a KMnO_4 concentration of 1.1 wt % as a result of mixing in the adjacent T4 cell. Interestingly, the post-treatment T3B5 groundwater sample was the only one within the biotreatment cells in which no TCE was detected.

4.1.4 Biodegradation vs Vapor Stripping

The amount of TCE stripped from the subsurface from the initial drilling and subsequent mixing of the T3 columns is difficult to quantify for reasons previously discussed. First, a limited number of off gas samples were analyzed with the GC (see Table 3.2). Second, the presence of other organic compounds (hydrocarbons and semivolatiles) in the off gas stream limit the value of the total VOC recorded by the FID for this purpose. Third, the lack of reliable off gas temperature and volume data due to previously discussed problems with the collapsed off gas tubing, make this estimation untenable.

While it is obvious that the initial drilling of the cells using 800 to 1000 cfm of air was responsible for the volatilization of TCE, it is apparent from the DAS graphic plots presented in Appendix C, that the subsequent passes with bacteria and air triggered less volatilization. The peak total VOCs recorded with the FID range from 10,000 ppm in T3C1 to 19,000 ppm in T3C2. The peaks were all associated with the initial drilling of the columns and correspond to a depth of about 20 ft bgs where some of the highest TCE concentrations were identified in the pre-treatment borings (Appendix B). The effects of stripping following the initial drilling with air appear to taper off considerably as the total VOCs measured in subsequent passes using air after bioaugmentation range from 2000 ppm in T3C1 to 5000 ppm in T3C3.

The amount of TCE degraded by G4 only could not be calculated directly from the off gas samples due to previously discussed problems with collapses in the off gas tubing. However, treatability studies have shown that 100 μ g of TCE could be degraded by 1 mL of G4 (at OD of 2) in 36 hrs. Assuming no loss of enzyme activity during scale-up, 300 gal of G4 at an OD = 2 would have degraded approximately 115 g of TCE. At the time of the first sampling event (i.e., 24 to 48 hrs after treatment), 2.5 and 1.8 kg of TCE were removed from Column T3C1 and T3C2, respectively. These amounts exceed the amount of TCE that could have been removed by G4 alone which suggest air stripping is responsible for a portion of the TCE mass removal.

4.1.5 Microbial Monitoring Results

Geoprobe soil cores were collected from inside and outside the three columns and shipped on ice to ORNL for microbiological analyses. Experiments determined the effects of bacterial addition and DSM treatment on the indigenous microbial population and survivability of G4 in the subsurface, as well as the potential distribution/migration of these microorganisms outside the treatment zone. Analyses consisted of blending 1 gm in a phosphate buffer saline. Serial dilutions of the blended samples were inoculated onto a non-selective growth media of 1% PTYG (peptone-tryptone-yeast extract-glucose) and a selective media of lactate+BSM (a G4 specific medium). Cultures that phenotypically resembled G4 underwent analyses

using the Biolog system (Bochner 1989). Finally, TCE degradation was investigated upon reacclimation, in the laboratory, of selected microorganisms isolated from the soil samples.

The microbiological experiments determined the presence of G4 at depths up to 13.5 ft bgs in the soil samples collected in the T3C1 and T3C2 columns during the first sampling event (two days). However, bacterial counts suggest that G4 had a low survivability in the subsurface matrix as depth increased. The highest numbers of microorganisms were observed in boreholes T3B1, T3B2, and T3B3 (depths between 5.5 and 10 ft) with CFU (colony forming unit) numbers ranging from 2.2 to 3.6×10^4 /g of soil. Interestingly, the post-treatment TCE concentrations for the previous depths in the latter boreholes ranges from 5 to 26 mg/kg (Appendix E). For depths below 13.5 ft, CFUs were $< 1 \times 10^2$ /g of soil and post-treatment TCE concentrations up to 279 mg/kg were reported (Appendix E). For Column T3C3, CFUs were $< 1 \times 10^2$ for all depths (boreholes T3B4 and T3B5). Several factors contribute to the low survivability of G4, including very high TCE concentrations with increasing depths and decreasing oxygen concentrations in the subsurface.

At the time of the second sampling (10 days post-treatment), G4 was still recoverable from Column T3C1 and T3C2; however, at much lower numbers. Additionally, comparison with background soil samples collected from the T3B6A and T3B7A soil borings indicates the microorganisms did not migrate outside the treatment zone.

Finally, bacteria isolated from three different soil cores and identified as G4 by the Biolog analysis were restarted in the laboratory using glucose and BSM to test for TCE degradation capabilities. From these field cultures, 1 and 5 ppm was degraded to below detection limits (< 5 ppb) within 24 hr. In a separate experiment, 80 to 98% of a 10 ppm TCE solution was also degraded. These experiments confirm that G4 was added to the subsurface and survived the DSM process where the TCE concentrations did not have toxic effects.

4.1.6 Evaluation of Cost for DSM Using Bioaugmentation

The estimated cost for DSM with bioaugmentation is based on operational cost estimates provided by Geo-Con. Geo-Con estimated equipment and crew costs at \$43/yd³ assuming 30,000 yd³ of soil and a treatment depth of 30 ft. Using a material (G4 bacteria) cost of \$10/yd³ (6.5 gal bacteria/yd³ of soil), and a multiplier of 1.45

to cover overhead, safety, quality control, supervision, and profit the overall estimated cost for DSM/bioaugmentation is approximately \$77/yd³.

4.2 DSM/KMnO₄ Demonstration Results

4.2.1 KMnO₄ Background Information

A chemical oxidation treatability study was completed in November 1995 to determine whether TCE and DCE could be degraded in contaminated soil from the KCP. Results of that study suggested that TCE removals greater than 90 wt % could be achieved using KMnO₄ solutions of at least 4 wt %, with oxidant loadings greater than 16 g KMnO₄/kg soil. During the demonstration, up to 69 % TCE removal in saturated soil and 83% TCE removal in unsaturated soil were achieved using a much lower average loading (6 g KMnO₄/kg soil). A lower oxidant loading was chosen for the field due to the limitation of the volume of oxidant which could be added to the low permeable soils. Thus, the 60% reduction in the oxidant loading used in the field still resulted in acceptable TCE reductions.

The KMnO₄ used for the field scale demonstration was supplied by Carus Chemical Company (Peru, Illinois) in free flowing grade (granular form) packaged in 3000 lb containers. Representatives from the manufacturer were on site to aid in the mixing of the KMnO₄ slurry which was accomplished by mixing 3000 lb of the granular KMnO₄ with 4000 gal of water in a colloidal mixer. Samples of each batch of KMnO₄ were collected for determination of concentration.

4.2.2 KMnO₄ Operational Information

The DSM/KMnO₄ demonstration was performed in the T4 and T5 cells illustrated in Fig. 4.3. The demonstration began with the treatment of T5 columns to a depth of 25 ft, followed by the treatment of the T4 columns to a depth of 47 ft.

DSM/KMnO₄ in the T5 cell was conducted July 12 and 13 in three overlapping test columns (T5C1, T5C2, and T5C3) with 8-ft diameters and 25-ft depths. Column T5C3 was treated first and was followed by column T5C1, and finally column T5C2.

Following are chronological summaries of mixing operations for each column in the T5 cell.

Fig. 4.3. T4 and T5 cell layouts with soil boring locations.

T5C3 Column

Elapsed time	Process description
0 to 21 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft, off gas tubing remains collapsed for the duration of the mix.
21 to 37 min	1440 gal KMnO_4 added between 24 ft and surface (60 gal/ft).
37 to 53 min	1263 gal KMnO_4 added between surface and 24 ft (40 gal/ft).
53 to 60 min	Mix column with no air or fluid from 24 ft to surface.
60 to 67 min	Drill from surface to 10 ft with air (800 to 1000 cfm).
67 to 80 min	1000 gal KMnO_4 added between 10 ft and 24 ft.
80 to 85 min	Rotate out from 24 ft to surface with no air or fluid, end mix.

Following the mixing of the T5C3 column, the mixing apparatus was moved to the T5C1 column located at the north end of the T5 cell. Off gas tubing is repaired with tape.

T5C1 Column

Elapsed time	Process description
0 to 14 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 10 ft, off gas tubing is collapsed again in spite of repair efforts.
14 to 19 min	Rotate to surface for shroud seal repair.
19 to 36 min	Drill from surface to 25 ft with air (700 to 1000 cfm).
36 to 44 min	560 gal KMnO_4 mixed from 24 to 10 ft.
44 to 55 min	Rotate to surface for repairs.
55 to 62 min	Complete repairs.
62 to 75 min	Drill with air from surface to 10 ft.
75 to 91 min	625 gal KMnO_4 mixed in from 10 ft to 25 ft (40 gal/ft).
91 to 97 min	705 gal KMnO_4 mixed in from 24 ft to 10 ft (50 gal/ft).
97 to 99 min	Rotate from 10 ft to 3 ft.
99 to 112 min	Rotate from 3 ft to 25 ft, add 64 gal KMnO_4 at 25 ft.
112 to 118 min	Rotate from 25 ft to surface with no air or fluid injection.
118 to 121 min	Lift auger above ground and clear ports with air pressure, end mix.

Following the mixing of the T5C1 column, the mixing apparatus was moved to the T5C2 column in the center of the T5 cell. Additional repair efforts to the off gas tubing include removal of slack in the line and more tape to cover torn portions.

T5C2 Column

Elapsed time	Process description
0 to 4 min	Prepare for drilling.
4 to 27 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft, off gas tubing continues to collapse in any area with too much slack.
27 to 35 min	570 gal KMnO_4 mixed in between 24 ft and 10 ft.
35 to 45 min	556 gal KMnO_4 mixed in between 10 ft and 23 ft.
45 to 50 min	Rotate from 23 ft to 8 ft with no air or fluid injection.
50 to 52 min	Rotate from 8 ft to 23 ft with no air or fluid injection.
52 to 59 min	Rotate from 23 ft to surface with no air or fluid injection.
59 to 63 min	Lift auger above ground and clear ports with air pressure, end mix.

Following treatment of the T5 cell, the mixing apparatus is moved to the T4 cell located to the west. The drilling subcontractor agrees to provide better tubing and maintenance of the off gas tubing for the next effort at the T4 cell.

DSM/ KMnO_4 in the T4 cell was conducted July 15 and 16 in three overlapping test columns (T4C1, T4C2, and T4C3) with 8-ft diameters and 47-ft depths. Column T4C3 was treated first and was followed by column T4C1, and finally column T4C2. The amount of slack in the off gas tubing is reduced. Following are chronological summaries of mixing operations for each column in the T4 cell.

T4C3 Column

Elapsed time	Process description
0 to 46 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 47 ft, off gas tubing now collapses at the inlet to the vacuum unit and Geo-Con calls the subcontractor for support which does not arrive until the T4 cell is completed.
46 to 77 min	1330 gal KMnO_4 mixed in between 47 ft and 14 ft (40 gal/ft).

77 to 96 min	627 gal KMnO_4 mixed in between 14 ft and 47 ft (19 gal/ft).
96 to 100 min	849 gal KMnO_4 mixed in between 47 ft and 33 ft (60.6 gal/ft).
100 to 125 min	Rotate out from 33 ft to surface with no injection of fluid or air.
125 to 139 min	977 gal KMnO_4 mixed in between 10 ft and 47 ft (26 gal/ft), 630 gal water added to tank to increase volume.
139 to 161 min	298 gal KMnO_4 mixed in between 47 ft and 10 ft (8 gal/ft).
161 to 169 min	570 gal KMnO_4 mixed in between 10 ft and 47 ft (15 gal/ft).
169 to 180 min	Rotate out from 47 ft to surface with no fluid or air injection, end of mix, (4651 gal total KMnO_4 injected).

Following the mixing of the T4C3 column, the mixing apparatus was moved to the T4C1 column at the north end of the T4 cell.

T4C1 Column

Elapsed time	Process description
0 to 43 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 47 ft, tubing collapsed at inlet to vacuum unit.
43 to 66 min	1880 gal KMnO_4 mixed from 47 ft to 10 ft (51 gal/ft).
66 to 76 min	Lift auger to surface, blow out ports with air, end of day.
0 to 17 min	Drill from surface to 10 ft.
17 to 41 min	782 gal KMnO_4 mixed from 10 ft to 47 ft (21 gal/ft).
41 to 58 min	816 gal KMnO_4 mixed from 47 ft to 10 ft (22 gal/ft).
58 to 62 min	Rotate out to surface, KMnO_4 flowing out under shroud.
62 to 97 min	Drill from surface to 47 ft with no air or fluid injection.
97 to 135 min	Rotate from 47 ft to surface with no air or fluid injection, end of mix.

Following the mixing of the T4C1 column, the mixing apparatus was moved to the T4C2 column in the center of the T4 cell.

T4C2 Column

Elapsed time	Process description
0 to 44 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 47 ft, tubing collapsed at inlet to vacuum unit.

44 to 58 min	1206 gal KMnO_4 mixed in between 47 ft and 10 ft (32.6 gal/ft).
58 to 68 min	Rotate out from 10 ft to 4 ft ,1200 gal water added to KMnO_4 mixing tank.
68 to 71 min	Rotate from 4 ft to 10 ft.
71 to 88 min	1162 gal KMnO_4 mixed in between 10 ft and 47 ft (31 gal/ft).
88 to 100 min	300 gal KMnO_4 mixed in between 47 ft and 10 ft (8 gal/ft).
100 to 103 min	Rotate out to 7 ft, 500 gal H_2O added to KMnO_4 mixing tank.
103 to 112 min	420 gal KMnO_4 mixed in between 7 ft and 47 ft (10.5 gal/ft).
112 to 128 min	Rotate out from 47 ft to surface with no air or fluid injection.
128 to 135 min	Clean out ports with air pressure, end of mix (3088 gal total KMnO_4 added).

Table 4.4 lists the operational data from the chemical oxidation treatment cells.

Table 4.4. KMnO_4 operational data

Treatment column	Mix date	KMnO_4 injected, L (gal)	No. of passes	KMnO_4 conc., wt% ^a	Loading rate, g KMnO_4 /kg soil
T5C1	7/13/96	7380 (1950 gal)	3	3.7	4.1
T5C2	7/13/96	4260 (1125 gal)	4	4.2	6.9
T5C3	7/12/96	14,000 (3700 gal)	5	4.7	10.0
T4C1	7/15 to 7/16/96	14,570 (3850 gal)	3	3.1	3.6
T4C2	7/16/96	11,689 (3088 gal)	1	3.4 (assumed)	6.1
T4C3	7/15/96	15,140 (4000 gal)	4	4.9	6.0

^a Measured using spectrophotometry, unless otherwise noted.

As previously discussed, the most significant problems associated with the off tubing collapses are the lack of data needed to calculate air volumes and contaminant mass in the off gas stream.

The calculations used to determine the KMnO_4 loading rates are presented in Appendix G. During the chemical oxidation demonstration, 25,640 L (6,775 gal) of KMnO_4 was applied to the three soil columns in the T5 cell (Fig. 4.3). Assuming a porosity of 30%, a particle density of 2.65 g/cm^3 , the respective KMnO_4 weight concentrations presented in Table 4.4, and the assumption that the C2 column (center) overlapped the adjacent columns by 60% (Fig. 4.3), this reagent volume results in a average field loading rate of $7.0 \text{ g KMnO}_4/\text{kg soil}$ for the T5 cell. However, it is estimated that up to 30% of the KMnO_4 added to the shallow test cells ponded on the surface of the treatment zone. The ponding resulted from the low-permeable soil's inability to adsorb the volume of reagent added. The excess reagent then followed paths of least resistance (up along the kelly bar) to the ground surface.

Because an estimated 30% of the oxidant returned to the surface, the actual loading rate may be as low as $4.9 \text{ g KMnO}_4/\text{kg soil}$ in the T5 cell. To avoid excessive reagent ponding, the deep test columns (T4 cell) were mixed and injected with only 41,399 L (10,938 gal) of KMnO_4 to yield an average in-situ oxidant loading rate of $5.2 \text{ g KMnO}_4/\text{kg soil}$. Thus, significant volumes of oxidant were not observed on the ground surface following treatment of the deep test cells.

The various analyses performed on the post-treatment soil samples from the oxidation cells are presented in Table 4.5. The procedures are either referenced or included in the results and discussion section. VOC and KMnO_4 analyses in the post-treatment samples were conducted on site in a mobile laboratory while the remaining analyses were performed at ORNL, Oak Ridge, Tenn.

The parameters in Table 4.5 were used to provide evidence of soil mixing efficiency and the effectiveness of the oxidation treatment. For example, increases in soil pH, moisture content, and manganese (Mn) concentration are indicative of soils which had interacted with the KMnO_4 treatment reagent. It was also expected that the overall organic content of soils treated with KMnO_4 would be reduced as this reagent is a non-specific oxidant that will consume both contaminants and natural soil organic matter (SOM). Microbial sampling and analyses were conducted to determine whether oxidation with KMnO_4 destroys or alters the bacterial population in the soil. Any intrinsic microbes present after initial treatment with KMnO_4 may be effective in further degrading any residual contamination present. Due to the close proximity of the T5 and T4 cells, post-treatment sampling of either test cell could not safely be conducted until both cells had been mixed. This resulted in a minimum delay of three days between mixing and post-treatment sampling. Post-treatment sampling information for each soil boring in the T5 and T4 cells is presented in Table 4.6.

Table 4.5. DSM post-treatment analyses and procedures

Analysis/Parameter	Method/Procedure
Soil pH (ASTM D4972)	1:1 wt/wt slurry (deionized water)
VOC concentration	GC (hexane extraction)
KMnO ₄ concentration	Spectrophotometry (0.01 M NaCl extraction)
Moisture content (ASTM D4959)	Gravimetric Analysis (100 C Drying)
Manganese (Mn) content (Carter 1993)	Exchangeable Cations (NH ₄ ⁺ Acetate extraction)
Total Carbon (TC) content	Dorhmann DC 190 Carbon Analyzer
Total Organic Carbon (TOC) content	Dorhmann DC 190 Carbon Analyzer (Acid prepped)
Microbial analyses	Aerobic and Anaerobic Plating and Counting

ASTM: American Society for Testing and Materials

Table 4.6. KMnO_4 sampling information

Soil boring	Associated column	Sampling date	Days after mixing
BKG-BH2	NA	7/16/96	NA
T5B1	T5C1	7/17/96	4.4
T5B2	T5C1	7/17/96	4.5
T5B3	T5C2	7/17/96	4.6
T5B4	T5C2	7/17/96	4.7
T5B5	T5C3	7/18/96	6.4
T5B6	NA	7/23/96	~10
T4B1	T4C1	7/18/96	3.6
T4B2	T4C1	7/18/96	3.7
T4B3	T4C2	7/19/96	3.4
T4B4	T4C2	7/19/96	3.4
T4B5	T4C3	7/19/96	3.6
T4B6	NA	7/20/96	~4

NA = not applicable

The following sections present the results of the various analyses performed on the post-treatment soil samples collected from the KMnO_4 treatment cells T4 and T5.

4.2.3 Post-Treatment VOC Results from KMnO_4 Cells

As previously discussed, the post-treatment boring locations were not intended to replicate the pre-treatment borings due to the redistributing effects of the mixing action. The post-treatment samples were, however, collected in similar fashion and locations as the pre-treatment samples. Furthermore, the inherent heterogeneity in the pre-treatment soil sample data combined with the redistribution of soil characteristics in the post-treatment soil sample data resulting from the mixing effects, required that the data sets be averaged to provide useful interpretation of the treatment effectiveness. The pre- and post-treatment VOC results for T5 and T4 cells are presented in Appendices B and E respectively. It should be noted that several pre-treatment samples from the T4 and T5 cells with detectable levels of *cis*-1,2-DCE

are presented in Appendix B. No *cis*-1,2-DCE, however, was detected in any of the post-treatment samples from the T4 and T5 cells. Thus, the VOC mass removal efficiency discussion is limited to TCE because there is insufficient data regarding *cis*-1,2-DCE to make any significant conclusion other than it was completely removed by the DSM/KMnO₄ treatment.

The average TCE concentration for each soil boring was calculated by summing the depth-specific TCE values provided in Appendices B and E and dividing by the number of depth intervals in each boring. The TCE results from the pre- and post-treatment soil borings were treated in the same manner as previously discussed in the bioaugmentation section. Using the data in Appendices B and E, pre- and post-treatment average TCE concentrations in soil for the T5 and T4 cells have been averaged and are presented in Tables 4.7 and 4.8, respectively. The soil boring locations for the T5 and T4 cells are presented in Fig. 4.3.

Table 4.7. Pre- and post-treatment average TCE concentrations in T5 Cell borings

T5C1 Column				T5C2 Column				T5C3 Column			
Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg
T5B3	118.0	T5B2	11.4	T5B4	35.0	T5B2	11.4	T5B5	0.05	T5B5	0.9
		T5B3	8.4			T5B3	8.4				
						T5B4	27.3				

Table 4.8. Pre- and post-treatment average TCE concentrations in T4 Cell borings

T4C1 Column				T4C2 Column				T4C3 Column			
Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg
T4B3	336.7	T4B1	210.7	T4B4	202.2	T4B2	42.6	T4B5	161.2	T4B4	62.1
		T4B2	42.6			T4B3	58.5			T4B5	11.8
						T4B4	62.1				

The average TCE concentrations for each pre-treatment boring in each of the T5 columns shown in Table 4.7 were then averaged to arrive at an average pre-treatment

TCE concentration for each column. The respective average pre-treatment TCE concentrations for the C1, C2, and C3 columns are 118, 35, and 0.05 mg/kg, which yield an average pre-treatment TCE concentration of 51 mg/kg for the T5 cell. The mass of soil for the T5 cell was calculated using three 25-ft deep columns with 8-ft diameters, a 60% overlap for the center column, a particle density of 2.65 g/cm³ and an estimated porosity of 30%. The resulting mass of soil in the T5 cell is 158,548 kg which when multiplied by the average TCE concentration (51 mg/kg) for the T5 cell yields a total pre-treatment TCE mass of 8.1 kg.

The average TCE concentrations from each of the post-treatment soil borings in the T5 columns shown in Table 4.7 were treated in the same fashion and yield respective average post-treatment TCE concentrations for the C1, C2, and C3 columns of 9.9, 15.7, and 0.9 mg/kg which yield an average post-treatment TCE concentration of 8.8 mg/kg in the T5 cell. The calculated total mass of TCE remaining after mixing in the T5 cell (8.8 mg/kg TCE $\times$ 158,548 kg soil) is 1.4 kg. Comparing the pre- and post-treatment TCE mass values of 8.1 and 1.4 indicates an overall removal of 83% or 6.7 kg of TCE from the unsaturated soil in the T5 cell.

The data presented in Table 4.8 represent the pre- and post-treatment TCE concentrations from soil borings in the three columns of the T4 cell. These data were treated in the same manner described above and are discussed below. The average pre-treatment TCE concentration for the T4 cell using the average C1, C2, and C3 column average TCE values (337, 202, and 161 mg/kg derived from Table 4.8) is 233 mg/kg of TCE. The mass of soil in the T4 cell was calculated to be 298,161 kg using the same previously discussed parameters with exception of the 47-ft depth variable. The resulting mass of pre-treatment TCE in the T4 cell was then calculated to be 69.5 kg.

The average post-treatment TCE concentration for the T4 cell results from the averaging of the C1, C2, and C3 column average TCE values (127, 54, and 37 mg/kg derived from Table 4.8) and is 72.7 mg/kg of TCE. The mass of post-treatment TCE in the T4 cell was calculated (72.7 mg/kg TCE $\times$ 298,161 kg soil) to be 21.7 kg TCE and represents a mass reduction of 69% or 47.8 kg of TCE from the saturated soil in the T4 cell.

The 83% and 69% reductions in TCE mass achieved by the DSM/KMnO₄ compare favorably with the treatment objective of 70%. It is useful to note that different TCE mass reductions could be represented with the data sets. For example, the values could be calculated on a per-column basis rather than a per cell basis and show that one column (T5C3) where the post-treatment TCE exceeds the pre-treatment TCE mass. However, because of the inherent heterogeneity in soil sampling and the redistribution of soil characteristics introduced by the soil mixing process, it is difficult to draw any significant conclusion from this approach. Moreover, the bulk of the

pre-and post-treatment data from the T4 and T5 cells suggest that treatment did in fact take place and, thus, indicate that treatment of the data on a per-cell basis is appropriate.

Post-treatment groundwater samples were to be collected after installing piezometers into the boreholes created as a result of the soil sampling event. Although piezometers were installed in boreholes T5B3 and T4B3, most of the boreholes collapsed before the wells could be installed because of the high moisture content of the treated soils. Two groundwater samples collected from the T5B3 borehole had an average TCE concentration of 3.2 mg/L, representing a 40% decrease over the pre-treatment TCE concentration in groundwater for that column.

Groundwater samples from borehole T4B3 contained 4.2 mg/L of TCE which represents a 99% decrease from the 630 mg/L average TCE concentration the pre-treatment boring T4B3. A thorough evaluation of whether oxidant and or contaminants migrated out the mixed area could not be made due to the limited number of samples available. However, a KMnO_4 concentration of 1.1 wt % was detected in a groundwater sample from one of the adjacent biotreatment boreholes (T3B5) located immediately west of the T4 cell. Interestingly, this groundwater sample was the only one within the biotreatment cells in which no TCE was detected. (The average post-treatment TCE concentration in groundwater for the biotreatment cell (T3) was 37 mg/L.)

To satisfy MDNR permitting criteria, groundwater samples were collected from two existing monitoring wells (KC84-018L and KC84-018U) located approximately 100 ft hydraulically downgradient or north east of the T4 cell. The samples were collected July 23 and reported Mn concentrations of 551 and 6810 $\mu\text{g/L}$ in 18U and 18L respectively. These values are comparable with historical data from these wells.

4.2.4 Oxidation vs Vapor Stripping

The amount of TCE stripped from the subsurface from the initial drilling and subsequent mixing of the T5 and T4 columns is difficult to quantify for the reasons previously discussed. First, a limited number of off gas samples were analyzed with the GC (see Table 3.2). Second, the presence of other organic compounds (hydrocarbons and semi-volatiles) in the off gas stream limit the value of the total VOC recorded by the FID. Third, the lack of consistent off gas temperature and volume data due to previously discussed operating conditions, make this estimation more difficult.

It is obvious that the initial drilling of the cells using 800 to 1000 cfm of air was responsible for the volatilization of TCE and other unknown VOCs. It is also apparent

from the DAS graphic plots presented in Appendix C, that the subsequent passes with KMnO_4 triggered less volatilization. The peak total VOCs recorded with the FID range from 12,000 ppm in T5C3 to 44,000 ppm in T4C1. The peaks were all associated with the initial drilling of the columns and correspond to a depth of about 20 ft bgs where the highest amounts of TCE were identified in the pre-treatment borings. The effects of stripping following the initial drilling with air appear to taper off considerably as the total VOCs recorded after the initial peaks are typically below 200 ppm.

4.2.5 Other Post-Treatment Sample Results from KMnO_4 Cells

Following are summaries of post-treatment sampling results that include KMnO_4 and Mn concentrations in soil, soil pH, soil moisture content, soil carbon/organic carbon content, and soil microbial analysis.

4.2.6 Soil KMnO_4 and Mn Concentrations

Results from the treatability study (Appendix F) indicated nearly complete oxidant degradation within 24 h when contacted with KCP soils. This phenomenon is largely caused by rapid oxidant consumption by the soil's high natural SOM content. In addition, the mixed regions were not sampled until a minimum of three days after oxidant injection. The concentration of KMnO_4 for each background sample and each post-treatment sample collected from the mixed regions was determined on-site immediately after sample collection. A known mass of soil was extracted with 0.01 M NaCl, filtered, and analyzed via ultra violet visible spectrophotometry (525 nm) for KMnO_4 . Although this method is quick and economical, it is limited by a rather crude detection limit of 0.1 mg/kg for KMnO_4 . As expected, the KMnO_4 concentrations for the background soil boring (BKGBH2 in Fig. 4.1) were non detectable (< 0.1 mg/kg) because the background boring should not have been affected by the demonstration activities, being located approximately 150 ft west of the near KMnO_4 treatment cell. However, the lack of any detectable KMnO_4 in the shallow and deep treatment cells indicated that another indicator be used.

Because KMnO_4 degrades rapidly, Mn was used as an alternative indicator for the distribution of the oxidant reagent. Thus, analyses for Mn in the background and post-treatment samples were performed. In addition to the post-treatment soil borings collected from the treatment zone, two more soil borings were drilled from an area outside of the treatment columns, approximately 1 to 3 ft from the mixed columns (post T5B6 and post T4B6 in Fig. 4.3). Analyzing these samples for Mn would be useful in determining the extent, if any, of KMnO_4 migration outside of the treatment zone.

The Mn content of the soils was determined using a cation exchange procedure (Carter 1993), because Mn deposited on the soil as a result of KMnO_4 addition would likely be loosely bound to the soil surfaces. The results of the Mn analyses are presented in Figs. 4.4 and 4.5, for the shallow and deep cells, respectively. For comparison, Mn data for the background soil boring (BKGBH2) located approximately 150 ft from the treatment cells, is also provided in each of these figures. Use of Mn analyses, however, is unfounded by the fact that naturally occurring manganese dissolved by the highly reducing subsurface conditions can be found at ppm levels at the KCP. Nevertheless, the soil boring collected outside of the shallow cells (post T5B6 in Fig. 4.3) suggests that some Mn migration because the Mn concentrations there are higher than background but not nearly as great as those observed for the soil borings inside of the treated columns. [The average Mn soil concentration outside of the shallow cells (119 mg/kg) is approximately 32% of that found within the T5 columns (376 mg/kg)].

A similar Mn distribution was also observed in and around the deeper T4 treatment cells. The average Mn concentration within the T4 region was 442 mg/kg while the amount of Mn outside of the T4 cell is approximately 106 mg/kg or 24% of that within the T4 cell.

4.2.7 Soil pH

Soil pH typically increases after mixing with KMnO_4 . The background and post-treatment soil pH data are presented in Figs. 4.6 and 4.7 for the T5 and T4 cells, respectively. With the exception of the post T4B1 boring with an average pH of 6.9, the pH of each post-treatment soil boring was elevated above the average background soil pH of 7.0. The average soil pH from the five post-treatment soil borings in the T5 cell increased to 7.6, while an average pH of 8.0 was measured for the four post-treatment borings collected from the T4 cell. The pH of the KMnO_4 used during the demonstration was not measured or recorded; however, the pH of a 5 wt % KMnO_4 solution prepared in the laboratory with distilled water was measured to be 8.04. Thus, it appears that values obtained from the post-treatment samples are reasonable.

4.2.8 Soil Moisture Content

Post-treatment soil moisture contents were also determined for each soil boring location (including post-T5B6 and post-T4B6 outside of the mixed cells) as another means to evaluate oxidant migration and/or mixing homogeneity. During the course of the demonstration, a total of 67,039 liters (17,710 gal) of solution were added to

Fig. 4.4. Mn concentrations of the post-treatment T5 soil borings.

Fig. 4.5. Mn concentrations of the post-treatment T4 soil borings.

Fig. 4.7. Soil pH values of the post-treatment T4 soil borings.

Fig. 4.6. Soil pH values of the post-treatment T5 soil borings.

the mixed regions. The average soil moisture content of the background, untreated soil boring was found to be 28.10 wt %. The moisture contents obtained for the post-treatment samples are presented in Figs. 4.8 and 4.9 for the shallow and deep cell, respectively. All samples from within the treatment zones yielded moisture values significantly greater than the background samples. The average increase in moisture within the T5 columns was found to be 21% greater than background. The moisture content of the T5B5 soil boring was particularly elevated (47% greater than background). This effect may be attributed to the significant ponding in the T5C3 column which was mixed first. In fact, notes recorded in the field for the post-treatment boring T5B5 in the 2.5 to 3 ft depth interval stated that this sample appeared to be "a lot more wet/slurried than any other sample collected from the T5 cell."

The moisture content of the T4 cell samples increased from an average 28% to 41%. These observed increases appear to be a direct result of oxidant injection, because field records indicated that no rainfall events occurred between the mixing and subsequent sampling of the KMnO_4 cells. The average standard deviations computed for the soil borings was nearly constant ($= 5.2$ wt %) for both the T4 and T5 cells, suggesting homogeneous mixing (i.e., little variation in moisture with depth).

4.2.9 Soil Carbon and Organic Carbon Content

Because KMnO_4 also reacts readily with natural SOM, the background and post-treatment samples were also subjected to TC and TOC analyses to evaluate the effect of chemical oxidation on this soil property. All TOC and TC analyses were performed using a DorhmannTM DC 190 carbon analyzer. The TC values for selected soil borings from the shallow and deep cells are presented in Figs. 4.10 and 4.11, respectively. Similarly, the TOC values for selected soil borings from the shallow and deep cells are presented in Figs. 4.12 and 4.13, respectively. The TOC samples were pre-treated with a 1:4 $\text{HCl}/\text{H}_2\text{O}$ solution while being heated and mixed to sparge the samples of any carbonate species. Upon examination of the results, it was found that a direct comparison of the treated samples with the background soil boring could not be made. The post-treatment TC and TOC values were higher than background, probably due to the presence of residual organic contaminants in the post treated soils. Thus, the TOC/TC ratio was computed for each sample and appears to be the best parameter for evaluating the post-treatment results. It is assumed that the extent of oxidation (of both SOM and organic contaminants) increases as the TOC/TC ratio decreases. The TOC/TC ratios obtained for selected shallow and deep soil borings are presented in Fig. 4.14. In nearly all cases, the TOC/TC ratio at each depth interval is less than that of background. The average TOC/TC ratio for the background soil boring was calculated to be 0.88 ($= 0.18$), while the average value for the shallow and deep soil borings was found to be 0.59 ($= 0.14$) and 0.69 ($= 0.19$), respectively. Comparing the TOC/TC ratio for each soil boring with the VOC

Fig.4.8. Moisture contents of the post-treatment T5 soil borings.

Fig.4.9. Moisture contents of the post-treatment T4 soil borings.

Fig. 4.10. Total carbon results for the post-treatment T5 soil borings.

Fig. 4.11. Total carbon results for the post-treatment T4 soil borings.

Fig. 4.12. Total organic carbon results for post-treatment T5 soil borings.

Fig. 4.13. Total organic carbon results for the post-treatment T4 soil borings.

Fig. 4.14. TOC/TC ratios for selected post-treatment T5 and T4 soil borings.

removal data reveals that borings with the lower ratios (e.g., T5B1, T4B5) also had the lowest VOC concentrations.

4.2.10 Soil Microbial Analyses

To examine the influence of KMnO_4 on the natural microbial populations present in the soil, both anaerobic and aerobic microbial analyses were performed for the shallow and deep treatment cells. Samples for microbial assays were aseptically taken on-site and shipped back to ORNL for analysis within 72 h. The presence of anaerobic microbes was determined by using a dilute heterotrophic media. The media was prepared by adding 0.1 g/L glucose, 0.1 g/L yeast extract, 0.05 g/L peptone, 0.05 g/L tryptone, 0.6 g/L magnesium sulfate, 0.07 g/L calcium chloride, 0.1 g/L MOPS, 1 mL/L vitamins, 10 mL/L minerals, and 2 mL/L resazurin. The media was heated to a boil under N_2/CO_2 conditions, 0.5 g/L cysteine HCl was added, autoclaved, 2 mM PO_4 was added, and the pH was adjusted to 7.3 to 7.6. The heterotrophic microbes which are capable of growing in this media are methanogens, sulfate reducers, iron reducers, and denitrifiers. For further verification of microbial presence in the media, samples were taken from the media and examined under a microscope to determine the shape and whether the bacteria were gram negative or gram positive. Table 4.9 contains the results of the anaerobic sampling. The results suggest that the KMnO_4 did not have an adverse effect on the anaerobic microbes in the treated soils. The uniform distribution of anaerobic microbes in both cells, especially in the surface samples where their presence would not be expected, may be attributed to the mixing/homogenization which took place.

The presence of aerobic microbes was examined by using a plating method developed by Balkwill et al. (1989). The samples were prepared by blending in 0.1% $\text{Na}_4\text{P}_2\text{O}_7$ (pH 7). Serial dilutions of the blended samples were then prepared in phosphate buffered saline [8.3 mM Na_2HPO_4 , 16 mM NaH_2PO_4 , 0.15 M NaCl (pH 7.2)]. For plate counting, the serial dilutions were spread on a dilute medium (1% PTYG: peptone-tryptone-yeast extract-glucose medium). Figures 4.15 and 4.16 suggest that the aerobic activity appears to be higher in the T5 cell than in the deeper T4 cell, as would be expected. The deep soils, which were initially lower in CFUs (see background boring plot), appears to have been mixed with other regions of the column with higher initial concentrations similar to the mixing/ dilution that was observed for the VOC removal. As with the anaerobic microbes, the aerobic microbes did not appear to be negatively influenced by the addition of KMnO_4 to the soil.

Table 4.9. Anaerobic microbial sample results

Sample	Depth	1:1	1:10	1:100	1:1000	Description
BKG-BH2	6.5-7.0	+	+	0	0	10*01 gram negative, long rods
BKG-BH2	26.5-27.0	+	+	+	0	No reading
BKG-BH2	31.5-32.0	+	+	+	+	10*03 gram negative, long rods
BKG-BH2	36.5-37.0	0	0	0	0	No reading
T5-B1	21.5-22.0	+	+	+	0	10*02 gram negative, short rods
T5-B2	21.5-22.0	+	+	+	+	10*03 gram negative, short rods
T5-B3	21.5-22.0	+	+	+	+	10*03 gram negative, short rods
T5-B4	21.5-22.0	0	0	0	0	No reading
T5-B5	21.5-22.0	+	+	+	+	10*03 gram negative, medium rods
T4-B1	11.5-12.0	+	0	0	0	10*00 gram positive, medium rods
T4-B1	21.5-22.0	+	+	0	0	10*02 gram positive, long and segmented rods
T4-B1	36.5-37.0	+	+	+	0	10*02 gram positive, short rods
T4-B2	11.5-12.0	+	+	0	0	10*01 gram positive, medium rods
T4-B2	36.5-37.0	+	0	0	0	No reading
T4-B3	11.5-12.0	+	+	+	0	10*02 gram negative, short rods
T4-B3	36.5-37.0	+	+	0	0	10*01 gram negative, short and medium rods
T4-B4	36.5-37.0	+	+	0	0	10*01 gram negative, cocci
T4-B5	11.5-12.0	+	+	0	0	10*01 gram negative, long and short rods; gram positive, long rods cocci
T4-B5	36.5-37.0	+	+	0	0	10*01 gram positive, cocci; gram negative, long rods

Fig.4.15. Aerobic bacteria results for the post-treatment T5 soil borings.

Fig. 4.16. Aerobic bacteria results for the post-treatment T4 soil borings.

4.2.11 Evaluation of Cost for DSM Using KMnO_4

Geo-Con estimated the cost of treatment using KMnO_4 to be \$128/yd³ of soil assuming 30,000 yd³ of soil and a treatment depth of 30 ft. This is based on a equipment and crew cost of \$43/yd³, plus a material (KMnO_4) cost of \$46/yd³ (for a 5% slurry of KMnO_4), and a multiplier of 1.45 to cover overhead, safety, quality control, supervision, and profit.

4.3 DSM/MRVS and Powdered Calcium Oxide Injection Demonstration Results

4.3.1 Background Information

The demonstration project was originally designed to evaluate soil mixing coupled with MRVS which had proven to be successful at removing VOCs in unsaturated silty clays (West et al. 1995). Treatability studies using soil cores from KCP, however, indicated that MRVS coupled with calcium oxide injection would improve the TCE removal efficiency in saturated silty clay soils (West et al. 1995). The hydration of the calcium oxide upon contact with wet soil reduces the amount of free moisture, thereby increasing soil air porosity and the friability of the soil. Results of the treatability study indicated removal rates of up to 90% could be achieved using MRVS in soils conditioned with calcium oxide which compared with removal rates of less than 40% using MRVS in unconditioned soils. The treatability study concluded that the successful implementation of the MRVS coupled with calcium oxide delivery would depend on the development of equipment that is capable of delivering powdered calcium oxide during soil mixing. Such equipment has been used already in the geotechnical arena (Broms 1991). It should be noted that the equipment used by Broms (1991) was designed for stabilization of soil with lime columns and the largest diameter mixing apparatus used did not exceed 3 ft. Additionally, the calcium oxide was conveyed using an auger feed mechanism to lift the powder to top of the kelly bar where it was gravity-fed directly out of the bottom of the mixing tool. However, to convey the volume of calcium oxide needed to achieve a 10% mass loading level for the DSM/MRVS demonstration, an entirely different approach was conceived. The system used was comprised of a 30 ton silo equipped with a rotary valve that delivered 130 lbs of powdered lime per revolution into a dry conveyor. The second air compressor forced the lime from the dry conveyor to a "y" in the main hose where air from the first compressor would assist to push the powder through the main hose to the top of the kelly bar and eventually out through the nozzles in the mixing blade.

The first attempt to deliver lime to the subsurface resulted in clogging of the lines with lime due to high backpressure inherent in the delivery system. The hoses were cleared and a number of alternate injection sequences were attempted with the mixing tool at various depths and with air pressure over 100 psi and air flows over 3000 cfm, all of which resulted in repeated clogging. Although the expected maximum backpressure had been calculated by the subcontractor be 30 psi, the combination of system and geostatic pressure could not be overcome with 100 psi of air pressure—which was the operational limit of the dry conveyor system. It should be noted that the system was able to convey lime to the mixing tool when the latter was above ground and not subjected to any geostatic pressure. Thus, after the repeated attempts to inject lime, it was agreed by all parties that the lime injection could not be performed and that the scope of the DSM/MRVS would be limited to one test cell (3 columns) to 25 ft using heated air.

Therefore, a key question answered by the DSM/MRVS demonstration was that the dry lime conveyor system as configured with the mixing tool was not a viable mechanism to deliver calcium oxide. However, it is evident that the system used could be redesigned with fewer turns and constrictions. For example, if the 90 degree turn at the bottom of the kelly bar into the air box on the mixing blade followed by another 90 degree turn to exit the air box through the nozzles were eliminated by routing the powder straight through the bottom of the pilot bit, a great deal of backpressure would be eliminated. This was suggested as a possibility but was deemed untenable by Geo-Con due to the design of the mixing tool in use and all other available tools.

4.3.2 DSM/MRVS Operational Information

DSM/MRVS was conducted July 19 and 20 in three overlapping test columns (T7C1, T7C2, and T7C3) with 8-ft diameters and 25-ft depths. Column T7C3 was treated first and was followed by column T3C1, and finally column T3C2. Figure 4.17 illustrates the location and orientation of the three columns. Following are brief chronological summaries of the mixing efforts conducted as part the DSM/MRVS demonstration.

Fig. 4.17. T7 cell layout with soil boring locations.

T7C3 Column

Elapsed time	Process description
0 to 20 min	An 8-ft diameter hole drilled with air (1500 to 1700 cfm) to a depth of 25 ft, continued collapsed off gas tubing prevails.
20 to 51 min	Attempt powdered lime injection from 25 to 22 ft but cannot overcome backpressure, no lime delivered.
51 to 71 min	Mix with air (1700 cfm) from 22 ft to surface.
71 to 82 min	Reconfigure air lines to maximize pressure and flow (100 psi, 3000 cfm).
82 to 89 min	Attempt powdered lime delivery from surface to 4 ft, cannot overcome backpressure, pull auger to surface and successfully test delivery system above ground.
89 to 257 min	Change nozzle size from 0.5 in. to 1 in. to reduce back-pressure.
257 to 277	Attempt powdered lime delivery from surface to 7 ft, cannot overcome backpressure pull auger to surface.
277 to 348 min	Change nozzle size back to 0.5 in. to proceed with air stripping only.
348 to 369 min	Mix column with air (1700 cfm) from surface to 25 ft.
369 to 388 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.
388 to 416 min	Mix column with air (1700 cfm) from 1 ft to 25 ft.
416 to 427 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.
427 to 448 min	Mix column with air (1700 cfm) from 1 ft to 25 ft.
448 to 460 min	Mix column with air (1700 cfm) from 25 ft to surface, end of mix.

Following treatment of T7C3, the mixing apparatus was moved and located over the T7C1 column at the north end of the T7 cell.

T7C1 Column

Elapsed time	Process description
0 to 9 min	Prepare for drilling.
9 to 44 min	An 8-ft diameter hole drilled with air (1500 to 1700 cfm) to a depth of 25 ft, off gas tubing is collapsed.
44 to 55 min	Mix with air (1700 cfm) from 25 ft to 1 ft.
55 to 81 min	Mix with air (1700 cfm) from 1 ft to 25 ft.
81 to 87 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.
87 to 108 min	Mix column with air (1700 cfm) from 1 ft to 25 ft.
108 to 114 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.

114 to 131 min	Mix column with air (1700 cfm) from 1 ft to 25 ft.
131 to 138 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.
138 to 152 min	Raise auger, blow out ports with air, end of mix.

Following treatment of the T7C1 column, the mixing apparatus was moved and located over the T7C2 column located in the center of the T7 cell.

T7C2 Column

Elapsed time	Process description
0 to 20 min	An 8-ft diameter hole drilled with air (1500 to 1700 cfm) to a depth of 25 ft, off gas tubing is collapsed.
20 to 27 min	Mix with air (1700 cfm) from 25 ft to 1 ft.
27 to 108 min	Break for lunch and minor rig repairs.
108 to 133 min	Mix with air (1700 cfm) from 1 ft to 25 ft.
133 to 151 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.
151 to 173 min	Mix column with air (1700 cfm) from 1 ft to 25 ft.
173 to 188 min	Mix column with air (1700 cfm) from 25 ft to 1 ft.
188 to 211 min	Mix column with air (1700 cfm) from 1 ft to 25 ft.
211 to 230 min	Mix column with air (1700 cfm) from 25 ft to 1 ft, end of mix.

Table 4.10 lists the operational data from the thermal vapor stripping treatment cell.

During the MRVS demonstration in the T7 cell, an estimated total of 16,563 m³ (584,800 ft³) of air with an average temperature of 85 °C (185 °F) was injected into the T7 cell.

Table 4.10. DSM/MRVS operational data

Treatment column	Mix date	Air injected, m ³ (ft ³)	No. of passes
T7C1	7/20/96	3996 (141,100 ft ³)	4
T7C2	7/20/96	7173 (253,300 ft ³)	4
T7C3	7/19/96	5932 (190,400 ft ³)	4

Due to the close proximity of the columns, post-treatment sampling could not safely be conducted until all three columns had been mixed. This resulted in a minimum delay of three days between mixing and sampling. Post-treatment sampling information for each soil boring in the T7 cell is presented in Table 4.11. The soil boring locations for the T7 cell are presented in Fig. 4.17.

Table 4.11. MRVS post-treatment sampling information

Soil boring	Associated column	Sampling date	Days after mixing
BKG-BH2	NA	7/16/96	NA
T7B1	T7C1	7/23/96	3.1
T7B2	T7C2	7/23/96	2.8
T7B3	T7C3	7/23/96	3.8

n.a.: not applicable

4.3.3 Post-Treatment VOC Results From MRVS Cell

As previously discussed, the post-treatment boring locations were not intended to replicate the pre-treatment borings due to the redistributing effects of the mixing action.

The post-treatment samples were, however, collected in similar fashion and locations as the pre-treatment samples. Furthermore, the inherent heterogeneity in the pre-treatment soil sample data combined with the redistribution of soil characteristics in the post-treatment soil sample data resulting from the mixing effects, required that the data sets be averaged to provide useful interpretation of the treatment effectiveness. The pre- and post-treatment VOC results for the T7 cell are presented in Appendices B and E respectively. It should be noted that no detectable levels of *cis*-1,2-DCE were reported in the pre- and post-treatment data. Thus, the VOC mass removal efficiency discussion is limited to TCE only.

The average TCE concentration for each soil boring was calculated by summing the depth-specific TCE values and dividing by the number of depth intervals in each boring. The data were treated in the same manner as the other previously discussed VOC data from the bioaugmentation and oxidation cells. Using the data in Appendices B and E, pre- and post-treatment average TCE concentrations in soil for the T7 cell are presented in Table 4.12. The soil boring locations for the T7 cell cells are presented in Fig. 4.17.

Table 4.12. Pre- and post-treatment average TCE concentrations in T7 Cell borings

T7C1 Column				T7C2 Column				T7C3 Column			
Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg	Pre-treat boring No.	Average TCE, mg/kg	Post-treat boring No.	Average TCE, mg/kg
T7B1	11.7	T7B1	5.6	T7B2	31.7	T7B2	5.6	T7B4	7.6	T7B3	2.6
T7B2	11.8			T7B3	8.5						

The average TCE concentrations for each pre-treatment boring in each of the T7 columns shown in Table 4.12 were averaged to arrive at an average pre-treatment TCE concentration for each column. The respective average pre-treatment TCE concentrations for the C1, C2 and C3 columns are 11.8, 20.1, and 7.6 mg/kg, which yield an average pre-treatment TCE concentration of 13.2 mg/kg for the T7 cell. The mass of soil for the T7 cell was calculated using three 25 ft deep columns with 8 ft diameters, a 60% overlap for the center column, a particle density of 2.65 g/cm³ and an estimated porosity of 30%. The resulting mass of soil in the T7 cell is 158,548 kg of soil which when multiplied by the average TCE concentration of 13.2 mg/kg yields a total pre-treatment TCE mass of 2.1 kg in the T7 cell.

The average TCE concentrations from each of the post-treatment soil borings in the T7 columns shown in Table 4.12 were treated in the same fashion and yield respective average post-treatment TCE concentrations for the C1, C2 and C3 columns of 5.6, 5.6, and 2.6 mg/kg; which yield an average post-treatment TCE concentration of 4.6 mg/kg for the T7 cell. The estimated total mass of post-treatment TCE in the T7 cell is calculated to be 0.73 kg using the same column dimensions and previously mentioned parameters. Comparing the pre- and post-treatment values of 2.1 and 0.73 kg TCE indicates an overall removal rate of 65% or 1.4 kg of TCE from the T7 cell.

Based on the treatability study results (West et al. 1995) which used the same KCP soils to achieve TCE removal rates of 90% or better with the addition of calcium oxide to condition the soil by reducing the moisture content, it could be concluded that the field demonstration had the potential to achieve similar removal rates had the dry powder delivery system been successful.

While the 65% reduction in TCE falls below the overall treatment objective of 70%, it is useful to note that TCE concentrations verify that VOC reductions did occur. Also, as previously discussed, it is useful to note that different TCE mass reductions could be represented with the same data set. For example, the values could be calculated on a per column basis rather than a per cell basis and show a range of TCE

removal efficiency from 53% in C1 to 72% in C2. However, due to the previously discussed aspects associated with heterogeneity in soil sampling and redistribution of soil characteristics introduced by the soil mixing process, it is difficult to draw any significant conclusion from this approach. Moreover, all of the pre-and post-treatment data from the T7 cell suggests that treatment did in fact take place and, thus, indicate that treatment of the data on a per-cell basis is appropriate.

When a straightforward comparison between the MRVS and KMnO_4 demonstration results for unsaturated soils are made it would appear that the mass of TCE reduced by the vapor stripping (65%) compares favorably with that reduced by chemical oxidation in the shallow test cell (83%). It should be noted, however, that the comparison applies to unsaturated soil only. Additionally, had the shallow chemical oxidation cell been exposed to the degree of vapor stripping applied in the MRVS test cell, a higher TCE mass reduction would have been expected in the former cell.

Post-treatment groundwater samples were to be collected after installing piezometers into the boreholes created as a result of the sampling event. Although piezometers were installed in boreholes T7B1, T7B2, and T7B3, the piezometers were still dry after waiting 24 hours, thus, no groundwater samples were collected.

4.3.4 Evaluation of Cost for DSM Using MRVS

Geo-Con estimated the cost of treatment using hot air injection alone to be \$62/yd³ of soil assuming 30,000 yd³ of soil and a treatment depth of 30 ft. This is based on equipment and crew costs of \$43/yd³, plus a multiplier of 1.45 to cover overhead, safety, quality control, supervision, and profit.

5. CONCLUSIONS

The DSM technology demonstration performed at the KCP answered numerous questions regarding the efficiency, costs, and equipment limitations of delivering three in situ treatment reagents in stiff clay soils. As a result of the demonstration the following answers were provided:

- It is possible to drill to 47 ft in stiff clay soils and mix such soils efficiently using an 8 ft diameter mixing tool.
- The biggest limitation for drilling and mixing to 47 ft in KCP soils is fluid control when using water for initial drilling and liquid reagent injection during mixing. In either case, the fluids must be introduced at lower pumping rates to prevent their return to the surface and flooding of the work site.
- The most serious equipment limitation regarding dry powder injection was overcoming system and geostatic back pressure build up which leads to clogging of lines. With additional testing and development this limitation could be overcome and provide a cost effective in situ treatment technology.
- TCE mass reductions of 70% or more were demonstrated by coupling DSM with chemical oxidation using KMnO_4 . Results of the laboratory treatability study suggested that TCE removals greater than 90 wt % could be achieved using KMnO_4 solutions of at least 4 wt %, with oxidant loadings greater than 16 g KMnO_4 /kg soil. During the demonstration, up to 69 % TCE removal in saturated soil and 83% TCE removal in unsaturated soil were achieved using a much lower average loading (6 g KMnO_4 /kg soil). A lower oxidant loading was chosen for the field due to the limitation of the volume of oxidant which could be added to the low permeable soils. Thus, the 60% reduction in the oxidant loading used in the field still resulted in acceptable TCE reductions.
- TCE mass reductions of 65% were demonstrated by coupling DSM with MRVS in soils with moisture content averaging 19%. Had the injection of powdered lime been achieved, treatability studies indicated that the mass reduction of TCE could be as high as 90%.
- TCE mass reductions of 38% were demonstrated by coupling DSM with bioaugmentation in soil TCE concentrations that are considered toxic to the injected bacterial population. Had the bioaugmentation been performed in soil with lower TCE concentrations, the mass removal rate may have reached the 70% objective.

- Based on the results of the DSM/Bioaugmentation demonstration it can be concluded that the chemical, physical and biological properties of the soil remain intact.
- Viable TCE degrading bacteria were recoverable from the upper treatment depths (0 to 13 ft bgs) for at least 10 days suggesting that TCE degradation could be continued if other limiting factors such as oxygen were augmented.
- Post-treatment microbiological studies determined that survivability of G4 below 13.5 ft was minimal probably due to the high TCE concentrations (up to 527 mg/kg) encountered at these depths. However, laboratory testing of surviving bacteria demonstrated successful degradation of TCE confirming that G4 was added to the subsurface and survived the DSM process where the TCE concentrations did not have toxic effects.
- Based on the results and observations of the field demonstration it can be concluded that treatment reagent migration beyond the boundary of the soil column is minimal. Reagent migration is limited to areas with inherent preferential flow networks such as fractures which are exploited and magnified by the high pressure/high volume flow of air used during initial drilling of the soil columns.
- Based on the results of the DSM/KMnO₄ demonstration it can be concluded that the physical and biological properties of the soil remain essentially intact. The results from both anaerobic and aerobic bacteria sampling indicate that neither were greatly influenced by the addition of the oxidant. The presence of the anaerobic microbes and the CFU values for the aerobic microbes suggest that the KMnO₄ treatment could be amended with a microbial remediation treatment. Microbial activity also appears to be more evenly distributed with soil depth as a result of the mixing process. Due to the low oxidant loading used and the high organic content of the pre-treated soil, KMnO₄ was not observed in the post-treatment samples, and a SOM fraction remained in the soils following treatment. Soil moisture was also affected during DSM, the average background soil moisture of 28% increased to 34% and 41% for the shallow and deep treatment cells, respectively. Increases in soil pH were also observed, due to addition of KMnO₄, and these increases were not greater than the pH of the oxidant which was added.
- Based on the results of the DSM/KMnO₄ demonstration it can be concluded that the treatment reagent was well distributed in the soil as manifested by the distribution of Mn.

- Based on the results of the DSM/KMnO₄ demonstration it can be concluded that treatment levels predicted from laboratory treatability studies can be achieved in the field.
- Although treatment costs using KMnO₄ are estimated to be \$128/yd³ of soil which is roughly twice the cost of the other treatments (bioaugmentation was \$77/yd³ and MRVS was \$62 yd³), it should be noted that the oxidation treatment was also applied in both saturated and unsaturated conditions and had the highest removal efficiency.

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Innovative Treatment for TCE-Contaminated Saturated Clay Soils in Emerging Technologies in Hazardous Waste Management VII Extended Abstracts presented for the Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society.

APPENDIX A

Pre-treatment Lithologic Borings

Prepared By: M. F. MURPHY Date: 4/15/95 Page: 1 OF 1
 Hole No.: Y1R1 Ground Elevation: _____
 Total Depth: 51' Rig Type: Model B-61 Location: NE Area Former Ponds
 Auger Size: 6.25" O.D. Sample Type: 5" CMF Continuous Barrel
 Project: KCF-DSM Data Verified By: D. R. Smuin Date: 5/15/95

DEPTH (FEET)	SAMPLE TYPE	SAMPLE DATA	LITHOLOGY	DESCRIPTION
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.
2	CS			
4				FILL: strong brown (7.5YR 5/6), firm to moderately stiff, damp, predominantly silty clay with common black organic debris, scattered coarse grained sand, occasional limonite staining, common small root hairs, no odors.
6	CS			
8				
10				Obstruction at 10', probable large cobble. Pull sampler and auger through.
12	CS			
14				Poor sample recovery from 10 to 15', debris from above obstruction blocking shoe. What small amount that was recovered appears to be predominantly fill grading into native soil.
16	CS			
18				ML CLAYEY SILT: dark to very dark gray (5Y 4/1 to 3/1), soft, moist, scattered small open pores <1mm, common very fine grained sand from approximately 17.5-19.2', visible oily sheen with a moderate to strong hydrocarbon odor in the same interval, decreases rapidly below 18.2', absent by 19, moisture content increasing with depth.
20	CS			
22				
24	CS			CL SILTY CLAY: color as above, moist, firm, medium plasticity, abundant roots and root pores up to 5mm in diameter, abundant carbonized wood fragments from 24-25', grades back to a clayey silt at 25', no pores.
26	CS			
28				
30	CS			ML CLAYEY SILT: very dark gray (5Y 3/1), soft, wet in the pore spaces at approximately 26', entire interval is wet by 29', fairly homogeneous, micaceous, scattered carbonaceous debris, occasional small roots and root pores <.5mm becoming absent by 27', scattered, open pores to 1mm.
32	CS			
34				ML CLAYEY SILT: very dark gray (5Y 3/1), soft, wet common small open pores usually 1mm or less, abundant small vertical fractures from 31-34', sides of the fractures and pores are FeO stained occasional fractures are FeO filled, scattered zones exhibit a granular texture due to numerous pebs, these zones have noticeably more free water, decreasing FeO staining by 35', absent below 35'.
36	CS			
38				
40	CS			ML CLAYEY SILT: color as above, very soft, wet, very homogeneous, sticky, occasional small open pores <1mm, beginning to see lenses of greenish gray sandy silt, lenses range in thickness from 2-5mm and are increasing with depth, entire interval becomes very sandy right above the gravel zone.
42	CS			
44				
46	CS			GM SILTY GRAVEL: dark greenish gray (5G 4/1), angular to subrounded limestone, sandstone and occasional chert gravels to 1" in a sandy to clayey silt matrix, wet, sand is predominantly fine grained subrounded quartz with some chert, scattered carbonaceous debris.
48	CS			
50	CS			Top of Bedrock 51', T.D. 51'.
52				
54				

orn1

Borehole Summary Information
OAK RIDGE NATIONAL LABORATORY

Prepared By: M.E. Mumby Date: 5/1/95 Page: 1 OF 1
 Hole No.: T7B3 Ground Elevation: _____
 Total Depth: 25' Rig Type: Mobil B-61 Location: NE Area Former Ponds
 Auger Size: 6.25" O.D. Sample Type: 5' CME Continuous Barrel
 Project: KCP-DSM Data Verified By: D.R. Smuin Date: 5/15/95

DEPTH (FEET)	SAMPLE TYPE	SAMPLE INTV	LITHOLOGY	DESCRIPTION
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.
2	CS			
4				FILL: very dark gray (10YR 3/1), stiff to very stiff, predominantly silty clay with common interbedded sand, gravel, and organic debris, occasional larger cobbles present, slight difficulty in drilling with sampler in hole, never to the point where it had to be removed, one cobble to 2" present in sampler.
6				
8	CS			
10				
12	CS			ML CLAYEY SILT: dark gray (5Y 4/1), firm, moist, becoming slightly crumbly, common small roots, <1mm, moderate hydrocarbon odor.
14				
16				ML CLAYEY SILT: dark gray (5Y 4/1), firm, moist, common open pores to 1.5mm, soil cohesiveness rapidly deteriorating below 15', visible product present in the pore spaces and on freshly broken sample faces from 15-20', very strong hydrocarbon odor.
18	CS			
20				
22	CS			ML CLAYEY SILT: color as above, soft, crumbly, becoming wet at approximately 23', entire sample interval from 20-25' is covered with an oily sheen, abundant free product is visible from 20-23', very little native structure left in the soil from 20-25', extremely strong hydrocarbon and solvent odor, crumbly texture due to the amount of product present.
24				T.D. 25'
26				
28				
30				

orn1

Borehole Summary Information

OAK RIDGE NATIONAL LABORATORY

Prepared By: M.E. Mumby		Date: 4/21/95		Page: 1 OF 1	
Hole No.: T5B3		Ground Elevation:			
Total Depth: 25'		Rig Type: Mobil B-61		Location: NE Area Former Ponds	
Auger Size: 6.25" O.D.		Sample Type: 5' CME Continuous Barrel			
Project: KCP-DSM		Data Verified By: D.R. Smuin		Date: 5/15/95	

DEPTH (FEET)	SAMPLE TYPE	SAMPLE INTV	LITHOLOGY	DESCRIPTION
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.
2	CS			FILL: brown (10YR 5/3), stiff, moist, silty clay with abundant organic debris, common roots up to 2mm in diameter.
4				
6	CS			FILL: very dark gray (10YR 3/1), stiff to very stiff, predominantly silty clay with abundant interbedded sand, gravel, and organic debris, largest gravels present in sampler were 3/4", no odors.
8				
10				ML CLAYEY SILT: very dark gray (5Y 3/1), firm, moist, blocky, appears re-worked.
12	CS			ML CLAYEY SILT: dark gray (5Y 4/1), firm, becoming slightly crumbly, common small roots, <1mm, moderate hydrocarbon odor.
14				
16	CS			ML CLAYEY SILT: dark gray (5Y 4/1), firm, moist, common open pores to 1.5mm, soil cohesiveness rapidly deteriorating below 15', visible product present in the pore spaces and on freshly broken sample faces from 15-20', very strong hydrocarbon odor.
18				
20	CS			ML CLAYEY SILT: color as above, soft, crumbly, becoming wet at approximately 23', entire sample interval from 20-25' is covered with an oily sheen, abundant free product is visible from 20-23', very little native structure left in the soil from 20-25', extremely strong hydrocarbon and solvent odor, crumbly texture due to the amount of product present.
22				
24				
26				T.O. 25'
28				
30				

orn1

OAK RIDGE NATIONAL LABORATORY

Borehole Summary Information

Prepared By: <u>M.E. Mumby</u>		Date: <u>4/24/95</u>		Page: <u>1 OF 1</u>	
Hole No.: <u>T4B2</u>		Ground Elevation: _____			
Total Depth: <u>47.5'</u>		Rig Type: <u>Mobil B-61</u>		Location: <u>NE Area Former Ponds</u>	
Auger Size: <u>6.25" O.D.</u>		Sample Type: <u>5' CME Continuous Barrel</u>			
Project: <u>KCP-DSM</u>		Data Verified By: <u>D.R. Smuin</u>		Date: <u>5/15/95</u>	
DEPTH (FEET)	SAMPLE TYPE	SAMPLE INTV	LITHOLOGY	DESCRIPTION	
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.	
2	CS			FILL: dark to very dark brown (7.5YR 4/6), stiff, slightly moist, predominantly silty clay with scattered coarse grained sand and small gravels to 1/8", common carbonaceous debris, scattered small roots <1mm.	
4					
6					
8	CS			FILL: very dark gray to black (10YR 3/1-2/1), very stiff, dry to a trace moist, predominantly silty clay with abundant interbedded gravels to 1.5" and coarse grained sand, slight hydrocarbon odor at 10', increasing with depth.	
10					
12	CS				
14					
16					
18	CS			ML CLAYEY SILT: dark gray (5Y 4/1), soft, slightly moist, scattered open pores and black argillans usually 1mm or less, starting to see visible product by 15', most concentrated in the pore spaces and argillans, soil is loosing its cohesiveness with depth due to the abundance of product present, very crumbly by 20'.	
20					
22	CS				
24					
26					
28	CS			ML CLAYEY SILT: dark gray (5Y 4/1), soft, very crumbly, difficult to distinguish any native structure in the soil, abundant free product above 23', very strong hydrocarbon odor, becomes wet at 23' with a very strong solvent odor solvent odor at 25', soil still very crumbly to 30' due to the amount of oil and solvent present, 25-30' sampler coated with oil.	
30					
32	CS			ML CLAYEY SILT: very dark gray (5Y 3/1), soft, wet, scattered open pores usually 1mm or less, occasional pores to 2-3mm, some vertical fracturing is present from 34-40', scattered FeO staining, pore spaces and fracture faces have an oily sheen present along with small pinpoint beads of brown oil, soil cohesiveness is far below what is usually present at this depth, very strong hydrocarbon and solvent odor is still present.	
34					
36					
38	CS				
40					
42	CS			ML CLAYEY SILT: grading from a very dark gray to a dark greenish gray (5GY 4/1) at approximately 41.5', scattered lenses of sandy silt present at 42' and are up to 4mm thick, becoming sandy at 42.5', sand is very fine to fine grained predominantly quartz with some chert, slight solvent odor.	
44					
46					
48	CS			GM SILTY GRAVEL: dark greenish gray (5BG 4/1), angular to sub-rounded limestone and sandstone gravels to 1" in a sandy silt matrix, saturated, grades to gravelly silt from approximately 47-47.5'.	
50				Top of bedrock 47.5', T.D. 47.5'.	

orn1

Borehole Summary Information
OAK RIDGE NATIONAL LABORATORY

Prepared By: M.E. Mumby Date: 4/20/95 Page: 1 OF 1
 Hole No.: T383 Ground Elevation: _____
 Total Depth: 25' Rig Type: Mobil 8-61 Location: NE Area Former Ponds
 Auger Size: 6.25" O.D. Sample Type: 5' CME Continuous Barrel
 Project: KCP-DSM Data Verified By: D.R. Smuin Date: 5/15/95

DEPTH (FEET)	SAMPLE TYPE	SAMPLE INTV	LITHOLOGY	DESCRIPTION
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.
2	CS			FILL: dark grayish brown (10YR 4/2) with common streaks of yellowish red (5YR 4/6) silty clay, stiff, slightly moist, common organic debris, occasional small roots 1mm or less.
4				
6				
8	CS			FILL: very dark gray (10YR 3/1), firm, moist, predominantly silty clay with abundant inter-bedded coarse grained sand and gravel to 1.5", occasional roots and root channels, slight solvent odor, no large cobbles encountered as in previous cells (T1, T2).
10				
12	CS			
14				ML CLAYEY SILT: dark gray (5Y 4/1), moderately stiff, moist, scattered open pores and black argillans, occasional small roots <1mm and very very fine grained sand, slight solvent odor increasing rapidly at approximately 15', visible product present in the pore spaces and argillans below 15'.
16				
18	CS			
20				ML CLAYEY SILT: color as above, soft, crumbly, visible oily sheen present on outside of sample, freshly broken faces appear wet but are saturated with product, extremely strong solvent odor at 20', sample is very saturated with product to 23', becomes wet at approximately 23', crumbly texture is most likely the result of the solvent breaking down the native structure of the soil, decreasing solvent odor at 25'.
22	CS			
24				
26				T.D. 25'.
28				
30				

ornl

Borehole Summary Information
OAK RIDGE NATIONAL LABORATORY

Prepared By: D.A. Pickering Date: 4/20/95 Page: 1 OF 1
 Hole No.: T2B3 Ground Elevation: _____
 Total Depth: 49' Rig Type: Mobil B-61 Location: NE Area Former Ponds
 Auger Size: 6.25" O.D. Sample Type: 5' CME Continuous Barrel
 Project: KCP-DSM Data Verified By: M.E. Mumby Date: 5/15/95

DEPTH (FEET)	SAMPLE TYPE	SAMPLE INTV	LITHOLOGY	DESCRIPTION
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.
2	CS			FILL: strong brown (7.5YR 4/6), firm to stiff, predominantly silty clay with common dark brown inclusions, damp, abundant roots and organic debris, occasional siltstone inclusions to 1', no odors.
4	CS			Obstruction at 6', pulled sampler and auger to 7'.
6				FILL: brown (7.5YR 5/2), stiff, dry, silty clay with abundant limestone and siltstone cobbles >3", crumbly, common FeO staining.
8	CS			Large obstruction at 10', could not auger through. Pulled augers and moved rig 1' to the west.
10				Augered to 12', very difficult drilling from approximately 10-12'. Ran sampler back in at 12', partial recovery from 12-15'. Appear to be out of the fill at approximately 14'?
12	CS			
14				
16	CS			ML CLAYEY SILT: very dark gray (2.5Y 4/1) damp, oily sheen on freshly broken sample faces, occasional very fine grained clear quartz sand grains from 15-17', occasionally mottled with FeO staining.
18				
20				
22	CS			PT PEAT: black (2.5Y 2.5/1), wood fragments and broken down organic material, occasional intact roots, wet, slight hydrocarbon odor.
24				
26				
28	CS			
30				ML CLAYEY SILT: very dark gray (5Y 3/1), soft, wet, common FeO staining increasing with depth, common pores up to 2mm lined with FeO stain.
32	CS			
34				
36				
38	CS			ML CLAYEY SILT: very dark gray (5Y 3/1), soft, plastic, wet, no visible FeO staining.
40				
42	CS			
44				
46	CS			GM GRAVELLY SILT: dark greenish gray (5GY 4/1), soft, sandy, gravels are predominantly limestone and sandstone up to 1", wet.
48				
50				Top of bedrock 48.5, T.D. 49'.

orn1

Borehole Summary Information

OAK RIDGE NATIONAL LABORATORY

Prepared By: <u>M.E. Mumby</u>		Date: <u>4/19/95</u>		Page: <u>1 OF 1</u>
Hole No.: <u>T183</u>		Ground Elevation: _____		
Total Depth: <u>25'</u>		Rig Type: <u>Mobil B-61</u>	Location: <u>NE Area Former Ponds</u>	
Auger Size: <u>6.25" O.D.</u>		Sample Type: <u>5' CME Continuous Barrel</u>		
Project: <u>KCP-DSM</u>		Data Verified By: <u>D.R. Smuin</u>	Date: <u>5/15/95</u>	

DEPTH (FEET)	SAMPLE TYPE	SAMPLE INTV	LITHOLOGY	DESCRIPTION
0				PT HUMUS: very dark gray (10YR 3/1), abundant grass, roots, and organic debris.
2	CS			FILL: strong brown (7.5YR 4/4), stiff, slightly moist, predominantly silty clay with scattered medium to coarse grained sand, occasional gravel to 1", common small roots 1mm or less, scattered carbonaceous debris.
4	CS			FILL: very dark gray (5Y 3/1), stiff slightly moist, silty clay/clayey silt with abundant interbedded sand and gravel.
6				Gravel layer from 6-8' difficult drilling, pulled sampler to auger through.
8	CS			FILL: very dark gray to black (5Y 3/1-2.5/1), soft predominantly silty clay with common coarse grained sand and wood fragments, occasional carbonaceous debris, interval from 8-13' exhibits an oily sheen which, appears wet from approximately 8-10' but is actually saturated with product which decreases rapidly below 10', very strong hydrocarbon odor present from 8-10', grades to a sulphurous/organic odor from 10-13'.
10				
12	CS			
14				
16				
18	CS			ML CLAYEY SILT: dark gray (5Y 4/1), moderately stiff, moist, scattered zones have a dark gray to gray (7.5YR 4/1-5/1) mottle, occasional black argillans, occasional small open pores <1mm, scattered FeO staining, no odors.
20				
22	CS			
24				ML CLAYEY SILT: very dark gray (5Y 4/1), soft, becoming wet at approximately 24', scattered small open pores <1mm, occasional small root hairs <1mm in diameter.
26				T.D. 25'.
28				
30				

APPENDIX B

Kansas City Plant Deep Soil Mixing Demonstration Project

Pre-treatment *cis*-1,2-DCE and TCE Content in Soil, $\mu\text{g/kg}$ and Groundwater, $\mu\text{g/L}$

APPENDIX B

Kansas City Plant Deep Soil Mixing Demonstration Project

Pre-treatment *cis*-1,2-DCE and TCE Content in Soil, $\mu\text{g/kg}$ and Groundwater, $\mu\text{g/L}$

Pre-Treatment samples from T1 Cell

Pre-T1B1

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
050	01	4.96	1x	<2000	<2000	<5.0	<5.0
052	10	3.85	1x	29,200	37,900	2J	2J
054	11	5.74	1x	22,800	19,850	2J	2J
056	15	4.51	1x	3420	3800	2J	2J
057	16	4.19	1x	2990	3550	2J	2J
058	19	5.04	1x	<2000	<2000	<5.0	<5.0
059	21	5.15	1x	<2000	<2000	<5.0	<5.0
060	21D	5.33	1x	<2000	<2000	<5.0	<5.0
061	25W	NA	1x	28,800	NA	<5.0	NA

Pre-T1B2

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
038	01	4.59	1x	<2000	<2000	2J	2J
040	06	4.81	1x	4950	5150	<5.0	<5.0
042	06D	3.88	1x	4110	5300	<5.0	<5.0
043	11	5.90	1x	<2000	<2000	<5.0	<5.0
045	16	4.96	1x	<2000	<2000	2J	2J
047	21	5.20	1x	<2000	<2000	<5.0	<5.0
049	25W	NA	1x	45,300	NA	2J	NA

B-2

Pre-T1B3

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
031	01	5.12	1x	<2000	<2000	2J	2J
032	06	4.31	1x	<2000	<2000	42	48.5
033	10	5.73	1x	<2000	<2000	<5.0	<5.0
034	11	3.95	1x	<2000	<2000	<5.0	<5.0
035	16	5.22	1x	<2000	<2000	<5.0	<5.0
036	21	4.59	1x	<2000	<2000	<5.0	<5.0
037	25	5.78	1x	<2000	<2000	<5.0	<5.0

Pre-T1B4

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
023	01	5.72	1x	<2000	<2000	<5.0	<5.0
024	06	6.36	1x	<2000	<2000	2J	2J
025	11	6.34	1x	<2000	<2000	<5.0	<5.0
026	16	5.57	1x	<2000	<2000	<5.0	<5.0
027	21	5.89	1x	<2000	<2000	<5.0	<5.0
028	21D	5.06	1x	<2000	<2000	<5.0	<5.0

Pre-T1B5

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
018	01	5.19	1x	<2000	<2000	<5.0	<5.0
019	06	5.31	1x	<2000	<2000	2J	2J
020	11	7.22	1x	<2000	<2000	<5.0	<5.0
021	16	6.17	1x	<2000	<2000	<5.0	<5.0
022	21	4.81	1x	<2000	<2000	<5.0	<5.0

D: soil sample duplicate

J: estimated concentration

NA: not applicable

W: groundwater sample (denoted by italics and shading)

Pre-treatment samples from T2 Cell

Pre-T2B1

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, μg/kg	TCE, gross	TCE, μg/kg
164	01	5.14	1x	<2000	<2000	2.6	1.0
165	11	6.32	100x	52,000	41,150	50,040	39,600
166	16	6.19	100x	<2000	<2000	3890	2640
167	21	5.51	1x	<2000	<2000	<5.0	<5.0
168	26	5.41	1x	<2000	<2000	<5.0	<5.0
171	31	6.31	1x	<2000	<2000	<5.0	<5.0
172	36	5.69	1x	<2000	<2000	<5.0	<5.0
174	41	5.26	1x	<2000	<2000	37	35
175	46	4.66	1x	<2000	<2000	<5.0	<5.0
169	30W	NA	1x	<2000	NA	212	NA
170	30WD	NA	1x	<2000	NA	236	NA
173	40W	NA	1x	<2000	NA	817	NA
176	50W	NA	1x	<2000	NA	622	NA

Pre-T2B2

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, μg/kg	TCE, gross	TCE, μg/kg
149	01	4.03	1x	<2000	<2000	2J	2J
150	11	5.41	10x	52,000	48,050	8420	7800
151	16	6.40	100x	<2000	<2000	13,150	10,250
152	21	5.75	1x	<2000	<2000	<5.0	<5.0
153	26	2.21	1x	<2000	<2000	<5.0	<5.0
155	31	6.06	1x	<2000	<2000	<5.0	<5.0
156	36	6.27	1x	<2000	<2000	<5.0	<5.0
159	41	6.00	1x	<2000	<2000	176	147
160	41D	5.28	1x	<2000	<2000	2J	2J
161	46	4.88	1x	<2000	<2000	<5.0	<5.0
162	49	5.83	1x	<2000	<2000	<5.0	<5.0
154	30W	NA	1x	<2000	NA	178	NA
158	40W	NA	1x	<2000	NA	632	NA
163	49W	NA	1x	<2000	NA	433	NA

Pre-T2B3

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, µg/kg	TCE, gross	TCE, µg/kg
062	01	5.57	1x	<2000	<2000	2J	2J
063	08	5.27	1x	27,110	18,650	530	365
064	13	5.97	1x	44,340	37,150	20,820	17,450
065	16	5.87	1x	16,900	14,400	25,740	21,950
066	21	4.67	1x	<2000	<2000	<5.0	<5.0
067	26	5.97	1x	<2000	<2000	<5.0	<5.0
069	31	4.27	1x	<2000	<2000	1.5J	2J
070	36	4.27	1x	<2000	<2000	<5.0	<5.0
072	41	4.82	1x	<2000	<2000	<5.0	<5.0
073	46	5.28	1x	<2000	<2000	<5.0	<5.0
074	46D	5.39	1x	<2000	<2000	<5.0	<5.0
075	49	5.54	1x	<2000	<2000	<5.0	<5.0
068	30W	NA	1x	39,890	NA	118	NA
071	40W	NA	1x	18,400	NA	102	NA
076	49W	NA	1x	15,580	NA	150	NA

Pre-T2B4

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, µg/kg	TCE, gross	TCE, µg/kg
133	01	5.83	1x	<2000	<2000	20	17
134	06	5.14	1x	8879	8650	132	129
135	10	4.11	10x	190,600	231,850	3760	4575
136	11	5.77	1x	87,920	76,200	120	104
137	16	6.65	100x	<2000	<2000	35,550	26,750
138	21	4.20	1x	<2000	<2000	<5.0	<5.0
139	26	4.94	1x	<2000	<2000	<5.0	<5.0
141	31	3.39	1x	<2000	<2000	<5.0	<5.0
142	36	4.78	1x	<2000	<2000	<5.0	<5.0
144	41	4.45	1x	<2000	<2000	<5.0	<5.0
145	41D	5.48	1x	<2000	<2000	<5.0	<5.0
146	46	5.36	1x	<2000	<2000	<5.0	<5.0
147	49	4.89	1x	<2000	<2000	<5.0	<5.0
140	30W	NA	1x	4280	NA	254	NA
143	40W	NA	1x	19,980	NA	869	NA
148	49W	NA	1x	7850	NA	516	NA

Pre-T2B5

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, μg/kg	TCE, gross	TCE, μg/kg
114	01	6.40	1x	<2000	<2000	2J	2J
115	06	5.64	10x	<2000	<2000	191	170
116	09	3.88	100x	433,000	558,000	103,200	133,000
117	11	4.09	100x	67,530	82,500	685	840
118	16	6.79	100x	<2000	<2000	37,000	27,250
119	20	4.51	100x	<2000	<2000	64	70
120	21	3.81	100x	<2000	<2000	<5.0	<5.0
121	21D	4.34	100x	<2000	<2000	33	40
123	26	5.63	1x	<2000	<2000	<5.0	<5.0
124	31	5.88	10x	<2000	<2000	<5.0	<5.0
126	36	6.28	10x	<2000	<2000	<5.0	<5.0
128	41	5.25	100x	<2000	<2000	<5.0	<5.0
129	46	4.97	1x	<2000	<2000	<5.0	<5.0
130	46D	5.63	1x	<2000	<2000	<5.0	<5.0
<i>122</i>	<i>25W</i>	<i>NA</i>	<i>1x</i>	<i>19,310</i>	<i>NA</i>	<i>1470</i>	<i>NA</i>
<i>127</i>	<i>40W</i>	<i>NA</i>	<i>1x</i>	<i>25,060</i>	<i>NA</i>	<i>2220</i>	<i>NA</i>
<i>131</i>	<i>50W</i>	<i>NA</i>	<i>10x</i>	<i>20,440</i>	<i>NA</i>	<i>1280</i>	<i>NA</i>

D: soil sample duplicate

J: estimated concentration

NA: not applicable

W: groundwater sample (denoted by italics and shading)

WD: groundwater sample duplicate

B-6

Pre-treatment samples from T3 Cell

Pre-T3B1

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
281	01	6.25	1x	<2000	<2000	150	120
282	06	6.36	100x	<2000	<2000	57,500	45,200
283	06D	5.85	100x	<2000	<2000	16,830	14,400
284	11	5.30	100x	<2000	<2000	9090	8600
285	16	5.64	1x	25,300	22,430	1J	1J
286	21	5.55	1x	65,570	59,070	101	91
287	25	5.82	1x	<2000	<2000	164	141
288	25W	NA	1x	<2000	NA	533	NA

Pre-T3B2

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
272	01	4.78	1x	<2000	<2000	34	35
273	06	5.32	10x	<2000	<2000	2640	2480
275	11	6.48	10x	<2000	<2000	8700	6700
276	16	5.19	100x	<2000	<2000	82,310	79,300
277	21	5.24	1000x	<2000	<2000	209,900	200,300
278	25	6.15	10x	<2000	<2000	891	725
279	25W	NA	10x	<20000	NA	6780	NA

Pre-T3B3

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
077	03	5.80	1x	<2000	<2000	31	27
078	07	6.03	1x	<2000	<2000	252	210
079	05	3.85	100x	4280	5550	40,380	52,450
080	11	5.91	1x	2210	1870	686	580
081	20	5.65	1000x	<2000	<2000	579,400	512,500
082	16	5.97	1000x	<2000	<2000	202,400	169,500
083	21	5.19	1000x	<2000	<2000	299,700	288,750
084	25W	NA	100x	<2000	NA	10,180	NA

Pre-T3B4

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
260	01	6.08	1x	<2000	<2000	<5.0	<5.0
261	06	5.92	1x	<2000	<2000	5.3	2J
262	11	5.96	1x	<2000	<2000	2J	2J
263	16	5.47	100x	<2000	<2000	41,550	38,000
264	16D	5.32	100x	<2000	<2000	60,170	56,550
265	21	5.55	1000x	<2000	<2000	141,700	127,650
266	25	4.45	1000x	<2000	<2000	322,000	361,800
268	26	5.72	1000x	<2000	<2000	603,600	527,500
267	25W	NA	10000x	<2000	NA	3,160,000	NA

Pre-T3B5

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
253	01	5.64	1x	<2000	<2000	<5.0	<5.0
254	06	5.03	1x	<2000	<2000	<5.0	<5.0
255	11	5.96	1x	<2000	<2000	<5.0	<5.0
256	16	5.80	1000x	<2000	<2000	181,200	156,200
257	21	5.03	1000x	<2000	<2000	263,320	261,750
258	25	4.61	100x	<2000	<2000	58,890	63,850
259	25W	NA	1000x	<2000	NA	683,100	NA

D: soil sample duplicate

J: estimated concentration

NA: not applicable

W: groundwater sample (denoted by italics and shading)

Pre-treatment samples from T4 Cell

Pre-T4B1

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
235	01	5.52	1x	<2000	<2000	<5.0	<5.0
236	06	6.04	1x	<2000	<2000	2J	2J
237	11	5.40	1x	<2000	<2000	<5.0	<5.0
238	11D	4.30	1x	<2000	<2000	<5.0	<5.0
239	15	6.22	1000x	<2000	<2000	213,400	171,500
240	16	6.36	1000x	<2000	<2000	118,350	93,050
241	20	6.19	1000x	<2000	<2000	655,700	529,500
242	21	5.71	1000x	<2000	<2000	1,331,000	1,165,500
243	26	6.12	100x	<2000	<2000	42,130	34,400
245	31	5.87	100x	<2000	<2000	65,000	55,350
246	33	5.90	100x	<2000	<2000	53,020	44,950
247	36	4.58	100x	<2000	<2000	61,290	66,900
249	41	4.30	1000x	<2000	<2000	98,700	114,750
250	46	5.44	1x	<2000	<2000	13,390	12,300
251	46D	5.63	1x	<2000	<2000	26,320	23,350
244	30W	NA	1000x	<2000	NA	384,600	NA
248	40W	NA	1000x	<2000	NA	562,500	NA
252	47W	NA	1000x	<2000	NA	250,700	NA

Pre-T4B2

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
217	01	5.37	1x	<2000	<2000	691	645
218	06	6.38	1x	<2000	<2000	<5.0	<5.0
219	11	6.40	1x	6850	5350	2J	2J
220	15	4.88	1000x	<2000	<2000	285,500	292,500
221	16	5.69	1000x	<2000	<2000	49,470	43,470
222	16D	5.27	1000x	<2000	<2000	61,160	58,000
223	21	5.51	1000x	<2000	<2000	142,450	129,250
224	26	6.03	1000x	<2000	<2000	276,200	229,000
227	31	5.67	1000x	<2000	<2000	208,600	183,950
228	36	4.26	100x	<200	<200	23,990	28,158
230	41	5.23	1x	7530	7200	1160	1110
231	46	5.50	100x	<2000	<2000	52,780	48,000
232	47	4.86	1x	<2000	<2000	1170	1200
226	30W	NA	10,000x	<2000	NA	1,600,000	NA
229	40W	NA	1000x	<2000	NA	1,202,000	NA
233	47.5W	NA	1000x	<2000	NA	563,600	NA
234	47.5WD	NA	1000x	<2000	NA	527,800	NA

Pre-T4B3

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
085	01	5.76	1x	<2000	<2000	<5.0	<5.0
086	07	4.69	1x	<2000	<2000	2J	2J
087	07D	5.25	1x	<2000	<2000	2J	2J
088	11	7.12	1x	6940	4875	7.0	5.0
089	15	5.68	1000x	<2000	<2000	628,200	553,000
090	16	5.18	1000x	<2000	<2000	827,200	798,500
091	20	5.08	1000x	<2000	<2000	674,900	664,500
092	21	4.83	1000x	<2000	<2000	920,300	952,500
093	22	3.52	1000x	<2000	<2000	171,600	243,750
095	31	6.04	1000x	<2000	<2000	619,200	512,500
096	36	5.83	1000x	<2000	<2000	374,300	321,000
098	041	5.92	1000x	<2000	<2000	214,500	181,200
099	46	5.17	100x	<2000	<2000	2J	2J
100	48	5.08	100x	<2000	<2000	83,900	77,600
101	48D	4.67	100x	<2000	<2000	140,700	150,650
094	30W	NA	1000x	<2000	<2000	539,400	NA
097	40W	NA	1000x	<2000	<2000	719,000	NA

Pre-T4B4

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
195	01	5.96	1x	<2000	<2000	<5.0	<5.0
196	06	5.28	1x	<2000	<2000	2J	2J
197	11	3.79	100x	<2000	<2000	14,640	19,300
198	11D	6.16	100x	<2000	<2000	24,290	19,700
199	15	5.98	1000x	<2000	<2000	304,900	254,950
200	16	5.13	1000x	<2000	<2000	571,200	556,500
201	21	6.30	100x	100,000J	79,450J	60,790	48,250
202	25	6.97	1000x	<2000	<2000	139,455	100,050
203	26	4.12	100x	<2000	<2000	109,100	132,400
204	30	3.75	1000x	<2000	<2000	1,250,000	1,666,500
206	31	5.82	1000x	<2000	<2000	353,000	303,250
207	31D	4.75	1000x	<2000	<2000	388,000	408,400
208	34	4.16	100x	<2000	<2000	38,300	46,050
209	35	5.49	100x	<2000	<2000	10,170	9250
210	36	5.76	1x	15,160	13,150	11.5	10
213	41	5.92	100x	<2000	<2000	103,600	87,500
214	46	6.00	1x	<2000	<2000	30.2	25
215	48	6.26	10x	<2000	<2000	13,310	10,650
205	30W	NA	10,000x	<2000	NA	12,450,000	NA
211	40W	NA	10,000x	<2000	NA	5,330,000	NA
216	48W	NA	10,000x	<2000	NA	2,530,000	NA

Pre-T4B5

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, μg/kg	TCE, gross	TCE, μg/kg
177	01	4.50	1x	<2000	<2000	<5.0	<5.0
178	06	4.65	1x	<2000	<2000	<5.0	<5.0
179	06D	6.61	1x	<2000	<2000	<5.0	<5.0
180	11	5.73	10x	24,200	21,100	<5.0	<5.0
181	15	5.79	100x	<2000	<2000	22,780	19,650
182	16	5.45	10x	87,190	80,000	15,000	14,750
183	20	5.05	1x	36,750	36,400	2J	2J
184	21	4.85	1x	26,120	26,950	9.3	10
185	26	5.71	100x	<2000	<2000	20,830	18,250
186	30	6.20	1000x	<2000	<2000	1,314,000	1,059,500
188	31	6.17	1000x	<2000	<2000	1,384,000	1,121,500
189	36	5.82	1x	3390	2910	2J	2J
191	41	4.98	10x	<2000	<2000	2630	2640
192	46	4.99	1x	<2000	<2000	9.0	10
193	47	5.84	100x	<2000	<2000	23,370	20,000
<i>187</i>	<i>30W</i>	<i>NA</i>	<i>10,000x</i>	<i><2000</i>	<i>NA</i>	<i>9,016,000</i>	<i>NA</i>
<i>190</i>	<i>40W</i>	<i>NA</i>	<i>10,000x</i>	<i><2000</i>	<i>NA</i>	<i>2,840,000</i>	<i>NA</i>
<i>194</i>	<i>48W</i>	<i>NA</i>	<i>10,000x</i>	<i><2000</i>	<i>NA</i>	<i>1,690,000</i>	<i>NA</i>

D: soil sample duplicate

J: estimated concentration

NA: not applicable

W: groundwater sample (denoted by italics and shading)

WD: groundwater sample duplicate

B-11

Pre-treatment samples from T5 Cell

Pre-T5B1

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
328	01	5.89	1x	<2000	<2000	<5.0	<5.0
329	06	5.84	1x	<2000	<2000	<5.0	<5.0
330	11	6.22	10x	<2000	<2000	12,730	10,230
331	15	6.00	1000x	<2000	<2000	601,700	501,400
332	16	6.07	1000x	<2000	<2000	107,800	88,800
333	21	5.49	1000x	<2000	<2000	37,050	33,740
334	25	6.90	10x	<2000	<2000	2590	1880
336	25W	NA	100x	<2000	<2000	57,200	NA

Pre-T5B2

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
308	01	6.01	1x	<2000	<2000	<5.0	<5.0
309	06	5.75	1x	<2000	<2000	<5.0	<5.0
310	11	5.69	100x	<2000	<2000	18,920	16,620
311	15	5.69	100x	<2000	<2000	34,700	30,490
312	16	6.65	1000x	<2000	<2000	264,300	198,700
317	21	5.82	100x	<2000	<2000	58,540	50,290
318	21D	unk	100x	<2000	unk	83,340	unk
319	25	5.83	1x	<2000	<2000	182	156
324	27	5.35	1x	<2000	<2000	562	525
320	25W	NA	10x	<2000	NA	11,170	NA
321	25WD	NA	10x	<2000	NA	13,020	NA

Pre-T5B3

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
104	01	4.55	1x	<2000	<2000	<5.0	<5.0
105	06	5.07	1x	<2000	<2000	225	220
106	11	6.14	100x	<2000	<2000	37,830	30,800
107	15	6.48	1000x	<2000	<2000	106,900	82,500
108	16	4.29	1000x	<2000	<2000	313,700	365,600
109	20	4.89	1000x	<2000	<2000	308,300	315,250
110	22	5.11	100x	247,200	241,900	29,030	28,400
111	24	6.45	1x	31,860	24,700	3440	2665
112	25W	NA	1x	22,250	NA	5370	NA
113	25WD	NA	1x	21,550	NA	5330	NA

Pre-T5B4

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
297	01	5.92	1x	<2000	<2000	<5.0	<5.0
298	06	5.41	1x	<2000	<2000	51.6	47.7
299	06D	5.83	1x	<2000	<2000	43.7	37.3
300	11	5.38	10x	<2000	<2000	11,860	11,020
304	16	5.23	1000x	<2000	<2000	197,400	188,700
305	25	5.42	1x	<2000	<2000	142	131
306	21	6.04	100x	<2000	<2000	11,840	9800
<i>307</i>	<i>25W</i>	<i>NA</i>	<i>10x</i>	<i><2000</i>	<i>NA</i>	<i>4900</i>	<i>NA</i>

Pre-T5B5

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
289	01	5.62	1x	<2000	<2000	<5.0	<5.0
290	06	5.14	1x	<2000	<2000	2J	2J
291	11	7.14	1x	<2000	<2000	340	238
292	16	6.01	1x	<2000	<2000	<5.0	<5.0
293	25	5.66	1x	<2000	<2000	<5.0	<5.0
294	25D	5.68	1x	<2000	<2000	<5.0	<5.0
<i>295</i>	<i>25W</i>	<i>NA</i>	<i>1x</i>	<i><2000</i>	<i>NA</i>	<i>7.1</i>	<i>NA</i>

D: soil sample duplicate

J: estimated concentration

NA: not applicable

unk: unknown

W: groundwater sample (denoted by italics and shading)

WD: groundwater sample duplicate

B-13

Pre-treatment samples from T6 Cell

Pre-T6B1

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
410	01	6.27	1x	<2000	<2000	<5.0	<5.0
411	06	5.89	1x	<2000	<2000	57	48
412	06D	6.55	1x	<2000	<2000	98	75
413	11	6.20	1x	<2000	<2000	5	5
414	16	5.60	10x	<2000	<2000	5220	4660
415	21	5.85	1000x	<2000	<2000	377,200	322,400
416	26	6.07	100x	<2000	<2000	19,600	16,100
418	31	5.03	10x	<2000	<2000	14,000	13,900
419	36	6.00	10x	<2000	<2000	5400	4500
421	41	3.83	1x	<2000	<2000	<5.0	<5.0
422	46	5.88	1x	<2000	<2000	199	169
423	47.5	6.15	10x	<2000	<2000	8190	6660
417	30W	NA	1000x	<2000	<2000	48,700	NA
420	40W	NA	100x	<2000	<2000	48,500	NA
424	47.5W	NA	100x	<2000	<2000	23,800	NA

Pre-T6B2

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
392	01	5.84	1x	<2000	<2000	<5.0	<5.0
393	06	4.64	1x	<2000	<2000	<5.0	<5.0
394	11	6.23	1x	<2000	<2000	<5.0	<5.0
395	15	5.88	100x	<2000	<2000	28,600	24,300
396	15D	5.95	100x	<2000	<2000	30,950	26,000
397	20	5.00	1000x	<2000	<2000	300,400	300,400
398	16	6.30	100x	<2000	<2000	34,300	27,200
399	21	6.04	1000x	<2000	<2000	804,150	665,700
400	26	6.79	100x	<2000	<2000	27,900	20,500
402	31	5.77	100x	<2000	<2000	113,900	98,700
403	36	6.50	100x	<2000	<2000	37,300	28,700
406	41	6.09	100x	<2000	<2000	200J	200J
407	46	5.29	1x	<2000	<2000	307	290
408	48	6.19	10x	<2000	<2000	7610	6150
401	30W	NA	1000x	<2000	<2000	251,200	NA
404	40W	NA	100x	<2000	<2000	161,200	NA
409	48W	NA	100x	<2000	<2000	80,100	NA

Pre-T6B3

Sample	Depth	Weight , g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, µg/kg	TCE, gross	TCE, µg/kg
374	01	6.91	1x	<2000	<2000	<5.0	<5.0
375	06	9.72	1x	<2000	<2000	2J	2J
376	15	6.45	100x	<2000	<2000	14,400	11,160
377	11	5.43	1x	<2000	<2000	<5.0	<5.0
378	16	5.95	100x	<2000	<2000	61,200	51,400
379	21	5.14	10,000x	<2000	<2000	1,004,000	976,700
380	21D	5.69	10,000x	<2000	<2000	915,000	804,000
381	30	5.02	100x	<2000	<2000	7240	7210
382	26	4.75	100x	<2000	<2000	1730	1820
384	31	3.93	100x	<2000	<2000	481,700	612,800
385	36	5.19	100x	<2000	<2000	82,800	79,800
387	41	5.43	1x	<2000	<2000	269	248
388	46	5.89	10x	<2000	<2000	2344	1990
389	48	6.58	1x	<2000	<2000	459	349
383	30W	NA	1000x	<2000	<2000	347,400	NA
386	40W	NA	1000x	<2000	<2000	605,800	NA
390	48W	NA	1000x	<2000	<2000	173,900	NA
391	48WD	NA	100x	<2000	<2000	183,800	NA

B-15

Pre-T6B4

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, μg/kg	TCE, gross	TCE, μg/kg
356	01	6.66	1x	<2000	<2000	<5.0	<5.0
357	06	6.06	1x	<2000	<2000	<5.0	<5.0
358	11	6.19	1x	<2000	<2000	<5.0	<5.0
359	16	5.72	1000x	<2000	<2000	541,600	473,400
360	20	5.33	1000x	<2000	<2000	242,100	227,000
361	21	5.24	100x	<2000	<2000	107,100	102,200
362	21D	5.43	1000x	<2000	<2000	239,000	220,100
363	26	5.98	1000x	<2000	<2000	3,100,000	2,600,000
365	31	5.88	1000x	<2000	<2000	625,500	531,900
366	36	4.83	1000x	<2000	<2000	419,000	433,700
367	36D	6.21	1000x	<2000	<2000	376,000	302,700
369	41	5.51	10x	<2000	<2000	235	213
370	45	6.35	100x	<2000	<2000	78,500	61,810
371	46	6.46	1x	<2000	<2000	169	130
372	48	6.12	1000x	<2000	<2000	469	383
364	30W	NA	10,000x	<2000	<2000	8,250,000	NA
368	40W	NA	10,000x	<2000	<2000	4,800,000	NA
373	48W	NA	10,000x	<2000	<2000	2,030,000	NA

Pre-T6B5

Sample	Depth	Weight , g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
337	01	3.09	1x	<2000	<2000	<5.0	<5.0
338	06	4.08	1x	<2000	<2000	<5.0	<5.0
339	11	5.51	1x	<2000	<2000	<5.0	<5.0
340	15	5.59	1000x	<2000	<2000	334,500	299,200
341	16	5.98	1000x	<2000	<2000	104,700	87,500
342	16D	5.98	1000x	<2000	<2000	130,300	109,000
343	21	4.38	1x	<2000	<2000	709	809
344	26	5.25	1000x	<2000	<2000	317,200	302,100
345	30	5.95	10,000x	<2000	<2000	1,700,000	1,400,000
347	31	5.25	10,000x	<2000	<2000	4,000,000	3,800,000
348	36	6.26	1000x	<2000	<2000	547,400	437,200
349	40	6.89	1000x	<2000	<2000	917,900	666,000
351	41	4.33	100x	<2000	<2000	45,300	52,400
352	46	5.77	1x	<2000	<2000	<5.0	<5.0
353	48.5	6.11	100x	<2000	<2000	18,130	14,800
346	30W	NA	100,000x	<2000	NA	11,200,000	NA
350	40W	NA	10,000x	<2000	NA	6,500,000	NA
355	48.5	NA	10,000x	<2000	NA	1,500,000	NA

D: soil sample duplicate

J: estimated concentration

NA: not applicable

W: groundwater sample (denoted by italics and shading)

WD: groundwater sample duplicate

B-17

Pre-treatment samples from T7 Cell

Pre-T7B1

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
441	01	6.18	1x	<2000	<2000	<5.0	<5.0
442	01D	6.31	1x	<2000	<2000	<5.0	<5.0
443	06	6.03	1x	<2000	<2000	<5.0	<5.0
444	11	6.31	100x	<2000	<2000	52,000	41,200
445	16	5.12	100x	<2000	<2000	28,315	27,700
446	21	4.19	10x	<2000	<2000	1317	1570
447	25	5.35	1x	<2000	<2000	<5.0	<5.0
448	25W	NA	10x	<2000	2000	1729	NA

Pre-T7B2

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
433	01	6.58	1x	<2000	<2000	<5.0	<5.0
434	06	5.75	1x	<2000	<2000	<5.0	<5.0
435	11	6.19	100x	<2000	<2000	28,700	23,200
436	15	4.90	100x	<2000	<2000	151,900	155,000
437	16	5.02	100x	<2000	<2000	42,900	42,800
438	21	7.03	10x	<2000	<2000	640	455
439	25	6.39	1x	<2000	<2000	595	466
440	25W	NA	10x	<2000	<2000	2179	NA

Pre-T7B3

Sample	Depth	Weight, g	Dilution	cis-DCE, gross	cis-DCE, µg/kg	TCE, gross	TCE, µg/kg
425	01	6.29	1x	<2000	<2000	<5.0	<5.0
426	06	6.55	1x	<2000	<2000	<5.0	<5.0
427	11	5.85	100x	<2000	<2000	17,480	14,900
428	11D	5.78	100x	<2000	<2000	16,210	14,000
429	16	5.49	100x	<2000	<2000	37,300	33,970
430	21	5.53	10x	<2000	<2000	1715	1550
431	25	6.36	10x	<2000	<2000	547	430
432	25W	NA	10x	<2000	<2000	975	NA

Pre-T7B4

Sample	Depth	Weight , g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
449	01	6.36	1x	<2000	<2000	<5.0	<5.0
450	06	5.75	1x	<2000	<2000	<5.0	<5.0
451	11	5.61	10x	<2000	<2000	11,530	10,280
452	16	5.77	100x	<2000	<2000	49,370	42,780
453	21	4.62	1x	<2000	<2000	188	174
454	21D	5.39	1x	<2000	<2000	156	145
455	25	5.76	1x	<2000	<2000	<5.0	<5.0
456	25W	NA	1x	<2000	<2000	497	NA
457	25WD	NA	1x	<2000	<2000	718	NA

Pre-T7B5

Sample	Depth	Weight , g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
458	01	5.87	1x	<2000	<2000	<5.0	<5.0
459	06	6.26	1x	<2000	<2000	<5.0	<5.0
460	11	5.47	100x	<2000	<2000	70,600	64,530
461	15	4.59	1000x	<2000	<2000	201,300	219,300
462	16	5.59	1000x	<2000	<2000	86,100	77,010
463	21	5.26	10x	<2000	<2000	3220	3060
464	25	6.13	10x	<2000	<2000	420	342
465	25W	NA	10x	<2000	<2000	2506	NA

D: soil sample duplicate

NA: not applicable

W: groundwater sample (denoted by italics and shading)

WD: groundwater sample duplicate

Pre-treatment samples from X1 Cell

Pre-X1B1

Sample	Depth	Weight , g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
003	01	6.15	1x	<2000	<2000	<5.0	<5.0
004	06	5.20	1x	<2000	<2000	<5.0	<5.0
005	11	5.32	1x	<2000	<2000	<5.0	<5.0
006	16	5.32	1x	<2000	<2000	<5.0	<5.0
007	21	5.83	1x	<2000	<2000	<5.0	<5.0
008	26	4.64	1x	<2000	<2000	<5.0	<5.0
010	31	5.32	1x	<2000	<2000	<5.0	<5.0
011	36	6.06	1x	<2000	<2000	<5.0	<5.0
013	41	5.24	1x	<2000	<2000	<5.0	<5.0
014	46	5.17	1x	<2000	<2000	<5.0	<5.0
015	46D	4.11	1x	<2000	<2000	<5.0	<5.0
016	51	4.40	1x	<2000	<2000	<5.0	<5.0
009	30W	NA	1x	<2000	NA	<5.0	<5.0
012	40W	NA	1x	<2000	NA	<5.0	<5.0
017	51W	NA	1x	<2000	NA	<5.0	<5.0

D: soil sample duplicate

NA: not applicable

W: groundwater sample (denoted by italics and shading)

APPENDIX C

Data Acquisition System FID vs Auger Depth Plots

Bio-C3 (T3C3) Summary

Date: 7-11-96

DAS time start: 10:29:14 = 0 min

DAS time stop: 14:13:07 = 223.88 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
11:06:46	00:37.53	12	ECD	7,500	ND
11:06:46	00:37.53	12	FID	7,500	ND
11:11:48	00:42.57	16	ECD	15,000	784
11:11:48	00:42.57	16	FID	15,000	759
14:03:27	03:57.00	16	ECD	2,000	286
14:03:27	03:57.00	16	FID	2,000	374

Process Summary:

Elapsed time	Process description
0 to 55 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft
55 to 66 min	Prepare for mixing
66 to 86 min	344 gal of bacteria mix added between 24 ft and 3 ft
86 to 174 min	Repair shroud seal
174 to 197 min	Mix column with air (800 to 1100 cfm) from surface to 24 ft
197 to 205 min	Mix column with air (800 to 1100 cfm) from 24 ft surface
205 to 219 min	Mix column with air (800 to 1100 cfm) from surface to 24 ft
219 to 224 min	Mix column with air (800 to 1100 cfm) from 24 ft to surface, end mix

Bio-C2 (T3C2) Summary

Date: 7-11-96

DAS time start: 17:36:57 = 0 min

DAS time stop: 18:35:30 = 58.55 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
18:00:29	00:23.50	24	ECD	6700	401
18:23:20	00:46.38	14	ECD	1300	148
18:31:50	00:54.889	8	ECD	2000	29

Process Summary:

Elapsed time	Process description
0 to 20 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 24 ft
20 to 31 min	Prepare for mixing
31 to 38 min	279 gal of bacteria mix added between 24 ft to surface
38 to 51 min	Mix column with air (800 to 1100 cfm) from surface to 24 ft
51 to 57 min	Mix column with air (800 to 1100 cfm) from 24 ft surface
57 to 59 min	Clear ports on auger blade, end mix

Bio-C1 (T3C1) Summary

Date: 7-11-96

DAS time start: 14:37:34 = 0 min

DAS time stop: 17:31:02 = 173.47 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
14:55:58	00:18:24	10	ECD	4500	906
14:55:58	00:18:24	10	FID	4500	585
15:10:34	00:33:00	19	ECD	8000	520
15:10:34	00:33:00	19	FID	8000	385
15:32:04	00:54:30	14	ECD	1400	64
15:32:04	00:54:30	14	FID	1400	54
17:04:28	02:45:00	8	ECD	1600	194

Process Summary:

Elapsed time	Process description
0 to 47 min	An 8-ft diameter hole drilled with air (800 to 1100 cfm) to a depth of 25 ft
47 to 64 min	266 gal bacteria mix added and mixed between 23 and 2.5 ft
64 to 140 min	Rig repair (shroud seal replaced)
140 to 165 min	Mix column with air (800 to 1100 cfm) from 1.5 to 23 ft
165 to 173 min	Mix column with air (800 to 1100 cfm) from 23 to 1.5 ft, end mixing

KMnO (T4C1A) Summary

Note: Because this mix spanned two days, the data is presented in two separate files (T4C1A and T4C1B) to provide better graphic resolution on the plots.

Date: 7-15-96

DAS time start: 14:49:39 min

DAS time stop: 16:05:35 = 75.93 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
15:09:38	00:20.15	12	ECD	12,000	1,112
15:25:42	00:36.22	35	ECD	12,000	656

Process Summary:

Elapsed time	Process description
0 to 43 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 47 ft
43 to 66 min	1880 gal KMnO ₄ mixed from 47 to 10 ft (51 gal/ft)
66 to 76 min	Lift auger to surface, blow out ports with air, end of day

KMnO (T4C1B) Summary

Note: Because this mix spanned two days, the data is presented in two separate files (T4C1A and T4C1B) to provide better graphic resolution on the plots.

Date: 7-16-96

DAS time start: 08:26:53 = 0 min

DAS time stop: 10:41:41 = 134.8 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
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No off-gas samples collected.

Process Summary:

Elapsed time	Process description
0 to 17 min	Drill from surface to 10 ft
17 to 41 min	782 gal KMnO ₄ mixed from 10 ft to 47 ft (21 gal/ft)
41 to 58 min	816 gal KMnO ₄ mixed from 47 to 10 ft (22 gal/ft)
58 to 62 min	Rotate out to surface, KMnO ₄ flowing out under shroud
62 to 97 min	Drill from surface to 47 ft with no air or fluid injection
97 to 135 min	Rotate from 47 ft to surface with no air or fluid injection, end of mix

KMnO (T4C2) Summary

Date: 7-16-96

DAS time start: 15:56:56 = 0 min

DAS time stop: 18:11:31 = 134.63 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
16:24:39	00:27.7	21	ECD	22,000	1,416
16:26:43	00:29.83	24	ECD	13,000	1,093
16:38:13	00:41.33	42	ECD	2,200	215

Process Summary:

Elapsed time	Process description
0 to 44 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 47 ft
44 to 58 min	1206 gal KMnO ₄ mixed in between 47 and 10 ft (32.6 gal/ft)
58 to 68 min	Rotate out from 10 ft to 4 ft, 1200 gal H ₂ O added to KmnO ₄ mixing tank
68 to 71 min	Rotate from 4 ft to 10 ft
71 to 88 min	1162 gal KMnO ₄ mixed in between 10 ft and 47 ft (31 gal/ft)
88 to 100 min	300 gal KMnO ₄ mixed in between 47 and 10 ft (8 gal/ft)
100 to 103 min	Rotate out to 7 ft, 500 gal H ₂ O added to KMnO ₄ mixing tank
103 to 112 min	420 gal KMnO ₄ mixed in between 7 and 47 ft (10.5 gal/ft)
112 to 128 min	Rotate out from 47 ft to surface with no air or fluid injection
128 to 135 min	Clean out ports with air pressure, end of mix (3088 gal total KMnO ₄ added)

KMnO (T4C3) Summary

Date: 7-15-96

DAS time start: 09:51:01 = 0 min

DAS time stop: 12:51:20 = 180.32 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
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No off-gas samples were collected from T4C3.

Process Summary:

Elapsed time	Process description
0 to 46 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 47 ft
46 to 77 min	1330 gal KMnO ₄ mixed in between 47 and 14 ft (40 gal/ft)
77 to 96 min	627 gal KMnO ₄ mixed in between 14 ft and 47 ft (19 gal/ft)
96 to 100 min	849 gal KMnO ₄ mixed in between 47 ft and 33 ft (60.6 gal ft)
100 to 125 min	Rotate out from 33 ft to surface with no injection of fluid or air
125 to 139 min	977 gal KMnO ₄ mixed in between 10 ft and 47 ft (26 gal/ft), 630 gal H ₂ O added to tank to increase volume
139 to 161 min	298 gal KMnO ₄ mixed in between 47 ft and 10 ft (8 gal/ft)
161 to 169 min	570 gal KMnO ₄ mixed in between 10 ft and 47 ft (15 gal/ft)
169 to 180 min	Rotate out from 47 ft to surface with no fluid or air injection, end of mix, (4651 gal total KMnO ₄ injected)

KMnO (T5C1) Summary

Date: 7-13-96

DAS time start: 10:59:26 = 0 min

DAS time stop: 13:09:14 = 129.8 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
11:25:21	00:25.92	14	ECD	13,000	948
11:25:21	00:25.92	14	FID	13,000	963
11:31:17	00:31.85	21	ECD	15,000	620
11:31:17	00:31.85	21	FID	15,000	491

Process Summary:

Elapsed time	Process description
0 to 14 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 10 ft
14 to 19 min	Rotate to surface for repair
19 to 36 min	Drill from surface to 25 ft with air (700 to 1000 cfm)
36 to 44 min	560 gal KMnO ₄ mixed from 24 to 10 ft
44 to 55 min	Rotate to surface for repairs
55 to 62 min	Complete repairs
62 to 75 min	Drill with air from surface to 10 ft
75 to 91 min	625 gal KMnO ₄ mixed in from 10 ft to 25 ft (40 gal/ft)
91 to 97 min	705 gal KMnO ₄ mixed in from 24 ft to 10 ft (50 gal/ft)
97 to 99 min	Rotate from 10 ft to 3 ft
99 to 112 min	Rotate from 3 ft to 25 ft, add 64 gal KMnO ₄ at 25 ft
112 to 118 min	Rotate from 25 ft to surface with no air or fluid injection
118 to 121 min	Lift auger above ground and clear ports with air pressure, end mix

KMnO (T5C2) Summary

Date: 7-13-96

DAS time start: 14:26:46 = 0 min

DAS time stop: 15:29:26 = 62.67 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
14:39:21	00:12.58	13	FID	6,400	539
14:42:56	00:16.17	11	FID	15,000	286

Process Summary:

Elapsed time	Process description
0 to 4 min	Prepare for drilling
4 to 27 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft
27 to 35 min	570 gal KMnO ₄ mixed in between 24 and 10 ft
35 to 45 min	556 gal KMnO ₄ mixed in between 10 and 23 ft
45 to 50 min	Rotate from 23 ft to 8 ft with no air or fluid injection
50 to 52 min	Rotate from 8 ft to 23 ft with no air or fluid injection
52 to 59 min	Rotate from 23 to surface with no air or fluid injection
59 to 63 min	Lift auger above ground and clear ports with air pressure, end mix

KMnO (T5C3) Summary

Date: 7-12-96

DAS time start: 16:50:27 = 0 min

DAS time stop: 18:15:00 = 84.55 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
17:10:51	00:20.40	23	ECD	8000	52
17:26:11	00:35.73	5	ECD	1200	11

Process Summary:

Elapsed time	Process description
0 to 21 min	An 8-ft diameter hole drilled with air (700 to 1000 cfm) to a depth of 25 ft
21 to 37 min	1440 gal KMnO ₄ added between 24 ft and surface (60 gal/ft)
37 to 53 min	1263 gal KMnO ₄ added between surface and 24 ft (40 gal/ft)
53 to 60 min	Mix column with no air or fluid from 24 ft to surface
60 to 67 min	Drill from surface to 10 ft with air (800 to 1000 cfm)
67 to 80 min	1000 gal KMnO ₄ added between 10 ft and 24 ft
80 to 85 min	Rotate out from 24 ft to surface with no air or fluid, end mix

Air T7C1 Summary

Date: 7-20-96

DAS time start: 08:55:43 = 0 min

DAS time stop: 11:27:24 = 151.68 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
10:11:01	00:75.30	18	ECD	1700	12

Process Summary:

Elapsed time	Process description
0 to 9 min	Prepare for drilling
9 to 44 min	An 8-ft diameter hole drilled with air (1500 to 1700 cfm) to a depth of 25 ft
44 to 55 min	Mix with air (1700 cfm) from 25 ft to 1 ft
55 to 81 min	Mix with air (1700 cfm) from 1 ft to 25 ft
81 to 87 min	Mix column with air (1700 cfm) from 25 ft to 1 ft
87 to 108 min	Mix column with air (1700 cfm) from 1 ft to 25 ft
108 to 114 min	Mix column with air (1700 cfm) from 25 ft to 1 ft
114 to 131 min	Mix column with air (1700 cfm) from 1 ft to 25 ft
131 to 138 min	Mix column with air (1700 cfm) from 25 ft to 1 ft
138 to 152 min	Raise auger, blow out ports with air, end of mix

Air T7C2 Summary

Date: 7-20-96

DAS time start: 11:29:39 = 0 min

DAS time stop: 15:20:04 = 230.42 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
14:55:55	03:44.00	20	ECD	600	12

Process Summary:

Elapsed time	Process description
0 to 20 min	An 8-ft diameter hole drilled with air (1500 to 1700 cfm) to a depth of 25 ft
20 to 27 min	Mix with air (1700 cfm) from 25 ft to 1 ft
27 to 108 min	Break for lunch and minor rig repairs
108 to 133 min	Mix with air (1700 cfm) from 1 ft to 25 ft
133 to 151 min	Mix column with air (1700 cfm) from 25 ft to 1 ft
151 to 173 min	Mix column with air (1700 cfm) from 1 ft to 25 ft
173 to 188 min	Mix column with air (1700 cfm) from 25 ft to 1 ft
188 to 211 min	Mix column with air (1700 cfm) from 1 ft to 25 ft
211 to 230 min	Mix column with air (1700 cfm) from 25 ft to 1ft, end of mix

Air T7C3 Summary

Date: 7-19-96

DAS time start: 09:06:11 = 0 min

DAS time stop: 16:46:23 = 460.2 min

Off-gas sample collection for TCE analysis:

Clock time	Elapsed time	Depth, ft	GC detector	FID reading, ppm	TCE, ppm
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No off-gas vapor sample collected.

Process Summary:

Elapsed time	Process description
0 to 20 min	An 8-ft diameter hole drilled with air (1500 to 1700 cfm) to a depth of 25 ft
20 to 51 min	Attempt lime from 25 to 22 ft but cannot overcome back-pressure, no lime delivered
51 to 71 min	Mix with air (1700 cfm) from 22 ft to surface
71 to 82 min	Reconfigure air lines to maximize pressure throughout lime delivery system
82 to 89 min	Attempt lime delivery from surface to 4 ft, cannot overcome backpressure, pull auger to surface
89 to 257 min	Change port size from 0.5 in. to 1 in. to reduce backpressure
257 to 277 min	Attempt lime delivery from surface to 7 ft, cannot overcome backpressure pull auger to surface
277 to 348 min	Change port size back to 0.5 in. and air strip the cell
348 to 369 min	Mix column with air (1700 cfm) from surface to 25 ft
369 to 388 min	Mix column with air (1700 cfm) from 25 ft to 1 ft
388 to 416 min	Mix column with air (1700 cfm) from 1 ft to 25 ft
416 to 427 min	Mix column with air (1700 cfm) from 25 ft to 1ft
427 to 448 min	Mix column with air (1700 cfm) from 1 ft to 25 ft
448 to 460 min	Mix column with air (1700 cfm) from 25 ft to surface, end of mix

APPENDIX D

Treatability Studies Examining the Biodegradation of Trichloroethylene: In Support of a Field Demonstration in Kansas City, MO

**Treatability Studies Examining the Biodegradation of Trichloroethylene:
In Support of a Field Demonstration in Kansas City, MO.**

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The degradation of trichloroethylene (TCE) was carried out under both aqueous and slurry conditions. The bacteria used to degrade the TCE was *Burkholderia cepacia* G4 PR1₃₀₁ (G4) [M. Shields, University of West Florida].

The bacteria were grown in continuous culture in basalt salt media (BSM) (Hareland et al., 1975) with 20 mM glucose as the sole carbon source. Liquid cultures were routinely started from agar plates of a complex growth media R2A (Difco laboratories, Detroit, MI) or a specialized growth media of BSM + 20 mM glucose, or 20 mM sodium lactate and 1.7% noble agar. The plates were scraped after 7 days and the bacteria resuspended in 10 mL of BSM + 20 mM glucose in a 15 mL sterile centrifuge tube. After a two-day incubation on a rotary shaker (250 rpm) at ambient temperature, the optical density (OD) measured at a wavelength of 600 nm increased from 0 to 0.2-0.5 (Gilford Response UV-Visible spectrophotometer, Oberlin, OH). These cultures were then transferred into 90 mL of fresh media in a 250 mL Erlenmeyer flask and returned to the shaker until $OD \geq 2.0$.

Expression of the enzyme responsible for TCE degradation, toluene ortho-monooxygenase, was measured using the TFMP (trifluoromethylphenol or m-hydroxy benzotrifluoride) oxidation assay. The rate of production of TFHA (7,7,7-trifluoro-2-hydroxy-6-oxo-2,4-heptadienoic acid), a yellow product, from TFMP oxidation correlates to the potential rate of TCE degradation by the enzyme (Shields et al., 1991; Shields and Reagin, 1992).

TCE biodegradation in aqueous and soil systems was monitored using gas chromatography. Standards and samples, prepared in triplicate, were prepared in 15 mL glass vials. Each vial contained 5 mL of a phosphate buffered solution (PBS, 1.2 g

Figure 1. Degradation of TCE in aqueous and slurry conditions (10% G4, 5 mL PBS, 0.5 g soil)

Figure 2. Degradation of TCE in aqueous and slurry conditions (10% G4, 5 mL PBS, 5.8 g of soil)

Na_2HPO_4 , 2.2 g NaH_2PO_4 , 8.7 g NaCl in 1 Liter deionized water), 10% active G4 inoculum, and TCE (various concentrations). In some experiments, Kansas City soil was also added to the vials. The vials were then inverted and allowed to equilibrate on a rotary shaker. Headspace samples (volume 30 μL) were analyzed using a Hewlett Packard gas chromatograph (HP5890 Series II Plus, San Fernando, CA) equipped with a DB624 capillary column (Alltech, Deerfield, IL) and an electron capture detector. TCE was also extracted over a 24-hr period with 3 mL of hexane + 1 mL methanol. A 1 μL extractant sample was injected into the gas chromatograph using an HP autosampler (HP 7673).

Figure 1 shows degradation to below the detection limits (<5 ppb) of TCE in aqueous solutions after a 48-hour incubation period. The samples contained 5 mL of the saline solution, a 10% G4 inoculum and TCE at concentrations ranging from 1 to 10 ppm. These concentrations correspond to the range of concentrations observed in Test Cell 7 (The Kansas City field demonstration where the bioremediation is planned). For both 1 and 5 ppm concentrations, TCE was degraded to below 10 ppb in 48 hours. This corresponds to a TCE biodegradation greater than 99.8%. For the 10 ppm concentration, 87.4% of the TCE was degraded during the same period of time (TCE final concentration = 1.28 ppm). Figure 1 also reports degradation of TCE under slurry conditions (0.5 g of sterile soil was added to the sample vials). The percent of TCE degraded ranged from 70 to 95%. It should be noted that these degradation experiments lasted 48 hours; however, enzymes will be active for several days. Indeed, Figure 2 shows that after ca. 100 hrs, 97 to 98% of TCE is degraded by G4. For this experiment, the soil-to-liquid volume ratio was 1 and the TCE concentrations were 1 and 5 ppm.

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APPENDIX E

Kansas City Plant Deep Soil Mixing Demonstration Project

Post-treatment *cis*-1,2-DCE and TCE Content in Soil, $\mu\text{g/kg}$ and Groundwater, $\mu\text{g/L}$

APPENDIX E

Kansas City Plant Deep Soil Mixing Demonstration Project

Post-treatment *cis*-1,2-DCE and TCE Content in Soil, $\mu\text{g/kg}$ and Groundwater, $\mu\text{g/L}$

Post-treatment samples from T3 Cell

Post-T3B1

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
5	6.5	4.45	10x	ND	ND	8549	9606
6	9.0	4.34	100x	ND	ND	22,754	26,214
7	12.0	4.33	10x	ND	ND	11,258	13,000
8	14.0	2.76	100x	ND	ND	104,231	188,824
9	17.0	3.70	100x	ND	ND	141,105	190,682
10	22.0	3.23	100x	ND	ND	62,417	96,621
11	27.0	3.88	1x	ND	ND	1570	2023
55	T3B1-01W	NA	100x	ND	ND	26,414 g/L	NA

Post-T3B2

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
12	5.0	5.13	100x	ND	ND	12,800	12,476
13	9.0	2.74	100x	ND	ND	9740	17,774
14	12.0	4.41	100x	ND	ND	64,500	73,129
15	14.0	4.12	100x	ND	ND	14,040	17,039
16	16.0	3.47	100x	ND	ND	121,500	175,072
17	22.0	4.16	100x	ND	ND	123,300	148,197
18	26.0	3.15	10x	ND	ND	2650	4206

Post-T3B3

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
19	5.0	4.20	10x	ND	ND	4400	5238
20	9.0	3.71	10x	ND	ND	7116	9590
21	12.0	3.17	10x	ND	ND	13,660	21,546
22	14.0	2.81	100x	ND	ND	37,793	67,247
23	17.0	4.50	100x	ND	ND	110,052	122,280
24	22.0	4.19	100x	ND	ND	140,741	167,949
25	27.0	4.66	10x	ND	ND	9311	9990
53	T3B3-01W	NA	100x	ND	ND	48,165 g/L	NA

Post-T3B4

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
26	5.0	3.34	10x	ND	ND	4188	6269
27	9.0	4.66	10x	ND	ND	5903	6334
28	15.0	3.47	100x	ND	ND	44,303	63,837
29	17.0	3.94	100x	ND	ND	123,837	157,154
30	23.0	3.75	100x	ND	ND	120,190	160,253
31	27.0	3.98	100x	ND	ND	43,702	54,902

Post-T3B5

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
32	5.0	2.95	10x	ND	ND	4420	7492
33	9.0	3.32	10x	ND	ND	10,437	15,718
34	17.0	4.85	1000x	ND	ND	238,152	245,518
35	22.0	4.13	1000x	ND	ND	168,834	204,400
36	27.0	3.83	100x	ND	ND	104,737	136,732
54 T3B5-01W		NA	1x	ND	ND	ND	NA

Post-T3B6

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, μg/kg	TCE, gross	TCE, μg/kg
38	5.0	3.93	10x	ND	ND	777	989
39	9.0	3.22	1x	ND	ND	243	377
40	12.0	1.84	10x	ND	ND	1525	4144
41	14.0	4.85	1000x	ND	ND	526,941	543,238
42	17.0	3.66	1000x	ND	ND	659,404	900,825
43	22.0	3.07	100x	ND	ND	16,433	26,764
44	27.0	4.67	100x	ND	ND	92,503	99,040

E-3

Post-T3B7

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
45	5.0	2.54	10x	ND	ND	7458	14,681
46	9.0	5.70	10x	ND	ND	7006	6146
47	11.0	5.34	100x	ND	ND	80,477	75,353
48	14.0	4.49	100x	ND	ND	91,851	102,284
49	17.0	4.03	100x	ND	ND	129,718	160,940
50	22.0	2.48	100x	D	ND	148,499	299,393
51	27.0	3.84	10x	ND	ND	10,736	13,979

Post-T3B5A

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
152	5.0	3.51	10x	ND	ND	6089	8674
153	9.0	3.84	10x	ND	ND	8941	11,642
154	12.0	4.30	100x	ND	ND	49,002	56,979
155	14.0	3.40	1000x	ND	ND	145,062	213,326
156	17.0	3.54	1000x	ND	ND	197,614	279,116
157	22.0	3.10	100x	ND	ND	99,674	160,765
158	27.0	3.38	100x	ND	ND	80,013	118,362

Post-T3B3A

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
159	5.0	3.65	10x	ND	ND	5616	7693
160	9.0	3.77	10x	ND	ND	6715	8906
161	12.0	4.25	100x	ND	ND	19,430	22,859
162	14.0	3.03	100x	ND	ND	81,933	135,203
163	17.0	3.44	100x	ND	ND	89,763	130,469
164	22.0	4.21	100x	ND	ND	96,293	114,362
165	27.0	2.84	100x	ND	ND	13,250	23,327

Post-T3B1A

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
166	5.0	3.29	10x	ND	ND	4186	6362
167	9.0	3.61	10x	ND	ND	112,64	15,601
168	12.0	3.69	100x	ND	ND	9522	12,902
169	14.0	4.06	100x	ND	ND	20,455	25,191
170	17.0	4.15	100x	ND	ND	101,568	122,371
171	22.0	3.58	100x	ND	ND	74,234	103,679
172	27.0	4.19	10x	ND	ND	4944	5900

Post-T3B6A

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
174	5.0	2.83	10x	ND	ND	1621	2864
175	9.0	3.33	10x	ND	ND	7530	11,306
176	12.0	3.02	10x	ND	ND	8581	14,207
177	14.0	3.05	100x	ND	ND	15,468	25,357
178	17.0	2.96	1000x	ND	ND	206,331	348,532
179	22.0	2.92	100x	ND	ND	14,457	24,755
180	27.0	3.06	100x	ND	ND	21,194	34,631

Post-T3B7A

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
181	5.0	3.68	10x	ND	ND	1023	1390
182	9.0	3.71	1x	ND	ND	876	1181
183	12.0	3.14	100x	ND	ND	9485	15,104
184	14.0	3.31	100x	ND	ND	96,891	146,361
185	17.0	3.31	100x	ND	ND	90,274	136,366
186	22.0	2.64	1000x	ND	ND	203,844	386,068
187	27.0	2.73	100x	ND	ND	15,842	29,015

D: soil sample duplicate

W: groundwater sample (denoted by italics and shading)

NA: not applicable

ND: not detected

Post-treatment samples from T4 Cell

Post-T4B1

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, µg/kg	TCE, gross	TCE, µg/kg
96	1.0	3.70	10x	ND	ND	1718	2322
97	3.0	3.65	10x	ND	ND	6551	8974
98	7.0	3.77	10x	ND	ND	5863	7776
99	12.0	4.69	1000x	ND	ND	897,368	956,682
100	17.0	3.69	1000x	ND	ND	206,312	279,556
101	22.0	3.70	100x	ND	ND	81,172	109,692
102	27.0	3.56	1000x	ND	ND	308,083	432,701
103	32.0	4.81	100x	ND	ND	78,650	81,757
104	37.0	2.93	10x	ND	ND	9819	16,756

Post-T4B2

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, µg/kg	TCE, gross	TCE, µg/kg
105	1.0	2.04	10x	ND	ND	1617	3963
106	3.0	2.85	10x	ND	ND	4068	7137
107	7.0	3.88	10x	ND	ND	4605	5934
108	12.0	3.34	100x	ND	ND	43,792	65,557
109	17.0	3.15	100x	ND	ND	44,525	70,675
110	22.0	2.70	10x	ND	ND	13,127	24,309
111	27.0	3.44	100x	ND	ND	41,469	60,275
112	32.0	4.90	100x	ND	ND	101,111	103,174
113	37.0	2.89	100x	ND	ND	24,646	42,640

Post-T4B3

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, µg/kg	TCE, gross	TCE, µg/kg
116	5.0	2.83	10x	ND	ND	6365	11,246
117	7.0	2.68	10x	ND	ND	6922	12,914
118	12.0	2.91	100x	ND	ND	40,490	69,570
119	17.0	3.17	100x	ND	ND	46,023	72,591
120	22.0	3.35	100x	ND	ND	51,678	77,131
121	27.0	5.01	100x	ND	ND	84,448	84,279
122	32.0	4.67	100x	ND	ND	91,959	98,457
123	37.0	3.95	100x	ND	ND	33,250	42,089
218 T4B3-02W		NA	10x	ND	ND	4196 µg/L	NA

Post-T4B4

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
124	1.0	3.77	10x	ND	ND	3392	4499
125	3.0	3.87	10x	ND	ND	3947	5099
126	7.0	4.10	10x	ND	ND	8662	10,563
127	12.0	4.70	100x	ND	ND	56,125	59,707
128	17.0	3.38	100x	ND	ND	116,193	171,883
129	22.0	3.82	100x	ND	ND	53,660	70,236
130	27.0	4.24	100x	ND	ND	127,128	149,915
131	32.0	4.71	100x	ND	ND	56,436	59,911
132	37.0	4.72	100x	ND	ND	25,612	27,131

Post-T4B5

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
133	1.0	3.70	1x	ND	ND	1041	1407
134	3.0	3.82	1x	ND	ND	895	1171
135	7.0	4.70	1x	ND	ND	772	821
136	12.0	3.76	10x	ND	ND	2181	2900
137	17.0	4.40	10x	ND	ND	6149	6988
138	22.0	2.96	10x	ND	ND	5172	8736
139	27.0	4.19	10x	ND	ND	8727	10,414
140	32.0	3.27	100x	ND	ND	44,222	67,618
141	37.0	4.50	10x	ND	ND	5221	5801

Post-T4B6

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
142	1.0	4.57	10x	ND	ND	6321	6916
143	3.0	3.86	10x	ND	ND	2746	3557
144	7.0	4.26	10x	ND	ND	10,132	11,892
145	12.0	4.35	100x	ND	ND	37,453	43,049
146	17.0	4.98	100x	ND	ND	74,652	74,952
147	22.0	6.06	100x	ND	ND	97,691	80,603
148	27.0	4.81	100x	ND	ND	110,625	114,995
149	32.0	4.76	100x	ND	ND	59,319	62,310
150	37.0	5.03	100x	ND	ND	30,515	30,333

D: soil sample duplicate

W: groundwater sample (denoted by italics and shading)

NA: not applicable

ND: not detected

Post-treatment samples from T5 Cell

Post-T5B1

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
65	3.0	2.77	10x	ND	ND	1091	1969
66	7.0	4.52	10x	ND	ND	3674	4064
67	12.0	2.33	10x	ND	ND	11,963	25,672
68	17.0	3.72	100x	ND	ND	45,262	60,836
69	25.0	2.96	10x	ND	ND	10,044	16,966
70	27.0	3.09	100x	ND	ND	46,565	75,348

Post-T5B2

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
72	7.0	2.98	100x	ND	ND	17,407	29,206
73	12.0	3.42	10x	ND	ND	1964	2871
74	17.0	3.08	10x	ND	ND	3918	6360
75	22.0	4.36	10x	ND	ND	4129	4735
76	27.0	4.93	100x	ND	ND	24,577	24,926

Post-T5B3

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
77	3.0	3.30	10x	ND	ND	455	689
78	7.0	4.80	10x	ND	ND	2439	2541
79	12.0	4.33	100x	ND	ND	14,497	16,740
80	17.0	2.03	10x	ND	ND	5895	14,520
81	22.0	1.90	10x	ND	ND	3571	9397
82	27.0	3.31	10x	ND	ND	4483	6772
114 T5B3-01W		NA	10x	ND	ND	4172 $\mu\text{g/L}$	NA
219 T5B3-02W		NA	10x	ND	ND	2145 $\mu\text{g/L}$	NA

Post-T5B4

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
84	3.0	4.20	10x	ND	ND	1025	1220
85	7.0	3.60	10x	ND	ND	2345	3257
86	12.0	2.67	100x	ND	ND	44,605	83,530
87	17.0	2.55	100x	ND	ND	34,367	67,386
88	22.0	3.32	10x	ND	ND	5316	8006
89	27.0	3.41	10x	ND	ND	248	364

Post-T5B5

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
90	3.0	4.08	1x	ND	ND	742	909
91	7.0	2.54	1x	ND	ND	449	884
92	12.0	1.84	1x	ND	ND	810	2201
93	17.0	2.83	1x	ND	ND	621	1097
94	22.0	3.38	1x	ND	ND	146	216
95	27.0	4.39	1x	ND	ND	559	637

Post-T5B6

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
211	3.0	3.80	1x	ND	ND	178	234
212	7.0	3.73	10x	ND	ND	4864	6520
213	12.0	3.63	1000x	ND	ND	160,615	221,233
214	17.0	3.06	100x	ND	ND	21,751	35,541
215	22.0	3.56	10x	ND	ND	9188	12,904
216	27.0	4.24	10x	ND	ND	25,446	30,007

D: soil sample duplicate

W: groundwater sample (denoted by italics and shading)

NA: not applicable

ND: not detected

Post-treatment samples from T7 Cell

Post-T7B1

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
204	1.0	2.78	1x	ND	ND	1157	2081
205	3.0	3.29	1x	ND	ND	1202	1827
206	7.0	3.25	10x	ND	ND	2355	3623
207	12.0	3.42	10x	ND	ND	11,792	17,240
208	17.0	3.60	10x	ND	ND	6271	8710
209	22.0	3.87	10x	ND	ND	3228	4171
210	27.0	4.43	10x	ND	ND	1166	1316

Post-T7B2

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
197	1.0	3.59	10x	ND	ND	1365	1901
198	3.0	3.79	10x	ND	ND	686	905
199	7.0	3.63	10x	ND	ND	1329	1831
200	12.0	3.69	100x	ND	ND	12,111	16,411
201	17.0	4.09	10x	ND	ND	9336	11,413
202	22.0	4.37	10x	ND	ND	3945	4514
203	27.0	4.65	10x	ND	ND	1846	1985

Post-T7B3

Sample	Depth	Weight, g	Dilution	<i>cis</i> -DCE, gross	<i>cis</i> -DCE, $\mu\text{g/kg}$	TCE, gross	TCE, $\mu\text{g/kg}$
190	1.0	2.94	1x	ND	ND	924	1571
191	3.0	3.38	1x	ND	ND	668	988
192	7.0	4.12	10x	ND	ND	1087	1319
193	12.0	3.83	10x	ND	ND	1603	2093
194	17.0	4.02	10x	ND	ND	4846	6027
195	22.0	3.70	10x	ND	ND	1834	2478
196	27.0	3.86	10x	ND	ND	3076	3984

D: soil sample duplicate

W: groundwater sample (denoted by italics and shading)

NA: not applicable

ND: not detected

APPENDIX F

Implementation of Deep Soil Mixing Innovative Remedial Technology at the Kansas City Plant

Chemical Oxidation Laboratory Treatability Study Results

**Implementation of Deep Soil Mixing Innovative Remedial Technology
at
the Kansas City Plant**

Chemical Oxidation Laboratory Treatability Study Results

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**Implementation of Deep Soil Mixing Innovative Remedial Technology
at
the Kansas City Plant**

Chemical Oxidation Laboratory Treatability Study Results

Objective

The objective of the chemical oxidation treatability studies was to determine if chemical oxidation treatment can be used to degrade DCE and TCE in contaminated soil from the DOE Kansas City Plant. The study objective was met by conducting three series of experiments 1)effect of oxidant type and concentration studies; 2)effect of oxidant volume studies and 3)oxidant persistence and effect on soil composition study. The first two studies were completed using zero-headspace extraction vessels loaded with either field or artificially contaminated soil from the Kansas City Plant. Oxidant solution(s) were added to the contaminated soil under gas-tight conditions and pre- and posttreatment contaminant concentrations were measured to determine chemical oxidation treatment efficiency. The final series of experiments was completed using a laboratory-scale soil mixing apparatus designed to replicate reagent injection and deep soil mixing.

Effect of Oxidant Type

In this study, field contaminated Kansas City soil was treated with either KMnO_4 , H_2O_2 , or H_2O_2 supplemented with FeSO_4 . A KMnO_4 concentration of 4% (wt basis) was selected for this study after considering the solubility of KMnO_4 at room temperature (~6%), and the expected purity of bulk (technical grade) KMnO_4 . A H_2O_2 concentration of 8.5% (wt basis) was selected so that the handling concerns and hazards associated with higher concentration H_2O_2 solutions could be avoided. During this initial screening study, only the reduction in TCE from a pre-treatment concentration of 14 mg/kg was evaluated. In Figure 1, the TCE removals obtained when the same volume (8 mL) of oxidant solution was added to 28 g of field moist soil are shown. The greatest TCE reduction (96.1%) was achieved when the soil was treated with the KMnO_4 solution. TCE reductions achieved with H_2O_2 and H_2O_2 + iron were 40.4% and 72.5% respectively. The improvement in H_2O_2 treatment observed with iron supplementation was probably due to the catalytic effect Fe^{2+} has on the decomposition of H_2O_2 to the hydroxyl radical (Fenton's process).

Figure 1. TCE removal from field contaminated soil

Effect of KMnO_4 Concentration

Because KMnO_4 appeared to be the most promising chemical oxidant for field application, all additional experiments in this treatability study were conducted using only KMnO_4 solutions. Additional studies completed using soil from another DOE site suggest that the H_2O_2 treatment levels can be further improved by adjusting the supplemental iron dose or using multiple H_2O_2 treatments. A more complete evaluation of H_2O_2 treatment of contaminated Kansas City soil can be completed in the future if needed.

Soil from field contaminated soil core number 269 was treated with several different concentrations of KMnO_4 solution. This experiment was completed to determine if the demonstration objectives could be met using lower KMnO_4 concentrations than those used in the previously described experiment. For this experiment, soil slurries (1:1, soil:water) were formed from the field contaminated soil, prior to oxidant addition. Soil slurries were used in this studies to ensure that complete mixing was achieved during treatment. The results of this study are plotted in Figure 2. It was observed that the TCE treatment efficiency increased as the oxidant concentration was increased from a low value of 34.9% removal with 0.5% KMnO_4 to a high of 95.6% removal with 4% KMnO_4 from an initial TCE concentration of 349 mg/kg. The proposed demonstration goal of >70% contaminant reductions was exceeded at the two highest KMnO_4 concentration evaluated for TCE. DCE removals of 100% from an initial concentration of 12 mg/kg was observed at all KMnO_4 concentrations.

The effect of KMnO_4 concentration experiment was repeated with soil slurries artificially contaminated with TCE. This was done to determine if uncontaminated Kansas City soil could be artificially contaminated and used in latter studies. The results of this experiment are also shown in Figure 2. The agreement observed between the treatment achieved in the field contaminated and artificially contaminated soil is quite good. The same trends were observed in both soil, although a significant difference (>20%) was found in the soils treated with the lowest concentration KMnO_4 solution. At the higher KMnO_4 concentrations, which are more relevant to the proposed field application, the agreement in results between field and artificially contaminated soil is less than 10%.

Effect of oxidant volume

This series of experiments was conducted to determine if the volume of oxidant solution added to the contaminated soil could be minimized or eliminated by treating the soil with greater than 4% KMnO_4 solutions or treating the soil with KMnO_4 crystals. Field contaminated soil from core number 270 was treated with 5%, 8% and 12% KMnO_4 solutions or dry KMnO_4 crystals. An additional series of experiments was completed with artificially contaminated Kansas City, since the initial contaminant concentrations in the field contaminated soil had decreased during storage.

Figure 2. VOC reduction in contaminated soil slurries treated with KMnO_4 solution. (8mL of oxidant solution added to 40 g of soil slurry)

During these experiments, field moist soils (no slurries) were treated in zero-headspace extraction vessels. The volume of oxidant solution and the mass of KMnO_4 crystals added to the soil were selected so that roughly equivalent doses (20 g KMnO_4 /kg soil) of oxidant were added to the soils during treatment. The volume of 5%, 8% and 12% KMnO_4 solution added to the soil was 8, 4, and 3 mL respectively. The KMnO_4 solutions with concentrations greater than 6% had to be prepared by heating the KMnO_4 /water solution to a temperature of approximately 40° C. The results of this study are shown in Figures 3 and 4. With all of the higher strength oxidant solutions, greater than 85% TCE removal (initial TCE = 536 mg/kg artificially contaminated, 14 mg/kg field contaminated) and 100% DCE removal (initial DCE = 124 mg/kg artificially contaminated, 9.7 mg/kg field contaminated) was observed. Although it may not be feasible to prepare higher concentration KMnO_4 solutions in the field, these experiments suggest that the demonstration objectives could be met by adding lower volumes of higher concentration oxidant solution. The advantages of adding lower volumes of oxidant include less potential to form a structurally unstable slurry in situ and decreased possibility of oxidant solutions and/or contaminants migrating from the treatment zone.

KMnO_4 Persistence in Field Moist Soil

One final series of experiments was completed to determine the persistence of KMnO_4 in field moist soil. In this experiments, uncontaminated Kansas City soil (field moist) was mixed with 3 different volumes of 4 wt% KMnO_4 using a laboratory-scale soil mixing apparatus. The volume of oxidant solution applied to the soil were 0.05, 0.1, and 0.15 mL oxidant/g soil (0.6, 1.2, and 1.8 gal/ft³). These volumetric loadings correspond to oxidant additions to the soil of 5, 10 and 15% on a weight basis (weight oxidant to weight of soil treated). Oxidant solutions were mixed directly into soil packed into 6 inch brass sleeves using a 2.5 inch diameter mixing blade. This arrangement allowed the field auger mixing and oxidant injection process to be evaluated at the laboratory scale. Soil samples were collected at regular intervals after oxidant addition so the moisture content and oxidant concentration could be monitored.

The increase in moisture content observed after oxidant addition correlated well with the volumes of oxidant added. The soil moisture content increased from an average pretreatment value of 25.2% to values of 25.5, 27.8 and 29.9% for the soils treated with 0.05, 0.1, and 0.15 mL oxidant/g soil respectively. The moisture content of the treated soils decreased with time. Seven days after oxidant injection the moisture content of the soils treated with 0.1 and 0.15 mL oxidant/ g soil oxidant injections were only 4.5 and 11.4% greater than the pretreatment value.

The oxidant concentration following injection and mixing was also evaluated to determine how long KMnO_4 could remain "active" in the Kansas City soil. After soil samples were collected from the treated cores, the soil solution was extracted (by the addition of 20 mL DI H_2O). The KMnO_4 concentrations in these extracts were measured colorimetrically. In the soils treated with 0.05 and 0.1 mL/g, the KMnO_4 concentration decreased by over

Figure 3.- TCE reduction in soil treated with different volumes of oxidant solution.
Note: The oxidant concentration was varied from 5 to 12% KMnO_4 in order to maintain an oxidant loading of 20 g KMnO_4 /kg soil treated.

Figure 4. DCE reduction in soil treated with different volumes of oxidant solution.
Note: The oxidant concentration was varied from 5 to 12% KMnO₄ in order to maintain an oxidant loading of 20 g KMnO₄/kg soil treated.

98% to 0.005 and 0.24 g/kg within 20 minutes of oxidant addition, indicating the rapid consumption of KMnO_4 in the soil. The soil treated with the higher volume of KMnO_4 had higher KMnO_4 concentrations after 20 minutes (1.1 g/kg). One day after oxidant injection no residual KMnO_4 was detected in the soils treated with 0.05 and 0.1 mL/g KMnO_4 . The KMnO_4 residual in the soil treated with 0.15 mL/g of KMnO_4 was 0.013 and 0.02 g KMnO_4 /kg soil 1 and 7 days after oxidant injection, respectively.

Conclusions

- KMnO_4 is more effective an oxidant than H_2O_2 or H_2O_2 + iron for the removal of TCE and DCE in contaminated soils from the Kansas City Plant.
- Under all but one of the experimental conditions evaluated, 100% of the DCE (initial concentration 12 -124 mg/kg) was removed from the Kansas City soil. Less the 100% DCE removal was observed in the soil treated with crystalline KMnO_4 .
- With KMnO_4 concentration of at least 4% and oxidant loading greater than 16 mg KMnO_4 /kg soil, TCE removals greater than 90% are possible.
- The volume of oxidant solution that is required to treat the Kansas City soil can be reduced by increasing the concentration of oxidant solution. In order to prepare solutions with KMnO_4 concentrations greater than 6% (by weight) the oxidant solution needs to be heated to 40° C.
- It is possible to treat the contaminated soil with crystalline KMnO_4 , however, TCE reductions are significantly lower than those achieved in soils treated with KMnO_4 solutions.
- KMnO_4 addition increases soil moisture content by an amount proportional to the oxidant volume and slightly increases soil pH. Additional studies would be required to determine the effect of KMnO_4 addition on the soil microbial population.

APPENDIX G

KMnO₄ Loading Rate Calculations for T5 and T4 Cells

KMnO₄ Loading Rate Calculations for T5 and T4 cells

T5 cell

Assumptions: Each cell is 8 by 25 ft cylinder (243.84 cm by 762 cm)
C2 cell overlaps 60%, yielding a net 40% for volume calc.
Particle density = 2.65 g/cm³
Effective porosity = 30%
25640 L of KMnO₄ @ 4.2% = (25,640 L) (42,000 mg/L) =
1,076,880 g KMnO₄

Volume Calc:

$$\begin{aligned}\text{Volume of 1 column} &= 3.14 (122 \text{ cm})^2 \times 762 \text{ cm} \\ &= 35,612,649 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Volume of C2 column} &= 35,612,649 \text{ cm}^3 (.4) \\ &= 14,245,060 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Total volume of C1, C2 and C3} &= 35,612,649 \text{ cm}^3 \times 2 + 14,245,060 \text{ cm}^3 \\ &= 85,470,358 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Subtract 30\% for effective porosity} &= 85,470,358 \text{ cm}^3 (.3) \\ &= 59,829,251 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Multiply by bulk density} &= 59,829,251 \text{ cm}^3 \times 2.65 \text{ g/cm}^3 \\ &= 158,547,515 \text{ g} \times 10^{-3} \\ &= 158,547.5 \text{ kg of soil}\end{aligned}$$

$$\text{KMnO}_4 \text{ Loading Calc: } 1,076,880 \text{ g KMnO}_4 / 158,547.5 \text{ kg soil} = 6.79 \text{ g KMnO}_4/\text{kg soil}$$

Substituting particle density with a total bulk density of 1.75 g/cm³ which accounts for void space and moisture content (28%) produces a loading rate of: 7.2 g KMnO₄/kg soil.

T5C1 column

$$\begin{aligned}35,612,649 \text{ cm}^3 - 30\% \times 2.65 \text{ g/cm}^3 &= 66,061,464 \text{ g} = 66,061.5 \text{ kg} \\ 7380 \text{ L} \times 37,000 \text{ mg/L} &= 273,060,000 \text{ mg} = 273,060 \text{ g KMnO}_4 \\ 273,060 \text{ g KMnO}_4 / 66,061.5 \text{ kg soil} &= 4.13 \text{ g KMnO}_4/\text{kg soil}\end{aligned}$$

T5C3 column

$$\begin{aligned}
 35,612,649 \text{ cm}^3 - 30\% \times 2.65 \text{ g/cm}^3 &= 66,061,464 \text{ g} = 66,061.5 \text{ kg} \\
 14,000 \text{ L} \times 47,000 \text{ mg/L} &= 658,000,000 \text{ mg} = 658,000 \text{ g KMnO}_4 \\
 658,000 \text{ g KMnO}_4 / 66,061.5 \text{ kg soil} &= \mathbf{9.96 \text{ g KMnO}_4/\text{kg soil}}
 \end{aligned}$$

T5C2 column

The overlap of the C2 column necessitates different treatment to calculate KMnO_4 loading rate. Essentially 30% of the C2 column overlaps the C1 column and 30% overlaps the C3 column. Using 30% of the total mass of each of these columns yields 19,818 kg ($66,061.5 \text{ kg} - 30\% = 19,818 \text{ kg soil}$). Thus, 19,818 kg soil in the overlap region with C1 column has 4.13 g KMnO_4 per kg/soil and 19,818 kg soil in the overlap region with C3 column has 9.96 kg KMnO_4 per kg soil. This translates to:

$$4.13 \text{ g KMnO}_4/\text{kg soil} \times 19,818 \text{ kg soil} = 81,848 \text{ g KMnO}_4 \text{ in the C1/C2 overlap region before C2 is mixed}$$

$$9.96 \text{ g KMnO}_4/\text{kg soil} \times 19,818 \text{ kg soil} = 197,387 \text{ g KMnO}_4 \text{ in the C1/C3 overlap region before C2 is mixed}$$

During the C2 mixing 4260 L KMnO_4 at 4.2 % (178,920 g KMnO_4) was mixed in with 66,061.5 kg soil which yields a loading rate of 2.71 g $\text{KMnO}_4/\text{kg soil}$ in C2. Therefore, the overlap regions have received an additional 2.71 g KMnO_4 per kg soil:

$$\begin{aligned}
 2.71 \text{ g KMnO}_4/\text{kg soil} \times 19,818 \text{ kg soil} &= 53,707 \text{ g KMnO}_4 \\
 53,707 \text{ g KMnO}_4 &\text{ must be added to the C1 and C3 overlap regions to determine the total KMnO}_4 \text{ added:}
 \end{aligned}$$

$$53,707 \text{ g KMnO}_4 + 81,848 \text{ g KMnO}_4 \text{ in the C1/C2 overlap region} = 135,555 \text{ g total in the C2/C1 overlap region}$$

$$53,707 \text{ g KMnO}_4 + 197,387 \text{ g KMnO}_4 \text{ in the C1/C3 overlap region} = 251,994 \text{ g total in the C2/C3 overlap region}$$

Loading rate for C2 calculated as follows:

$$\begin{aligned}
 \text{C2/C1 overlap region: } 135,555 \text{ g KMnO}_4 / 19,818 \text{ kg soil} &= 6.84 \text{ g KMnO}_4/\text{kg soil} \\
 \text{C2/C3 overlap region: } 251,994 \text{ g KMnO}_4 / 19,818 \text{ kg soil} &= 12.72 \text{ g KMnO}_4/\text{kg soil} \\
 \text{C2 nonoverlap area is } 2.71 \text{ g KMnO}_4/\text{kg soil}
 \end{aligned}$$

Weighted average loading rate for the C2 column: (30%) 6.84 g + (30%) 12.72 g + (40%) 2.71 g = 6.85 g KMnO_4 /kg soil

T4 Cell

Assumptions: Each cell is 8 by 47 ft cylinder (243.84 cm by 1433 cm)
 C2 cell overlaps 60%, yielding a net 40% for volume calc.
 Particle density = 2.65 g/cm³
 Effective porosity = 30%
 41399 of KMnO_4 @ 3.8% = (41,399 L) (38,000 mg/L) =
 1,573,162 g KMnO_4

Volume Calc:

$$\begin{aligned}\text{Volume of 1 column} &= 3.14 (122 \text{ cm})^2 \times 1433 \text{ cm} \\ &= 66,972,344 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Volume of C2 column} &= 66,972,344 \text{ cm}^3 (.4) \\ &= 26,788,938 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Total volume of C1, C2 and C3} &= 66,972,344 \text{ cm}^3 (2) + 26,788,938 \text{ cm}^3 \\ &= 160,733,626 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Subtract 30\% for effective porosity} &= 160,733,626 \text{ cm}^3 (.3) \\ &= 112,513,538 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Multiply by bulk density} &= 112,513,538 \text{ cm}^3 \times 2.65 \text{ g/cm}^3 \\ &= 298,160,876 \text{ g} \times 10^{-3} \\ &= 298,160.9 \text{ kg of soil}\end{aligned}$$

KMnO_4 Loading Calc: 1,573,162 g KMnO_4 /298,160.9 kg soil = 5.28 g KMnO_4 /kg soil

Substituting particle density with a total bulk density of 1.75 g/cm³ which accounts for void space and moisture content (28%) produces a loading rate of: 5.6 g KMnO_4 /kg soil.

T4C1 column

$$\begin{aligned}
 66,972,344 \text{ cm}^3 - 30\% \times 2.65 \text{ g/cm}^3 &= 124,233,698 \text{ g} = 124,233.7 \text{ kg} \\
 14,570 \text{ L} \times 31,000 \text{ mg/L} &= 451,670,000 \text{ mg} = 451,670 \text{ g KMnO}_4 \\
 451,670 \text{ g KMnO}_4 / 124,233.7 \text{ kg soil} &= \mathbf{3.64 \text{ g KMnO}_4/\text{kg soil}}
 \end{aligned}$$

T4C3 column

$$\begin{aligned}
 66,972,344 \text{ cm}^3 - 30\% \times 2.65 \text{ g/cm}^3 &= 124,233,698 \text{ g} = 124,233.7 \text{ kg} \\
 15,140 \text{ L} \times 49,000 \text{ mg/L} &= 741,860,000 \text{ mg} = 741,860 \text{ g KMnO}_4 \\
 741,860 \text{ g KMnO}_4 / 124,233.7 \text{ kg soil} &= \mathbf{5.97 \text{ g KMnO}_4/\text{kg soil}}
 \end{aligned}$$

T4C2 column

The overlap of the C2 column necessitates different treatment to calculate KMnO_4 loading rate. Essentially 30% of the C2 column overlaps the C1 column and 30% overlaps the C3 column. Using 30% of the total mass of each of these columns yields 37,270 kg ($124,233.7 \text{ kg} \times 30\% = 37,270 \text{ kg soil}$). Thus 37,270 kg soil in the overlap region with C1 column has 3.64 g KMnO_4 per kg/soil and 37,270 kg soil in the overlap region with C3 column has 5.97 kg KMnO_4 per kg soil. This translates to:

$$3.64 \text{ g KMnO}_4/\text{kg soil} \times 37,270 \text{ kg soil} = 135,663 \text{ g KMnO}_4 \text{ in the C1/C2 overlap region before C2 is mixed}$$

$$5.97 \text{ g KMnO}_4/\text{kg soil} \times 37,270 \text{ kg soil} = 222,502 \text{ g KMnO}_4 \text{ in the C1/C3 overlap region before C2 is mixed}$$

During the C2 mixing 11,689 L KMnO_4 at 3.4% (397,426 g KMnO_4) was mixed in with 124,233.7 kg soil which yields a loading rate of 3.2 g $\text{KMnO}_4/\text{kg soil}$ in C2. Therefore, the overlap regions have received an additional 3.2 g KMnO_4 per kg soil:

$$\begin{aligned}
 3.2 \text{ g KMnO}_4/\text{kg soil} \times 37,270 \text{ kg soil} &= 119,227 \text{ g KMnO}_4 \\
 119,227 \text{ g KMnO}_4 &\text{ must be added to the C1 and C3 overlap regions to determine the total KMnO}_4 \text{ added:}
 \end{aligned}$$

$$119,227 \text{ g KMnO}_4 + 135,663 \text{ g KMnO}_4 \text{ in the C1/C2 overlap region} = 254,890 \text{ g total in the C2/C1 overlap region}$$

119,227 g KMnO_4 + 222,502 g KMnO_4 in the C1/C3 overlap region = 341,729 g
total in the C2/C3 overlap region

Loading rate for C2 calculated as follows:

C2/C1 overlap region: 254,890 g KMnO_4 /37,270 kg soil = 6.84 g KMnO_4 /kg soil

C2/C3 overlap region: 341,729 g KMnO_4 /37,270 kg soil = 9.17 g KMnO_4 /kg soil

C2 nonoverlap area is 3.2 g KMnO_4 /kg soil

Weighted average loading rate for the C2 column: (30%) 6.84 g + (30%) 9.17 g +
(40%) 3.2 g = 6.1 g KMnO_4 /kg soil

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