

The Lasagna Technology for In Situ Soil Remediation. 1. Small Field Test

SA V. HO,*[†] CHRISTOPHER ATHMER,[†]
P. WAYNE SHERIDAN,[†]
B. MASON HUGHES,[†] ROBERT ORTH,[†]
DAVID MCKENZIE,[†]
PHILIP H. BRODSKY,[†]
ANDREW SHAPIRO,[‡] ROY THORNTON,[‡]
JOSEPH SALVO,[‡] DALE SCHULTZ,[§]
RICHARD LANDIS,[§] RON GRIFFITH,[§] AND
STEVE SHOEMAKER[§]

Monsanto Company, 800 N. Lindbergh Blvd.,
St. Louis, Missouri 63167, General Electric Corporate R&D,
P.O. Box 8, Schenectady, New York 12301, and
DuPont, Corporate Remediation Group,
140 Cypress Station Drive, Suite 135, Houston, Texas 77090

A novel, in situ remediation technology called Lasagna is being developed for cleaning up contamination in heterogeneous or low-permeability soils. The technology uses electrical current to drive contaminants from the soil into treatment zones installed directly in the contaminated area. The collaboration between a consortium of industry (Monsanto, DuPont, and General Electric) with the Department of Energy (DOE) and the Environmental Protection Agency (EPA) has led to two field tests at a DOE plant, chosen for its combination of low-permeability soil and trichloroethylene (TCE) as the sole contaminant. This paper describes the first field test in which TCE in the contaminated soil was transported into carbon-containing treatment zones where it was trapped. The test was very successful, removing over 98% TCE from the contaminated soil, with most treated samples showing greater than 99% removal. The success of this test paved the way for the second and much larger field test in which TCE was degraded in place.

Introduction

A novel, in situ remediation technology is being developed for cleaning up contamination in heterogeneous or low-permeability soils. Called Lasagna because of its layered configurations, the technology couples electrokinetics for contaminant transport in the soil matrix with in situ treatment zones that are installed directly in the contaminated soil. Electrokinetics includes the transport of water (electroosmosis) and ions (electromigration) as a result of an applied electric field. The use of electrokinetics as an in situ method for soil remediation has received increasing attention because of its unique applicability to low-permeability soils (1–9). Advantages of electroosmosis include relatively uniform water flow through heterogeneous/low-permeability soils, high degree of control of the flow direction, and very low power consumption.

* Corresponding author phone: (314) 694-5179; fax: (314) 694-1531; e-mail: sa.v.ho@monsanto.com.

[†] Monsanto Company.

[‡] General Electric.

[§] DuPont.

With its in situ treatment approach, the Lasagna technology offers many advantages over conventional electrokinetics that have been discussed in detail in a previous publication (10). Various configurations of the technology have been studied at both bench and pilot scale, including solid (graphite or steel plate) and granular carbon electrodes; adsorption and degradation treatment zones; and various soil matrixes such as homogeneous clay, sand mixed with clay, and a number of actual soils (10–14).

To help accelerate the development of this technology for field implementation, a consortium of industry (Monsanto, DuPont, and General Electric) was formed in collaboration with the Department of Energy (DOE) and the Environmental Protection Agency (EPA). The Paducah gaseous diffusion plant (PGDP) location was chosen from a list of DOE sites on the basis of two major criteria: low-permeability soil and a single chlorinated contaminant without heavy metals or radionuclides present. In addition to making the Paducah site available, DOE also contributed by providing soil sampling and analysis support (through Martin Marietta) and funds through a Research and Opportunity Announcement (ROA) grant. CDM-Federal, Inc., was hired by the consortium to construct and manage the field experiments. The first test unit was constructed in November and December 1994, began operating in January 1995, and was completed in May 1995. This paper documents this Phase I Lasagna field experiment.

Objectives of the Field Experiment. This initial field experiment tested the coupling of electroosmotic removal of TCE from the contaminated soil with in situ adsorption by carbon-containing treatment zones. This basically represents the simplest Lasagna configuration. Important operating issues include design and installation of treatment zones, electrical effects (e.g., voltage, current, power, soil conductivity, and heating) and electrokinetic effects (e.g., electroosmotic flow, pH profile, solution conductivity, responses to polarity and flow reversal, and long-term operation). Issues related to TCE removal include extent of soil cleanup, effectiveness of carbon adsorption in an electroosmotic environment, and overall mass balance. Field data would also be useful for the development of a mathematical model of the process.

Experimental Methods

Analytical Procedures. Soil sampling was carried out by Oak Ridge National Laboratory (ORNL) under the direction of Martin Marietta Energy Systems (MMES). TCE levels in soil were determined by extracting the soil samples with hexane then analyzing on site using a gas chromatograph equipped with an electron capture detector (GC-EC). Carbon sampling was performed by ORNL and Monsanto. TCE levels adsorbed on carbon were determined by extracting the carbon samples with hexane then analyzing off site (Monsanto analytical laboratory in St. Louis, MO) using GC-EC. TCE adsorption isotherms on soil were obtained using ¹⁴C-labeled TCE. A standard mixture of labeled and nonlabeled TCE was contacted with the soil in gas-tight centrifuge tubes for three days, then the amount of TCE left in solution was determined with a liquid scintillation counter.

Field Setup. The field test covered a soil block 15 ft (4.6 m) long × 10 ft (3 m) wide × 15 ft (4.6 m) deep. Figure 1 shows the actual layout of the field setup and locations of boreholes for soil sampling.

Electrodes and Treatment Zones. The two electrodes were set 10 ft (3 m) apart with four treatment zones installed at equidistance (2 ft or 61 cm) between the electrodes. Each

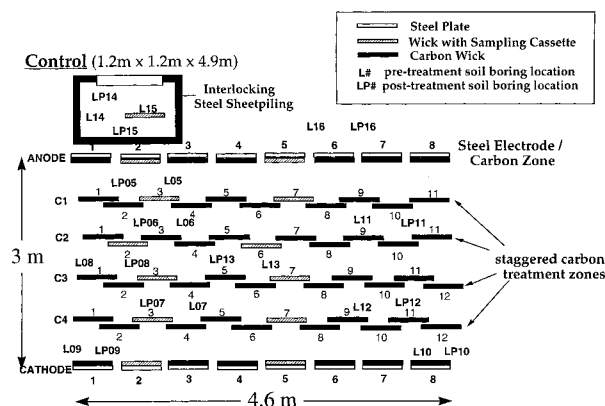


FIGURE 1. Layout of the field setup with sampling borehole locations (top view).

treatment zone consisted of a series of 11 or 12 individual "wicks" 46 cm wide and 4.6 m long placed vertically next to each other in a staggered configuration to create a curtain 4.6 m wide, 4.6 m deep, and 2.5 cm thick. The wick material was made from a roll of Hydraway wick drain material manufactured by Monsanto. The wicks were cut to length, filled with granular activated carbon (FiltruSorb-400 from Calgon), and encased in a geosynthetic filter fabric cover (Tygar from Remay). Each wick also had a 5 m length of 1/2 in. (1.27 cm) polyethylene tubing running the full length of the wick to allow water samples to be taken from any wick and for water level control in the electrode wicks. Each treatment row also contained two special sampling cassettes made of stainless steel shell with 50% open area that was constructed to hold a 15.2 cm wide section of wickdrain. These cassettes could be retrieved during or at the end of the experiment for TCE analysis.

Each electrode consisted of eight steel panels installed side by side with about 1/2 in. gap between panels, which covered the 4.6 m span. The panels were each 1/4 in. thick (0.635 cm), 18 in. wide (45.7 cm), and 16 ft long (4.88 m). Attached to the front of each steel panel was a wickdrain that contained activated carbon and acted as a treatment zone to trap TCE, preventing it from being degraded at the electrodes.

A control area was set up at the west end of the unit and was isolated hydraulically by a wall of 5 m deep sheet piling surrounding three-fourths of the perimeter of the control zone. A sampling cassette was inserted in the middle of the control zone for monitoring TCE removal under passive conditions.

The installation of electrode and treatment panels was carried out using a modified sheet piling method by NILEX corporation of Englewood, CO. A 10 ton vibratory hammer mounted on an 8 m high mast tower was connected to a steel mandrel sleeve that moved vertically. A steel shoe was designed to open the hole and allow the mandrel to penetrate through the gravel and clay layers to a depth of about 5 m below grade. The wick was then inserted into the mandrel, and the mandrel was removed, leaving the shoe and wick in place. A total of 46 treatment wicks and 16 electrode wicks were installed for this test.

Water Management System. For fluid circulation, individual overflow tubes were inserted each into a cathode panel down to about the clay level. A pump was used to lift liquid from the cathode compartments into the cathode collection tank, which overflowed by gravity into the anode supply tank through an electromagnetic flowmeter. Another pump was used to circulate the liquid on the anode side through the anode tank.

In order to keep the water handling systems from freezing during the winter, a temporary plastic enclosure was

TABLE 1. Characteristics of Paducah WKWMA Clean Soil

soil type	clay loam
sand content	22%
silt content	46%
clay content	32%
moisture content	15–18%
organic carbon content	0.2%
cation exchange capacity	13.4 meq/100 g
porosity	0.4
bulk density	2.0 g/cm ³

constructed over the test site, including the water tanks. The air discharge from the cooling radiator for the electrical generator was used to blow warm air into the enclosure. A vent was placed at the opposite corner to allow air to leave the enclosure. This vent was later used to monitor TCE volatilization.

Power Supply and Data Acquisition System. Power to the test site was supplied with a diesel-run Kubota Power Generator GV-3190Q rated at 18 kW. Two Sorenson 300 V, 35 amp power supplies provided the DC power to the field unit. The power supplies were connected in parallel to provide the required current.

A total of 12 thermocouples and seven multi-depth voltage probes were installed in the unit. The thermocouples were installed at various depths and locations to monitor the temperature rise in the soil due to resistive heating. Each voltage probe measured the voltage potential at 2-ft (0.6 m) intervals vertically. A PC-based data acquisition system was installed to monitor the operation of the unit. Twelve channels were monitored by the data acquisition system: eight temperature points, total voltage, current for each power supply, and total flow rate. Duplicate manual measurements were made periodically along with the voltage potentials and the pH and conductivity of the electrode fluids.

Electroosmotic Permeability Calculation. The electroosmotic permeability can be calculated using the following equation:

$$Q = k_e \Delta E A \quad (1)$$

where Q = volumetric flow rate by electroosmosis (cm³/s); k_e = coefficient of electroosmotic permeability (cm²/V s⁻¹); ΔE = voltage gradient applied across the soil mass (V/cm); A = cross-sectional area perpendicular to the direction of flow (cm²).

Note that the electroosmotic flow is proportional to the applied voltage gradient, and that the electroosmotic permeability has the units of velocity over field strength (cm/s over V/cm).

The cross sectional area for this field unit was 2.09×10^5 cm², compared to about 81 cm² for the bench-scale laboratory unit and 2600 cm² for the pilot unit.

Results and Discussion

Site and Soil Characteristics. The Paducah test site consisted of 1.5 m of a mixture of gravel and clay over about 12 m of TCE contaminated sandy clay loam. The hydraulic conductivity of the sandy clay loam is estimated to be about 1×10^{-7} cm/s. The hydraulic conductivity of the gravel/clay overflow has not been determined.

Clean Soil. Prior to the field test, a load of clean soil was obtained from the Western Kentucky Wildlife Management Area (WKWMA) site near the PDGP. This soil was judged to be similar to the contaminated soil at the Paducah plant. Table 1 summarizes some properties of this clean soil, which was characterized as a clay loam and contained approximately 0.2% organic carbon. Because of its very low organic content, the soil adsorbs very little TCE. The Langmuir fit of

the TCE adsorption data gives the following equation:

$$C_s = \frac{4.53C_w}{4.73 + C_w} \quad (2)$$

where C_s is the concentration of TCE adsorbed on soil (mg/kg) and C_w is the TCE concentration in soil pore water (mg/L).

The average TCE level in the contaminated soil at the test site was over 80 mg/kg, which translates to an average concentration in the pore water of almost 400 mg/L. The amount of TCE actually adsorbed on the soil would then be (from eq 2) about 4.5 mg/kg soil, or 5.6% of the measured level. Thus, most of the TCE present at the site was probably not bound to the soil and should readily move with the passing water. This clean soil was also used in the pilot unit for assessing long-term electroosmotic performance and heating effects (13).

Contaminated Soil. Four intact soil cores from the contaminated site were taken for analysis. They had an average density of 1.983 g/cm³, a moisture content of 18.5 wt %, and a solid density of 2.6 g/cm³. The pH of the soil samples ranged from 5.8 to 7.2. The electrical conductivity of one core, measured as a function of temperature using the four-point method (15), was found to increase steadily with temperature from 4 °C to 70 °C and can be fitted with the following equation:

$$\log_{10} \left(\frac{\sigma T}{\sigma_{20} \text{ } ^\circ\text{C}} \right) = \frac{1.3273(T - 20 \text{ } ^\circ\text{C}) + 0.001053(T - 20 \text{ } ^\circ\text{C})^2}{(T - 20 \text{ } ^\circ\text{C}) + 125} \quad (3)$$

where σT is the soil electrical conductivity at the temperature T in Celsius and $\sigma_{20} \text{ } ^\circ\text{C} = 0.026 \text{ S/m}$.

Electroosmotic experiments were conducted in the laboratory with slices of the contaminated soil cores repacked in a glass electroosmosis unit (9 cm inside diameter, 14.5 cm long for the soil column). Steel plates were used as electrodes, and four activated carbon zones, each 1 cm thick and 3–3.5 cm apart, were packed with the soil. For an applied voltage of 10 V, the current stabilized overnight to 11 mA. The electroosmotic permeability obtained was calculated to be $1.2 \times 10^{-5} \text{ cm}^2/\text{V s}^{-1}$, which is a fairly typical value for clayey soils.

Field Results. The field installation was carried out during November and December 1994. The power was turned on in January 1995, and the test lasted four months. Before the power was turned off, the voltage was reversed for about one week, primarily to collect voltage and current data. Key operating characteristics of the field test are reported below.

Voltage and Current. The test was conducted in a constant current mode. With the current held constant at 40 amps, the initial voltage started out at 138 V then slowly decreased with time, stabilizing at 105 V after one month of operation. The lower voltage at constant current was due to the soil being heated up (discussed below), which increased the electrical conductivity of the soil. The voltage gradient ranged from 0.45 to 0.35 V/cm. The voltage drop across the unit was fairly linear and did not change over the course of the experiment.

Electroosmotic Flow. During the first month, an electroosmotic flow rate of about 2 L/h was measured, which was less than half of the predicted value based on the bench-scale data. This low flow rate was later found to result from plugging of the cathode siphon tubes, causing water to “overflow” at the cathode wicks. Once this problem was corrected, the flow rate averaged approximately 4–5 L/h, corresponding to an electroosmotic permeability of $\sim 1.2 \times 10^{-5} \text{ cm}^2/\text{V s}^{-1}$, which agrees very well with the laboratory

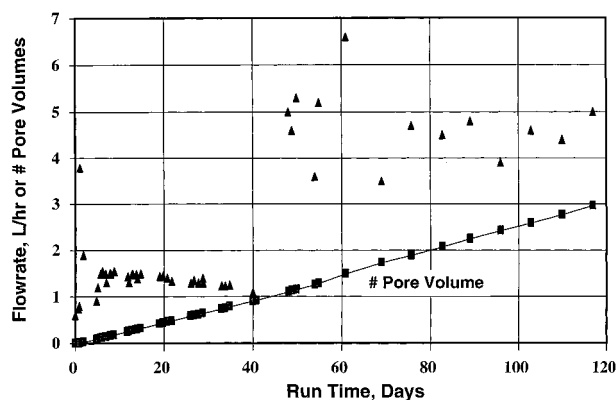


FIGURE 2. Electroosmotic flow rate measured as a function of time. Number of pore volumes was calculated using an electroosmotic flow rate of 4 L/h for the first 40 days.

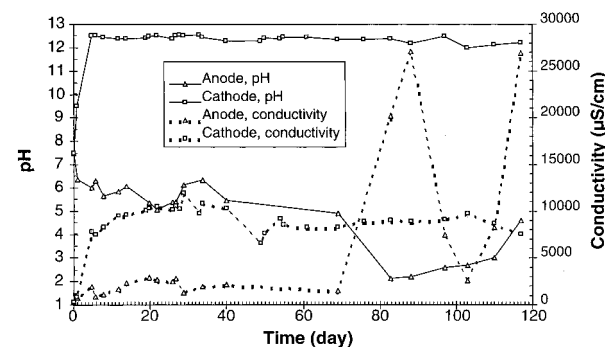


FIGURE 3. pH and conductivity of the electrode fluids as a function of time.

data. With the flow rate for the first 40 days corrected to a value of 4 L/h, the unit moved three pore volumes of water (between adjacent treatment zones) over the four month operating period (Figure 2).

Conductivity and pH. The pH of the anode fluid decreased from near neutral at the beginning to 5–6 for most of the test. This mild pH behavior was due to iron corrosion rather than water electrolysis as the predominant anodic reaction, which had also been observed in laboratory units (13). During the last month of the test, however, the anode fluid pH dipped rather unexplainably down to 2–3 before climbing back up to a more normal range near the end of the test. The pH of the cathode fluid increased rapidly to around 12 within a few days and stayed there for the whole experiment, a consequence of the electrolysis of water generating OH[−] at the cathode.

The conductivity of the anode solution ranged between 1000 and 3000 μS/cm for most of the test, except near the end when it fluctuated widely with occasional spikes up to 25 000 μS/cm. The prime ion species found were iron and chloride. This behavior was probably related to the low pH noted above during this period, which led to solubilization of many salts. The cathode solution conductivity was fairly constant at around 10 000 μS/cm with the primary ion species being sodium. These values were consistent with laboratory data. At the end of the test, water samples were taken from every wick to determine the distribution of anions, cations, pH, and specific conductance. Values of pH and conductivity of the anode and cathode fluids over time are shown in Figure 3.

Temperature Effects. The temperature rise at various locations due to the electrical input is shown in Figure 4. The initial temperature of the soil at the 3-m depth was 15 °C. The core temperature (hottest spot) reached a maximum of 45.2 °C at the end of the test. Notice the control zone

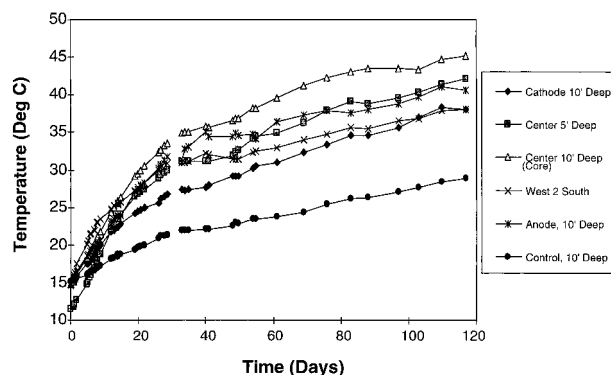


FIGURE 4. Temperature versus time at various locations.

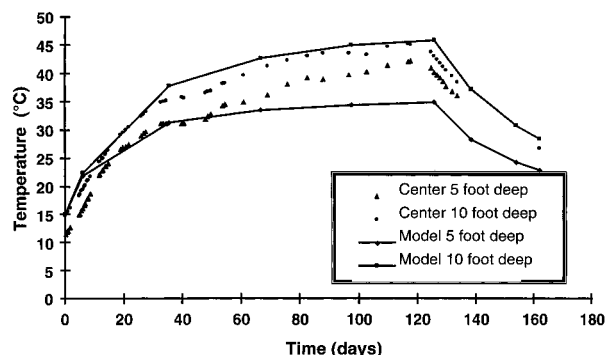


FIGURE 5. Comparison of model prediction and measured temperatures at the center of the test unit.

temperature also increased, probably because of stray current and/or thermal conduction, since the control zone was less than 30 cm from the anode.

To predict temperature rises in the field experiment, a mathematical model was developed using FIDAP, a commercial computational fluid dynamics program. The governing equations included energy transport by conduction, electroosmotic convection, and heat generation from Joule heating. Temperature dependencies of electrical conductivity and electroosmotic permeability were accounted for. The model description and the corresponding equations were reported in a previous publication (13). Specific examples simulating possible scenarios for the Lasagna pilot test in Paducah, KY, were studied. On the basis of the lab k_e value and estimated thermal conductivity and heat capacity of the soil, the operating current was set to 40 amps, which would keep the temperature of the unit below 50 °C. The model predictions correspond reasonably well with the field data as shown in Figure 5, including the cooling-off period when power was turned off at the end of the test.

Polarity Reversal. The electrical polarity of the field unit was reversed at the end of the test and held for 1 week. At a current of 39 amps, the reverse voltage was only 90 V instead of 105 V, which indicated an increase in electrical conductivity of the whole unit (soil plus electrodes) when the polarity was reversed. Also, as expected, pH at the electrodes was shifting from high to low at the new anode and from low to high at the new cathode. The overall behavior was very similar to what was observed in bench and pilot experiments (10, 13). These results indicate that polarity reversal can be utilized in the field, if needed, for reversing flow or neutralizing pH and/or osmotic gradients.

TCE Removal and Mass Balance. Pretest Soil Samples. Prior to the field installation, soil samples were taken and analyzed by ORNL personnel. A total of 12 boreholes were made with samples taken every foot (0.3 m) to a depth of 15 ft (4.6 m) below ground surface. Nine boreholes were drilled

TABLE 2. Average TCE Levels in Soil Cores Prior to Treatment

depth (ft)	TCE (mg/kg soil)			est TCE in water (mg/kg) max
	min	max	mean	
4	8.60	61.6	22.8	308.0
5	1.00	63.1	34.5	315.5
6	1.00	79.4	38.3	397.0
7	2.60	114.5	45.1	572.5
8	2.30	79.4	44.4	397.0
9	5.90	129	60.3	645.0
10	7.80	138.9	79.5	694.5
11	6.90	165.1	109.7	825.5
12	2.60	292	140.6	1460.0
13	4.70	402.5	150.2	2012.5
14	2.10	507.3	151.4	2536.5
15	3.20	237.3	123.2	1186.5
average	4.06	189.2	83.3	

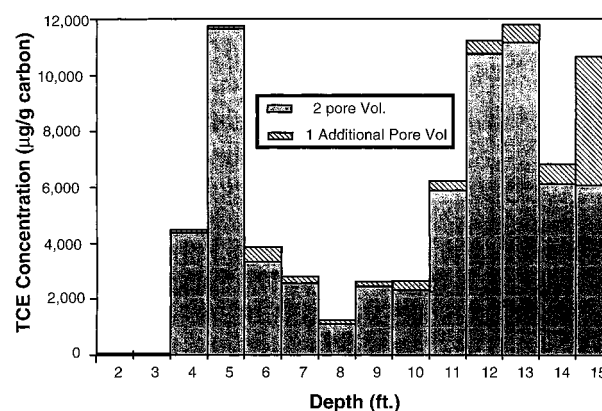


FIGURE 6. TCE levels measured on carbon samples from C4-7 sampling cassette. Calculations were made assuming that the carbon samples contained 50% moisture and the extraction efficiency was 33.3%.

within the test area, one on the outside and two in the control area. Figure 1 shows the locations of the boreholes with respect to the wicks. Shown in Table 2, TCE concentrations in the soil ranged from 1 mg/kg to over 500 mg/kg with an overall average of 83.3 mg/kg for the 12 boreholes from 4 to 15 ft (1.2–4.6 m) depths. Note that some samples at and below 12 ft deep show TCE concentrations in water exceeding its solubility limit (1100 ppm), suggesting the presence of DNAPLs. The total mass of TCE within the test site (4.6 m \times 4.6 m \times 3 m) was estimated to be about 9.25 kg.

Intermediate Carbon Samples. In order to assess the progress of the test, the carbon cassette from wick C4-7 was removed for analysis after two pore volumes of water exchange had occurred. Carbon samples were taken every 1 ft (0.3 m) from 3 to 15 ft. TCE levels on the carbon were found to be quite high, ranging from several thousand to over 10 000 mg TCE/kg carbon (Figure 6). This indicates that TCE was being effectively flushed from the soil and trapped on the carbon. When the cassette was refilled with fresh carbon and exposed for another pore volume, very little additional TCE was captured by the carbon except at the lowest depth. This indicates that the soil was probably clean of TCE. On the basis of these carbon results, the test was stopped.

Post-Test Soil and Carbon Samples. At the completion of the test, all carbon sampling cassettes were removed and analyzed in the same manner as were the intermediate samples. Soil samples were also taken. Twelve boreholes were dug near the original pretest boreholes (Figure 1) to take samples at every 1 ft to slightly deeper than 15 ft. The results obtained (Table 3) show very high degrees of TCE removal

TABLE 3. Summary of TCE Removal Based on Soil Core Data. Values Shown are the Averages of Samples from 4 to 15 ft for Each Location

borehole number	boreholes within test boundary									borehole outside unit		
	L-05	L-06	L-07	L-08	L-01	L-10	L-11	L-12	L-13	L-14	L-15	L-16
pre-test concentration (mg/kg)												
high	169.4	167.3	176.7	368.6	113.1	7.6	144.3	76.9	140.2	178.2	196.8	114.2
low	20.3	4.9	37.2	3.0	13.7	1.0	4.1	12.0	38.3	10.4	43.7	10.6
av	73.0	82.0	101.6	110.4	66.6	4.0	72.2	44.8	99.1	108.2	118.6	63.0
post-test concentration (mg/kg)												
High	0.29	1.22	8.62	17.40	15.20	0.47	1.84	5.23	2.29	101.7	109.5	50.8
low	0.004	0.21	0.055	0.018	0.002	0.042	0.40	0.002	0.038	24.6	6.7	2.6
av	0.14	0.50	1.06	2.07	3.73	0.30	0.89	0.89	0.64	80.0	58.0	20.1
TCE removal (%)	99.8	99.4	99.0	98.1	94.4	92.4	98.8	98.0	99.4	26.1	51.1	68.1

TABLE 4. Estimated TCE Concentrations in Soil from Kriged Data^a

carbon wick no.	wick TCE		pre-test soil TCE		post-test soil TCE		TCE mass removed from soil (gm)	TCE material balance (%)
	concn (mg/kg)	mass (gm)	concn (mg/kg)	mass (gm)	concn (mg/kg)	mass (gm)		
C1-3	1694	10.0	95.5	52.1	0.14	0.074	52.0	19.4
C1-7	1861	11.0	90.3	49.2	0.14	0.074	49.1	22.5
C2-2	4273	25.2	121.1	66.0	0.50	0.27	65.7	38.6
C2-6	4239	25.0	91.2	49.7	0.89	0.49	49.2	51.3
C3-3	4757	28.1	106.8	58.2	2.10	1.1	57.1	50.2
C3-7	6788	40.1	95.8	52.2	0.64	0.35	51.9	77.5
C4-3	2239	13.2	106.6	58.1	1.10	0.58	57.5	23.7
C4-7	5862	34.6	87.8	47.9	0.89	0.48	47.4	73.3
cathode-2	5652	33.4	99.4	54.2	3.70	2.0	52.2	65.3
cathode-5	6005	35.4	84.3	46.0	0.30	0.16	45.8	77.4
overall av	4337	25.6	97.9	53.4	1.04	0.558	52.8	49.0

^a TCE soil mass is figured using 6-in. wide × 21-in. long × 11-ft deep zone of soil in front (upstream) of the 6-in. wide sampling cassette and the average TCE concentration based on the pretest soil core kriged data.

from the treated soil. The final soil concentrations were generally below 1 mg/kg, with an average of 1.1 mg/kg for the nine boreholes within the test boundary. TCE removal ranged from 92.4 to 99.8%, with an overall average of 98.4%. The soil samples taken either outside or deeper than the test zone (below 15 feet) still showed substantial amounts of TCE present, with 26% and 51% removal from the two spots in the control zone and 68% from behind the anode. TCE removal in the control zone was probably due to diffusion into the carbon wick (see modeling below). The removal in the location behind the anode (L16) was probably due to both migration and diffusion from the anode area and/or sampling inaccuracies. Despite significant removal from the control areas, the definite contrast between TCE levels in the soils within the treated area and outside (or deeper) is quite remarkable and shows conclusively the effectiveness of the process for cleanup of the contaminated soil.

Several of the pretest soil samples showed TCE concentrations greater than 225 mg/kg (12–15 ft samples of borehole L-08). These values would indicate a residual DNAPL situation because a soil TCE concentration of 225 mg/kg corresponds to an equilibrium pore water concentration of 1100 mg/L, based on a bulk soil density of 2 g/cm³, a porosity of 0.4, and accounting for the 4.5 mg TCE/kg soil due to adsorption. In these likely DNAPL locations, TCE levels were reduced to less than 1 mg/kg, except for the 15-ft sample that was 17.4 mg/kg, probably because of upward diffusion of TCE from contaminated soil at lower depths. These results are intriguing and suggest that further work should be done to assess the effectiveness of this process for treating DNAPL TCE.

TCE Mass Balance. Special attempts were made in this study to determine the mass balance for TCE, taking into account the amounts in the soil before and after the test and the amounts trapped on the carbon. This was an important task for this field test because the major objective was to

demonstrate the ability of electrokinetics to transport TCE from the soil matrix into carbon trapping zones. However, rigorous mass balance analysis was not possible because of the following complexity of the field situation: (a) TCE levels in the soil varied in all directions. In addition, not all the soil samples were taken directly in front of the corresponding carbon cassettes. Thus, estimation of TCE concentrations at various locations was needed. For this we used a kriging method to obtain contour maps of TCE levels in the treated area. (b) The carbon cassettes were installed at the site about one month before the experiment actually started. So some TCE from the soil was lost because of passive diffusion to the carbon cassettes in the back row, which were not sampled, opposite to the direction of electroosmotic flow. On the basis of diffusion modeling (Table 5 below), the loss could be about 5%. (c) TCE degradation from reactions such as dechlorination due to iron present in the soil and iron introduced by the anodic reaction is possible (16). The extent of this loss is unknown. (d) Volatilization of TCE from the soil into the atmosphere was measured twice during the test. The first one gave an emission rate of 2.3 g TCE/d when the core temperature of the soil mass was 29.5 °C. The second sampling, when the core temperature was 35 °C, showed a TCE emission rate of 3.2 g/d, which, for a period of four months, would result in approximately 4% loss of TCE through volatilization. It should be noted that the above emission rates correspond to TCE concentrations in the air that are much lower than the maximum allowable limit.

Table 4 shows the mass balances obtained for various locations, each from 4 to 15 ft depth. As can be seen, the mass balance ranges from 20 to 80%, with an overall average of about 50%. These numbers are judged to be excellent considering the uncertainties mentioned above.

Role of Diffusion on TCE Removal. The removal of TCE from the contaminated soil by diffusion in the absence of an

TABLE 5. Model of TCE Removal from Soil by Diffusion with No Electroosmosis^a

A. % TCE removal at indicated soil temp (carbon zone spacing = 22 in. (0.56 m))				
exposure time	15 °C	25 °C	40 °C	60 °C
1 wk	7.8	8.2	8.8	9.7
4 mo	20.6	23.7	28.3	34.2
1 yr	35.9	41.3	49.3	59.4
5 yr	76.8	84.5	92.3	97.4
10 yr	93.4	97.0	99.3	99.9

B. % TCE removal at 25 °C			
exposure time	3-ft (0.91 m) spacing	5-ft (1.52 m) spacing	7-ft (2.13 m) spacing
1 wk	7.3	6.9	6.8
4 mo	14.7	10.0	8.4
1 yr	25.3	15.4	11.6
5 yr	56.3	33.9	24.2
10 yr	76.5	47.9	34.2

^a Model assumptions and parameters: diffusion in slab, carbon treatment zones as infinite sinks, no retardation of TCE from interaction with the soil matrix, soil porosity = 0.4, soil tortuosity = 3, $D_{TCE} = 9.96 \times 10^{-6}$ cm²/s at 25 °C.

imposed electric field was modeled. The problem is similar to the unsteady state heat conduction in the slab. With the soil between two treatment zones modeled as a slab at a uniform initial concentration of TCE and bracketed on both sides with infinite sinks (due to rapid adsorption relative to electroosmotic flow and carbon's capacity of 500 mg TCE/g carbon compared to <15 mg TCE/g carbon in soil), an analytical solution can be obtained (17). The effects of temperature on TCE diffusion were estimated using the Hayduk-Laudie equation (18) for TCE diffusivity: $D_b = (13.26 \times 10^{-5}) \mu_{H_2O}^{-1.14} V_{TCE}^{-0.589}$, where V_{TCE} is the molal volume of TCE at its normal boiling point and is equal to 101.5 cm³/gmol.

Table 5a shows that for the carbon zone spacing of 22 in. (55.9 cm), TCE removal by diffusion after four months is 20.6% at 15 °C, 23.7% at 25 °C, and 28.3% at 40 °C. These levels are significantly lower than the removal levels obtained in the treated soil. It is interesting that in 10 years, passive diffusion can remove over 90% of TCE in the soil at 15 °C for the 22-in. spacing. However, larger and more realistic treatment zone spacings of 5–7 ft (1.52–2.13 m) drastically

reduce the amounts of TCE possibly removed by passive diffusion. As shown in Table 5b, after 10 years at 25 °C, the TCE removal by diffusion alone is less than 50% for a 5-ft spacing and about 34% for the 7-ft spacing.

Acknowledgments

The authors thank our companies (Monsanto, GE, and DuPont) for their support on this project, and the teams at CDM Federal, API, Nilex, Martin Marietta, ORLN, WKMMA, EPA-Cincinnati, Clean Sites, Battelle-PNL, SAIC, and University of Cincinnati for their outstanding technical contributions. Last but not least, this project would have not been possible without DOE's financial support through contract number 21-94MC31185 as well as valuable logistic support from the Paducah plant.

Literature Cited

- (1) Casagrande, L. J. *BSCE* **1952**, 39, 51.
- (2) Shapiro, A. P.; Renaud, P.; Probst, R. *PhysicoChem. Hydrodyn.* **1989**, 11 (5/6), 785.
- (3) Hamed, J.; Acar, Y. B.; Gale, R. J. *ASCE* **1991**, 112, 241.
- (4) Bruell, C. J.; Segall, B. A. *J. Environ. Eng.* **1992**, 118 (1), 68.
- (5) Segall, B. A.; Bruell, C. J. *J. Environ. Eng.* **1992**, 118 (1), 84.
- (6) Acar, Y. B.; Li, H.; Gale, R. J. *ASCE* **1992**, 118 (11), 1837.
- (7) Shapiro, A. P.; Probst, R. F. *Environ. Sci. Technol.* **1993**, 27, 283.
- (8) Lageman, R. *Environ. Sci. Technol.* **1993**, 27 (13), 2648.
- (9) Acar, Y. B.; Alshawabkeh, A. N. *Environ. Sci. Technol.* **1993**, 27(13), 2638.
- (10) Ho, S. V.; Sheridan, P. W.; Athmer, C. J.; Heitkamp, M. A.; Brackin, J. M.; Weber, D.; Brodsky, P. H. *Environ. Sci. Technol.* **1995**, 29 (10), 2528.
- (11) Brodsky, P. H.; Ho, S. V. U.S. Patent 5,398,756, 1995.
- (12) Ho, S. V.; Brodsky, P. H. U.S. Patent 5,476,992, 1995.
- (13) Ho, S. V.; Athmer, C. J.; Sheridan, P. W.; Shapiro, A. P. *J. Hazard. Mater.* **1997**, 55, 39.
- (14) Ho, S. V.; Athmer, C. J.; Brackin, J. M.; Heitkamp, M. A.; Sheridan, P. W.; Weber, D.; Brodsky, P. H. In *Bioremediation Technologies*; Sikdar, S. K., Irvine, R. L., Eds.; Technomic Publishing Co., Inc.: Lancaster, PA, 1998; Vol III, pp 393–417.
- (15) Telford, W. M.; Geldard, L. P.; Sheriff, R. E. In *Applied Geophysics*, 2nd ed.; Cambridge University Press: New York, 1990; Chapter 5, p 288.
- (16) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, 32, 958.
- (17) McCabe, W. L.; Smith, J. C.; Harriott, P. In *Unit Operations of Chemical Engineering*, 5th ed.; McGraw-Hill: New York, 1993; Chapter 10, p 301.
- (18) Hayduk, W.; Laudie, H. *AIChE J.*, **1974**, 20, 611.

Received for review April 2, 1998. Revised manuscript received November 30, 1998. Accepted January 18, 1999.

ES980332S