

Soil Heating for Enhanced Remediation of Chlorinated Solvents: A Laboratory Study on Resistive Heating and Vapor Extraction in a Silty, Low-Permeable Soil Contaminated with Trichloroethylene

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Thermally enhanced remediation of trichloroethylene (TCE) from a 50 cm deep silty soil was demonstrated in a two-dimensional laboratory tank. Volatilized TCE was captured by vapor extraction in an overlaying coarse sand layer. Soil vapor extraction was first tested alone at 23 °C, showing very little efficiency due to the low-permeable layer and an estimated cleanup time of more than 1 year. By injecting electric current, the temperature was increased to 85 and 100 °C in steps, and the fluxes of TCE increased by factors of 2.6 and 19, respectively. After 37 days of heating, the mass of TCE in the soil was reduced from 35 to 0.072 g, corresponding to 99.8% mass removal. Average soil TCE concentrations were reduced from 273 to 0.6 mg/kg. Steam production by boiling of pore water and a 9-fold increase in the Henry's law constant of TCE were identified as the major mechanisms for overcoming mass-transfer limitations. The silty soil did not dry out due to water addition at the current electrodes, which is promising for the use of thermal enhancements for remediation of water-saturated clay layers and in shallow groundwater. In-situ thermal cleanups can be done in a few months, at costs typically below \$100/m³, and with very high removal efficiency for volatile and semivolatile organics.

Introduction

Soil vapor extraction is the most commonly used technique for remediation of unsaturated soils contaminated with volatile and semivolatile organics (1). The limiting factors for efficient removal include slow desorption of contaminants, slow diffusion of contaminants from low-permeable

layers into areas with vapor exchange, vapor-phase retardation due to adsorption, and limited volatility of the contaminant at in-situ temperatures (2, 3). The presence of low-permeable soil layers leads to incomplete contaminant removal since such layers often have high water saturations and potentially may retain significant amounts of organics not directly affected by the airflow in the surrounding permeable layers. Thermally enhanced remediation has recently been studied for overcoming the mass-transfer limitations (4–8). Recently, temperature effects on these physical parameters were investigated using trichloroethylene as a model compound (9, 10). It was shown that heating the soil from 20 to 100 °C would increase the volatility by a factor of 11–18, would increase diffusion coefficients in air and water by factors of 1.3–1.5, and would reduce partitioning coefficients leading to enhanced desorption and lower retardation of TCE moving in a vapor phase (10). Thus, there is an obvious potential for enhancing soil vapor extraction by applying heat to the contaminated areas.

The ways of applying heat to contaminated sites include thermal conduction using heat blankets or thermal wells, injection of hot air or steam, hot water injection, low-frequency electrical heating, radio frequency heating, and microwave heating (1, 7, 8, 11–13). Injection of hot fluids (air, steam, or water) suffers from the major disadvantage that the heat only can be injected directly into relatively permeable zones. Excellent research and field demonstrations of steam-enhanced extraction have been published by Udell and co-workers (7, 14, 15). However, low-permeable silt/clay layers of more than 0.5 m thickness will typically be heated solely by thermal conduction, which is a slow process since soil is a good insulator and has a high heat capacity. Therefore, alternative methods for heating low-permeable areas would be desirable.

Electrical heating techniques are based on resistive (Joule, ohmic) heating of the soil when an alternating current (ac) is applied. Whereas silty and clayey deposits are low-permeable to fluids, they are typically electrically more conductive than quartz sand due to the higher charge density of mineral surfaces and to higher water contents caused by capillary forces. This fact may be exploited by preferentially heating fine-grained layers by low-frequency ac heating (6, 16–18).

Resistive heating has been demonstrated to clean up a 3 m thick clay layer contaminated with trichloroethylene and perchloroethylene by heating the clays in-situ to 100–105 °C (16), and several authors have shown that heating can be achieved (17–20). However, there is still a major need to understand the processes taking place during heating and remediation, as indicated by a comprehensive recent review (7).

This paper presents a laboratory study on powerline (60 Hz) resistive heating of a low-permeable silty soil contaminated with TCE. We simulate the most problematic part of a vadose zone subject to soil vapor extraction; a silt/clay layer at high water saturation contaminated with TCE at concentrations close to the solubility limit. This is the case when the low-permeable layer receives infiltrating water from a zone with residual or pooled DNAPL. The effect of heating the soil to 85 and 100 °C to enhance soil vapor extraction is demonstrated, and the mechanisms for overcoming mass-transfer limitations are identified.

Materials and Methods

An overview of the laboratory setup is given in Figure 1. Soil vapor extraction was driven by the vacuum pump, leading

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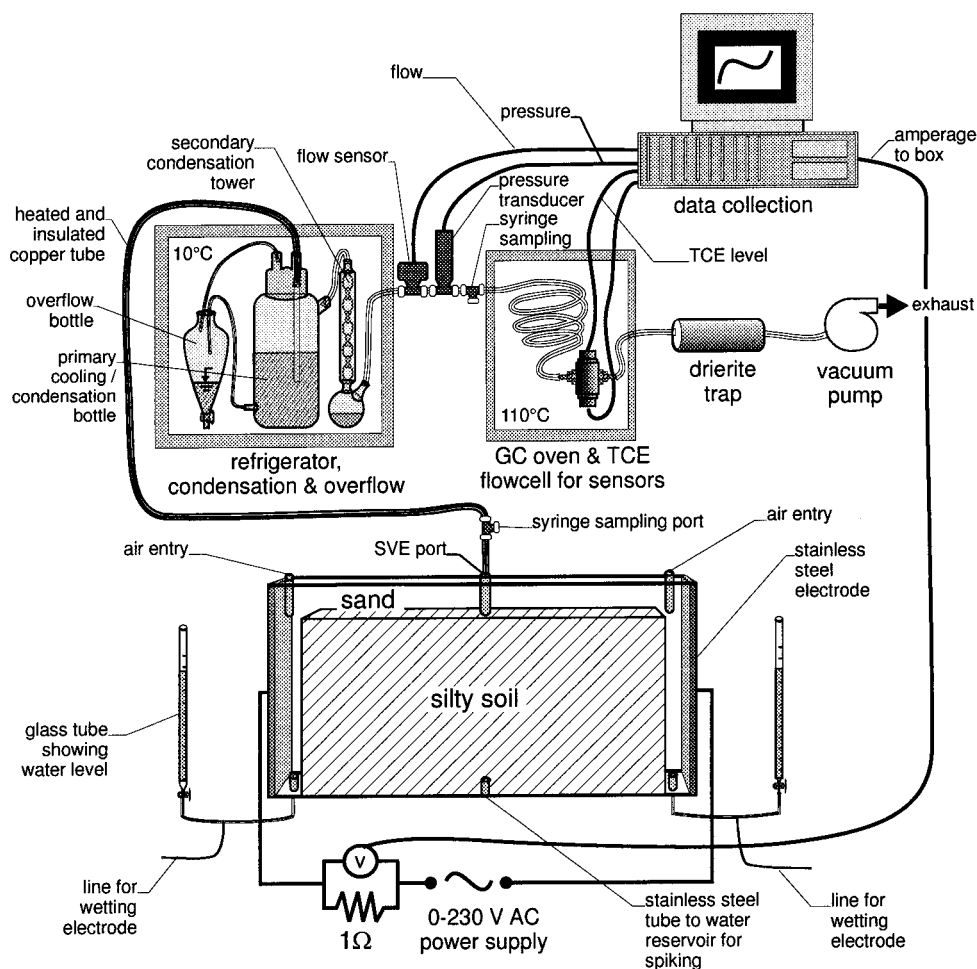


FIGURE 1. Laboratory setup overview for simulation of soil vapor extraction and resistive heating of a TCE-contaminated silty soil. The box was 120 cm wide, 60 cm high, and 12 cm deep.

to an airflow through the entire system from the air inlet ports, sweeping across the top sand layer in the box and through the central vent into the vapor treatment line where excess moisture was removed by condensation, and TCE concentrations were measured by gas sensors placed in a GC oven. Finally, the air was passed through a drierite trap for removal of residual moisture and on to an exhaust vent.

Box Construction: Details. The two-dimensional tank (117 cm by 57 cm by 12.6 cm) contained 84 L of soil, only contacted by Teflon, stainless steel, and Viton rubber. Forty ports for sampling water and vapor were inserted in the front Teflon plate. A piece of sintered stainless steel (opening mesh 10 μm) wrapped with Teflon tape and pressed into the open end of a thermocouple connector (stainless steel) was used as capillary barrier, allowing for sampling of water in the unsaturated soil through a GC septum using a gastight GC syringe. In the back Teflon plate, 48 ports with thermocouples sticking into the center of the soil permitted temperature recording using a DigiSense Thermocouple meter. The vapor in/outlet ports in the top coarse sand layer and the three bottom in/outlet ports were constructed from sintered stainless steel (opening mesh 100 μm) pressed into a PVC connector sealed by a Viton O-ring. The PVC connectors were screwed into tapped holes in the Teflon top and bottom bars, yielding gastight connections. Stainless steel electrodes were used as in previous field application of resistive heating (17). Joints between Teflon and stainless steel were sealed by a Viton rubber O-ring pressed in place tightly by a supporting plexiglass construction. Holes drilled in the plexiglass plates allowed for sampling of the front ports

and for thermocouple cables to run straight back into the insulation surrounding the entire box. Plexiglass is not an ideal material since it deforms at temperatures close to 100 $^{\circ}\text{C}$, but no better material was found at the time of construction. Polyisocyanate sheets were used for insulation around the entire box.

Soil Packing and Addition of Water and TCE. The box was packed with an uncontaminated silty soil (0.2% sand, 81% silt, 18.8% clay) with a low content of organic carbon (0.028% w/w measured according to ref 21) and a BET surface area of 14.4 m^2/g at 40 $^{\circ}\text{C}$. The permeability of this silty soil was 10^{-5} Darcy (determined by a simple constant head setup, triplicate columns). Coarse silica sand (ASTM 20–30, U.S. Silica, PA) was used at the ends next to the electrodes (4 cm width) and for the top 5 cm, where the vapor extraction was conducted (Figure 1). Carbon dioxide was flushed through the soil for 5 days to avoid nonwetted areas with trapped air. During water addition, trapped CO_2 dissolved readily in the water, leading to a more uniform water distribution. By comparing ingoing and outgoing volumetric CO_2 flows, it was confirmed that the box was gastight. A saturated solution of TCE (1120 mg/L) in water with the ratio of cations and a pH matching a saturated soil extract but with a salinity typical for groundwater (total dissolved solids 250 mg/L, pH 4.0, $[\text{Ca}^{2+}] = 42 \text{ mg/L}$, $[\text{Na}^+] = 33 \text{ mg/L}$, $[\text{Mg}^{2+}] = 14 \text{ mg/L}$, $[\text{Cl}^-] = 126 \text{ mg/L}$, and electrical conductivity of 765 $\mu\text{S}/\text{cm}$) was added through the central bottom port using capillary rise as the main driving force. After 3 days, the water addition was accelerated by application of a slight hydraulic head of 5–10 cm. The water entered the box and spread radially out

from the bottom port, reaching the sides and the top of the silty sand layer at the same time. This indicated a very homogeneous packing and symmetry in the box. The TCE concentrations in the inlet water were monitored by frequent water samples taken from the water line and analyzed as given below. No significant changes in the TCE concentration were observed during the 7 days of water addition.

Power Supply and Electrode Wetting. A variable power supply capable of supplying 230 V at up to 8 A was used to inject electric current at 60 Hz between the two electrodes. The injected current was determined by measuring the voltage drop over a 1 Ω resistor placed in series with the electrodes (Figure 1). The voltage was read by a multimeter connected directly to the poles of the transformer. Water was added to the electrodes through the bottom corner inlets by connecting the steel tubes to a constant head bottle containing water with the same salt content as the spiking water, but no TCE. A valve was opened manually when electrode wetting was needed and was shut when the desired level was reached.

Vapor Treatment and Monitoring System. The warm, moist air leaving the soil through the central vent was run through a heated (120 °C) 1/8 in. copper tube where the high temperature prevented condensation of water and clogging of the tube. A sampling port consisting of a stainless steel T with a GC septum was placed at the outlet port. Vapor samples were taken in a 1000- μ L gastight GC syringe equipped with a stop valve (wetted parts glass and Teflon only). The SVE line was run through a refrigerator (9–10 °C) where the air was brought to equilibrium with water at 10 °C for removal of moisture, which could affect TCE measurement in subsequent units of the equipment (22). The main condensation bottle was filled with 6 mm glass beads to minimize the retention time in the bottle, maintaining a high heat capacity. The temperature in the water was measured with a thermocouple dipped into the center of the bottle. A constant head connection allowed for removal and quantification of the condensed water in a volumetric overflow flask. The cooled air was passed through a secondary condensation tower to ensure condensation of excess water vapor. In a GC oven maintained at 110 °C, the air was heated in a 10 m long stainless steel coil and then passed through a sensing unit consisting of two semiconductive tin dioxide Figaro TGS 823 gas sensors in a custom-built stainless steel flow cell. The sensors were used for continuous, nondestructive monitoring of the TCE concentration in the air. Data were stored using the LabView data collection system (22). After leaving the oven, the air was sent through a trap containing drierite (anhydrous CaSO_4) for removal of residual water and organics before passing through the vacuum pump to a fume hood. Between the refrigerator and the oven, continuous monitoring of the airflow rate and pressure was done by a Ryton turbine wheel-type gas flow sensor (400–2000 mL/min; Cole-Parmer) and a stainless steel vacuum pressure transmitter (Cole-Parmer) connected to the automated data collection system. The pressure was also measured manually (mercury barometer) at the outlet sampling port, between the refrigerator and the oven, and between the oven and the drierite trap. Airflow was measured by means of direct reading glass flow tubes (0–1000 mL/min; Cole Parmer) before and after the oven. Mass fluxes of TCE were then calculated as the airflow rate times the TCE concentration.

Water and Vapor Sampling. Water samples were collected through the sampling ports in the silty layer, and vapor samples were collected in the outlet port. Vapor samples were taken in a 1000- μ L gastight GC syringe equipped with a stop valve (wetted parts glass and Teflon only) for closure and injected immediately into a GC with a capillary column and FID detector. Water samples (1 mL) were extracted in

0.25 mL of pentane in 2-mL GC vials with Teflon-coated crimp caps, and 5 μ L of the pentane extract was injected into a GC with a capillary column and FID detector. Water samples were cooled in the glass syringe for 30 s in an ice bath before extraction, thereby preventing boiling and loss of pentane after mixing in the extraction vial. Heat losses during sampling with the front side partly open (typically 2 h) led to maximum temperature decreases in the center of the soil of 2 °C.

Soil Sampling and Analysis. After the heating time and a cool-down period, the soil was sampled destructively for water content and TCE concentration. The sampling ports on the front side were screwed out, and soil was sampled through the holes using a cork-bore. Samples for TCE were injected quickly into vials containing 2 mL of pentane floating on top of 20 mL of water and extracted during 2 h of shaking and 24 h of overend-tumbling. The pentane extracts were analyzed on a Finnigan 4615 GC–MS using a capillary column and a negative ion ionization detector. Water contents were determined gravimetrically after soil drying at 105 °C for 48 h.

Results and Discussion

Initial TCE Concentrations and Saturations. The two-dimensional box was spiked with 31.8 L of water containing 35.5 g of dissolved TCE, and then allowed to equilibrate for 8 days prior to the onset of soil vapor extraction on day 0. The box was kept airtight with all ports closed to prevent losses. The initial box temperature was 23 °C (Figures 2 and 3). The distribution of dissolved TCE was highly nonuniform (Figure 3). Because the TCE-containing water was added from the bottom center port (Figure 1), it entered and spread radially as observed in a duplicate box equipped with transparent glass walls. Symmetric half-circular fronts indicated a very homogeneous packing of the soil and confirmed that the water entered the soil driven by capillary forces in the silty sand.

The decreasing TCE concentrations with distance from the inlet port may be explained by two mechanisms. First, diffusive losses of TCE into the vapor phase at the wetting front would be expected to lead to lower concentrations in the water. Second, adsorption of TCE onto the soil will reduce the concentration in the water. If sorption mechanisms would have led to a rapid approach to equilibrium, dissolved TCE concentrations in the bottom center of the box would have been close to 1120 mg/L, the average concentration in the inlet water. But at day 0, after 8 days of equilibration, aqueous concentrations were below 800 mg/L, which represents a drop by 29%. This decrease was not due to diffusive losses from the box, as documented by a very good mass balance for the experiment. Such decreases could be caused by kinetically controlled sorption, as previously observed by several authors (23–26).

No free liquid-phase TCE was formed during the experiment. Inlet concentrations were 1120 mg/L, well below the solubility limit at the actual temperature (1265 mg/L, ref 9). Adsorption of part of the TCE onto soil particles led to dissolved concentrations below 800 mg/L in all ports at all times during the experiment.

Soil samples from a duplicate box indicated a fairly homogeneous water content in the silty layer with an average saturation of 0.87 (data not shown). On the basis of the soil volume and the added amount of water, an initial saturation of 0.90 was estimated (porosity = 0.38).

Performance of SVE Alone (Days 0–8). Soil vapor extraction in the top sand layer resulted in little removal of TCE (6.8%) from the box (Figures 2 and 3) and did not affect the water saturations significantly. A total of 2.4 g of TCE was recovered by the vapor treatment system, and the mass of dissolved TCE decreased by 1.5 g, with a decrease of 0.9

TABLE 1. Mass Balance for the Total Box at Selected Times during the Soil Vapor Extraction—Resistive Heating Experiment^a

day	temp (°C)	Henry's law constant, H (—)	partitioning coeff, K_d (L/kg)	obs total TCE mass in box (g)	obs dissolved TCE mass (g)	calcd vapor mass (g)	calcd dissolved mass (g)	calcd mass on solids (g)
0	23	0.38	0.40	35.5	14.6	0.55	13.7	21.3
8	23	0.38	0.40	33.1	13.1	0.51	12.8	19.8
21	80	2.33	0.35	21.7	4.5	2.0	8.3	11.3
35	85	2.61	0.35	15.9	2.6	1.7	6.0	8.2
45	99	3.47	0.34	0.072	0.027	0.010	0.027	0.035
60	23	0.38	0.40	0.072	0.028	0.001	0.028	0.043

^a Equations 1 and 2 were used, and the overall mass recovery of 94% was used to correct the masses left in the box, assuming a constant mass loss with time.

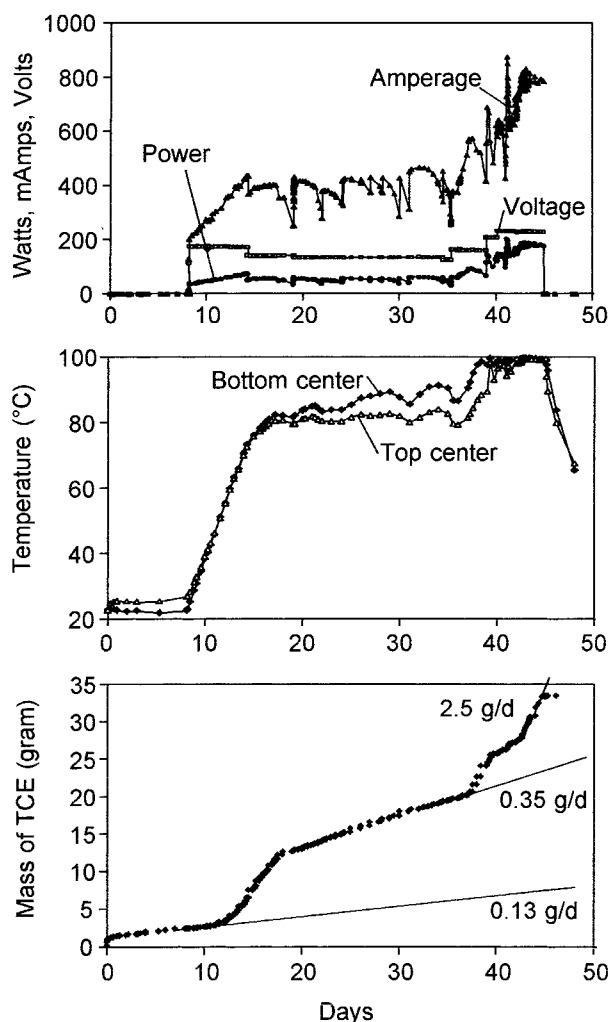


FIGURE 2. Performance of the two-dimensional Joule heating–soil vapor extraction reactor: The power input by electrical heating, the development of temperatures at selected locations in the box, and the accumulated mass of TCE recovered from the central vent during the experiment. A total of 35.5 g of TCE was added to the box. Steady-state fluxes out of the central SVE port increase from 0.13 to 2.5 mg of TCE per day when heating from 23 to 99 °C.

g in the adsorbed and vapor phases (mass balance given in Table 1). The most obvious mass removal occurred in the top of the box where clean air entered through the top inlet ports and swept across the top of the silt layer. When the stagnant air in the SVE layer was replaced, the removal flux dropped to very low levels and stabilized at 0.13 g/d (Figure 2). This flux was relatively constant over a week of extraction and indicated that it would take close to 1 year to remove the TCE from the silty layer, assuming that this flux could be maintained. Practically, diffusion-rate limitations and kinetic

desorption would lead to reduced fluxes over time, and we believe that a cleanup time of several years or decades would be required. This shows that soil vapor extraction would be impractical as the sole remediation technique for a fine-grained, almost saturated layer of this thickness (50 cm). Note that the elevated temperatures around the SVE port (Figure 3) were caused by the conduction of heat from the heated SVE line (heat traced at 120 °C).

Resistive Heating Reaching 85 °C. The electrical heating was initiated on day 8, leading to a rapid increase of the temperatures in the entire box, until a steady temperature was reached around day 21 (Figures 2 and 3). The temperatures in the upper part of the soil were typically 8–12 deg lower than at the bottom, due to the cooling effect of the clean air entering from the top corner inlet ports and the fact that the power dissipation predominantly occurred in the lower part of the box where the soil next to the electrodes was water-saturated. The distribution of TCE in the dissolved phase (Figure 3) indicated dramatic mass reductions, and the heating was continued.

The increased temperatures dramatically increased the TCE flux out of the box, as a peak lasting for about 1 week was observed (Figure 2). When the flux leveled off, steady-state fluxes were still high (0.35 g/d) as compared to the SVE flux (0.13 g/d) at 23 °C. On day 35, after 28 days of heating, the mass of dissolved TCE had dropped from 14.6 to 2.6 g, and a total of 19.6 g of TCE had been recovered by the vapor treatment system (Figure 2, Table 1). The distribution of dissolved TCE shows that concentrations had been lowered in the entire box and that TCE concentrations at the edges of the silty layer were very low (Figure 3). The edges were more exposed to the vapor extraction and to water vapor moving upward from the water table at the electrodes.

Twenty-eight days of heating to 80–90 °C resulted in removal of 55% of the total TCE in the box, and the steady-state flux of 0.35 g/d reached indicated a total cleanup time of at least another 50 days, assuming that a constant TCE flux could be maintained. At this point, it was decided to try to speed remediation by increasing the temperature in the box.

Resistive Heating Reaching 99–100 °C. By increasing the voltage to 230 V, we were able to inject 180 W of electrical power and reach temperatures of 99–100 °C in the entire box between days 39 and 45 (Figures 2 and 3). Boiling of water led to steam production, and about 20 L of water was removed in 5 days. To maintain the high current flow into the box, clean water with the same salinity as the spiking water was added to the electrodes through the bottom inlet ports (Figure 1). The added water equalled the mass of water condensed in the vapor treatment system, so overall the soil did not dry out significantly. During the 5 days during which temperatures were maintained above 99 °C, the flux of TCE peaked and 13.9 g of TCE was removed. The relatively high flux of TCE out of the box, even when residual concentrations dropped to low values, was very encouraging. The results indicated that removal of low residual amounts of organics

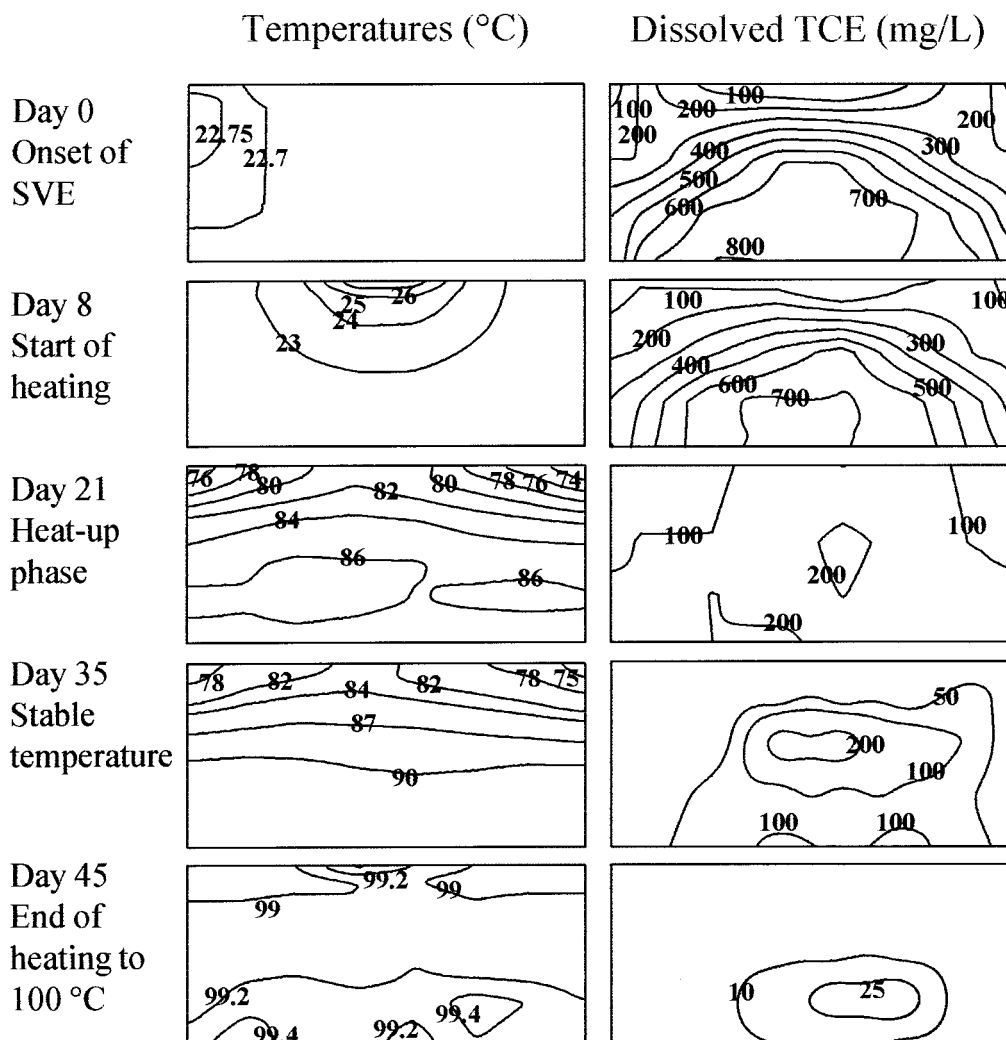


FIGURE 3. Temperature distribution measured using a 48-point thermocouple grid and distribution of dissolved trichloroethylene measured by gas chromatography in pentane extracts of water from the 40 sampling ports in the two-dimensional Joule heating–soil vapor extraction reactor at selected times. The box was 120 cm wide, 60 cm high, and 12 cm deep.

may be rapid at 99–100 °C and that the tailing observed using soil vapor extraction alone may be much less significant at higher temperatures.

Performance after Power Shutdown. Immediately after the power was shut off, temperatures near the SVE screen dropped below 99 °C, and the steam production ceased. The flux of TCE decreased rapidly to below detection limits within 24 h, as the box had cooled to 90 °C (Figure 2). A small amount of water vapor was recovered by the SVE system, and when the water flux approached the detection limit, the vapor extraction was stopped. The insulation was kept in place for slowed cooling in order to prevent movement of water induced by thermal gradients within the box. In 2 weeks, the box cooled to below 25 °C. The residual soil contents of TCE showed that 0.072 g of TCE was left in the soil (Figure 4), as compared to the initial 35.5 g. This equals a 99.8% removal of TCE from the silty soil, without significant drying out as shown by the water balance. The highest TCE concentrations were found in the central bottom part, where water saturations were highest (above 0.95, data not shown), and diffusive paths to the coarse sand were longest.

Mass Balances for TCE and Water. The final distribution of dissolved TCE (Figure 3) and total soil TCE (Figure 4) indicated not only an efficient TCE removal of 99.8% but also that the soil closest to the most permeable layers essentially was clean. Average soil concentrations were reduced from an initial 273 to 0.6 mg/kg. The vapor extraction

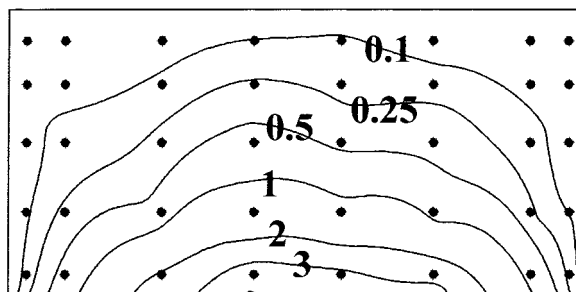


FIGURE 4. Distribution of trichloroethylene in soil samples (mg/kg dry weight) from the silty soil after 45 days of soil vapor extraction including 36 days of electrical heating. The soil was allowed to cool slowly for 15 days prior to sampling on day 60. Dots indicate soil sampling points. The box was 120 cm wide, 60 cm high, and 12 cm deep.

system recovered 33.5 g of TCE, which led to 94% recovery, since only 0.072 g was left in the soil after the heating period. A mass balance for the entire experiment was developed from the experimental data on days 0, 8, 21, 35, 45, and 60 and simple calculations using the equations for the soil–water distribution coefficient K_d , and the dimensionless Henry's law constant H for TCE experimentally determined between 10 and 95 °C by Heron et al. (9, 10):

TABLE 2. Observed Fluxes of TCE in the SVE Line and Calculated Physical Property Changes with Temperature at Times of Steady-State Conditions

temp in the soil (°C)	TCE steady-state flux (g/day)	obsd enhancement factor (flux/flux ₂₃)	Henry's law constant increase factor (H/H_{23})	partitioning coeff decrease factor ($K_{d,23}/K_d$)	gaseous diffusion increase factor (D/D_{23})	combined, multiplied H, K_d , and D increase factor
23	0.133	1	1	1	1	1
85	0.352	2.65	6.8	1.15	1.33	10.4
99	2.5	18.8	9.0	1.18	1.41	15.0

$$K_d = 0.4 \exp(-\Delta H_s/R_g(1/T - 1/T_o)) \quad (\text{L/kg}) \quad (1)$$

$$\ln H = 108.21 - 7975/T - 14.45 \ln T \quad (\text{dimensionless}) \quad (2)$$

where ΔH_s is the enthalpy of sorption for TCE onto the soil in question (-2 kJ/mol used for TCE as a moderately sorbate in a low-organic carbon soil, ref 10), R_g is the gas constant (8.314 J/(mol K)), and T is temperature in Kelvins. Negative ΔH_s values (exothermic adsorption process) means that the K_d decreases with increasing temperatures, as supported by experimental work on soil and clay solids (27). The value 0.4 L/kg for K_d was determined experimentally at 23°C (this study, data not shown). The results are given in Table 1, along with experimentally determined data for the mass of dissolved TCE (integrated from the data in Figure 3). Heating the soil favored the transport of TCE to the gaseous phase and reduced the importance of adsorption onto the soil. However, even at 99°C more TCE was found in the adsorbed state than dissolved (on a mixed media basis). This showed that sorption was still a dominant mechanism, even when the volatility was increased 9-fold. The total mass of TCE was diminished by the removal through the vapor extraction port, and only traces of TCE were found in the vapor, water, and soil. Overall, all three phases were reduced simultaneously, even though TCE was only removed as vapor.

Rate-Limiting Mechanisms and Compound Properties.

Diffusion of organic compounds in the vapor phase is 4 orders of magnitude faster than aqueous diffusion (28, 29). Thus, shifting the equilibrium toward the vapor phase (eq 2) during heatup may lead to higher fluxes out of the soil. Also, lowering the partitioning coefficient K_d may lead to enhanced desorption and higher mobility of the TCE (eq 1). The gaseous diffusivity of TCE goes up no more than a factor of 1.5 from 20 to 100°C , as calculated in ref 10:

$$D = D_o(T/T_o)^{1.5} \quad (3)$$

The calculated values for D , H , and K_d and the observed fluxes are given in Tables 1 and 2. The increased fluxes cannot be explained by the diffusivity increase or sorption decrease alone. The increased volatility was the dominant factor, since Henry's law constants increased by factors of 6.8 and 9 from 23 to 85 and 99°C , respectively. Combining the effects by multiplying the factors for each property leads to enhancement factors in the same range as the observed flux increases (Table 2). At 85°C , the enhancement seems to be overestimated, since the flux only increased 2.65-fold as compared to the calculated increase of 10.4-fold. This shows that not all three properties were limiting the removal rate at this temperature. Potentially, the Henry's law constant was high enough to shift the equilibrium toward the vapor phase. It may be that diffusion paths to the upper layer were not sufficiently fast for a similar flux increase. At 99°C , however, the predicted enhancement factor agreed reasonably with the observed one. We speculate that the formation of gas bubbles in the soil due to volatilization of dissolved gases may produce air-filled pores or even channels for fast gaseous

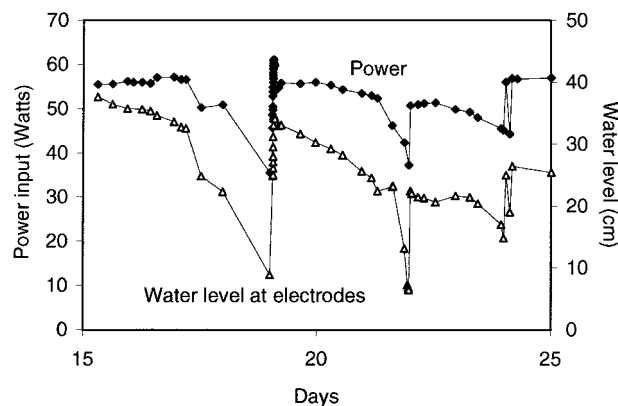


FIGURE 5. Example of how the water level at the power electrodes influences the power input for a selected fraction of the heating period.

diffusion and maybe even advection of steam and hot air within the soil. Such channels could not be positively identified during the excavation of the soil. Both the small-scale difficulties in manual excavation and the fact that such bubbles may have been redissolved during cooling prevented testing of this hypothesis.

Recent results indicate that very little drying out was required for almost complete removal of organics from soil (7). A theoretical study showed that the concentration (C) of contaminants in the dissolved phase was reduced by orders of magnitude when the soil dried from a water mass m_o to m_i following

$$\frac{C_i}{C_o} = \left(\frac{m_i}{m_o}\right)^{(H(\rho_{\text{water}}/\rho_{\text{vapor}}) - 1)} \quad (4)$$

where H is the dimensionless Henry's law constant and ρ is density (7). At 99°C , the exponent may be estimated to 5640 for TCE, assuming that the vapor is pure steam and performs as an ideal gas. Drying out of 1% of the water in the soil would lead to a concentration drop to well below detection limits in the water. Although a very simplified calculation, this supported our observation that very little mass-transfer limitations occurred in the later stages when the soil was heated to 99°C .

Electrode Operation, Design, and Power Input. The energy dissipated within the soil is directly dependent on the water levels at the electrodes (Figure 5). Drying out leads to increased resistivity of the sand since the water conducts the bulk of the current. Since the power supply was at a fixed voltage (E, V), drying out the electrodes and the subsequent resistivity increase (R, Ω) led to lower current (I, A) into the box and thus to a lower power input (P, W):

$$P = EI = RI^2 \quad (5)$$

The fixed voltage power source was selected for safety reasons, since the other alternative for power control (fixed current) could potentially lead to great hazards. Assuming constant current and increasing resistivity, the power supply would

automatically increase the voltage to maintain the set current. Thus, drying out would lead to increasing power input (eq 5) and thus to even quicker evaporation. This situation would be highly unstable unless controlled by thermostats at several locations in order to prevent overheating and electrode melting. Melting of injection electrodes was observed in the field (17, 30) where temperatures as high as 1000 °C at the electrodes were indicated by in-situ measurements.

The maintenance of a relatively constant power input was essential for the production of steam when the temperature approached 100 °C. Drying out at the electrodes quickly led to lower power input (Figure 5) and shut down steam production, since the temperature at the top SVE extraction point dropped below 99 °C. Thus, to keep temperatures high and for optimal steam production, it is important to maintain good electrical contact to the formation. This has been done by adding water to the electrodes (16, 17, 31) and by packing graphite around the electrodes (17). Since most of the water evaporates close to the electrodes, it is not essential that the formation is permeable enough to conduct the injected water.

Effect of Steam Production on TCE Fluxes. In this study, steam production greatly enhanced the recovery of TCE from the soil. When the temperatures dropped slightly and steam production ceased, the TCE flux would decrease similarly. So in this case it was crucial to maintain a high, constant power input to maintain high TCE recovery rates. An important mechanism for the TCE movement may be the expansion of water as it evaporates. One gram of liquid water occupies 1 mL. Once evaporated at 100 °C, the same gram of water behaves as an ideal gas and thus occupies 1.7 L as steam at 1 atm pressure, which is a 1700-fold volume expansion. This expansion may push out large amounts of soil vapor in the surrounding areas and thus be a very important mechanism for the enhanced contaminant recovery at steam temperatures, as previously discussed in refs 7 and 15.

Potential for Removal of Higher Boiling Point Compounds. The enhancement of the TCE recovery by heating does not directly depend on exceeding the boiling point of TCE (87 °C), since there was no free-phase TCE and thus not a direct boiling of such a phase. Actually, Figure 2 shows that the TCE fluxes picked up dramatically long before 87 °C was reached. This indicates that similar enhancement factors can be achieved for other compounds with higher boiling points. Independent of the boiling point, properties such as the Henry's constant, vapor pressure, and diffusion coefficients will increase with temperature in a manner similar to those of TCE. Adsorption onto the soil will decrease, also leading to faster removal. Actually, the stronger the contaminant sorbs (high $-\Delta H_s$), the stronger the effect of heating on K_d (eq 1, ref 10). Thus, electrical heating is very promising for accelerating removal of a wide range of organic compounds, including semivolatile compounds.

Potential for Resistive Heating below the Water Table. Drying out was not necessary for almost complete TCE removal from the silty soil. In fact, even the 100% saturated bottom parts of the silty layer were cleaned to very low residual TCE levels (Figure 4). This is encouraging for the application to groundwater plumes where desaturation would be hard to achieve without lowering the water table hydraulically to below the target area. Resistive heating may thus be feasible in the upper part of aquifers, overlaid by an unsaturated zone suited for soil vapor extraction. Where a vapor phase is important for contaminant removal, air sparging may be a promising technology to combine with heating.

Heat Capacity and Cost of Thermal Remediation. A typical concern on thermal remediation is the cost of heating soil. However, simple calculations show that approximately

80 kWh is needed for heating 1 m³ of water-saturated soil from 10 to 100 °C (heat capacity of soil and water of 1000 and 4200 kJ/(kg K), respectively; ref 32). This equals a cost of \$8/m³ when heated using electricity and a cost of \$3/m³ when the heat is supplied as steam. When significant evaporation of water occurs, the heat of vaporization may lead to greater energy consumption. Field-scale applications show that thermal cleanup can be done with a total treatment cost in the range of \$45–150/m³, including the cost of research and development (31, 33). A recent study on the cost of thermal methods concluded that, in all five scenarios presented, thermal remediation was cheaper than the best comparable technology (34). In conclusion, it appears that not only are thermal methods efficient for removal of organics from low-permeable soils that presently cannot be remediated by other techniques, they are also economically very competitive. The main reason for this is the low treatment time needed when elevated temperatures speed up mass removal, leading to much lower long-term expenses (34).

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