

USING ELEVATED TEMPERATURES TO ENHANCE IN-
SITU REMEDIATION IN LOW-PERMEABILITY SOILS AND
GROUNDWATER

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1. INTRODUCTION

Contamination of soil and groundwater by organics is recognized as a major threat to the environment. Where contamination is severe and occurs deep or below buildings, excavation and off-site treatment is impractical. In-situ remediation is the only alternative to abandoning the area and containing the spread of contamination.

The most commonly used remediation techniques are (1) pump and treat, (2) air sparging, (3) vacuum extraction, and (4) stimulation of biological degradation. The physical-chemical remediation techniques suffer from three major limitations. Firstly, when circulating water or air through a geologic formation, the fluid will predominantly flow in the highly permeable layers, rendering layers of low-permeable soil largely unaffected by the treatment. Often organic contaminants bind stronger onto low-permeable, organic and clay-rich lenses and layers. Even if the moving fluid totally cleans the major part of the formation, the slow diffusion of contaminants from low- to high-permeable layers may be rate-limiting for the total clean-up (DiGiulio, 1992; Gibson et al., 1993). Secondly, limited volatility of the contaminants (low vapor pressure and Henry's law constants) at the in-situ temperature may prevent a sufficiently rapid clean-up, even when target areas are flushed with air. Thirdly, sorption of contaminants onto soil and aquifer sediment may dramatically retard the movement with the fluid. Both the wet adsorption coefficients (K_d) and the vapor sorption coefficient (K'_g) are important parameters. For many compounds, retardation factors in the range of 10 to several thousands may prevent efficient clean-up. Recently, Davis (1997a) reviewed the effect of heat on the distribution of organics in soils and groundwater.

This paper summarizes the effect of heating on the distribution of organics in the subsurface, briefly reviews technologies used to inject heat in-situ, and finally illustrates the dramatic effect of heating on contaminant removal rates using a controlled laboratory simulation. These results are currently submitted for publication elsewhere (Heron et al., 1997a; Heron et al., 1997b).

2. EFFECT OF TEMPERATURE ON PHYSICAL PROPERTIES OF CONTAMINANTS

In terms of basic physical-chemical parameters, the recovery of contaminants from soils and aquifers may be controlled by the following: (1) vapor pressure, (2) solubility, (3) Henry's law constant, (4) diffusion coefficients in water and air, and (5) sorption coefficients for dissolved and vapor-phase contaminants, or the kinetic expressions related to these parameters. We will now briefly review the importance of temperature for each parameter, supported by Table 1, summarizing the temperature dependency as determined for TCE in a recent study (Heron et al., 1997a).

2.1. Vapor pressure

The vapor pressure of an organic compound is a measure of its volatility when present as a free phase liquid. Vapor pressure (P_v , measured in mmHg or Atm) varies strongly with temperature, generally following the integrated form of the Clausius-Clapeyron equation. When ΔH_{vap} (enthalpy/heat of vaporization) may be assumed constant over a narrow temperature interval.

Table 1. Hypothetical enhancement factors for contaminant removal rates based on changes in the physical properties of organic compounds with increasing temperature. Values are based on data determined for trichloroethylene in this study. Calculations are based on initial temperature of 20 °C. Data taken from Heron et al. (1997a).

Parameter	In-situ temperature reached		
	50°C	100°C	200°C
Solubility increase	1.1	1.4	-
Increased diffusion coefficient, air and water ¹	1.16	1.44	2.05
Henry's law equilibrium change	2.5	11	-
Increased vapor pressure	3.7	18	110
Decreased sorption coefficient K_d' , dry soil ²	6	58	1360
Decreased sorption coefficient K_d , wet soil ³	1.1	1.2	-
Decreased retardation in vapor phase, dry soil	6	57	915

- 1) Using the power $n = 1.5$ in the temperature equation
- 2) Assuming heat of sorption of -46.2 kJ/mole
- 3) Assuming heat of sorption of -2 kJ/mole

integration yields:

$$P_v = C \cdot \exp(-\Delta H_{\text{vap}}/R_g T)$$

where C is an experimentally determined constant, R_g is the natural gas constant, and T temperature in Kelvins. Vapor pressures have also been approximated by other exponential equations (CRC, 1994; Dean, 1985). These equations are precise for temperatures below the boiling point of the contaminant, but may be in error at higher temperatures (Heron et al., 1997a).

As an example, raising the temperature from 20 to 50, 100 and 200 °C would lead to an increased vapor pressure for TCE by factors of 3.7, 18 and 110, respectively (Table 1). Thus, if free liquid TCE is present, and the volatility is limiting the contaminant removal rate, the heating would lead to equivalent enhancement factors, speeding up the removal significantly.

2.2 Solubility in water

When the in-situ temperature changes, the solubility of organics as free phases may also change. There is no unique relationship between solubility and temperature. It was shown that the solubility of TCE increases by 40% between 0 and 100 °C (Table 1). However, no general rule exists for organic contaminants, but for compounds with a positive heat of solution in the 20-100 °C range, solubility may be significantly enhanced by soil heating, but probably not more than by a factor of 2 (Heron et al., 1997a).

2.3 Henry's law constant

When volatilization of contaminants from an aqueous phase governs the removal rate during remediation, the air-water partitioning coefficient, the Henry's law constant H is the critical parameter. Henry's law constant is defined as the ratio of the gas-phase concentration to the dissolved concentration in equilibrium over a flat water surface. Two forms are typically used, one is the dimensionless Henry's constant H , the other k_{H1} has the unit of $\text{atm} \cdot \text{m}^3/\text{mol}$ (Mackay & Shiu, 1981):

$$H = C_g/C_w \quad \text{or} \quad k_{H1} = P_v/C_w \quad \text{where} \quad k_{H1} = H \cdot R_g T$$

where C_g and C_w have the units of mg/L or mol/m^3 , and P_v the unit of atm . Using this equation for a saturated liquid/vapor system, it appears that Henry's law constant is equal to vapor pressure divided by the solubility.

Henry's law constants for TCE increase with temperature between 0 and 100 °C. Raising the temperature from 20 to 50 and 100 °C would lead to increases in Henry's law constants for TCE by factors of 2.5 and 11, respectively (Table 1). Similar effects may be expected for other organic compounds, since the Henry's law constant largely follows the increasing vapor pressure. Thus, volatilization from a dissolved phase may be accelerated significantly by applying heat. At temperatures above 100 °C at atmospheric pressure, the use of Henry's law becomes questionable, since the water will boil off and the soil start to dry out.

2.4 Diffusion coefficients in water and air

Diffusion in water or air may be limiting for the removal rate of organics. For instance if free phase contaminants are trapped in regions without water and gas movement (e.g. clay strata), the diffusive transport through water or air to portions of the subsurface with moving fluid may govern the overall removal rate.

Aqueous diffusion is typically four orders of magnitude slower than gaseous diffusion at 20 °C (Peterson et al., 1988; Grifol & Cohen, 1994). Thus, in unsaturated soils, the apparent diffusion coefficient D is strongly related to the saturation (Millington & Quirk, 1961):

$$D = D_o \cdot \theta_{\text{gas}}^{10/3} \cdot \theta_{\text{tot}}^{-2}$$

where D_o is the diffusion coefficient in air, and θ_{gas} and θ_{tot} are the gas-filled and total porosity, respectively. The temperature effect on D_o has been approximated by (Falta et al., 1992):

$$D_o(T) = D_o(T_o) \cdot (T/T_o)^n$$

where n is an experimental constant, typically between 1 and 1.7 for aqueous diffusion and 1.5-1.6 for gaseous diffusion (Heron et al., 1997a). Assuming $n = 1.5$, raising the temperature from 20 to 50, 100 and 200 °C will increase the diffusion coefficient by factors of 1.16, 1.44, and 2.05, respectively (Table 1). This is not a dramatic increase, and since the apparent diffusion coefficient

also is strongly dependent on the moisture content, other physical changes such as drying of the soil are supposed to dominate over the change in the diffusion coefficient at higher temperatures.

3.5. Sorption and retardation

Partitioning of organics onto soils affects remedial actions in several ways. Desorption rates affect release of contaminants from target areas. Once released from the soil, the organic may be removed by advection in either an aqueous or gaseous phase, and in both phases may be retarded by adsorption onto soils. The moisture content of the soil and the soil gas are important parameters when discussing sorption, since vapor-sorption differs significantly from sorption in an aqueous phase.

First we consider sorption in wet soils. The partitioning coefficient is given by:

$$K_d = C_s / C_w$$

where the concentrations on the solid (C_s) and in the water (C_w) are in equilibrium. Assuming constant heat of sorption, it was shown that (Heron et al., 1997a):

$$K_d = C \cdot \exp(-\Delta H_{sorp} / R_g T)$$

Values for heat of sorption for saturated conditions are typically smaller (from 0 to -10 kJ/mole) than for dry soils (from -20 to -65 kJ/mole for TCE vapor sorption onto dry soil minerals: Goss, 1992; Ong & Lion, 1991). If we assume -2 kJ/mole for TCE in groundwater and -46 kJ/mole for TCE in dry soil (as shown by Heron et al., 1997a), very different temperature dependencies are seen (Table 1). Under saturated conditions, the K_d is reduced by factors of 1.1 and 1.2 for a temperature increase from 20 to 50 and 100 °C. When we approach 100 °C, K_d is no longer a reasonable parameter, since the soil will start to dry as the water boils off. In unsaturated and dry soils, the mobile phase will be the soil vapor.

Equilibrium partitioning of organics involving vapor, soil moisture, and soil may be described by the vapor sorption coefficient K'_d :

$$K'_d = C_s / C_{vap}$$

where C_{vap} is the vapor phase concentration of the contaminant. With a heat of sorption of -46 kJ/mole, the partitioning coefficient decreases by factors of 6, 58 and 1360 when the temperature is increased from 20 to 50, 100 and 200 °C, respectively (Table 1). Again, the stronger the adsorptive forces, the stronger the temperature dependency.

Lowering of the K_d and K'_d leads to a lowering of the retardation of the organic compound in moving water or air, given by the retardation factor R:

$$R = 1 + K \cdot \rho / \theta$$

where K is the partitioning coefficient, ρ is bulk density, and θ the porosity of the aquifer material.

In dry soil, the R decreases by factors of 57 and 915 for temperature increases from 20 to 100 and 200 °C, respectively. Thus, recovery of contaminants through a vapor stream through dry soils would be dramatically accelerated by heating if retardation in the vapor was limiting, even for a moderately sorbing compound such as TCE. Even higher effects can be expected for heavier contaminants such as oil components.

OVERVIEW OF REMOVAL ACCELERATING MECHANISMS

As shown in the previous section, especially increased volatility (vapor pressure and Henry's law constant) and decreased adsorption (lower partitioning coefficients and retardation factors) would lead to major changes in the behavior of organic compounds in soils and groundwater. However, four other mechanisms during heating in-situ may be equally important (Heron et al., 1997b):

- heating groundwater may lead to formation of air/gas bubbles from dissolved gases such as methane, oxygen, nitrogen and carbon dioxide and from vaporization of the water itself. Heating lowers the solubility of most gases in water, and bubble formation may lead to increased advection and diffusion in pores or even channels.
- when the boiling point of water is reached, the groundwater is converted into steam, which is pushed out by the positive pressure generated. One mL of water occupies 1 mL as a liquid, but 1,700 mL as steam at 100 °C. This 1,700 fold volume expansion leads to dramatic fluxes of steam through the soil, which may potentially carry contaminants out of even very low-permeable soils as shown by Heron et al. (1997b).
- drying of soil layers opens up pores to vapor flow, and may expose free phase droplets present as residual NAPL. For remediations based on air flow (air sparging and vacuum extraction) this may be a very important accelerating mechanism.
- heating and drying may induce physical changes in clay minerals and fractures in clay layers, greatly increasing the exposed surface area of such formations. This would lead to increased air and water flow, and thus to enhanced removal of contaminants.

4. HOW TO APPLY HEAT TO THE TARGET VOLUMES

We now briefly review the technologies for heating soils and groundwater in-situ. Temperatures reached during thermally enhanced in-situ remediation vary substantially, as reviewed below.

4.1. Thermal conduction using heat blankets or thermal wells

High temperatures (up to 1000 °C) may be reached using thermal blankets or wells, using electrical heaters and simple thermal conduction through the soil from the hot areas into cooler areas (Iben et al., 1995; Vinegar et al., 1993). The heat moves away from the blanket/well, and vacuum extraction through slots or screens draws the hot air from the subsurface. Thermal desorption is achieved by reaching temperatures of up to 300 °C up to 1 m away from the heat source. During

movement of desorbed contaminants towards the heat source, thermal destruction may lead to complete contaminant removal in-situ. This technique is currently being tested in Houston, Texas by Shell and General Electric. Its major disadvantage is the limited treatment volumes, caused by the low thermal conductivity of most soils. Also application below the water table is questionable, since large amounts of water would be vaporized before temperatures above 100 °C can be reached.

4.2 Injection of hot air and steam

Injection of hot air or steam can be done with injection temperatures of up to 650 °C (Clarke et al., 1994), but the temperature reached in the formation may be much lower due to the limited heat capacity of air and steam. Injection of a hot fluids (air, steam or water) suffers from the major disadvantage that the heat only can be injected directly into relatively permeable zones. Low-permeable silt/clay layers will typically be heated solely by thermal conduction, which is a slow process since soil is a good insulator (thermal conductivity typically between 0.25 and 3 W/mK; De Vries, 1963). This problem was partly overcome by combining steam injection with resistive heating of clay layers during the Dynamic Underground Stripping project, leading to a very successful clean-up at a gasoline spill site (Newmark et al., 1994).

Other field trials on steam injection have been less convincing (EPA, 1991; EPA, 1995c; EPA, 1995d; Lingenini & Dhir, 1992; Udell & Stewart, 1989). The major problem has been difficulties in controlling the direction of steam flow and to get the target volumes up to steam temperature. Another challenge is controlling the condensation front that moves ahead of the injected air or steam. Generally, steam breakthrough to extraction wells and subsequent flushing of several pore volumes is needed for successful contaminant removal.

4.3 Hot water injection

Injecting hot water may lead to mobilization of free phase contaminants such as oils (Davis, 1997b). Some oils are denser than water at ambient temperature, but lighter at elevated temperatures. Thus, heating oils may make them float to the top of the groundwater table for removal by separation pumping. However, no good field evidence of this approach has yet been published.

4.4. Low-frequency electrical (resistive) AC heating

Electrical heating techniques are based on resistive (Joule, ohmic) heating of the soil when an AC current is applied. Whereas silty and clayey deposits are low-permeable to fluids, they are typically electrically more conductive than quartz sand due to higher amounts of clay minerals (electrically conductive double layers) and to higher water contents due to stronger capillary forces. This fact may be explored by preferentially heating fine-grained layers by low-frequency AC heating (Gauglitz et al., 1994; Newmark et al., 1994; Phelan & Webb, 1994; Buettner & Daily, 1995).

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 (Gauglitz et al., 1994), and several other authors show that heating can be achieved (Aines et al., 1992; Bergsman

et al., 1993; Newmark et al. 1994; Buettner and Daily, 1995). However, there is still a major need to understand the processes taking place during heating and remediation. Also, electrical hazards caused by the high currents applied pose challenges to the design of field equipment. Electrode meltdown is another problem observed in the field (Newmark et al., 1994).

Soil resistivity is strongly dependent on soil water content, since the current predominantly flows in the soil water. Practically, this limits the use of low-frequency electrical heating to temperatures below or close to the boiling point of water, since drying the soil will increase soil resistivity dramatically and reduce current flow (Chute & Vermeulen, 1988; Aines et al., 1992; Edelstein et al., 1994).

4.5 Radio-frequency heating

Radio-frequency heating can be used to reach higher temperatures. The higher the frequency of the applied current, the lower the effect of moisture content on the resistivity (Edelstein et al., 1994). Therefore, radio-frequency (typically between 1 MHz and 2.45 GHz) electrical heating has been used for heating soil in-situ to temperatures of 140 °C (Edelstein et al., 1994), 200 °C (Sresty et al., 1986), 250 °C (Snow et al., 1993), and potentially as high as 400 °C (Chute & Vermeulen, 1988). However, the high frequency electrical heating requires expensive current sources and matching networks (Edelstein et al., 1994; EPA, 1995a; EPA, 1995b) and is less energy-efficient than 50-60 Hz heating. Also, high electrical frequencies pose challenges to field equipment such as temperature sensors, pressure transducers, tiltmeters, well material and wires. Temperatures as high as 1000 °C have been observed at the injection antennas, where melting and corrosion of brass and stainless steel have been reported (Snow et al., 1993; Edelstein et al., 1994).

Once these engineering challenges are overcome, the high in-situ temperatures will lead to efficient thermal desorption, high volatility of contaminants, and substantial steam drives out of all heated soil layers. Snow et al. (1993) showed 97-99 % removal of volatile and semi-volatile organics from silts, sands and gravel heated to at least 250 °C at Rocky Mountain Arsenal, Colorado. Similar results were shown by Dev et al. (1988, 1989) for BTEX and JP-4 fuel in a sandy soil at Volk Air NGB, Wisconsin.

4.6 Microwave heating

Using microwaves (typically 2.45 GHz) injected by antennas may heat soil and groundwater in a manner similar to the heating of foods in microwave ovens. Two approaches are possible. One is similar to radiofrequency heating, where microwave heating is used in combination with vapor extraction or air sparging (George et al., 1992). Another approach is to form a vapor blob below the water table, where microwaves heat and vaporize water and contaminants at the interface between vapor and water (Kearl & Ensley, 1996). The generated pressure drives water vapor and contaminants to the screened antenna, where it is extracted and treated on-site. Both techniques still lack field demonstration.

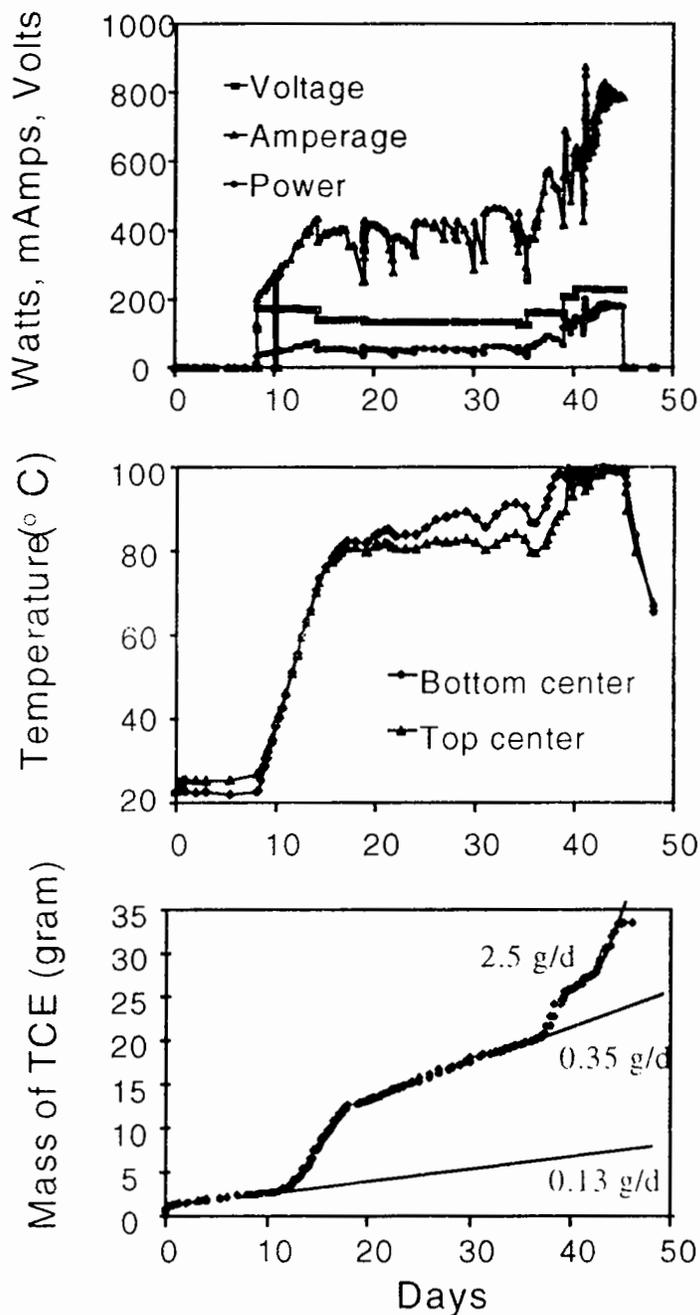


Figure 2. Power input, resulting soil temperature and mass flux of TCE out of the 2D box (Heron et al., 1997b).

At day 8, the electrical power was switched on, and the box was heated at a rate of 8 °C/day until 80 °C was reached on day 18, followed by slower heating to 85 °C on day 21 (Figure 2). This resulted in dramatically increased fluxes of TCE out of the central vent between days 10 and 20, dropping off towards a steady flux of about 0.35 g/d (Figure 2). The temperature was kept almost constant until day 35, where a total of 20 grams had been removed, and 15 gram of TCE remained in the box. 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

The 2-dimensional box was spiked with water and then left to equilibrate for 8 days prior to onset of soil vapor extraction. Figure 3 shows the dissolved TCE concentrations. The shape is dominated by the fact that water and TCE was added from the bottom central screen, and kinetic adsorption of TCE onto the soil (Heron et al., 1997b).

Soil vapor extraction alone (days 0-8) removed 2.4 g of TCE from the box (7 % of the added TCE). Clean air entered through the top inlet ports and quickly concentrations in the outlet port dropped to very low levels with a flux of about 0.13 g/d. This flux was relatively constant over a week of extraction, and indicated that it would take at least 250 days to clean 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 supposedly to a clean-up time of several years or decades, showing that soil vapor extraction would be inefficient as the sole remediation technique for a fine-grained, almost saturated layer of this thickness (50 cm).

At day 8, the electrical power was switched on, and the box was heated at a rate of 8 °C/day until 80 °C was reached on day 18, followed by

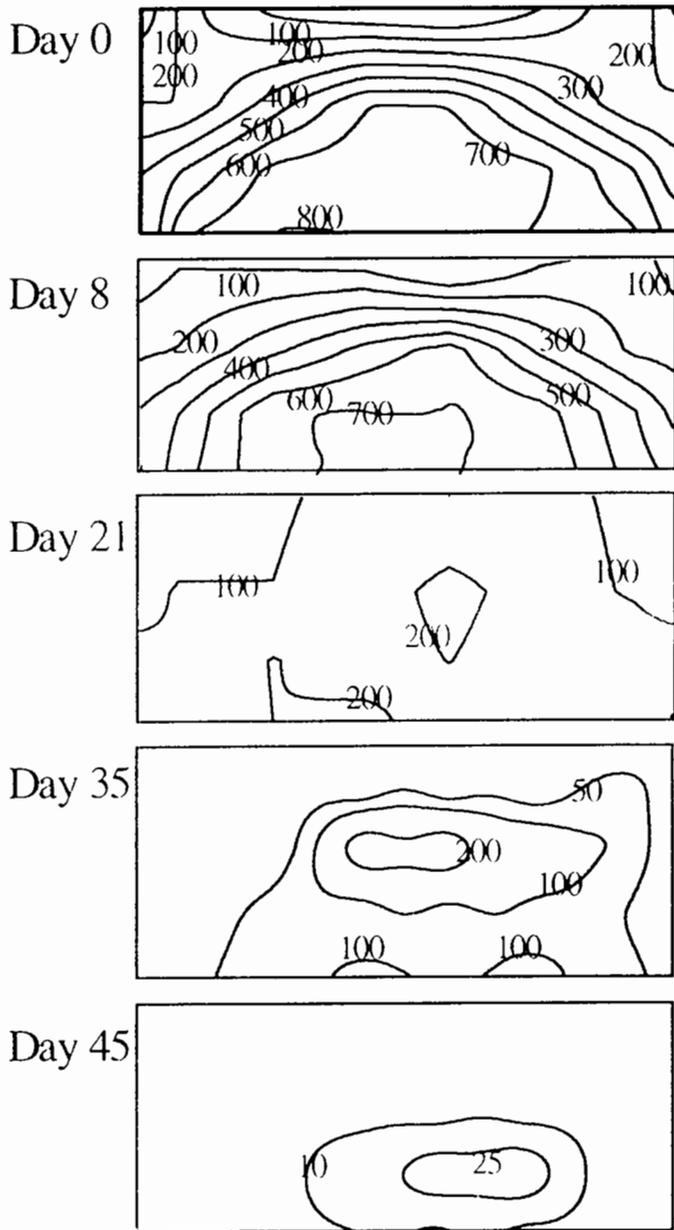
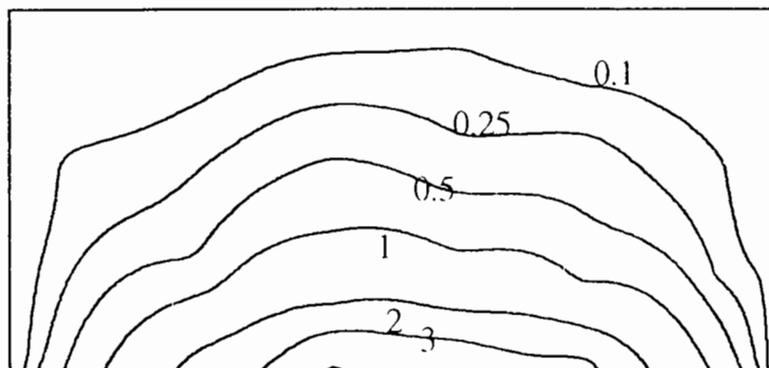


Figure 3. Distribution of dissolved TCE (mg/L) in water sampled from the 2D box (Heron et al., 1997b)

Figure 4. Soil concentrations of TCE (in $\mu\text{g/g}$) at the end of the soil heating (Heron et al., 1997b).



TCE flux could be maintained. At this point, we decided to try to speed the remediation up by raising the temperature in the box further.

Then the power was increased, and 99-100 °C was reached and maintained through days 39-45 (Figure 2). This led to another peak in the flux and later to stabilization around 2.5 g/d. The power was shut off on day 45, since the mass balance indicated that only trace amounts of TCE remained in the soil (Figure 3). The box was left to cool down slowly over a 2 week period. The soil vapor extraction was discontinued on day 48 after the flux of TCE out of the box had dropped to below detection limits, and finally soil samples were collected for determination of TCE levels in the treated soil. These showed that the water content was unchanged (due to wetting of the electrodes during heating), and that only 70 mg of TCE remained in the soil (Figure 4).

The TCE mass balance indicated an overall recovery of 94.3 % by the SVE system, and a remediation efficiency of 99.8% with a residual TCE content of 70 mg in the soil compared to the initial 35.5 g on day 0 (Figure 4).

This study demonstrated the effect of electric heating for heating up low-permeable soil for enhanced removal of TCE. The cleanup time was reduced dramatically compared to soil vapor extraction alone when the silty soil was heated to 85 and 99 °C. As temperatures rise, the physical properties of TCE and the soil change towards increased volatility, reduced sorption, and increased diffusivity. In addition, a steam drive created when soil water boils pushes out the surrounding soil vapor, leading to high TCE fluxes out of the soil. Since desaturation is not critical for enhanced removal, electric heating may also be promising in shallow groundwater.

6. SUMMARY

Elevated temperatures may potentially be used to overcome the rate-limiting mechanisms during in-situ remediation. Heating increases contaminant volatility and diffusivity, reduces adsorption and retardation, and creates driving forces for soil vapor and contaminants. Applying the heat to target subsurface areas poses several engineering challenges, and very few field trials have been successful in documenting efficient removal of organic contaminants. However, where these difficulties were overcome, very promising results were found.

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16. ABSTRACT Contamination of soil and groundwater by organics is recognized as a major threat to the environment. Where contamination is severe and occurs deep or below building, excavation and off-site treatment is impractical. In-situ remediation is the only alternative to abandoning the area and containing the spread of contamination. The physical-chemical remediation techniques suffer from three major limitations. Firstly, when circulating water or air through a geologic formation, the fluid will predominantly flow in the highly permeable layers, rendering layers of low-permeable soil largely unaffected by the treatment. Often organic contaminants bind stronger onto low-permeable, organic and clay-rich lenses and layers. Even if the moving fluid totally cleans the major part of the formation, the slow diffusion of contaminants from low-to high-permeable layers may be rate limiting for the total clean-up (DiGiulio, 1992; Gibson et al., 1993). Secondly, limited volatility of the contaminants (low vapor pressure and Henry's law constants) at the in-situ temperature may prevent a sufficiently rapid clean-up, even when target areas are flushed with air. Thirdly, sorption of contaminants onto soil and aquifer sediment may dramatically retard the movement with the fluid. Both the wet adsorption coefficients (K_d) and the vaapor sorption coefficient (K') are important parameters. For many compounds, retardation factors in the range of 10 to several thousands may prevent efficient clean-up. This paper summarizes the effect of heating on the distribution of organics in the subsurface, briefly reviews technologies used to inject heat in-situ, and finally illustrates the dramatic effect of heating on contaminant removal rates using a controlled laboratory simulation.		
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