Full-Scale Removal of DNAPL Constituents Using Steam-Enhanced Extraction and Electrical Resistance Heating

by Gorm Heron, Steven Carroll, and Steffen G. Nielsen

Abstract

In 2003, the United States Department of Energy completed a full-scale non–aqueous phase liquid (NAPL) remediation of Area A of the Northeast Site at the Young-Rainey STAR Center, Largo, Florida. Area A covered an area of 930 m² (10,000 square feet) and extended to a depth of 10.7 m (35 feet), representing a total cleanup volume of 9930 m³ (12,960 cubic yards). The site was contaminated with ~2500 kg (5500 lb) of NAPL constituents such as trichloroethylene, cis-1,2-dichloroethylene, methylene chloride, toluene, and petroleum hydrocarbons. The site consists of a fine-grained sand aquifer underlain by a Hawthorn clay at 9 m (30 feet) depth. The upper 1.5 m (5 feet) of this clay formed part of the remediation volume, as dense non–aqueous phase liquid was present in this layer. The site was remediated using a combination of steam-enhanced extraction and electrical resistance heating. Operations lasted 4.5 months. The site was heated to the target temperatures within 6 weeks, at which time the mass removal rate increased more than 1000-fold. After the target volume had been heated to or near boiling temperatures, pressure cycles were used to increase the mass removal rates, until a final phase of diminishing returns was reached. Postoperational sampling of soil and ground water at randomly selected locations showed the concentrations of all contaminants of concern (COC) to be well below the remedial goals. The majority of the ground water samples were below maximum contaminant level (MCL) for all the COC. The estimate of volatile organic contaminant (VOC) mass removed from the site (1130 kg = 2500 lb) agreed well with the estimate of VOC present before operation (1170 kg = 2580 lb). The postoperational sampling showed that ~0.5 kg (1 pound) of VOCs remained in the remedial volume, and showed remedial efficiencies of between 99.85% and 99.99% for the four chemicals of concern. Since the postoperational sampling shows all concentrations to be below or close to ground water MCLs, the thermal remedy may be satisfactory for site closure without a polishing phase.

Introduction

The release of man-made chemicals in the form of non–aqueous phase liquid (NAPL) to the subsurface has created great environmental concerns. Soil and ground water contaminated with NAPL are relatively slow to remediate naturally, with typical plume life expected to be hundreds or thousands of years. The longevity of NAPL source zones is primarily caused by the environmental stability of the NAPL, its immobility in the subsurface, low dissolution rate into moving ground water, and its low vaporization rate when located below the water table (Hunt et al. 1988a; Mercer and Cohen 1990; Pankow and Cherry 1996).

Conventional in situ remediation techniques have used fluid injection and extraction at ambient temperature and therefore often suffer from mass-transfer limitations. Flushing with water and air has limited effect since the NAPL is relatively immobile and the constituents dissolve and vaporize slowly at ambient temperature. Heating the subsurface to temperatures around the boiling point of water leads to dramatic changes in the thermodynamic conditions and makes NAPL much more mobile. The major effects are

- The vapor pressure of the NAPL increases markedly with temperature. As the subsurface is heated from 20°C to an average temperature of 100°C, the vapor pressure of the contaminants will increase by between 10- and 30-fold (Udell 1996).
- In locations where both NAPL and water are present, boiling and complete NAPL removal can occur at temperatures below 100°C, where the vapor pressure of the NAPL and water phases summed exceeds formation pressure. For instance, a mixture of trichloroethylene (TCE) (pure-phase boiling point 87°C) and water will boil at 73°C, as demonstrated in controlled experiments (DeVoe and Udell 1998).
- Adsorption coefficients are reduced during heating, leading to release of contaminants from the soil or rock matrix (Heron et al. 1998b).
- Viscosity of NAPLs is reduced by heating. The higher the initial viscosity, the higher the reduction. For moderately viscous NAPL, viscosity is typically reduced from 30 centistokes to 3 centistokes by heating from ambient to steam temperature (Davis 2005). For TCE and other chlorinated solvents with low viscosity at ambient temperature, the viscosity typically is reduced by about a factor of 2 (Heron et al. 1998c).
- Dense non-aqueous phase liquid (DNAPL) density is reduced during heating for improved floatation and displacement. For chlorinated solvents, the effect is modest, with less than 10% swelling of the DNAPL.
- NAPL-water interfacial tensions are lowered, allowing for improved hydraulic removal of NAPLs (Davis 1997; Sleep and Ma 1997).
- Water solubility increases for organic contaminants at elevated temperatures, and dissolution rates go up two to five times, leading to faster NAPL dissolution and removal (Imhoff et al. 1997).

These physical effects lead to several ways the NAPL is removed from the subsurface:

- By displacement as a NAPL phase and extraction with the pumped ground water (Hunt et al. 1988b; Udell et al. 1997)
- By vaporization and extraction in the vapor phase
- By volatilization, migration in the steam phase, and condensation in water that is subsequently removed by pumping
- By dissolution and desorption and removal with the extracted water.

In addition to the aforementioned physical removal, biological and chemical degradation may occur during and after thermal remediation. These degradation mechanisms include

- Microbial mineralization of NAPL components
- Hydrous pyrolysis oxidation, an oxidation reaction initiated by the introduction of excess oxygen to the previously steam-heated subsurface, an important destruction mechanism for chlorinated solvents (Knauss et al. 1999a), creosote, and oil hydrocarbons (Knauss et al. 1997; Leif et al. 1998)
- Hydrolysis at elevated temperature. This is particularly relevant for chemicals with short half-lives such as 1,1,1-trichloroethane and methylene chloride (Marrone et al. 1998).

Heating of sites that contain substantial volumes of both sands and clays requires a combination of heating techniques. Steam has been used to heat the more permeable zones, which are typically sandy layers with relatively low clay and mineral contents. The in situ process using steam injection and aggressive fluids extraction was named steam-enhanced extraction (Udell et al. 1991). The mechanisms were studied intensively in laboratory and theoretical experiments (Udell 1983; Hunt et al. 1988b; Stewart and Udell 1988; Basel and Udell 1989; Basel 1991; Yuan and Udell 1993), and summarized by Udell (1996). Field demonstrations of this technology proceeded in the late 80s and 90s (Udell and Stewart 1989; Newmark 1994; Udell et al. 1997; BERC 2000; Heron et al. 2000). Mass removal efficiency was demonstrated at a large, full-scale creosote-contaminated site in California (Newmark and Aines 1998; Eaker 2003) and at the Savannah River Site (Oochs et al. 2003). Recently, steam injection has been field tested at fractured rock sites contaminated with DNAPL and light non-aqueous phase liquid (LNAPL) (Earth Tech and SteamTech 2003; U.S. EPA 2003). Recently, the co-injection of air during steam injection has been tested and applied both in laboratory studies (Schmidt et al. 2002; Kaslusky and Udell 2002) and in the field (Earth Tech and SteamTech 2003; U.S. EPA 2003). The air injection is performed to reduce the risk of forming condensation banks containing NAPL, and in order to enhance vapor transport between injection and extraction points.

Both three-phase and six-phase electrical heating were developed as robust techniques for heating low-permeable layers in the 90s (Bergsman et al. 1993; Gauglitz et al. 1994; Buettner and Daily 1995). Laboratory studies demonstrated that thermodynamic changes induced by electrical heating can lead to very effective removal of chlorinated solvents from silts and clays (Heron et al. 1998b). Since the late 90s, several commercial full-scale implementations of both three- and six-phase heating were completed (U.S. ACE 2003; McGee 2003).

The combination of steam and electrical heating is a patented technology named Dynamic Underground Stripping, and was demonstrated at a gasoline spill that had resulted in LNAPL contamination above and below a rising water table at the Livermore Gas Pad (Newmark 1994; Daily et al. 1995). Since that demonstration, no field-scale implementations of the combined heating approach have been documented.

This paper presents the results of a full-scale remediation for DNAPL-impacted soil and ground water using steam-enhanced extraction and electrical resistance heating in combination. The heating techniques were combined with a robust vapor and liquid extraction strategy that ensured that hydraulic and pneumatic control was maintained during remediation, preventing spreading of the mobilized contaminants. This is the first DNAPL remediation using steam and electrical heating, with a performance evaluation based on numeric soil and ground water cleanup goals.

**Young-Rainey STAR Center Site Description**

**Site Background**

The Young-Rainey STAR Center (formerly the Department of Energy [DOE] Pinellas Plant) operated as a DOE site. In the late 1960s, drums of waste and construction debris were disposed of in a swampy area of the Northeast Site. The East Pond was excavated in 1968 as a borrow pit. In 1986, an expansion of the East Pond was initiated to create additional storm water retention capacity. Excavation activities were stopped when contamination was...
detected directly west of the East Pond. An interim groundwater recovery system was installed in 1992 and operated until 1997. In 1995, a portion of the Northeast Site was excavated to remove debris and other materials that could inhibit future corrective measures. A larger pump-and-treat system was constructed and became operational in 1997 with nine extraction wells.

During 1997, anaerobic bioremediation and rotary steam stripping pilot tests were conducted in the northern and southern portions of the Northeast Site, but were not selected for scale-up treatment at this site (U.S. DOE 1998a, 1998b).

An Interim Measures Work Plan for Remediation of NAPL at the Northeast Site was approved in 2002. It supported the long-term corrective action to remediate the dissolved-phase contamination in the surficial aquifer to Florida Department of Environmental Protection drinking water maximum contaminant levels (MCLs). Without this measure, NAPLs will continue to act as a source of dissolved-phase contamination, resulting in contaminant concentrations in ground water significantly above the MCLs.

At the Northeast site, two distinct NAPL areas have been identified. This paper describes the remediation of the smaller of the areas, Area A.

Geology

Figure 1 shows a schematic of the subsurface geology and the well types used for remediation of Area A. It shows an upper silty and sandy layer that extends to between 8.5 and 10.7 m (28 and 35 feet) depth (the surficial sands). It is underlain by a continuous silty clay layer, which rests on silty, sandy, and carbonaceous clays at a depth of ~12 m (40 feet). The lower permeability clay layers lying below 10.7 m (35 feet) depth form part of the uppermost Hawthorn Group.

Hydrology

Ground water elevations vary between 3 and 4.5 m (10 and 15 feet) mean sea level (MSL) at the site, corresponding to depths between 0.3 to 2 m (1 and 6 feet) below grade. The ground water level is strongly influenced by rainfall, with rapid rises of several feet observed during storm events. The unconfined surficial sand and silt aquifer has hydraulic conductivity in the $10^{-4}$ to $10^{-3}$ cm/s range, corresponding to about 0.1 to 1 darcy intrinsic permeability. The Hawthorn clays and silts are of low permeability, with hydraulic conductivity in the $10^{-8}$ to $10^{-6}$ cm/s range. The Hawthorn Group clay forms a laterally extensive aquitard at the Northeast site.

Contaminants

The buried waste contained a wide range of synthetic chemicals, including oils, solvents, resins used for boat manufacture, and solids. The estimate of contaminant mass was around 1,200 kg (2,600 lbs) of volatile organics (Table 1). Both DNAPL and LNAPL were positively identified, as they accumulated in on-site wells (U.S. DOE 2000). The contaminants of concern (COC) selected for this site are TCE, toluene, cis-1,2-dichloroethylene (cis-1,2-DCE), methylene chloride, and petroleum range
organics. Tables 2 and 3 show the numeric standards established for Area A remediation. These concentrations were determined by DOE to represent levels below which NAPL should not persist in the subsurface.

**Treatment Volume Definition and Objectives**

The distribution of the NAPL and dissolved contaminants was assessed by intensive soil and groundwater sampling (U.S. DOE 2003c). An approach was adapted to delineate the outer boundaries of the treatment volume, horizontally and vertically. It was then assumed that NAPL and contaminants could exist anywhere inside the volume defined and that thermal remediation should address the entire volume. The resulting treatment area is shown in Figure 2. The treatment depth was defined from land surface to a depth of 1.5 m (5 feet) into the Hawthorn Group, representing a total depth of ~10.7 m (35 feet). The treatment area was 930 m² (10,000 square feet), and the treatment volume was 9930 m³ (12,960 yard³). After thermal remediation, a statistically valid sampling and analysis approach was used to determine whether the numeric remedial goals were met.

**Description of Field Implementation**

Steam was used to deliver energy at high rates to the surficial aquifer, both inside and outside of Area A. Electrical resistance heating was used to heat the Hawthorn Group clay layer, to preheat the perimeter of Area A prior to steam injection, and to deliver energy to a relatively low-permeability sand zone located between 3 and 6 m (10 and 20 feet) depth within the surficial sand aquifer.

At the onset of operations, the wellfield for Area A consisted of a network of 66 operational boreholes and 44 monitoring locations (Figure 2):

- Fifteen steam injection wells around the perimeter of Area A
- Twenty-eight extraction wells with electrodes below the screened interval to heat the Hawthorn Group and the base of the surficial aquifer
- Twenty-one combined steam injection-electrode wells to heat the surficial sands
- Two deep electrodes to augment Hawthorn Group heating, added to improve the three-phase electrical heating coverage
- Thirty-six temperature monitoring boreholes equipped with thermocouples at 1.2-m (4 feet) vertical spacing
- Eight (four pairs) ground water monitoring wells installed outside Area A.

Borehole design features for the injection and extraction wells are shown in Figure 1. Note that electrodes were placed in both injection wells and extraction wells. This design was chosen in order to optimize the heating and minimize drilling and construction costs.

### Table 1

<table>
<thead>
<tr>
<th>Sink</th>
<th>Total VOC</th>
<th>TCE</th>
<th>Toluene</th>
<th>Methylene Chloride</th>
<th>cis-1,2-DCE</th>
<th>Other VOCs¹</th>
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<td>Accumulation in the NAPL tanks (lb)</td>
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<td>1191</td>
<td>677</td>
<td>230</td>
<td>117</td>
<td>77</td>
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<td>Trapping in the spent liquid-phase carbon (lb)</td>
<td>206</td>
<td>92</td>
<td>32</td>
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<td>3</td>
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<td>Trapping in the spent vapor-phase carbon (lb)</td>
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<td>111</td>
<td>2.5</td>
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<td>13.5</td>
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<td>Emission to atmosphere (lb)</td>
<td>156</td>
<td>85</td>
<td>1.6</td>
<td>52</td>
<td>11</td>
<td>6.4</td>
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<td>Discharge with treated water (lb)</td>
<td>1.9</td>
<td>0.0003</td>
<td>0.01</td>
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<td>Total estimates (lb)</td>
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<td>1283</td>
<td>709</td>
<td>287</td>
<td>139</td>
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<td>Mass estimate before treatment (lb)</td>
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<td>Mass estimate posttreatment (lb)</td>
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<td>0.14</td>
<td>0.89</td>
<td>0.03</td>
<td>0.19</td>
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¹Quantified using EPA method 8260B.

### Table 2

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<th>cis-1,2-Dichloroethene (µg/kg)</th>
<th>Methylene Chloride (µg/kg)</th>
<th>Toluene (µg/kg)</th>
<th>Trichloroethene (µg/kg)</th>
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<td>Preoperation Maximum concentration</td>
<td>68,000</td>
<td>650,000</td>
<td>72,000</td>
<td>250,000</td>
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<tr>
<td>Preoperation Average concentration</td>
<td>1239</td>
<td>3444</td>
<td>825</td>
<td>2753</td>
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<td>Postoperation Maximum concentration</td>
<td>120</td>
<td>8.2</td>
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<td>Postoperation Average concentration</td>
<td>4.4</td>
<td>0.8</td>
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<td>Soil cleanup goal</td>
<td>71,000</td>
<td>227,000</td>
<td>15,000</td>
<td>20,400</td>
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Table 3
Postoperational Ground Water Sampling Results from the 16 Wells Located Inside Area A Compared to Cleanup Goals and Ground Water MCLs

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<tr>
<th>Location</th>
<th>cis-1,2-Dichlorethene (µg/L)</th>
<th>Methylene Chloride (µg/L)</th>
<th>Toluene (µg/L)</th>
<th>TCE (µg/L)</th>
<th>FL-PRO (µg/L)</th>
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<td></td>
<td>April 16-17 May 13 to 14 July 23 to 24</td>
<td>April 16-17 May 13 to 14 July 23 to 24</td>
<td>April 16-17 May 13 to 14 July 23 to 24</td>
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<td>April 16-17 May 13 to 14 July 23 to 24</td>
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<td>PIN15-CS-01</td>
<td>ND 3.3 76 ND 0.40 JB ND 0.20 J</td>
<td>ND 0.49 JB ND 0.38 J ND 0.13 J</td>
<td>ND 0.63 J ND 0.35 J ND 3.6</td>
<td>ND 120 J 140 J ND ND</td>
<td></td>
</tr>
<tr>
<td>PIN15-CS-02</td>
<td>ND 0.74 J 52 ND 0.49 JB ND 0.38 J</td>
<td>ND 1.2 JB 11 1.3 ND ND ND 0.58 J</td>
<td>ND 0.49 J 52 ND 0.49 J 52 ND 0.49 J 52</td>
<td>ND 340 J 510 J 2000</td>
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<tr>
<td>PIN15-CS-03</td>
<td>ND ND ND 16 ND 1.2 JB ND 1.3 ND</td>
<td>ND 1.3 JB 11 1.3 ND ND ND 0.58 J</td>
<td>ND 0.49 J 52 ND 0.49 J 52 ND 0.49 J 52</td>
<td>ND 340 J 510 J 2000</td>
<td></td>
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<tr>
<td>PIN15-CS-04</td>
<td>0.3 J 0.45 J 0.18 J ND 0.49 JB ND 0.38 J</td>
<td>ND 1.3 JB 11 1.3 ND ND ND 0.58 J</td>
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<td>ND 340 J 510 J 2000</td>
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</tr>
<tr>
<td>PIN15-CS-05</td>
<td>23 9.9 8.6 13 3.8 JB ND 1.5</td>
<td>ND 1.2 JB 11 1.3 ND ND ND 0.58 J</td>
<td>ND 0.49 J 52 ND 0.49 J 52 ND 0.49 J 52</td>
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<tr>
<td>PIN15-CS-06</td>
<td>0.5 J 36 27 4.2 J 150 B 12 0.59 J</td>
<td>ND 1.2 JB 11 1.3 ND ND ND 0.58 J</td>
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<td>PIN15-CS-07</td>
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<td>PIN15-CS-09</td>
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<td>PIN15-CS-11</td>
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<td>PIN15-CS-15</td>
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<td>ND 0.49 J 52 ND 0.49 J 52 ND 0.49 J 52</td>
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<td>ND 1.2 JB 11 1.3 ND ND ND 0.58 J</td>
<td>ND 0.49 J 52 ND 0.49 J 52 ND 0.49 J 52</td>
<td>ND 340 J 510 J 2000</td>
<td></td>
</tr>
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</table>

Remediation Goals

- cis-1,2-Dichlorethene: 50,000
- Methylene Chloride: 20,000
- Toluene: 5500
- TCE: 11,000
- FL-PRO: 50,000

Ground water MCLS:

- cis-1,2-Dichlorethene: 70
- Methylene Chloride: 3
- Toluene: 1000
- TCE: 5

1No MCL is established for this site: the listed value represents typical MCL for this chemical group in Florida.

J = result less than reporting limit and greater than the method detection limit; B = analyte was detected in associated method blank; ND = not detected.
An asphalt vapor cap was installed over Area A to prevent storm water infiltration into the treatment area, to minimize surface vapor leakage, and to prevent steam and contaminant-laden vapor from escaping into the atmosphere through the surface soils. The vapor cap extended 9 m (30 feet) beyond each edge of Area A. Storm water was directed to the nearby East Pond.

The process equipment used is shown in Figure 3. Steam was generated from softened water using a diesel-fired boiler system with four units, each rated for 2400 kg/h (5000 lb/h) of steam production. Steam was piped to the injection wells using steel pipe, and the pressure was regulated at each wellhead. Steam flow rates were measured for each injection interval using orifice plates with differential pressure gauges. Electrical power was delivered by five substations, each delivering power to between 9 and 12 electrodes. Proprietary equipment under the trade name of ET-DSPTM (McMillan-McGee Corporation, Calgary, Canada) was used for the three-phase electrical heating component. The power delivery was automatically controlled and recorded. Each substation was capable of delivering 400 amperes per phase at varying voltages with >400 kW of power. Water was added to each electrode (0.4 to 1.2 L/min; 0.1 to 0.3 gpm) using a pressure pump and a simple manifold system. Liquids were extracted at rates between 0.4 to 12 L/min (0.1 and 3 gpm) per well from the 28 extraction wells using downhole positive displacement pumps and liquid entrainment tubes. Vapor was extracted at rates of 1 to 35 m³/h (0.5 to 20 standard cubic feet per minute [scfm]) per well by vacuum extraction. The extracted fluids were cooled, condensed, and separated in an on-site treatment system. NAPL was separated from the water in an oil-water separator and a large holding tank. Water treatment was by air stripping and activated charcoal filtration. Vapor treatment was by activated charcoal filtration, using on-site steam regeneration to reduce the amount of charcoal used. The vapor treatment capacity was 850 m³/h (500 scfm), and the water treatment capacity was 11.3 m³/h (50 gpm).

Subsurface temperatures were recorded using thermocouples installed in 36 dedicated monitoring holes. The subsurface temperatures were posted on a project Web site in near real time. Ground water elevation was recorded using interface probes, and by a bubbler system.

The sampling and monitoring program for this project is described in SteamTech Environmental Services (2002a, 2002b, 2002c). For hot samples, a simple cooling loop consisting of a stainless steel coil in an ice bath was used to bring the water temperature below 20°C before sampling. Halogenated and volatile organics were analyzed by EPA Method 8021. Petroleum range organics were analyzed using the Florida-Range Petroleum Organics method (FL-PRO; Severn Trent Laboratories, Tampa Bay, Florida). Vapor samples were analyzed for halogenated and aromatic volatiles by EPA Method TO-14. In addition, vapor samples were screened using a handheld photoionization detector (PID) (MiniRae 2000) calibrated to a 100 ppmv isobutylene standard gas. Water samples were screened for volatile contaminants using a headspace PID reading.
on a 0.5-L sample in a 1-L bottle. Warm samples were allowed to cool to below 25°C prior to analysis.

Results

Operations lasted 4.5 months and followed a strategy where contaminant spreading was minimized and recovery was maximized (SteamTech Environmental Services 2002d). The main objectives were
1. Establish hydraulic and pneumatic control by liquid and vapor extraction. This was achieved after 3 d of continuous extraction on October 3, 2002.

Figure 3. Process flow diagram for the steam injection, electrical resistance heating, and effluent treatment systems.
2. Heat the perimeter and bottom of the treatment volume, while maintaining hydraulic control. Electrical resistance heating was used to heat the upper 1.5 m (5 feet) of the Hawthorn clay, and a combination of electrical resistance heating and steam injection was used to heat the perimeter of Area A. Acceptable heating was achieved after 33 d of heating on November 6, 2002.

3. Heat entire Area A to target temperature, using steam injection and electrical resistance heating in combination, while maintaining hydraulic and pneumatic control. This was achieved after a total of 42 d of heating on November 15, when the average temperature inside Area A had reached 84°C, with the zone below 3 m (10 feet) depth generally above 100°C.

4. Pressure cycling and mass removal optimization phase. The pressure cycling was performed by varying the steam injection rates and the electrical power delivery, and the applied vacuum and liquid extraction rate. Mass recovery was high at times of depressurization and during times of heating of subareas that had previously remained cool. This phase lasted for 60 d, until the end of heating on February 17, 2003, when diminishing returns were achieved. The extraction of vapor and liquids continued another 7 d.

5. Cool-down and polishing, involving continued vapor and liquid extraction combined with air and cold water injection. This active cooling lasted 7 d and was completed on March 24, 2003.

Interim progress reports were used to document the field implementation (U.S. DOE 2002; 2003a, 2003b). A complete data set and interpretation are contained in the Final Report (U.S. DOE 2003c).

Injection and Liquid Extraction Rates

The steam injection and water extraction rates are shown in Figure 4 along with the overall water balance for the remediation volume. Steam injection rates varied between 45 and 2300 kg/h (100 and 5000 lb/h). The highest rates were achieved in November, during the stage when heating was targeted at Area A, and later during the pressurization phases of each of the pressure cycles. During depressurization events, injection rates were reduced to between 115 and 450 kg/h (250 and 1000 lb/h). This was sufficient to ensure that the steam piping remained hot and also to prevent silting of injection wells.

Before the site was heated, liquid extraction rates typically ranged between 1.8 and 4.1 m³/h (8 and 18 gpm). With the addition of more extraction wells, and heating of the site through mid-November, the extraction rate increased to about 6.8 m³/h (30 gpm). During pressure cycling events, the extraction rate was typically varied between 2.3 and 9.1 m³/h (10 to 40 gpm), with a peak extraction rate of 12.5 m³/h (55 gpm).

The water balance shows that a total of 15,500 m³ (4.1 million gallons) of water was extracted from the subsurface (Figure 4). A total of 2550 m³ (674,000 gallons) of water was injected in the form of steam. The volume of water injected at the electrodes was 5670 m³ (1.5 million gallons). This water was injected to keep the electrodes cool and wet, thereby preventing the electrical resistivity in the vicinity of the electrodes from increasing, and the power flow from being reduced. The net liquid extraction shows a steady increase during operations. A net total of 7200 m³ (1.9 million gallons) of water was extracted from the site. This water infiltrated from the surface or entered horizontally due to the drawdown established by the extraction system, creating inward ground water flow throughout operations.

Energy Balance

As the electrodes were energized to heat the uppermost Hawthorn Formation, they delivered about 500 kW, and
the site heated as expected. When steam injection was initiated around the perimeter at rates of about 1460 kg/h (3000 lb/h), the total enthalpy input rose to a peak rate of 2000 kW (equivalent to 6.9 million BTU/h [British thermal units per hour]). During depressurization events, and during cool-down, the net enthalpy flux was negative, as more energy was extracted than injected, and the average temperature decreased.

During the pressure cycling events from mid-November to late January, the average net enthalpy rate was close to zero, supporting the assumption that most of the target volume had been heated and maintained at a relatively constant temperature. However, the cumulative energy balance calculation (Figure 5) indicated that the average temperature of the target volume was between 90°C and 100°C, which is less than the observed temperatures in the thermocouples inside Area A. These data would suggest that a subvolume of the Area A target zone had not been heated sufficiently, and that this volume had not been penetrated by temperature sensors. During the interim drilling conducted on January 20, 2003, this assumption was confirmed by the discovery of a resin layer on the northeast side of Area A, and observations that the soils immediately above and below this layer were cooler than the surrounding soils.

After additional steam injection wells became operational, steam was delivered to the cool areas and the site heated to an average calculated temperature of 121°C by February 19, 2003. The energy balance showed that the energy demand calculated for heating the site to above boiling temperatures had been delivered.

A total of 6000 and 4940 GJ (5700 and 4700 million BTU) was delivered to the subsurface using steam injection and electrical resistance heating, respectively. A total of 6640 GJ (6100 million BTU) was extracted in the form of heated water and vapor, and steam. At the time of maximum heating, the site contained about 4750 GJ (4500 million BTU) more than at ambient temperature. A simple heat capacity calculation shows that this energy addition should raise the average temperature in the target volume to around 120°C (Figure 5).

After cessation of heating on February 19, the site started to cool as hot fluids continued to be extracted. Energy removal rates ranged between 300 and 900 kW, and the site initially cooled at a rate of about 1°C/d. Active cooling in the period March 17 to 24 by air and cold water injection reduced the temperatures sufficiently (below 100°C) to allow confirmatory soil sampling to proceed safely.

Subsurface Temperatures

Figure 6 shows the progression of the site heating for selected depth intervals and times. Heating began on October 3. By October 23, the temperatures had increased substantially at depths of 26 to 34 feet, showing that the heating of the top of the clay layer was successful. The November 6 slices show how the steam injection had created a more uniform heating from 14 feet downward. On November 20, the depth interval from 14 to 34 feet was above 95°C. Finally, after another 4 weeks of heating and pressure cycles, the shallower locations reached temperatures above 60°C on December 16. As seen by the relatively modest temperatures for the upper 2-foot interval on January 29, the surface was not heated to steam temperature. Instead, this unsaturated zone was flushed with air and kept under vacuum at all times. Overall, the thermocouple data showed that the site was heated very uniformly and that the target temperatures were achieved across the entire Area A, from depths between 6 and 38 feet below grade.

Contaminant Extraction and Concentrations

Screening of V-1 vapor samples using a PID yielded data for every 2 h of operation during the most intense periods (Figure 7). The PID readings were low (less 100 ppmv) during the first 5 weeks of operation, until November 7, 2002. The PID readings then increased dramatically as the site heated, and increased to above 10,000 ppmv on November 17. They were generally above 1000 ppmv during the second half of November, when the first two pressure cycles were conducted.

In December 2002, the PID readings decreased, with the highest readings occurring during depressurization events and the lowest rates occurring during periods of steam injection for pressurization. After addition of the shallow steam injection points to the operations in late December, another large peak in the PID readings occurred as the site was heated to a higher average temperature (Figure 6). After February 18, where the site reached its maximum average temperature, the PID readings declined steadily with only minor increases over short periods. Several pressure cycles were conducted without producing a significant response in the mass removal rate. This was interpreted to indicate that very little COC mass remained in the target treatment volume.

The analytical data from the V-1 samples are shown in Figure 8. The data are much more sparse than the PID screening data but confirm that high concentrations of TCE and toluene were extracted at times of high PID readings. The maximum concentrations of TCE (280,000 ppbv), methylene chloride (61,000 ppbv), and toluene (240,000 ppbv) occurred on November 29, 2003, during the third depressurization phase, where a large spike in the V-1 PID readings was seen (Figure 7). Near the completion of the
remediation period, the V-1 concentrations decreased to below 4500 ppbv for all analytes.

The analytical data from the L-1 water samples presented in Figure 8 show high concentrations of COCs from the onset of extraction, with the TCE concentration reaching a maximum after 10 d (44,000 μg/L on October 10). The COC concentrations then declined until November 7, after which an increase occurred at the time of the first large vapor-phase removal events. After the two first pressure cycles, L-1 COC concentrations decreased by 1 to
2 orders of magnitude (to less than 100 µg/L). Two spikes in the concentrations were seen during the following pressure cycling and shallow heating events, until the very last samples from February 24. The last sample showed less than 13 µg/L for all four COCs.

Estimated Mass Removed

There are a limited number of sinks for the chemicals that were extracted from the subsurface (Table 1):

1. Accumulation in the NAPL tanks. This was evaluated by volume measurements after separation (760 L = 200 gallons) and the density of the NAPL (1.2 kg/L used).

2. Trapping in the spent liquid-phase carbon. This was estimated by the amount of spent carbon, using appropriate trapping capacity numbers for the type of granular activated charcoal (GAC) and contaminants (2% assumed due to relatively high iron concentrations and GAC replacement before breakthrough occurred in the polishers). The resulting mass estimate was 191 kg (420 lb).

3. Trapping in the spent vapor-phase carbon (vapor polisher). This was estimated by the amount of spent carbon, using appropriate trapping capacity numbers for the type of GAC and contaminants (4% assumed due to significant loading of the carbon, as evidenced by breakthrough). The resulting estimate was 200 kg (440 lb).

4. Emission to atmosphere, based on analytical results and PID screening data monitored at sample point V-3. The resulting estimate was 163 kg (360 lb).

5. Discharge with treated water, based on analytical data from the discharge samples. The resulting estimate was 0.86 kg (1.9 lb).

An estimated total of 2500 lb (1130 kg) of volatile organic contaminant (VOC) was recovered. The available data are insufficient to allow for estimation of the recovered total petroleum hydrocarbons (TPH) mass in the vapor stream.

Concentrations in Extraction and Monitoring Wells

In order to screen each extraction well for the presence of COCs, water samples were collected at each wellhead every week during operation. These data were used to screen the water for VOC concentrations using a PID headspace method, without the expense associated with laboratory analysis. Three wells nearest the proposed hot-spot area on the east side of Area A (EE-6, 9, and 17) had the highest readings, exceeding the range on the PID instrument (10,000 ppmv). After December 2, all readings decreased to below 700 ppmv for the rest of operations. For the last round of samples collected on February 21, 2003, all values were below 25 ppmv, indicating that very little VOC was being extracted in the water from all the wells.

Concentrations of VOCs varied between the wells, with the highest concentrations of 37,000 µg/L TCE measured in EE-17. Overall, several wells underwent large increases in COC concentration during the period from November through January, while all wells ended with low concentrations at the last two sampling rounds. The analytical data for the most contaminated well, EE-17, are shown.
in Figure 9. These data were taken as an indicator that the ground water lying within Area A was sufficiently remediated.

During and after remediation, ground water samples were collected from eight monitoring wells located outside Area A every 3 weeks. Sample locations are shown in Figure 2 (labeled Stoller monitoring wells). All concentrations remained below 100 µg/L throughout the project, well below the remediation goals listed in Table 3.

**Interim Soil Sampling—Addition of Steam Injection Screens**

In order to examine the progress of the remediation, interim soil samples were collected both on December 22, 2002, and January 20, 2003, from characterization boreholes drilled to approximately 4.6 m = 15 feet. Some of the collected samples showed high PID readings, and laboratory analysis confirmed that TCE and toluene soil concentrations exceeded the cleanup goals. The areas of high concentration in the soil coincided with the location of a 0.3-m (1 feet)−thick resin layer observed during drilling. A sample of the resin material was analyzed and found to contain high concentrations of methylene chloride and TCE. On February 2, six additional shallow screens for steam and air injection or vapor extraction were installed and then used to deliver steam and air to the areas that apparently had been stagnant and that had resisted remediation. This resulted in more complete heating of the small problem area. During cool-down, air was injected into the shallow screens in order to enhance volatilization and prevent COCs from condensing in the subsurface.

**Postoperative Soil Samples**

Postoperative soil sampling was carried out in the 36 confirmatory borings at locations selected by random number generation laid out on a regular grid. The holes were drilled and sampled between March 24 and April 10, 2003. All postoperational soil contaminant concentrations were substantially below NAPL remediation goals (VOC data shown in Table 2). Chlorinated VOC concentrations nowhere exceeded 1% of the remediation goals, while toluene and petroleum range organics nowhere exceeded 20% of the remediation goals.

![Figure 9. Analytical data for VOCs in the most contaminated extraction well (EE-17) during operation.](image-url)
water and chemicals present in the treatment volume. Within a few hours of slowing the steam injection, vapor-phase PID readings on V-1 samples typically increased by orders of magnitude, indicating that boiling of pore fluids in the subsurface had led to vaporization of large amounts of contaminants. Figure 10 shows the relation between the steam injection rate and the calculated VOC removal rate in the vapor stream at the V-1 sample location. Increases in the mass removal rate correlate with times when the steam injection rate was decreased, as shown by the vertical lines on the figure.

The pressure cycling mode of operation increased the mass removal rates significantly, thereby allowing the target volume to be treated more rapidly than if the heating had been conducted at steady rates. Furthermore, pressure cycling influenced temperatures in both the low-permeability zones and the sandy zones. This was shown by the temperature swings observed in the upper 4 feet of the Hawthorn Group. The temperature would increase and decrease ~1°C to 3°C with the same frequency as the steam pressure cycles (data not shown). These temperature swings indicate that boiling was occurring in the pores of the clays. The heating was caused by the heat added using the deep electrodes, but the mass removal was ultimately driven by the lowering of the overall pressure in the water-bearing zone above. Such boiling would lead to formation of steam vapor, which would have a tendency to migrate upward due to its buoyancy. COC-laden vapors would then migrate through the sand zones toward extraction wells for recovery. This is an important mechanism for DNAPL and COC removal from aquitards. Details of the mechanisms were described by Itamura and Udell (1995).

The solubility of chlorinated solvents such as TCE and cis-1,2-DCE increase by between 50% and 100% when heating from ambient to 90°C (Heron et al 1998a; Knauss et al. 1999b). Also, experimental data on PCE showed that the rate of dissolution increased by about 400% in a controlled laboratory column experiment (Imhoff et al. 1997). Overall, the limited data available would suggest that, at best, the ground water concentrations would increase by a factor of 10 or so, when heating from ambient to near the boiling point of water. Thus, dissolution was likely not an important mechanism for the NAPL removal.

In situ reactions, biological or chemical, could have contributed to the removal of COCs from the subsurface. However, since such reactions would result in the disappearance of the COCs, without any well-established by-products other than water, carbonate, and hydrogen ions, data could not be obtained to provide proof of such reactions.

The reaction kinetics of methylene chloride are favorable for hydrolysis rates to be significant, rendering hydrolysis reactions of particular interest for that compound (Marrone et al. 1998). The kinetics can be reasonable, predicted by the Arrhenius equation (Fells and Moelwyn-Hughes 1958) and therefore the half-life at higher temperatures can be estimated from:

$$t_{1/2}(T) = t_{1/2}(T_0) \times \exp\left(\frac{E_a}{R \times (1/T - 1/T_0)}\right)$$

where $t_{1/2}$ = half-life (years), $T$ = absolute temperature (degrees K), $E_a$ = activation energy for the hydrolysis reaction (kJ/mol), and $R$ = the gas constant (8.314 J/mol/K).

By using a half-life of 1 to 2 years at 25°C and an activation energy of 100 to 120 kJ/mol (assumption based on values cited by Fells and Moelwyn-Hughes 1958 and Marrone et al. 1998), the half-life at a temperature of 70°C is estimated as approximately 1 d. At 90°C, the half-life is 2 h.

Subsurface temperatures were in the 50°C to 90°C range during times when methylene chloride was abundant in the extracted water and presented a problem by breaking through the liquid-phase GAC system. At this time, the operators reduced the liquid extraction rate from the wells suspected of producing water with high concentrations of methylene chloride. These wells were selected by analysis of preoperational soil samples and PID screening of water samples collected at each extraction well. The purpose was to allow the methylene chloride to hydrolyze in situ at the elevated temperature, since the half-life at this temperature was estimated at about 2 h. After restart of extraction from the suspect wells, the methylene chloride concentrations in the extracted water were negligible (documented by sampling at location L-1). Although no proof of the operation of these mechanisms can be provided, it is postulated that a substantial amount of methylene chloride was degraded by hydrolysis. This mechanism can be very useful for optimizing the remedial results and for reducing the risk of liquid-phase GAC breakthrough. Wells that are heated and contain high methylene chloride concentrations may

![Figure 10](image-url)
simply be turned off for 1 to 3 d, during which time the concentrations would decline due to hydrolysis. Extraction can then be resumed.

Air Injection Benefits
The injection of air into the steam injection wells potentially had three effects:

1. Air sweep through the heated zones carried some of the COCs to the extraction wells, thereby reducing the amount of vaporized COCs that would recondense or redissolve. This would reduce the risk of forming NAPL zones where the steam condensed (Schmidt et al. 2002; Kaslusky and Udell 2002).
2. By injecting air, which was then extracted at the vacuum wells, vapor flow between the injection and extraction points would assist in VOC removal.
3. Air injection would add oxygen to the subsurface, potentially creating aerobic conditions favorable for both hydrous pyrolysis oxidation and aerobic biodegradation.

The operational data suggest that the air injection was particularly effective in the shallow steam injection screens and assisted in remediation of the upper 2 m (6 feet) of the target volume, where temperatures did not reach the boiling point of water. This was indicated by the large changes observed in the soil concentrations between the time of the interim soil sampling (December to January) and the post-operation sampling (March). The shallow air injection was performed during this time.

Potential for Spreading of Contaminants
The hydraulic and pneumatic control of the site was implemented as designed, with overall net movement of water and soil vapors into the treatment volume from the surrounding soil. The observed ground water concentrations in the eight surrounding monitoring wells stayed below 100 µg/L for all volatile contaminants, while TCE concentrations as high as 44,000 µg/L were seen in the water extracted from the wellfield (location L-1; Figure 8). This indicates that the preheating of the treatment cell perimeter, plus the horizontal inward sweep of water and vapor, was effective in preventing chemicals from migrating beyond the treatment volume. Deep soil sampling from the bottom clay layer and from the base of the surficial sands showed that very low concentrations of VOCs remained after treatment. These data indicate that downward movement of DNAPL was effectively prevented by the creation of a heated zone in the Hawthorn clays prior to injecting steam in the surficial sands. In conclusion, all the collected data indicate that contaminant spreading, both vertically and horizontally, was effectively prevented.

Conclusions and Recommendations
This is the first full-scale remediation of a DNAPL site by a combination of steam-enhanced extraction and electrical heating. Using steam to deliver energy to the permeable zones, and electrical heating to heat low-permeable zones, can lead to very effective and uniform heating. More importantly, by focusing the heating at the treatment zone perimeter and bottom first, heated barriers can be created around the DNAPL-containing volume. This can effectively minimize the risk of contaminant spreading, both horizontally and vertically.

This study showed the importance of pressure cycling for accelerating mass removal and shortening the operational time. During the induced pressure cycles, mass removal rates were many times higher than during constant injection and extraction of steam and electrical power. This phenomenon has been well published for 12 years (Udell et al. 1991, Udell 1996) but apparently has not been used effectively in several recent steam projects.

By the removal of about 1130 kg (2500 lb) of volatile contaminants in 4.5 months, soil and ground water concentrations were lowered to concentrations believed to be at least 100 times lower than levels that would allow DNAPL to exist. Complete DNAPL removal was apparently achieved in the entire treatment volume. Three rounds of ground water samples were used to document that rebound did not occur within the 6 months of sampling and showed that ground water concentrations were lowered to below MCL in the majority of the samples. By such effective remediation estimated at an average mass removal efficacy of 99.9% for the volatile contaminants, polishing steps may not be necessary.

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