Cost and Performance Summary Report Radio Frequency Heating in Fractured Rock at an Active Manufacturing Facility Impacted by Residual TCA DNAPL

Executive Summary [1, 2, 3, 4, and 5]

A historical release of 1,1,1-trichloroethane (TCA) occurred at an active manufacturing facility. Using the NAPL FLUTe[™] inverting liner site characterization tool, residual TCA dense, nonaqueous phase liquid (DNAPL) contamination was identified in an approximate 232 square-meter source area at concentrations between 410 to 1,100 milligrams per liter (mg/L). The target treatment area was located beneath an occupied commercial building.

After evaluating several in-situ treatment technologies, an integrated Radio Frequency (RF) heating and soil vapor extraction (SVE) system was designed, constructed and began operation in December 2003. According to the vendor, this system is the first in situ application of RF heating to treat TCA DNAPL in fractured bedrock. The treatment system included a network of nine, 100-foot deep, eight-inch diameter boreholes, an RF generator, a four-probe transmitter array, and a SVE system for control and treatment of vapors. The RF heating system consisted of a 27 Megahertz (MHz) four channel, 20-kilowatt (kW) RF equipment trailer, transmission lines, four water-tight antennae, applicators, and fiber optic thermometry. The RF heating system operated for 36 months at a maximum output of 19 kW.

Ground water temperature was monitored during the course of the treatment. Temperatures in the heated area increased at the rate of 1 degree Celsius (°C) per week from an ambient temperature of 21°C at the maximum power of 19 kW. The maximum ground water temperature achieved was 52°C. The total volume of ground water heated using the RF heating system was nearly 8,400 cubic meters (approximately 11,000 cubic yards). Based on three years of post treatment monitoring, TCA concentration in source area ground water had decreased to 2.4 mg/L. The decrease in TCA is attributed to the increased ground water temperatures and accelerated dissolution rate of TCA DNAPL, making it more susceptible to biodegradation and abiotic transformation. With every 10°C rise in temperature, a nearly two-fold increase is observed in biodegradation rates. In addition, above 25°C abiotic degradation rates of TCA are also higher. Above 55°C, the half-life of TCA is reduced to a period of days.

Background Information [1 and 3]

A historical release of TCA occurred at an active manufacturing facility. Both residual DNAPL and elevated dissolved phase concentrations were identified in the source area, which extended across approximately 232 square meters. The historical average TCA concentration in ground water within and around the source area was 250 mg/L, which is equivalent to approximately 19 percent of TCA's aqueous solubility of 1,334 mg/L at 25° C [6]. Residual DNAPL (discontinuous ganglia) in bedrock fractures was identified

by coupling the results of geophysical imaging logs with data collected using immisciblefluid absorbent liners such as the NAPL FLUTeTM. Residual DNAPL was noted in five of the nine boreholes where FLUTeTM liners were installed. Extensive subsurface investigation and removal actions within the source area suggested that release(s) of solvents had migrated vertically through the unconsolidated overburden into the underlying bedrock. Lateral migration in bedrock appears to have been restricted by a bowl-shaped bedrock depression and the high competency, low yield of the bedrock beneath the source area. TCA concentrations in source area wells containing residual DNAPL were found to be between 410 to 1,100 milligrams per liter (mg/L). The target treatment area was located beneath an occupied commercial building.

Extensive technology screening, laboratory treatability studies and field pilot tests were conducted to assess the feasibility of applying in situ remedial technologies to treat the residual TCA DNAPL source area at the site. Three in-situ treatment technologies were evaluated in detail: (1) in-situ chemical oxidation (ISCO) with heat-catalyzed sodium persulfate and/or Fenton's Reagent, (2) thermal degradation at temperatures of 35°C or higher using RF heating; and, (3) biodegradation using lactate or emulsified soybean oil plus an enrichment culture. The results from these evaluations confirmed that the tight, discontinuous nature of the bedrock fracture network limited the effectiveness of technologies dependent on physical push/pull delivery of treatment medium such as injection and/or mass withdrawal based technologies. Therefore, the ISCO and biodegradation were not retained for further evaluation because they were not expected to overcome the physical constraints posed by the poorly connected, low yield bedrock.

RF heating was selected because of several advantages including:

- 1. RF heating preferentially heats polar molecules (e.g., water), focusing the thermal energy on the target (impacted ground water in bedrock fractures) rather than the host (bedrock),
- 2. RF generates heat within an elliptical volume of field propagation, largely independent of the physical constraints of the host, thereby overcoming the physical constraints posed by the poor degree of fracture interconnectivity and low yield of the bedrock, and
- 3. RF heating efficiency was enhanced by several site hydrogeologic characteristics which included:
 - The low yield of the bedrock;
 - The overlying building acting as a cap and minimizing infiltration of precipitation; and
 - The hyrologic location of the site, at the upper edge of a drainage basin divide, a low recharge area, thereby minimizing flushing of that portion of the aquifer.

Timeline [2]

| Date | Activity |
|---------------|-----------------------------|
| December 2003 | RF heating system activated |
| November 2006 | RF system shutdown |

Factors That Affected Technology Cost or Performance [2]

The site surficial geology consists of glacial outwash and till with an estimated thickness of 4.5 to 9 meters. Bedrock is composed of late Precambrian- to Devonian-aged rocks characterized by intensely sheared parent rock. The primary porosity of the rock is estimated at 0.5 percent. The bedrock aquifer consists of the interconnected secondary porosity. The "residual" DNAPL consisted of discontinuous films, ganglia, or globules of separate phase solvent. DNAPL thickness could not be measured due to presence of poorly connected fractured crystalline bedrock of very low-yield (less than 1 gallon per minute).

Listed below are the parameters that define the key matrix characteristics affecting RF heating and the values measured for each parameter during site characterization.

| Parameter | Value | | |
|------------------------|---|--|--|
| Soil classification | Crystalline bedrock | | |
| Depth to ground water | 9 m below ground surface (bgs) | | |
| Depth of interest | 9 m to 30 m bgs | | |
| Volume of interest | Approximately 11,000 cubic yards (cy) | | |
| Primary porosity | 0.5 percent | | |
| Electrical Resistivity | Average of 1,716 ohm metre ($\Omega \cdot m$) (unfractured core | | |
| | sample), average of 598 Ω ·m (fractured core sample) based | | |
| | on laboratory testing. | | |
| Composition of DNAPL | 1,1,1- Trichloroethane (TCA) | | |
| Areal extent of DNAPL | Approximately 232 square meters based on observed | | |
| | DNAPL and aqueous solubility of TCA | | |

Matrix Characteristics Affecting Technology Cost or Performance [2, 3, 4, 5]

Treatment Technology Description [1, 2, 3, 4, 5, 7]

RF heating uses electromagnetic energy in the radio frequency spectrum to heat media. The electromagnetic radiation is directed toward a non-conducting material (such as bedrock). Part of the applied electromagnetic energy is transmitted through the material, part of it is reflected, and part of it is absorbed. Majority of the absorbed energy is converted into heat energy that in turn heats the target conductive material (in this case, ground water contaminated with TCA DNAPL). Thermal degradation of TCA is substantially accelerated (half-life from years to days) via hydrolysis and abiotic elimination at temperatures of 50°C to 60°C and is therefore amenable to relatively low temperature thermal treatment. TCA DNAPL is depleted in situ by accelerated dissolution and volatilization, followed by natural degradation of the dissolved phase. In addition, TCA is also susceptible to increased biodegradation due to the increase in temperature.

The treatment system includes a network of nine, 30.5-meter deep, 20-cm diameter boreholes, an RF generator, a four-probe transmitter array, and a SVE system for control and treatment of vapors.

The RF heating system employed at the site consists of a 27 Megahertz (MHz) four channel, 20-kilowatt (kW) RF equipment trailer, transmission lines, four water-tight antennae, applicators, and fiber optic thermometry. The antennae are placed in the boreholes and are spaced approximately 4.5 meters apart in a square array. Each antenna was typically 3 meters long and 6.5 centimeters in diameter and received a maximum of 5 kW from the RF generator module. The antennae were placed in eight boreholes at a depth of 30.5 meters in deep open bedrock and produced a vertical and a horizontal electrical field distribution of 4.6 meters. The electrical field generated from the RF heating system simultaneously targeted 860 cubic meters of fractured bedrock. The RF heating system was activated in December 2003 and operated for 36 months at a maximum output of 19 kW.

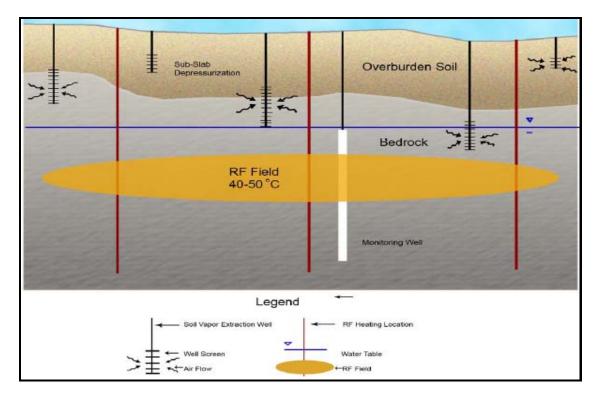


Figure 1: Cross section of the RF heating system at the treatment site [3]

The SVE system consists of a total of 26 vacuum extraction points. The sub-slab depressurization system consists of 12 shallow (screened from 2 to 10 feet below grade) overburden extraction wells. The SVE system also includes 14 deep overburden and shallow bedrock extraction wells located within the targeted remediation area focused on abating VOC impacts within the vadose zone.

The vacuum extraction points are connected above-grade to the SVE system equipment via 1 ¹/₄- or 2-inch diameter polyvinyl chloride (PVC), schedule 40 pipe.

The SVE equipment includes the following:

- two ¹/₄ -horsepower (hp) air-cooled heat exchangers
- moisture separator
- air intake and filters
- 5-hp rotary lobe blower with discharge silencer;
- 2-hp air-cooled heat exchanger;
- vapor-phase carbon vessels (2 in series, 1 as stand-by); and
- 2-hp regenerative blower.

Operating Parameters [2, 7]

Listed below are the key operating parameters for RF heating and the SVE system.

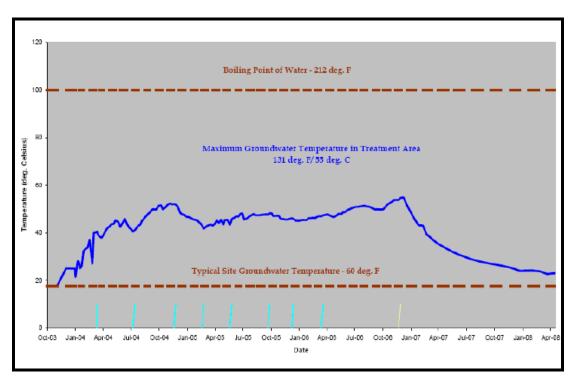
| Parameter | Value | | | |
|-----------------------------|---|--|--|--|
| RF heating | | | | |
| Temperature | 52 degrees Celsius | | | |
| Radio frequency power input | power input 19 kilowatts | | | |
| SVE system | | | | |
| Flow rate | 110 and 140 cubic feet per minute (cfm) | | | |

Performance Information [2, 3]

Ground water temperature was continuously monitored during the course of the treatment. Ground water temperatures in the heated area increased at the rate of 1°C per week at the maximum power of 19 kW. Maximum ground water temperature observed was 52°C. Elevated groundwater temperatures were measured over an area of approximately 400 square meters and at a 21 meter (~68 feet) vertical interval from the water table starting at 9 meters (30 feet) bgs to 30 meters (98 feet) bgs. Figure 2 shows the source area ground water temperature over time. The total volume of ground water heated using the RF heating system was nearly 8,400 cubic meters (approximately 11,000 cubic yards).

The average source area TCA, 1,1-dichloroethene (DCE), and 1,1-dichloroethane (DCA) concentrations in ground water over time during the treatment period are shown in the table below [3]:

| Date | TCA concentrations (µg/L) | DCE concentration (µg/L) | DCA concentration (µg/L) |
|---------------|------------------------------|-----------------------------|-----------------------------|
| May 2003 | 146800 | 11200 | 5100 |
| May 2004 | 35600 | 4200 | 1400 |
| May 2005 | 14300 | 4500 | 760 |
| May 2006 | 1000 | 1600 | 140 |
| May 2007 | 3000 | 2000 | 160 |
| June 2008 | 4800 | 1600 | 170 |
| May 2009 | 8300 | 2200 | 430 |
| February 2010 | 3300 | 870 | 160 |



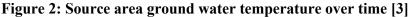


Figure 3 shows concentrations of TCA in source area ground water. The decrease in TCA (and other VOCs) is attributed to the increased ground water temperatures and accelerated dissolution rate of TCA DNAPL into dissolved phase TCA, potentially increasing biodegradation rates and also making it more susceptible to abiotic transformation [1, 4, 5]. An evaluation of the data shows both abiotic and biotic degradation of TCA to DCE, acetic acid and DCA. Vinyl Chloride (VC) concentrations were non-detect in the groundwater samples. The samples were not analyzed for ethane or ethane.

The typical influent concentration of TCA into the SVE system ranged from 2.83 μ g/L (January 2006) to 0.03 μ g/L (June 2006). The SVE system was intended to capture any volatile compounds released by the RF heating system. A total of 144 pounds of VOC were captured from December 2003 to November 2006. Figure 4 shows the cumulative VOC removed (lbs) and the VOC Removal Rate (lbs/day) from October 2003 to November 2006.

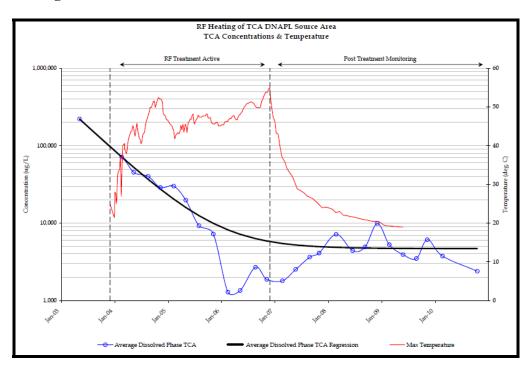
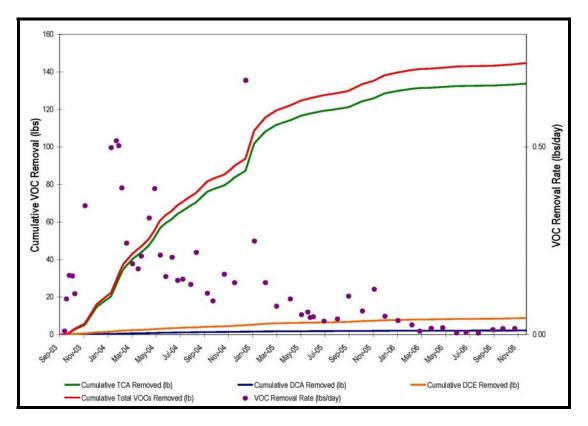


Figure 3: Concentrations of Dissolved Phase TCA in the Source Area





Performance Data Quality

No exceptions to established quality assurance/quality control (QA/QC) procedures were noted in the available references.

Cost Information

According to the vendor, typical remediation costs using RF heating are \$100 - \$150 per cubic yard. This cost includes bench-scale testing; field-scale design; RF equipment mobilization, start-up and testing, operation and maintenance (including remote telemetry), and demobilization. Any costs associated with subsurface investigations, drilling, groundwater monitoring, and the SVE system are not included.

Observations and Lessons Learned [1, 3]

By May 2010, TCA concentrations in source area ground water were reduced by 97%. The decrease in TCA is attributed to the increased ground water temperatures and accelerated dissolution rate of TCA DNAPL into dissolved phase TCA, making it more susceptible to abiotic transformation.

Success in the application of RF treatment at this site was largely due to a match between the advantages and benefits afforded by RF and the characteristics of the target contaminant and the site. Key considerations included: 1) the rapid reduction in TCA half-life with low temperature thermal treatment (from years to days at 50°C to 60°C) and ability accelerate the dissolution rate of TCA DNAPL; 2) treatment in low yield, poor connectivity fractured bedrock and the ability of RF to heat over a volume in the host material independent of bedrock physical constraints; 3) the relatively small size of the treatment area (400 square meters); and 4) the presence of DNAPL as a residual and low potential for mobilization during treatment.

Aspects that could improve the efficiency of the technology include: 1) treatment of multiple cells, use of probes at multiple depths and multiple RF generators to simultaneously maximize the overlap benefits (approximately twice the heating energy in the overlap between cells/probes) to reduce operating time; 2) increasing system power at sites where it is safe to do so (this application was operated beneath an occupied building) and 3) application of heat activated catalysts to treat fringes of the source area, reduce generation of daughter products and utilize latent heat in the system.

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