

Groundwater Issue Paper

In Situ Thermal Remediation

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Section 1.0 Introduction

In situ thermal remediation technologies rely on the addition of energy to the subsurface to change the phase distribution and other physical properties of volatile and semivolatile organic contaminants to mobilize them and aid in their recovery. The most commonly used in situ thermal remediation technologies today are Steam Enhanced Extraction (SEE), electrical resistance heating (ERH), and thermal conductive heating (TCH; sometimes called in situ thermal desorption, ISTD). These three most commonly used technologies are applicable to and have been proven for a wide variety of organic contaminants and in a wide variety of hydrogeologic settings, both above and below the water table. In addition, there is an emerging thermal technology called Self-sustaining Technology for Active Remediation (STAR), that results in the in situ combustion of liquid contaminants that have significant fuel value in porous media. Each of these technologies will be summarized.

Thermal remediation technologies are very aggressive and are most applicable for contaminated sites (or portions of sites) where contaminant concentrations are the greatest, generally areas where nonaqueous phase liquids (NAPLs) are present. The NAPLs can be either lighter than water (LNAPLs, such as petroleum hydrocarbons) or denser than water (DNAPLs, such as chlorinated solvents or coal tar-based products). LNAPLs can be volatile organic compounds (VOCs) such as gasoline, semivolatile organic compounds (SVOCs) such as diesel fuel, or longer chain hydrocarbons that are less volatile such as oil and grease compounds. Chlorinated solvents are generally VOCs, while coal tar and its derivative creosote are SVOCs. NAPLs, and in particular DNAPLs below the water table in heterogeneous hydrogeologic settings which include low permeability soils or fractured bedrock can be some of the most difficult organic contaminants to remediate. At the same time, these scenarios can create significant risk of exposure to contaminated groundwater, elevated contaminant concentrations in indoor air, or discharge of contaminants to surface waters, thus increasing the need for

effective remediation. Thermal remediation technologies have the advantages of being fast, with most VOC remediations requiring six months or less of operation. Large percentages of the contaminant mass can be recovered, leaving behind only dissolved and/or adsorbed phases. Using temperature measurements to ensure treatment of all the target area greatly increases the certainty of the remediation.

The purpose of this paper is to briefly describe these commonly used in situ thermal remediation technologies, and how they are deployed to remediate VOC and SVOC contaminated sites. The effects of temperature on the physical properties of common organic contaminants that result in the effectiveness of these technologies for the recovery or destruction of contaminants are also briefly described. A case study is provided for each of the thermal technologies discussed. In addition, guidance is provided on evaluating, contracting, and implementing thermal technologies within the Superfund process of evaluating alternative technologies, including preparing bid documents for thermal remediation services, reviewing designs, and monitoring the implementation of the remedy. Most of this information will also apply to sites that are covered by other regulatory programs or are outside of the regulatory process. Factors that affect the costs of thermal remediation are also discussed. Advice based on experience gained from sites where these technologies have been implemented is provided on soliciting thermal remediation services, how to determine the area/volume to be treated, and when to terminate the heating portion of the remediation. This paper includes both information gathered from other published papers and knowledge gained from the author's extensive experience of technical support for thermal remediation.

Section 2.0 In Situ Thermal Technology Descriptions and Their Implementation

Steam enhanced extraction, electrical resistance heating, and thermal conductive heating are all adaptations of technologies that have been used in the oil industry for enhanced oil recovery. While all these technologies have the objective of increasing the mobility of contaminants either by reducing the viscosity of a liquid phase for SVOCs or by causing a phase change to a vapor for VOCs, they differ in the manner in which the energy is injected into the subsurface to bring about these changes. Some chemical reactions may also be enhanced at the temperatures used for thermal remediation. All these technologies include extraction of the contaminants in the vapor and/or liquid phase via soil vacuum extraction (SVE) or multiphase extraction (MPE), and above ground treatment of the effluent stream(s). Each of the methods of heating the subsurface has certain advantages or disadvantages in certain situations; however, there is also overlap between the applicability of the technologies to specific sites. In this section, each of the three heating techniques that are commonly used today will be described, as well as the emerging STAR technology, along with some advantages and disadvantages of each. Also discussed is when combining thermal technologies may be the most effective means to treat a site.

Section 2.1 Steam Enhanced Extraction.

Steam Enhanced Extraction (SEE) involves the injection of steam under pressure with the concurrent extraction of groundwater, NAPL, and vapors (Davis, 1998). Ideally, steam injection wells are constructed in relatively clean soils surrounding the contaminated area to be treated, while multiphase extraction (MPE) wells are constructed centrally located of the steam injection wells within the contaminated area (Figure 1). For sites that are larger than the radius of influence of the injected steam, a 7-spot pattern is recommended (Figure 2). Thus, each multiphase extraction well, which extracts ground water, NAPL, and vapors, ideally is surrounded by four to six injection wells. As steam

is injected under pressure into the subsurface through vertical injection wells, initially the steam condenses and gives up the heat of condensation to the soils. When the soil reaches steam temperature, steam will begin to move radially into the subsurface from the injection well. With continued steam injection, three different temperature zones form: closest to the injection well is the steam zone which is at steam temperature; next is a narrow variable temperature zone which goes from steam temperature to ambient temperatures, and further from the well is the ambient temperature zone (Udell, 1996; Udell and Stewart, 1989; 1990). Pore fluids (water and NAPL) will be displaced by the steam and condensate, pushing it towards the extraction wells.

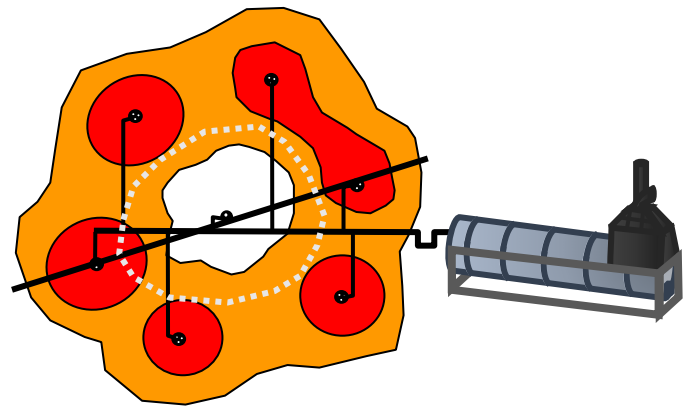


Figure 1. This figure illustrates the development of a steam zone as steam is injected into the subsurface using vertical injection wells that are installed in a 7-spot pattern (see Figure 2). The boundary of the NAPL-contaminated area (shown by the dotted line) is surrounded by the injection wells, and the sharp steam front displaces the NAPL to the centrally-located multiphase extraction well. Steam enters the formation radially from the injection well, so part of the steam does not enter the thermal treatment area. Each injection well may accept differing amounts of steam. Volatile components of the residual liquid saturation left behind the displacement front are volatilized when the steam front reaches it, and the vapors are transported to the steam front for extraction. As steam injection continues, steam will breakthrough at the extraction well. After breakthrough, the steam injection rate is reduced to decrease the pressure in the subsurface and allow more of the contaminants to volatilize from low permeability zones and be transported to the extraction wells. Several cycles of decreased and then increased steam injection (called pressure cycling) are normally performed until reducing the injection pressure does not significantly increase contaminant extraction rates.

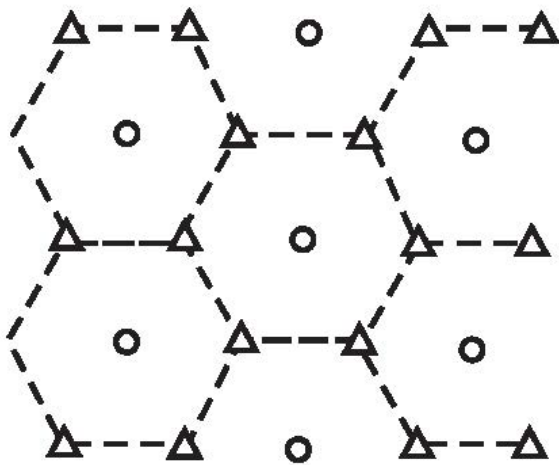


Figure 2. When the NAPL-contaminated area to be treated is larger than the maximum spacing for steam injection wells, a 7-spot pattern is generally used, as illustrated, where the triangles represent steam injection wells and the circles represent multiphase extraction wells. This pattern with multiple injection wells surrounding the extraction wells improves the distribution of steam within the treatment area. The outer periphery of wells outside of the treatment area should be steam injections wells, and they should be outside of the NAPL-contaminated area.

Liquid NAPL that is displaced will leave behind residual liquid saturation, which is typically 10 to 20 percent of the pore space. As the steam front reaches this residual saturation, it will volatilize the more volatile components of the residual liquids and these vapors will be transported to the steam front. When the contaminant is a mixture of volatile and semivolatile compounds, such as diesel fuel, creosote, or spent chlorinated solvents, the volatile components of the mixture (which would include benzene, toluene, ethylbenzene, and xylene (BTEX) compounds in fuels or naphthalene in creosote) will be volatilized, and transported to the front of the steam zone, where they are recovered with the rest of the mobilized NAPL. Volatile compounds with a boiling point of less than approximately 150°C will be essentially fully recovered by the passage of the steam front (Yuan and Udell, 1993), while higher boiling compounds are likely to remain in the soil pores. With continued steam injection, essentially all the volatiles will eventually be stripped from the residual NAPL.

The steam injection technology employs all the mechanisms for contaminant mobilization that come from raising the temperature of the subsurface (Section 3), and also employs a displacement mechanism that can be very effective for recovery of NAPLs composed of semivolatile compounds such as creosote (Udell and Stewart, 1989). SEE is most effective in more permeable soils with hydraulic conductivity greater than about 10^{-3} centimeters per second (cm/sec). Steam propagation is governed by heat transfer to the formation, and thus, injection of steam into the subsurface is a stable and predictable process (Heron et al., 2005). A potential disadvantage of steam injection is that when the preferred arrangement of injection and extraction wells is employed, with steam injected around the outside of the area to be treated, a portion of that steam will heat the area outside of the treatment zone. Thus, not all the energy injected goes within the treatment zone due to the radial flow of steam at the injection wells. These injection wells are generally in contaminated groundwater, and these dissolved phase contaminants can be pushed away from the treatment area and recovery wells. However, when pressure cycling (terminating or reducing steam injection while continuing to aggressive extract liquids and vapors) is performed, the collapse or reduction in the steam zone will pull these contaminants back to the treatment area where they can be recovered. Pressure cycling will also enhance the vaporization of contaminants in low permeability zones and their transport to the more permeable zones so that they can be recovered via vacuum extraction (Itamura and Udell, 1995).

Steam, due to its high specific enthalpy, is a very efficient means of heating the subsurface (Class and Helmig, 2002). Steam injection is the most cost effective technology for large, deep sites with sufficient permeability, due to the fact that greater spacings between injection and extraction wells can be used. However, SEE has also been successfully used at shallow sites where there is sufficient permeability to allow sufficient steam injection at low injection pressures. Steam injection below the water table will impede the inflow of ground water,

allowing steam temperatures to be reached even in high permeability aquifers. Still, to maintain hydraulic control, the groundwater extraction rate must exceed the steam injection rate by a factor of 1.5 to 2.5 in order to maintain hydraulic control by recovering also the groundwater displaced by the growth of the steam zone. The heating rate is dependent on the ability to inject steam, which is dependent on the hydraulic conductivity of the formation and the steam injection pressure. The steam injection pressure in turn is dependent on the depth of injection; the injection pressure cannot exceed the overburden pressure. Because overburden pressure increases with depth, higher injection pressures can be used at deeper sites, which will allow a greater spacing between injection and extraction wells, and reduce the amount of drilling and above ground infrastructure required. However, the effects of soil anisotropy on steam migration may necessitate closer injection well spacing. Typical steam injection well spacing for shallow sites are between 20 and 30 feet, while full scale applications at large, deep (treatment depths of 100 to 200 feet below ground surface) sites have been implemented with wells spacings exceeding 80 to 90 feet.

Superfund sites where steam injection remediation has been used include Southern California Edison's Visalia Pole Yard Superfund Site to recover creosote (now deleted from the National Priority List), the former Williams Air Force Base to recover jet fuel (the largest at 413,000 cubic yards and deepest at a maximum of 240 feet below ground surface steam injection remediation to date), and at the Beede Waste Oil Superfund site to recover waste oil and chlorinated solvents (see SEE Case Study). Also, a steam injection research project was performed in fractured rock at the Quarry site at the former Loring Air Force Base (Davis et al., 2005).

Section 2.2 Electrical Resistance

Heating. The Electrical Resistance Heating (ERH) technology was first developed by Pacific Northwest National Laboratory in the early 1990s. Generally, the electrodes are installed vertically in a hexagonal pattern, spaced 12 to 20 feet apart (Figure 3). Originally, 6-phase current was used with a different phase applied to each of the 6 electrodes in the hexagonal array. Eventually 3-phase alternating current was adopted for most application, as it allows for a better current distribution in irregularly-shaped treatment areas. ERH relies on water in the pore spaces to carry current between the electrodes. Soils are naturally resistant to the current flow, and this resistance dissipates the current energy as heat. Volatile contaminants are vaporized and extracted via soil vapor extraction (SVE). The presence of ions in clay soils can make clays more conductive to electricity than more permeable sandy soils, which ensures that current flows through clay zones and they are heated. Temperatures equivalent to the boiling point of water can be achieved with this technology, but water must be maintained in the pores for current to continue to flow. Thus, in low permeability soils or when treating soils above the ground water table, water or an electrolyte solution is usually added at the electrodes to ensure that contact is maintained between the electrodes and thus heating is maintained (Morgenstern et al., 2007). Some versions of the ERH technology also rely on water injection to convectively carry energy from the electrodes, and thus greater water injection rates are used (McGee et al., 2000; Mejac et al., 2008). In this case, ground water extraction is always used in conjunction with vapor phase extraction.

A variety of electrode constructions have been used, including steel pipe or copper plate, with a backfill of conductive materials such as graphite or steel shot in the borehole annulus to increase the effective diameter of the electrode (typically 10 to

Electrical Resistance Heating

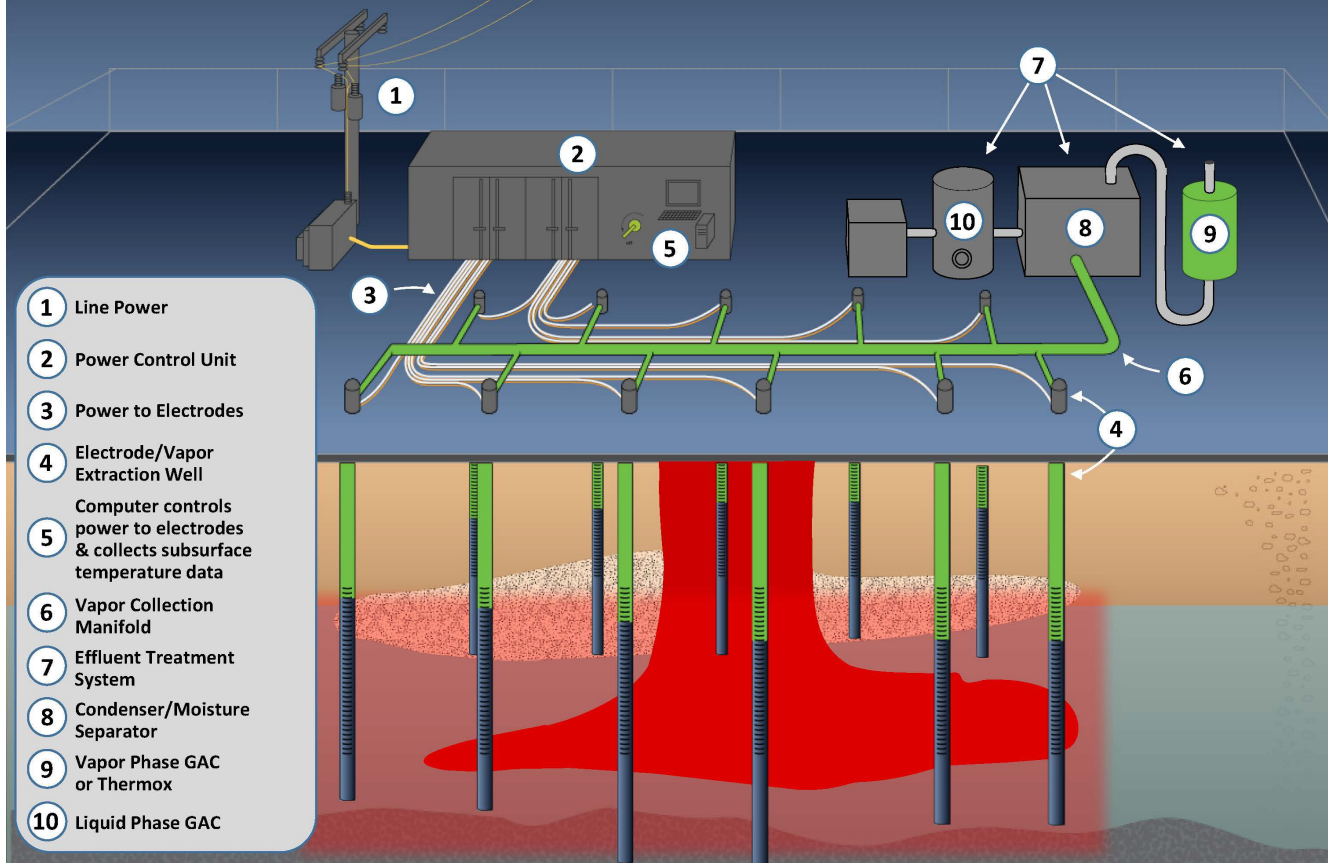


Figure 3. This figure illustrates an ERH system. Three phase alternating electrical current from the power grid is distributed to electrodes installed vertically (or at angle to reach under a building or other infrastructure) in the subsurface in a triangular pattern. Current flows within the soil pore water connecting electrodes of different phases. The natural resistance of the soil to current flow causes the current to be dissipated to the soils as heat. Current flow will stop if the pore water is totally removed, limiting the temperature that can be achieved with this technology to the boiling point of water. Vapors are collected by vacuum extraction, and transported to the effluent treatment system, where the condensable vapors (steam) are separated from the air and volatile contaminants. The noncondensable vapors are then treated through vapor phase granular activated carbon (GAC) and discharged. At large sites the vapors can be destroyed on site in a thermal or catalytic oxidizer. Condensed steam is treated by liquid phase granular activated carbon before discharge.

12 inch diameter). Sheet piling has also been used for electrodes in relatively permeable soils, which has the advantage of a greater surface area for contact with the soil and thus greater current flow (Cacciatore et al., 2008). For deep sites or sites with changes in geology and therefore electrical resistivity parameters with depth, the installation of stacked electrodes is required to properly heat the full treatment depth. Bored electrodes can also be vapor recovery wells, and vapor recovery is accomplished using conventional SVE techniques. Vapor recovery can also be done by the installation

of separate vapor extraction wells between electrodes. ERH can be performed either above or below the water table, and can be used to treat both zones simultaneously. A major advantage of ERH is its ability to treat low permeability silts and clays effectively, reaching contaminants that are difficult to contact and treat through the injection of liquids or conventional SVE. Pressures created by the vaporization of ground water and contaminants will force the flow of vapors to the extraction points. Drying of the soils will also aid in increasing its permeability to vapors, however, as mentioned

previously, some water must be maintained in the pore spaces to carry current between the electrodes. Ground water flow rates greater than approximately 1 foot per day are challenging for ERH systems and may limit the system's ability to reach the boiling point of water and/or can lead to a loss of hydraulic control. In these situations groundwater extraction upgradient of the treatment area with reinjection downgradient may flatten the hydraulic gradient and extend the use of this technology to more permeable saturated formations. Another option may be to limit groundwater flow into the treatment area by installing an upgradient hydraulic barrier such as a sheet pile wall or slurry wall.

Superfund sites where ERH has been used include East Gate Disposal Yard at the Fort Lewis Army Depot where waste oil and chlorinated solvents were recovered, Cleburn Street Well site where chlorinated solvents were recovered (see ERH Case Study), the South Municipal Well Superfund Site where chlorinated solvents were recovered, and the Hamilton-Labree Superfund site where chlorinated solvents were recovered (TerraTherm, 2022).

Section 2.3. Thermal Conductive

Heating. As the name implies, this technology relies on heat conduction through the soil to heat the target treatment area. This technology was first developed primarily by Shell Oil Company in the 1990s with the participation of a variety of other companies (Stegemeier and Vinegar, 2001). The basis for using heat conduction for applying energy to the subsurface is the fact that the thermal conductivity of different soil types is fairly uniform, varying only by approximately a factor of two to five (dry sandy soil will have a thermal conductivity of 0.5 – 1.0 Watt per meter-Kelvin (W/mK) while wet silt/clay is closer to 2.0 – 2.5 W/mK). This allows for a relatively more uniform heating rate in highly heterogeneous soils than can be achieved by the injection of energy as a fluid, such as by hot water or steam injection. However, the thermal conductivity of soils is low, which necessitates a steep temperature gradient (thus high temperatures) at the points of energy application in order to transport energy away from the points of

application (Heron et al., 2015). Thus, heater temperatures in the range of 500 to 800°C are typically used (Figure 4), with heater spacings on the order of 6 to 20 feet, depending on time available for remediation (larger spacing will require longer remedial timeframes to reach the same endpoint).

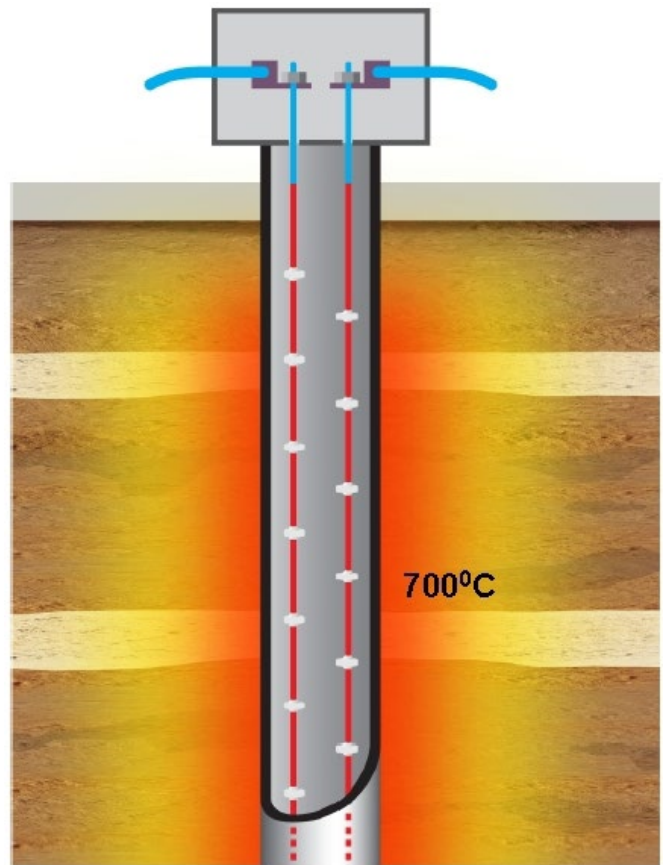


Figure 4. This figure illustrates an electrical thermal conduction heating (TCH) heating well installed in heterogeneous soils. The temperature of the heater well is in the range of 700°C in order to increase the conduction of heat into the soils. The thermal conductivity of soils is relatively uniform, thus different soil types will heat at about the same rate. Most TCH systems rely on electrical energy, however, one version of the technology uses natural gas or propane combustion at the well heads to provide the energy. The heater wells are installed in a triangular pattern at spacings of 12 to 20 feet with extraction wells located throughout the treatment area, generally at the midpoints between the heater wells. When installed above the water table, treatment temperature up to 350 – 400°C can be reached to treat higher boiling compounds.

TCH is the only one of the three commonly used technologies that can reach temperatures above the boiling point of water, and in the higher temperature applications (with target temperatures up to 350 – 400°C) the heater spacing is typically between 8 to 12 feet. Also, multiple well patterns are generally used to increase heating effectiveness and efficiency through superposition of heat/energy. Vapor extraction is used to recover the vaporized contaminants. A significant advantage of this technology is that because it does not rely on water for energy application or convection, temperatures in excess of the boiling point of water can be achieved when the soils are unsaturated. This allows not only VOCs but also SVOCs to be treated by this technology to achieve very low residual soil concentrations by raising the temperature to 250 – 350°C (Baker and Heron, 2004). Semivolatile contaminants such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and dioxins and furans have been treated using TCH technologies.

Various types of TCH systems available from the thermal technology vendors. In general terms, the TCH technology is implemented in situ by installing heater wells in vertical boreholes. Angled or horizontal wells can also be used, particularly for extending under buildings or other structures. The wells are installed in triangular patterns, creating a repeating series of hexagons. Energy applied to the heater wells creates temperatures of 500 – 800°C at the wells, but due to the steep temperature gradient, only soils within approximately 6 to 12 inches of the heater wells reaches temperatures above the boiling point of water in a typical VOC treatment application. This heat is conducted into the soil, resulting in a relatively uniform radial heating pattern even in heterogeneous soils. Contaminants are vaporized and recovered by SVE. Vacuum extraction can be built into the heater wells, so that all wells are dual purpose, or they may be adjacent to (within three feet of) or at centroid locations between the heater wells. Most variations of TCH use electrical energy, however, one variation of the TCH technology uses natural gas, propane or other fuel combustion at the well heads as the energy source. This can be

advantageous in areas where electrical power is not readily available, however, natural gas may also be limited in the winter months in colder areas.

Generally treatment durations range from several months to about a year, depending on the temperature required for volatilization of the contaminants and the selected well spacing. When treating below the water table, higher permeability soils – and the resulting higher ground water flow rates – will result in longer treatment times or necessitate a tighter well spacing, as water flow through the treatment area will cause heat to migrate from the treatment area. The TCH technology is applicable for groundwater flow rates less than 0.1 to 1 foot per day. Where higher flow rates are encountered, barriers such as sheet piles or slurry walls or pumping wells to flatten the hydraulic gradient have been used to reduce the effects of groundwater flow.

For the recovery of SVOCs such as polychlorinated biphenyls (PCBs) or coal tar contaminants, the target temperature may be as high as 350°C, depending on the boiling point of the contaminant and the degree of treatment desired (Stegemeier and Vinegar, 2001). These high treatment temperatures can only be achieved above the water table, or when the water table is controlled to eliminate ground water flow into the treatment area. Recently, the treatment of Per- and Polyfluoroalkyl Substances (PFAS) soil contamination using TCH was demonstrated (ESTCP project ER20-D1-5198). PFAS concentrations in soil were reduced from an average of 232 micrograms per kilogram ($\mu\text{g}/\text{kg}$) to 4.1 $\mu\text{g}/\text{kg}$ (range of 20 $\mu\text{g}/\text{kg}$ to nondetect at 0.5 $\mu\text{g}/\text{kg}$). PFAS compounds were observed to react and breakdown over a wide temperature range (Heron, 2023).

Superfund sites where TCH has been used include Solvent Recovery Services of New England (see TCH Case Study), Memphis Depot Superfund site (Heron et al., 2009), the Velsicol Superfund Site where chlorinated solvents were recovered, and Mare Island Naval Shipyard where PCBs were recovered.

Section 2.4. Self-Sustaining Technology for Active Remediation (STAR) is an emerging technology that may be applicable for sites that are heavily contaminated with NAPLs that have low volatility and significant fuel value, which includes longer chain petroleum hydrocarbons, coal tar, and creosote. This technology relies on

smoldering combustion processes, where a liquid or solid fuel within a porous matrix is slowly combusted. The combustion processes, which are dominated by pyrolysis and oxidation, are initiated by the addition of heat (typically approximately 250 to 400°C) at the ignition point and sustained by the heat generated by the combustion process itself and the injection of air (Figure 5).

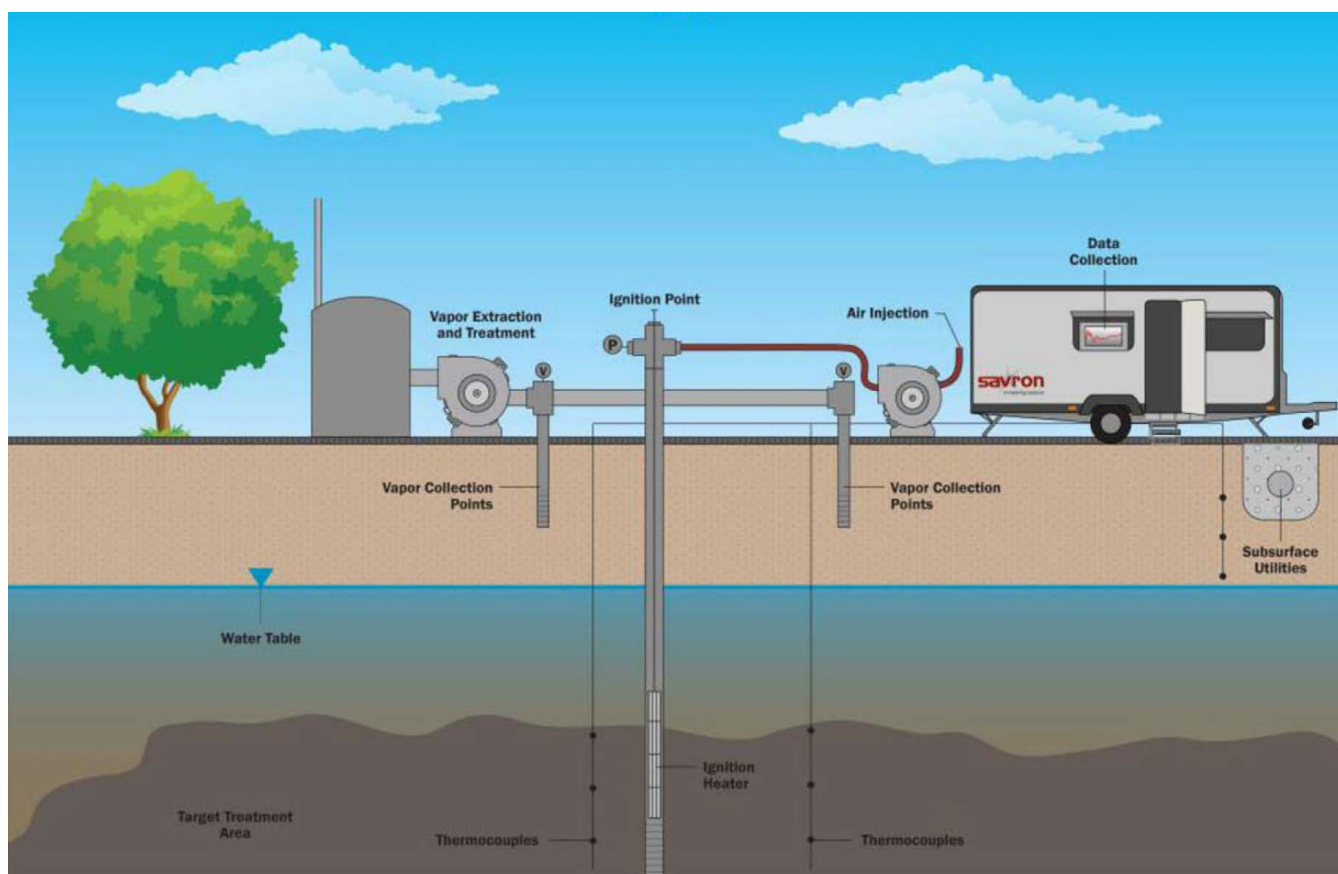


Figure 5. This figure illustrates the emerging smoldering combustion technology called Self-Sustaining Treatment for Active Remediation (STAR). This technology is applicable to SVOCs such as coal-tar based products or heavy petroleum hydrocarbons that have more limited volatility but significant fuel value. At the ignition point, a heater is inserted to start the combustion process. The combustion process itself produces the energy required to continue the combustion of the contaminants as the combustion front migrates away from the ignition point. Air must be injected to sustain the process. This process works above and below the water table. Volatile compounds are collected via vacuum extraction along with the products of combustion, which are treated through vapor phase GAC before discharge.

Smoldering combustion requires that the fuel have a large surface area exposed to the oxidizer (air), a condition which can be attained when the fuel is contained within a porous matrix such as soils. The smoldering combustion process destroys the higher boiling point NAPL components in situ, producing carbon dioxide, carbon monoxide, and water vapor. Lighter components of the NAPL, such as benzene,

toluene, ethylbenzene, and xylene (BTEX) are generally volatilized before the combustion front reaches them. The combustion products as well as the volatile components of the NAPL (typically less than two percent of coal tar) are extracted via vacuum extraction. Typically, this technology requires NAPL concentrations of the higher boiling compounds in excess of 3,000 to 5,000 milligram

per kilogram (mg/kg) total petroleum hydrocarbon (TPH) in order to produce the heat required in situ to sustain the combustion front as it migrates from the ignition point. Due to limitations with injecting air, this technology requires a more permeable soil, with grain sizes ranging from silty sands to gravels, but even then the typical radius of influence of an ignition point is around 10 feet, depending somewhat on lithology. The combustion process can be sustained below the water table because the heat produced will dry the nearby soils, and vapors generated by the process displace the groundwater, allowing the combustion to proceed.

Oxygen is required to sustain the process, so the smoldering combustion process can be extinguished by terminating air injection. Heterogeneity of the permeability to air can cause reduced air flow in lower permeability soils that can limit the combustion process. Final soil concentrations are generally reduced by 99 percent, with concentrations ranging from nondetect to a few tens to hundreds of mg/kg of TPH (Scholes et al., 2015; Grant et al., 2016).

Section 2.5. Other Thermal

Technologies. A number of other methods for heating the subsurface for enhanced oil recovery and/or remediation have been the focus of research by a variety of researchers. Radio Frequency (RF) heating has been applied to remediate a limited number of sites, but is not currently commercially available. More recent research has shown that RF heating is not as energy efficient as ERH, due to the energy losses (on the order of 40 to 50 percent) to convert power line frequency to RF (Roland et al., 2011). Microwave heating has been studied extensively in the laboratory where it has been found to be successful for heating the soil and removing volatile contaminants, however, microwave energy has a very limited penetration into soils (Falciglia et al., 2016) that so far has limited its applicability in the field. Hot air injection and hot water injection for remediation have also been the subject of research and attempts in the field (Davis and Lien, 1993; Johnson, 1994). While hot water injection can aid in the reduction of the viscosity of NAPLs which may aid in their recovery,

these low energy methods are not as effective as other thermal remediation technologies that are more energy intensive. Low energy thermal methods are not generally used today.

Other low energy methods with objectives such as enhancing biodegradation or other chemical reactions such as hydrolysis have received considerable interest by researchers but have been found to be only marginally less costly than thermal remediation at temperatures of the boiling point of water when applied to source areas. Also, there is less certainty in treatment performance and life cycle costs associated with low temperature applications meant to increase biotic and/or abiotic reaction rates to destroy contaminants in situ (Macbeth et al., 2012). Moderate temperature increases have been used enhanced biodegradation in the dissolved phase plume downgradient of thermal treatment areas (Heron, 2023), however, temperatures above approximately 35°C have been found to decrease or eliminate biological dechlorination of some chlorinated solvents (Pennell et al., 2009). Low energy, low temperature thermal systems usually try to reduce costs by not extracting vapors, which increases the risk of fugitive emissions. Even at ambient temperatures, soil gas concentrations of volatile contaminants can pose a risk to indoor air. Any increase in temperature will increase the partitioning of volatiles to soil gas, possibly causing fugitive emission to the atmosphere or to indoor air if vapor extraction is not used.

ERH and TCH can also be used to treat soils that have been excavated. Ex situ application of these technologies takes place within an engineered, above ground, fully enclosed treatment pile structure (Figure 6). Ex situ treatment has been used for contaminated shallow soils that cannot be practically treated in situ. Ex situ treatment may be more appropriate for high boiling compounds such as PCBs, dioxins and furans, or PFAS, that are more easily excavated without causing excessive fugitive emissions of volatile contaminants, but for which off site disposal is not an option or is very costly. The principles of the system are the same as for in situ treatment, in that electrodes or heater wells

are installed to heat the soil, and vaporized contaminants are extracted under vacuum. For high temperature ex situ TCH applications at temperatures greater than 200°C, degradation processes such as pyrolysis and oxidation have also been found to be important. Treatment piles

typically range in size from 50 cubic yards (yd³) to 70,000 yd³, and treatment times will depend on the treatment temperature required and the remedial goals. A noteworthy example is the treatment of dioxin-contaminated soils and sediments at the Danang airport in Vietnam (Sorensen et al., 2018).

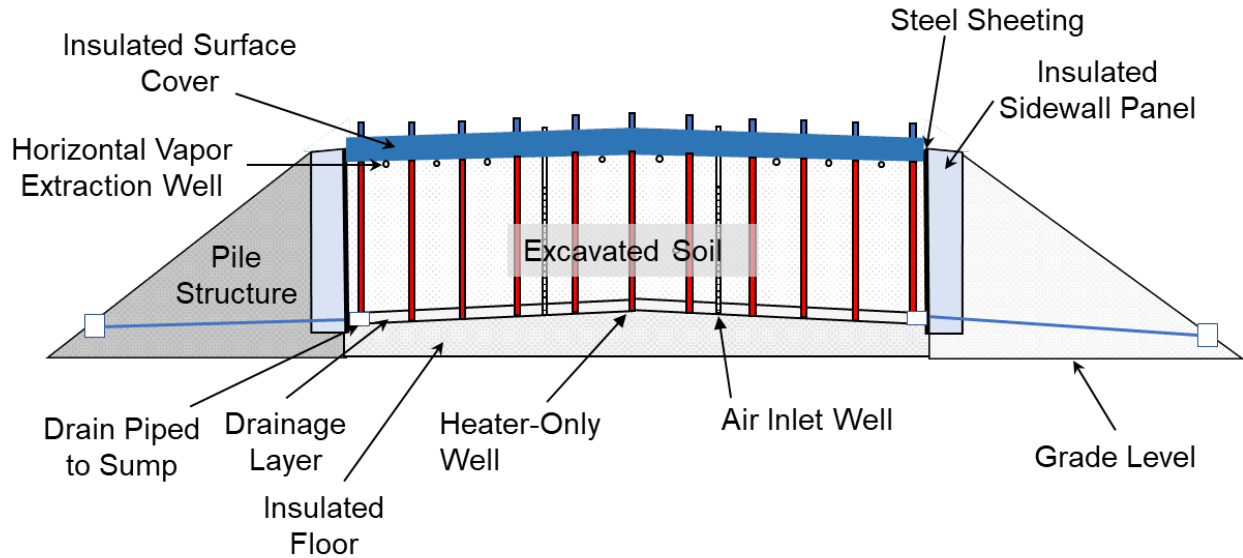


Figure 6. This is an example of how excavated soils or sediments can be thermally treated. In this particular application, ex situ treatment was used to treat dioxins. The use of herbicides during the Vietnam war left surface soils in parts of the country contaminated with highly toxic dioxins. Contaminated surface soils and sediments were excavated, then placed in the concrete foundation to create an ex situ thermal treatment pile. The soils were treated using thermal conductive heating (TCH) at temperatures exceeding 300C to reduce the 2,3,7,8-TCDD concentrations from as high as 157,000 parts per trillion (ppt) to less than 150 ppt (Sorensen et al., 2018).

Section 2.6. Which technology is Appropriate for a Given Site? While ERH and TCH are more applicable in lower permeability soils, and SEE requires more permeable soils, there is overlap in the applicability of these technologies depending on the contaminant to be remediated, the geologic and hydrogeologic setting, and the remedial action goals. Best practice is to allow the thermal vendors to propose how they would address the site during the bidding process, allowing them to determine whether or not they believe their technology, or which of the technologies they offer, is best suited for the site. When treating VOCs such as chlorinated solvents, their volatility can be exploited to recover them in the vapor phase with any of the three commonly used in situ thermal technologies, and the choice of

technology will be more dependent on the hydrogeologic setting.

For SVOCs, the permeability of the soils, the hydrogeologic setting, and the remedial goals will all be important in selecting the technology. If the remedial goal is to recover mobile NAPL, either ERH or TCH may be used effectively to reduce the viscosity of the NAPL to enhance its migration to extraction wells and increase its ability to be recovered by pumping. Recovery as a NAPL will generally aid in recovering more of the higher boiling components of the NAPL with less energy input. When more stringent cleanup criteria are to be achieved, once the recoverable NAPL and groundwater has been extracted, the temperature can be raised further using TCH to recover the contaminants in the vapor phase (Baker et al.,

2006). TCH, however, can only achieve temperatures above the boiling point of water when implemented above the water table, since a continuous inflow of groundwater would buffer the temperature at the boiling point as the water is boiled off. In permeable soils, SEE has been used successfully to recover contaminants such as creosote. Where there are higher levels of contamination in more permeable soils either above or below the water table, STAR may be applicable and able to achieve stringent soil cleanup criteria. However, the STAR technology may not be able to treat zones with source material at TPH concentrations less 3,000 mg/kg.

For sites where the contamination resides both in high permeability and low permeability soils, a combination of thermal technologies may be used. SEE for the more permeable zone can be combined with either ERH or TCH in the low permeability zone for volatile contaminants (Newmark et al., 1994; Newmark and Aines, 1997; Heron et al., 2005; Heron et al., 2012), while a combination of TCH and STAR may be applicable at sites of varying hydraulic conductivity that are contaminated by semivolatile contaminants. It may be advantages at some sites to combine ERH and TCH. For example, ERH may be used at sites with large zones with VOCs where the boiling point of water is sufficient for treatment, and TCH can be used for smaller areas with SVOCs needing treatment at higher temperatures. Another example would be shallow PCBs in topsoil which could be treated at high temperatures using TCH and solvents at deeper depths can be treated with ERH. ERH is more cost-effective for the VOC source zones in most cases, particularly for clay and silt soils and where the subsurface is really wet (vadose zone and saturated zone). ERH can also tolerate a lot more water flow before the cooling reduces efficiencies. At one site ERH was used to treat a large area and TCH to heat below a creek, as not having electrodes close to the surface water reduced the electrical risks (since that time, methods have been developed for grounding electrodes and prevention of electrical shock hazards when operating close to surface water or other electricity- conducting materials) (Heron, 2023).

SEE, ERH and TCH have all been successfully used to remediate fractured rock. Again, the appropriate technology for the site is heavily influenced by the permeability of the fractured rock. Highly fractured rock with significant groundwater flow will favor SEE, while competent rock with relatively few fractures will favor TCH or ERH. If the rock is of low porosity and thus low water content, the electrical resistivity of the rock may be high, making ERH application more difficult, and favoring TCH. Sampling of the rock matrix at various sites has shown that contaminants generally do not migrate significantly from the fracture surface into the rock matrix (Davis et al., 2005), and steam temperatures can be conducted considerable distances into the rock matrix (Stephenson et al., 2006), so steam injection may be very effective for recovering the contaminants from fracture zones without heating the entire rock matrix (Kluger and Beyke, 2010; Lebron et al., 2012; Beyke et al., 2014).

Section 2.7. Above Ground Treatment of Extracted Contaminants.

All of the thermal remediation technologies include above ground treatment of the extracted vapors and groundwater to separate the contaminants from the air and water before discharge. The applied vacuum to the subsurface varies by application but vapor extraction mechanisms cannot be compared with traditional ambient temperature SVE systems, especially not in low permeability geology settings. During the thermal remedy the extraction points can be considered pressure release points and vapor pathways out of the tight formations, rather than active extraction points to pull air and vapors through the soil with a given radius of influence. For that reason the extraction point density is more dense than for traditional SVE systems, with well spacings typically between 15 and 30 feet.

Commonly used treatment trains include vapor-water separators, heat exchangers, oil/water separators, and granular activated carbon for both the vapors and water, in that order. For larger sites where the use of carbon may be cost-prohibitive, a thermal oxidizer, catalytic oxidizer, or thermal accelerator may be used to destroy the contaminant vapors. Steam-regenerated granular

activated carbon (GAC) systems with multiple adsorption vessels can be used to minimize GAC usage. These systems that are used on site can regenerate spent GAC in 4 to 8 hours while adsorbing and treating extracted vapors. This produces liquid wastes (NAPL and water condensate) for treatment and disposal. Alternatively, a cooling, compressing, and condensing system has also been used at some sites to condense the vapors to a liquid which is then disposed off site. Fuel hydrocarbons may have recycle value, making one of these alternatives which convert vapors to liquids especially attractive. However, for many types of mixed waste contaminants, this may not be advantageous. Some communities have objected to having a thermal oxidizer or one of its variations at a local site to destroy the recovered contaminants, but where these systems can be used, the onsite destruction of contaminants will eliminate the need to transport the liquid wastes via truck through the community, which may be inherently safer.

Initially contaminant mass recovery rates may be small, however, at large sites, hundreds of pounds of contaminants may be extracted per day as the site reaches treatment temperature and recovery rates reach their peak. If the contaminants are VOCs, most of the mass will be recovered in the vapor phase, while SVOCs may be recovered as a liquid. SEE remediation systems will also tend to recover more of the contaminants as a liquid due to the displacement of liquids ahead of the steam front. Robust above ground treatment systems are required even if the estimates of mass to be recovered are low or moderate, as estimates of contaminant mass in the ground are notoriously inaccurate. Contaminants recovered as a NAPL may be emulsions in groundwater due to biological growth, requiring biocides or some other emulsion breaker to treat the emulsions. Organoclay filters may be used to improve the separation of the NAPL from water. Heating the aquifer may also increase the dissolved phase concentrations of naturally occurring elements such as arsenic, which may require treatment before the water can be discharged.

For Superfund sites undergoing remediation, air and water discharge permits are not required. However, non-condensable vapors that are discharged to the air and water that is discharged to a publicly owned treatment works (POTW), a storm sewer, to surface water, or reinjected to the aquifer, must meet state and/or local discharge criteria. Weekly or monthly monitoring of the air and water discharge streams is generally required to ensure that the air and water discharge criteria are met.

Section 2.8. Monitoring of Thermal Remediation Systems. In addition to monitoring the air and water discharges to ensure the above ground treatment system is containing the contaminants, subsurface monitoring is required to ensure that the entire target treatment area is being heated, and to verify that hydraulic and pneumatic control are being maintained so that contaminants are not lost as fugitive emission or by migrating away from the treatment area. The extraction rate of contaminants is also monitored throughout the remediation to aid in determining when the remediation reaches 'diminishing returns'. This section describes the commonly used means to monitor subsurface conditions and the rate of contaminant mass recovery.

Section 2.8.1. Temperature Monitoring. Subsurface temperatures are used to verify that the energy injected to the subsurface is reaching the entire target treatment area. All in situ and ex situ thermal remediation systems include temperature monitoring points (TMPs) in the treatment zone. Temperature monitoring strings are inserted in boreholes throughout the treatment areas, with thermocouples, fiber optic temperature measuring systems, or other temperature measuring devices spaced every 3 to 5 feet vertically, starting a little above the treatment area and commonly extending about 1 to 5 feet below the treatment area. Temperature monitoring strings generally are placed at the centroids between wells where the energy is applied to the subsurface, one string for every 1,000 to 3,000 square feet of treatment area depending on the heterogeneity of the subsurface and the thermal technology used. Temperatures

are normally measured and recorded automatically at pre-set intervals, which may be as short as 15 minutes or less. Sometimes real time subsurface temperature data is available to the site owner on the vendor's website. The vendor should be expected to monitor the temperature data on a regular basis (usually daily) to ensure that the subsurface is heating at the desired rate, and that the target temperature for the remediation is achieved throughout the treatment area.

Section 2.8.2. Pneumatic and Hydraulic Control Monitoring. Subsurface monitoring should also include monitoring to verify that hydraulic and pneumatic control are being maintained throughout the remediation to ensure that contaminants are being captured and are not migrating away from the treatment area. Best practice is to start the extraction system(s) at least several days before heating is initiated to demonstrate that the vacuum extraction system creates a vacuum throughout the treatment area, however, it is not always possible to measure vacuum at pressure monitoring points before heating starts in low permeability soils. If multiphase extraction is to be used, the amount of extracted groundwater during this time should be documented along with an estimate of the water extracted as steam during the remediation. It is not possible to open monitoring wells within the thermal treatment area during heating to measure the groundwater elevation within the treatment area, so groundwater elevations cannot be used to determine if hydraulic control is being maintained. Pressure buildup in the subsurface due to heating and the generation of vapors makes it dangerous to open monitoring wells to the atmosphere while the groundwater temperature is elevated. The sudden release of pressure caused by the opening of the well can allow hot groundwater to flash to steam which can escape through the well casing. Pressure transducers or bubblers within the monitoring wells can sometimes be used, however, the harsh conditions in the hot groundwater can damage the transducers.

A more reliable and safer method of determining if hydraulic control is being maintained is to measure

temperatures surrounding the treatment area with thermocouple strings similar to those used within the treatment area. Some temperature increase outside of the thermal treatment area can be expected during heating due to conductive heating, but sudden increases in groundwater temperature are likely to be due to the migration of hot groundwater from the treatment area (Figure 7), which may carry elevated contaminant concentrations with it. Thus, thermocouple strings located exterior to the treatment area and co-located with monitoring wells are recommended surrounding the treatment area.

Vapor monitoring points that allow measurement of soil gas pressure/vacuum should also be included at these exterior monitoring points – as well as interior to the treatment area - to demonstrate that pneumatic control is being maintained. It should be noted that a small pressure build-up within the treatment zone is expected especially in low permeability soils due to the steam production and transport of vaporized contaminants in the steam phase to the extraction points.

Section 2.8.3. Contaminant Mass Recovery Rate. Monitoring the extraction rate of contaminants as a function of time is critical for aiding in determining when the thermal system has accomplished what it reasonably can in terms of recovery of contaminants. When a majority of the contamination is located above the water table in higher permeability soils, vapor extraction rates may be significant right from the time that vapor extraction is initiated. When most of the contamination is located below the water table, initial extraction rates may be low. In both cases, the extraction rate should be expected to increase as the subsurface is heated. The maximum extraction rate may correspond roughly to around the time that temperatures in the subsurface approach the co-boiling point of the NAPL (see Section 3.1). Extraction rates can then be expected to decrease gradually as the contaminants within the treatment area are depleted. The extraction rate can be expected to reach a continuous low rate when the majority of the subsurface mass has been depleted, at which point the remediation is

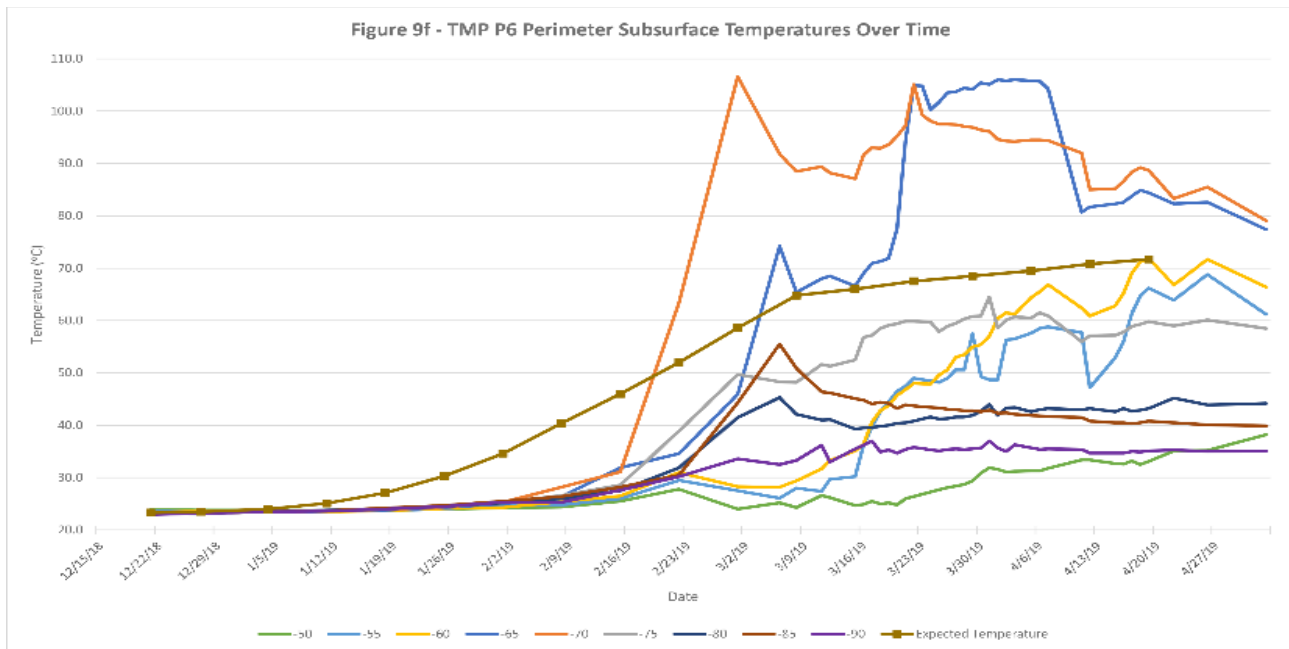


Figure 7. For this small scale pilot ERH, temperature monitoring points (TMPs) were placed surrounding the thermal treatment area. A thermal model was used to predict the temperature at these exterior TMPs over time due to conductive heating from the treatment area as the site heated; these results are shown with squares in the graph. The actual temperatures recorded at these TMPs were lower than predicted during the first four months of operation, likely as a result of groundwater flow towards the treatment area carrying the heat back towards the treatment area. After that time, the temperature graphs show rapid temperature increases at some depths, indicating that hot water migrated from the treatment area. This graph illustrates the fact that generally TMPs exterior to the treatment area provide a reliable means of determining if hydraulic control is being maintained, and the difference between the expected conductive heating and loss of hydraulic control of hot water is clearly differentiated. Soil samples were taken adjacent to these exterior TMPs post treatment, and it was found that contaminants had not been transported outside of the treatment area.

considered to have reached ‘diminishing returns’. If target temperatures have been reached throughout the treatment area and groundwater concentration have decreased to low levels, then the remediation has likely accomplished most of what it can, and heating can be terminated. Extraction should continue during at least the early stages of cool down, while subsurface temperatures remain above the boiling point of water.

To determine the extraction rate, photoionization detector (PID) or flame ionization detector (FID) readings of the vapor flow into the vapor treatment system are normally made every day that an operator is on site (normally 5 days a week). Flow rates are also measured, so that mass extracted can be calculated. Also, weekly summa canister samples are obtained and analyzed for the site contaminants to verify the PID or FID readings. Groundwater concentrations should also be monitored during the remediation. As with vapor

extraction rates, the concentrations should be expected to increase during heating, then decrease as the contaminant mass in the subsurface is depleted. Monitoring wells must be constructed to be able to obtain groundwater samples without opening the wells during heating due to safety concerns (see Section 2.8.2). If multiphase extraction wells are installed as part of the thermal system, sample ports at the wellhead may allow for groundwater sampling. Hot groundwater sampling techniques should be used, which generally involve running the groundwater through a stainless steel or copper coil immersed in an ice bath to cool it to ambient temperatures before obtaining the sample for analysis. Hot soil samples techniques can also be used to obtain interim and/or confirmation soil samples by obtaining the samples within a stainless steel sleeve, immediately capping both ends tightly, and then cooling the soil on ice before opening the sleeves to obtain samples for analysis (Gaberell et al., 2002).

Section 3.0 Mechanisms for Increased Contaminant Recovery during Thermal Remediation

Generally the most important property of an organic compound that determines whether or not it is amenable to thermal remediation is the boiling point, which is directly related to its vapor pressure (Hunt et al., 1988; Davis, 1997). The boiling point or vapor pressure will also influence the temperature required for the effective recovery of the compound. Volatile organic compounds (VOCs) which are only slightly soluble in water and which have boiling points less than about 150°C are generally amenable to volatilization at temperatures less than or equal to the boiling point of water (100°C at standard atmospheric pressure) and can be readily recovered in the vapor phase using thermal technologies. Some compounds with higher boiling points, such as naphthalene (boiling point 218°C), have also been recovered at temperatures around 100°C. For semivolatile organic compounds, such as coal tar or creosote, viscosity reduction and displacement of the liquid phase may be more important as a recovery mechanism during thermal remediation at temperatures up to approximately 100°C, and vaporization only becomes important at significantly higher temperatures.

Section 3.1. Increased Vaporization and Co-boiling of NAPL and Groundwater.

The vapor pressure of organic compounds is an exponential function of temperature. For VOCs, as the temperature is increased above about 50 – 60°C, the vapor pressure of most of these compounds will increase rapidly (Figure 8), facilitating their recovery in the vapor phase via vacuum extraction. When two separate liquid phases are present such as when VOC NAPLs are present at or below the water table, the vapor pressure from each liquid contributes to the overall vapor pressure (Figure 9), and the combined liquids will boil when the total of their vapor pressures equals the local pressure (Atkins, 1986; DeVoe and Udell, 1998). This temperature can be called the co-boiling temperature. The temperature at which co-

boiling of a VOC NAPL occurs is always less than the boiling point of water, and the lower the boiling point of the NAPL, the lower the co-boiling temperature (Table 1).

Table 1. Boiling points and co-boiling points for some organic compounds of environmental interest at atmospheric pressure (760 mm Hg)

Chemical	Boiling Point (°C)	Co-boiling Point (°C)
Methylene Chloride	40	38
cis-1,2-Dichloroethylene	60	55-56
1,2-Dichloropropane	96.8	78
Tetrachloroethylene	121.3	88
Benzene	80.1	69
Trichloroethylene	87.3	73-74
Toluene	110.6	84-85
Naphthalene	218	99
Xylenes	138 – 144	92-94
Chlorobenzene	131.7	91
Carbon Tetrachloride	76.8	67
1,1,2-Trichloroethane	114	86
1,1,1,2-Tetrachloroethane	148	94-95

Thus, when VOC NAPL is present in porous media along with water, the NAPL and water will boil when their combined vapor pressures equal the local pressure. When temperatures exceed the co-boiling temperature, the NAPL phase has been removed, however, dissolved and adsorbed phase contamination will remain in the subsurface. Maximum removal rates and removal efficiency requires increasing the temperature to at least the boiling point of groundwater under the conditions of the remediation, which maximizes steam stripping, the process by which steam aids in transporting the vapors to the extraction points.

The same principles apply to SVOC NAPLs such as the PAHs that comprise creosote or coal tar, but higher temperatures are required to create the significant increase in vapor pressure (Figure 8). Thus, for SVOC NAPLs, their vapor pressure is not high enough at 100°C to cause a decrease in the co-boiling point with groundwater. Significant volatilization of SVOCs in order to recover them effectively requires higher temperatures. Coal tar, creosote, PCBs, and dioxins have all been successfully recovered in the vapor phase at temperatures in the range of 300 – 375°C. The volatilization behavior of per- and polyfluoroalkyl compounds, commonly referred to as PFAS, varies

depending on their alkyl chain length and their functional group. Laboratory testing found that 10 to 14 days of heating at temperatures of 350°C and above reduced soil concentrations of PFAS by as much as 99 percent (Crowner et al., 2019). A recent field demonstration of TCH treatment of PFAS-contaminated soils showed that similar reductions are possible in the field (Heron, 2023).

1,4-Dioxane is a contaminant that is commonly co-located with chlorinated solvents, having been added to products such as 1,1,1-trichloroethane in low concentrations as a stabilizer. 1,4-Dioxane has a boiling point of 101°C, but is much more soluble in water than most chlorinated solvent VOCs, giving it a very low Henry’s constant at ambient temperatures. However, under the thermal treatment conditions normally used for the recovery of chlorinated solvents, 1,4-dioxane in soil and groundwater have been found to be reduced by as much as 99 percent (Oberle et al., 2015).

Increased vaporization of contaminants and groundwater due to increases in temperature in low

permeability soils will increase the pressure if the vapors cannot readily migrate from the low permeability soil. This increase in pressure can create microfractures and/or vugg porosity in clay soils (Figure 10), which increases the permeability of the soils and allows the vapors to be collected via vacuum extraction. This increase in pressure in low permeability soils as the soils are heated makes thermal remediation of low permeability soils much more effective than SVE at ambient temperatures, which relies on sufficient permeability in order to pull air and vapors through the soil pores (Heron et al., 2013).

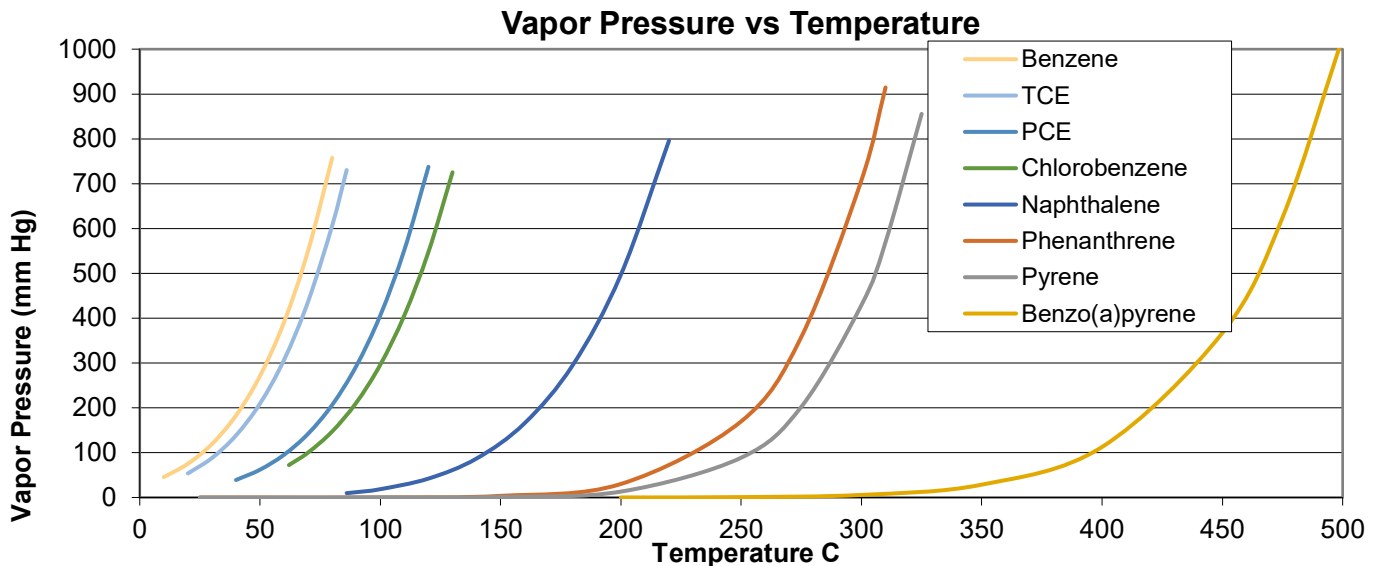


Figure 8. This figure shows the vapor pressure as a function of temperature for a variety of organic chemicals of environmental interest. Volatile compounds such as benzene and TCE can accumulate in soil gas and intrude into buildings at concentrations that are hazardous to health even at ambient temperatures. As vapor pressures increase exponentially with temperature, driving these chemicals into the vapor phase, there is greater potential for vapor intrusion from these chemicals. For compounds like benzene and TCE, the increase in vapor pressure even at more moderate temperature increases is substantial. However, it is also easier to recover these chemicals using soil vacuum extraction when they are driven into the vapor phase. SVOCs such as the higher-molecular weight PAHs require significantly higher temperatures to volatilize them to a significant extent.

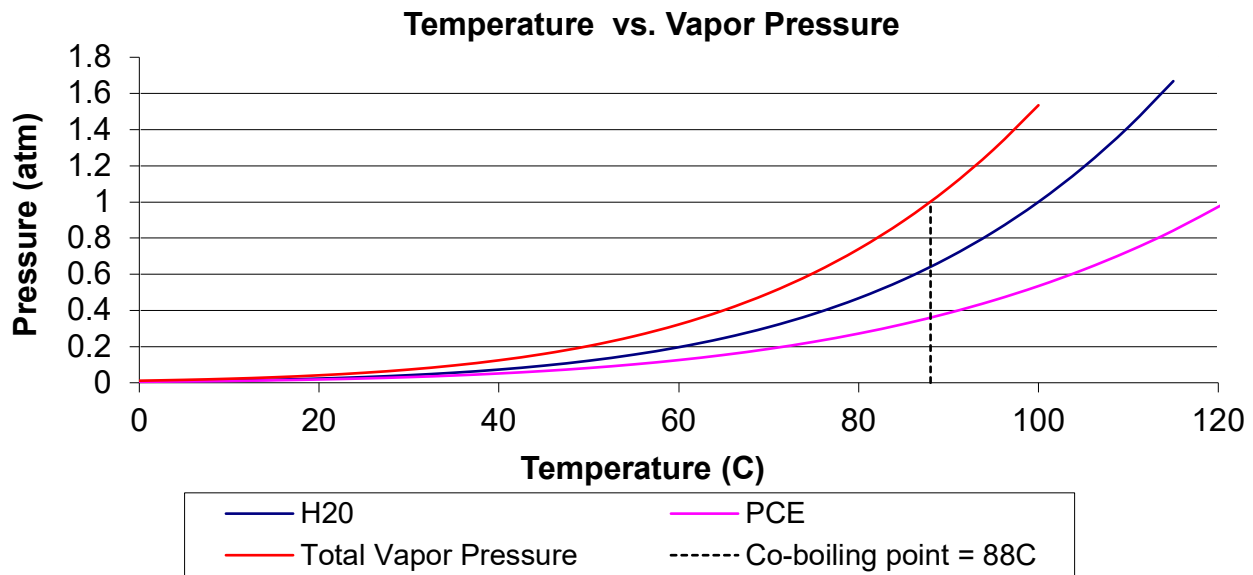


Figure 9. This figure illustrates the additive effect of vapors coming from separate liquid phases to the total vapor pressure, which creates boiling of the two liquid phases when their combined vapor pressures equal the ambient pressure. When water and a separate phase volatile organic compound are both present, the boiling point of the combined liquids will always be less than the boiling point of water. This temperature can be called the co-boiling temperature. During thermal remediation of a site containing NAPL, when the temperature reaches the co-boiling point, it will remain at that temperature until the NAPL is removed by converting it to vapor. When the temperature reaches the boiling point of water alone, the NAPL has been boiled off. This figure shows that the co-boiling point of PCE DNAPL and water at atmospheric pressure is 88C. Below the water table, where hydrostatic pressure causes overall higher pressures, the co-boiling temperatures is higher.

Section 3.2. Decreased viscosity of groundwater and NAPL. As the temperature increases, the viscosity of water and organic liquids will typically decrease exponentially. Many of the chlorinated VOCs and petroleum hydrocarbons have relatively low viscosities even at ambient temperatures, ranging from about 0.5 to about 1.5 centipoise, which is similar to that of water at the same temperature. Thus, even the exponential decrease in viscosity with temperature may not be significant with respect to flow rate of these liquids. However, many SVOCs, including creosote and coal tar, may have a very high viscosity at groundwater temperatures which decrease exponentially as the temperature increases (Figure 11). For these contaminants, the decrease in viscosity at temperatures of 50 to 80°C can significantly increase the mobility of the liquid, allowing it to be more readily recovered in the liquid phase. This approach, which has been used in enhanced oil recovery, has also been used to recover coal tar and creosote in the liquid phase, which has the advantage of being able to recover more of the

higher boiling compounds that are difficult to vaporize, and to recover them with less energy input.



Figure 10. Sample of clay recovered from 25 feet below ground surface after 30 days heating by ERH. Steam bubble formation and escape created microfractures and vuggy porosity. It was noted that the vacuum pressure on the subsurface decreased and the flow rate increased as heating of the clays progressed, with concurrent release of steam and vaporized contaminants (McGee et al., 2006).

Creosote Viscosity as a function of Temperature

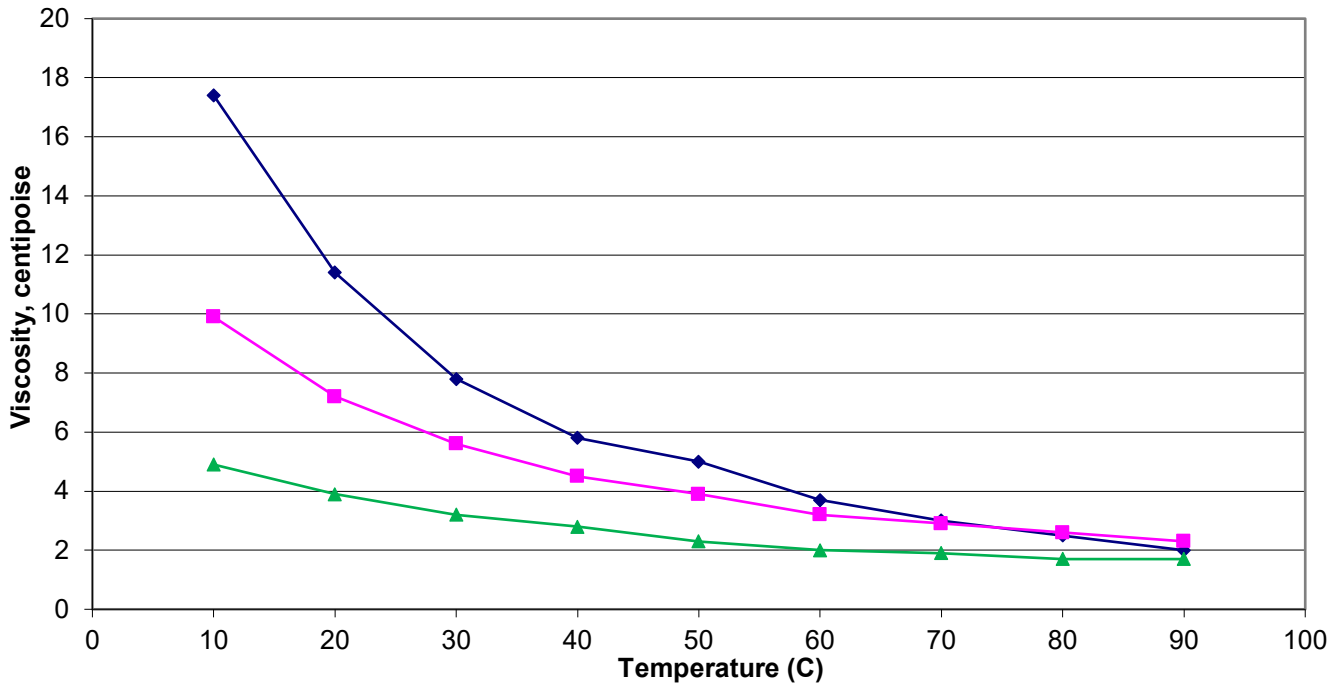


Figure 11. Viscosity as a function of temperature for creosote product recovered from a Superfund site. Generally, the more viscous a liquid is at ambient temperatures, the greater will be the viscosity reduction as the temperature increases, allowing the liquid to flow more readily to wells. This reduction in viscosity will also allow it to be pumped to the surface more readily.

Section 3.3. Other Mechanisms. Other mechanisms that may aid in the thermal remediation process include increased solubility and solubilization rates (Imhoff et al., 1997), and increased Henry’s constant which increases the volatilization from water (Heron et al., 1998). Research has also shown that there may be increased desorption of chemicals of environmental interest from soils (Cornelissen et al., 1997; Pennell et al., 2009). Increases in solubility and solubilization rates generally cause increases in groundwater concentrations during the initial stages of heating as NAPL dissolves and/or contaminants are desorbed from soil surfaces. The groundwater concentration increases may be more than an order of magnitude. Once the NAPL has been essentially depleted, decreasing groundwater concentrations trends will be observed, although it can be expected that there will be considerable variation in concentrations during heating.

Heating contaminated groundwater causes evolution of gases from the groundwater as well as the formation of VOC and water vapors. The gases and vapors are buoyant relative to the groundwater, and as the bubbles migrate upward they can carry NAPL with them at the interface of the bubble and water (Figure 12). This basic principle is used in Dissolved Air Flootation, a well-known process which is used to separate solids and nonaqueous phase liquids from water (Metcalf & Eddy, Inc, 1972). This process has been demonstrated at ambient temperatures when an air bubble is present at the interface of a volatile compound and water in open water, in capillary tubes, and in porous media. When the liquids are heated, it has been observed that PCE and water vapors generated at the interface of the water and liquid-phase PCE in a 0.5 millimeter capillary tube had liquid PCE attached to the bubble, and the combined PCE liquid and vapor migrated slowly upward (Udell, 2006).

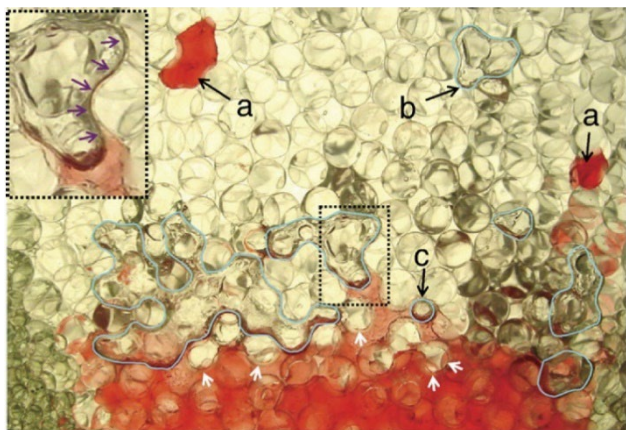


Figure 12. In this laboratory experiment chlorinated solvent DNAPL (dyed red) was emplaced in a two dimensional model containing glass beads and air-free water. Once an air bubble was introduced into the model, it was observed to grow in size as the DNAPL volatilized into it. When the bubble was large enough to overcome the capillary pressure, part of the bubble broke off and migrated upward in the porous media, forming the residual DNAPL blobs shown (labeled a in the photo). DNAPL was also dragged upward as a thin film at the interface between the bubble and water as shown in the inset picture (Roy and Smith, 2006)

Pakkala (2007) demonstrated that trichloroethene can attach to air bubbles and migrate upward in a packed bed of glass beads 2 millimeters diameter. The bubbles can be formed by introducing air at the bottom of the packed bed or by heating the water and causing the liberation of air and other dissolved gases. Insoluble compounds such as DDT have been shown to be carried upward when dissolved in a solvent such as chlorobenzene that has accumulated at the air-water interface of bubbles (Valsaraj et al., 1986). This type of ‘bubble floatation’ was believed to contribute to the coalescing of fuel oil in the subsurface during an ERH remediation, allowing more of the liquid fuel to be recovered (Beyke and Fleming, 2002), and likely helps to account for the lack of downward migration by DNAPL during heating.

Increased rates of biotic and/or abiotic reactions may also be observed for some contaminants. The dechlorination daughter products of chlorinated solvents may be observed during or after thermal remediation. Hydrolysis rates can increase exponentially as the temperature increases (Washington, 1995). Hydrolysis of chlorinated ethanes 1,1,1-trichloroethane or 1,1,2-

trichloroethane will form 1,1-dichloroethene (1,1-DCE). 1,1-DCE does not hydrolyze further, and is more toxic than the ethanes from which it is formed. 1,1-DCE is also more volatile than the parent compounds, will readily volatilize from water, and can readily be recovered during thermal remediation.

Carefully performed and controlled laboratory experiments have shown that chlorinated compounds such as TCE or PCE do not readily break down at temperatures used for their recovery via thermal remediation (Costanza et al., 2007), unless an appropriate form of iron is present to aid in abiotic degradation processes. However, laboratory experiments have shown that when polynuclear aromatic hydrocarbons (PAHs) are treated by thermal remediation, oxygenated and/or hydroxylated PAHs may be formed (Trine et al., 2019).

During TCH, temperatures near the heater casings can be as high as 400 to 800°C. This creates a zone immediately surrounding the heater wells where oxidation and pyrolysis may occur. Systems can be designed to minimize contaminant presence in the vicinity of the heaters, thus avoiding heated vacuum wells. If the heating and extraction wells are co-located, contaminants are pulled to the very high temperature zones, and some chemical degradation would be expected. In the case of halogenated contaminants, some acid production can occur, leading to corrosion of wells and piping.

Section 4.0 Defining the Area to be Treated by Thermal Remediation

Appropriately defining the area to be treated by thermal remediation is essential to the overall success of the project, and in making the remedial action cost effective. These aggressive, more costly technologies are generally applied to source areas, defined as the areas containing appreciable NAPL, although there are times when these technologies have been applied to lower levels of contamination, particularly in low permeability soils and/or below the water table. The cost of applying these

technologies is generally proportional to the size of the area and volume that must be treated, so areas that are only lightly contaminated generally are not included in the treatment zone. Examples of exceptions to that are when high dissolved phase concentrations are in low permeability soils that are not amenable to other types of remediation such as pump-and-treat, when a rapid and complete remediation is required in order to transfer the property or for reuse of the site, or any other time that a rapid remediation is preferred. Multiple lines of evidence of NAPL, including soil borings, are generally the best way to determine where NAPL is present in the soils, while groundwater data provides an additional line of evidence as to whether NAPL is present or not. The extent of the NAPL should be fully defined with soil borings exhibiting only low concentrations – or concentrations below the cleanup criteria – just outside of the delineated treatment area.

NAPL presence in wells is an obvious indication of mobile NAPL in the vicinity, but should not be interpreted as the full extent of NAPL. Thermal treatment zones must extend outside of the area where NAPL exists in wells. For DNAPLs, wells that do not contain sumps may not be adequate for the detection of mobile DNAPL, as it may migrate through the well at times when the well is not being gauged for product. Where DNAPL is suspected or known to be present, monitoring wells should be constructed with sumps to allow detection of DNAPL migrating into the well.

At sites where a high concentration dissolved phase plume exists adjacent to the NAPL contaminated area, it may be appropriate to extend the thermal treatment area to include this area. This may be especially true where the high concentration dissolved phase plume is in low permeability soils, which may be difficult to treat using pump-and-treat or where it would be difficult to inject treatment fluids.

Section 4.1. Characterization Techniques to Determine NAPL Presence.

While it is not the purpose of this paper to discuss characterization techniques in

detail, some discussion of NAPL detection techniques and potential problems with characterization efforts is provided based on experiences in the field. It has been found that not all characterization tools are equally effective in all hydrogeologic settings and/or when searching for different types of NAPLs (i.e., chlorinated solvents versus coal-tar based products). Field work for characterization is often delegated to the least experienced environmental professionals. However, this does not mean that this work is not critical to the overall remedial efforts. Proper sampling procedures for soil and groundwater sampling must be followed, and proper documentation must be provided of the work that was performed, including boring logs, well sampling logs, and groundwater gauging reports. It must be ensured that the tools being used for characterization are capable of detecting the contaminants that are believed to be present. The Triad approach (EPA, 2004) is recommended to allow the investigation to be driven by the results that are being found as the investigation proceeds. Briefly, with a Triad approach, the investigation would start where it is known that there is NAPL, to verify that the tool being used can detect the contaminant(s) of concern. Then the investigation continues by stepping out in all directions from there until the extent of contamination is determined. Generally 40 to 50 foot spacings are used for characterization locations for moderate to large sites, smaller sites may use closer spacings.

When little is known about the location of NAPL on a site, it may be appropriate to obtain screening data using a membrane interface probe (MIP) or laser induced fluorescence (LIF), as these tools provide continuous inference of contaminant presence and relative permeability of the soils. However, this screening data alone should not be relied on to determine if NAPL is present. Correlating MIP response to soil concentrations has been found to be problematic, thus the instrument response must be verified by comparison with soil samples (Myers et al., 2002; Mumford et al., 2022). One aspect of the problem is that the PID detectors employed in MIPs have a maximum value which does not allow it to distinguish between high

aqueous concentrations and the presence of NAPL (Mumford et al., 2022).

Some NAPLs such as creosote or coal tar may be readily visible as a dark liquid or sheen in soil cores, and the NAPL-contaminated area may be defined based on visual observation of NAPL in the soil core. LIF can be a powerful screening tool for screening soils for the presence of PAHs such as creosote and coal tar. The fact that these NAPLs have a low interfacial tension and thus can penetrate a wider range of pore spaces, leading to greater saturations and areas where greater pools are formed, may make them more likely to be detected by an LIF instrument. Chlorinated solvent NAPLs such as TCE or fuels such as gasoline are generally much more difficult to see visually in soils, and the neat liquids do not fluoresce, and due to their higher interfacial tension they may have a more heterogeneous distribution in the soil. DyeLIF is a relatively new method for chlorinated solvent NAPL investigations, but successful use of this screening tool relies on additional lines of evidence of NAPL occurrence, generally comprised of benchtop testing of the DyeLIF response to the NAPL, PID readings, and analytical samples (Einarson et al., 2018; Dakota Technologies, 2022).

A photoionization detector (PID) or flame ionization detector (FID) should be employed to screen the length of the soil core at closely spaced intervals to determine where the most contaminants are located within the soil column. Soil samples should be obtained by the appropriate method approximately every five to ten feet along the soil core where the PID/FID shows the maximum concentrations may reside, and submitted to the laboratory for analysis. When the contaminant is a volatile compound, care should be taken to scan the core quickly, then open the core to the center to quickly obtain the analytical sample in order to try to minimize vaporization losses. An additional line of evidence of the presence of chlorinated compound NAPLs may be obtained by inserting a piece of FLUTE ribbon in the soil core; a reaction can be seen on the ribbon when DNAPL is present. However, the reaction between the NAPL and the ribbon only occurs when there is direct contact between them,

as the ribbon will not wick the NAPL. Soils can be screened for NAPL using oil red dyes, however, for chlorinated solvents such as PCE false negative results may be obtained (EPA, 2004).

Soil gas samples may also be used for screening, however, soil gases may migrate much more readily than the liquid contaminant, spreading a significant distance from the NAPL. Additionally, the soil gas may linger after the NAPL has vaporized. Soil gas data must be confirmed by soil or groundwater data. Direct push technology (DPT) may be applicable at some sites for obtaining soil cores, however, the small diameter of the core may mask the presence of NAPL that can be detected in larger diameter cores as can be obtained using rotosonic drilling. For some soils, the recovery using DPT may be poor. When the contaminant is a DNAPL, DPT may meet refusal before the vertical extent of the DNAPL has been defined. This is particularly true when the DNAPL has reached a zone of weathered bedrock and migrated into the bedrock itself. Rotosonic drilling can produce heat which potentially can vaporize VOC contaminants, however, the larger diameter cores produced by this drilling method may be better in many soils for detecting the presence of NAPL. The cores can be halved lengthwise to expose a fresh surface for screening with a PID. The other half of the core can be covered to reduce vaporization of contaminants until the screening is completed, then soil samples can be collected when the PID response was the greatest. Generally rotosonic drilling includes an outer casing from the core barrel, so if DNAPL is drilled through it cannot migrate down the borehole. When drilling through DNAPL or through a low permeability zone into more permeable soils, a bentonite plug can be set in the casing to ensure that DNAPL does not migrate downward through the borehole. Polypropylene liners within the sonic core barrel are not recommended.

The continued discharge of highly viscous, low density coal tar and creosote NAPLs to surface water demonstrates that these NAPLs can continue to migrate in the subsurface for more than a hundred years (Gerhard et al., 2007). However, a commonly held belief is that low viscosity NAPLs

released to the ground surface do not continue to migrate over long time periods, but will reach residual saturations rather quickly. This is thought to be especially true for less viscous and more dense chlorinated solvent DNAPLs. The assumption seems to be that the NAPL will not have sufficient head to continue migrating long term, but will pool on top of low permeability zones and not migrate further. In contrast to this belief, numerical modelling has suggested that these types of NAPLs can continue to migrate vertically in heterogeneous porous media for decades (Reynolds and Kueper, 2004). Observations at a couple sites where large amounts of NAPL were discharged to the subsurface seem to support these modeling results. Examples

of continued migration of NAPLs include the appearance of chlorobenzene and DDT DNAPL in a well at least 300 feet from the known source zone 40 years after the closure of the DDT manufacturing facility (Figure 13), and jet fuel migration over a 10 year period between when the characterization work was done and when the full scale SEE remediation system was constructed (Figure 14). Thus, the age of the characterization data used to delineate the NAPL-contaminated area to determine the thermal treatment area must be considered. Also, it is possible that where there are NAPL saturations greater than residual saturation, investigation activities (i.e., drilling, open boreholes) or groundwater pumping can cause or allow NAPLs

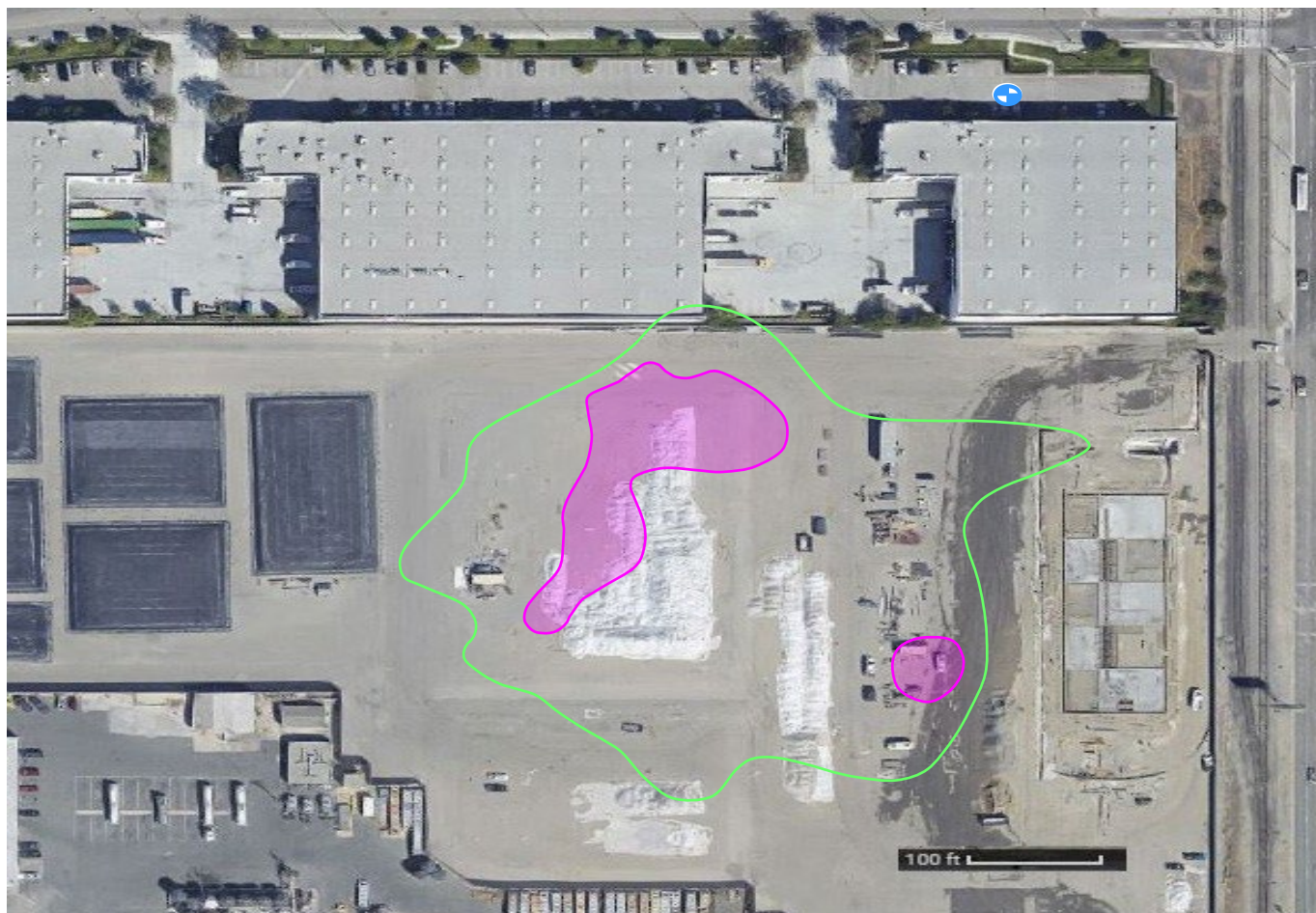


Figure 13. This Superfund site is a former DDT manufacturing facility which ceased operating in 1982. An investigation to determine the extent of DNAPL was carried out in 2005. The green line delineates the area below the water table where DNAPL was found within an aquitard. The pink areas show where mobile DNAPL was found to exist based on the occurrence of DNAPL in wells and/or soil concentrations above 53,000 mg/kg. In 2017, DNAPL was first detected in the well shown by the blue and white circle approximately 200 feet to the north of the previously-defined DNAPL contaminated area, and DNAPL continues to be periodically recovered from this well, demonstrating the continued migration of DNAPL for years after the discharge occurred.

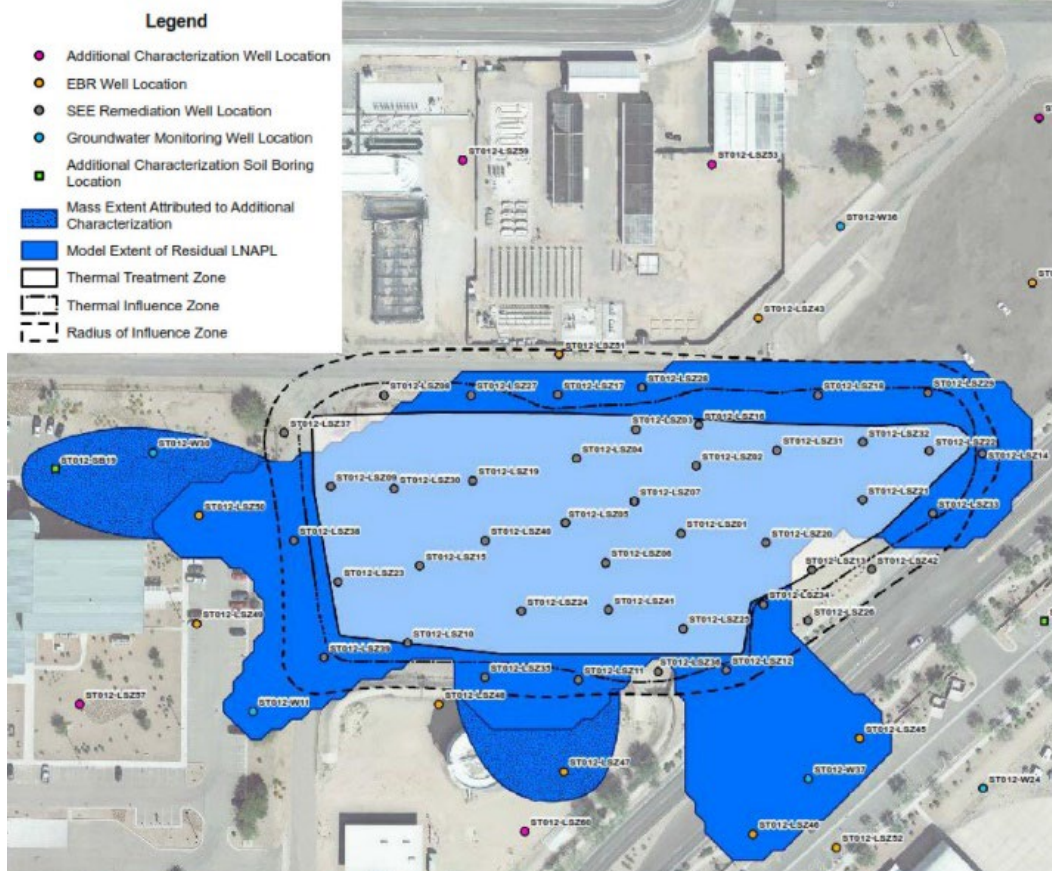


Figure 14. At this former Air Force Base, a large jet fuel leak migrated to depths as great as 235 feet bgs. As the water table subsequently rose, jet fuel was trapped below low permeability zones. More than 30 years after the leaking was terminated, jet fuel continues to migrate to the southeast where it is periodically collected from wells. Two and a half million pounds of jet fuel were recovered using SEE (the SEE treatment area is shown in light blue). The dark blue areas continue to contain mobile LNAPL that is collected routinely from wells that were installed after the termination of SEE.

to migrate. Sometimes early investigation activities did not totally delineate the extent of NAPL (Horst et al., 2021). If significant time has elapsed since the NAPL delineation was carried out, additional delineation can be carried out during the installation of the thermal remediation system to ensure that the treatment area contains essentially all of the NAPL.

Section 5.0 Treatability Studies

According to EPA guidance (EPA, 1992), laboratory scale treatability studies can be conducted during the remedial investigation/feasibility study stage to indicate whether a given technology can meet the expected cleanup goals, while field scale treatability studies can be performed during the remedial design/remedial action stage to establish the design

and operating parameters for a sound, cost effective implementation of the remedy. The Guide recommends a three-tiered approach, the first of which is bench-scale tests to determine qualitatively if a certain technology can achieve the performance goals. The second tier is remedy selection testing which can be done at either (or both) the laboratory and/or field scale to “provide quantitative data for use in determining whether a technology can meet the operable unit’s cleanup criteria and at what cost.” The third tier of RD/RA testing is performed by the technology vendors to pre-qualify them, or to support the detailed design specifications.

While laboratory and field testing may be very important and informative for some situations, in situ thermal technologies have been used

extensively enough in a wide variety of geologic and hydrogeologic conditions (Horst et al., 2021) that they can be efficiently applied to many common sites without prior laboratory and/or field scale testing. When laboratory or field testing is to be performed, the testing should be carefully designed in order to obtain valid data. Problems with non-representative conditions during laboratory testing can start with the normal procedures of homogenizing soil samples brought in from the field for testing. When the contaminants are volatile, much of the contamination may be lost during the sampling and homogenizing process, thus the soils tested may not represent the 'worst case' or even common contaminant concentrations. In some cases, enough of the contaminants can be lost during the sampling and homogenization process that the pre-test soils already meet the soil cleanup criteria. For thermal remediation, there can be tradeoffs between treatment time and temperature to reach cleanup goals – lower temperatures may meet the same treatment goal if a longer treatment time is allowed. Testing time at temperature in the laboratory is generally on the order of a couple hours to a couple days, while treatment times in the field are generally several weeks or more at temperature. Thus, laboratory testing may not reveal the optimum combination of treatment time and temperature for meeting the treatment goals. One approach to better correlate laboratory testing with field conditions is on the basis of energy density, which translates into the amount of pore volumes of steam generated and removed.

Section 5.1. Laboratory Testing. For thermal remediation, bench scale tests that would fall into the category of tier one testing have been performed by heating a contaminated soil sample in an oven to determine if the contaminants can be volatilized at the thermal treatment temperature, or conversely to determine the treatment temperature required to meet the remedial goals. Steam injection treatability tests have also been performed in the laboratory that would be considered tier one testing. In general, tier one bench scale treatability testing is only

recommended for semivolatile contaminants, and the purpose would be to determine the temperature that is needed to effectively volatilize the contaminants. When use of the STAR technology is being evaluated for the remediation of SVOCs, one dimensional column studies are used to determine if the contaminants can sustain in situ combustion (Grant et al., 2016). For VOCs, adequate experience has been obtained during field scale remediations that thermal remediation systems can be designed with confidence without site specific treatability studies.

When steam injection testing using a one dimensional column is performed, it must be ensured that a steam front is formed in the column. The formation of a steam zone is dependent on the pressure and thus the temperature of the steam being high enough to overcome the back pressure created by the permeability of the soils – the lower the permeability of the soils, the higher the temperature and pressure must be to form a steam front. The steam injection should be performed with the steam injected at the top of the column and with the effluent recovered at the bottom. One reliable way to demonstrate that a steam front has been formed within the column is to track the amount of effluent condensed and collected and to compare that to the amount of steam injected on a condensed basis (Figure 15). Steam has a volume approximately 1500 times that of liquid water. When a steam front forms in the column, it will displace in front of it the water from the pores of the soil sample, and more effluent volume will be collected than the amount of water injected as steam. If the amount of effluent liquid collected is the same as the volume of water injected as steam, a hot water flood was conducted, not a steam flood. One dimensional column studies in the laboratory have demonstrated that hot water flooding is much less effective at recovering contaminants than steam. Thus, if a laboratory steam injection is not performed correctly, erroneous conclusions may be drawn from the laboratory experiment.

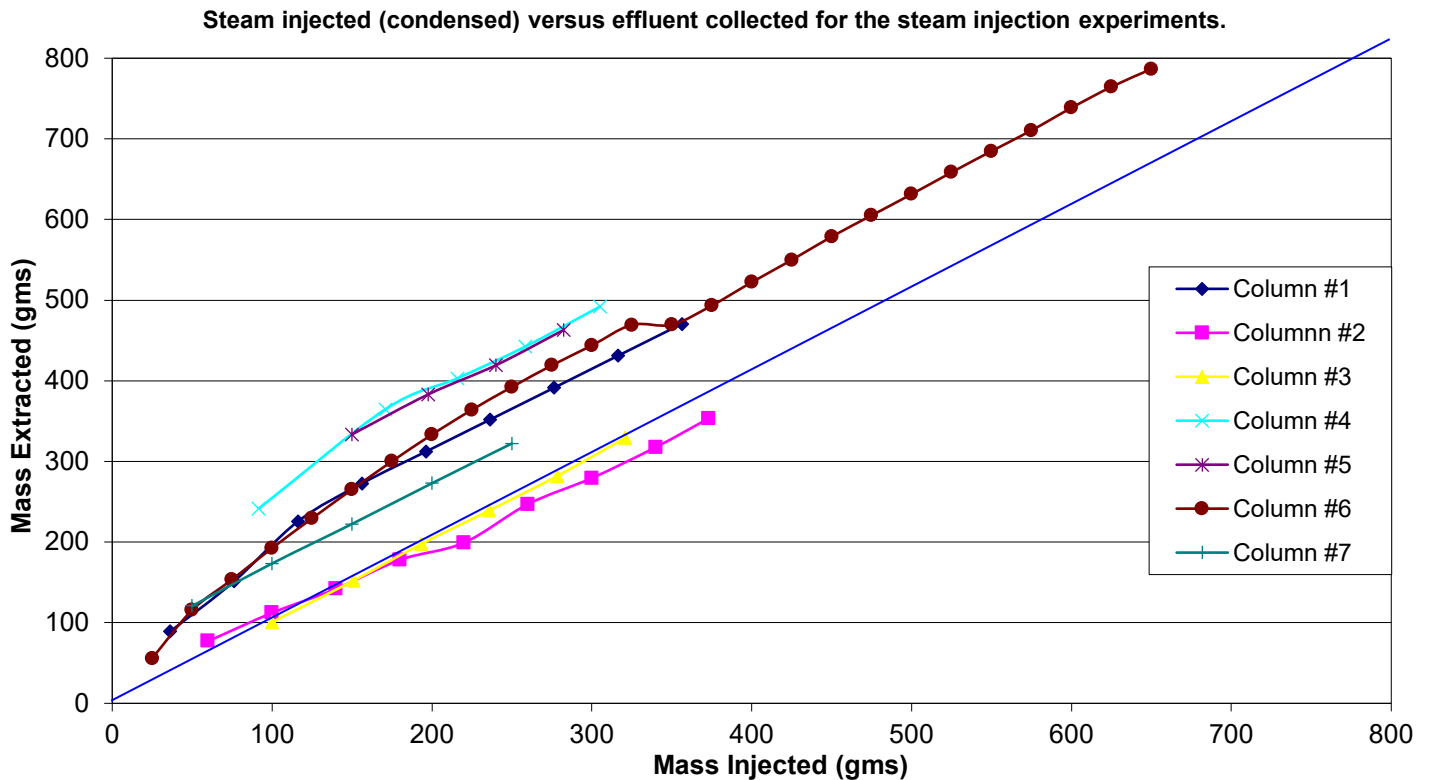


Figure 15. This graph displays data from one dimensional column steam injection treatability tests. The formation of a steam front in the column is indicated for the column experiments where the mass of effluent collected exceeds the mass injected. Steam has a volume approximately 1500 times that of water, thus the formation of a steam front within the column displaces in front of it the water from the pore spaces of the soil, and more water is collected in the effluent than steam injected (considered as condensed to water). If the pressure in the column is sufficient to condense the steam to hot water, the mass of effluent collected will be essentially the same as the mass of steam injected, as shown for column #2 and #3, which track the line showing the mass of water injected as being the same as the mass extracted. Steam injection was shown to recover much more of the contaminant mass than hot water flooding.

The results of one dimensional steam injection column experiments – even when a steam front is formed in the column – cannot be directly extrapolated to the field in terms of the amount of steam injection required to reach a remedial endpoint. In the field, steam injected into a well will flow radially from the well. Thus, as the steam front expands from the well, the radius gets larger but the amount of steam reaching a given area is less. The area closer to the steam injection well will receive more treatment than the areas further away.

Section 5.2. Field Testing. The EPA guidance states, “Field testing, however, is important for an adequate evaluation of in situ treatment. Because of the unique difficulties associated with simulating

in situ conditions and monitoring effectiveness of in situ treatment in the laboratory, field testing often may be the only way to obtain the critical information needed for the detailed analysis of alternatives . . .”. Tier two/three testing for in situ thermal technologies would generally consist of a field test on a portion of the area to be remediated in order to determine the amount of energy that is required to reach the target treatment temperature. This test might also be used to confirm that the contaminants can be effectively recovered at the target temperature. Valuable information may be obtained from these tests to determine the required electrode or heater well spacing and vacuum extraction requirements. However, due to the high costs associated with field scale pilot testing, it only recommended when the

field conditions are somehow unusual from the more commonly treated sites. Experience obtained at a large number of field sites and the use of models to predict heating rates as a function of energy input and the configuration of the site allows the thermal remediation vendors to design and implement these remedies at most sites successfully without obtaining site specific field data from a pilot.

Whether or not a pilot scale is recommended for a particular site can be discussed with the vendors of the technologies. Examples of when field testing may be recommended include when the contaminants at a particular site have not been treated previously using thermal technologies, for contaminants such as PFAS for which all the removal mechanisms are not understood, sites with high permeability water bearing zones where it must be determined if steam injection or groundwater extraction is required, and sites where the possibility of subsidence must be evaluated. For unusual contaminants that have not been treated by thermal remediation previously, laboratory and/or field testing may be recommended before thermal remediation is chosen as the remedy. Often the questions about treatment of exotic contaminants can be answered by less-costly laboratory tests rather than field tests. For design questions about the need for steam injection or groundwater extraction, the field scale test may occur after thermal remediation has been chosen as the remedy. In some cases, a field test is desired by the site owner as 'proof of concept' before investing in a full scale remediation at a large site.

When steam injection is the preferred technology, steam injection rate as a function of injection pressure of the steam as well as steam migration through the formation is usually evaluated through field scale treatability tests. This type of data can be very useful for designing SEE remediation systems, especially in setting such as fractured rock, but steam injection pilot tests have also been used to determine the extent of steam buoyancy in highly permeable sand and gravel aquifers. Generally one or two steam injection wells are constructed with

several thermocouple strings surrounding them at varying distances from the injection wells. The use of temperature monitoring points surrounding the injection wells allows the vendors to compare results with the radius of influence (ROI) and steam shape obtained from steam modeling and back-calculate the anisotropy ratio, which is then used for scale-up modeling. Steam may exhibit very irregular flow patterns in the subsurface depending on the distribution of hydraulic conductivity. Temperature is the best means of determining where the steam will flow spatially and vertically. Steam injection rates as a function of injection pressure is also critical to determine the well spacing and expected breakthrough time of the steam at extraction wells. These short term steam injection tests, with a typical duration between 2 and 7 days, can be performed without simultaneous groundwater extraction. The wells and TMPs used for the pilot test are then incorporated into the full scale design.

When field treatability testing is desired, often the approach proposed by the site owner is to conduct the pilot in the middle of the most contaminated area of the site. This can be problematic for several reasons. Performing a pilot in the most contaminated area can demonstrate that the thermal technology can recover the contaminants effectively, but it cannot demonstrate that soil cleanup criteria can be met because contamination from outside the treatment area will continuously be pulled into the pilot area if hydraulic and pneumatic control of the pilot area are maintained. If hydraulic and pneumatic control are not maintained, contaminants may be spread to previously uncontaminated areas. Then, due to recontamination, the pilot area would have to be re-treated during the full scale remediation. Another potential problem is the recovery of significant quantities of contaminants that must be treated at the surface.

It is recommended that when a field scale pilot treatability study is to be performed, an upgradient area of the contaminated site be chosen to lessen the likelihood of recontamination and enhance the probability of reaching cleanup criteria during the

pilot. Starting in an area with less contaminant mass increases the likelihood of being able to successfully treat the contaminants that are recovered aboveground, while learning more about how to treat the recovered wastes. This will help in designing and sizing the treatment system for the full-scale remediation.

The size of a field scale treatability study should also be carefully considered along with the objectives of the pilot. For example, the in situ thermal technologies generally rely on superposition of heat or energy, meaning that heat reaches an area from all sides. Thus, if the pilot scale is to determine if the site can be heated to the desired temperature, or how much energy is required to heat the area, the pilot scale should be large enough that multiple heat injection points are used to simulate what would occur at full scale. Thus, thermal technology pilot scale implementations that rely on one hexagonal array of the wells providing energy to the subsurface, whether they are electrodes, heater wells, or steam injection wells, may not provide data that can be directly scaled up to the full scale implementation.

Section 6.0 Thermal Remediation Services and the Superfund Process

Successful implementation of thermal remediation technologies requires substantial expertise in the design and operation of these technologies as well as specially designed equipment. Several specialty vendors offer thermal remediation services, and most now offer more than one thermal technology. This section discusses a general procedure for procuring thermal remediation services through the Superfund process, but most of the discussion will also apply to sites under other regulatory programs and even sites that are not regulated.

When thermal technologies are being evaluated for a particular NAPL-contaminated site, the evaluation process and decision documents, such as a Feasibility Study (FS) and Record of Decision (ROD) or Engineering Evaluation/Cost Analysis (EE/CA), best practice is for the document(s) to specify

thermal remediation in general but not a particular thermal technology. There is some overlap in applicability of the thermal technologies, particularly for low permeability soils where both ERH and TCH are both generally applicable. When a particular thermal technology is not specified, the thermal vendors can then propose during the bidding process the technology they believe is best suited for a particular hydrogeologic setting, contaminant, and remedial goal. This allows the vendors to put forward their best technical proposal for the site. This will also allow more of the vendors to bid on the project if they believe their technology is applicable.

The contract for the thermal vendor must be a design/build/operate contract. While there is more than one vendor for each technology type, each vendor applies the technology somewhat differently, and they have their own specialty equipment designed for their process. The vendors generally will not bid on a design produced by others, or if they do, the design will be redone. A thermal vendor will not generally guarantee that performance standards such as temperature goals or soil cleanup standards can be met when working with a design they did not develop themselves.

A basis of design (BOD) should be prepared that is part of the package that will be used to solicit bids from the thermal vendors for the design/build/operate contract. The BOD must not include a conceptual design – as stated previously, each of the vendors has their own method of designing and operating their technology, and they will not generally bid on a design produced by others. The BOD should contain a concise but complete conceptual site model (CSM) for the site, including a description of the site geology and hydrogeology, the contaminant(s), their distribution in the subsurface, and their concentrations in soil and groundwater along with a breakdown and best estimate of the total contaminant mass. Plane views and cross sections containing all of this information are a good way to present this information in a readily understandable way. Three dimensional models or presentations are less valuable for bidding and design purposes as they

may leave openings for interpretation of the footprint and treatment depth of the target treatment area, and as a result may make it difficult to compare the bids that are prepared by different vendors. Surface structures and subsurface infrastructure within and immediately surrounding the area to be treated should be identified on figures. Access to and size of electrical, water, sewer, and natural gas utilities should be discussed. It should be noted that the large but temporary power demands of these technologies, electrical and/or natural gas (or possibly propane), particularly for larger sites, may be problematic. Electrical power requirements may have a long lead time to get the power drop. Discussions with the utility companies should be initiated even as thermal remediation is evaluated for its applicability for a given site to determine the availability of the power required for the remediation.

Section 6.1. Remedial Goals. The BOD should clearly define the remedial goals. For Superfund sites, Remedial Action Objectives (RAOs) are defined by the ROD, and generally include statements of protection of human health and restoration of groundwater resources. At sites where NAPL is present, particularly for chlorinated solvents, there is usually a downgradient dissolved phase plume that is not being addressed by the thermal remediation. A remedial goal should be defined to specifically state what the thermal remediation is intended to accomplish. Where soil remedial goals have been established which are meant to protect groundwater by eliminating or reducing leaching from soils, these soil cleanup criteria may be appropriate endpoints for the thermal remediation within the thermal treatment zone. Soil concentration goals are to date the most common hard criteria for thermal remediation completion. However, if these criteria are extremely low, as in the tens of parts per billion range, long thermal treatment times may be required due to slow desorption rates, and it may not be cost effective to continue heating until these very low concentrations are achieved.

For most Superfund sites, restoration of groundwater is one of the ultimate goals of the

remedial activities. Maximum concentration levels (MCLs) for chlorinated solvents such as PCE and TCE or volatile petroleum hydrocarbons such as benzene are very low (5 micrograms per liter, ug/l), which is five to six orders of magnitude less than the solubility limit for the compounds. Reaching these concentrations in a groundwater system that has been contaminated by NAPL for a long period of time, which allows adsorption onto the soil particles and diffusion into low permeability soil strata, will likely require extended treatment times due to the slow desorption process. Also, experience at thermal remediation sites has shown that groundwater concentrations will vary significantly during thermal remediation both spatially and over time, making it difficult to use a groundwater concentration as a remedial objective.

Percent mass recovery or a percent reduction in soil and groundwater concentrations have also been used or proposed as remedial goals for thermal remediation. The heterogeneity of NAPL distribution in the subsurface and our limited abilities to determine its actual distribution and saturation within the soil pores even with our most advanced and/or most prolific sampling procedures frustrates attempts to calculate the mass of contaminants in the subsurface. Thus, clean up criteria tied to a percent mass recovery or a percent reduction in soil concentrations can be extremely difficult to verify and document.

For many sites, particularly larger sites, a more cost effective approach may be to terminate the thermal remediation system when the system reaches 'diminishing returns'. This remedial endpoint is especially appropriate if the remedial objective is to remove contaminant mass to reduce the contaminant mass flow into the downgradient plume. To reach 'diminishing returns', first a site must reach the target temperature throughout the treatment area. For chlorinated solvents or light petroleum hydrocarbons, such as BTEX compounds, the target temperature should be the boiling point of water at the local pressure condition. As the site heats up, the mass recovery rate is monitored, and

an increase in the recovery rate is generally noted. When the site temperature exceeds the co-boil point for the NAPL, the NAPL has been eliminated, and mass recovery rates will start to decrease. Groundwater samples analyzed during the heatup phase would be expected to increase due to enhanced dissolution rates during heating, and then decrease when the NAPL is eliminated and only dissolved and adsorbed phases remain. Once recovery rates have reached a low rate, and groundwater concentrations are well below concentrations that would be indicative of NAPL presence, it may be most cost effective to terminate the thermal remediation at that time and to reduce groundwater concentrations further by groundwater extraction. Extracting the heated groundwater will recover contaminant mass that is desorbing from the soil particles, and aid in reaching MCLs. Pump-and-treat systems in general are effective for recovery of contaminants that are in the dissolved phase, and the process will likely be enhanced by higher temperatures.

For SVOCs, including PAHs, PCBs, and dioxins, the target temperature may be 300°C or greater. Temperatures in excess of the boiling point of water can only be achieved by the TCH technology or by STAR, the in situ combustion technology. For TCH, these higher temperatures can only be achieved when groundwater is not present. Table 2 shows pre- and post-treatment PAH concentrations for a coal tar site treated by TCH at temperatures of 325°C. At the Mare Island Naval Shipyard Superfund site, TCH reduced PCB concentrations by as much as four orders of magnitude, to concentrations less than 0.033 milligrams per kilogram (mg/kg).

Table 2. Pre- and Post-Treatment Soil Concentrations of Coal Tar Components Within the Construction Worker Exposure Depth

Constituent	Average Concentrations		Reduction %
	Pre-Treatment mg/kg	Post-Treatment mg/kg	
Benzene	2068	0.35	99.98%
Anthracene	19	0.48	97.47%
Benzo(a)anthracene	20	0.51	97.45%
Benzo(a)pyrene	20	0.33	98.35%
Chrysene	20	0.71	96.45%
Fluoranthene	43	1.02	97.63%
Naphthalene	679	5.7	99.16%
Phenanthrene	107	3.82	96.43%
Pyrene	65	1.12	98.28%
C11-C22 Aromatics, unadj.	4000	43.15	98.92%

Section 6.2. What to Look for in a Remedial Action Work Plan/Remedial Design. Normally during the remedial design (RD) phase, several rounds of review by the regulatory agency are conducted. These reviews should inform the responsible party or regulatory agency of the details of the design and operation of the thermal remediation system, however, it should not be viewed as opportunity to tell the vendor how to design or operate their system – the vendors are the experts on these systems. Attempts to dictate to them the design or operation of the system may result in liability on the part of the responsible party or regulatory agency. However, what should be of particular interest to the site owner and regulatory agency is the monitoring system. Monitoring should include performance monitoring to show progress toward meeting the remedial goals, and operational monitoring to show that the above ground treatment system is operating as designed and is meeting the discharge criteria for air and water (Section 2.8). At sites where the community is close by, or near occupied facilities, ambient air monitoring and/or indoor air monitoring may also be recommended.

Performance monitoring to show progress toward meeting the remedial objectives includes subsurface temperature monitoring, monitoring to show that pneumatic and hydraulic control are being maintained, and contaminant extraction rates over time. Most thermal remediations will also

include groundwater concentrations over time to track remedial progress. Interim soil samples may also be used to monitor the progress of the system, especially when the target treatment zone is above the water table and the cleanup criteria are soil concentrations. Subsurface temperatures are monitored automatically on a continuous basis by thermocouples or by other temperature measuring techniques such as fiberoptic temperature monitoring systems that are installed in the subsurface in vertical borings with the temperature sensor spaced vertically every 3 to 5 feet. These temperature monitoring points are often co-located with piezometers to measure subsurface vacuum to demonstrate pneumatic control. Weekly progress reports from the vendor should include figures showing the current subsurface temperatures spatially and vertically. Demonstrations of pneumatic and hydraulic control are best achieved by including temperature and pressure monitoring points around the thermal treatment area, as well as within the treatment area. While some temperature increase is expected outside of the thermal treatment area (due to heat conduction from ERH and TCH systems or radial injection of steam during SEE remediation), higher rates of temperature increase than expected are a reliable indication of the loss of hydraulic control (Figure 7). These vacuum and temperature measurements should be made and reported on a weekly basis. How many monitoring points are installed will depend on the system size, but a general guideline may be one per every 1000 to 2000 square feet. The heterogeneity of the system and the cost of installing monitoring points should also be considered when determining the frequency of the temperature monitoring points. Where there are sensitive areas adjacent to the treatment area, additional monitoring may be warranted.

Contaminants extracted in the vapor, liquid (dissolved) and NAPL phase should be measured and reported at least on a weekly basis. Commonly, PID readings are taken of the vapors as they enter the final treatment stage (thermal oxidizer or vapor phase granular activated carbon) on a daily basis. Summa canister samples for laboratory analysis are generally obtained on a weekly basis. Water

entering the final treatment phase (commonly liquid phase granular activated carbon) is generally sampled weekly as well. NAPL accumulation is also measured weekly to determine the total contaminant recovery rate and the cumulative contaminants recovered. When the NAPL is eliminated, this should be reflected in overall decreases in groundwater concentrations, although there may be significant variations in groundwater concentrations even during this stage of the remediation. When the concentrations remain well below the concentrations that are indicative of NAPL presence and the mass extraction rates are low, diminishing returns have been achieved and the application of heat can be terminated. As groundwater concentrations and mass recovery rates decrease, it may also be desirable to obtain soil samples for analysis. Note that groundwater and soil samples obtained during and after thermal remediation need to follow hot groundwater and soil sampling standard operating procedures (SOPs) that are available from the thermal vendors.

Section 6.3. How Does Thermal Remediation Affect the Community?

Thermal remediation technologies are frequently implemented in commercial, industrial and residential areas (Figure 16).



Figure 16. Thermal remediation technologies have been used in residential, commercial, and industrial setting. In most cases, the remediation has been able to proceed without displacing the residents.

In a few cases, sensitive possible receptors have been relocated during construction and operation of the thermal remediation, but in many cases the thermal system design, construction and operation

can be conducted in a manner to reduce the impact to the residents or business to accommodate them remaining in their residence or business. Design elements to reduce the impact to existing infrastructure include angled or horizontal boreholes under buildings when the building cannot be accessed by drill rigs to install borings vertically (Figure 17), and subsurface completions of wells to allow safe access to the area. Construction schedules can be altered to accommodate businesses, for example by doing the construction at night when the business is not open. In contrast, in a residential area, construction activities may be restricted to normal business hours so that residents experience less disruption in the early morning and evenings when they are more likely to be home. Constraints on construction and where access to the public must be maintained must be detailed in project bid documents.

While construction can be limited to specific times of the day or week, operation of thermal remediation systems is normally continuous, and some of the components, such as blowers, can produce considerable noise. Noise-producing equipment can be placed away from the property boundary and/or within structures, or sound barriers can be built around them to reduce the noise level at the property boundary. Monitoring of noise continuously or on an as needed basis can also be included in the project remedial action work plan (RAWP).

Ambient and/or indoor air monitoring is usually warranted when the public will have access to areas adjacent to or within buildings above the remediation area. Continuous monitoring via PID or FID readings at the perimeter of the property boundary is commonly used when a residential area is adjacent to the site, however, these readings do not distinguish between the different types of VOCs that may be present and the differences in their toxicity. Summa canister samples of air can determine what specific chemicals are present and can be used periodically to support the PID or FID data, but these samples are generally short term and thus not representative of the long term air quality. Also the turnaround time on the analysis can be as much as three weeks. Absorbent medium samplers which average the concentrations over the time that they are deployed can be used for air samples to provide data on the specific compounds that are present, but again, this is not real time data. When there is significant risk of exposure in buildings that overlay or are adjacent to the treatment area, real time data can be obtained by an automated gas chromatograph system. This system can be set up to obtain air samples from a variety of locations on a rotating basis and provide essentially real time data on VOCs concentrations in air in sensitive areas. The system can also provide notifications when concentrations of specific compounds exceed a threshold (Kram et al., 2019).



Figure 17. Thermal remediation systems have been installed vertically in warehouses where there is access for a drill rig and under active manufacturing buildings using angled borings.

Some communities may object to having a thermal oxidizer or catalytic oxidizer on site during remediation to destroy the vaporized contaminants as they are recovered from the subsurface. Vapor phase activated carbon (VGAC) can be used on the back end of these systems to help alleviate the concerns. Destruction of the vapors on site may be a more environmentally safe option for the community than to have the vapors condensed to a liquid hazardous waste that is stored on site until being transported by truck through the community to an off site disposal facility.

Section 7.0 How Do We Know When We are Done?

When to turn off the thermal treatment system – or at least when to terminate heating – is a commonly asked question. Regardless of the objectives of the thermal remediation, there can be benefits to continuing the remediation until ‘diminishing returns’ have been met. When the objective of the remediation is mass recovery to the extent practical, ‘diminishing returns’ would be the best indication that the remediation has reached that point. The first criteria that must be met is that the target temperature should be met throughout the treatment area (Heron et al., 2006). The design energy input for the system should be compared to the amount of energy that has been input. If the design energy – or at least enough energy to heat the entire area plus some extra for heat losses - has not been applied, that may be an indication that there are significant cold areas in between the temperature monitoring points. Once the energy demand has been achieved, then the mass recovery rate and groundwater and/or soil concentrations should be considered in determining if ‘diminishing returns’ has been achieved. ‘Diminishing returns’ is indicated by mass recovery rates and groundwater concentrations that are low and remain low (Heron et al., 2023). Groundwater samples can be obtained from monitoring wells or if groundwater extraction is being used, samples can be collected from the multiphase extraction wells which would already have high temperature pumps installed and operating. Several rounds of groundwater samples, spaced over a couple weeks, should indicate that

the concentrations are well below that which would indicate the presence of NAPL. Then confirmation soil sampling can also be performed.

Section 7.1. Should We Specify Soil or Groundwater Cleanup Criteria? How to specify cleanup criteria is another frequently asked question. There are advantages and disadvantages to using either media for the cleanup criteria. Soil concentrations, such as the concentrations for leaching to groundwater, have been used at many thermal sites. Drawbacks to the use of soil criteria include the fact that extremely small soil samples are analyzed, which makes it very difficult to account for the natural heterogeneity of contaminant distributions. This is particularly true if a percent reduction in soil concentrations is used as the cleanup criteria (which is not recommended). If soil samples are utilized to document cleanup levels, enough samples should be obtained for the results to be statistically valid (EPA, 2002). When the contaminants are VOCs, the soil samples should be obtained from the sections of the core that screening with a PID shows has the highest remaining contaminant concentrations. Standard operating procedures (SOPs) have been developed for obtaining hot soil samples and obtaining valid soil concentration data (Gaberell et al., 2002), but a drill rig must be mobilized to the site, and there will likely be issues with access to some sections of the site due to the site infrastructure.

Groundwater concentrations have an advantage over soil concentrations in that they interrogate concentrations over larger areas. As discussed previously, groundwater concentrations can be expected to vary considerably during a thermal remediation, making trying to meet groundwater concentration criteria a ‘moving target.’ A groundwater criteria would be even more problematic if there were upgradient sources of contamination that could recontaminate the treatment area. When groundwater criteria are used, consideration must be given to the fact that the treatment area will remain hot potentially for years after heating has been terminated, and the solubility of some contaminants is greater at higher temperatures. Overall, contaminant concentrations

should be expected to decrease as the site cools. If the groundwater concentration goals are met while the groundwater is still at elevated temperatures, the goals should continue to be met as the site cools, as long as there are no upgradient sources.

Other criteria that have been proposed for shut down of a thermal system are that a specified amount of mass be recovered, or that the mass in the ground be reduced by a certain percentage. Both of these criteria suffer from the fact that it is extremely difficult to determine the mass of contaminants in the subsurface (unless a spill of a known size recently occurred) due to the heterogeneity of soil and thus contaminant distribution. The mass of contaminants in the subsurface has both been over and under estimated when compared to the amount of mass that was recovered via thermal remediation. Another closely related issue is that the mass of contaminants recovered is also an estimate.

Most of the thermal vendors have performed guaranteed remediations to meet low soil or groundwater concentrations. This can have the advantage of a set cost up front to complete the remediation. However, when the risk of being able to meet the cleanup goals is placed on the vendor in this manner, the costs will be increased over a remediation that is not guaranteed. Thus, the remediation is more costly whether it needs to be or not. The least costly implementation is typically achieved when a risk sharing and partnering approach are considered between the responsible party and the thermal vendor.

Section 7.2. What Happens to Groundwater Concentrations After Heating is Terminated? After an aggressive thermal remediation of the NAPL-contaminated subsurface, groundwater concentrations have been shown to have an overall downward trend, even as some variability in concentrations can be expected. Figure 18 shows groundwater concentrations of TCE at the East Gate Disposal Yard after ERH remediation of two source areas, and documents the increase in concentrations in the first treatment area during heating, then the decrease in

concentrations that occurred after heating was terminated. The figure shows that in this high permeability sand and gravel aquifer, TCE MCLs were reached in the source zones in a few years after thermal treatment. Heron et al. (2016) documents the decreasing dissolved phase plume concentrations of PCE and its daughter products after thermal remediation. Natural attenuation of PCE in the dissolved phase plume had been occurring before thermal remediation was implemented in the source zone, and continued at a rapid rate after thermal treatment. Five years after thermal treatment was completed, only one monitoring well still had vinyl chloride concentrations above the MCL. The authors concluded that back diffusion is not necessarily a barrier to reaching groundwater goals.

Baker et al. (2016) document the effects of thermal remediation of five source zones on groundwater concentrations, showing that the mass flux of contaminants from the source zone into the downgradient plume can be reduced sufficiently so that natural groundwater flushing can lead to restoration of the plume within the time frame of a decade or so. These five case studies also demonstrate that back diffusion is not necessarily a barrier to groundwater restoration, despite common belief.

These examples show that aggressive source zone remediation is justifiable, as it can lead to restoration of groundwater, both within the treatment zone and within the downgradient plume. Aggressive treatment of essentially the entire NAPL source zone can lead to groundwater restoration in a reasonable timeframe.

Section 7.3. Can Thermal Remediation Lead to Site Closure? Thermal remediation of the source zone can in some cases be the sole remedial action that is needed to close a site with a notice of No Further Action (NFA) or de-listing from the National Priorities List (NPL), if there are no other contaminants (for example, metals) that are not addressed by thermal remediation, and if there is no dissolved phase plume that is above

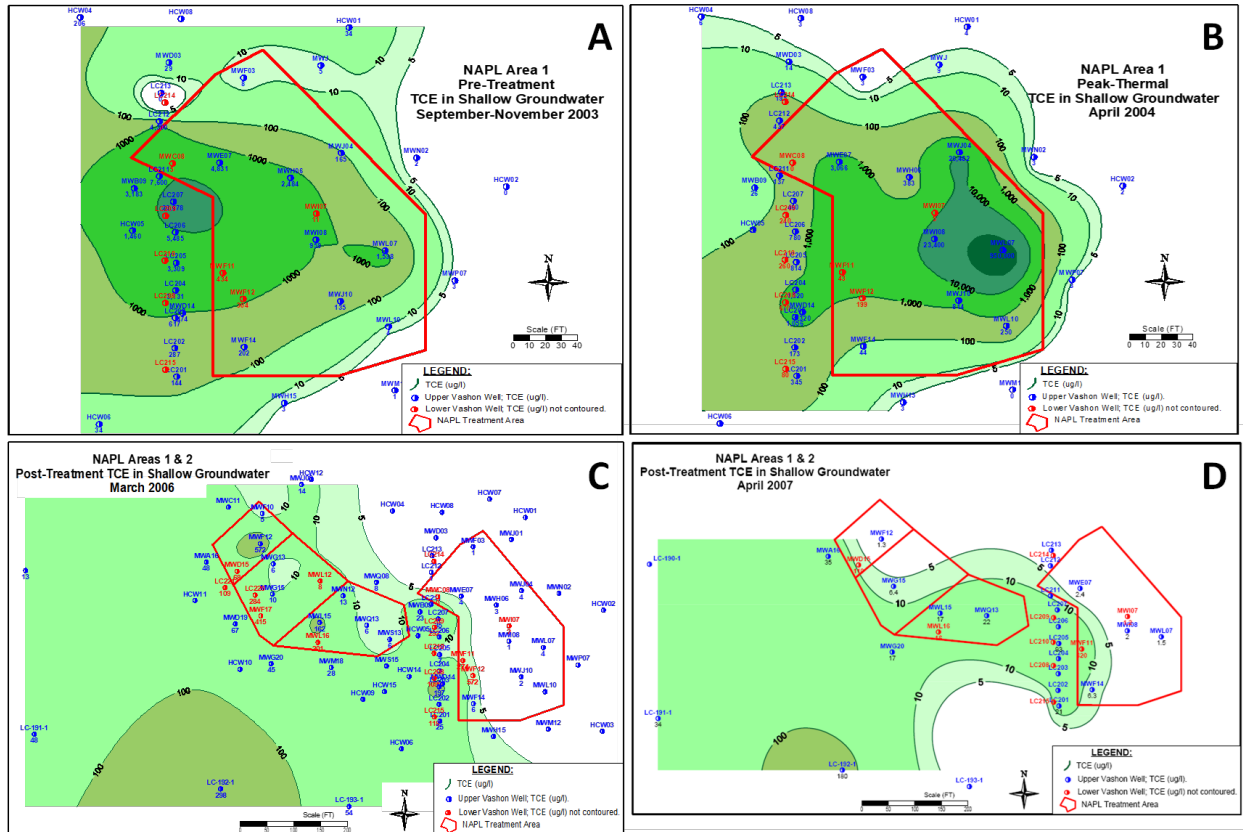


Figure 18. In one of the earliest deployments of thermal technologies at a Superfund site, ERH was used to remediate TCE from a disposal facility for waste oils. Figure 18A shows the baseline TCE concentrations within and immediately downgradient of the first NAPL-contaminated area to be treated. Note that the highest pre-treatment groundwater concentration was found just outside of the treatment area. Figure 18B shows the groundwater concentrations after heating was initiated. Heating increases the solubility and solubilization rate of chlorinated solvents, thus increasing groundwater concentrations are typically seen after heating is initiated in the immediate vicinity of NAPL. Heating was terminated when groundwater concentrations were less than about 400 ug/L. Figure 18C shows TCE concentrations 2 years after heating was terminated in the first treatment area, and 1 year after treatment was terminated in the second adjacent treatment area. In this sand and gravel aquifer with a relatively high groundwater flow rate, the dissolved phase TCE that remained in the first treatment area was rapidly flushed from the area. Figure 18D shows that a year later, most of the remaining TCE was flushed from the second treatment area as well.

groundwater goals. An example of this is a former wood treatment site with creosote contamination in the vadose zone only, which was comprised of a tight clay. Because the contamination was in the vadose zone and groundwater was not affected, TCH remediation of the creosote in the vadose zone was sufficient to reduce contaminants of concern concentrations in the soil to below the cleanup goals, and no further action was necessary. In other cases, treatment of the source zone has allowed for re-use of the site.

Many Superfund sites, however, have more than one contaminant of concern, and many have downgradient dissolved phase plumes that are not cost effective to treat with thermal remediation. In

these cases, multiple treatment methods may be necessary to achieve site closure. Another former wood treater site with creosote below the water table and a downgradient dissolved phase plume used a combination of steam injection below the water table to recover the creosote NAPL, pump-and-treat to recover downgradient dissolved phase contaminants, and a soil cover to inhibit leaching of contaminants from the vadose zone to groundwater to achieve the groundwater cleanup criteria throughout the former source zone which allowed the site to be deleted the site from the National Priorities List (NPL).

Section 8.0 Factors Affecting Costs

Many factors come into consideration when determining the costs of thermal remediation. The size and dimension of the treatment area (surface area and depth), the depth to groundwater and the groundwater flow velocity, type and quantity of contaminants, wellfield access, and the project goals will all affect the total project costs. Some of the largest sites treated (250,000 to 400,000 cubic yards (yd³)) have had the lowest costs on a per cubic yard basis (\$75/yd³ and \$60/yd³, respectively), while small pilot scale sites may approach \$2000/yd³. The reasons for this include the fact that some costs, such as mobilization and demobilization, costs of document production (design reports, completion reports) are not scalable, as well as factors such as greater percentage heat losses on small sites. Sites above the water table or with limited groundwater flow rates generally require less energy than sites which include significant depths below the water table and significant groundwater flow. An energy usage of approximately 220 to 250 kiloWatt-hour per cubic yard (kWh/yd³) is typically required for VOC treatment at the boiling point of water no matter which heating technology is used. Treatment of the lower-boiling SVOCs at their boiling point typically requires an energy usage between 300 and 400 kWh/yd³. For higher temperature (300°C and higher) TCH SVOC treatment, energy requirements may be as much as 500 to 600 kWh/yd³. When treatment is required to the ground surface, there can be significant heat losses to the atmosphere and the added expense of a cap at the surface. SVOC sites typically have unit costs that are 50 to 100 percent higher than costs for VOCs due to the greater energy requirements to reach higher temperatures. The cleanup criteria will also affect the costs of thermal remediation. For one site, cost estimates were obtained from the vendors for two different remedial end points, which showed that reducing the groundwater cleanup goal from 300 ug/L to 3 ug/L increased the estimated energy costs by approximately 30 percent.

Section 8.1. General Cost Information for Thermal Remediation.

The costs associated with in situ thermal remediation were discussed during a seminar in July 2021 put on by one of the thermal vendors, and the following information comes from that presentation. Costs for ERH and TCH are generally similar, and will vary based on the size and depth of the site, the amount of groundwater flow through the site, the recalcitrance of the contaminants to be treated, and the remedial goals. Large, deep sites allow the fixed costs to be spread over a larger volume, and costs may be in the range of \$85/yd³. Significant groundwater flow into the treatment area is a heat sink, and will tend to increase treatment costs either because more energy is used to offset the heat losses or because a combination of technologies (TCH and SEE or ERH and SEE) are required in high groundwater flow regimes to meet the remedial goals. Higher boiling point compounds or more stringent remedial goals will also increase the costs per unit volume. Smaller sites with volatile compounds may have treatment costs in the range of \$150/yd³ to 350/yd³.

Several contracting strategies can be used to reduce overall costs. One approach is to pay for as many costs as possible directly rather than passing the cost to the thermal vendor. This includes the cost for power (which is generally approximately 10 to 30 percent of the total costs - the larger the site volume, the higher the percentage); the costs of establishing temporary electrical, natural gas, or potable water service; permitting; waste management and disposal, including granular activated carbon; and the costs of laboratory analysis. Another strategy to reduce costs is to reduce the risk to the vendor. The vendor takes on risk when stringent remedial criteria must be met, as by a guaranteed remediation. Also, the more uncertain the site characteristics are, the greater the uncertainty in achieving temperature goals and thus cleanup criteria, and the greater the costs.

Section 9.0 Life Cycle Analysis of Thermal Remediation Technologies

According to Lemming et al. (2013), “The LCA translates the environmental exchanges during the life-cycle of the remediation project (use of finite resources, emissions to air, soil and water) to a number of environmental impacts including global warming, ozone formation, acidification, eutrophication, respiratory impacts, human- and ecotoxicity and resources depletion.” However, that definition fails to mention the primary environmental impacts from the contamination itself. From a groundwater contamination and remediation perspective, primary environmental impacts are defined as the local impacts related to the contaminants in groundwater before and after remediation. Cadotte et al. (2007) found that primary impacts can represent a very significant portion of the total global impacts, however, impacts to groundwater are not included in established impact analysis methods (Godin et al., 2004; Lemming et al., 2010).

According to this definition, secondary impacts arise from the remedial efforts, which includes resource use and emissions from all the remedial stages (Volkwein et al., 1999). Most studies comparing the Life Cycle Analysis (LCA) of remedial technologies have not evaluated the effects of different remedial timeframe or different remedial efficiencies (Cadotte et al., 2007), thus, caution must be used when comparing the LCA of remedial technologies.

The results of an LCA will depend on a large number of site specific factors, including the size and depth of the contamination, the location of the site, its accessibility, and the cleanup criteria. LCA of thermal technologies found that in situ thermal treatment becomes more environmentally efficient for larger sites. SEE was found to have lower environmental impacts per unit volume of soil remediated than the other commonly used thermal

technologies due to the wider spacing of wells that is possible when SEE is used at large, deep sites. Non-toxic environmental impacts are generated due to the energy consumption necessary to heat the soils, however, these impacts are highly dependent on the mix of sources for energy production in the area where the remediation takes place. Additional impacts are due to the above grade materials used to treat the recovered contaminants (Lemming et al., 2013).

Lemming et al. (2013) also evaluated which aspects of in situ thermal technologies had the highest secondary environmental impacts. Concrete use, particularly as a vapor cap when treating close to the surface, activated carbon for liquid and vapor treatment, and the materials for wells and above grade manifolds all contribute to the environmental footprint of these technologies. Substitutions of cap materials and the use of bio-based granular activated carbon will help to reduce these environmental impacts. Re-use of above ground treatment systems at a significant number of remedial sites also helps to reduce the environmental footprint of these remediations. This evaluation also concluded that delineating the contaminated area carefully so that only the soil volume that needs treatment is remediated is important for reducing the overall environmental impacts of remediation.

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Steam Enhanced Extraction (SEE) Case Study



The Beede Waste Oil Superfund Site is located in Plaistow, New Hampshire, within a predominantly residential area. Prior commercial operations at the site from 1926 to 1994 included storage and distribution of fuel oil and recycling of used oil. Spills, leaks from storage tanks, and discharges to lagoons on the site created subsurface plumes of light nonaqueous phase liquids (LNAPL) that contained a wide variety of petroleum hydrocarbons, PCBs, and chlorinated solvents and which covered approximately three acres. Between 2001 and 2005, a vacuum extraction system recovered approximately 90,000 gallons of LNAPL. The Record of Decision (ROD) chose soil vapor extraction (SVE) to remediate the smear zone of LNAPL, with a contingency for thermal enhancements if it was determined during the design stage that this was needed in order to meet the site soil cleanup goals. The ROD also included a groundwater extraction system to extract the downgradient dissolved phase plume.

Bench scale treatability studies demonstrated that thermal remediation of the soils was capable of reducing contaminant concentrations to meet the cleanup criteria, however, SVE at ambient temperatures was not. Subsequently, Steam Enhanced Extraction (SEE) was chosen as the remediation technique for two LNAPL-

contaminated areas. In 2015 – 2016, SEE was used to successfully meet the soil cleanup criteria in the 13,300 cubic yard Phase 1 area, a former lagoon (Phase 1 treatment area and above ground treatment system are shown in the photograph). More than 150,000 pounds of contaminants were recovered by the injection of 28.7 million pounds of steam. In Phase 2, 66.3 million pounds of steam were injected to recover approximately 37,000 gallons of contaminants from 21,456 cubic yards in the former landfill.

Groundwater from the downgradient extraction system was used for the steam. Most of the contaminants were recovered as an LNAPL which was then shipped off site for disposal, while recovered contaminant vapors were destroyed in a thermal oxidizer. In addition to the petroleum hydrocarbons and chlorinated VOCs contaminants, the recovered groundwater also contained naturally occurring arsenic and bromide which were mobilized by the heat. Additional treatment for these compounds was required before the water could be reinjected.

After the soil cleanup criteria were met in Phase 1, it was found that a small amount of LNAPL remained in the treatment area; approximately 80 gallons were recovered by bailing. This can be attributed to the fact that the pumps have to be set deep enough in the extraction wells to provide the amount of recovery needed to maintain hydraulic control, which does not always allow all of the LNAPL to enter the pump so it can be extracted. To alleviate this problem, Phase 2 included a 'slurper' system at the wells, so that any LNAPL floating on the groundwater table above the pump intakes could be recovered by inserting a slurper tube and applying vacuum extraction.

LNAPL from the Phase 2 area had been discharging to surface water at Kelley Brook. In order to reduce the effects of heat on the surface water to the extent practicable, the SEE treatment area stopped approximately 100 feet from the Brook. A sheet pile wall was constructed to separate the portion of the landfill that was to be treated by SEE from the

portion closer to the Brook that would be excavated. Extraction wells on the Brook side of the sheet pile wall helped to remove LNAPL and heat from that area. While the sheet pile wall aided in protecting the Brook from heat and LNAPL, it would have been more effective had it been extended further past the steam injection area, and if the joints had been sealed.

Even after the strict soil cleanup criteria that were meant to be protective of groundwater were met

and the SEE system was terminated, groundwater concentrations of naphthalene remained above the New Hampshire State standard. The elevated temperature of the groundwater following SEE likely increased the solubility of naphthalene. Pumps were re-installed in several of the extraction wells with higher naphthalene concentrations and extraction continued until the groundwater standard was met.

Electrical Resistance Heating (ERH) Case Study.



South Municipal Water Supply Well Superfund Site is located in Peterborough, New Hampshire. In 1982, more than 100 parts per billion (ppb) total chlorinated VOCs were found in the South Well, causing it to be taken out of service. The nearby New Hampshire Ball Bearing (NHBB) manufacturing facility was found to be the source of the contaminants. Chlorinated solvents including 1,1,1-trichloroethane (1,1,1-TCA), trichloroethene (TCE), and tetrachloroethene (PCE) were used at the facility for degreasing during the manufacturing process, and had been discharged to the ground. NHBB had been established in 1957 and expanded several times, necessitating the relocation of a creek on site and changes to outfall locations, which contributed to widespread contamination. Soil Vapor Extraction (SVE) was implemented in the vadose zone soils, but in 1997 an Explanation of

Significant Difference (ESD) was signed that issued a Technical Impracticability (TI) waiver for the site due to the presence of DNAPL below the water table that cannot be remediated by SVE. The ESD called for the groundwater contamination to be contained on site using extraction wells, however, biofouling of the wells reduced their efficiency and the extraction rates needed to contain the plume could not be maintained.

In 2009 an amended Record of Decision (ROD) was signed which called for in situ thermal treatment of DNAPL source areas. A pre-design investigation identified a mainly TCE source area under the central part of the building, and just immediately to the north was a PCE DNAPL source zone which extended into the parking lot. An SVE system was installed to address the TCE mass and to control vapor intrusion into the building, and ERH was used to remediate the PCE DNAPL. Angled, bored electrodes were used under the building, and sheet piles were used as electrodes in the parking lot. A few of the electrodes were completed below grade so traffic flow around the building could be maintained. The ERH system recovered approximately 4,500 pounds of contaminants, including the 1,4-dioxane which was co-located with the PCE DNAPL.

Indoor air was initially monitored using summa canisters, which showed elevated contaminant concentrations within the building soon after heating started. A well within the building was resealed, and changes were made to the HVAC

system to bring the indoor air levels to acceptable concentrations. An automated gas chromatography system was installed that provided real time air quality data from various locations within the building, and it was found that the ERH system did not contribute unacceptable levels of contaminant vapors to the indoor air throughout the remaining treatment time.

ERH was terminated in November 2016 after six months of heating based on 'multiple lines of evidence' – the treatment area was heated to and maintained at the target temperature of the boiling point of water, mass recovery rates had declined to low levels, and groundwater concentrations had decreased significantly and were no longer indicative of DNAPL presence. Post-treatment groundwater sampling, however, showed increasing concentrations PCE and its break down products in

some treatment area wells within a year after treatment was terminated. The wells affected by these elevated concentrations sometimes varied from one quarterly sampling period to the next. A limited investigation to the northwest of the treatment area located a smaller area which appears to contain PCE DNAPL, which appears to be the source of the post-ERH elevated concentrations. Continued water table elevation measurements seem to show that a water table mound sometimes exists in the area of an outfall that is between the parking lot and a wetlands, which may be the cause of the changes in which wells are affected by this dissolved phase plume coming from the northern source zone. The recontamination of the treatment area by elevated dissolved phase concentrations illustrates the importance of addressing all of the source zone to prevent recontamination.

Thermal Conductive Heating (TCH) Case Study.



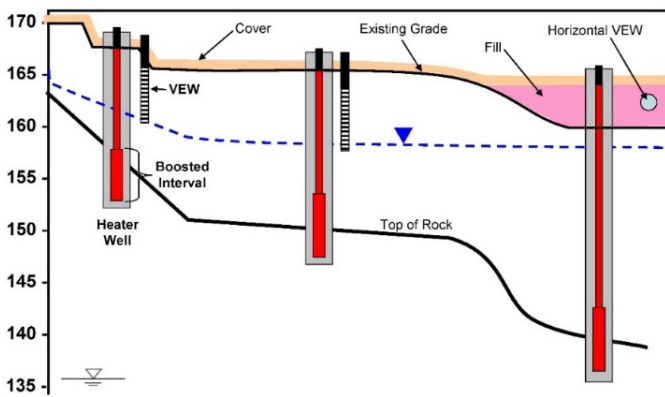
The Solvent Recovery Services of New England Superfund Site located in Southington, Connecticut, is a former waste oil recovery facility that operated from 1955 to 1991. The facility redistilled approximately 100 million gallons of solvents. Spills and discharges of solvents to lagoons during operations discharged more than 500,000 pounds of contaminants to the subsurface, which included chlorinated solvents and petroleum hydrocarbons. A dissolved contaminant plume reached downgradient municipal water supply wells, causing them to be shut down. Non-Time-Critical Removal

Actions completed in the 1990s provided hydraulic containment of the plume, but non-aqueous phase liquid (NAPL) wastes remaining on site in the overburden were a continuous source of contamination to the groundwater. Technical support efforts by ORD personnel on remedial technologies resulted in *in situ* thermal remediation being chosen by the Region in the 2005 Record of Decision (ROD) for remediation of the overburden soils. The objective of the thermal remediation was to reduce the soil concentration of contaminants to below levels that indicated the presence of NAPL.

In order to determine the area that required thermal treatment, Direct Push Technology (DPT) was used to obtain continuous soil cores which were visually inspected to determine if NAPL was present. When NAPL was present, a step out boring was completed further out from the area of known NAPL presence until the extent of the NAPL was delineated, an area of approximately 1.7 acres. TCH was chosen as the treatment technology for the low permeability soils. It was known that DNAPL was pooled on top of the bedrock, so a drilling protocol was developed to avoid the downward migration of DNAPL into bedrock during the installation of the TCH system. Sonic drilling was used, with outer

casing installed ahead of the core barrel to a depth of two feet into the bedrock. The bottom of the borehole was then checked for DNAPL, and if it was present, it was recovered. The heater casing was then installed before the outer casing was pulled. The DPT rig used for characterization had met refusal at the top of weathered bedrock, while the sonic rig used for system installation allowed the actual depth to top of bedrock to be determined and included within the treatment area. Ultimately this added another 20 percent to the total volume to be treated and caused some adjustments to the design.

The successful thermal remediation was completed in 2015, and recovered an estimated 496,400 pounds of contaminants. Final soil concentrations were significantly below concentrations that would be indicative of NAPL presence. Recent microbial data collected from the site show that remaining contaminants are being degraded, and contaminant concentrations in the hydraulic control wells have decreased substantially. A cap was constructed on the site in 2017, and the site, along with the adjacent former railway right of way, has been converted to trails, as part of the “Rails to Trails” program for former railroad lines.



Due to the large volume of contaminants present, the treatment area was divided into two phases, and heating of the second phase was started only after the mass of contaminants being recovered from the first phase had decreased from the peak extraction rate. This extended the total operational time, but allowed a smaller above ground treatment system to be used. The recovered vapors were destroyed in a thermal oxidizer on site. Despite the use of a phased startup of heating, the large amount of petroleum hydrocarbons entering the thermal oxidizer caused combustion in the pre-oxidizer heat exchanger which damaged the daisy wheel at the oxidizer inlet. To avoid future occurrences, an organoclay filter was added after the oil-water separator, a temperature sensor was added at the oxidizer inlet, and the heat exchanger temperature set point was reduced. During the five weeks that it took to repair the system, heating was discontinued, but vapor extraction was continued with the use of the backup vapor phase granular activated carbon that was already on site.