The Science behind Low Temperature Thermal Remediation

Eva Davis, PhD
US EPA
Kerr Environmental Research Center

Potential advantages of low temperature thermal remediation

- Less energy use equates to less green house gas emissions which makes thermal technologies more ‘sustainable’
- Less volatilization means that vapor collection & aboveground treatment is not necessary
- Enhanced rate of hydrolysis
- Enhanced rate of biodegradation
- Lower costs due to less energy use & no vapor collection & treatment

EPA United States Environmental Protection Agency

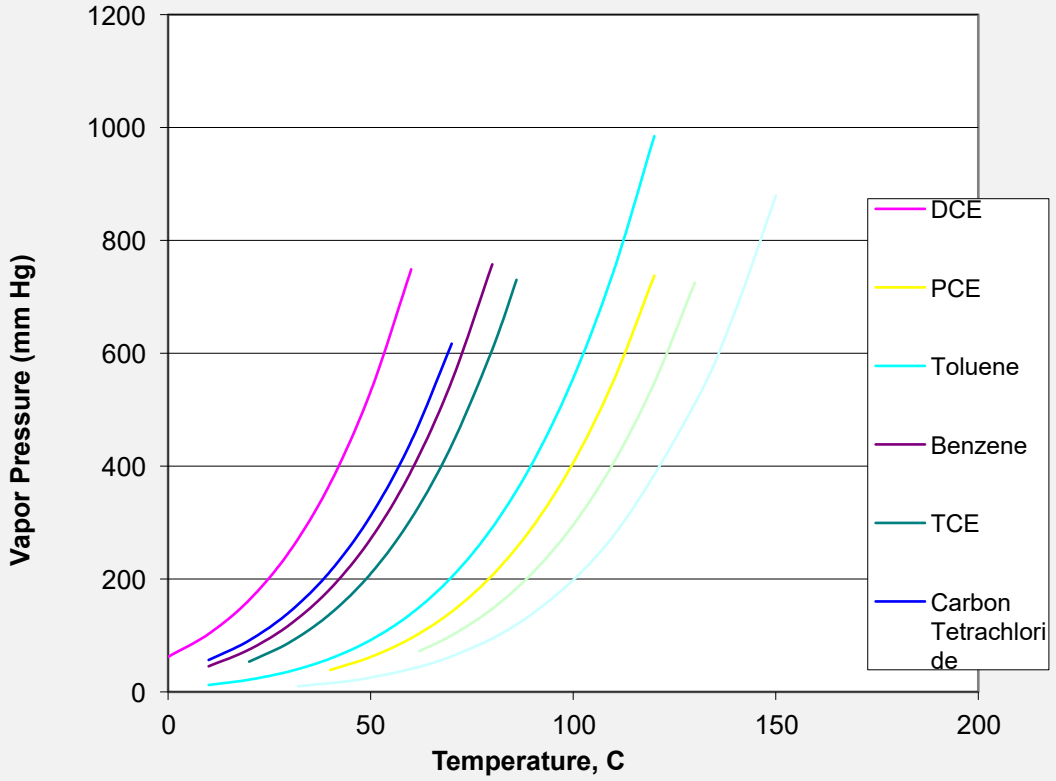
Sustainability is much more than green house gas emissions

- From the environmental perspective, we use Life Cycle Analysis (LCA) to evaluate sustainability
- LCA must be done on a site by site basis
- LCA to compare remedial alternatives must be based on achieving the same endpoint
  - If a less stringent endpoint is used for low temperature thermal, then a direct LCA comparison cannot be made
- Environmental impact of contaminant mass left behind must be taken into account in LCA

Vapor pressure increases for VOCs are moderate over the small temperature range

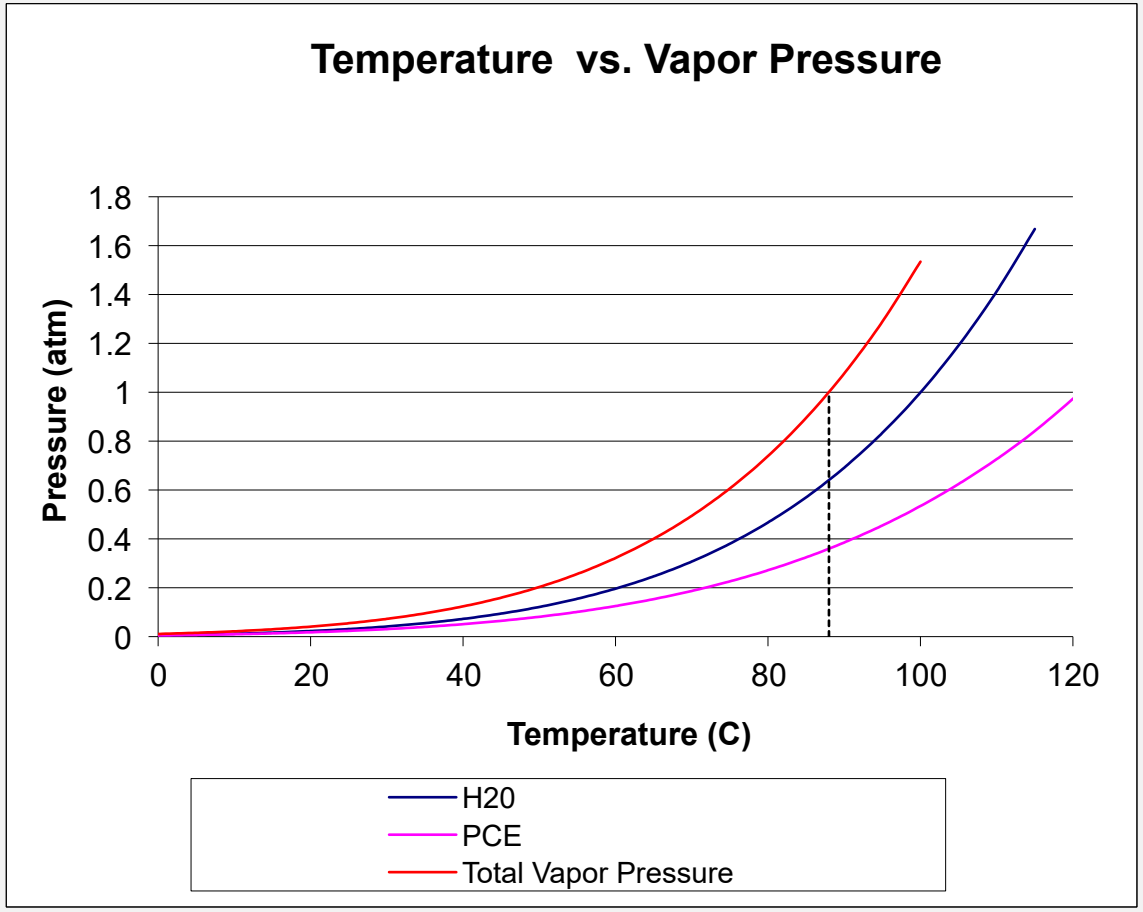
- Even at ambient temperatures VOCs produce vapors that can cause Vapor Intrusion (VI) into building
- Even these small to moderate increases in vapor pressure can create additional risk of VI & fugitive emissions to the atmosphere

Figure 1. Vapor Pressure vs. Temperature



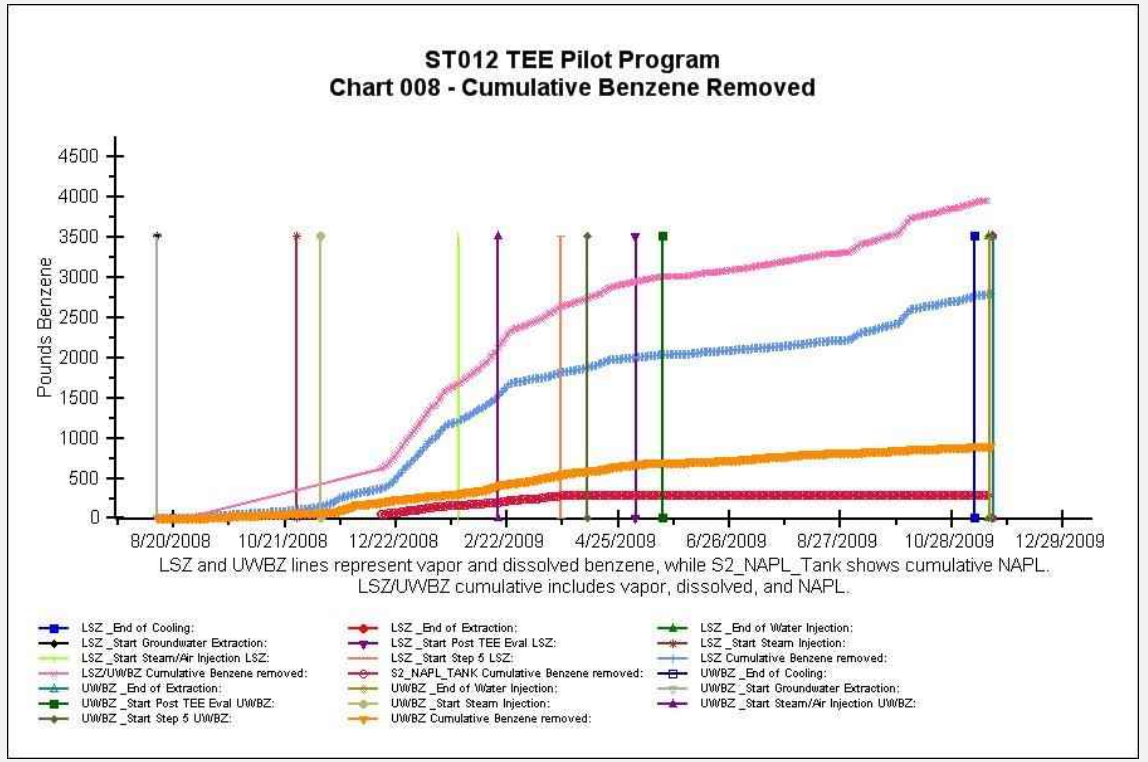
Co-boiling of NAPL when present with water

- Co-boiling occurs when the total vapor pressure from 2 liquids equals the total pressure
- The co-boiling temperature for a VOC & water is always less than that of water alone
- VOC NAPLs can be eliminated by raising the temperature to the co-boiling point with water
- When the temperature reaches the boiling point of water, a volatile, immiscible phase liquid cannot exist in the presence of groundwater



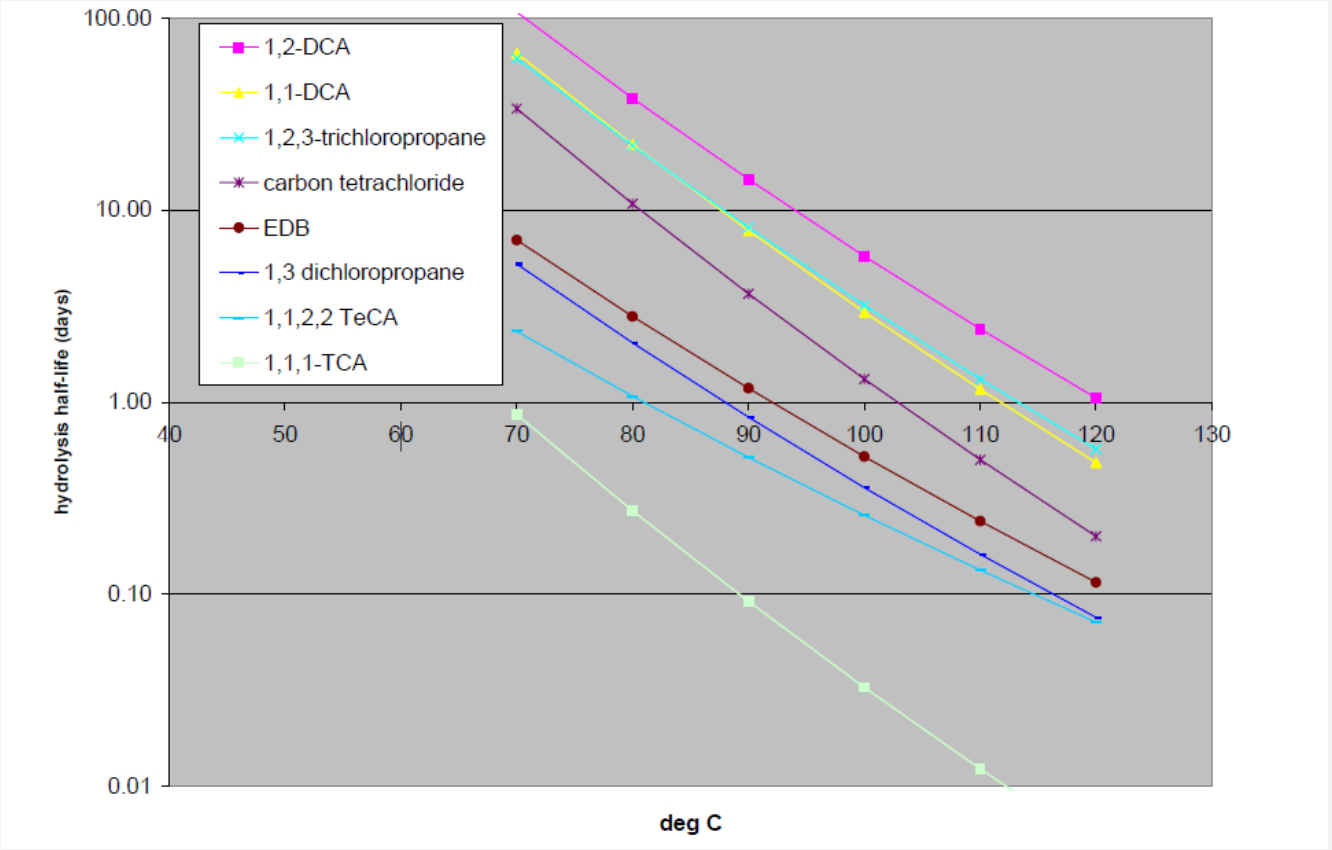
Thermal Enhanced Extraction of Jet Fuel Pilot Scale Demonstration

- Thermal technology used was steam injection – less steam (energy) injected
- Compared benzene dissolution before & after, insufficient reduction in dissolved phase benzene to meet remedial goals
- Theoretical evaluation showed that energy needed to reduce dissolved phase concentrations similar to conventional thermal remediation energy requirements



Hydrolysis rates increase with temperature

- Hydrolysis rates, given in terms of half lives, increase exponentially as a function of temperature
- Hydrolysis occurs in dissolved phase, NAPL must dissolve for this to occur
- Even at 100C hydrolysis rates are still measured in terms of days



After Beyke & Crownover, 2006

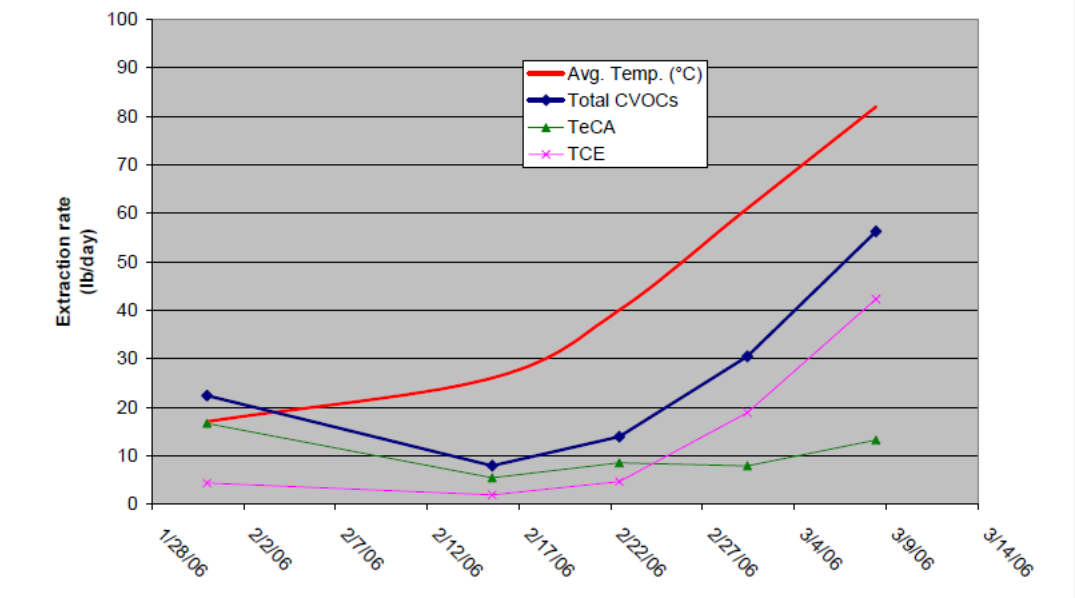
Half life comparison: Hydrolysis vs Evaporation

- Evaporation half life at ambient temperatures is far less than the hydrolysis rate at 100C
- Chlorinated ethenes (PCE, TCE, DCE) do not hydrolyze
- Ethanes do not mineralize by these processes, product is a toxic compound that does not hydrolyze furtherer

Contaminant	MCL	Hydrolysis Half Life at 100°C (days)[e]	Daughter Product	Evaporation half life 25°C (minutes)[h]
Methylene chloride	5 µg/l	35	mineralizes	18 - 25
Carbon Tetrachloride	5 µg/l	1.3	mineralizes	29[i]
1,1-Dichloroethane	5 µg/l[a] 50 µg/l[b]	2.9	acetaldehyde	
1,2-Dichloroethane	5 µg/l	6	Ethylene glycol	
1,1-Dichloroethene	7 µg/l	100,000		~ 25
cis-1,2-Dichloroethene *trans*-1,2-Dichloroethene	70 µg/l[c] 100 µg/l	20,000,000		19.4[i] 24[i]
1,1,1-Trichloroethane	200 µg/l	0.09	1,1-Dichloroethene	20 +/- 3
1,1,2-Trichloroethane	5 µg/l	39	1,1-Dichloroethene	35[i]
Trichloroethene	5 µg/l	5,000		21 +/- 3
1,1,1,2-Tetrachloroethane	70 µg/l[d]	5	Trichloroethene	~ 60
1,1,2,2-Tetrachlroethane	1 µg/l[a,b]	0.3	Trichloroethene	~ 50
Tetrachloroethene	5 µg/l	2,000,000		~ 25

Thermal Remediation of 1,1,2,2-Tetrachloroethane

- 1,1,2,2-TeCA hydrolyzes to TCE, half life at 100C is 0.3 days (7.2 hrs)
- TeCA is more toxic than TCE, but TCE is still highly toxic!
- Hydrolysis allowed a less toxic, more volatile compound to be recovered, does not eliminate the need for vapor extraction & treatment
- 1,1,2,2-TeCA was still being recovered – all of it was not hydrolyzed



Beyke & Crownover, 2006

EPA United States Environmental Protection Agency

Thermal Enhancement of Biodegradation

- Generally true that raising the temperature of a microcosm in the lab by 10C will double the biodegradation rate
- For CVOCs, maximum temperature for biodegradation ~30 – 35C, so at best can quadruple the biodegradation rate
- Biodegradation occurs in the aqueous phase, NAPL must dissolve for it to occur
- When treating petroleum hydrocarbons, aerobic degradation may be desired which requires oxygen

EPA United States Environmental Protection Agency

Thermally Enhanced Biodegradation Case Study

- From thermal vendor website for a confidential client:
- Contaminants were xylene, ethylbenzene, toluene
- Goal was to reduce soil concentrations of all COCs to below 1000 mg/kg
  - Soil goal is greater than initial concentration for many thermal remediations
- Temperature goal was 30 – 35C, technology was Thermal Conductive Heating
- Air injected to enhance aerobic degradation
  - Injected air will flow through largest soil pores, most of soil will not be contacted by additional oxygen
  - Injected air will volatilize these COCs

Water Solubility of Xylene as a function of temperature

- Biodegradation occurs in the aqueous phase
- IUPAC-NIST Solubilities Database
- Xylene solubility does not significantly increase over the temperature range that can be used in an attempt to increase biodegradation rates, which is a limiting factor on biodegradation

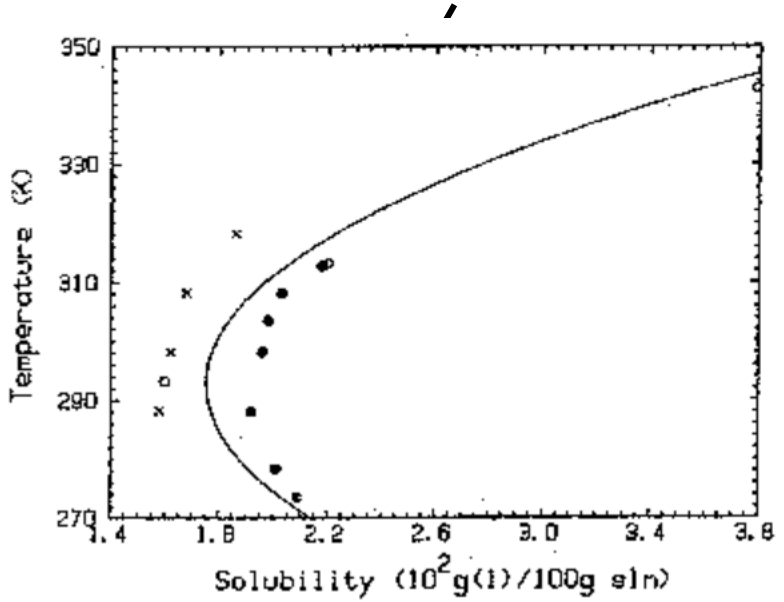
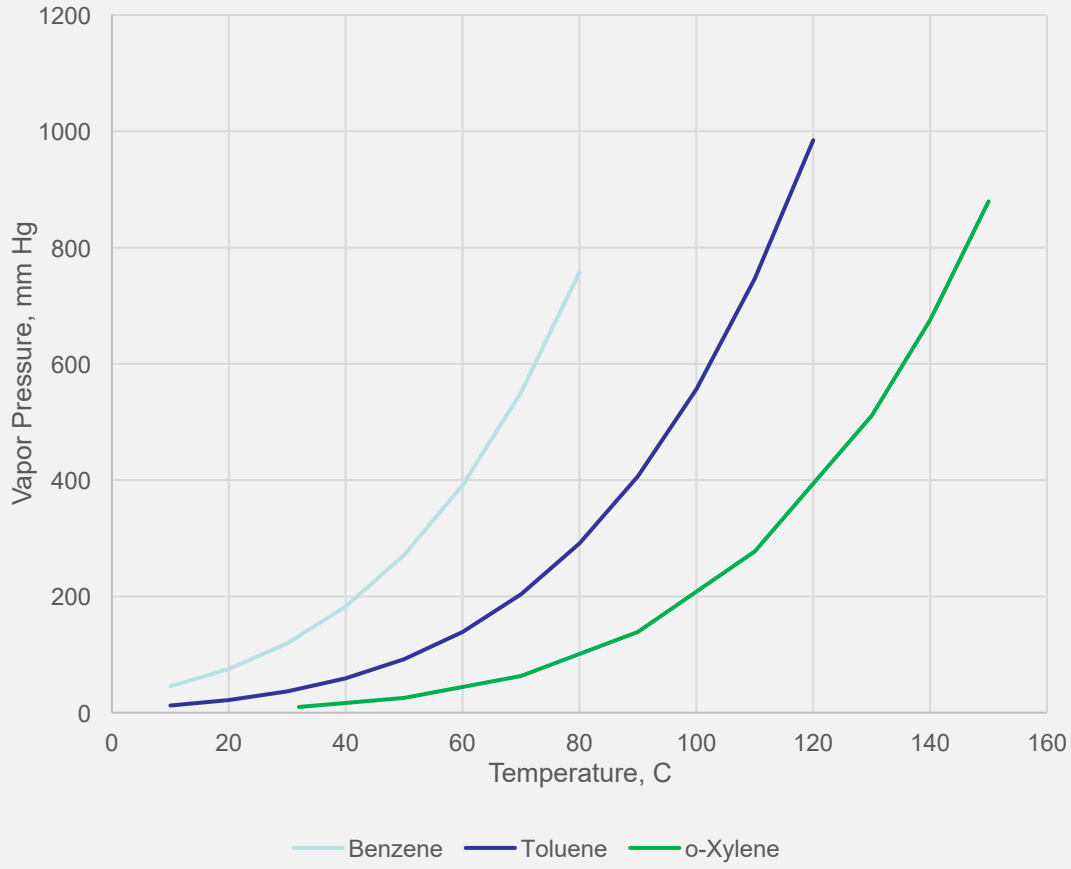


FIGURE 1. Solubility of m-xylene in water; selected data: ref 2 (•); ref 9 (○); ref 12 (x). Solid curve fitted to "Best" values (Table 2).

Vapor Pressures as a function of temperature

- Xylene's boiling point – 144C
- Xylene vapor pressure at ambient temperatures is less than 10 mm Hg
- Minimal increase in vapor pressure over the temperature range used here
- Even at these moderate temperatures, the SVE system collected 3,650 pounds of xylene in the vapor phase



EPA United States Environmental Protection Agency

Goals of the remediation were achieved, but . . .

- 18 months of operation were required – significantly longer than would be required for a conventional thermal remediation at 100C
  - Longer remedial time frame can have LCA impacts including societal impacts
- Vapor extraction & treatment system were part of the system
- NAPL would likely remain at soil concentrations of 1000 mg/kg
- Groundwater would not be protected at these soil concentrations
  - Xylene concentration in soil to protect groundwater - 1.6 mg/kg
  - Dissolved xylene concentrations would likely exceed the MCL
  - Environmental impacts due to contamination remain

EPA United States Environmental Protection Agency

Are total costs reduced by using low temperature thermal remediation?

- Low temperature thermal remediation of source zones is only marginally less costly than conventional thermal remediation
- There is less certainty in treatment performance and life cycle costs with low temperature thermal remediation
- Macbeth, T., M. Truex, T. Powell, and M. Michalsen, Combining low-energy electrical resistance heating with biotic and abiotic reactions for treatment of chlorinated solvent DNAPL source areas, ESTCP Project ER-200719, December 2012.

EPA United States Environmental Protection Agency

Conclusions on Low Temperature Thermal Remediation

- At these temperatures, VOCs will still produce significant vapors that should be captured
- Much greater concentration reductions can be achieved in shorter times by using higher temperatures
- Use of low temperature thermal remediation may require a lowering of the standard for success
- Cost reductions may only be incremental