# Overview of In-Situ Thermal Remediation Technologies

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## Introduction

- Technology Overview
- Governing Processes
  - Contaminant properties
  - Subsurface conditions
- Technology Applications


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# Thermal Technologies

- Heat facilitates contaminant mobilization, dissolution, removal, destruction and/or degradation
  - Volatilize liquid contaminants – the vapors are captured in the vadose zone and treated at the surface.
  - Lower the viscosity of long-chain hydrocarbons – liquid phase contaminants are removed by standard pumping systems.
  - Increase chemical reaction rates – biotic and abiotic degradation
- Thermal technologies include:
  - Steam Enhanced Extraction (SEE) } ≤ 100ºC
  - Electrical Resistive Heating (ERH) } ≤ 100ºC
  - Thermal Conductive Heating (TCH or ISTD) } Can exceed 100ºC
  - Radio Frequency (RF) Heating } Can exceed 100ºC
  - In Situ Smoldering (STAR) } Can exceed 100ºC

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# Thermal Technologies

- Typically applied in NAPL source areas
- Implemented in conjunction with Soil Vapor Extraction (SVE) systems to contain and recover vapors

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# Contaminant Types

- Volatile Organic Compounds (VOCs)
  - Aromatic and aliphatic compounds
  - Chlorinated VOCs (PCE, TCE, Carbon Tet., etc.)
- Semi-volatile Organic Compounds (SVOCs)
  - Polynuclear aromatic hydrocarbons (PAHs)
  - Phthalates
  - Tars (includes combinations of heavy organics)
  - Explosives (HMX, RDX, TNT)
- Polychlorinated biphenyls (PCBs)
- Pesticides
- Metals and Other Inorganics

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# Applicable Contaminants

- Volatile Organic Compounds (VOCs)
  - Aromatic and aliphatic compounds
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# Why Thermal?

- Heavy organic compounds not amenable to other technologies (e.g., coal tar)
- Complex mixtures of organic contaminants (e.g., mixed drum sites)
- To overcome matrix diffusion limitations

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# Think Thermal When…

✓ You have a Source Zone, or Hot Spots
✓ Site is Heterogeneous and/or Low in Permeability
✓ Stringent Cleanup Levels Must be Achieved, Quickly (or you just need to remove a lot of mass)
✓ Excavation is Ruled Out or Impractical

## Thermal is Especially Well Suited if:

✓ The Treatment Zone is Deep
✓ There's a Mixture of Contaminants
✓ The Site is Complex, and/or
✓ Long-Term O&M is Too Costly

Courtesy of TerraTherm

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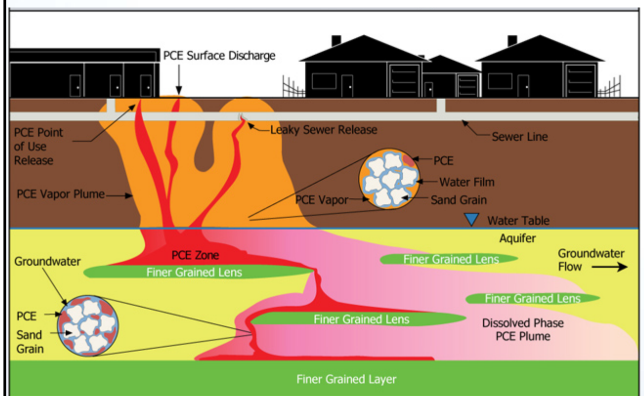
# Matrix Diffusion




Source: http://www.washoecounty.us/water/pce_background.htm

Interbedded sandstone and shale

Sale, et al (2006)

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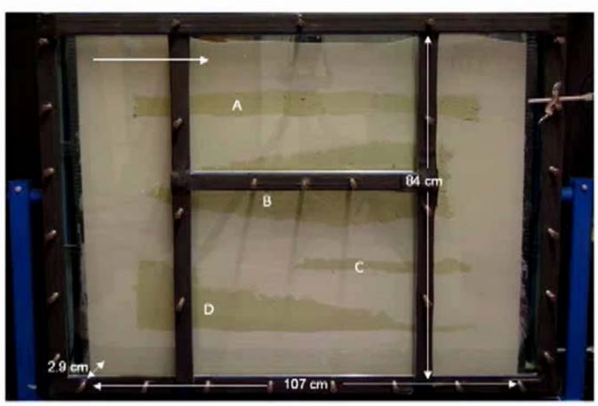
# Matrix Diffusion




Courtesy of Tom Sale, Colorado State University

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# Equilibrium Properties

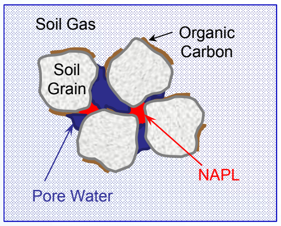
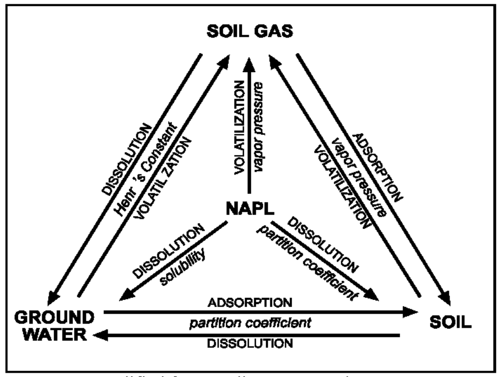



**Figure 2-2: Phase Equilibrium Mechanisms and Properties of Chlorinated Solvents**




Source: Modified from Huling, S.G., and J.W. Weaver 1991

From U.S. EPA (2004)

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# Heat-Induced Changes

**Table 2-3. Thermal Effects on Chlorinated Solvent Properties**

| Fate and Transport Property | Effect as Temperature Increases |
|---|---|
| Liquid density | Decreases moderately (less than 100 percent) |
| Vapor pressure | Increases significantly (10 to 20 fold) |
| Liquid viscosity | Decreases significantly until boiling point and drops markedly upon conversion from liquid to vapor |
| Vapor viscosity | Increases slightly as vapor temperature increases |
| Diffusivity | Increases |
| Solubility | Increases as temperature increases |
| Henry's constant | Increases (more likely to volatilize from water) |
| Partition coefficient | Decreases (less likely to partition to organic matter in soil) |
| Biological degradation | Increases (may decrease at higher temperatures) |
| Abiotic degradation | Increases |

Source: Derived from Davis 1997

From U.S. EPA (2004)

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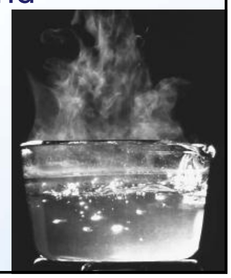
# Heat-Induced Changes

- CVOCs typically have a 5 to 7 times greater vapor pressure at 50˚C than at 10˚C.
- Liquid viscosity generally decreases by 1 percent per ˚C (up to its boiling point).
- CVOCs occupy larger volume in the gas phase than as liquid, resulting in expansion and advective flow.



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# Heat-Induced Changes

- The viscosity of a chlorinated solvent as a gas is generally 2 orders of magnitude less than that of a liquid.
- Viscosity and diffusivity rates (in air) allow for more efficient flow of chlorinated solvents as a gas than as a liquid.
- Increasing the temperature from 10 to 100˚C will increase the diffusion in the vapor phase by approximately 50 percent (Davis 1997).

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# Heat-Induced Changes

**Table 2-4. Heterogeneous Azeotropes of Common Chlorinated Solvents**

| Chlorinated Solvent | Pure Substance Boiling Point (°C) | Heterogeneous Azeotrope with Water | |
|---|---|---|---|
| | | Boiling Point (°C) | Molar Concentration of Chlorinated Solvent in Liquid/Vapor (%) |
| PCE | 121 | 88 | 83 |
| TCE | 87 | 73 | 94 |
| 1,1,2-TCA | 114 | 86 | 84 |
| CT | 77 | 67 | 96 |
| CF | 61 | 56 | 97 |
| MC | 40 | 39 | 99 |

Source: Gmehling and Onken 1977

From U.S. EPA (2004)

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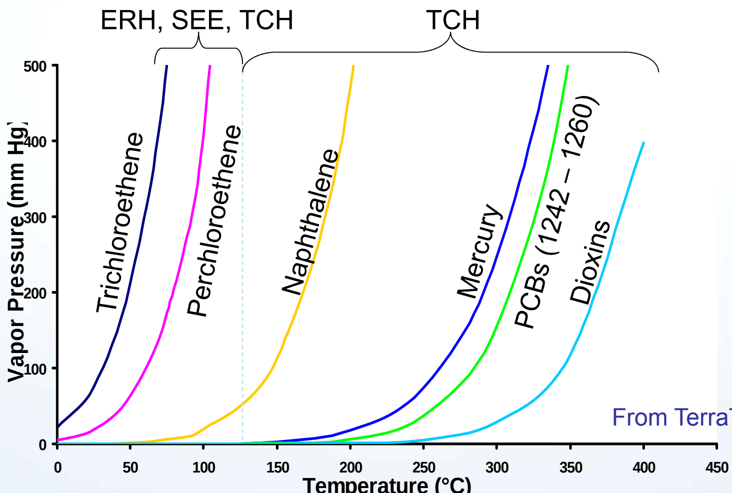
## Vapor Pressure vs. Temperature




From TerraTherm, Inc.

Vapor pressures increase exponentially during heating

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# Physical Processes/Changes (below 120ºC)

| Component property | Oil based LNAPL | Chlorinated solvents | Creosote | Coal tar | PCB | Comment |
|---|---|---|---|---|---|---|
| Vapor pressure increase factor | 20-80 | 20-100 | 20-300 | 20-300 | 2000 | Abundance of data in literature |
| Solubility increase factor | 2-100? | 1.5-3 | 10-1000 | 10-1000 | 10-1000 | Chlorinated solvent less affected than larger hydrocarbons |
| Henry's constant increase factors | | 10-20 | 0-10 | 0-10 | 0-10 | Data absent for most compounds, some decrease? |
| Viscosity reduction factor | 2 to 100+ | 1.3-3 | 5-10 | 20-100+ | 3-100 | The higher initial viscosity, the more reduction |
| Interfacial tension reduction factor | <2 | <2 | 2-5 | 1-5 | <5 | Typically not dramatic effect (less than factor 2) |
| Density reduction (%) | 10-20 | 10-20 | 10-20 | 10-20 | 10-20 | Note that DNAPL may become LNAPL |
| $K_d$ (reduction factor) | ? | 1-10 | 5-100 | 5-100 | NA | Estimates based on limited data |

**Note:** Abiotic and biological reactions not listed

Courtesy of TerraTherm

Udell (1989, 1991, 1993, 1996)
Davis (1997, 1999)
Imhoff et al. (1997)
Sleep and Ma (1997)
Heron et al. (1998, 2000)
Stegemeier and Vinegar (2001)

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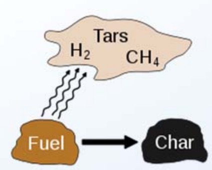
# Degradation Enhancement

- Abiotic Mechanisms:
  - Hydrolysis
  - Hydrous Pyrolysis/Oxidation (HPO)
  - Oxidation
  - Pyrolysis


Thermal Oxidation




Pyrolysis

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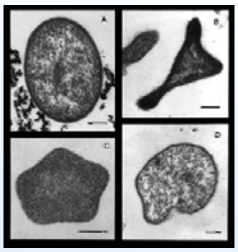
# Degradation Enhancement

- Biological Degradation:
  - For every 10˚C increase in temperature, there is roughly a two-fold increase in biological activity (EPA 1997).
  - Most microbes benefit from elevated temperatures at the fringe of a thermal treatment area.
  - Extremely high temperatures may sterilize soils of some microbes.



Thermophiles from Yellowstone National Park

Source: http://planetquest1.jpl.nasa.gov

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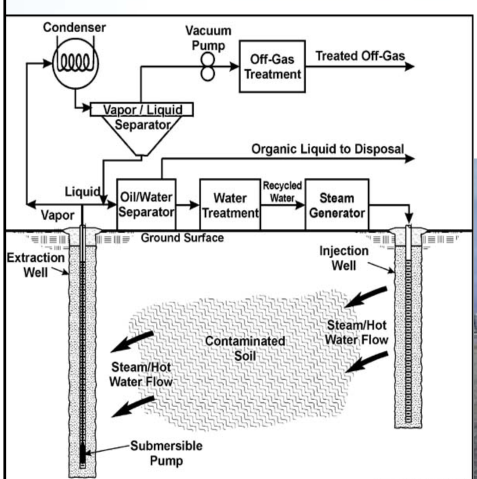
# Steam Enhanced Extraction




Steam injected into source zone to dissolve, vaporize and mobilize contaminants that are recovered using SVE

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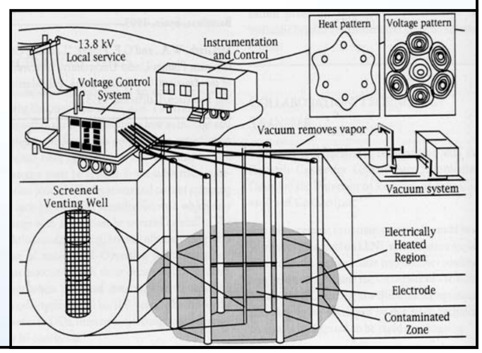
# Electrical Resistive Heating

- Application of electrical current through subsurface generates heat
- Steam generation dissolves, vaporizes and mobilizes contaminants which are recovered using SVE

From www.thermalrs.com

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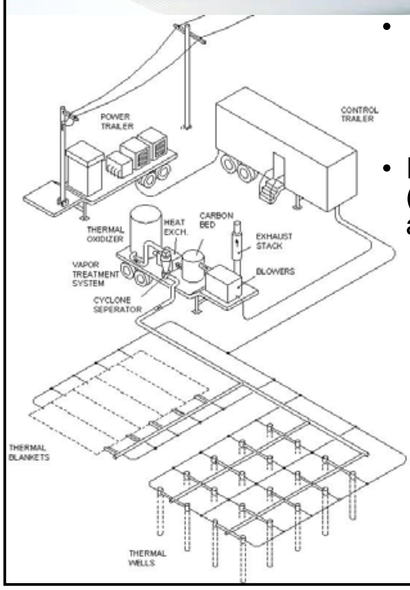
# In Situ Thermal Desorption




- Application of heat using:
  - array of vertical heater elements and vacuum wells; or
  - a surface blanket of heaters and vacuum shroud at surface (less common)
- ISTD can achieve high temperatures (>500 ºC) - causes contaminant oxidation and pyrolysis

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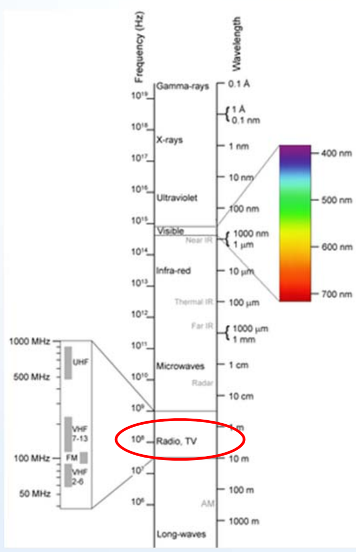
# Radio Frequency Heating




- Antennae emit high-frequency radio waves into the subsurface:
  - Absorbtion of RF energy generates heat
  - Some conductive heating also occurs
- Can achieve temperatures >100ºC

From www.ecologia-environmental.com

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# Engineering Considerations

- Investment in additional Site Characterization to reduce volumes requiring aggressive treatment can pay BIG dividends
- Pilot-scale studies can provide valuable site-specific engineering design insights to support full-scale deployment (may not be needed at 'simple' sites)
- Insulating covers are essential to prevent heat losses and water infiltration

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## Engineering Considerations

- Materials of construction: High concentrations of chlorinated solvents may result in high temp, low pH waste stream requiring hastalloy
- Phase changes in the ground and in above ground capture/treatment units:
  - Multi-component wastes like coal tar and creosote can result in naphthalene crystallization and plugging in non heat-traced piping
  - Condensation of unrecovered vapors in the subsurface can redistribute contamination

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## Engineering Considerations

- High subsurface GW flow regimes:
  - May hamper achieving requisite temperature and prevent achieving cleanup goals
  - Additional cost to divert and/or dewater
- Temperature serves as an important metric for in-situ process control
- Fractured rock remediation is possible

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# Engineering Considerations

- Power requirements can be significant
  - Coordinate with local electric utility during feasibility evaluation
  - May require electric infrastructure upgrades (transformers, power lines)
- Potential for short circuiting of steam
- Potential impacts on subsurface structures or utilities
- "Hot sampling"

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# Hot Sampling





From TRS

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# References


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  http://www.epa.gov/tio/download/remed/epa542r04010.pdf
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- U.S. EPA (1998), "In Situ Thermal Treatment and Thermal Enhancement Technologies: Notes on an Engineering Forum Roundtable Discussion"

  http://www.epa.gov/tio/tsp/download/stamnes.pdf


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