United States Environmental Protection Agency

Thermal Remediation

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2023 Superfund Report

Table 3: Source Remedies Selected Most Frequently in Recent Decision Documents (FY 2018-2020)

Selected Remedy	Number	Percent
Treatment	**86**	**50%**
In Situ Treatment	58	34%
Thermal Treatment	18	10%
Soil Vapor Extraction	13	8%
Solidification/Stabilization	13	8%
Chemical Treatment	10	6%
Bioremediation	9	5%
Amended Caps	4	2%
Ex Situ Treatment	46	27%
Physical Separation	24	14%
Solidification/Stabilization	12	7%
Recycling	5	3%
Source P&T	4	2%
Thermal Treatment	2	1%
Containment/Disposal	**115**	**67%**
Disposal (off-site)	89	52%
Containment (on-site)	67	39%
MNA/MNR/EMNR	**4**	**2%**
Institutional Controls	**119**	**69%**
Other	**35**	**20%**

- Percentages based on 172 source decision documents issued in FYs 2018 through 2020.

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Presentation Outline

- Important mechanisms for enhanced recovery of organic contaminants during in situ thermal remediation
- Description of the commonly used thermal technologies
- Brief case studies for each of these technologies
- Q & A

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In Situ Thermal Remediation

Applications

- Aggressive technologies:
  - Generally applied to Source Zones to Recover NAPL
  - Only in situ technologies applicable to NAPLs
- Applicable to VOCs and SVOCs
- Applicable in wide variety of hydrogeologic conditions
  - Simple and highly heterogeneous lithology
  - Above and below water table
  - Sites with surface structures
  - Fractured bedrock

Expected Outcome in Porous Media

- Large percentage of mass recovered
- Orders of magnitude reductions in soil and groundwater concentrations
- Orders of magnitude reduction in mass flux to downgradient plume
- P&T or Monitored Natural Attenuation (MNA) effective for remaining dissolved phase & downgradient plume

Mechanisms for Enhancing Recovery of VOCs & SVOCs by Thermal Remediation

- Increasing the temperature:
  - Exponential increase in vapor pressure
    - For VOCs, vapor pressure increases more than an order of magnitude going from ambient temperature to 100°C
  - Exponential decrease in viscosity of water and NAPL
    - Most significant for viscous NAPLs
  - Increased solubility of contaminants
    - Increased rate of solubilization
  - Decreases adsorption
    - May also increase desorption rate

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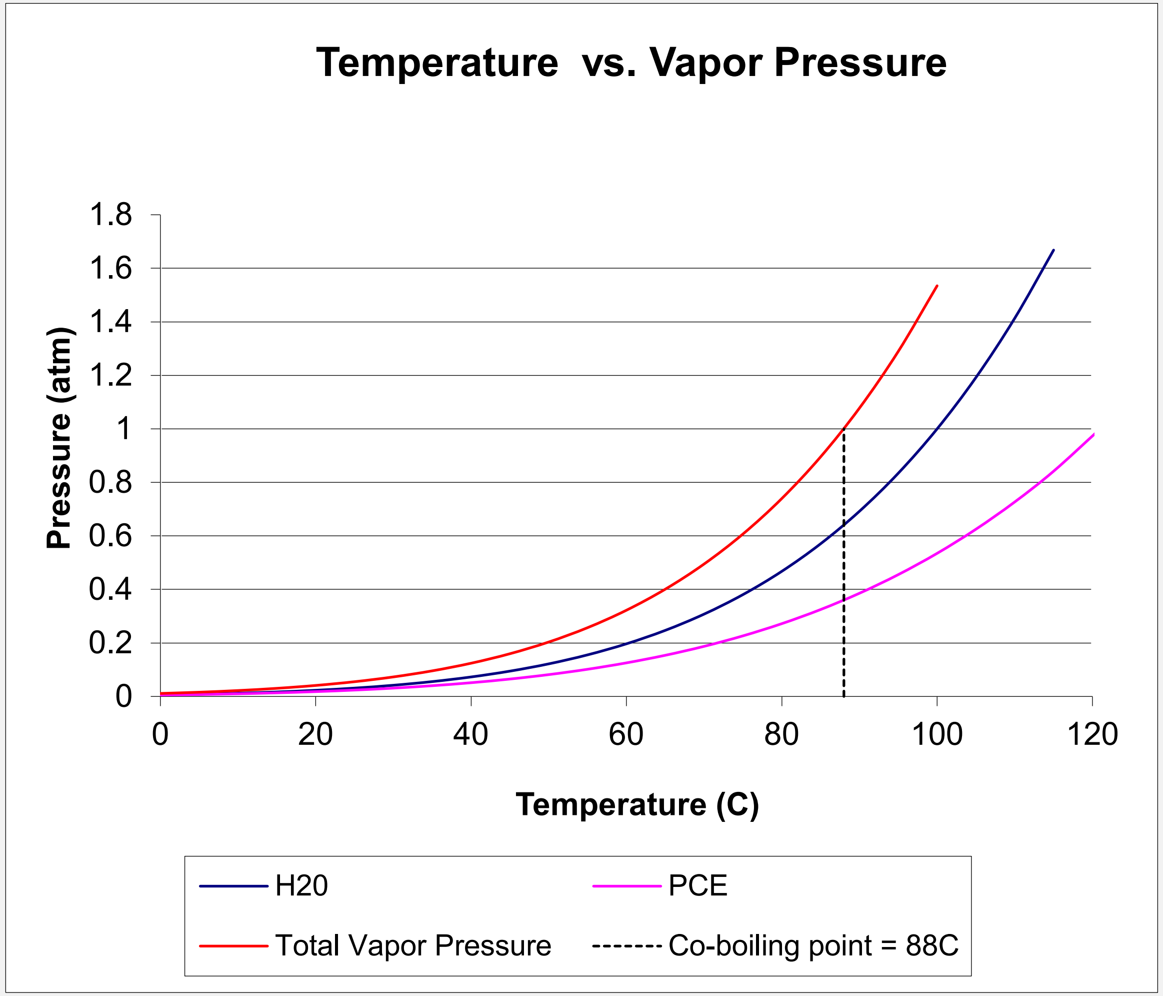
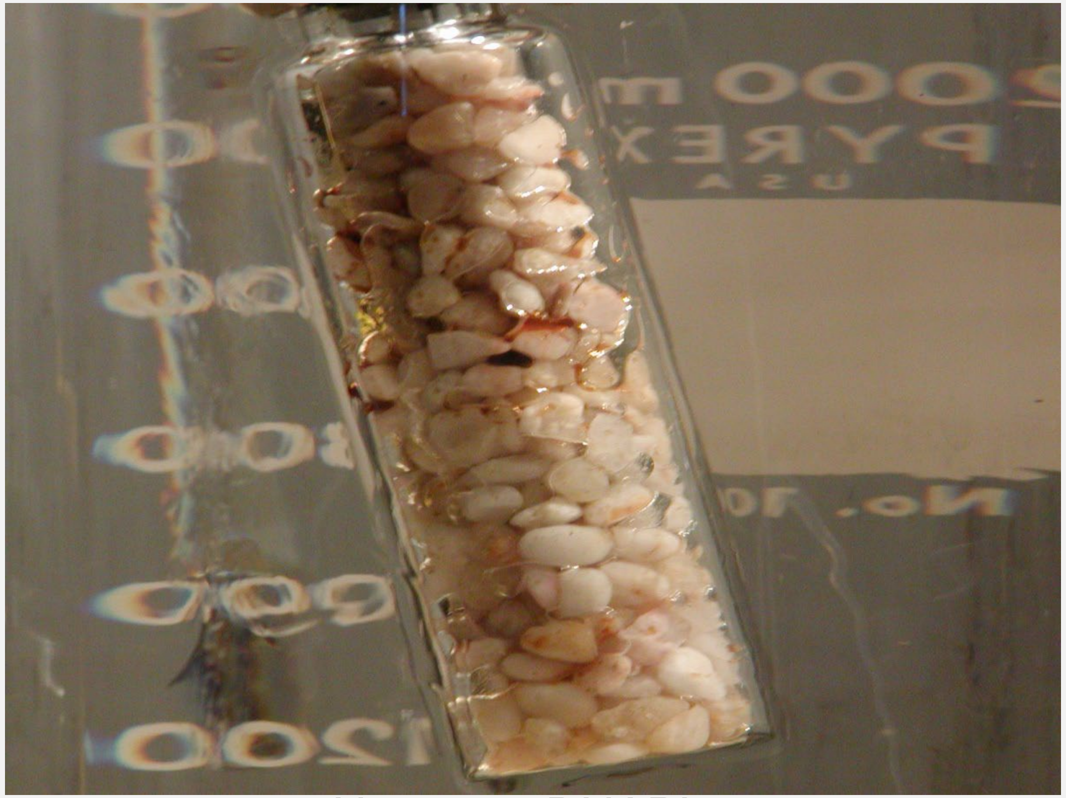
Co-boiling of VOC NAPLs during Thermal Remediation



- When a VOC NAPL is present with groundwater:
- Boiling occurs when the combined vapor pressure from the 2 liquids equals the local pressure
  - Thus, a VOC NAPL boils at temperatures less than the boiling point of water
  - For PCE, which has a boiling point of 121C, DNAPL/groundwater boils at 88C

The boiling point of water is recommended target temperature when remediating VOCs

- When the temperature reaches the co-boiling point with water, a volatile NAPL cannot exist in the presence of groundwater
- Dissolved, adsorbed phase remain, groundwater concentration likely orders of magnitude above MCLs
- Continue heating to boiling point of water to recover dissolved & absorbed contaminants



Note less DNAPL seems present at bottom of vial

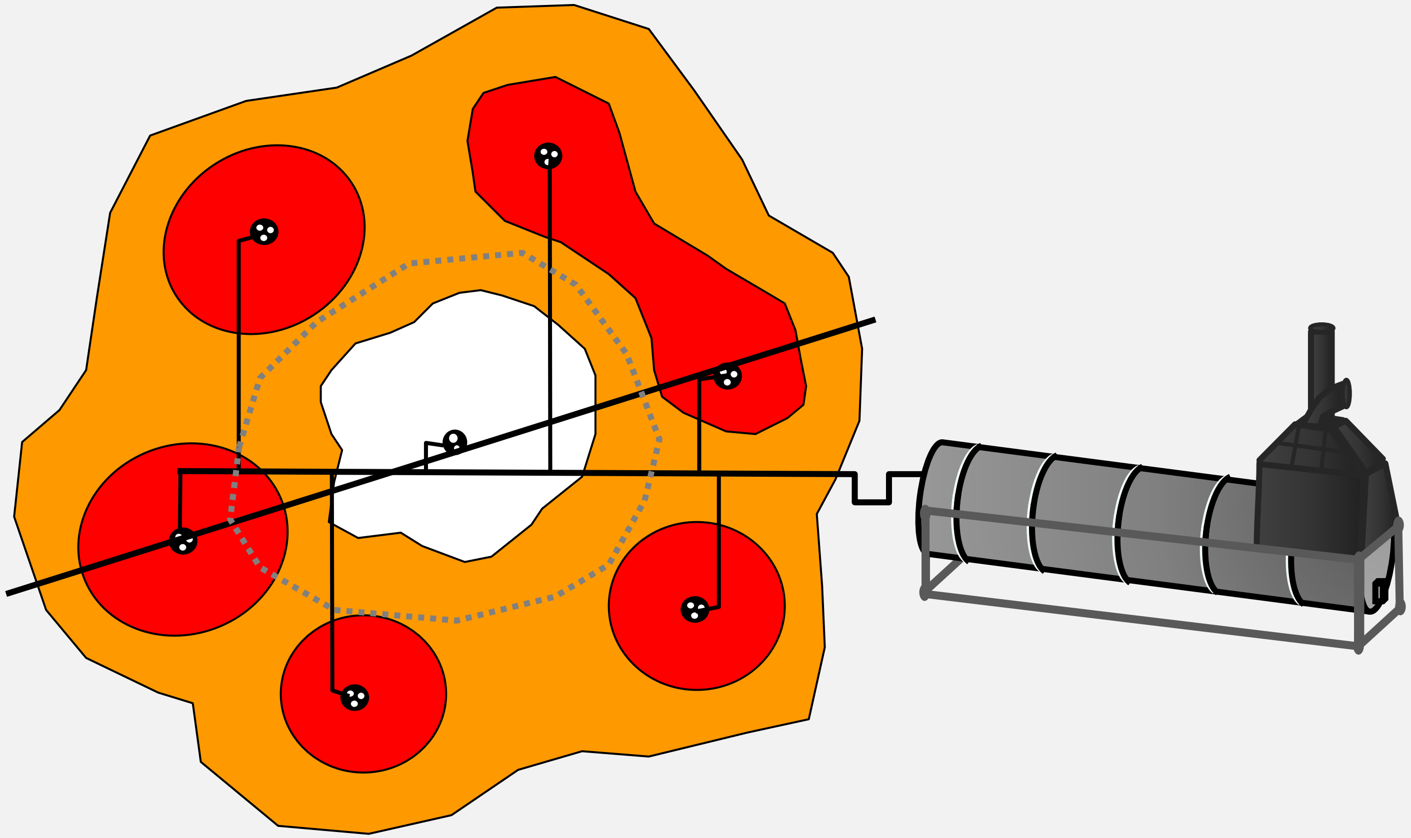
Thermal Technologies

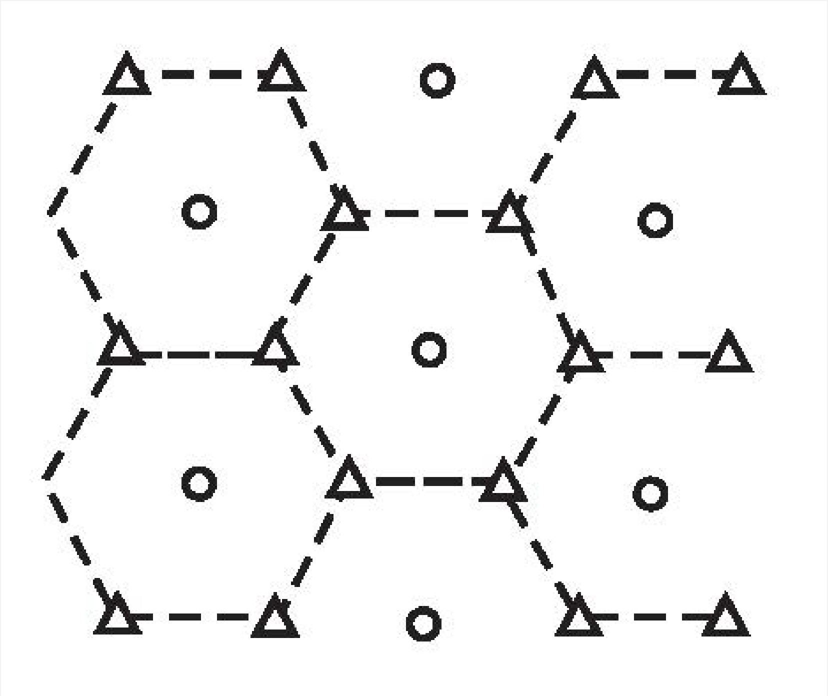
- Three main technologies in use today:
  - Steam Enhanced Extraction (SEE)
  - Electrical Resistance Heating (ERH)
  - Thermal Conductive Heating (TCH)
- Differ in the means by which energy is added to the subsurface
- Innovative thermal technology: Self-Sustaining Treatment for Active Remediation (STAR)
- All thermal technologies include:
  - Thermocouples in the subsurface to monitoring temperature
  - Extraction of vapors, steam using vacuum extraction
  - Treatment of vapors and steam above ground

Steam Enhanced Extraction (SEE)

- Additional recovery mechanism of displacement
- Steam injected, groundwater, NAPL and vapors extracted
- Steam flows in more permeable strata, less permeable zones heated by conduction
  - Minimum hydraulic conductivity for steam injection 10^{-5} cm/sec (silty sands)
- Pressure cycling (reducing steam injection, while continuing extraction) helps to recover contaminants from low permeability zones
- Most appropriate for large, deep sites – significantly greater well spacings
- Applicable to highly permeable sands & gravels with high groundwater flow rates
- Best way to get large amount of energy into the subsurface

Preferred SEE approach: Surround NAPL with injection wells, central extraction well

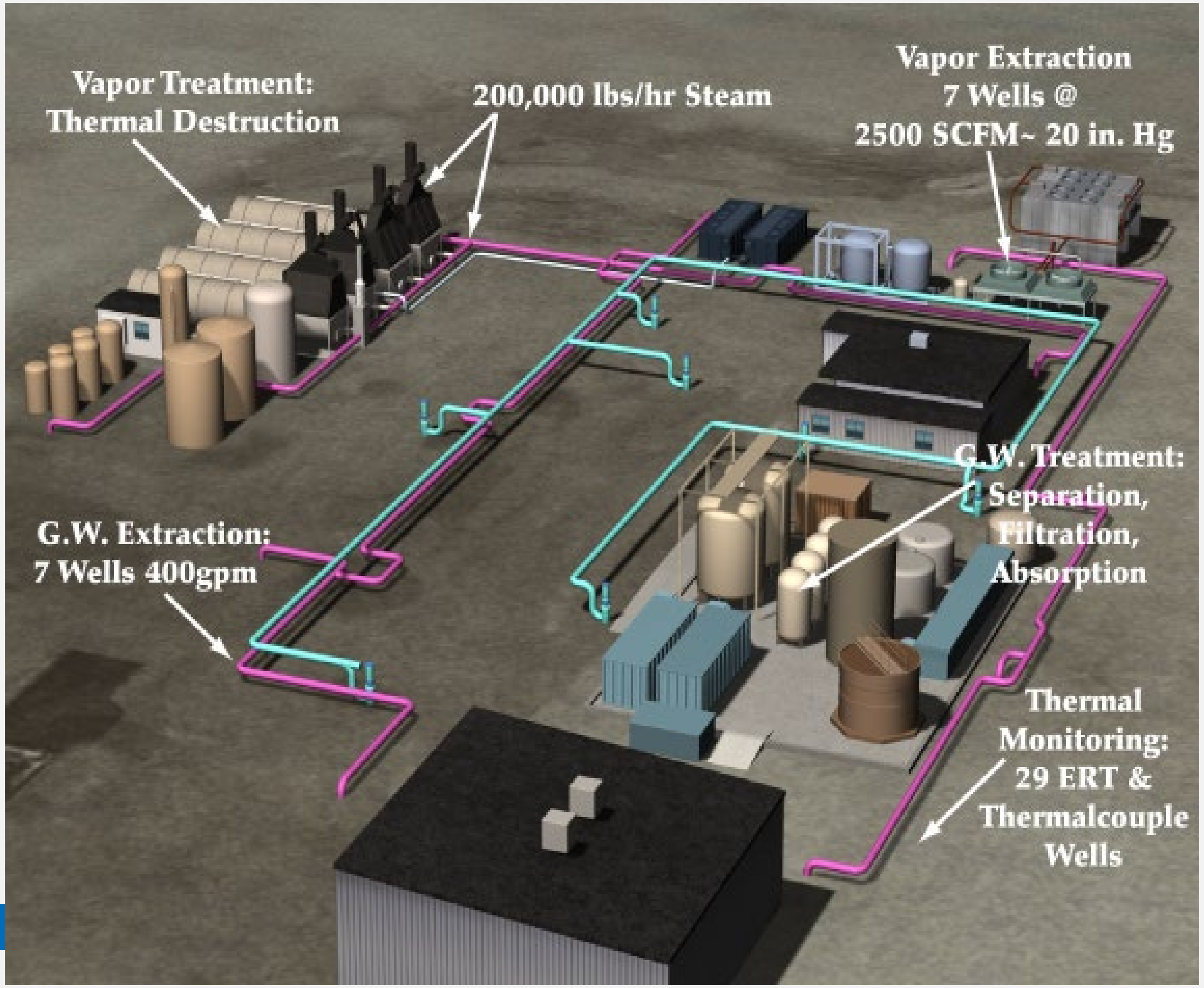




Seven Spot Pattern

Southern California Edison Steam Injection Remediation

Visalia, CA



- From May 1997 to June 2000, ~ 660 million pounds of steam were injected
- ~ 1.33 million pounds of wood preservative chemicals recovered
- Enhanced biological degradation with air injection
- Continued operation of P&T through 2003

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Visalia Post Steam Injection Site Chronology

- P&T: 1975 – 1990
  - ~ $1M/yr
- Steam injection: 1997 – 2000
- Continued P&T: 2000 - 2004
- Remedial Action Report and Final Close Out Completed: 2009
- Visalia Pole Yard De-Listed from National Priorities List: 2010

- Total SEE Project Cost - $21.5 million
  1996 through mid-2001
- Unit Cost per Cubic Yard of Soil Treated
  - Actual Costs $57
  - With Lessons Learned $38
- Comparative Cost per Gallon of Creosote Removed
  - Pump and Treat $26,000
  - Steam Injection $130
- Estimated Time to Remove 1.2 M lbs of Creosote
  - Pump and Treat 3,250 years
  - SEE 3 years

Beede Waste Oil Superfund Site

Plaistow, NH

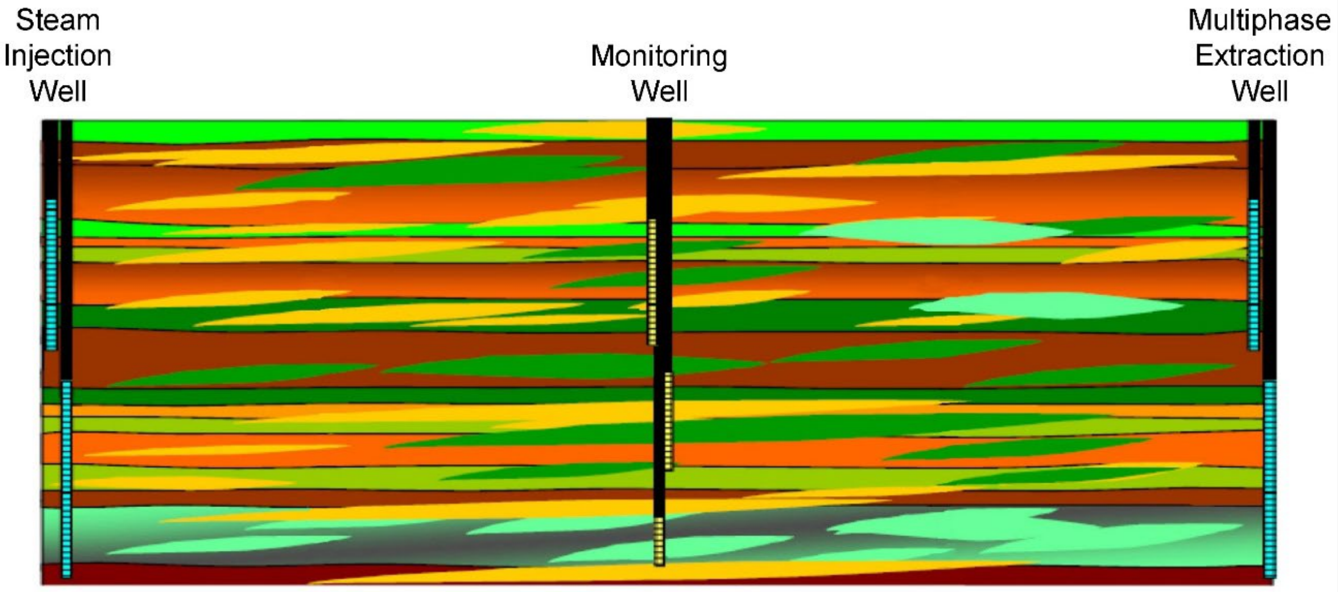
- 2 Phases of SEE completed
- Waste oil, CVOCs, PCBs
- ~95 M lbs steam injected
- ~54,000 gallons NAPL recovered
- Strict soil cleanup criteria were met

Phase 1 See

Former Williams Air Force Base Site ST-12

Mesa, AZ

- Jet Fuel spill, reached depths of 240 feet below ground surface
- Highly heterogeneous soil strata did not stop downward migration of fuel, but low permeability zones trapped LNAPL below water table as the water table subsequently rose
- Water table at ~160 ft bgs at time of SEE



Williams Air Force Base Remedial Actions

Previous Remedial Actions

- SVE in vadose zone, ~370,000 gallons of JP-4 removed since 2005
- Attempt to use horizontal wells to recover LNAPL was unsuccessful
- Steam pilot scale demonstrated that SEE can effectively recover LNAPL

Thermox used to destroy fuel vapors from the SVE system

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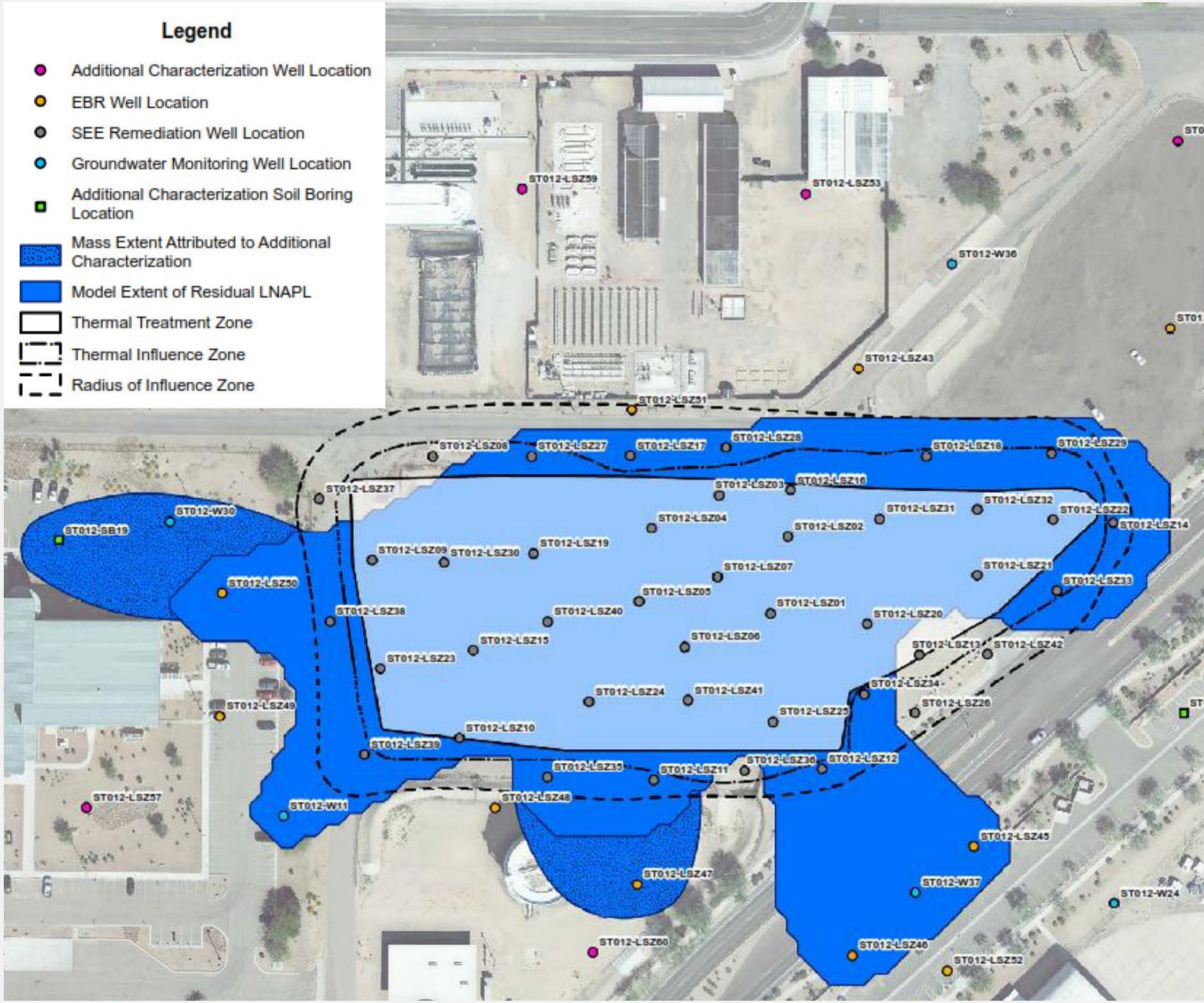
Williams AFB: Largest, Deepest SEE Remediation

- 2013 RODA selected SEE to recover jet fuel from below the water table
- ~410,000 yd^3 treatment area
  - 160 – 240 ft bgs
- >300 M lbs of steam injected
- >2.5 M lbs of petroleum hydrocarbons recovered, half as LNAPL, most of the rest as vapors

Complication to Remedial Efforts: NAPL outside of treatment area

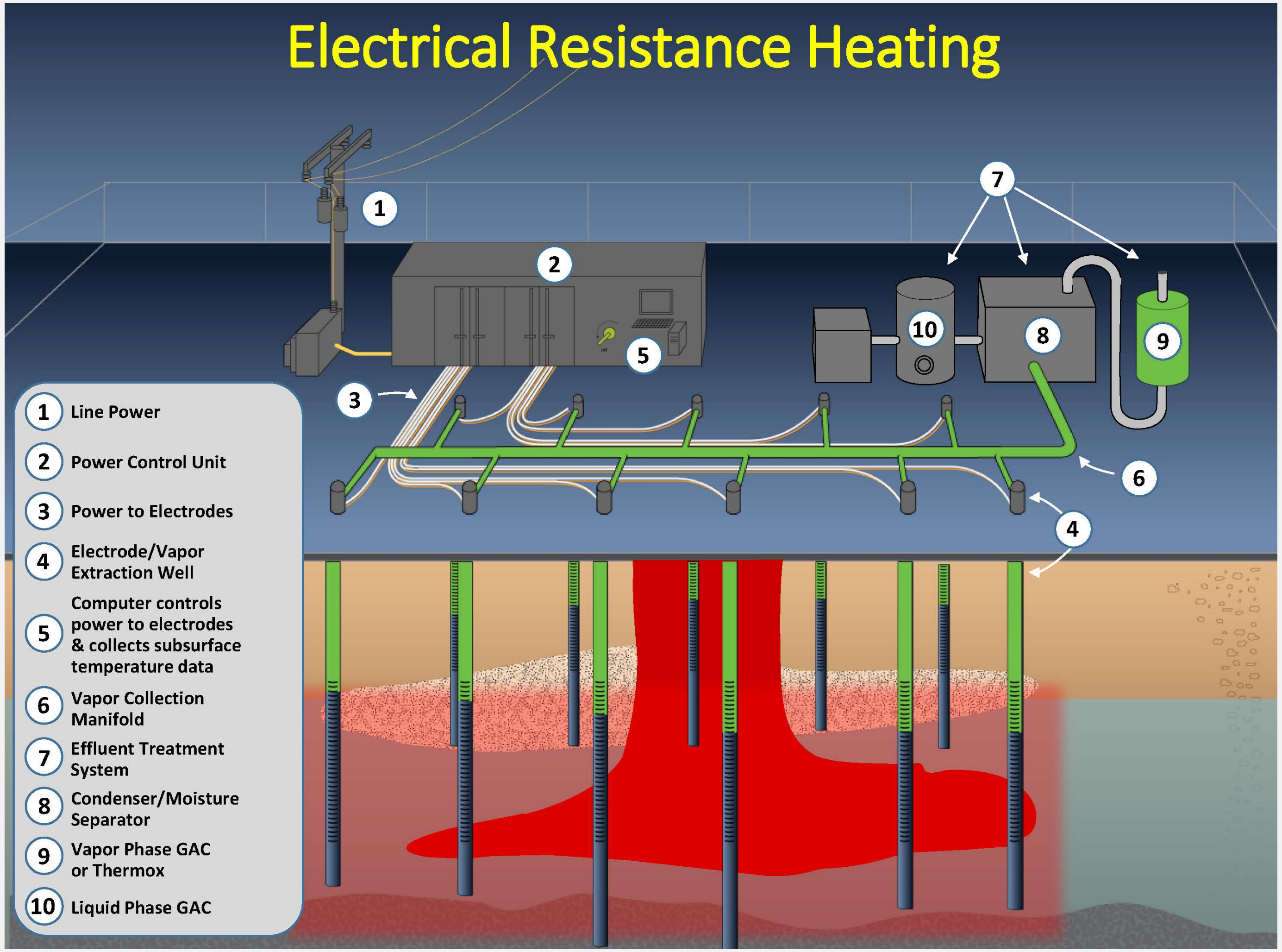
Light blue – SEE treated area

Dark blue - LNAPL extent



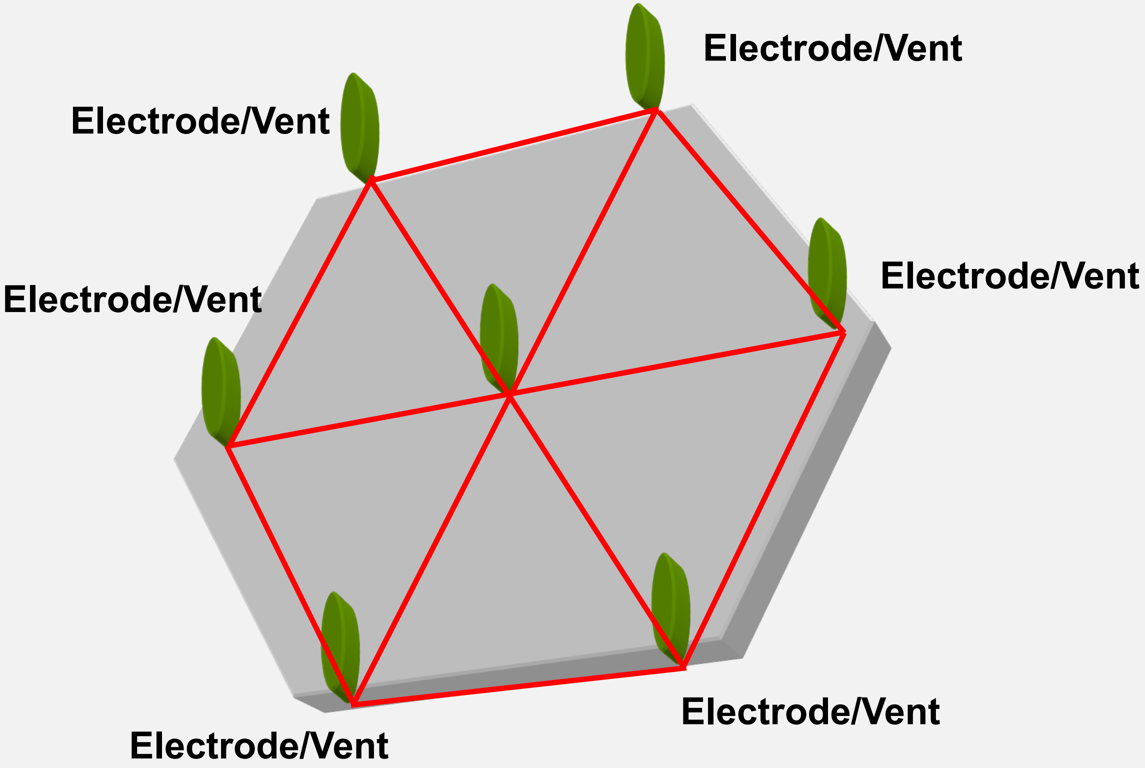
Electrical Resistance Heating (ERH) for Remediation

- Electrodes installed in subsurface
- Alternating current applied to electrodes
- Current carried between electrodes by water in pore spaces
- Resistance of soils to current flow produces heat
- Full scale application uses 3 phase current



How Does Electrical Heating Work ?

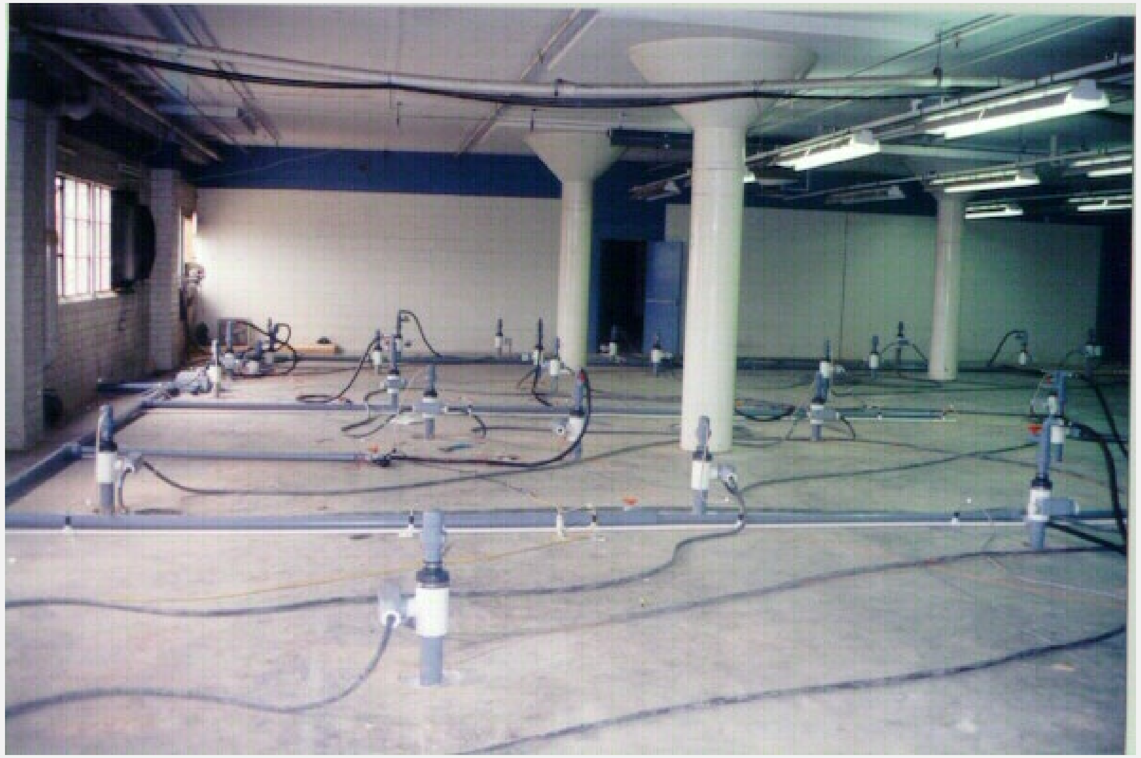
- Vertical or angled electrodes in triangular/hexagonal array
- A typical array diameter is 20 – 40 feet
- Typically 100 – 600 volts applied per electrode
- Steam temperatures reached in ~ 3 – 6 months
- Vapor extraction at electrodes or MPE wells between electrodes



Electrical Heating of Soils

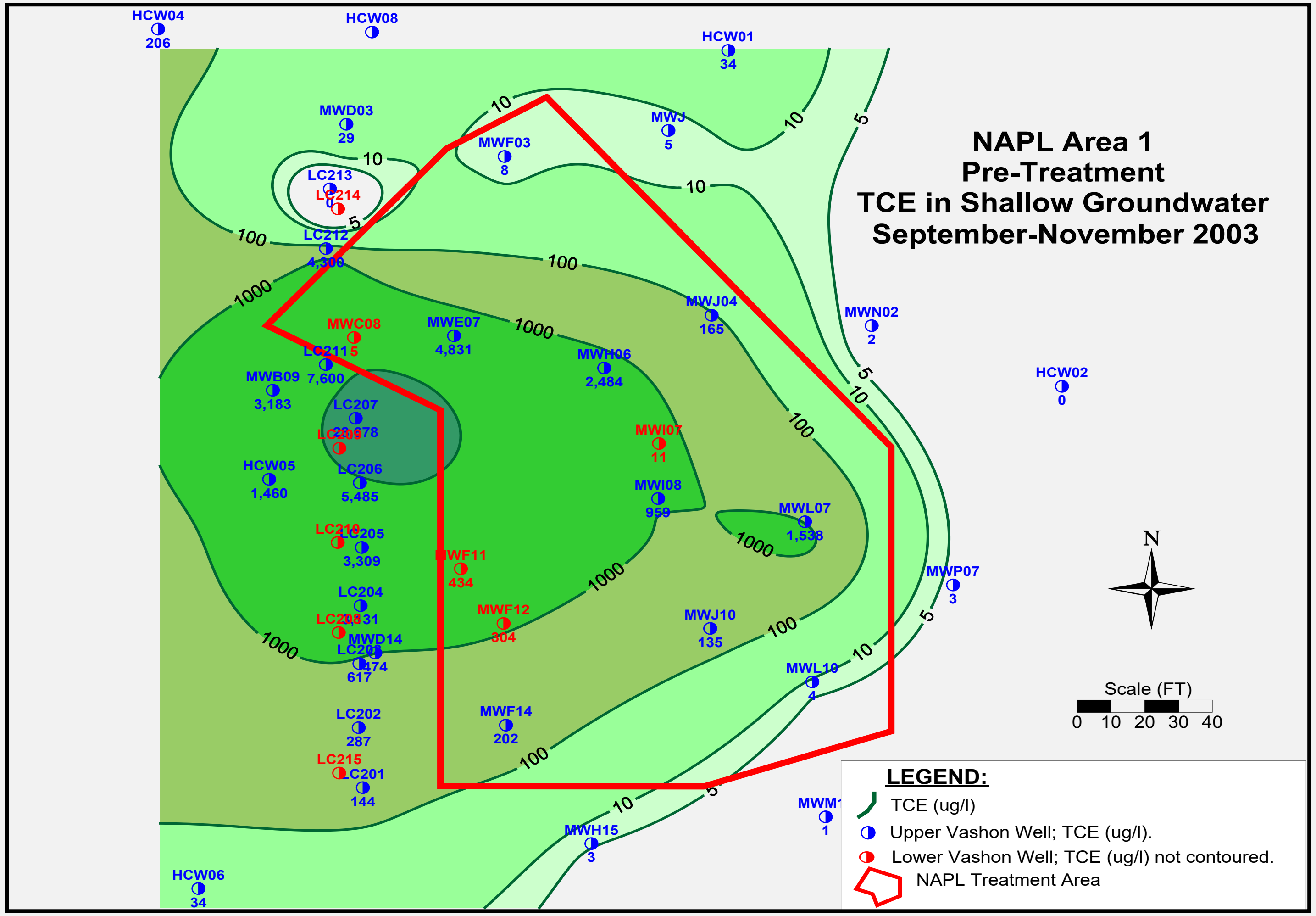
- Heating dependent on electrical conductivity of water in pore space: low permeability zones often heated first due to higher cation content, less groundwater flow
- Works above and below water table
- Temperature limited to boiling point of water as water in the pores is needed to conduct current
- Contaminants collected as vapors
- Where groundwater flow rate is high, groundwater also extracted, can extract NAPL
- Challenged by groundwater flow rates greater than 1 ft/day
  - Works very well in low permeability soils

ERH Under Building



Fort Lewis Army Logistics Center
Fort Lewis, WA

- Waste oils & chlorinated solvents
  - ~ 6,600 lbs CVOCs & 88,500 lbs TPH recovered by ERH
- Highly permeable soils, high groundwater flow rate
- Upgradient groundwater extraction used to reduce flow rate through thermal treatment area
- Remediation was a mass removal exercise, treated to 'diminishing returns'



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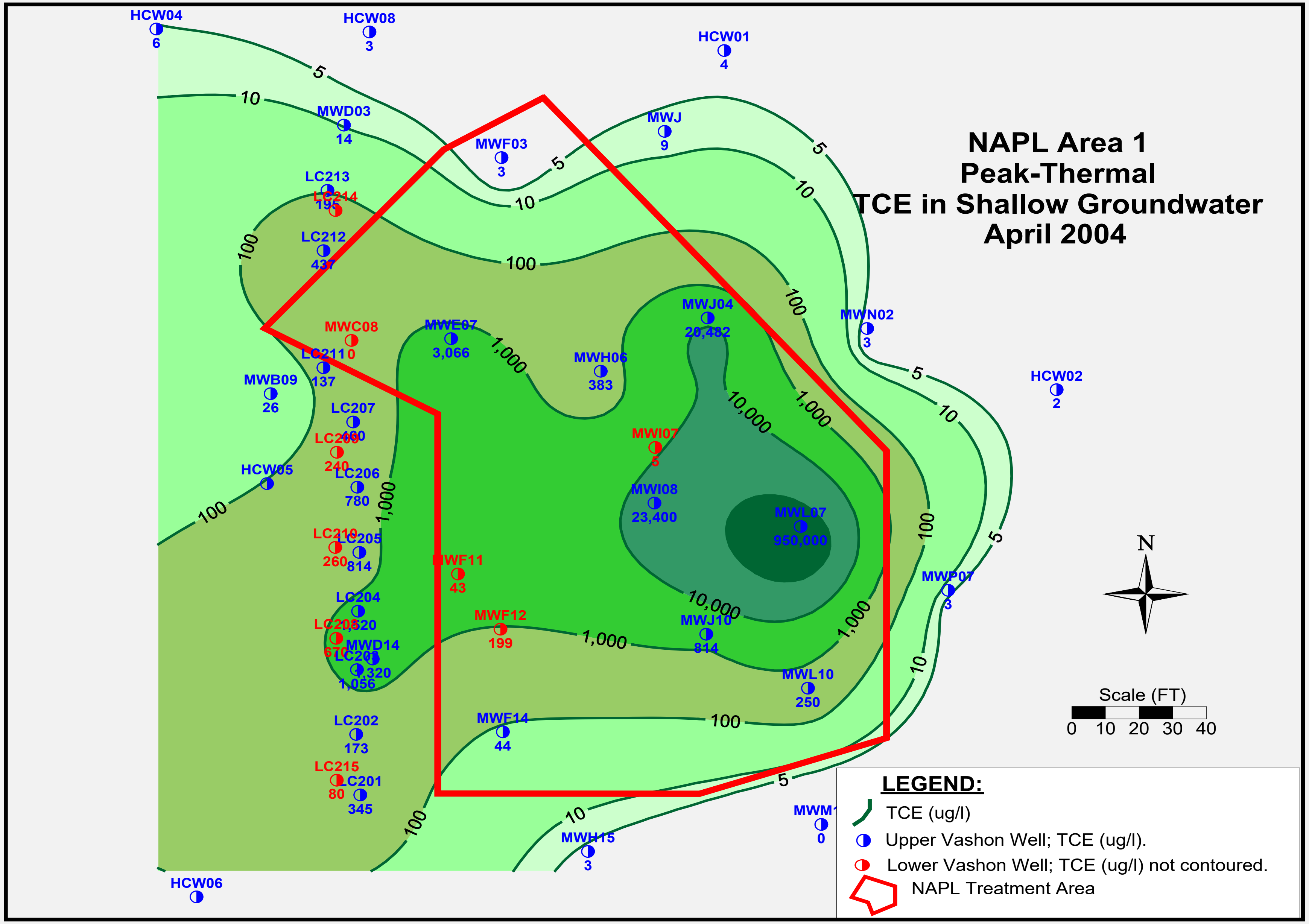
Ft Lewis

Maximum TCE concentrations during heating > 100,000 ug/L



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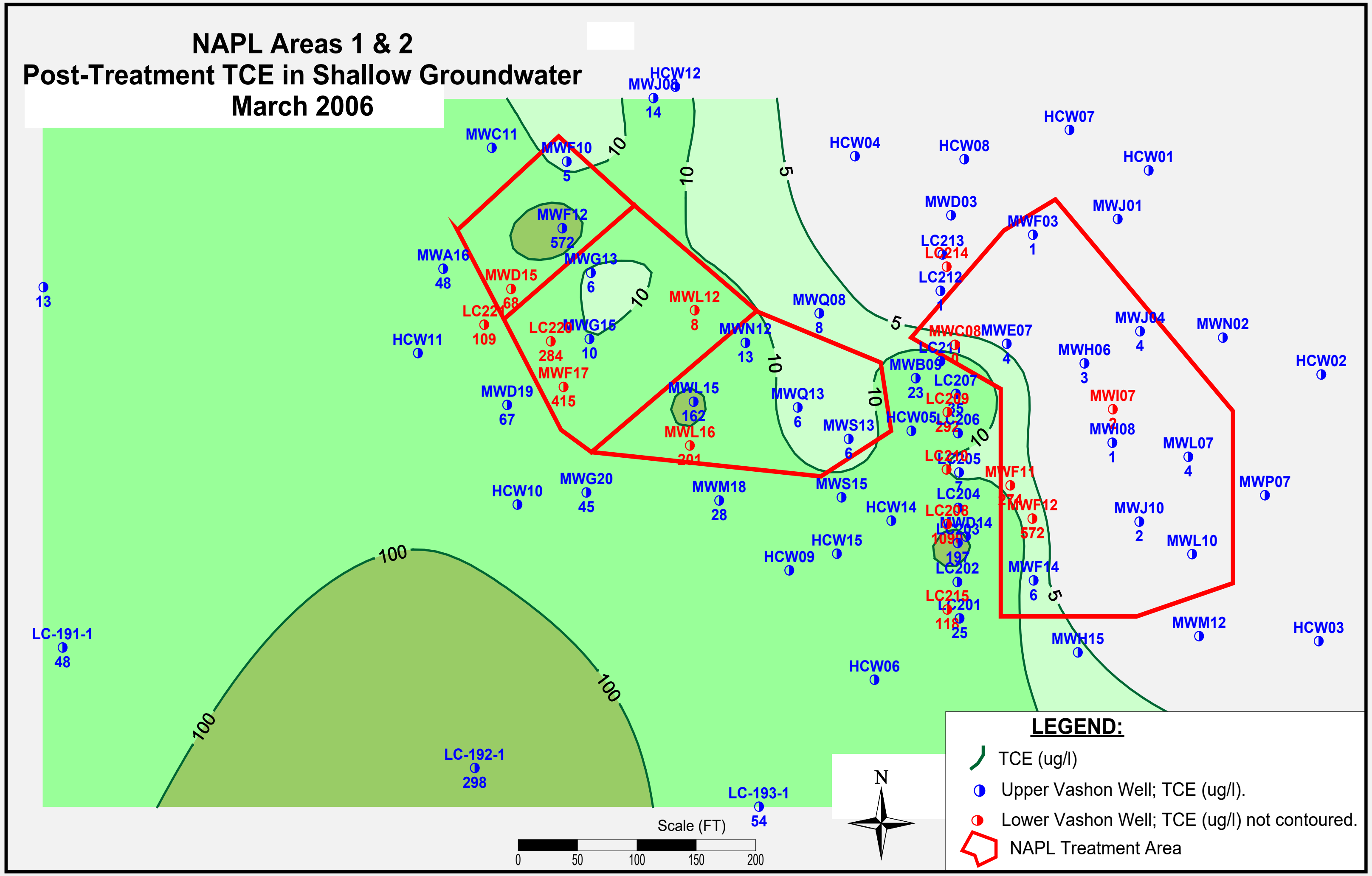
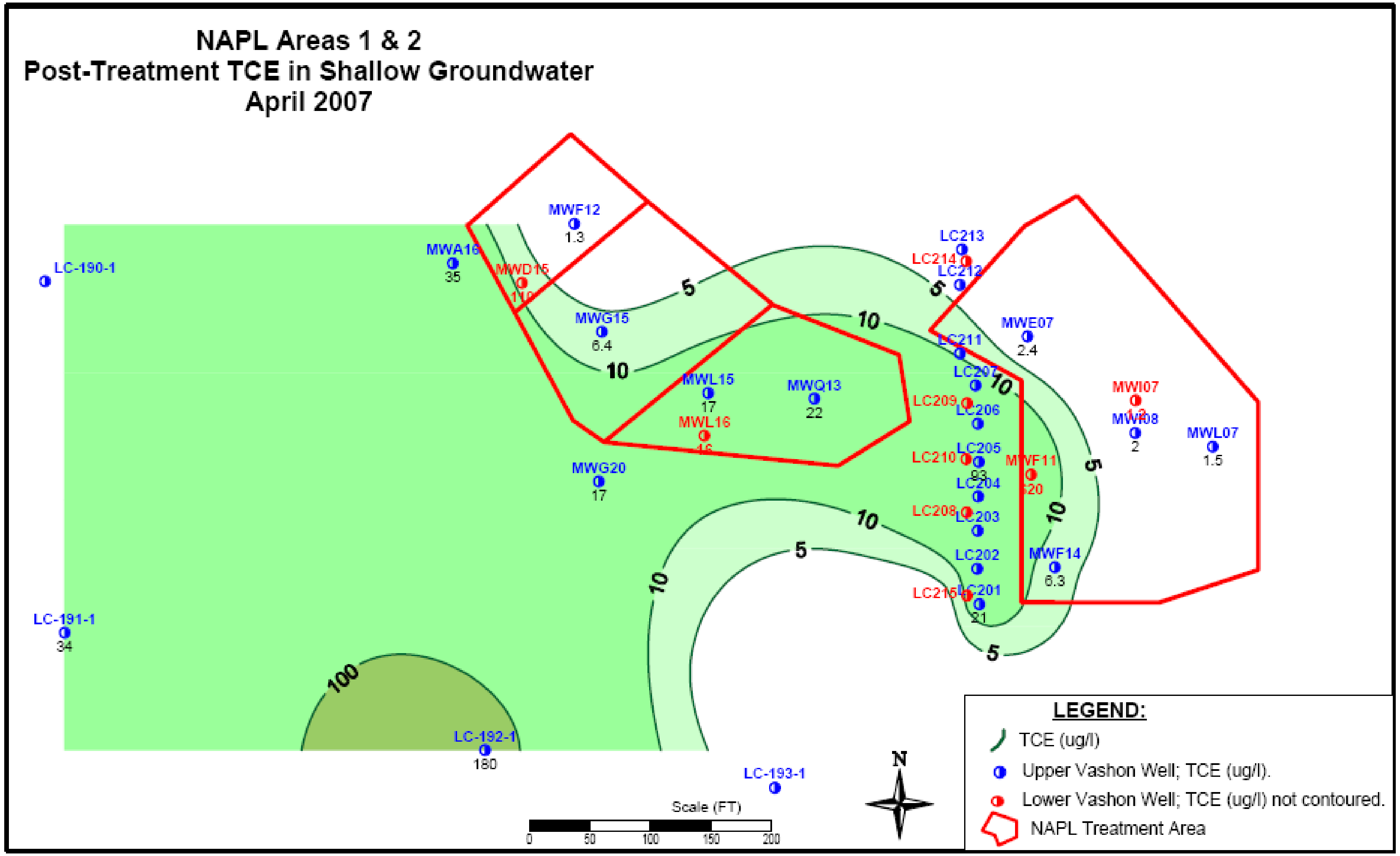
Ft Lewis

Groundwater TCE concentration contours 1.5 years after remediation.

MCL reached throughout most of first thermal treatment area.



Groundwater TCE concentration contours 2.5 years after thermal remediation



Camelot Cleaners

Fargo, ND

- Tight, fat clay, little groundwater; overlying aquifer which provides Fargo's water supply
- Initial concentrations of PCE as high as 2200 mg/kg
- > 5,000 lbs of PCE recovered by ERH
- Of 80 confirmation samples, 57 were ND, 2 exceeded cleanup goal of 3 ppm

Cleburn St: Success with Thermal!

Hastings, NE

- Chlorinated solvents recovered via ERH in low permeability soils, SEE in underlying aquifer
- 99% reduction in contamination
- 2nd order effects up to 300 yards downgradient:
  - from 7,000 ppb to 700 ppb outside thermal treatment zone
- No rebound

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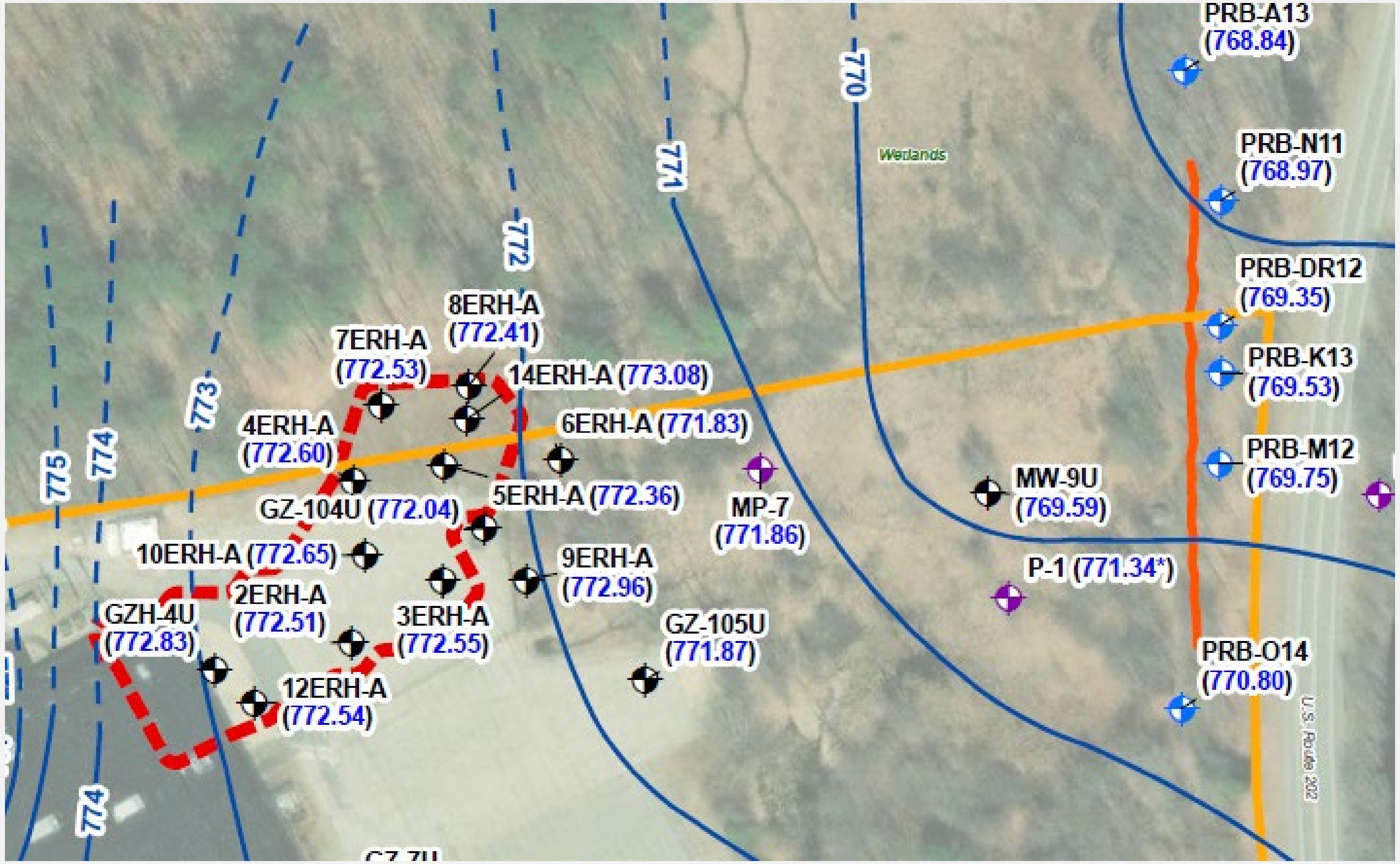
South Municipal Well Superfund Site
Peterborough, NH

- Active manufacturing facility
- Chlorinated solvents (mostly PCE) impacting municipal well
- TI Wavier, P&T for hydraulic containment, could not maintain pumping due to biofouling of wells
- Thermal remediation of source zone, permeable reactive barrier at fence line
  - ~ 4,500 lbs recovered by ERH
- Angled electrodes to address source zone under building

Permeable Reactive Barrier (PRB) at TI Wavier Boundary



- Thin zero valent iron (ZVI) wall was not treating contaminants
- Groundwater flow direction changed – A wells to north now contaminated
- 1,4-dioxane not treated by ZVI

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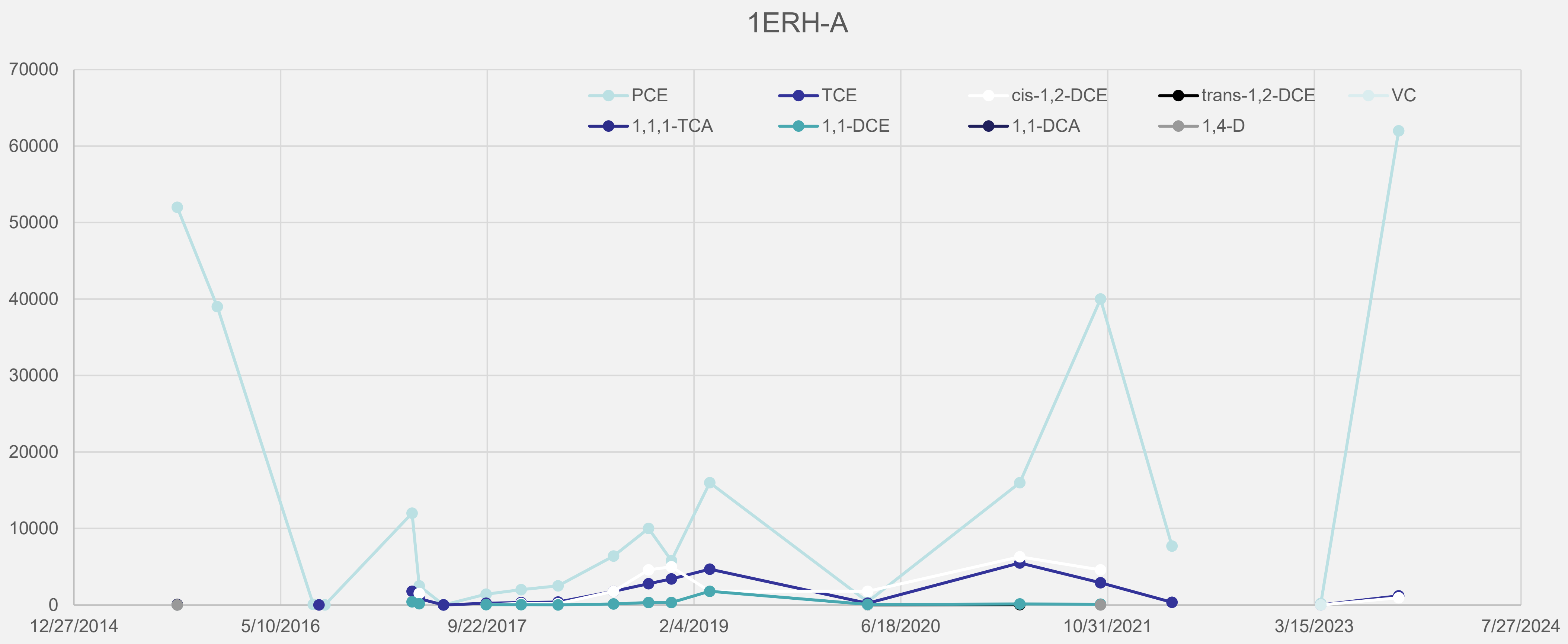
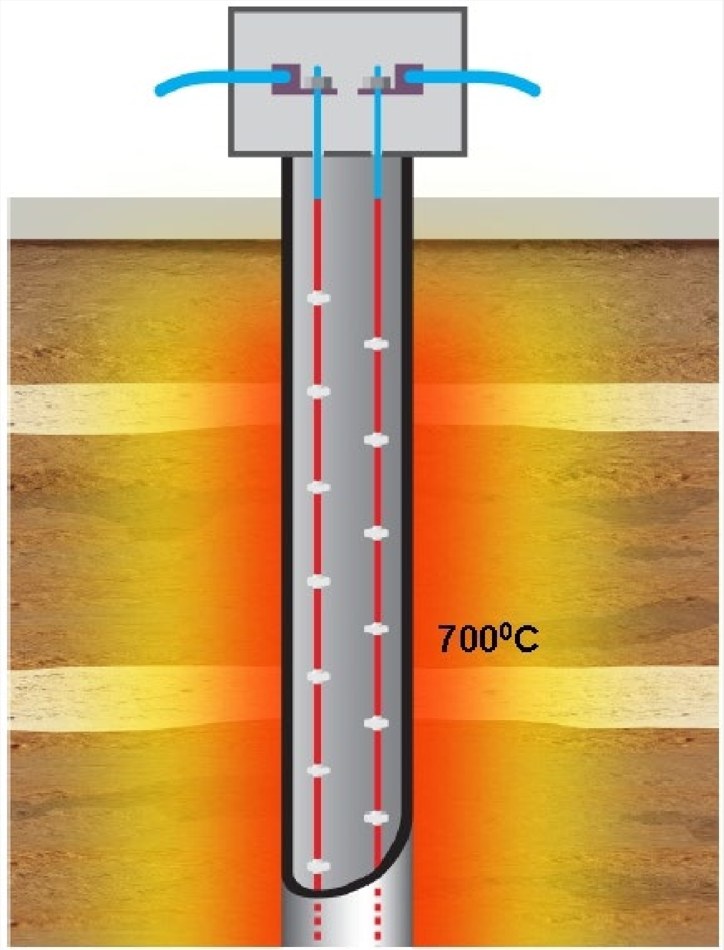
Concentrations have fluctuated widely



Thermal Conductive Heating (TCH)

- Heat is conducted from the heater well to the soil, dependent on soil thermal conductivity
- Heater wells with temperature of ~700°C installed in triangular pattern, 12 – 20 ft spacing
- Co-located vapor extraction wells
- Can be electrical or gas combustion fueled
- Temperatures greater than 300C can be reached in vadose zone



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Thermal Conductive Heating

- Relies on thermal conductivity of soil to heat ground
  - Thermal conductivity of soils/rocks fairly uniform – thus more uniform heating of subsurface
  - But low, ~10^{-6} m^2/s
- Requires high temperature (~700°C or greater) at point of application, close well spacing (10 – 12 ft)
- Triangular/hexagonal arrays
- Vapor extraction wells co-located with heater wells
- Treatment temperatures > 300°C possible above the water table
  - Can vaporize SVOCs such as PCBs, PAHs, dioxins

TCH via natural gas combustion at the wellhead

- Has a real advantage where electrical power is limited or not readily available
- Diaz Superfund Site:
  - –Unusual SVOCs containing fluoride
  - –Pilot study used to determine temperature requirement
  - –Site is in residential area

Solvent Recovery Services of New England

Southington, CT

- Waste oil Superfund Site
- ~1.7 acres, >700 heater wells, >430,000 lbs of CVOCs, petroleum hydrocarbons recovered
- Objective was mass recovery, eliminate NAPL
- Soil cleanup criteria exceeded by orders of magnitude

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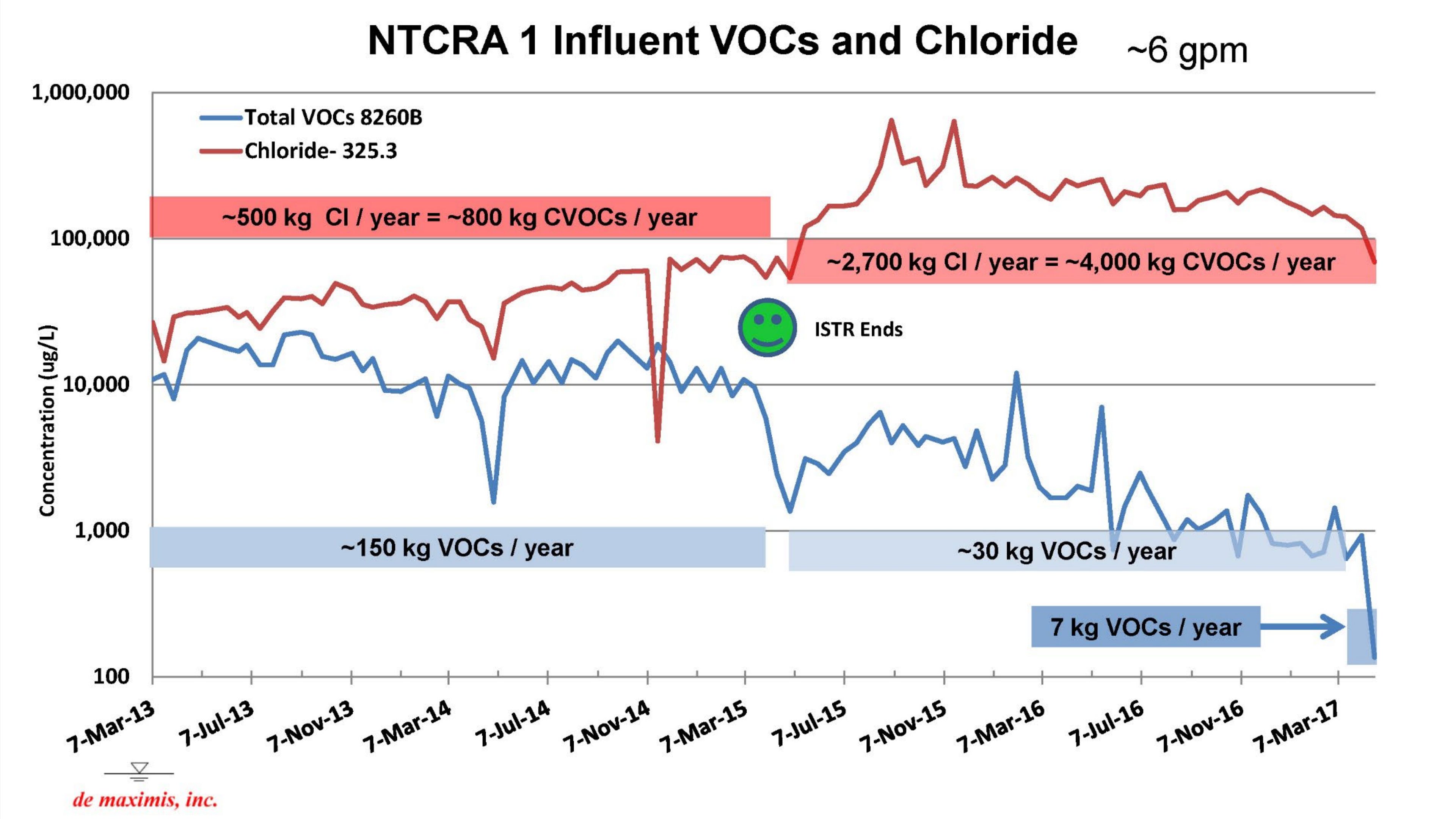
P&T influent concentrations show that significant NAPL did not remain after thermal treatment



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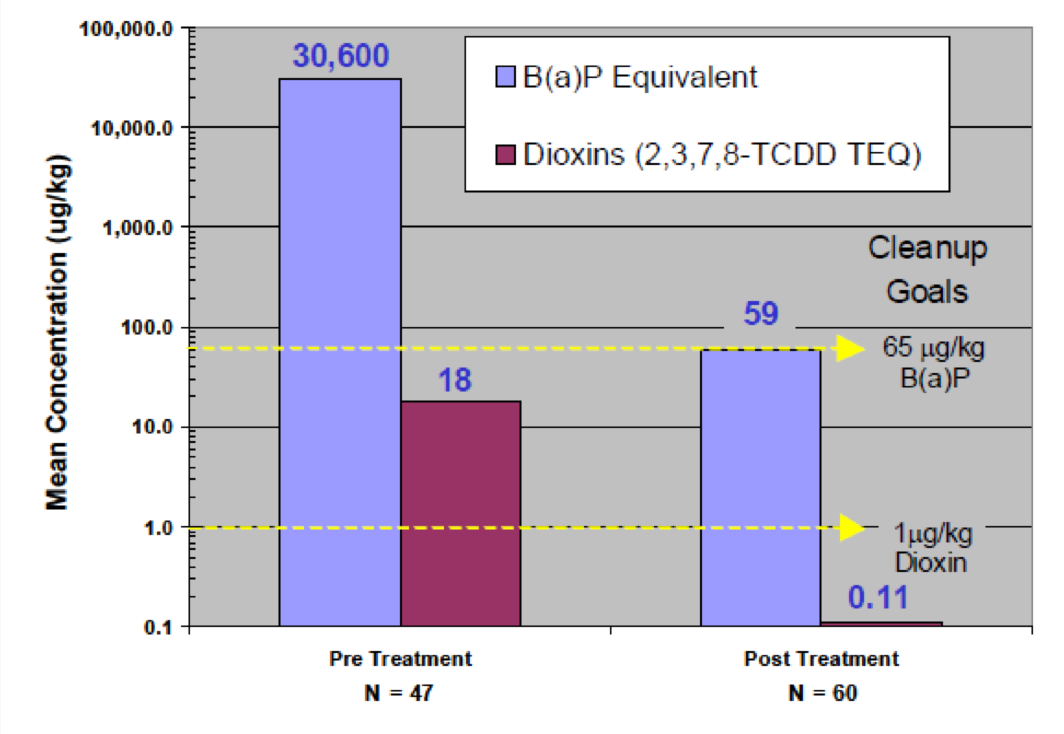
Southern California Edison's Alhambra Wood Preserving Site

Alhambra, CA

Creosote contamination to a depth of >100 feet

TCH remediated soils to stringent cleanup goals – target temperature > 300C



Coal Tar Remediation at former Manufactured Gas Plant (MGP)

North Adams, MA

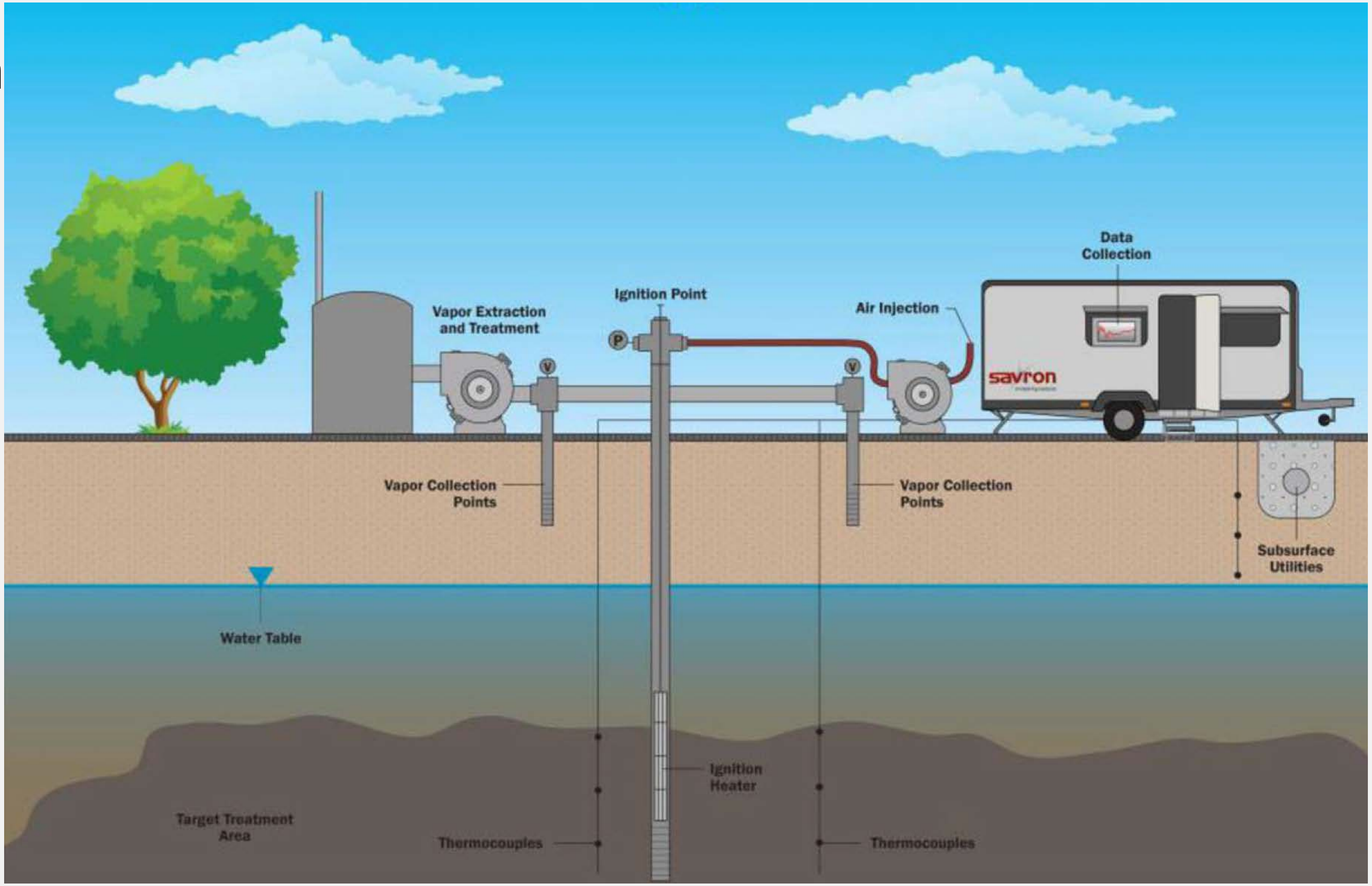
- Treatment area was former gas holder which held coal tar
- Temperature ramped up in 3 phases
  - –Dewatering at 80C
  - –Liquid coal tar recovery at 100C via viscosity reduction
  - –Vaporization at 325C to recover high boiling PAHs

Ex-Situ Thermal Desorption
Danang, Vietnam

- Agent Orange, dioxin contamination
- Topsoil excavated, placed in concrete foundation
- Thermal Conductive Heating (TCH) to 350C

STAR - Self-Sustaining Treatment for Active Remediation

- Smoldering Combustion
- Applicable to creosote, coal tar, heavy hydrocarbons at concentrations > 3000 mg/kg
- Air injection, vapor extraction required
- ROI ~ 10 feet
- Works above & below water table



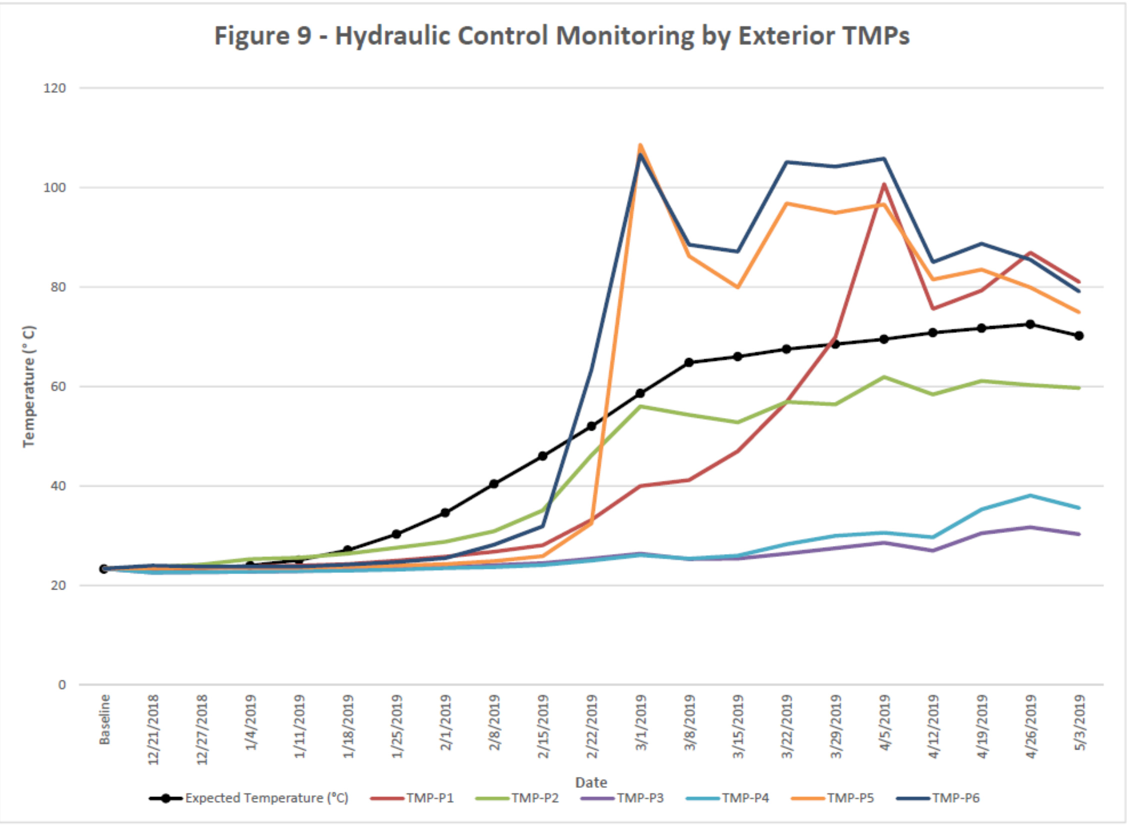
Combining Thermal Technologies

- It's critical to heat the entire contaminated area
- When the area to be treated includes both low & high permeability soils:
  - –ERH or TCH can be used in the low permeability soils
  - –Steam injection (SEE) is used in the high permeability soils

Monitoring thermal remediation operation

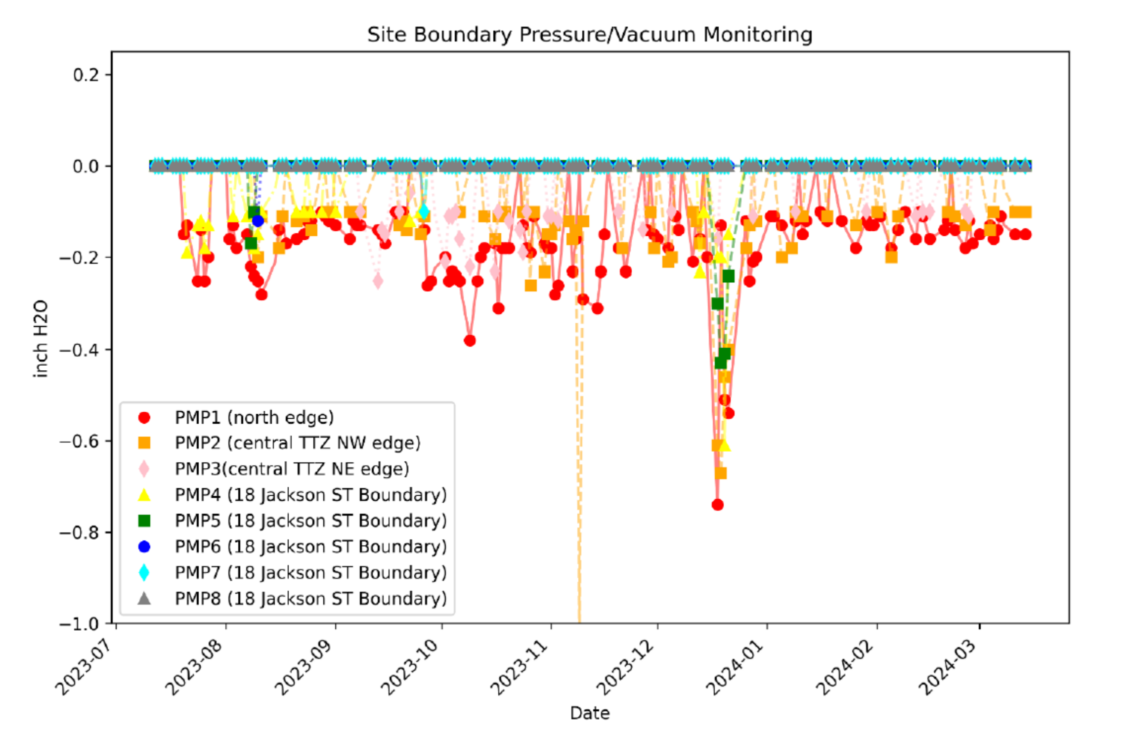
- Subsurface temperature distribution
  - Thermocouple strings throughout treatment area
- Hydraulic control maintained
  - Thermocouple string outside thermal treatment area
- Pneumatic control maintained
  - Vacuum measurements outside treatment area
- Contaminant extraction rates
  - NAPL, vapor, and aqueous phases
- Groundwater concentrations
  - Expect concentrations to increase during initial heating then decrease as mass in subsurface is depleted
- Soil concentrations

Temperature monitoring outside treatment area to verify hydraulic control



- Some heating outside treatment area expected due to thermal conduction
- Thermal conduction outside treatment area may be reduced by groundwater flow towards the treatment area
- Significant loss of hydraulic control obvious in temperature history
- No contamination lost here

Soil vacuum monitoring outside of treatment area



- Ensure soil vapor pressure does not increase outside of thermal treatment area

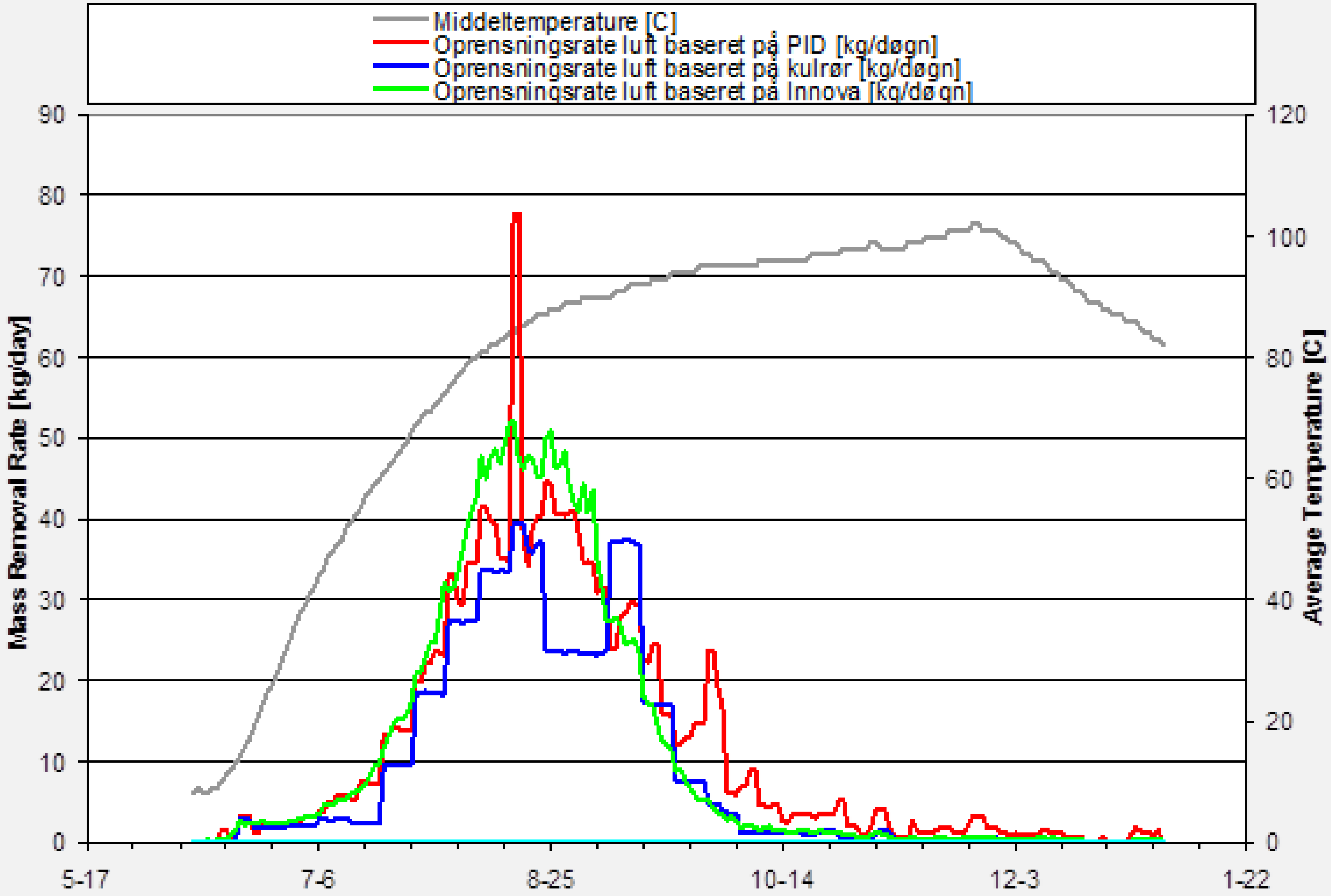
How many monitoring points?

- No one size fits all response to this question
- Things to consider:
  - Size of treatment area
  - Heterogeneity of soils in treatment area
  - Cost of installing the monitoring point
    - Depth
  - Consequences of not knowing/area to be protected
    - Are there sensitive areas around the treatment zone that need to be protected?

How do we know when we are done?

- First criteria: have temperature goals been met throughout treatment area?
- Diminishing returns
  - Recovery rate reduced to small amount
  - Groundwater concentrations have peaked and then decreased
  - More than one round of groundwater samples showing low concentrations
  - Soil concentrations can also be measured

What diminishing mass recovery looks like



Successful Thermal Remediation requires:

- Site must be characterized adequately
- Apply thermal to all areas with significant NAPL
  - NAPL adjacent to the treated area will be pulled into the treatment area by the extraction system
  - Inffluent and groundwater concentration will remain high for an extended period during treatment
  - Contamination remaining upgradient will recontaminate the treated area

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Successful Thermal Remediation requires:

- Implement appropriate thermal technology to reach target temperature
  - Dependent on temperature needed, site geology & hydrogeology
  - Heterogeneous site hydrogeology may require combining thermal technologies
- Design of heating and extraction system is crucial: all NAPL areas must be heated, all mobilized contaminants must be extracted
- For VOCs, heat to the boiling point of water throughout the treatment area, including low permeability zones
- SVOCs generally require higher temperatures
  - Use energy balance to ensure all areas are heated

Lessons Learned

- Defining the area to be treated
  - NAPL contaminated area – NAPL can continue to migrate!
  - Dependent on objectives of the remediation
- Characterization methods
  - Soil data vs groundwater data
  - Screening tools vs sonic cores
- Estimating mass in the ground, mass recovered
  - Over- or under-estimating can be a problem, especially with screening data such as MIP, soil samples are critical for NAPL delineation & mass estimation
  - Contaminants not detected by common analytical methods
- Above Ground Treatment Methods
  - Destruction via thermal oxidation vs condensing to reuse or dispose

Questions?

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