Results from the LLNL Gasoline Spill Cleanup

A worked example of thermal remediation and site closure for NAPL below the water table.

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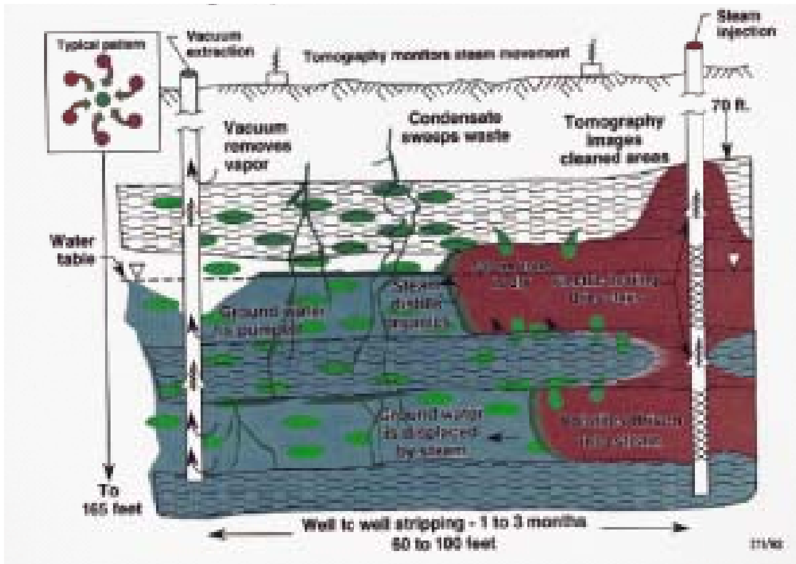
LLNL

A Collaborative Effort By LLNL and UC Berkeley, Funded by DOE EM 50

The Gas Pad cleanup provides examples of the major benefits of thermal methods:

- Increased volatility of contaminants
- Rapid mass transfer
- Rapid diffusion and evaporation
- Boiling of formation
- Lower viscosity of water and contaminants
- Faster chemical reactions

Dynamic Underground Stripping: Steam & Electric Heat, Vacuum Extraction, Monitoring & Control



The LLNL Gasoline Spill

http://geosciences.llnl.gov/envtech/dynstrip/index.html

> 140 ft depth

Water table at 100 ft

Active shipping and receiving yard

Gasoline (auto and airplane) with DCE and DCA

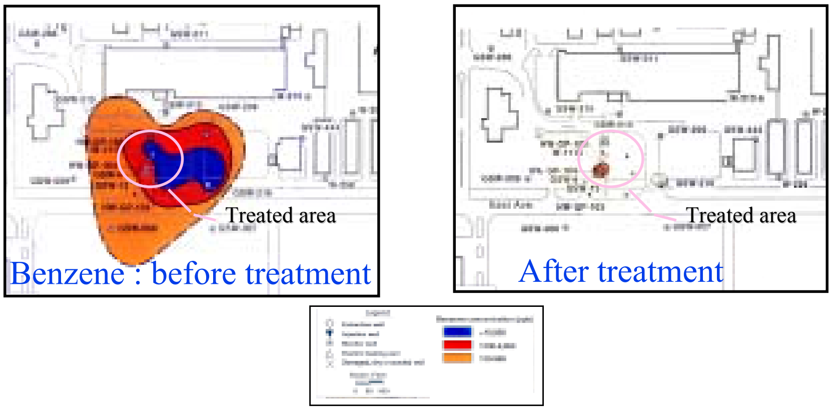
7000 gallons removed in one year of operation

Steam system mated to existing pump-and-treat with vacuum extraction

Full report at:

http://geosciences.llnl.gov/envtech/dynstrip/index.html

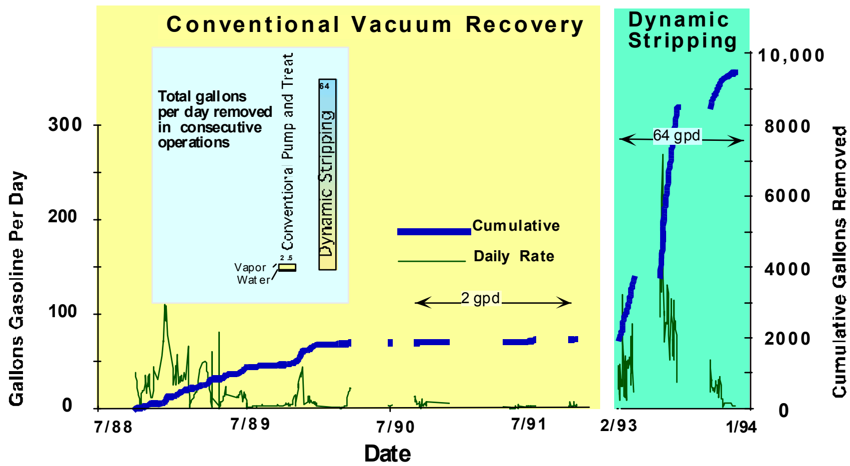
Both the source and surrounding plume were removed: only the source was targeted



Thermal remediation at LLNL removed NAPL source region from up to 30 ft below the water table, allowing rapid elimination of surrounding plume.

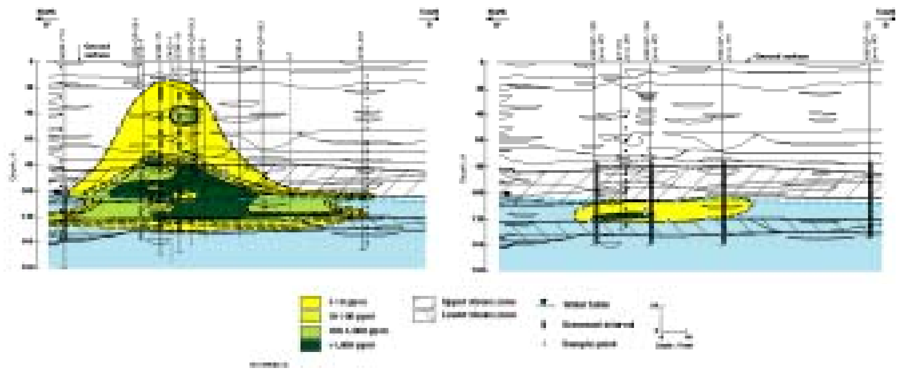
Dynamic Underground Stripping vs Conventional Recovery Methods

LLNL Gasoline Spill Site



Dynamic Underground Stripping removed vadose zone contamination at ~ 15 times the rate of conventional methods, and groundwater contamination at greater than 60 times the conventional rate.

Contaminant Was Herded To The Spill Center, and Rapidly Removed From The Vadose Zone



LLNL Gasoline Spill Site Before and After Experimental Dynamic Underground Stripping Treatment (1992-1994)

Heat moves readily - you don't have to place it carefully

Heated volumes scale by tens of meters; pinpoint location of contamination not required.

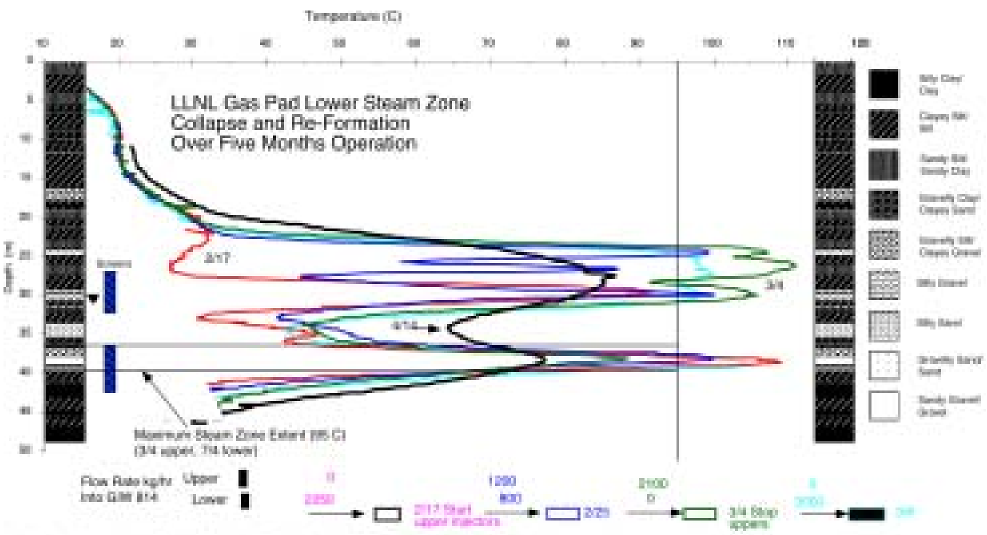
Even the most impermeable locations can be heated and treated by thermal conduction.

Steam tends to trace out the permeable pathways: electricity tends to focus on least permeable material.

Primary removal mechanism for VOCs is vaporization: vapor is readily collected and removed.

Thermal methods do not require you to spend your entire budget precisely locating the problem - most vendors adjust coverage during system installation.

Steam moves rapidly into permeable zones; conduction enlarges the heated volume over time



All plots adjusted to 20 C at 10 M depth. Steam flow to GIW 814 in period before date of temperature log.
7/4 and 5/10 data adjusted down 1-2 m to align with 38 m steam zone trend.

Is there a best way to add heat?

NO!

It's a lot like drilling; site and vendor specifics can make more difference than technique.

Energy flux is important: one yard^3 of soil requires ~100 KW-hour to reach 100°C - ***whether you use steam, electricity, microwaves or hot air.***

- **Steam tends to dominate for deep applications.**
- **Electricity has been more widely used for shallow sites.**
- **Hot air and hot water carry less heat, work slowly.**

Fundamental requirements for effective thermal remediation

Enough heat: ***don't skimp here***

- **The goal is to reach boiling in all contaminated areas**
- **Low-heat methods help, but fail to realize full potential**

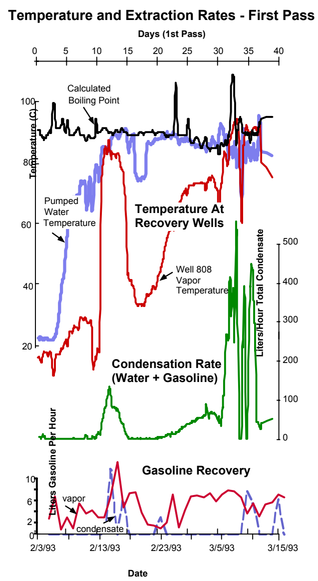
Good process monitoring: ***protects client investment***

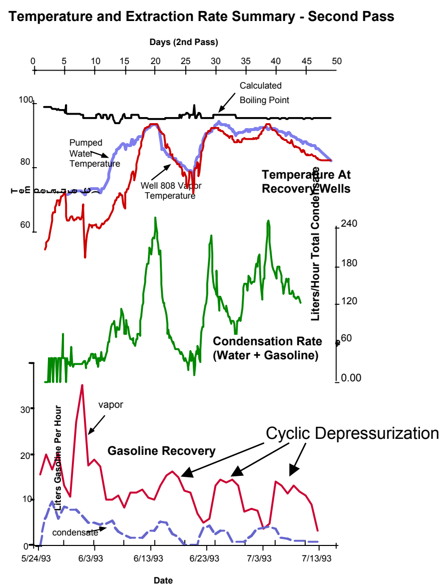
- **Heating flux (power input) in each well**
- **Heated areas**
- **Extraction temperatures and contaminant load**

Good engineering practice: ***don't try this at home***

- **Temperature-compatible materials**
- **Large treatment systems to catch all that contaminant!**
- **Installers and operators familiar with safety issues**

Recovery increased when boiling temperatures reached the extraction wells, zoomed after heat soak. Patience pays.





What about mobilization?

Mobilizing contaminants is the <u>purpose</u> of thermal enhancement.

Just like pump-and-treat, hydraulic control is required.

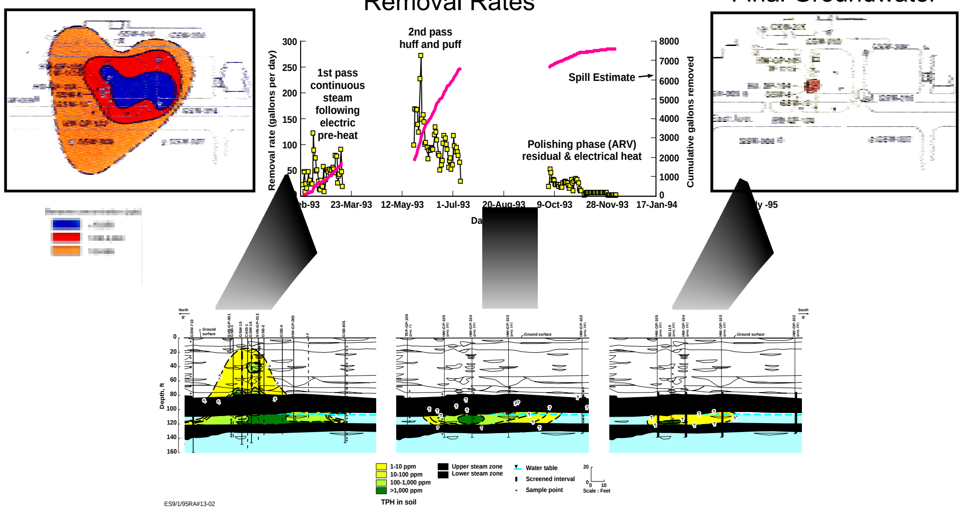
- **Concentrations always increase due to heating, even outside target area in warm water or air.**
- **Vapor can spread if vacuum control is lost.**
- **No instances of NAPL spreading.**

Mid-process drilling showed that contaminant was moved toward the center for removal

Initial Groundwater

Removal Rates

Final Groundwater

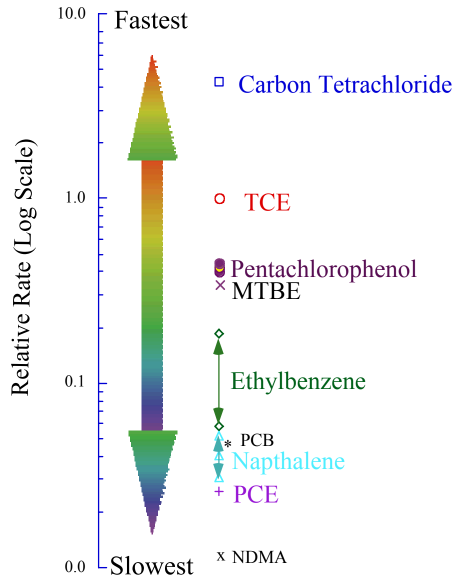


Soil Chemistry

LLNL Gasoline Cleanup Findings

- ✓ Easy to build steam zone below water table
- ✓ Rapid removal of free product, mostly as vapor
- ✓ Electric heating of aquitards effective
- ✓ Vadose zone extremely easy to clean
- ✓ Increased biological activity
- ➔ We should have measured CO_2 from in situ oxidation (physical or biological mechanisms)
- ✓ Continued attenuation after heating ended
- ✓ Cleanup of groundwater to MCL
- ✓ Site closed three years after remediation start

Disappearance of DCE (and common sense) led us to investigate the slow oxidation of organics in water



<u>Hydrous Pyrolysis/Oxidation</u>
Every chemical tested has been destroyed by to below MCL, at varying rates

Carbon dioxide and chloride ion are the observed products

Passive destruction is always part of an active removal scheme.

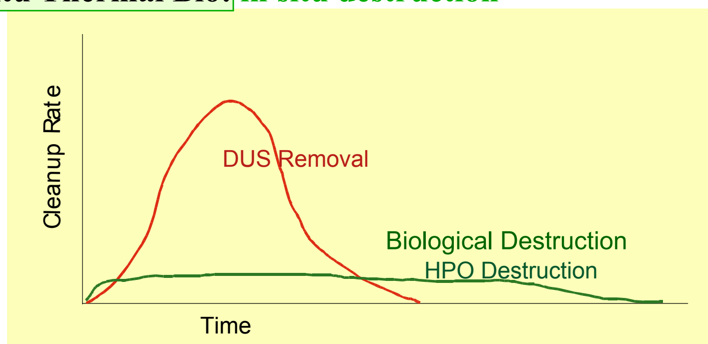
Thermal Remediation: mobilizes organics for removal.

✚

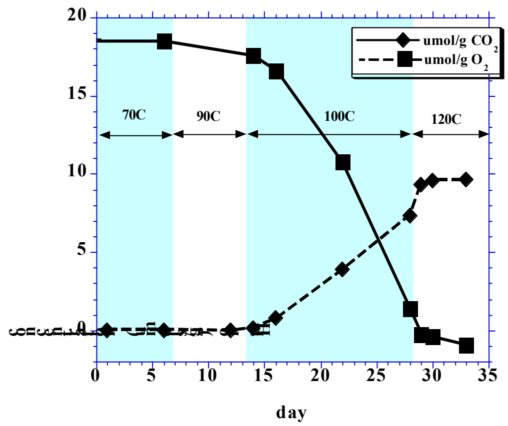
Hydrous Pyrolysis/Oxidation: in situ destruction.

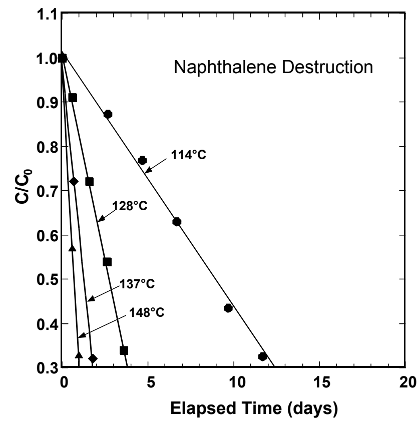
✚

In Situ Thermal Bio: in situ destruction



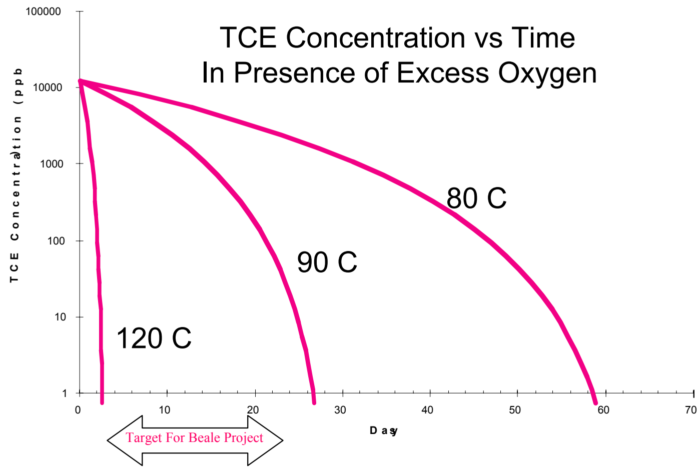
Physical oxidation of dissolved naphthalene begins at 90ºC





Destruction of dissolved pole-treating chemicals by HPO

Complete oxidation of dissolved TCE: typically on the order of a few weeks



Conclusions

Thermal methods can rapidly clean source areas, including NAPL and DNAPL.

Rapid source removal can be extremely cost effective; may be the perfect complement to monitored natural attenuation.

A variety of heating methods have been shown to be effective - the key is reaching boiling temperatures in soil.

Vendors now have considerable experience.

Applicable contaminants include VOCs, fuels, creosote and PAHs, and more recalcitrant organics.

Visalia - Large Scale Remediation of DNAPL Creosote and Related Compounds

Craig Eaker

Southern California Edison Co.

Southern California Edison Company
Visalia Steam Remediation Project (VSRP)

History
- Former Wood Treatment Site
- Superfund "NPL Listing" No. 199
- RAP/ROD - $45M (npv) for Enhanced In-Situ Bio
  - EISB would not work

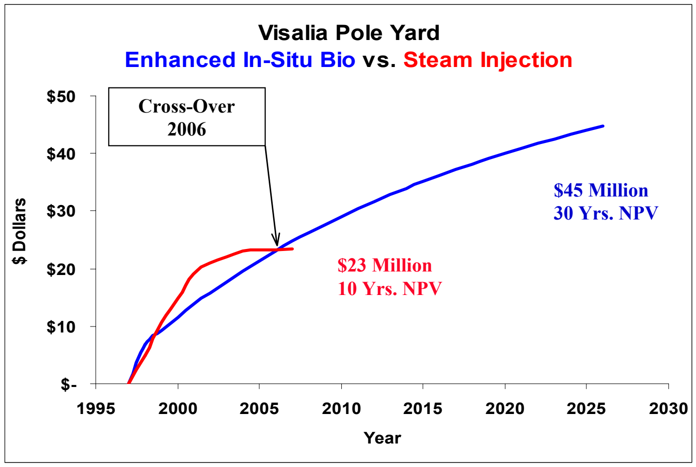
Superfund Process
- Very High Benchmark ($45 M)
  - Too Expensive
  - EISB Wasn't Going Work (Especially GW)
- We Needed an Alternative Process
  - Cost Effective, Meets Project Goals

A Great Recovery Mechanism
- 90% / 10 % Ratepayer and Shareholder Split
- Insurance Recovery

Thermal Made Sense
- Cut Costs by ~50%
- Provided Technical Solution
- Goals were achievable
- Manageable Timeframe
- Reduced - Environmental Liability"Book Value"

Implemented VSRP
- Injected 700 M lbs. Steam
- Extracted 1,400,000 lbs. (PAHs, PCP, Diesel, Dioxins, and Furans)
- Accelerated Mass Removal by 3500 years
- Thermal Treatment Cost $57/yd3

The Visalia Investment Was Driven By Favorable Cost Analysis

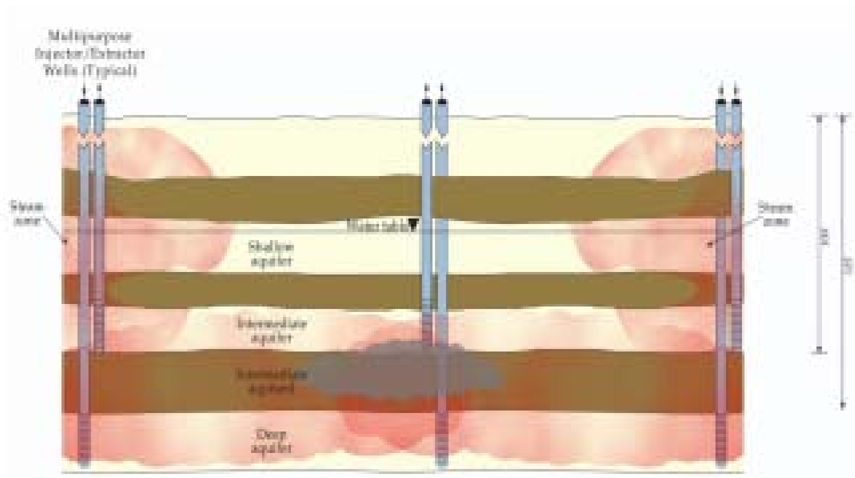


Project Success Formula

The "Right Stuff"

- Environmentally Conscious Company
- Pro-Active Management
  - Willing to take an "Educated Risk"
- State Directed Superfund
  - Results Driven Enforcement
- A Superior Team
  - LLNL, UCB, SCE Engineering
- No Entrenched Thinking or Culture
  - A "Can Do" Attitude

Phase II Steam Injection Cross-Section



Visalia 1995-97: *Source cleanup of a major superfund groundwater site: 1,200,000 lb creosote removed*

A yield equivalent to 3500 years of pump-and-treat

Prior to steam injection the removal rate was approximately <u>10 lb per week</u>

204,000 lb
Vapor Hydrocarbon
Burned In Boilers

210,000 lb
In Situ Destruction
(Removed CO_2)

607,000 lb
Free Product
LNAPL & DNAPL

195,000 lb
Dissolved Hydrocarbon
Activated Carbon Filtration

Free product recovered at Visalia was an oil-in-water emulsion; this was a key aspect of DNAPL recovery.

Control is important

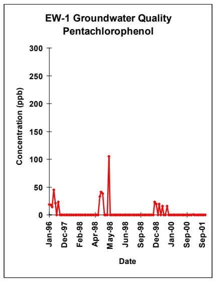
Monitoring of heated zone; treat the whole zone!

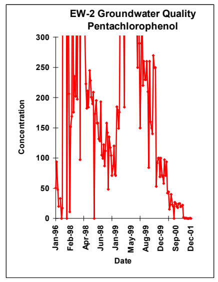
Vapor control - it moves! Suck it up.

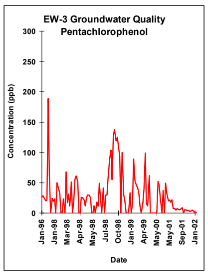
Hydraulic control - just like pump and treat

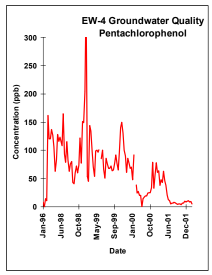
Vapor extraction system at Visalia exchanged the vadose zone air once a day.

Visalia Steam Remediation Project
Progress Report – Groundwater Quality





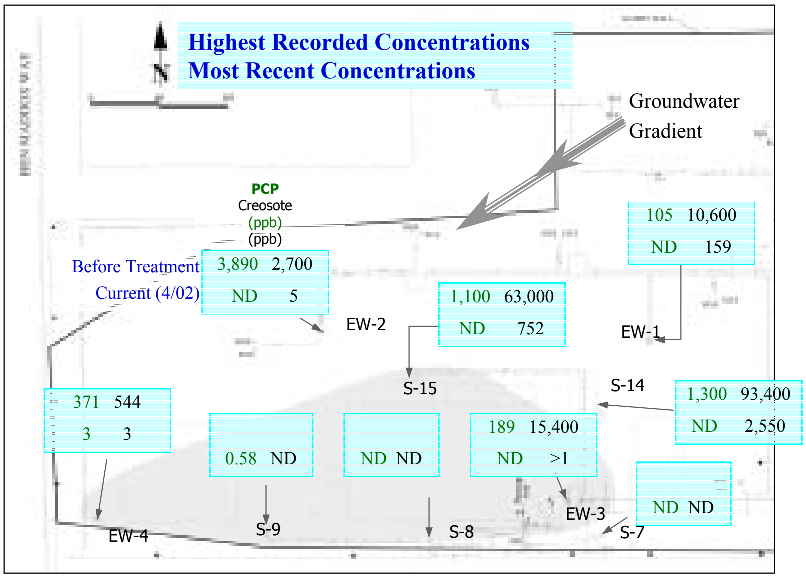




- Benzo(a)pyrene and pentachlorophenol are the regulatory drivers

- Only pentachlorophenol remains a concern. Levels are greatly reduced and continuing to drop in post-treatment phase.

Visalia Progress **Groundwater Quality - Pentachlorophenol & Creosote**



Costs at Visalia

- Total 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
  - SER $130
- Estimated Time to Remove 1.2 Million Pounds of Creosote
  - Pump and Treat 3,250 years
  - SER 3 years