Innovative Approaches to PHC Remediation

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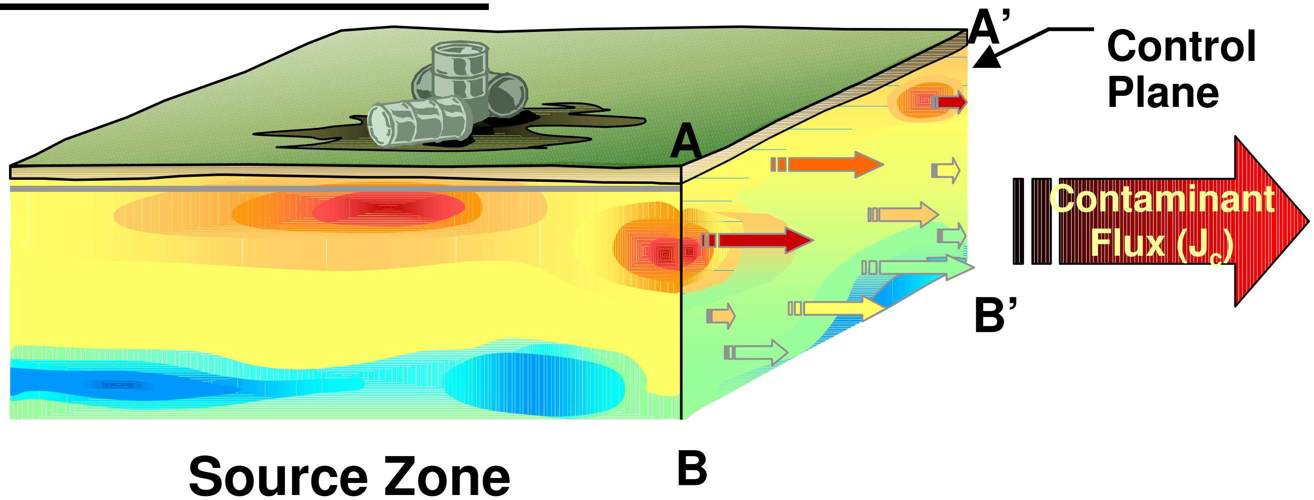
Technology Innovation Office/USEPA

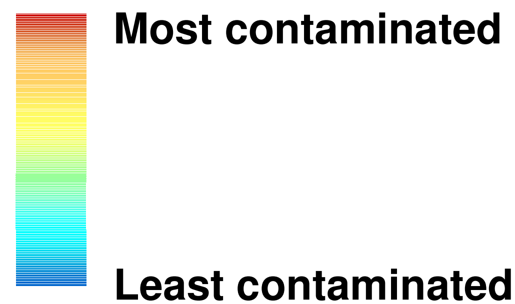
R 6/8 Refinery Workshop

July 2002

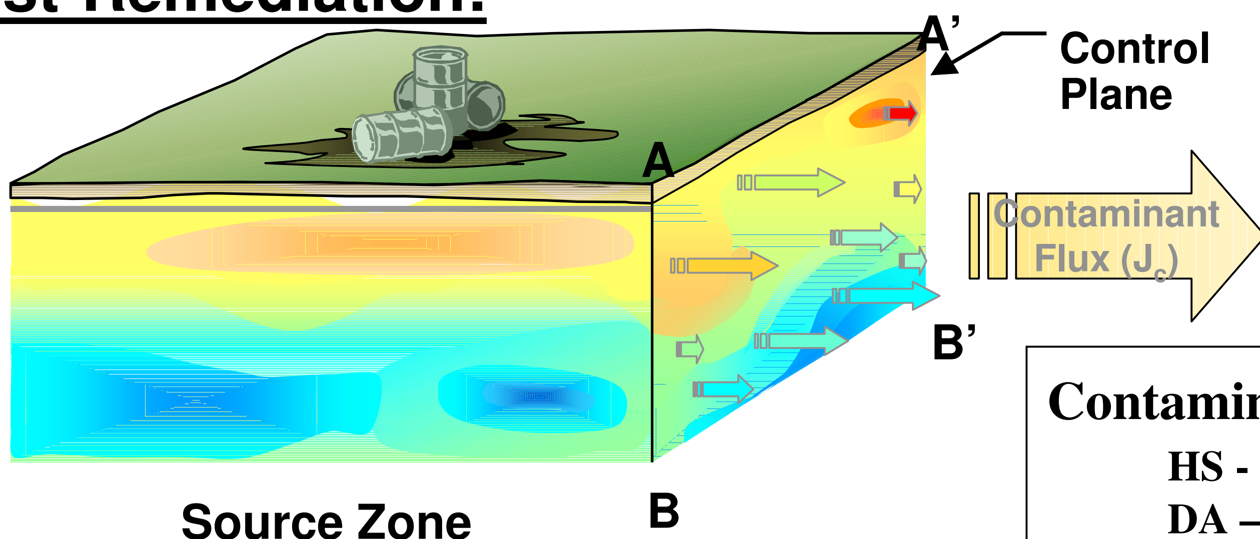
Mass Reduction vs Mass Flux

Pre-Remediation:





Post-Remediation:



Contaminant flux = f (HS, DA)

HS - hydrodynamic structure

DA – DNAPL architecture

What's New

- Potential to address vadose zone SVOC contamination not amenable to SVE
- Potential to address contamination in the saturated zone below the water table
- Ability to address contamination at depths below those amenable to excavation

STEAM ENHANCED EXTRACTION

Why Thermal Remediation?

Thermal remediation methods are effective due to a variety of factors:

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

Results from the LLNL Gasoline Spill Cleanup

Roger Aines

Robin Newmark

LLNL

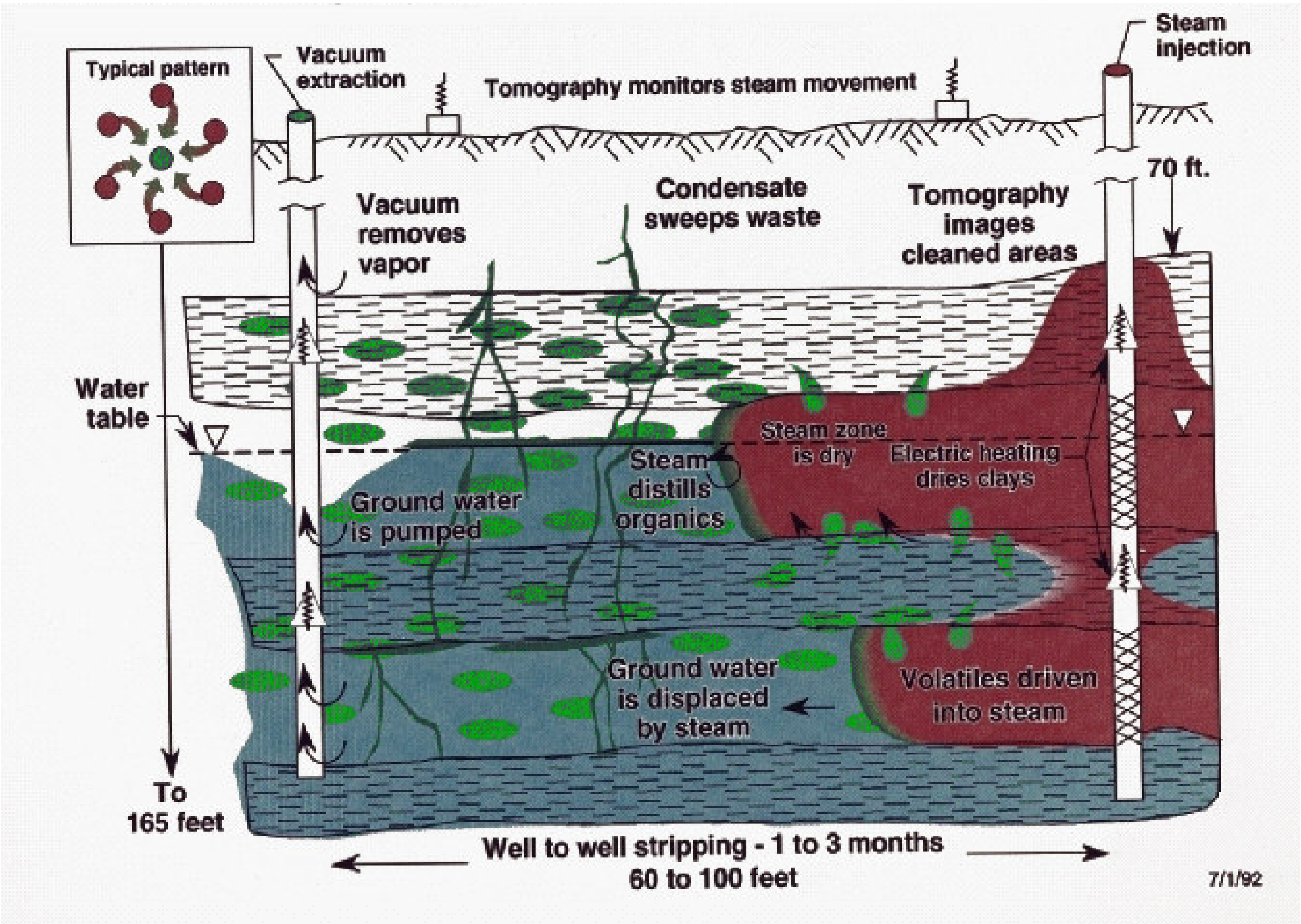
LLNL deep gasoline spill:

7000 gallons removed, 1 yr

50 x increase in removal rate

Site closed

Dynamic Underground Stripping Mobilizes Contaminant For Rapid Extraction



The LLNL Gasoline Spill:

> 140 ft depth

Water table at 100 ft

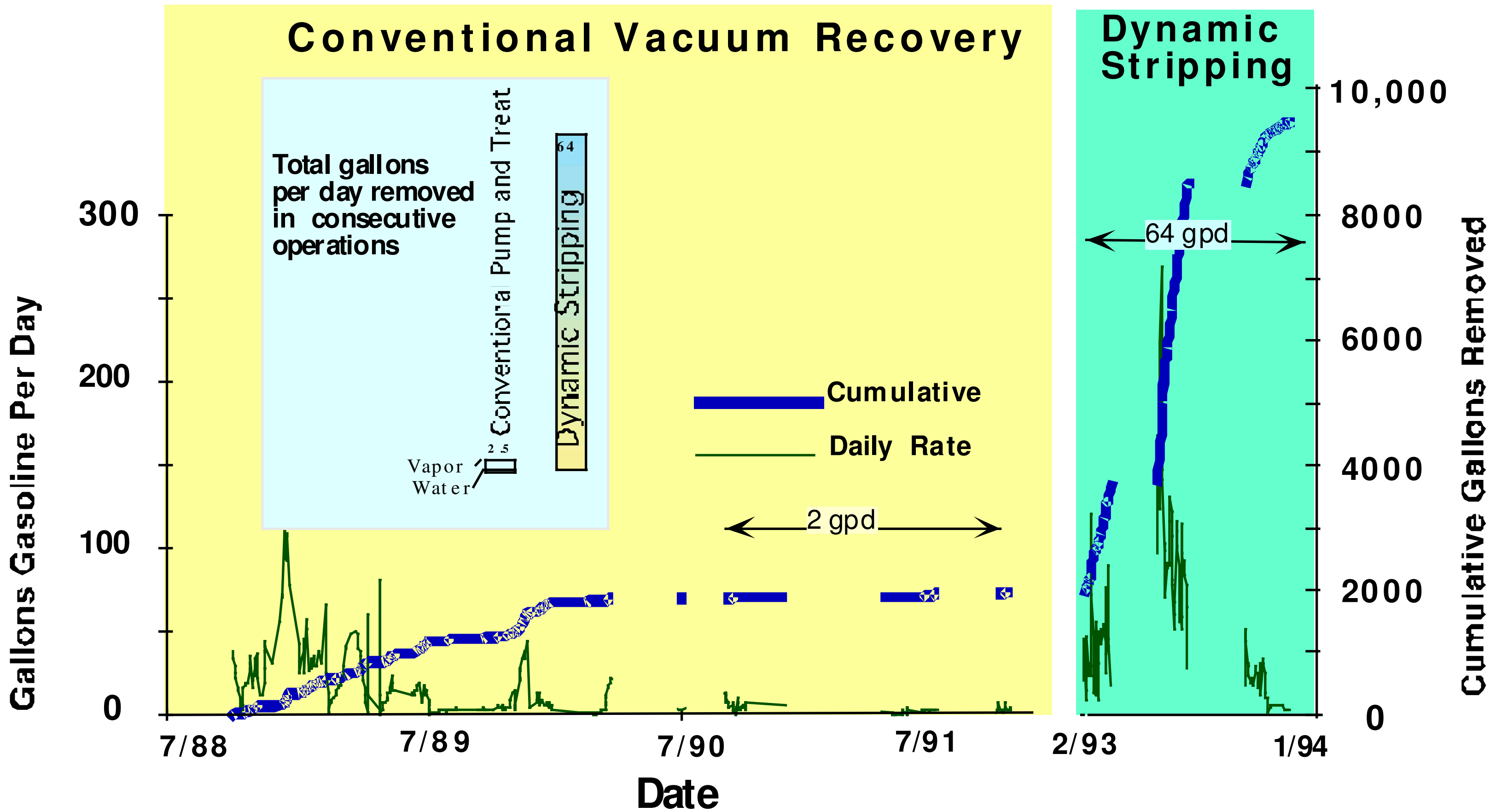
Active shipping and receiving yard

Gasoline (auto and airplane) with DCE and DCE

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

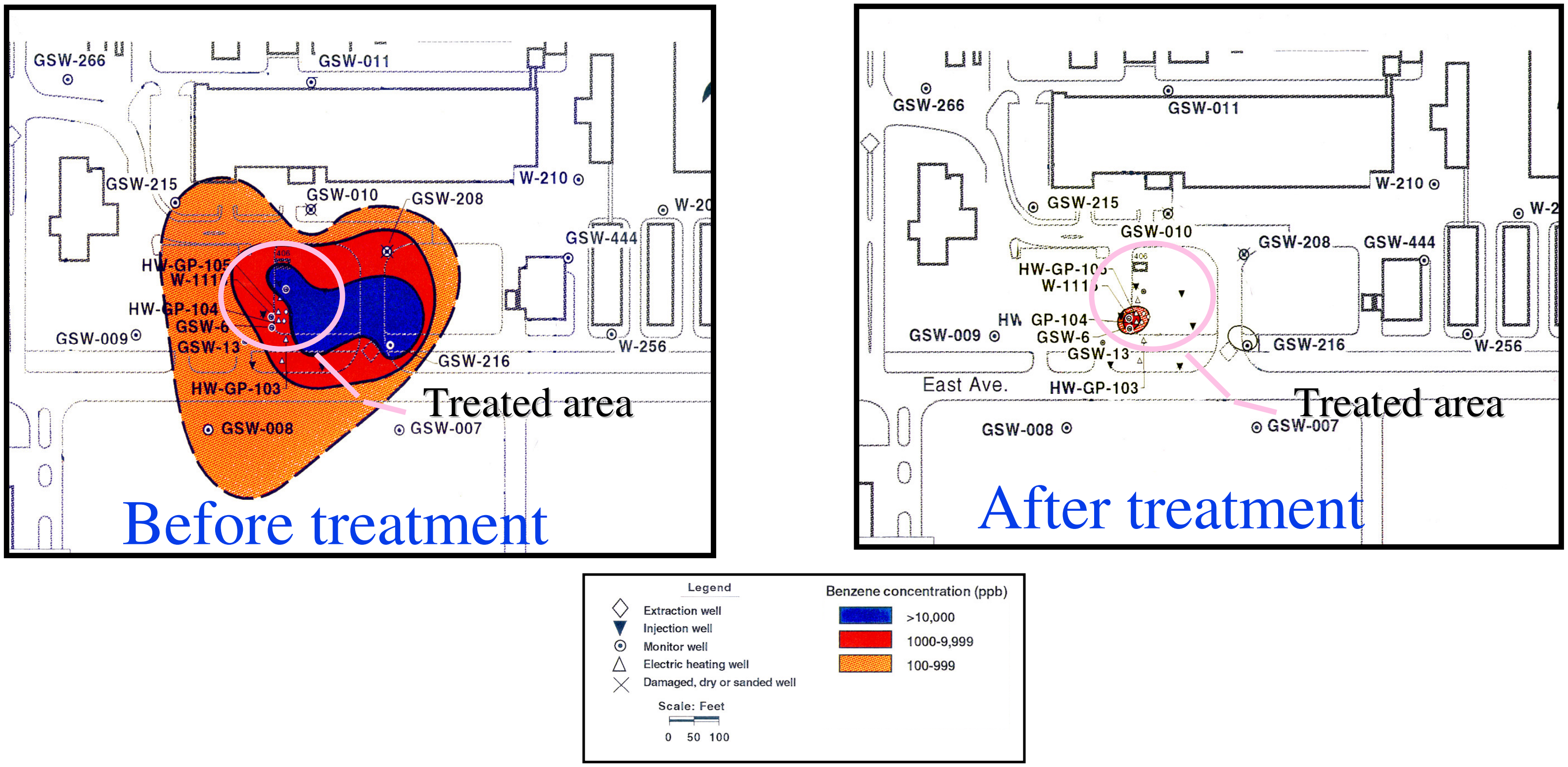
Dynamic Underground Stripping vs Conventional Recovery Methods

LLNL Gasoline Spill Site



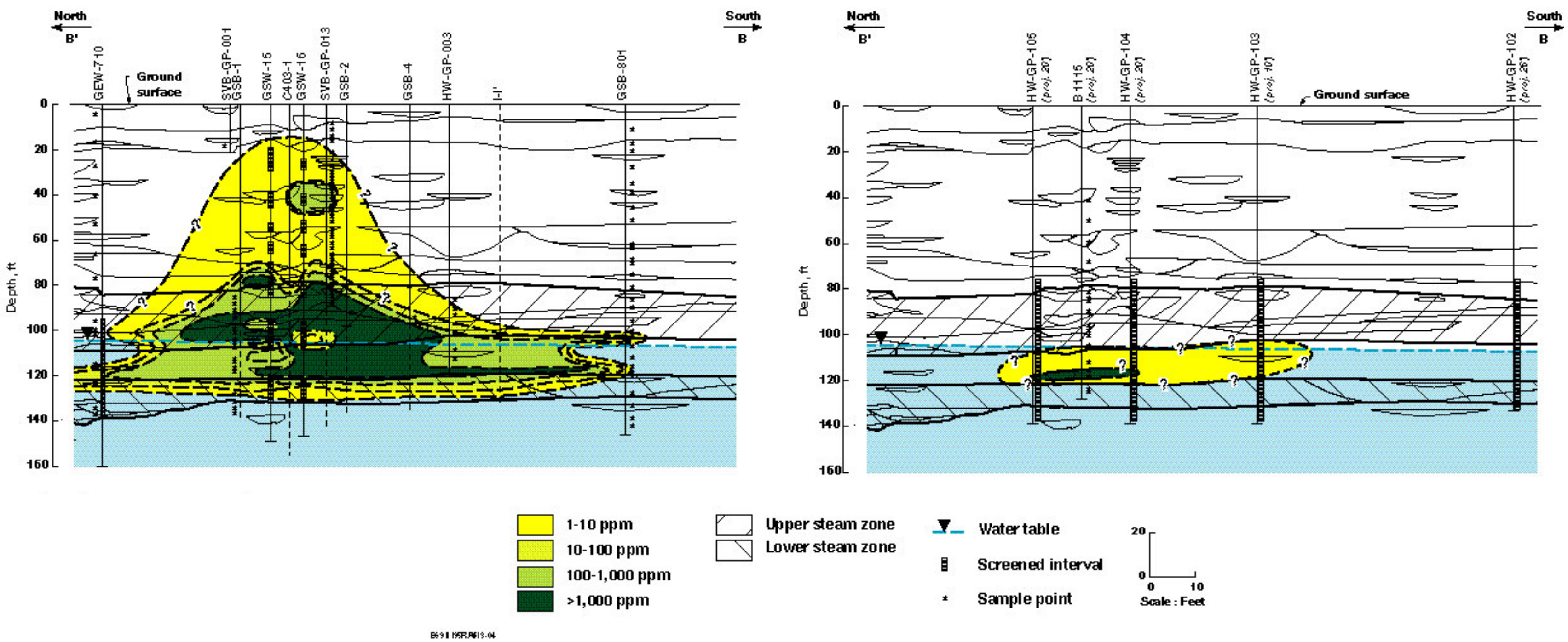
Dynamic Underground Stripping removed vadose zone contamination at ~ 15 times the rate of conventional methods, and groundwater contamination at greater than 60 times the conventional rate.

A Success Story: LLNL Gasoline Spill Cleanup and Closure



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

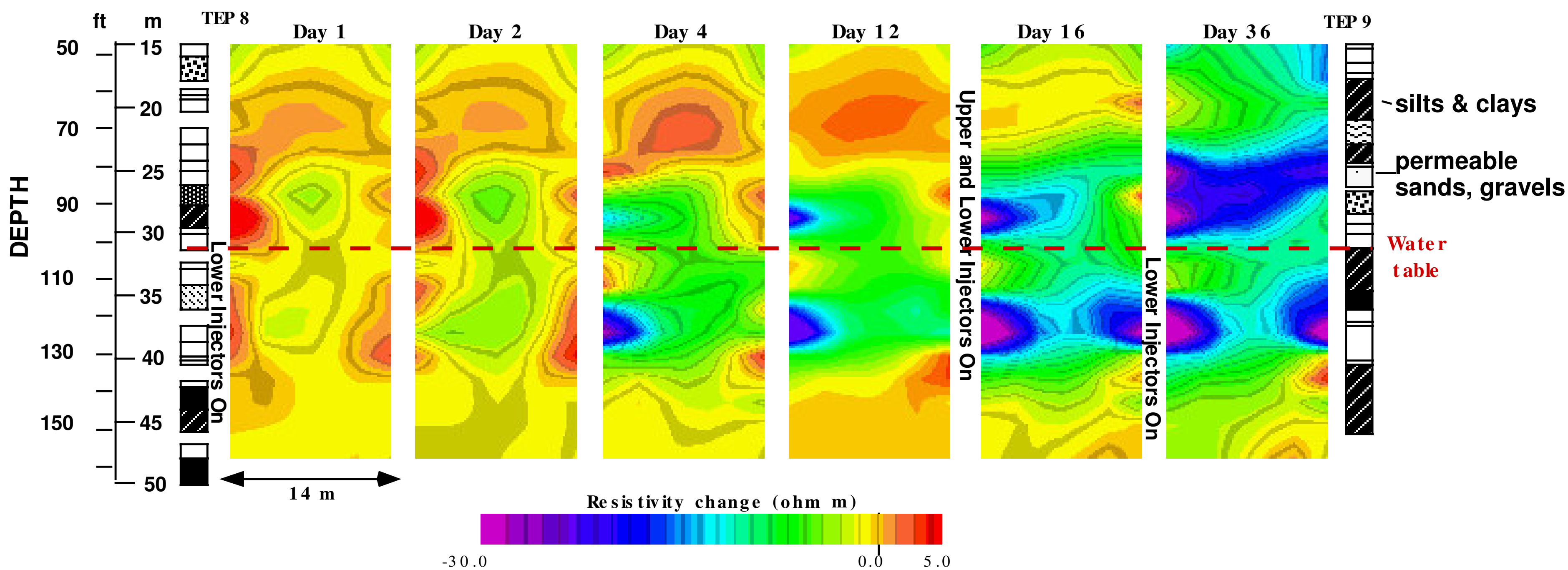
Contaminant Was Herded To The Spill Center, and Rapidly Removed From The Vadose Zone



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

Gas Pad Chronology - Cleanup to Closure 30 Months

Differential ERT was deployed to map steam movement



➪ Steam immediately broke through from lower to upper injection zones

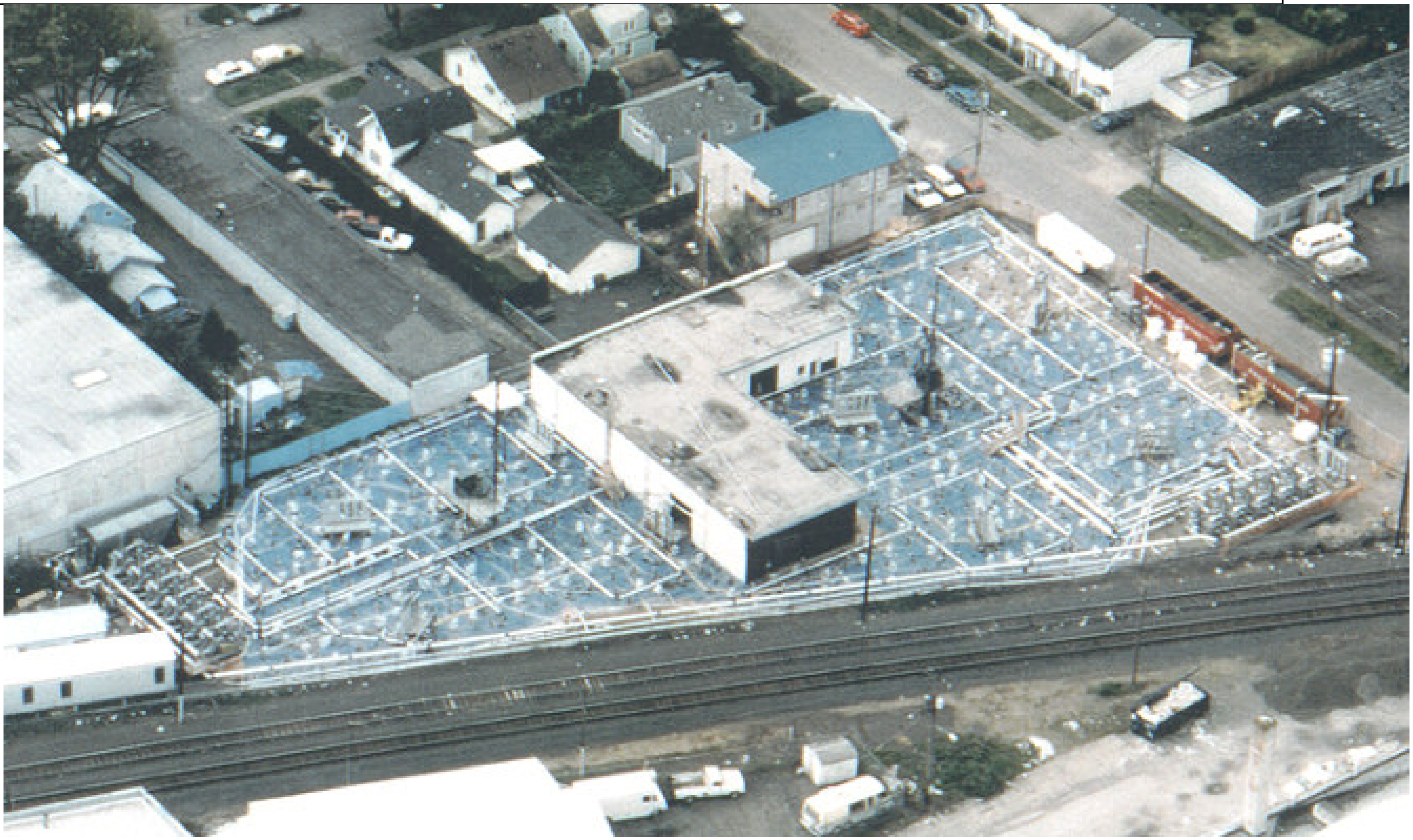
➪ Anastamosing permeable zones are traced above and below the water table

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
- Benefited, not diminished biological activity
- Vadose zone extremely easy to clean
- Continued attenuation after heating ended
- Cleanup of groundwater to MCL
- Site closed three years after remediation start

THERMAL CONDUCTIVE HEATING

Shell Bulk Fuel Facility, Eugene OR



Overview of Project

- Former Shell Bulk Storage Terminal for middle and heavy hydrocarbon distillates
- Diesel Range Organics (DRO), gasoline and benzene:
  - in soil and groundwater to depths up to 12 feet bgs;
  - maximum concentrations of 9,300 mg/kg (DRO), 3,500 mg/kg (gasoline) and 1,300 μg/kg (benzene in groundwater);
  - as much as 7.9 ft of free product in monitoring wells.
- Gravel layer 1-4', over silt to ~11-16' bgs.
- Perched groundwater encountered in the unconfined top gravel and silt layers.

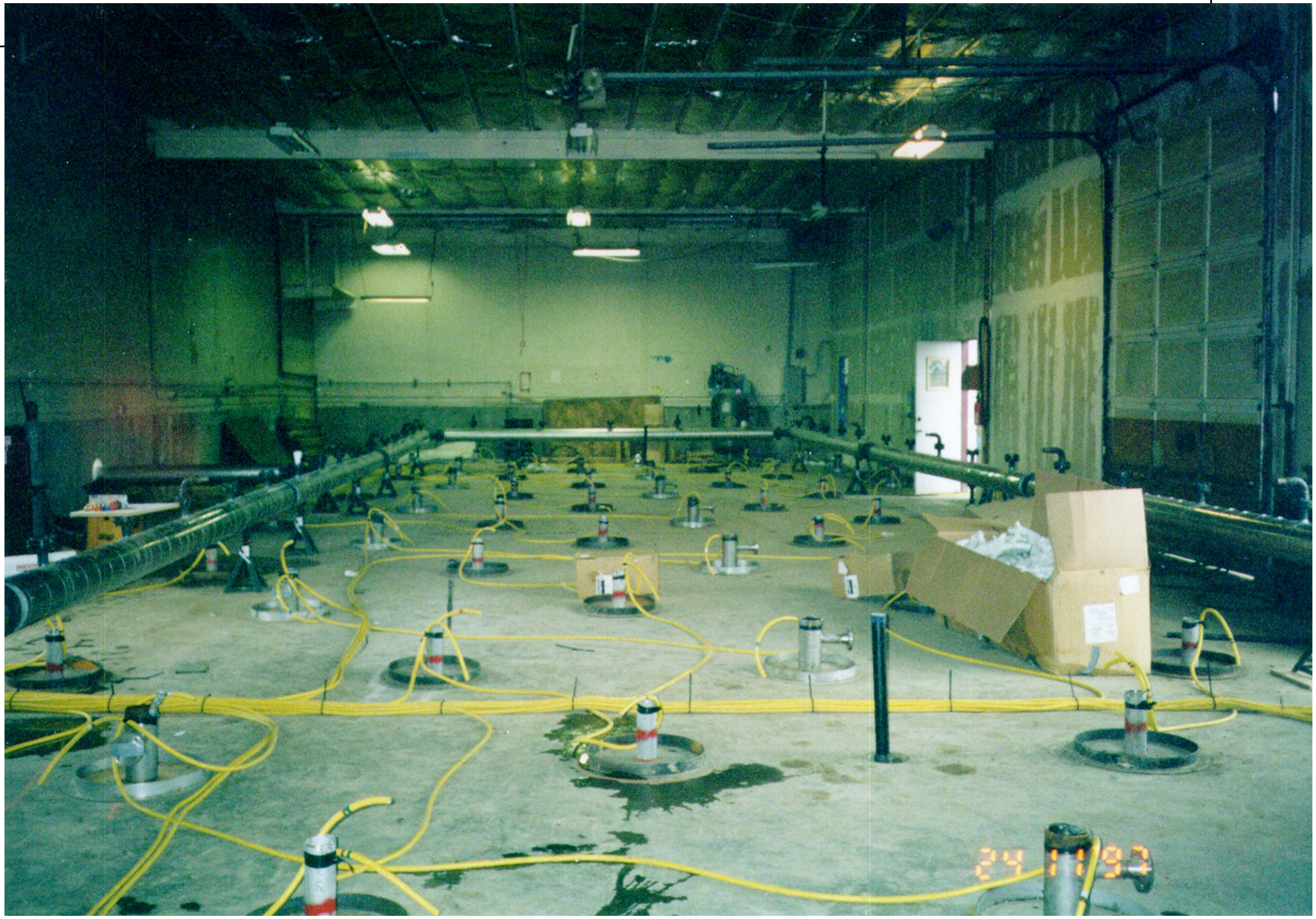
Overview of Project (cont.)

- Project goal was removal of free product and benzene, and closure of the site under RBCA UST program with Oregon DEQ.
- TerraTherm Environmental Services Inc.:
  - mobilized to the site Sept '97;
  - installed 277 vacuum-heater wells and 484 heater-only cans, at 7-ft spacing, to 10-12 ft bgs;
  - conducted dewatering during treatment;
  - operated from June through August '98;
  - demobilized by Oct. '98.

Project Results

- Thermal well system achieved an average in-situ temperature of ~500 °F.
- Free phase LNAPL removed from the entire site.
- Est. 200,000 lbs of hydrocarbons removed/treated during the 120-day heating cycle.
- All confirmation (post-remediation) soil/groundwater samples were below the ODEQ's Tier 1 Risk-Based Concentrations:
  - Benzene concentrations in GW w/in the treatment area were reduced from 1,300 μg/L to 2.14 μg/L.
  - All post-treatment off-site GW samples (4 quarterly rounds) were below the analytical detection limit (i.e., <0.5 μg/L).
- Oregon DEQ issued a "No Further Action" letter on March 14, 2000.
- Turnkey cost (design, permitting, operation, demobilization, reporting): $2,971,000 (~$200/cy).

Thermal Wells inside Warehouse



Eugene, OR Fuel Depot (gasoline, diesel) – ¾ acre area treated

ISTD Near Residences, Fuel Depot, Eugene, OR

Other In Situ Thermal PHC Applications

- #2 Fuel Oil, Atlanta, Ga (completed) - Electrical Resistive Heating (aka 'Six-Phase Heating)
- Yorktown, Va (Navy Special Fuel Oil) (ongoing) - Steam In Horizontal SS Wells to Drive NSFO to Recovery Trenches
- Guadalupe Oil Field (prospective) - Steam Pilot Under Design

SURFACTANT/COSOLVENT FLUSHING

Golden, OK UST Site
Starting Point

- Gasoline free phase: thickness on water table 2.7 to 3.3 ft
- Shallow zone (< 15 ft) - silt:benzene, 2,000 to 36,000 µg/L in GW; TPH, non-detect to 345 mg/L
- Deep zone - sand/gravel: benzene, 50 to 3,000 µg/L; TPH, non-detect to 30 mg/L
- Surfactant Flushing Zone: 1.5 acres (22,300 ft^2)

Case Study
Golden UST Site, Oklahoma

Project Goals

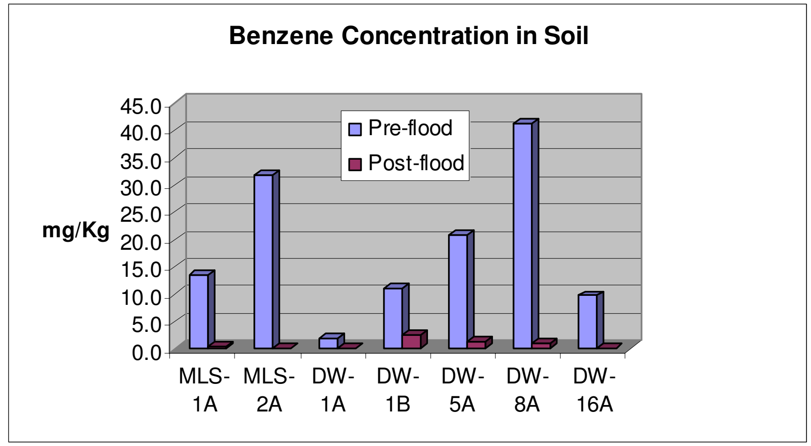
- Primary: Remove all free phase gasoline
- Secondary: Significant decrease in soil and groundwater concentrations (one to two order magnitude)
- Tertiary: See how low we can get the soil and groundwater concentrations -- Primary Drinking Water Standard?

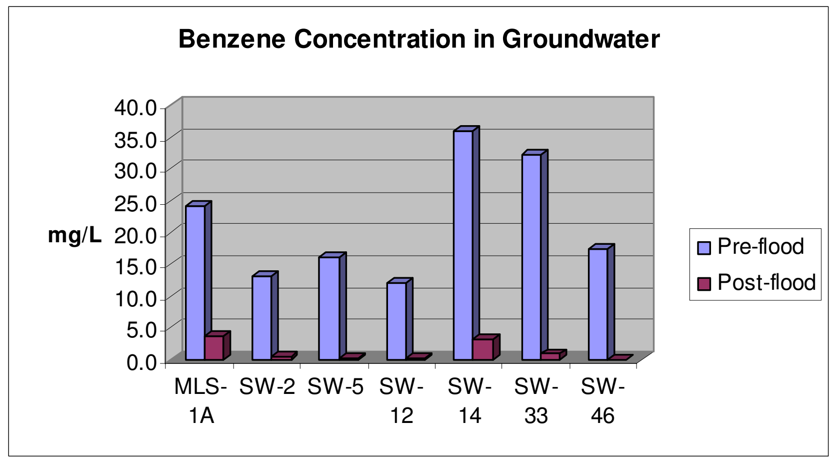
Recent Low Surfactant / Integrated Technology Approach

- Improve economics by using low surfactant concentrations (0.1 to 1 wt% versus 3 to 8 wt% in earlier SESR projects)
- Polishing step: injection of low chemical oxidant (< 1 wt%) and/or bioamendment to polish remaining residual / dilute NAPL plume

Golden, OK UST Site
Approach / Results

- Surfactant used: 0.75% AOT / 0.19% Calfax 16L-35/1.2% NaCl
- 1 PV (190,000 gallons) – 60 days flushing
- Polishing: shallow -- low level chemical oxidation (0.8% Fenton's Reagent); deep – bioamendments (H_2O_2/Na_2SO_4)
- Soil and ground water concentrations reduced by one to three orders of magnitude





Golden, OK UST Site
Results

Results versus Goals:

- **Primary: no visible or instrument evidence of free phase gasoline in all but three wells after three-month shut-down (25 with no trace of NAPL)**
- **> 6,000 gallons gasoline extracted**
- **Secondary: GW--70% to 99% reduction in benzene concentration**
- **Final Polishing (Chem Oxid/Bioamendment) to approach MCL (8/02-expected)**
- **Cost Info**
  - **Total Project - $712k**
  - **Surfactant zone - $36/yd**
  - **Total vol treated (surf+chem ox+bio) - $14/yd**

In Situ Chemical Oxidation (ISCO)

- ISCO has been used at 100's of BTEX UST Cleanups
- Stoichiometrically problematic at large PHC sites

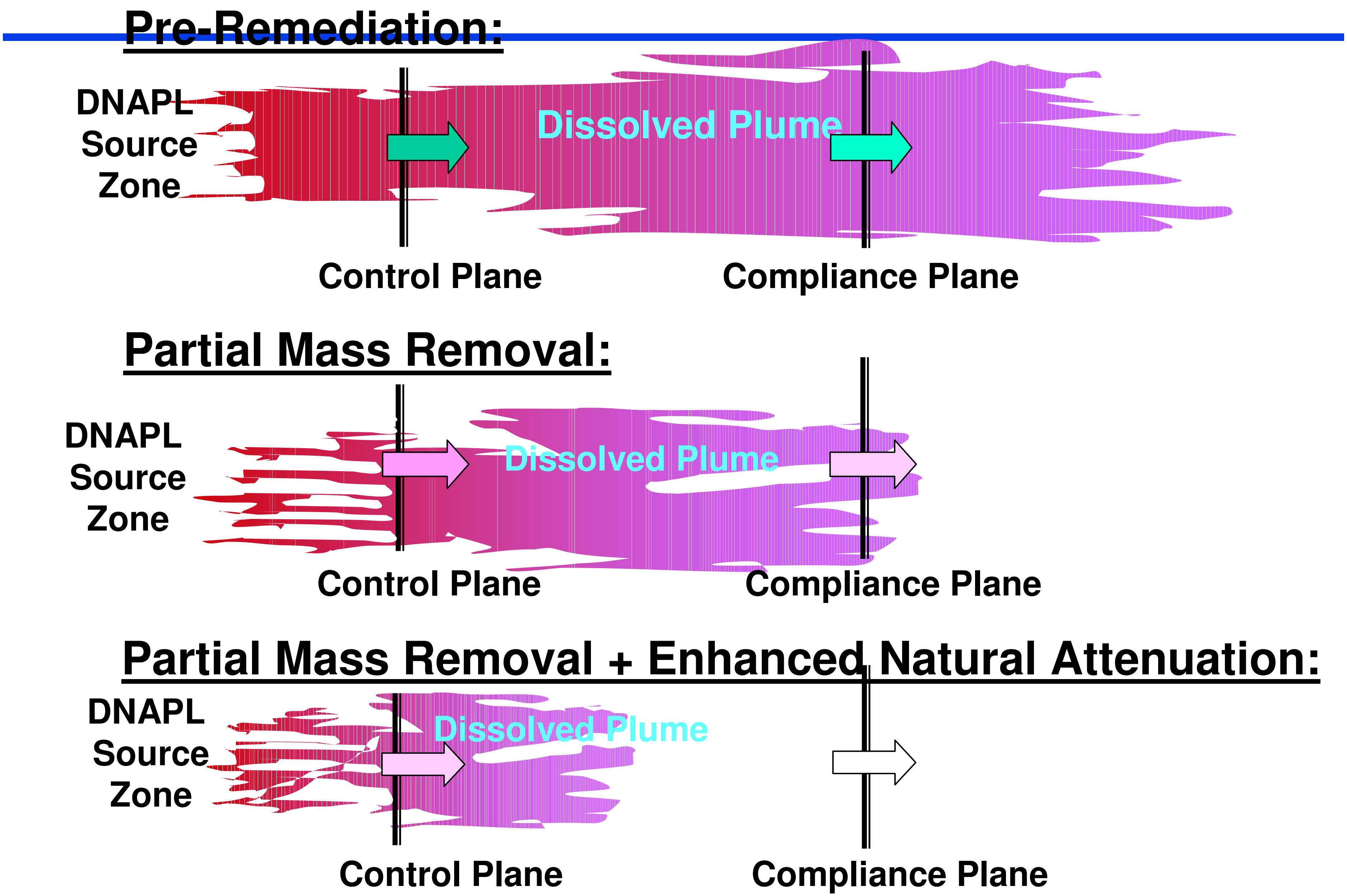
THE $64K ?: What to Do About the Large Sites – i.e. the Ones with Lots of Contamination

- Petroleum Refineries
- Wood Treaters
- Manufactured Gas Plants (MGPs)
- Large Solvent Recyclers

Desired End State/Least Cost Solutions

- Adequate Use of Robust Source Term Removal Technologies
- Timely transition to cost-effective ‘polishing’ step(s)
- Reduce/Eliminate Need for Pump and Treat
- Appropriate Reliance on MNA

PLUME RESPONSE



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- In Situ Oxidation and Surfactant/Cosolvent Flushing Databases Under Development