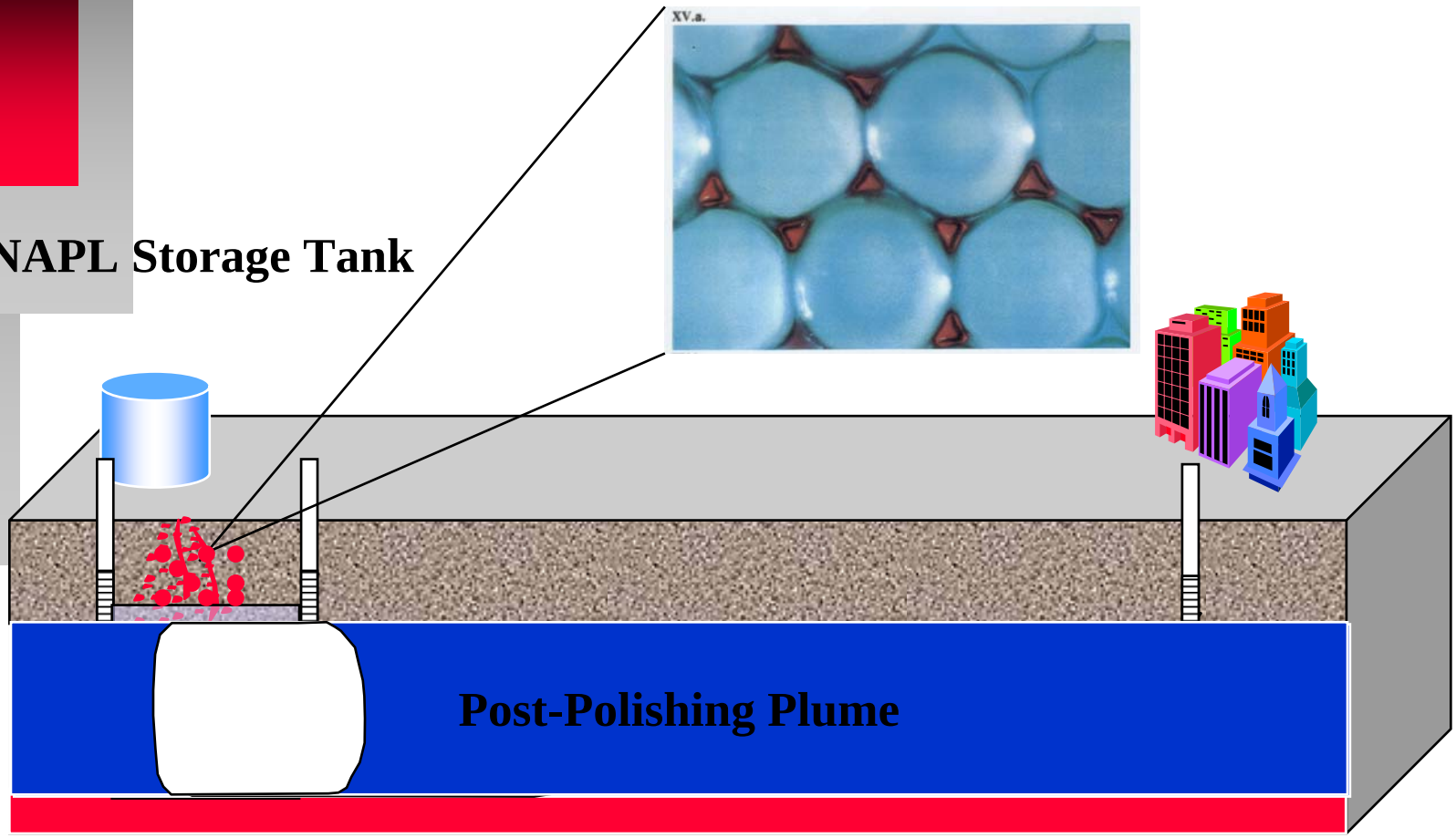
# Surfactant Enhanced Subsurface Remediation for Source Zone Removal: Fundamentals and Case Studies

Surbec Environmental and The University of Oklahoma
Norman, Oklahoma

# Problem / Approach

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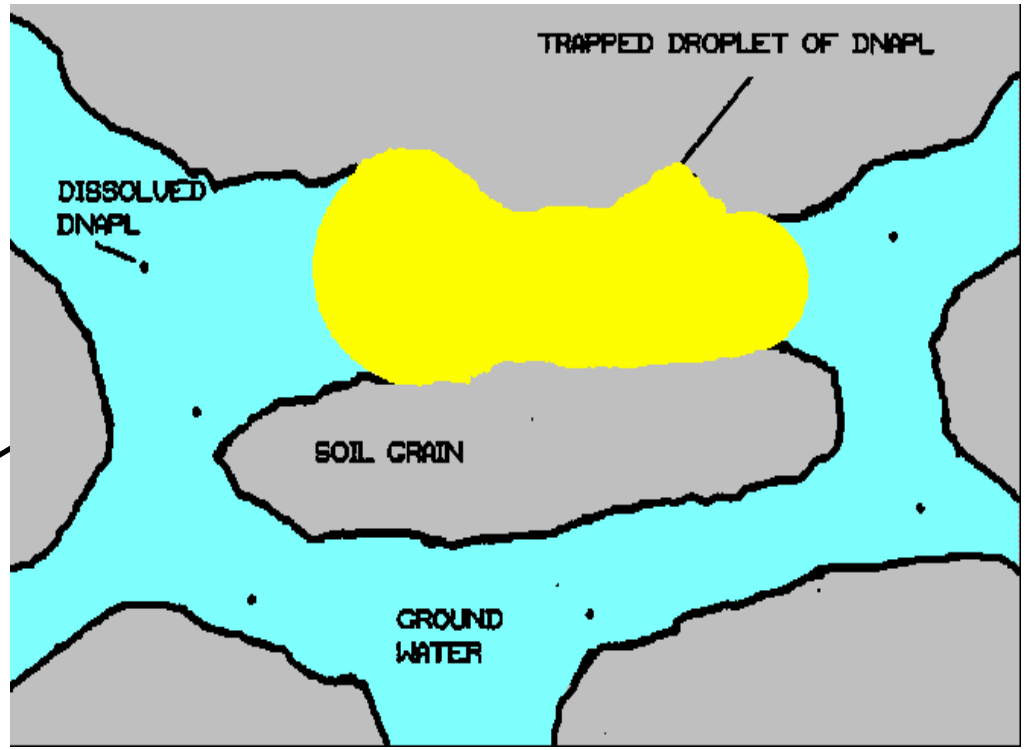
# NAPL is Trapped by "Capillary Forces"

**High o/w interfacial tension makes the oil immobile.**




**Low water solubility -- 100s to 1000s of flushings (years) to dissolve oil.**

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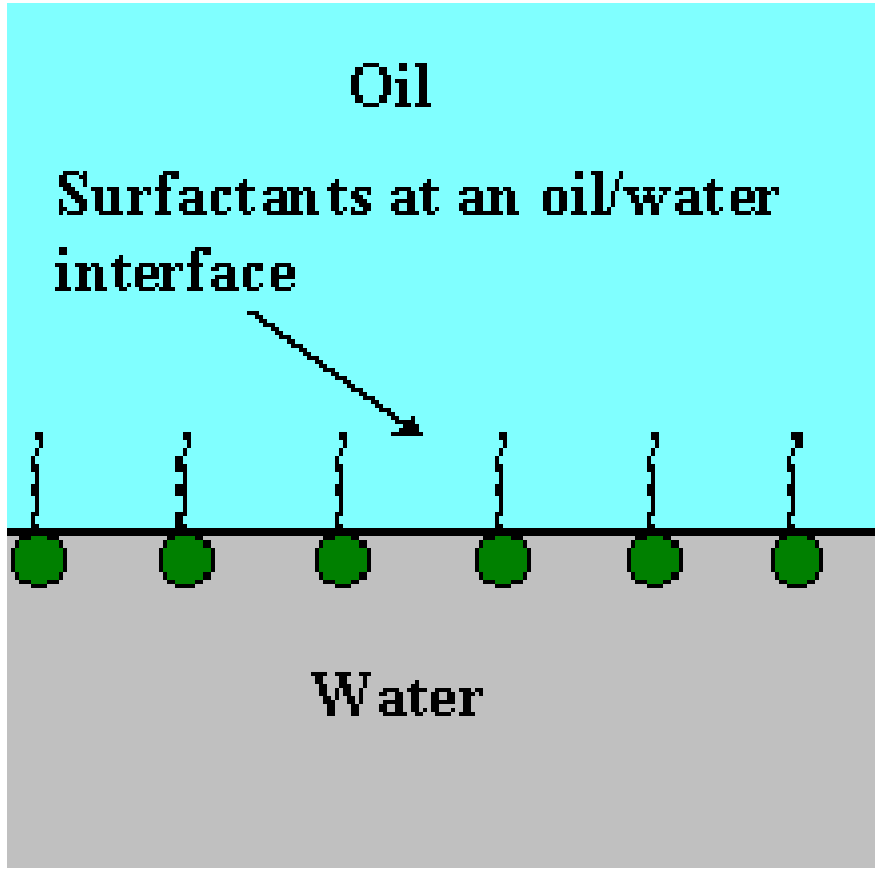
# A Surface Active Agent

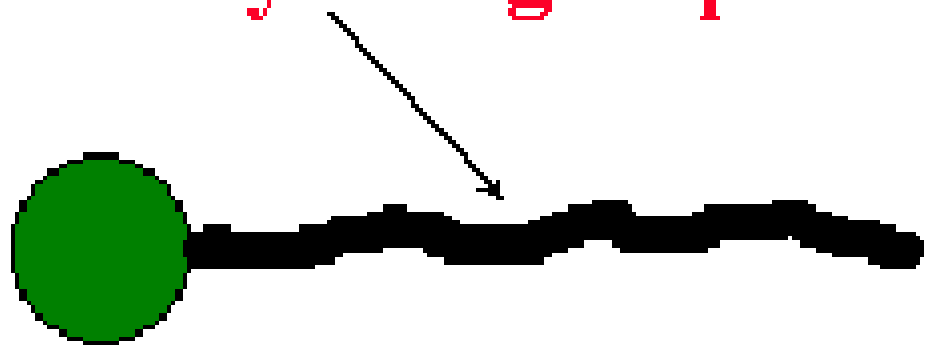
The word SurfActAnt is constructed from the phrase "Surface Active Agent". The word "surfactant" is meant to teach us that a surfactant is a molecule that seeks out and goes to a surface.



# Lauric Acid, found in milk and coconut oil, is a naturally occurring surfactant:

Dodecyl tail group--oil loving

Lauric acid is a naturally occurring food lipid.

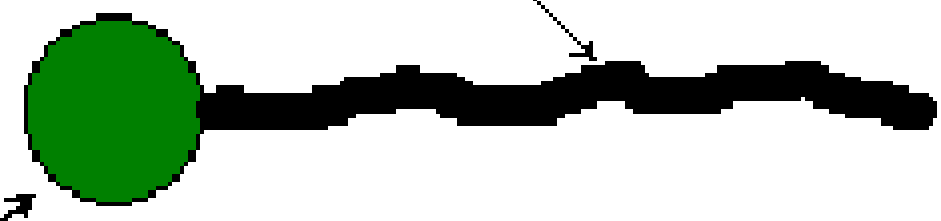


Carboxylic head group--water loving

$$\boxed{HOOC}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

# Sodium Lauryl Sulfate, made from coconut oil, is a good example:

Dodecyl tail group--oil loving

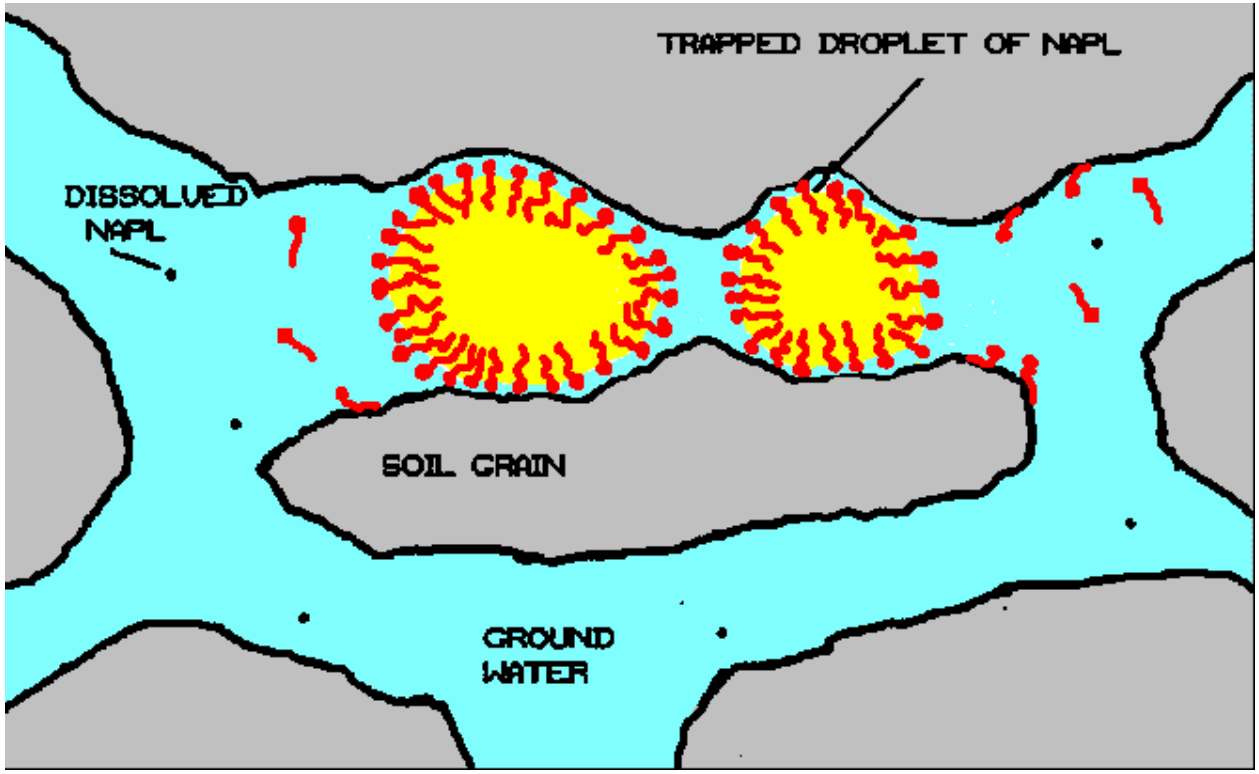


Sodium sulfate head group--water loving

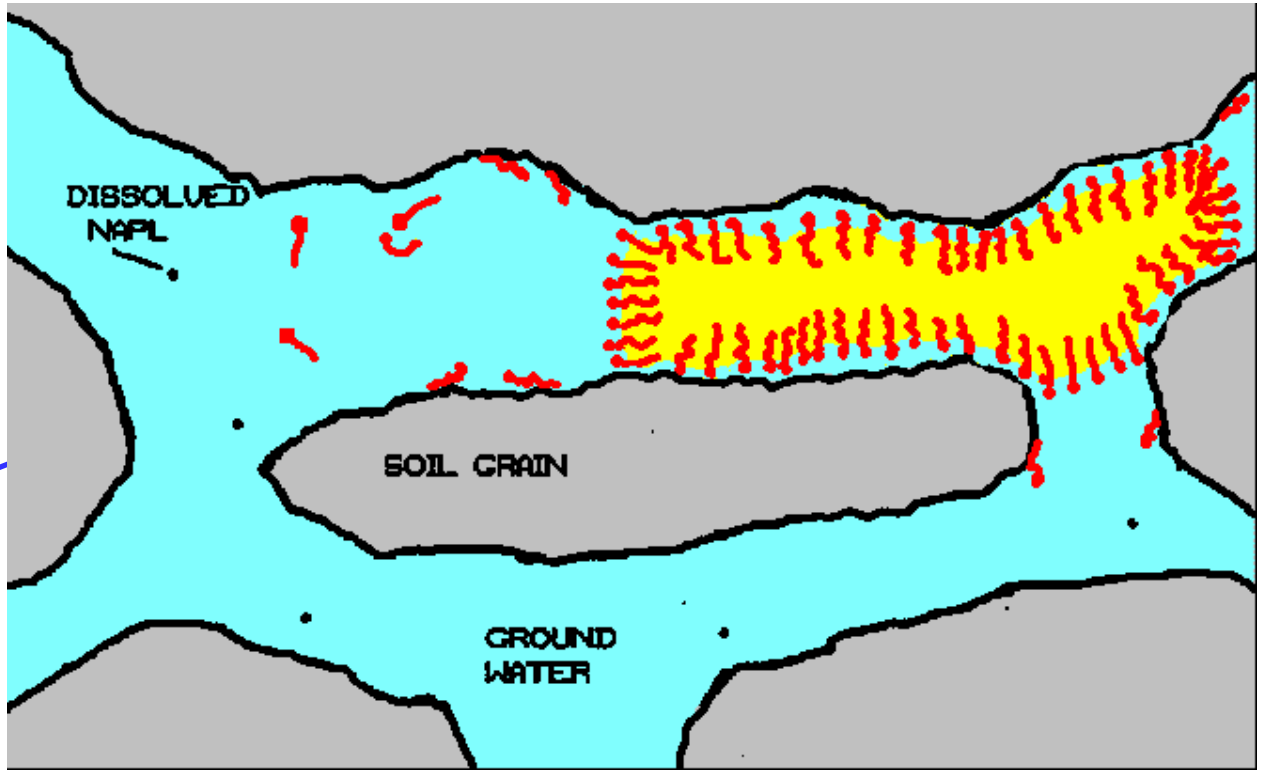
$NaSO_4$ $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

# Surfactant adsorption lowers oil/water IFT

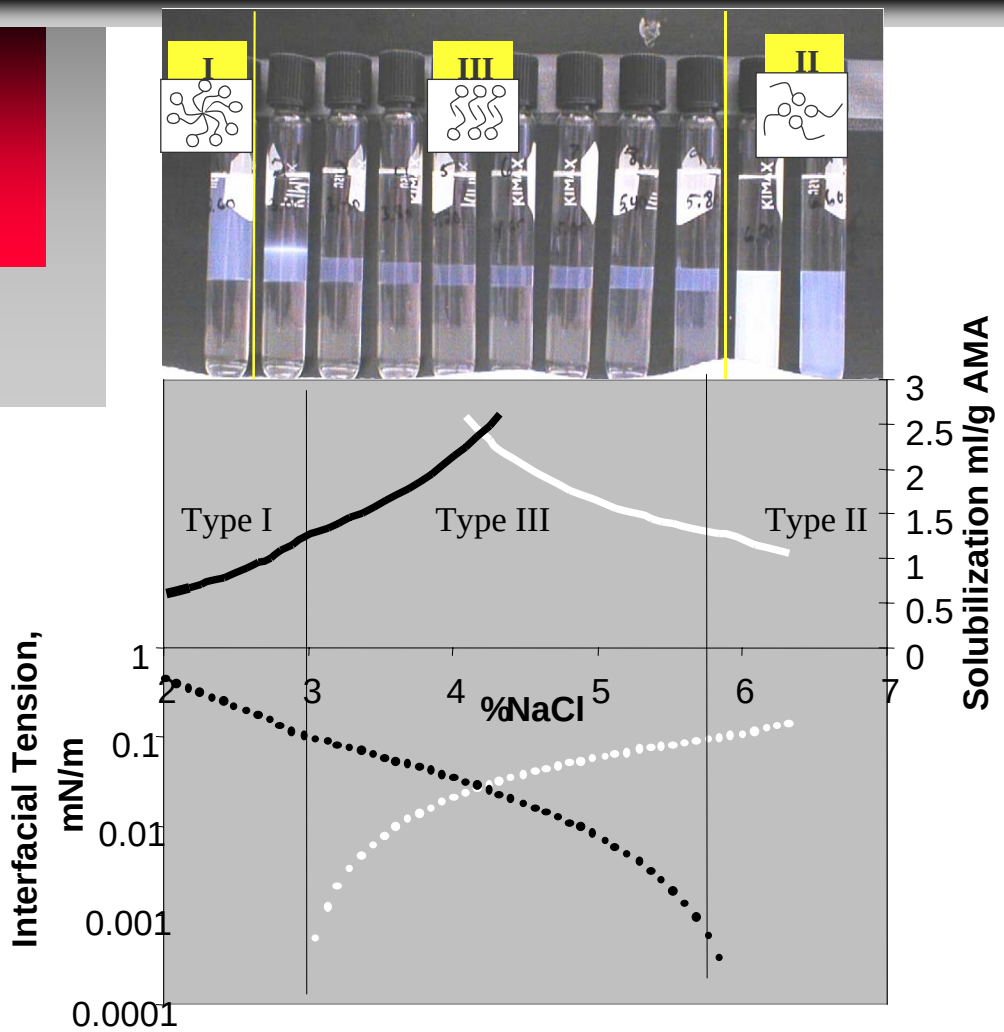
Dense monolayer lowers interfacial energy.



# Droplet is mobilized, begins to flow.



# Phase Scan: IFT / Solubilization




- Winsor Type I, III and II phases
- Solubilization enhancement maximum, IFT minimum -- Type III
- Type I to III boundary – solubility enhanced, IFT reduced versus "micelles"

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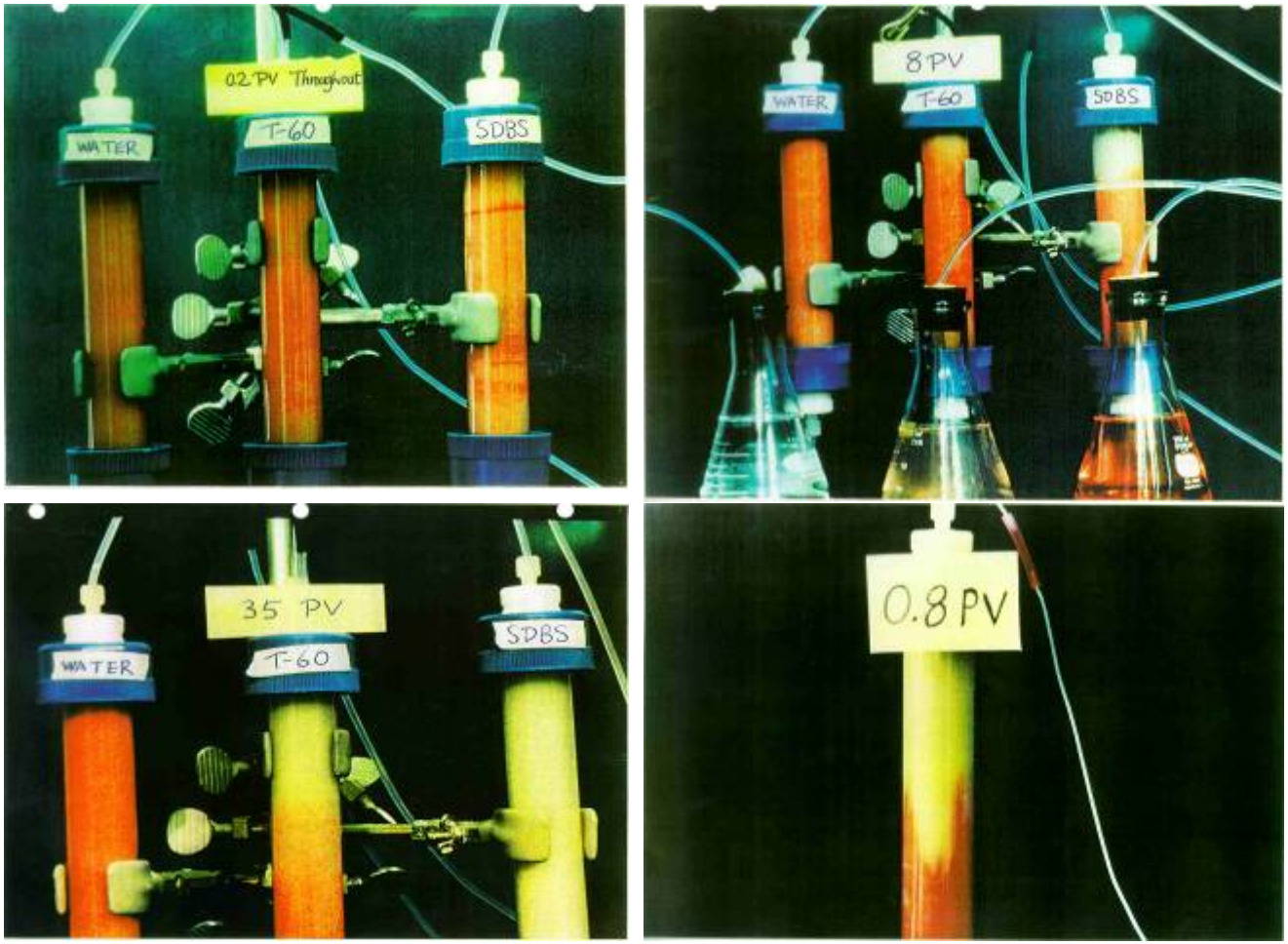
# Column Comparison

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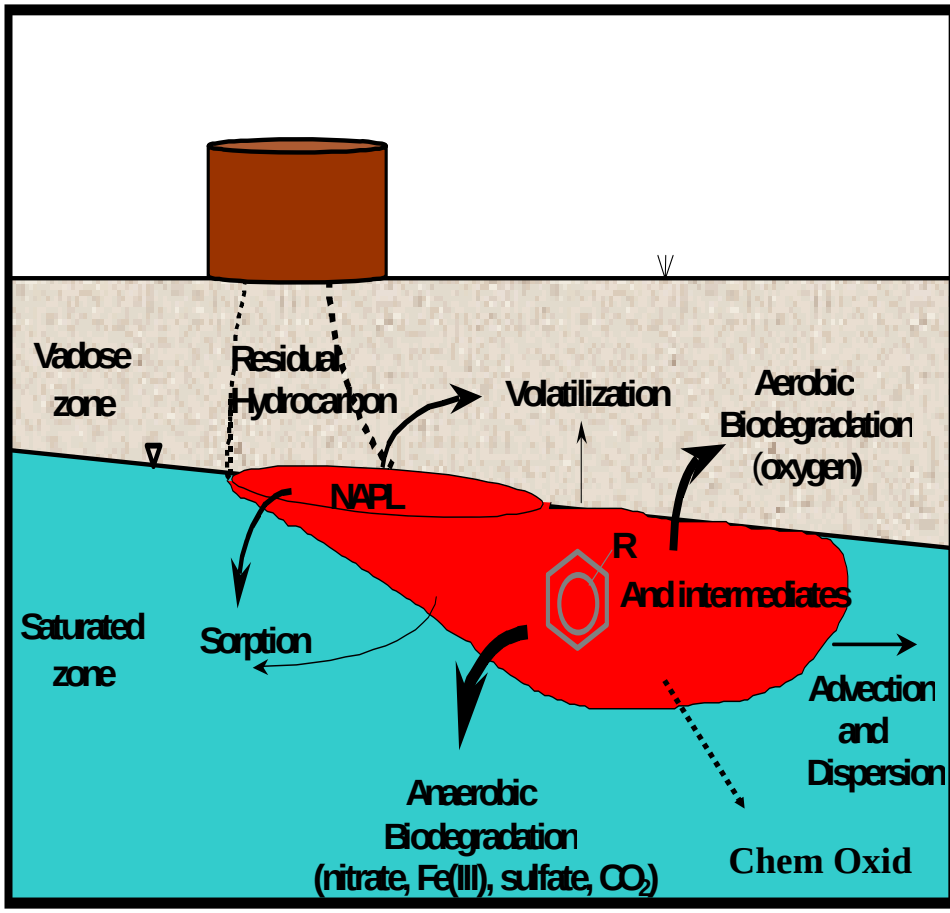
THE UNIVERSITY OF OKLAHOMA 1890

# Design Factors

- Contaminant chemistry, distribution
- Surfactant Chemistry is Critical!
- Site Hydrogeology: adsorption, heterogeneities, injection rates, sweep efficiency
- Scale-up Approach (avoid failure)
  - Batch, column, field scale – tracer test, pilot-scale test

# Integrated Low Surfactant/Chemical Oxidation Approach*/Bioamendment

- Surfactant flushing is not suitable for dilute plume remediation
- Polishing step: injection of low chemical oxidant (< 1 wt%) and/or bioamendment to polish remaining residual / dilute NAPL plume




*Surbec U.S. Patent No. 6,913,419

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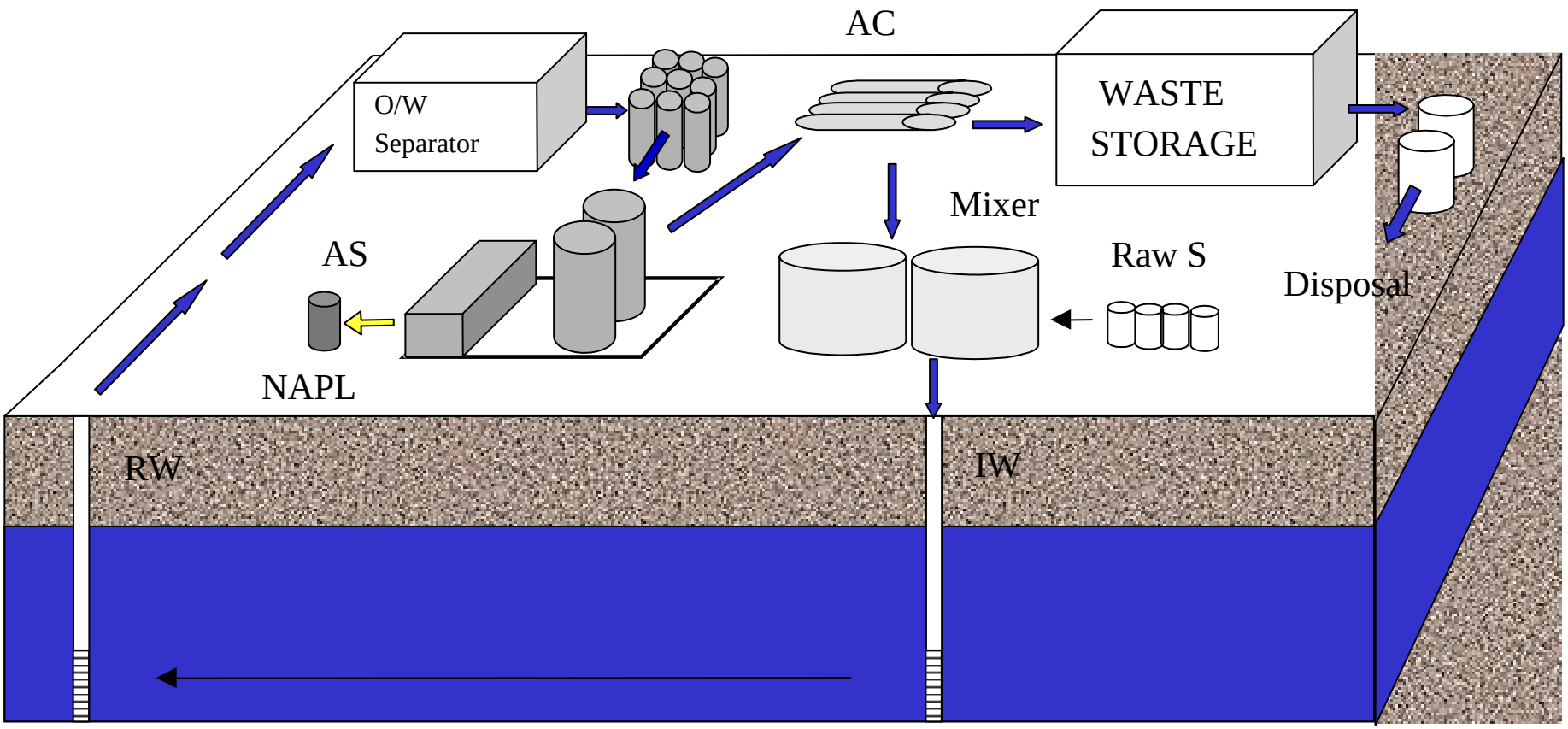
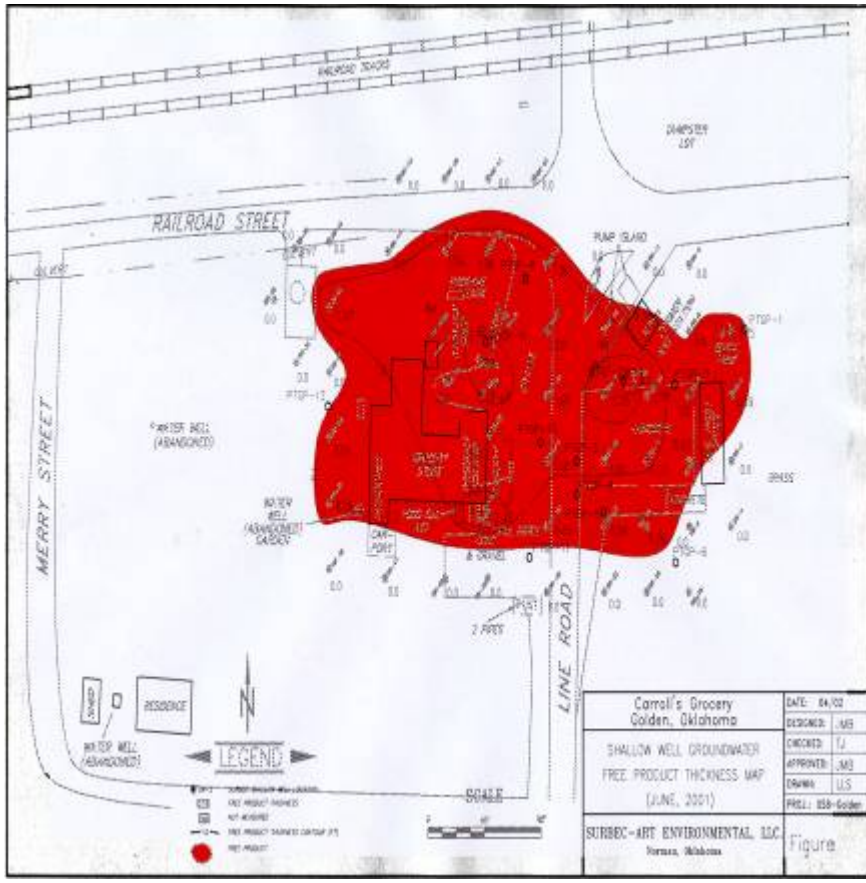
# Surfactant Flushing Integrated Process



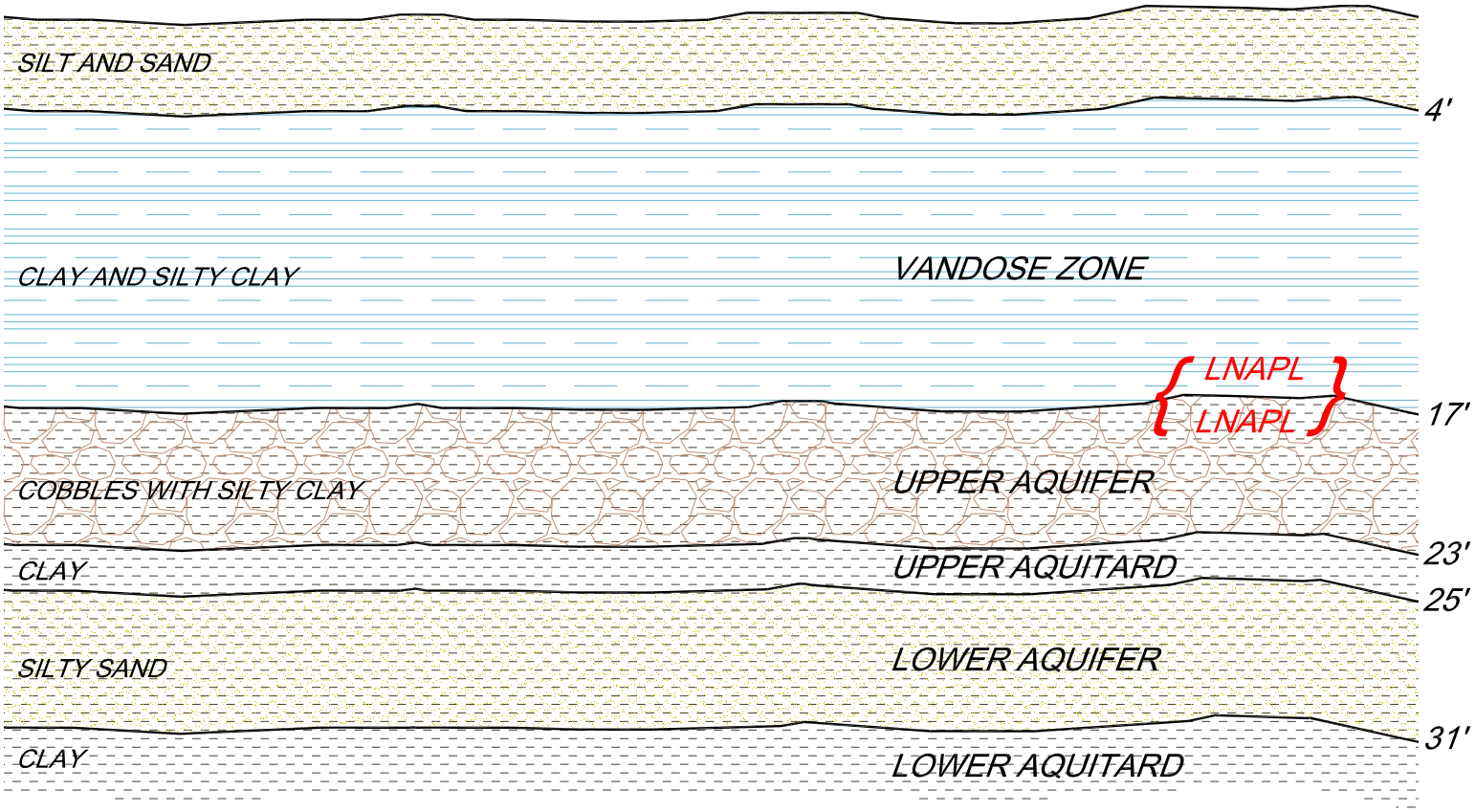
# Golden, OK UST Site
# Starting Point (LNAPL)-- 2-acre site

- 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




Golden Free Product Map

# SITE GEOLOGY AT GOLDEN

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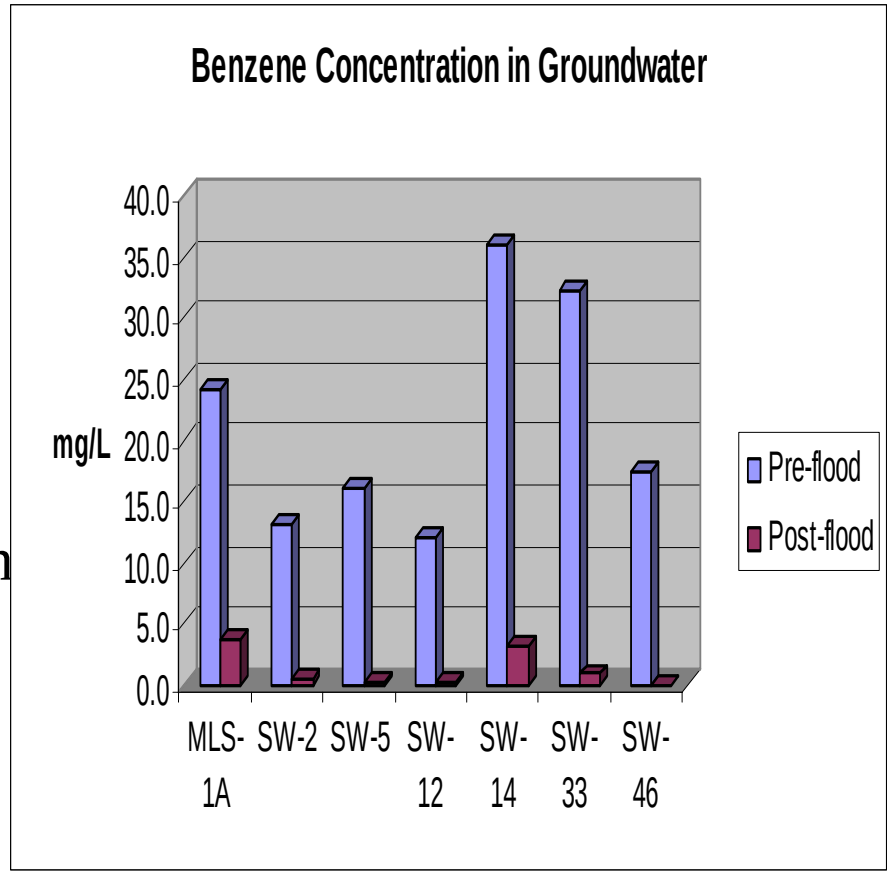
# Golden, OK UST Site Approach / Results

- Low level (< 1 wt%) surfactant/cosurfactant mixture
- 1 PV (190,000 gallons) – 60 days flushing
- Polishing: shallow -- low level chemical oxidation; deep – bioammendments (Phase I); chemical oxidation (Phase II)
- Soil and ground water concentrations reduced by one to three orders of magnitude




Data collected on 06/27/02

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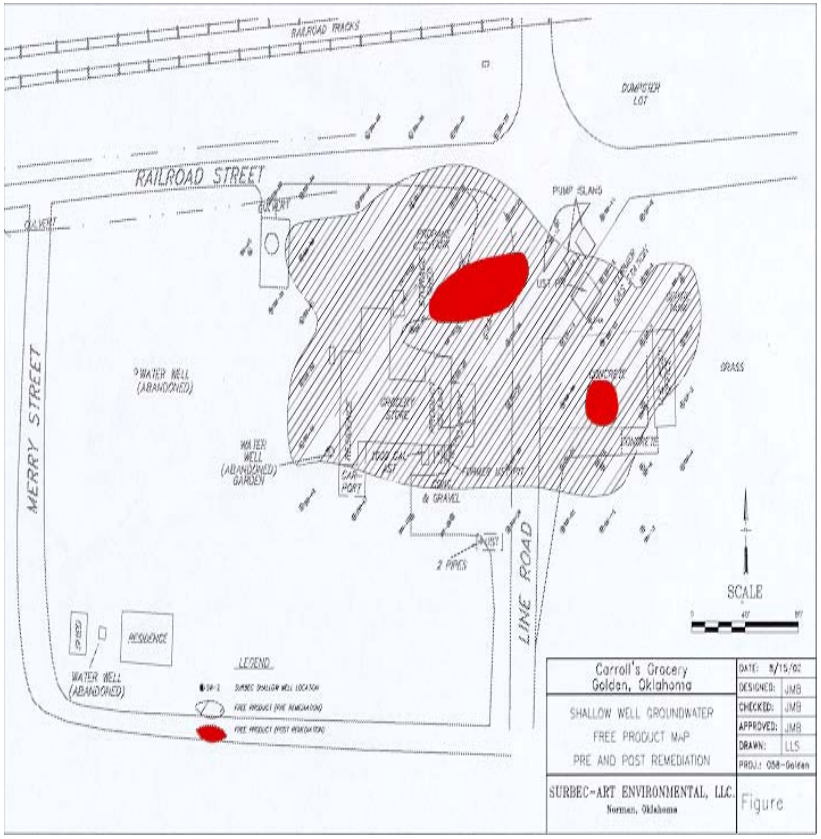
# Golden, OK UST Site
# Results vs Goals

- Primary: no visible or instrumental evidence of free phase gasoline in 22 wells after three-month shut-down (3 had trace levels of NAPL)



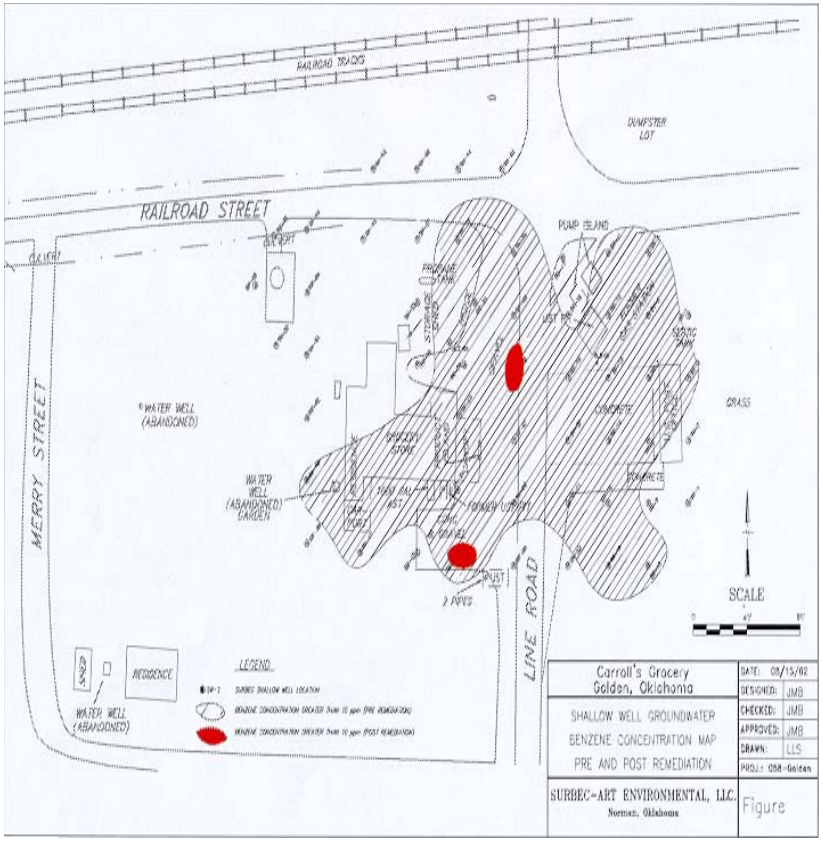

Post Flush Free Product Map
(06/02 data collected)

# Golden, OK UST Site Results (cont.)

- Secondary:

  Groundwater

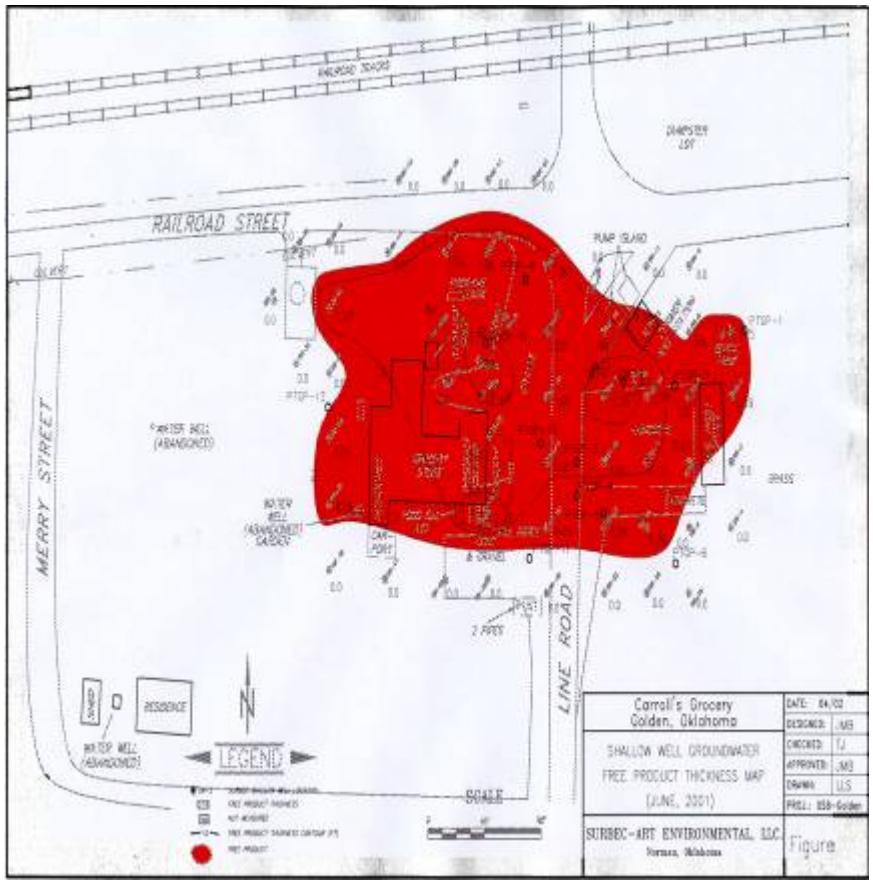
  70% to 99% reduction in benzene concentration
- Final Polishing (Chem. Oxid.) to approach MCL



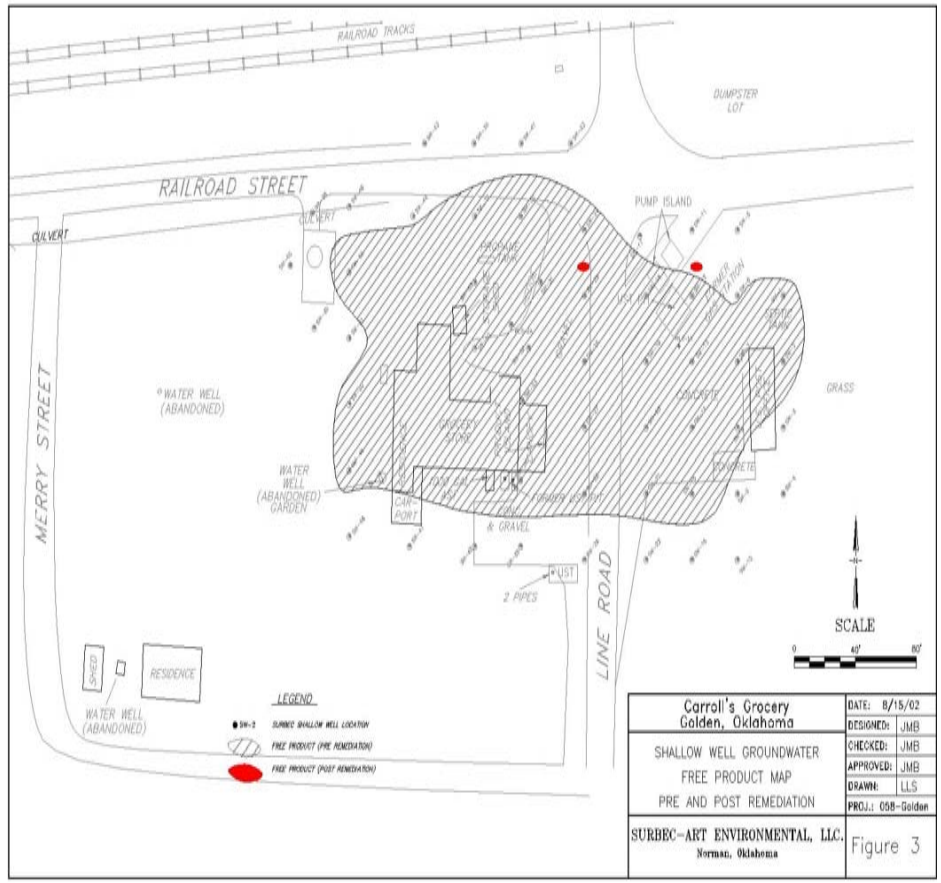

Post Flush Benzene Map
(06/02 data collected)

# Free Product Four Years Later

**September 2001**




**January 2006**




**Water Table: 11 feet**

**Water Table: 16 feet**

Bixby, Oklahoma
UST Site

# Bixby UST Site
# Bixby, Oklahoma

SURFACE (MW-10)

BROWN SANDY CLAY TO OLIVE GRAY SILTY CLAY

8’

LIGHT BROWN TO ORANGE MEDIUM SAND

13’

BROWN COURSE SAND

14’

GRAY COURSE SAND

20’

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# Bixby UST Site, Bixby, OK (LNAPL)

## Treatment

- NAPL: mixed gasoline and kerosene
- Geology: silty clay to coarse sand
- Free product: 0.5 to 2.2 ft in MWs, extent 120 ft x 85 ft
- Surfactant flushing: 0.94 wt%, 120,000 gallons (1.5 PV) over 13 days
- Polishing: 0.4 wt% Fenton's Reagent, 130,000 gallons over 6 days

## Results

- No free product was observed after surfactant flushing
- Post surfactant flushing: GW Benzene conc. 50 ug/L to 20 mg/L
- Post chem ox polishing: GW Benzene conc. ND to 1.8 mg/L (SSTL 5.6 mg/L)
- Project completed in 2.5 months

# Douglass HS Site, OKC

- 3.1 acres school campus impacted by an upgradient UST facility
- Soil volume treated: 19,444 $yd^3$, fine to silty sand between 22’-28’
- Goal: free product gasoline removal
- Initial product thickness: 0.02’ to 1.3’ in eleven monitoring wells

Douglass HS

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# Douglass HS (cont.)

- Surfactant injection: 1.23 PV (921,500 gallons) between six months (10/04 – 03/05)
- No free product gasoline were present in ten monitoring wells
- Confirmatory soil borings indicated low contaminant level is ready for site closure after surfactant flushing (data collected in 05/05)

Douglass HS

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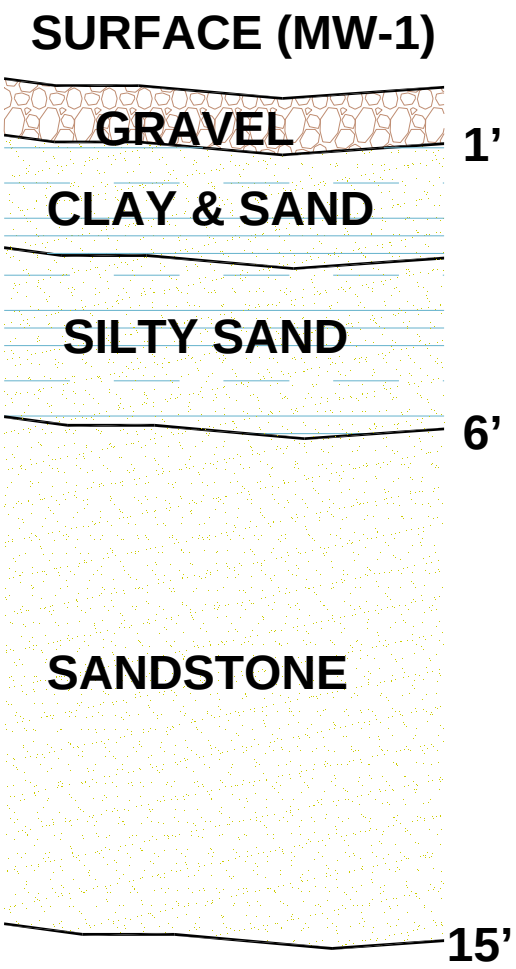
# BRISTOW, OK




- Fracture Sandstone
- Surfactant Flush
- Free product removed
- 3 months from mobilization to demob

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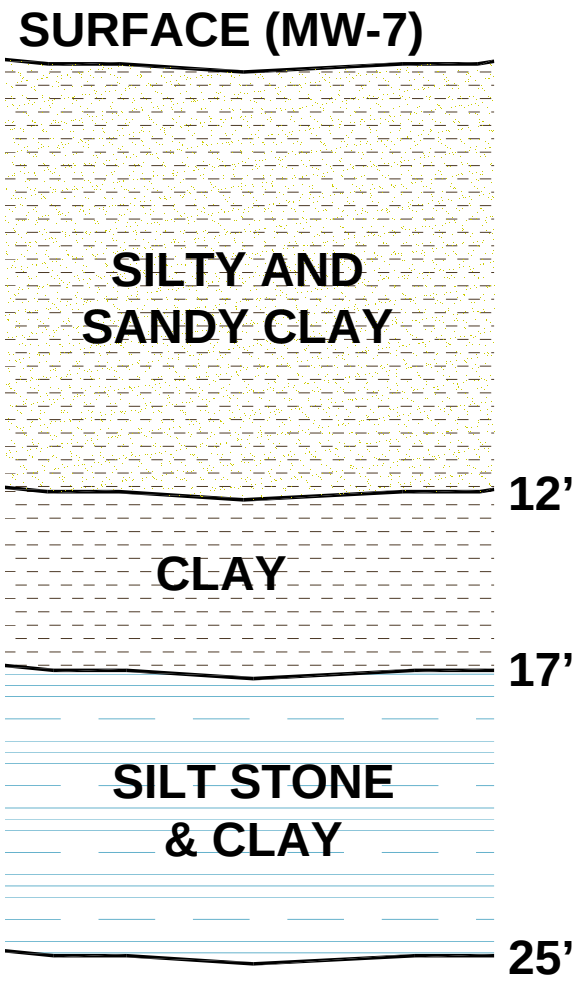
# HOLDENVILLE, OK




- Remediation requirement: free product removal, GW SSTLs (5.5 ppm benzene)
- Flush + Chem. Ox.
- Mob to Demob 6 months

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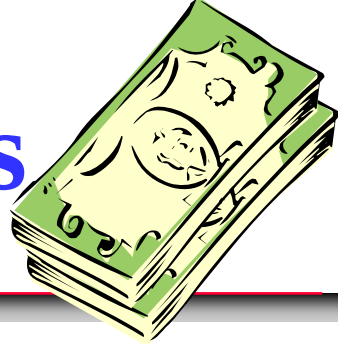
# Site Specific LNAPL Costs



| UST | project cost | $yd^3$ | $/$yd^3$ † |
|---|---|---|---|
| Douglas | $1,453 K | 19,440 | 75 |
| Golden | $712 K | 15,550 | 36 |
| Bixby | $275 K | 5,400 | 51* |
| Bristow | $258 K | 2,900 | 89 |
| Holdenville | $390 K | 1,642 | 238* |

**Figures are *total* cost for project, site investigation to demob, including waste disposal**

† varies with size, NAPL, lithology, Clean-up level

*cost included chem oxid

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# Excellent Track Record with DNAPLS

Ground Water Monitoring&Remediation

## Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites

*by Travis M. McGuire, James M. McDade, and Charles J. Newell*


### Abstract

Performance and rebound of intensive source depletion technologies were evaluated at 59 chlorinated solvent sites where remediation targeted dense non–aqueous phase liquid (DNAPL) source zones. The four technologies included in the study are chemical oxidation, enhanced bioremediation, thermal treatment, and surfactant/cosolvent flushing. Performance was evaluated by examining temporal ground water concentration data before and after source remediation was performed. Results indicated that all four technologies have median concentration reductions of 88% or greater for the parent chlorinated volatile organic compound (CVOC). Approximately 75% of the source depletion projects were able to achieve a 70% reduction in parent compound concentrations. A median reduction in total CVOC concentrations (parent plus daughter compounds) of 72% was observed at 12 chemical oxidation sites and 62% at 21 enhanced bioremediation sites. Rebound was assessed at sites having at least 1 year of posttreatment data. Rebound occurrence was most prevalent at sites implementing chemical oxidation. At chemical oxidation sites where rebound was evaluated ($n = 7$), the median parent CVOC concentration reduction was 90% immediately following treatment compared to 78% at the end of posttreatment monitoring (i.e., 1 to 5 years after treatment). For enhanced bioremediation sites where rebound was evaluated ($n = 10$), median parent CVOC concentration reduction changed from 77% to 96% over the posttreatment monitoring period. Minimal concentration change was observed over the posttreatment monitoring period at surfactant/cosolvent sites ($n = 2$) and thermal treatment sites ($n = 1$) evaluated for rebound. Based on current data, none of the 59 source depletion projects was able to meet maximum contaminant levels throughout the treatment zone for all CVOCs.

# Three Significant Conclusions:

- Surfactant flushing best record for mass removal (>95%)
- Ground water concentration reduction proportional to mass removal
- No rebound observed for surfactant sites

**McGuire, T.M., McDade, J.M., Newell, C.J., 2006. "Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent Impacted Sites."** ***Ground Water Monitoring & Remediation*** **26: 73 -84.**

- Surfactant Flushing is fast--significant NAPL mass removal can be achieved in ***weeks***
- Economically--very competitive with other technologies including pump-and-treat and dig-and-haul
- Combination of Surfactant Flushing (source removal) with Chemical Oxidation and/or Bioamendments (contaminant plume polishing) will expedite site closure
- Safe—all surfactants used have direct or indirect food additive status and pass EPA biodegradation tests
- Compatible with built infrastructure
- Chemistry and hydrogeology critical

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# Tank Pit Flushing

- **Pollution Prevention**:
  - Free phase removal (gasoline & diesel pits)
  - Love's Country Store (OKC, Completed--10/02)

Love's Tank Pit

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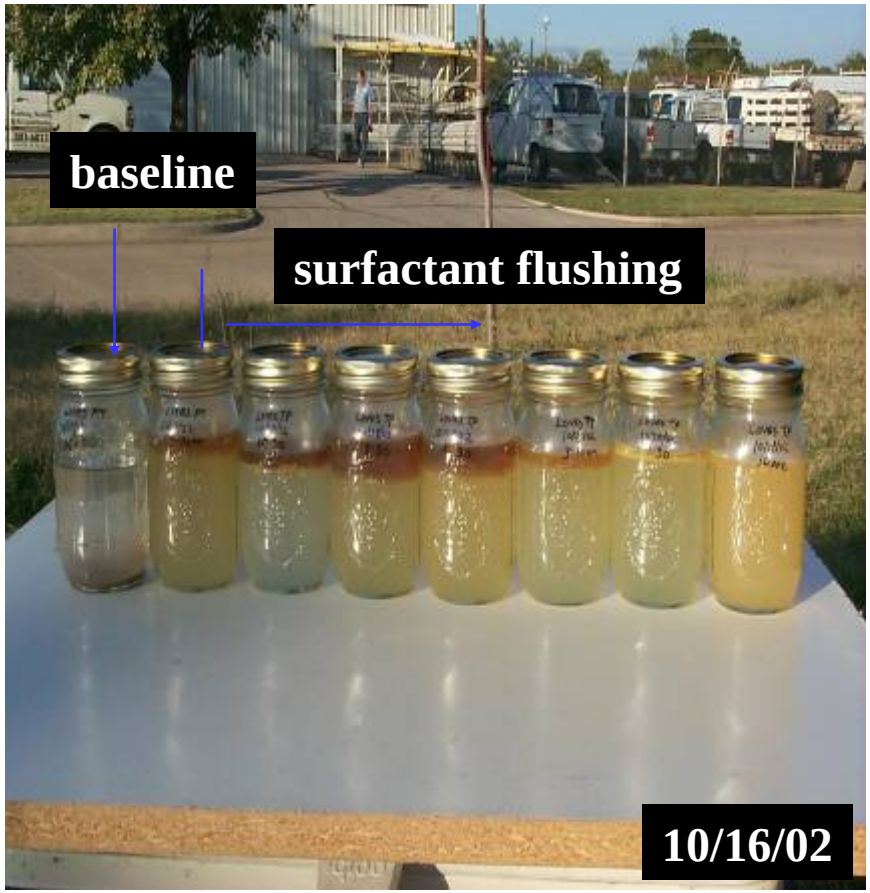
# Tank Pit Flushing (cont.)

- Approach: low surfactant conc. (1PV)
- Different surfactant systems for gasoline and diesel pits
- Low cost (< $ 50K)
- Recycling/ reuse of recovered water
- Compact design without interrupting the routine activity




Tank Pit Effluent

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# Questions

- For copies of the presentation:

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