



Surfactant-Enhanced Site Remediation

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Roadmap



Surfactant-Enhanced Remediation

- **Enhancement Strategy:** Surfactant-Enhanced Remediation to facilitate fast capture of residual petroleum fuel mass (LNAPL and sorbed)

- **Presentation Focus:**
 - Description of Surfactants (What)
 - Need for Enhancements (Why)
 - Application Methods (How)
 - Successful Situations (When)

SURFACTANTS

Surfactant-Enhanced Remediation

- Surfactants, or surface-active agents, are chemical compounds that have the potential to alter the properties of fluid interfaces.
- Surfactant usage dates back to the 1960s when sulfonate surfactants attained widespread use for enhanced oil recovery efforts. Use in environmental applications dates to the 1980s.
- Surfactants are composed of a strongly hydrophilic (water loving) group, and a strongly hydrophobic (water fearing) group

Hydrophobic "tail" group



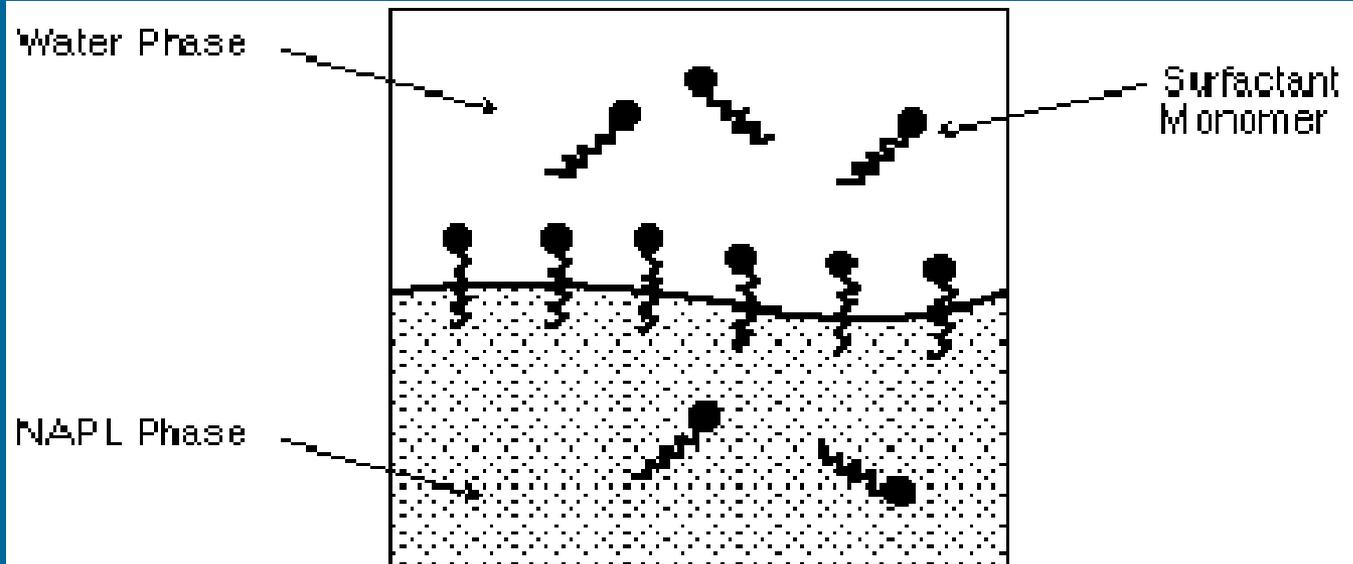
*Hydrophilic
"head" group*

Surfactants at NAPL-Water Interface

Surfactant-Enhanced Remediation

When a sufficient amount of surfactant is added to an aqueous solution, surfactant micelles will form

The threshold concentration for micelle formation is termed the CMC



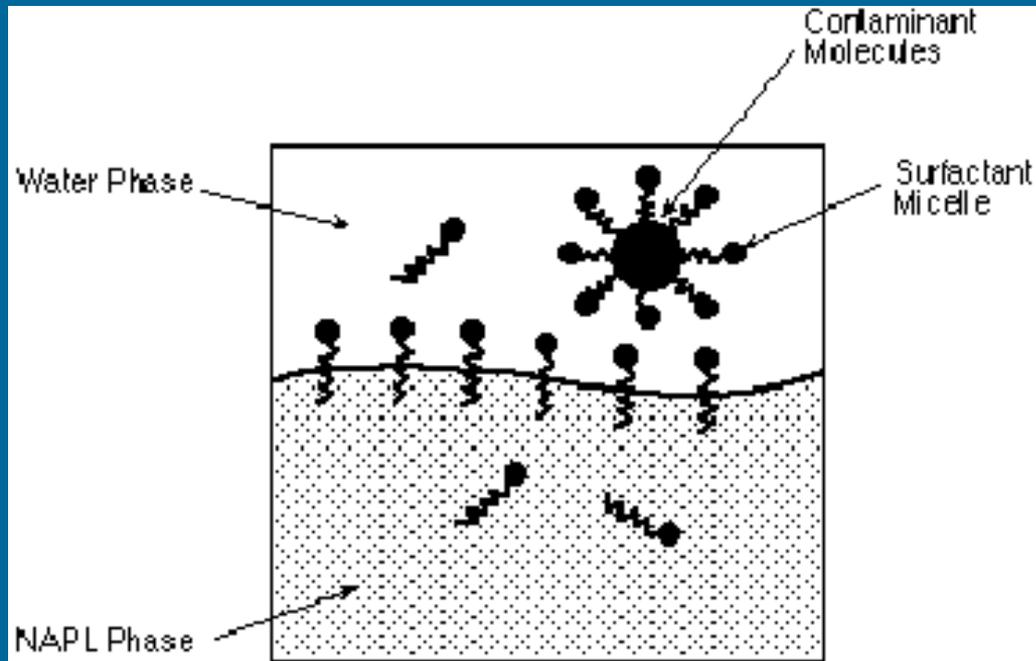
Surfactant monomer accumulation at the NAPL-water interface

NAPL Solubilization/Mobilization

Surfactant-Enhanced Remediation

Micelles are oriented with hydrophobic tails pointed toward interior of micelle

This produces a hydrophobic interior where organic molecules can form (increases total solubility of target NAPL by 10 to 100 times)



Surfactant monomers and micelles in equilibrium with contaminant molecules and solution interface

PETROSOLV™

Surfactant-Enhanced Remediation

PetroSOLV™ BioSurfactant

- Biodegradable
- Concentrated
- Off-the-shelf recipe for gasoline/diesel
- Adjustable formula for other fuels (motor oil, hydraulic oil, fuel mixtures, etc.) – no additional cost.
- Available in small quantities or large bulk quantities (5-gal, drums, totes)
- Low Cost (\$20-\$35/gallon based on quantity)



ETEC Biological Enhancements

Surfactant-Enhanced Remediation

- **CUSTOM BLEND NUTRIENTS - CBN™**
 - Contains ~65% electron acceptors (nitrate and sulfate)
 - N, P, K, and micronutrient blend in correct microbial ratio (100:25:5)
 - Fully Soluble



Need for Surfactant

Surfactant-Enhanced Remediation

➤ EQUILIBRIUM & INTERFACIAL TENSION

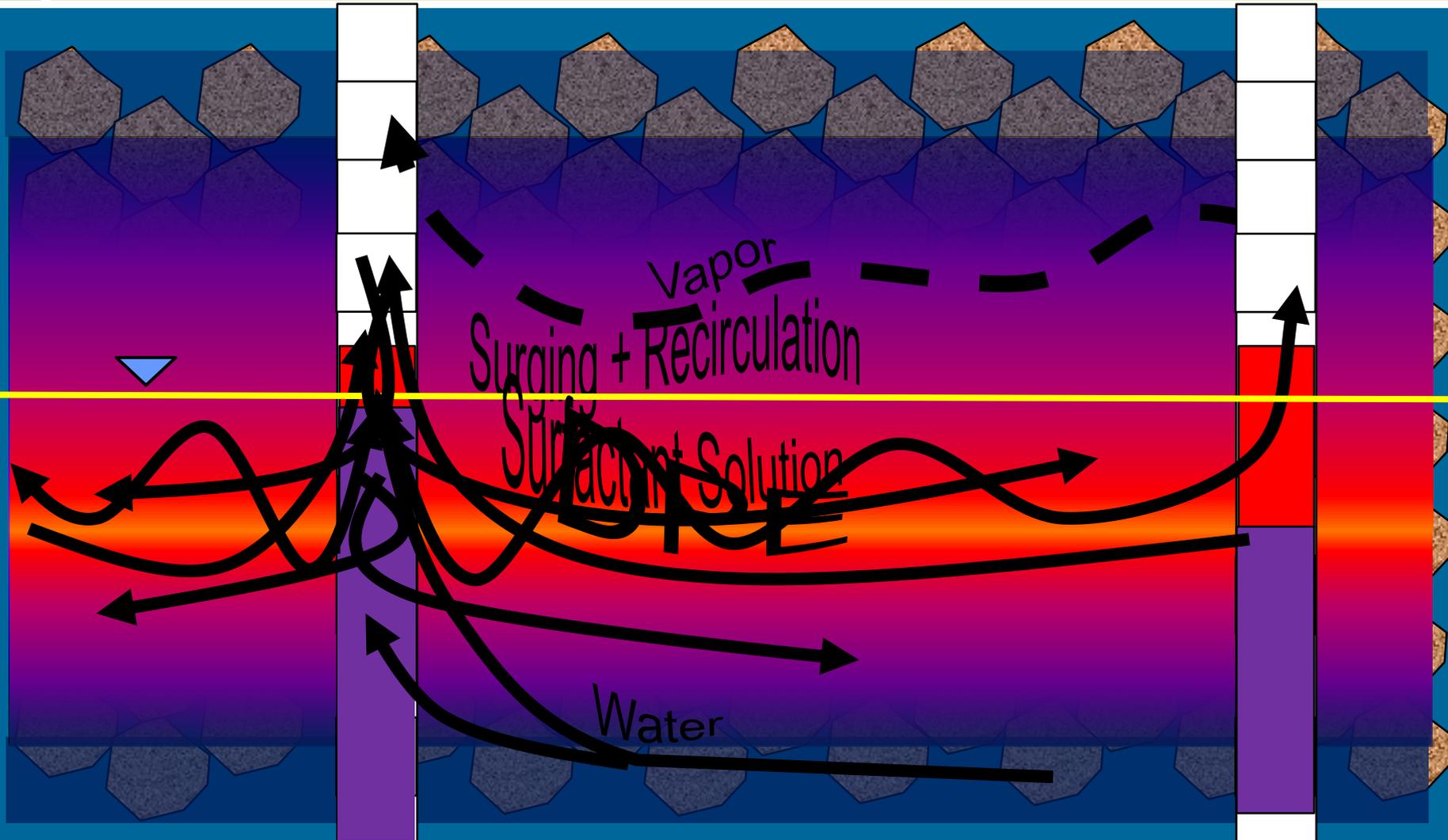
- LNAPL has sorbed to soil, produced dissolved-phase contaminants, and often filled soil pore space
- Installation of wells creates “void” that allows fuel to temporarily accumulate
- LNAPL is hydrophobic, so it won't readily mix with water
- Even under high vacuum, LNAPL can often linger for long time period
- LNAPL, soil and GW are in steady-state equilibrium – aged plumes, so LNAPL sorbed, trapped or “comfortably situated” in the smear zone

➤ LOW GW VELOCITY/GRADIENT AND SOIL CONDITIONS

- Heterogeneous subsurface consists of layers/zones of soil material with differing properties
 - Sorption
 - Hydraulic Conductivity
- Impacted smear-zone soil is often submerged for portions of the year – capillary pressure keeps LNAPL trapped - difficult for DPE alone to capture

Contaminated Site Realities

Surfactant-Enhanced Remediation



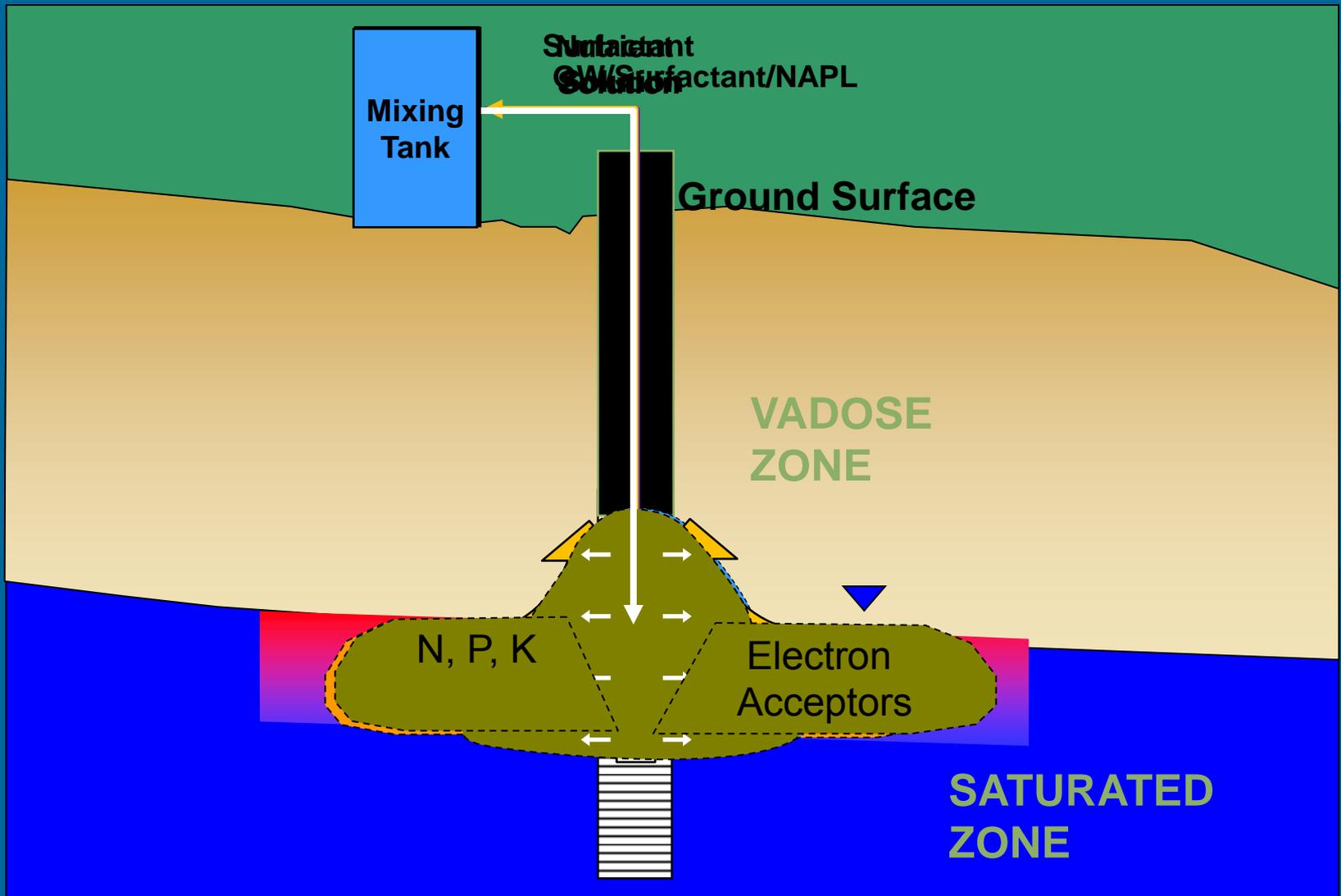
FIELD APPLICATION TECHNIQUES

Surfactant-Enhanced Remediation

- **PUSH-PULL**
 - Applicable for small free product areas with only 1 or 2 impacted wells
 - Requires limited equipment and time (1-2 days)
- **GW RECIRCULATION**
 - Necessary for large free product areas with multiple impacted wells
 - Requires injection and extraction equipment, and large holding tanks
 - An effective recirculation event usually takes 3-5 days minimum to implement
- **COMBINED WITH MOBILE/FIXED DUAL-PHASE EXTRACTION**
 - Surfactant can be injected into existing DPE wells
 - Agitation & Contact time = maximum solubilization/mobilization of NAPL
 - Fluid Extraction followed by DPE activation – increased TOV/VOC concentrations

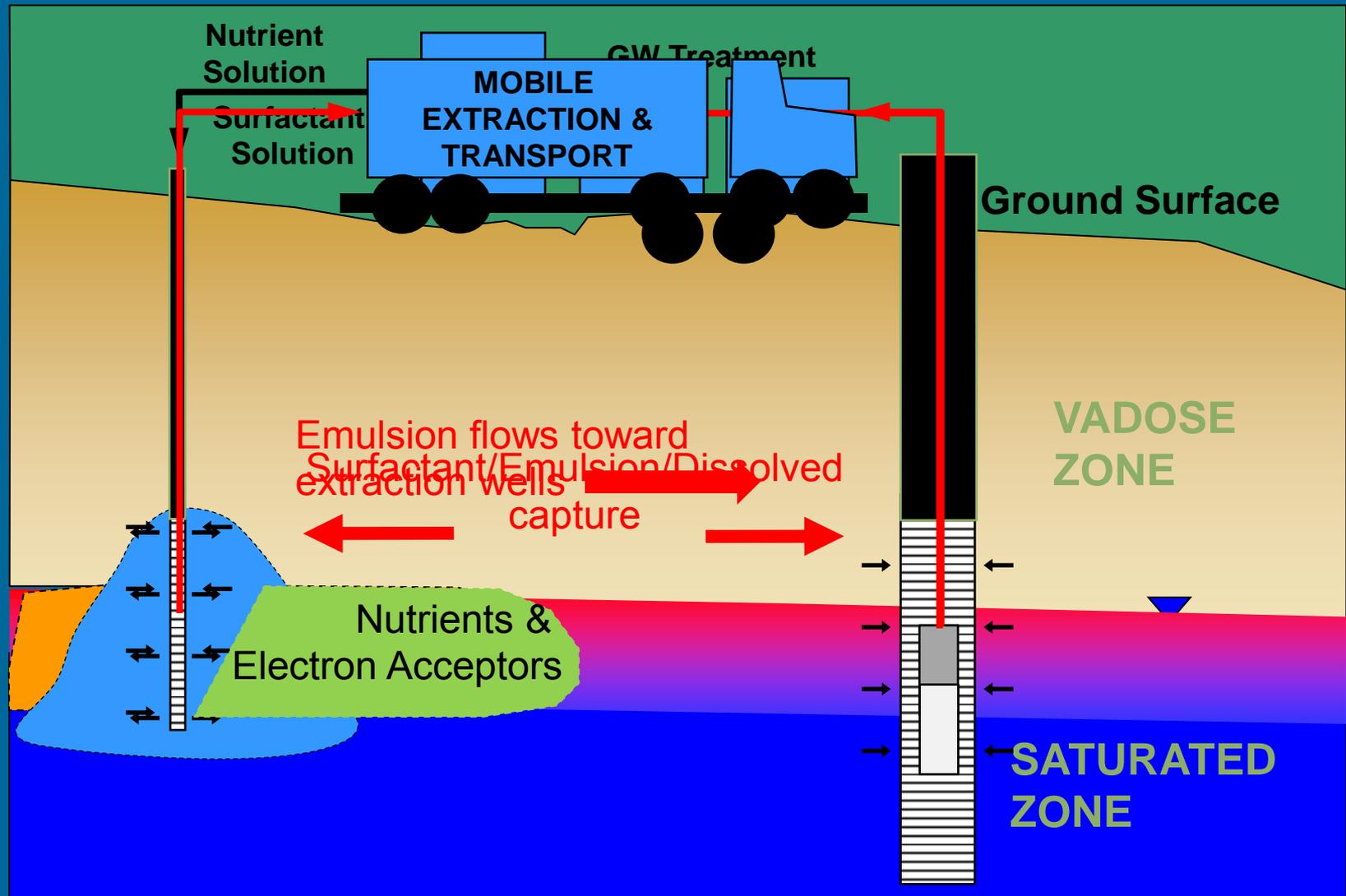
PUSH-PULL for NAPL Capture

Surfactant-Enhanced Remediation



GW RECIRCULATION for NAPL Capture

Surfactant-Enhanced Remediation



KEY FIELD CONSIDERATIONS

Surfactant-Enhanced Remediation

- **GW ELEVATION**
 - Surfactant injection when smear zone is submerged – impossible to mound GW.
 - Optimum contact with sorbed fuel & trapped NAPL
- **SUBSURFACE AGITATION and PRESSURE INJECTION**
 - Vigorous surging (surge block) forces surfactant thru NAPL-saturated soil
 - Localized soil washing = larger and larger contact ROI for surfactant
- **INJECTATE VOLUME**
 - More fuel/NAPL = more surfactant fluid
 - Chase water is effective to minimize costs, maximize fluid flow
 - With surfactant injection, the groundwater fluid can temporarily carry significant fuel mass (opposite of normal DPE operation)

KEY FIELD CONSIDERATIONS



Surfactant-Enhanced Remediation

- **LOCALIZED HYDRAULIC CONTROL IS CRITICAL**
 - Fluid Recovered > Fluid Injected
 - Active GW extraction of 1.5 to 3 times the injectate volume = successful capture zone & enhanced fuel mass recovery
- **POST-INJECTION ENHANCEMENT**
 - Provide long-term remediation process, abates 5-25 equiv. gallons of fuel
 - Minimal Cost (typically \$1,000 - \$3,000)

ETEC DESIGN/PROPOSAL PROCESS

Surfactant-Enhanced Remediation

➤ Site Data

- Boring Logs
- Water/LNAPL Levels
- Historic BTEX/TPH Data
- Pump Test/Mobile DPE Data (Fluid Volumes)

➤ Detailed Proposal

- Estimated Horizontal Target Zone
- Estimated Vertical Target Zone (smear zone)
- Best time to perform event (based on annual hydrograph)
- Costs for ETEC implementation or Products Only or Products + Trailer
- Detailed Scope of Work for given injection event



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Surfactant-Enhanced NAPL Oil Recovery at Active Industrial Facility - NJ

FACILITY: Active Power Plant
LOCATION: New Jersey
EQUIPMENT: Mobile Trailer Unit
PRODUCTS: PETROSOLV™



CASE STUDY

Project Background

Surfactant-Enhanced Remediation

- Active Power Plant Facility with 2 distinct NAPL areas
 - Area 1 contained ~ 0.5' diesel free product, likely from overflow of adjacent generator
 - Area 2 contained ~ 3.0' used motor oil from used oil drum storage area
 - Monitoring wells and soil borings installed in each area to delineate NAPL plume
 - Manual Bailing and several Mobile High Vacuum Recovery (HVR) events applied to wells in Area 1 and Area 2, NAPL persisted.
- Hydrogeology
 - Silty sand
 - DTW ranged from 5 feet to 8 feet bgs
- NAPL Plume Size
 - Area 1: 15 feet x 15 feet
 - Area 2: 20 feet x 20 feet
- Remediation Goals
 - Remove NAPL to less than 0.01 feet in Area 1 & Area 2

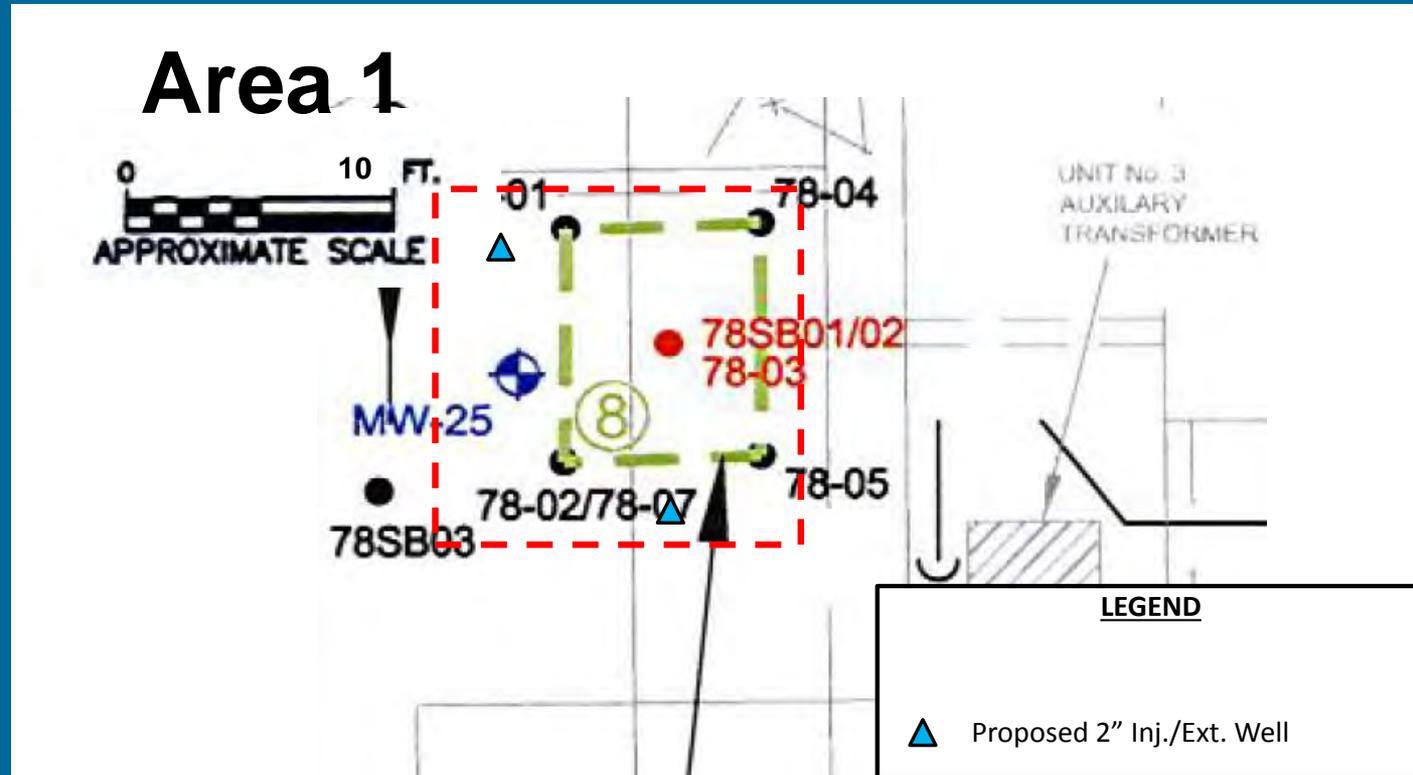


Site Figure – Area 1

Surfactant-Enhanced Remediation

NAPL was historically persistent at thicknesses ranging from 0.11 to 1.00 feet in MW-25. Free product at ~0.5 feet prior to surfactant event.

Two injection/extraction wells were subsequently installed in Area 1 for NAPL capture.

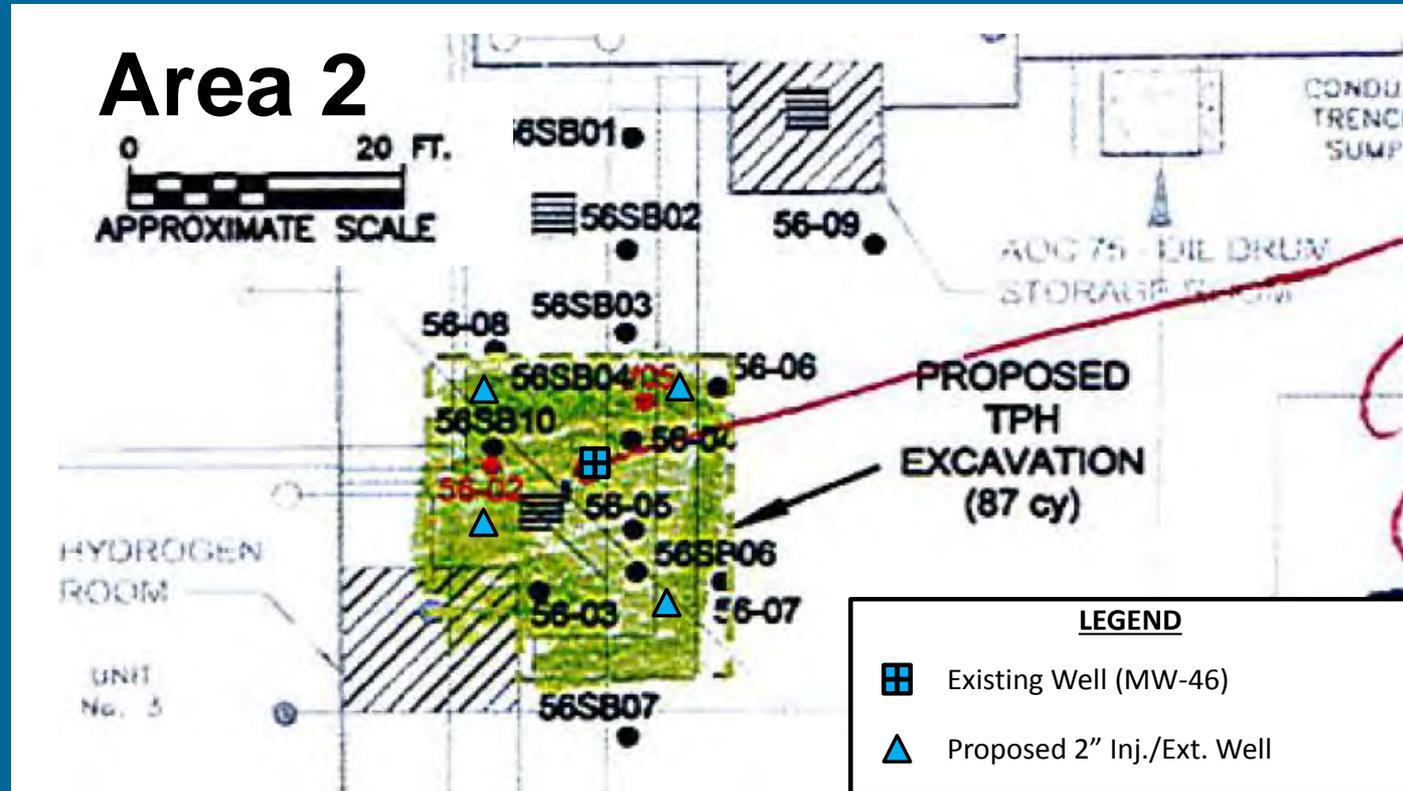


Site Figure – Area 2

Surfactant-Enhanced Remediation

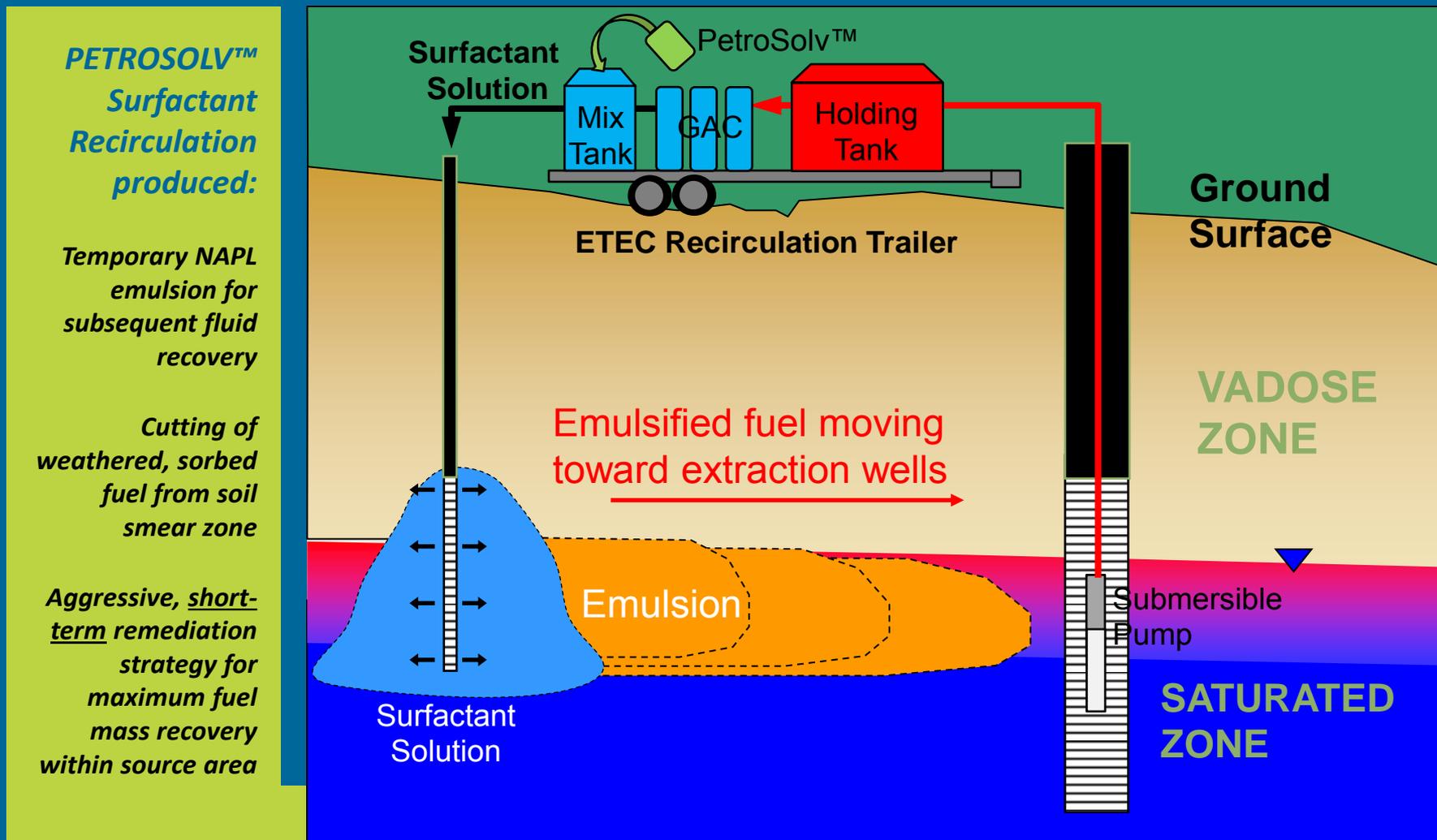
NAPL was historically persistent at thicknesses ranging from 2.00 to 4.00 feet in MW-46. Following 8-hour HVR events, NAPL re-accumulation typically took several weeks. Free product at ~3.0 feet prior to surfactant event.

Four injection/extraction wells were subsequently installed in Area 2 for NAPL capture.



Process Diagram – Part 1

Surfactant-Enhanced Remediation



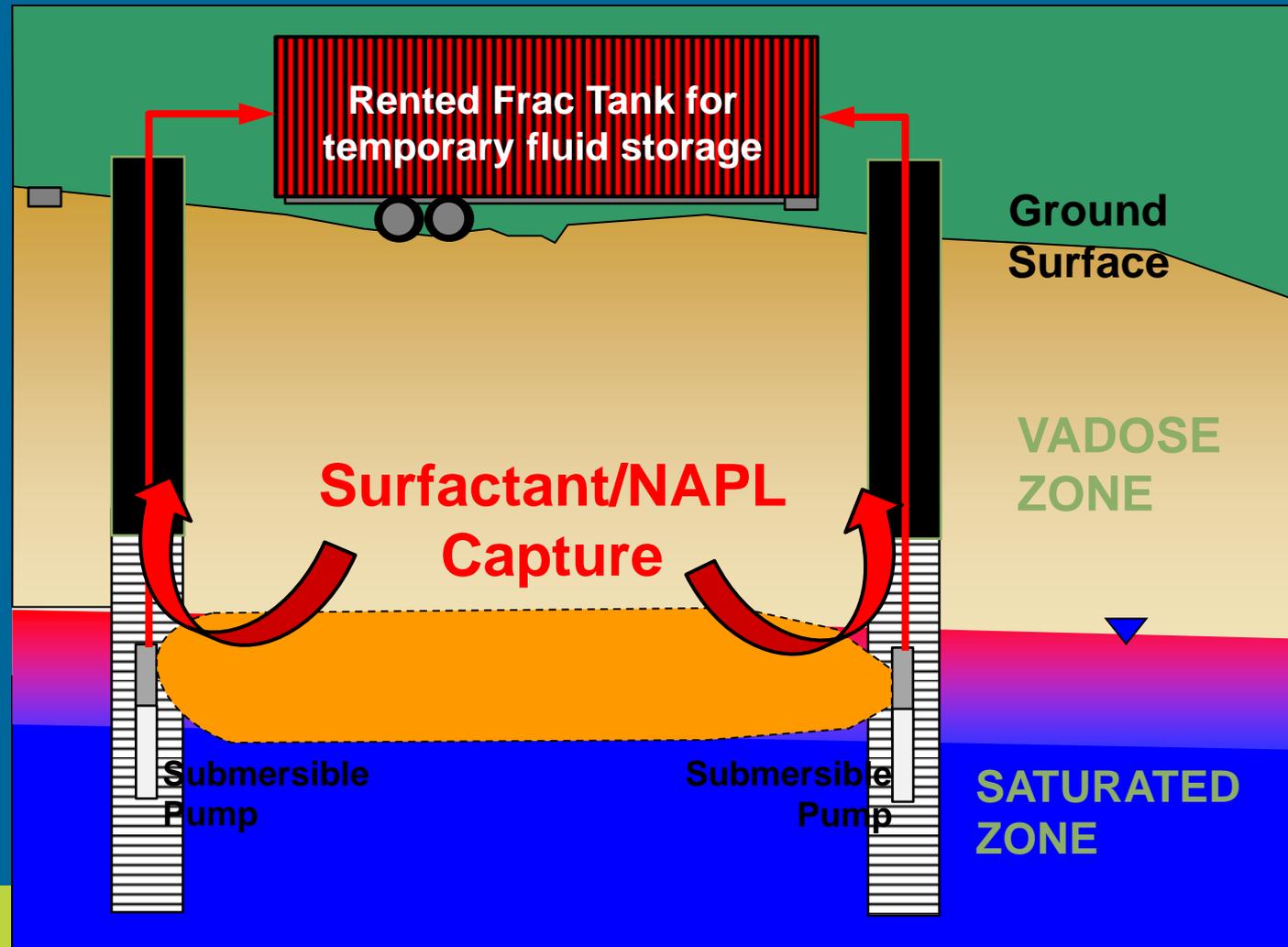
Process Diagram – Part 2

Surfactant-Enhanced Remediation

Follow-up Fluid Extraction events provide:

Optimum recovery of injected surfactant fluid and emulsified NAPL mass.

Maximized pore volume flushes/exchanges (goal is extraction of 1.5 to 3 times the fluid volume that was injected).



Field Work

Surfactant-Enhanced Remediation

5-Day Surfactant Injection Event Statistics:

*Used ETEC's
Mobile
Recirculation Unit
to recirculate and
inject surfactant
solution into Area
1 (3,000 gallons)
and Area 2 (5,000
gallons).*

*Used standard
PetroSolv
formulation for
Area 1 (diesel),
and adjusted
formulation for
Area 2 (motor oil)*



Field Work

Surfactant-Enhanced Remediation

5-Day Surfactant Injection Event Statistics:

*Performed
simultaneous GW
extraction from
adjacent wells
during surfactant
injection into
target wells.*

*Rotated injection
or extraction in
different wells to
optimize
subsurface
surfactant contact
and distribution*



Field Work

Surfactant-Enhanced Remediation

6-Day Follow-up Fluid Recovery Period:

Area 1: Recovered ~5,000 gallons of GW fluid from target area over period of 4 days.

Area 2: Recovered ~10,000 gallons of GW fluid from target area over period of 6 days.



Results

Surfactant-Enhanced Remediation

- No NAPL detected in Area 1 and Area 2 for 10 months after injection/extraction event (October 2014-August 2015)
- Fuel odor decreased dramatically by end of extraction event (2 weeks), confirming contact and capture
- Significant layer of NAPL in aboveground frac tank (used for temporary storage of extracted fluid), indicating successful capture of NAPL mass in Area 1 and Area 2.

Conclusions

Surfactant-Enhanced Remediation

- **Critical Elements for Success**
 - Closely-spaced wells for injection/extraction
 - Surfactant Formulation (used different PetroSolv mixtures for Area 1 & Area 2)
 - **Pore Volume Exchanges!!!** Injected 1 pore volume, extracted ~2 pore volumes in each Area.
 - Extended GW extraction over 1-week period provided consistent emulsified NAPL recovery
- **Regulatory Status**
 - Closure monitoring activities complete as of April 2015, site closure and No Further Action (NFA) status pending
- **Cost:**
 - 2-week event cost (amendments, labor, equipment) - \$35,000



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Episodic Surfactant Case Study: Truck Stop in GA

PRESENTER: David Laughlin, P.E.



Site Background/Infrastructure

Surfactant-Enhanced Remediation

HISTORY:
Diesel Fuel in
UST Cavity

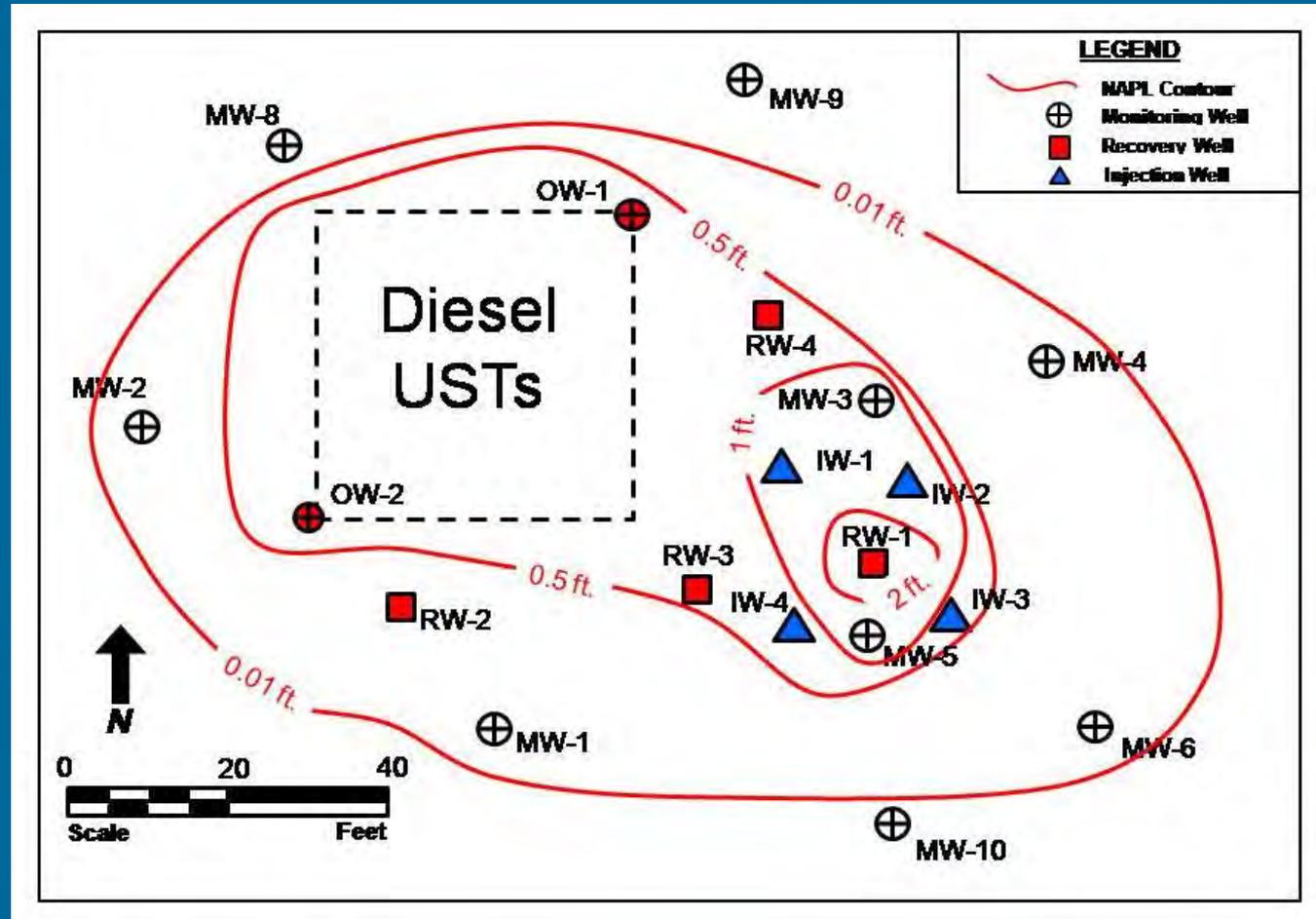
**DIESEL NAPL
THICKNESS :**
0.6' in UST
OWs & 1-2' in
dwngnrdt. MWs

LITHOLOGY:
Sandy Silt
(saprolitic)
underlain by
fractured
bedrock

DTW: 13-16'
bgs

PLUME: 60' x
50'

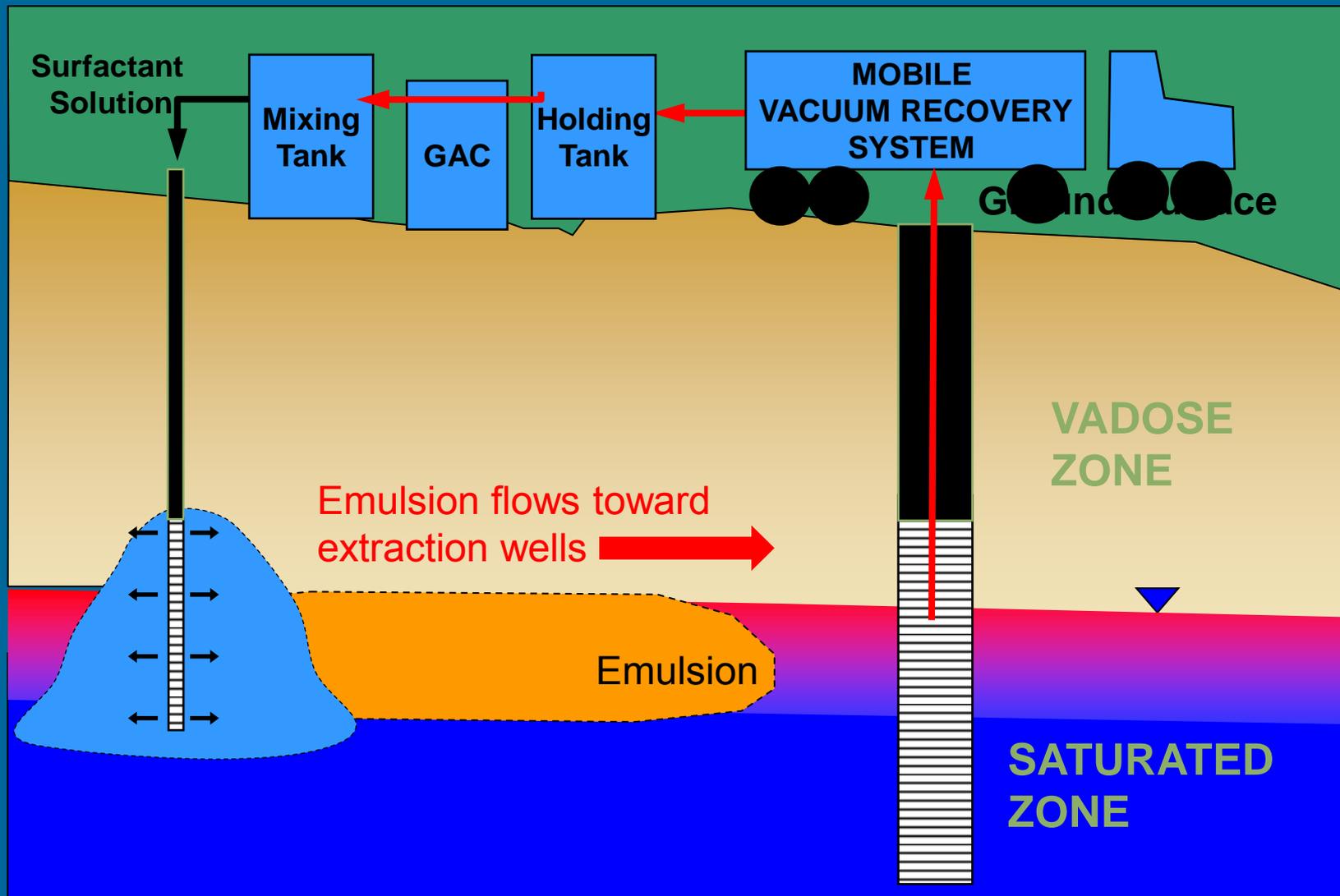
GOALS:
Remove NAPL
to < 0.01' in all
site wells



Surfactant-Enhanced Remediation

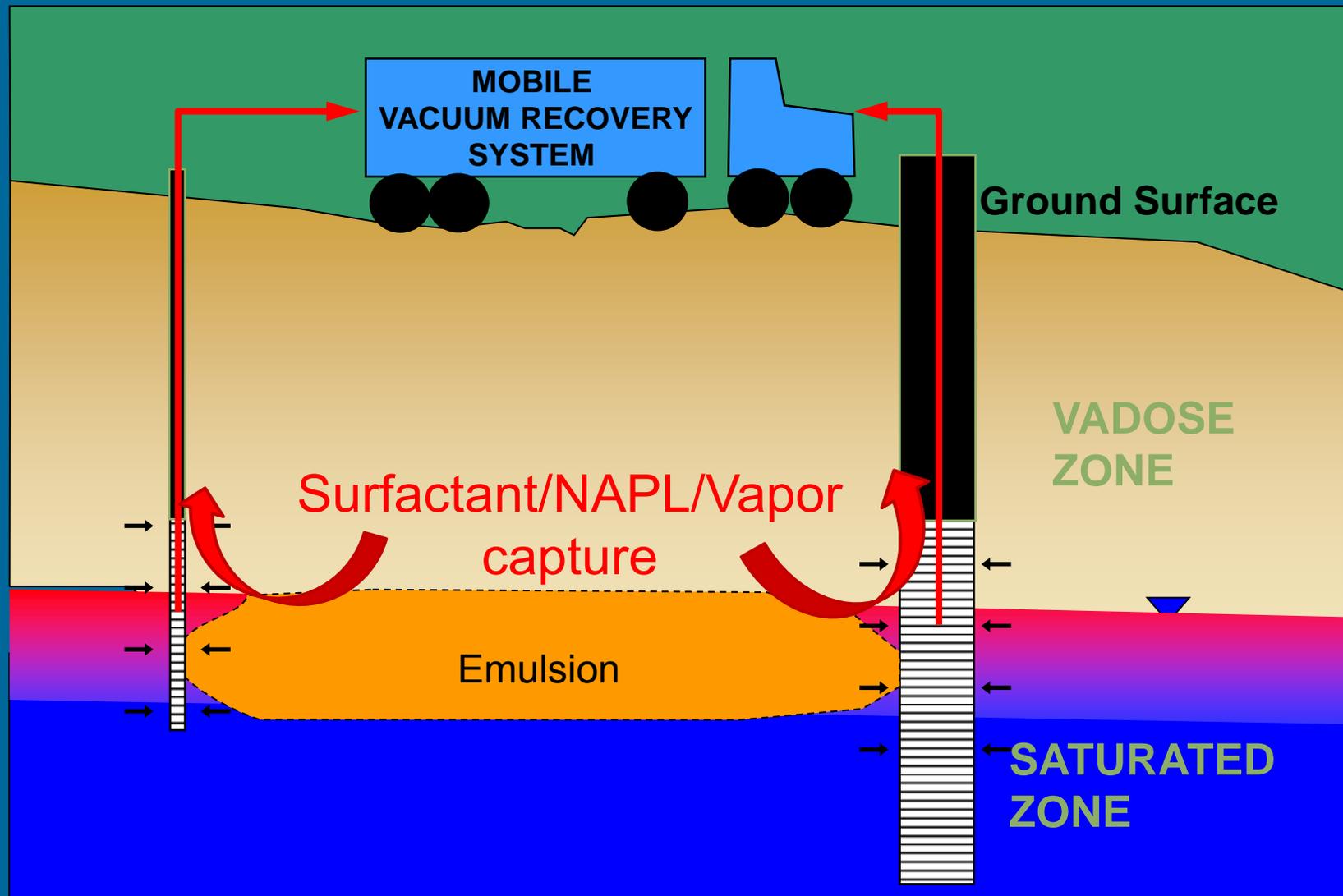
REMEDIATION STEP 1: Surfactant Recirculation

Surfactant-Enhanced Remediation



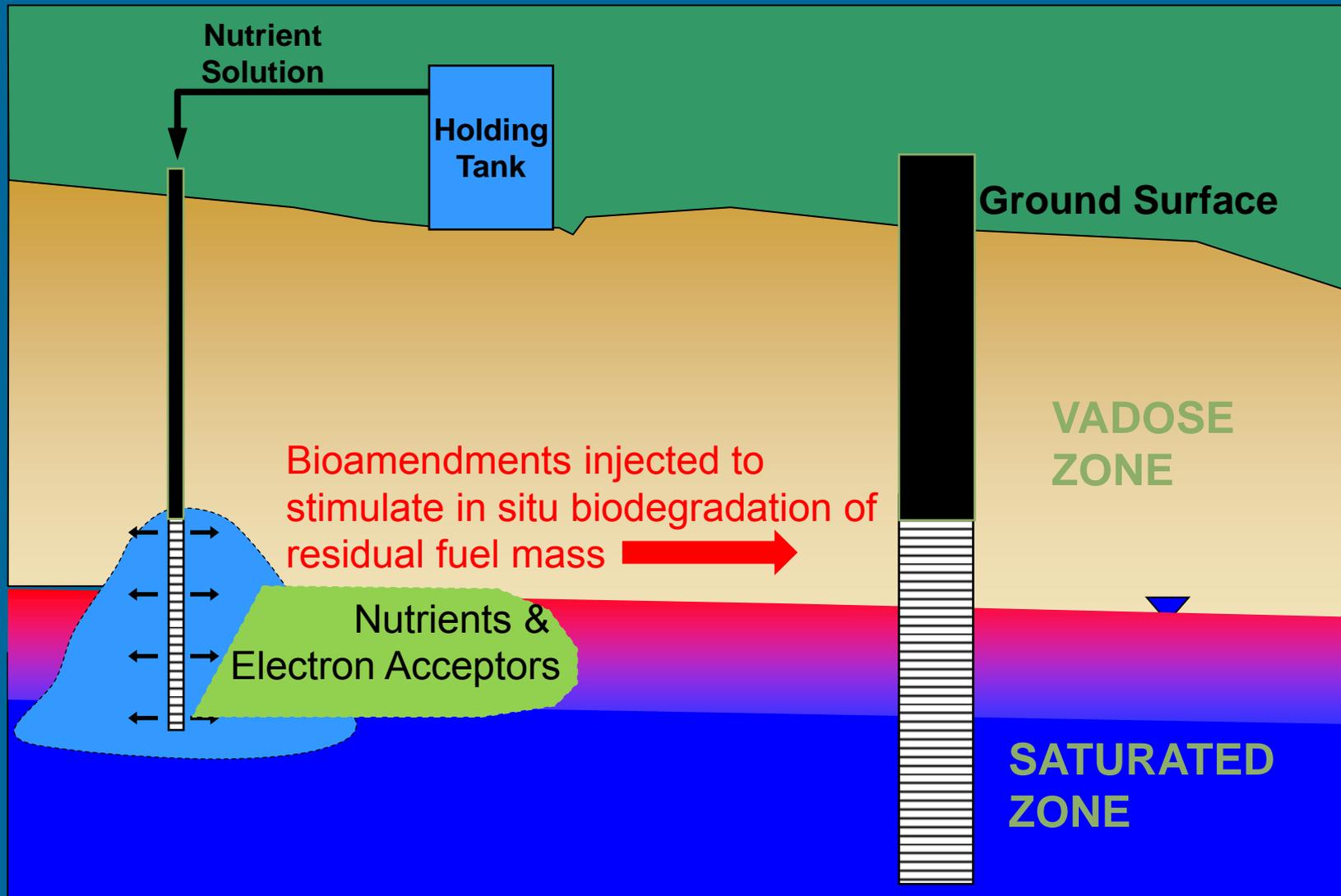
REMEDIATION STEP 2: Aggressive Fluid Extraction

Surfactant-Enhanced Remediation



REMEDIATION STEP 3: Bioamendment Recirculation

Surfactant-Enhanced Remediation



Remedial Process

Surfactant-Enhanced Remediation

- Conducted Bail-Down test at Monitoring Well with thickest NAPL layer
 - Evaluate NAPL recharge capacity
- Performed slug tests from several un-impacted wells to determine hydraulic conductivity (3.8×10^{-5} cm/s)
- Installed one extraction well and four injection wells
- 24-hour Surfactant Recirculation Pilot Test
 - Evaluate injection and extraction rates from various wells
 - Evaluate NAPL recovery via pre- and post-recirculation gauging of NAPL thickness (4 consecutive weeks after pilot test)
- Full-Scale Recirculation Events
 - Based on information obtained from Bail-down tests and Pilot Test, regulatory agency approved 3 full-scale recirculation events focused on plume-wide NAPL removal

Site Background/Infrastructure

Surfactant-Enhanced Remediation

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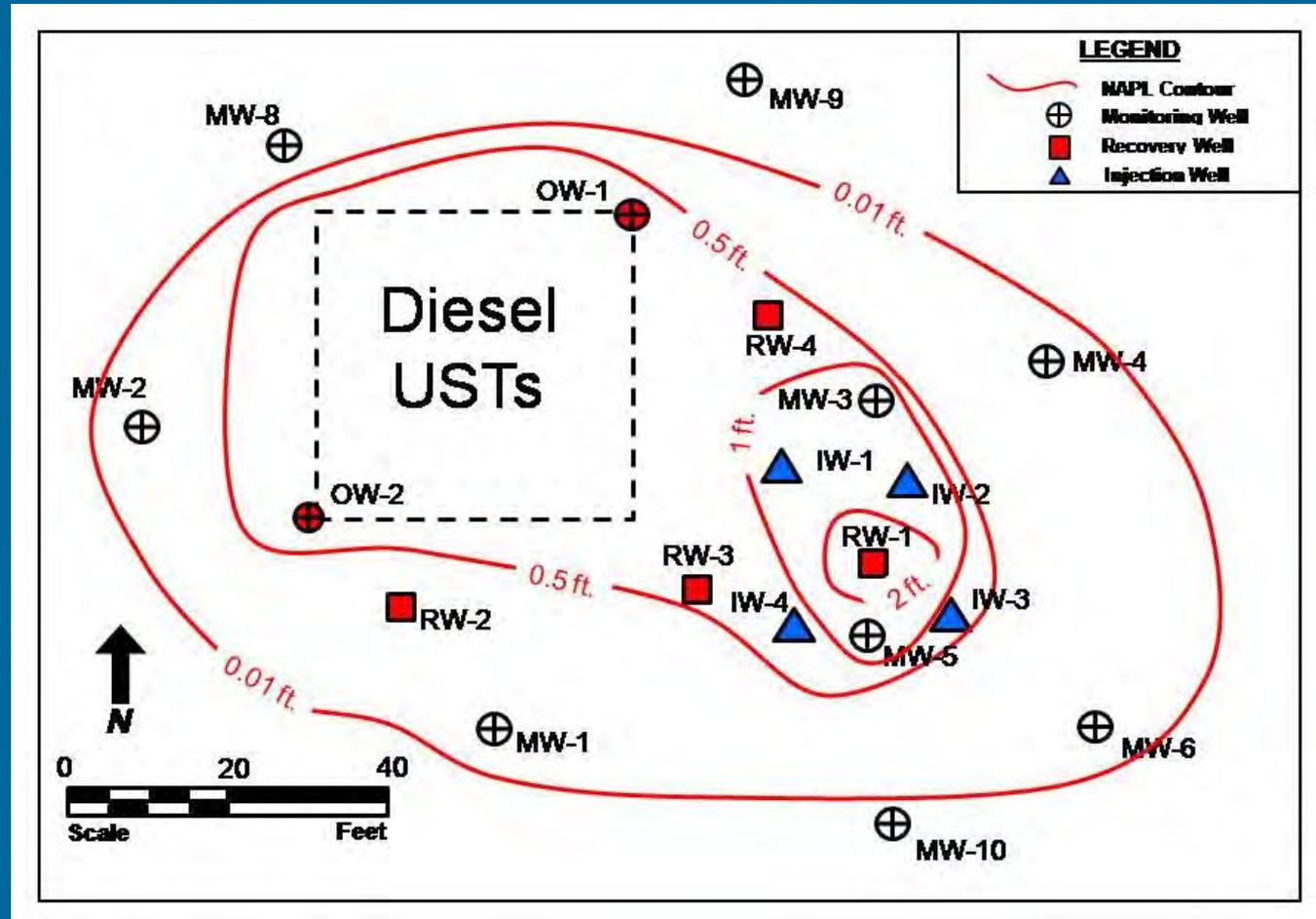
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0.6' in UST
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underlain by
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DTW: 13-16'
bgs

PLUME: 60' x
50'

GOALS:
Remove NAPL
to < 0.01' in all
site wells



Surfactant-Enhanced Remediation

Pilot Test Results

Surfactant-Enhanced Remediation

- 24-hour event
- Extracted 8,500 gallons from RW-1, MW-3, and MW-5 over 24-hour period
- Injected 3,000 gallons of 5% surfactant solution followed by 3,000 gallons of clean water into IW-1, IW-2, IW-3, IW-4

	MW-3	MW-5	RW-1	IW-2
Baseline NAPL Thickness	0.58 ft.	1.37 ft.	2.01 ft.	ND
Post-injection NAPL Thickness (4 weeks after Pilot Test)	ND	0.07 ft.	0.14 ft.	0.10 ft.

Full-Scale Summary

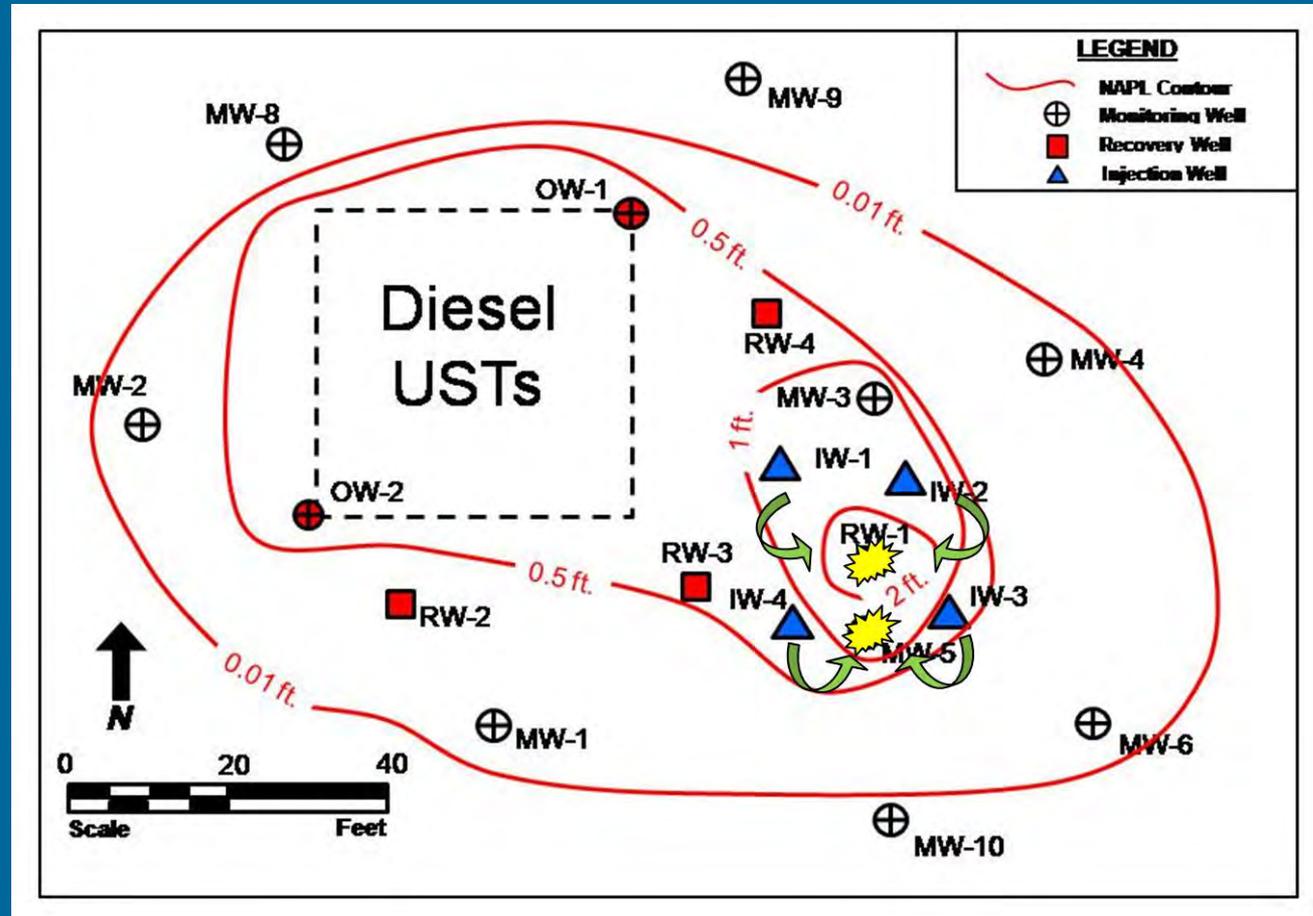
Surfactant-Enhanced Remediation

Two (2) 72-hour events.

1st 24 Hours:

12 hours extraction from all wells containing product

12 hours extraction from MW-5 and RW-1, with injection of 2,000 gallons of 5% surfactant solution into IW-1, IW-2, IW-3, IW-4



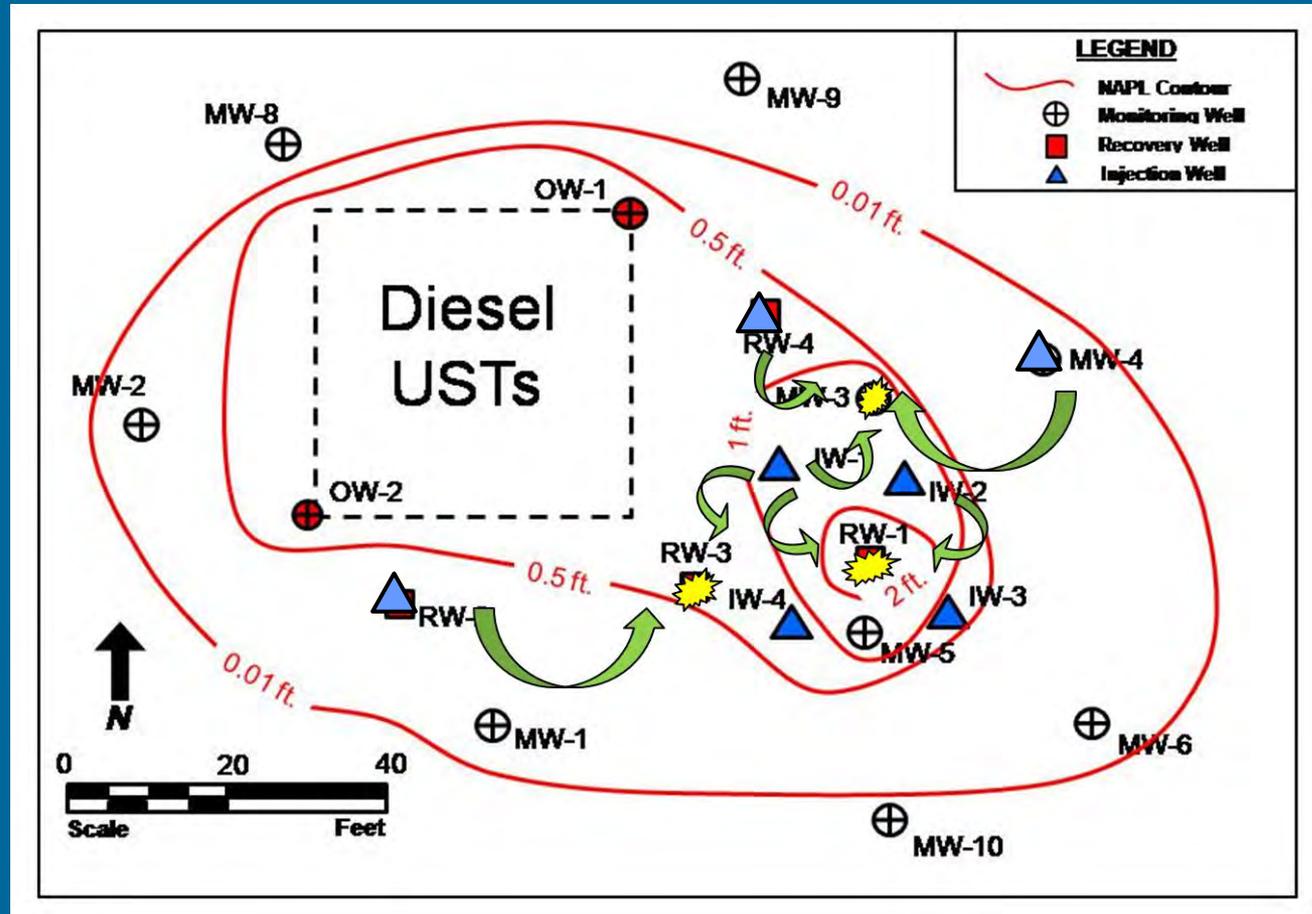
Surfactant-Enhanced Remediation

Full-Scale Summary

Surfactant-Enhanced Remediation

24-36 Hours:

*12 hours
extraction from
MW-3, RW-1
and RW-3, with
injection of
2,000 gallons
of 5%
surfactant
solution into
MW-4, RW-2,
RW-4, IW-1
and IW-2*



Full-Scale Summary

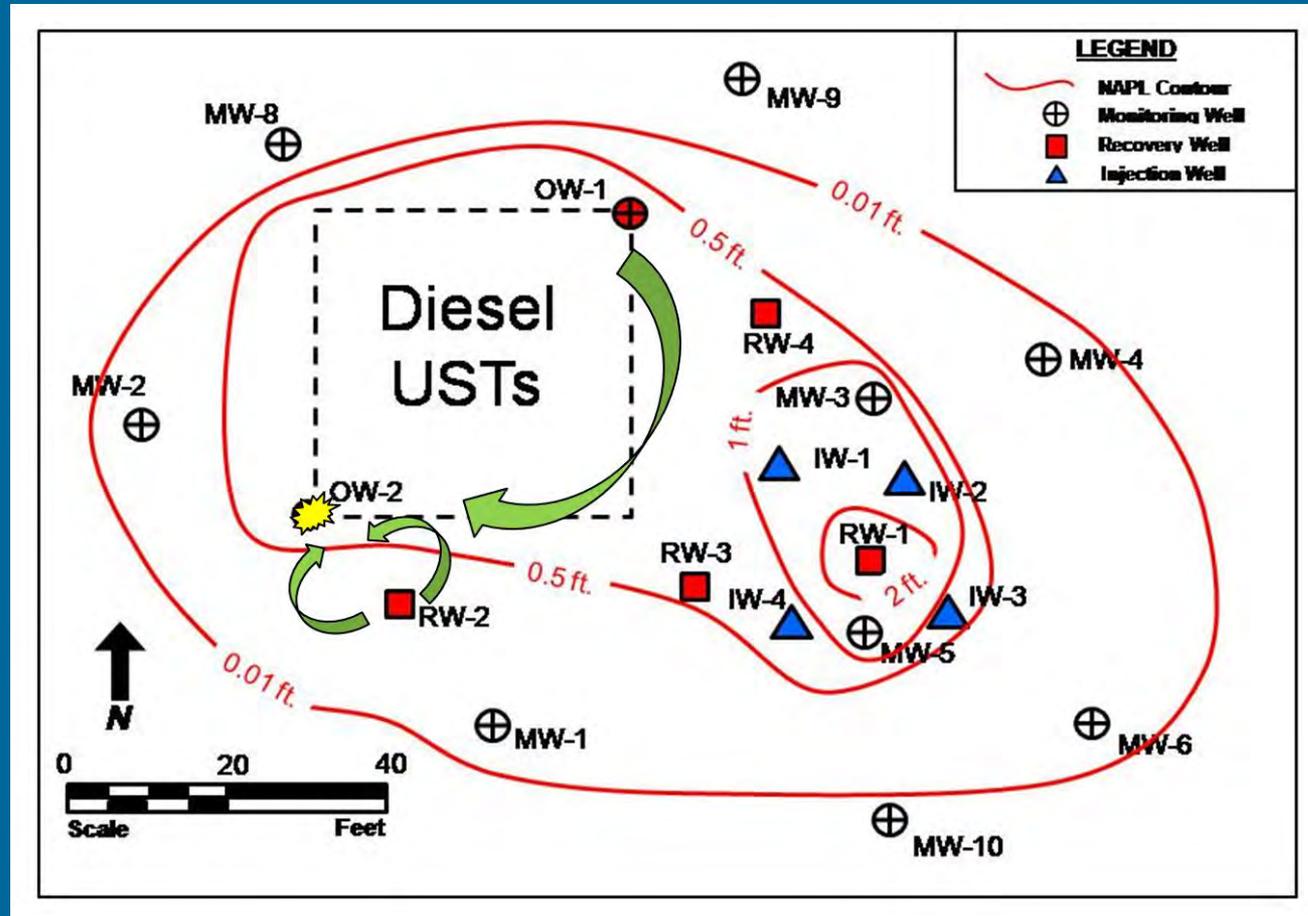
Surfactant-Enhanced Remediation

36-72 Hours:

12 hours
extraction from
OW-1 & OW-2

12 hours
extraction from
OW-2, with
injection of
2,000 gallons of
5% surfactant
solution into
OW-1 & RW-2

12 hours
injection of
2,000 gallons of
nutrient solution
into IWs, RWs,
and OWs



NAPL Recovery Data

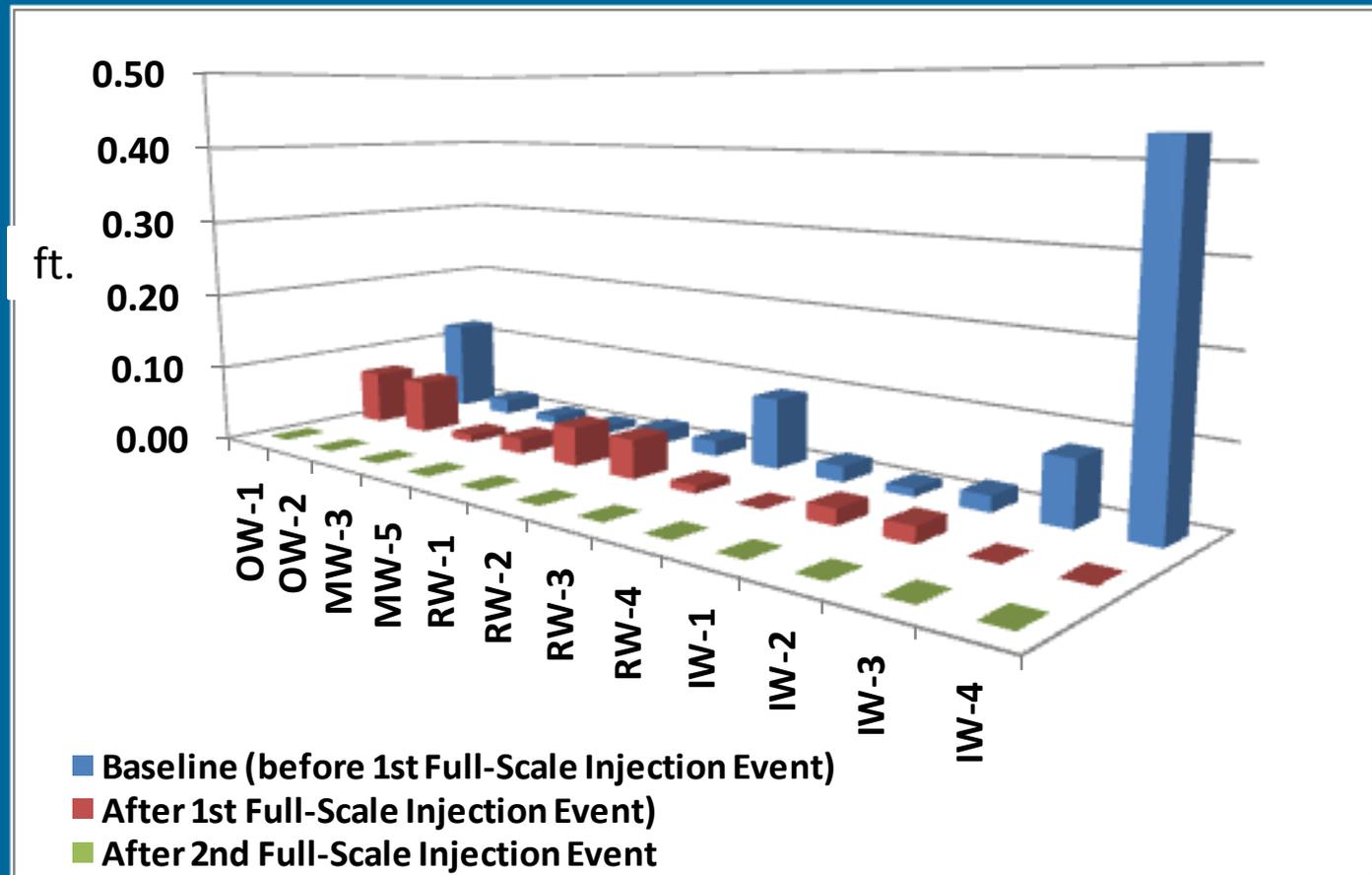
Surfactant-Enhanced Remediation

NAPL fully removed from all site wells with 1 pilot-scale and 2 full-scale events

No NAPL rebound

No residual dissolved VOC/PAH constituents

Site Received NFA in 2012



Conclusions

Surfactant-Enhanced Remediation

Critical Elements for Success

- Infrastructure
 - Tight soil conditions required multiple IWs/RWs
- Surfactant Concentration (2-5%)
- Solution Volume (~8,000 gallons/event)

- Costs
 - Surfactant and Nutrients (for Pilot Test + 2 Full-Scale Events): ~\$12,000
 - Field Labor/Mobile DPE/Fluid Disposal (for Pilot Test + 2 Full Scale Events): \$35,000

Expectations

Surfactant-Enhanced Remediation

- Several events (2-3) are usually needed to fully capture LNAPL and heavily-sorbed fuel mass, especially in silt/clay.
- Must have reasonable Well Infrastructure (maximum 15 ft. ROI for sand/silt, maximum 5-10 ft. ROI for silt/clay)
- Not typically effective for thick LNAPL layers (i.e. >1-2 ft.) – perform mechanical LNAPL removal first
- Episodic Surfactant Injection with Mobile DPE is excellent for LNAPL removal and reducing dissolved BTEX concentrations from High (>50,000 ppb) to Medium (<20,000 ppb). **Not good for reducing dissolved concentrations from High to Very Low (<500 ppb) by itself.** Low BTEX concentrations require surfactant + fixed DPE, AS/SVE, etc.