Surfactant-Enhanced Aquifer Remediation (SEAR) for DNAPL Removal

Naval Facilities Engineering Service Center

Duke Engineering & Services

I. Characterization of DNAPL Zones

II. Surfactant-Enhanced Aquifer Remediation (SEAR)

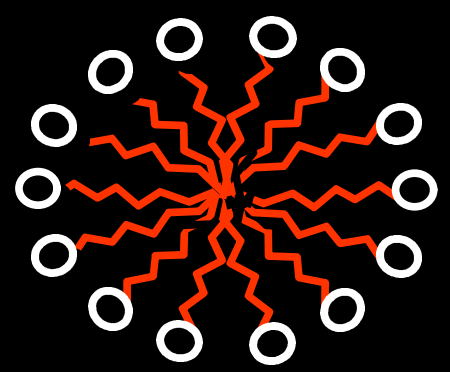
Presentation Overview
II. Surfactant-Enhanced Aquifer Remediation (SEAR)

- **Introduction**
- Principles
- Applicability
- Technology implementation
  - Site characterization
  - Design objectives and approach
  - Field operations
  - Costs
- Case study
- New developments

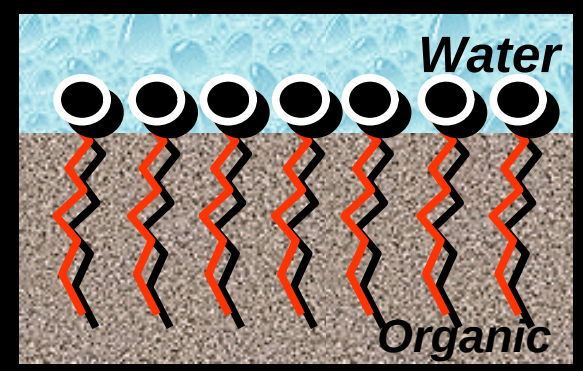
What are surfactants?

Surfactants are surface active agents, molecules composed of two differing parts: a hydrophilic head and a hydrophobic tail. This leads to their interesting behavior.

A surfactant molecule



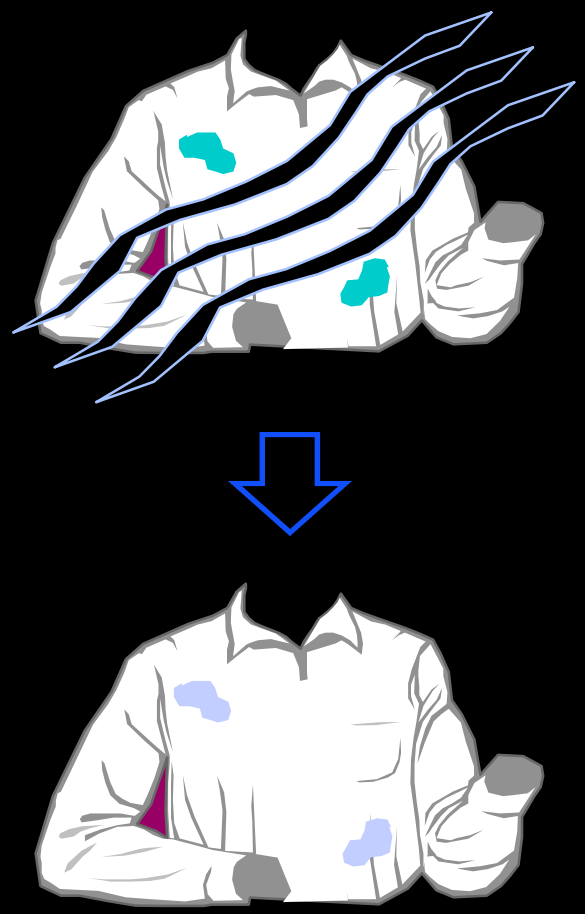
Micelle



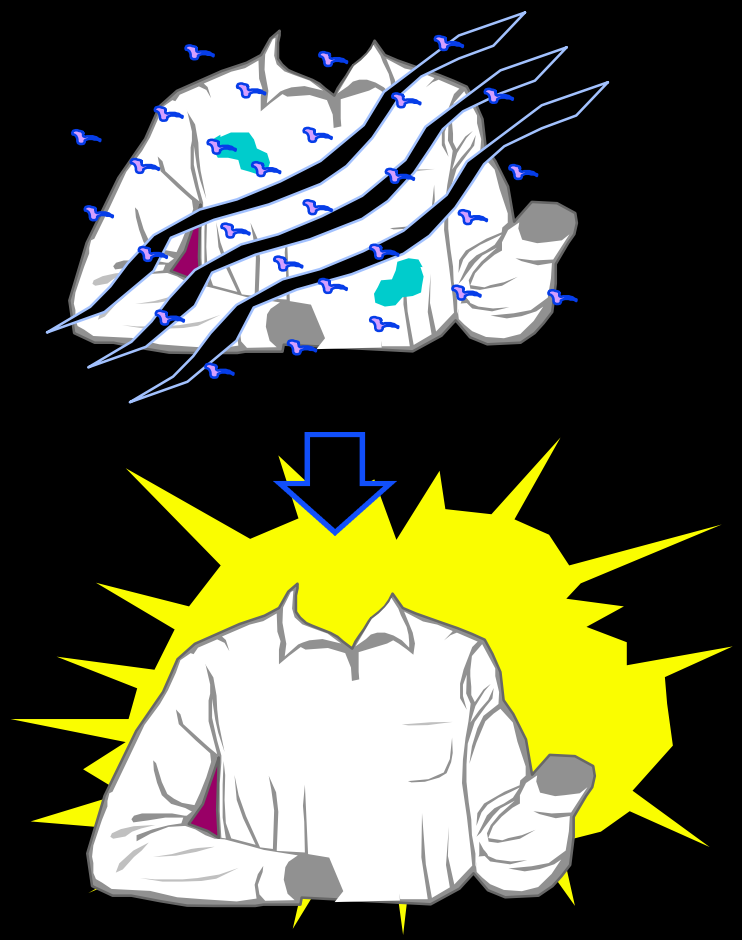
Surfactants Reduce Interfacial Tension

A familiar example of surfactants

Water Only



Water & Detergent



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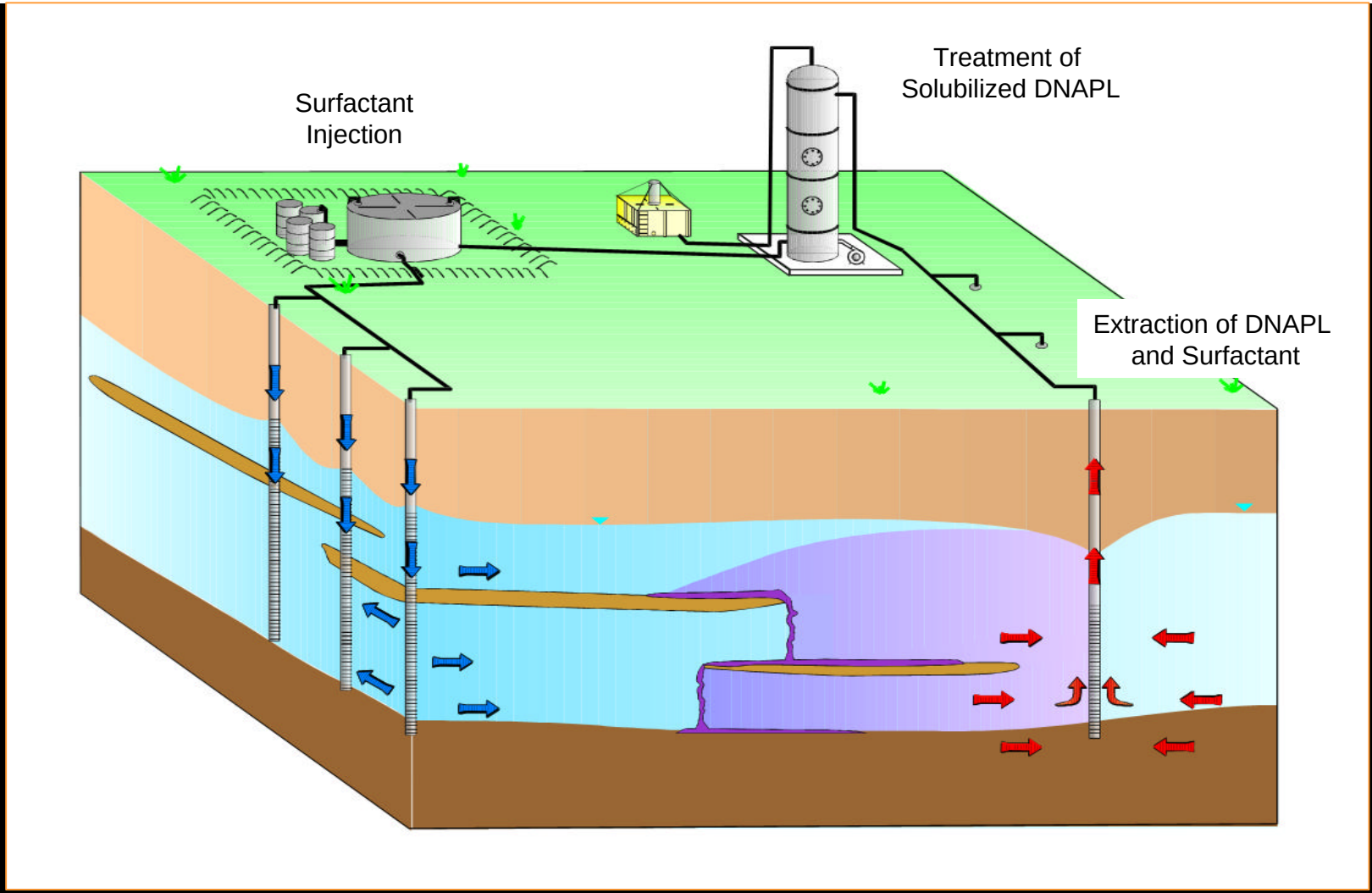
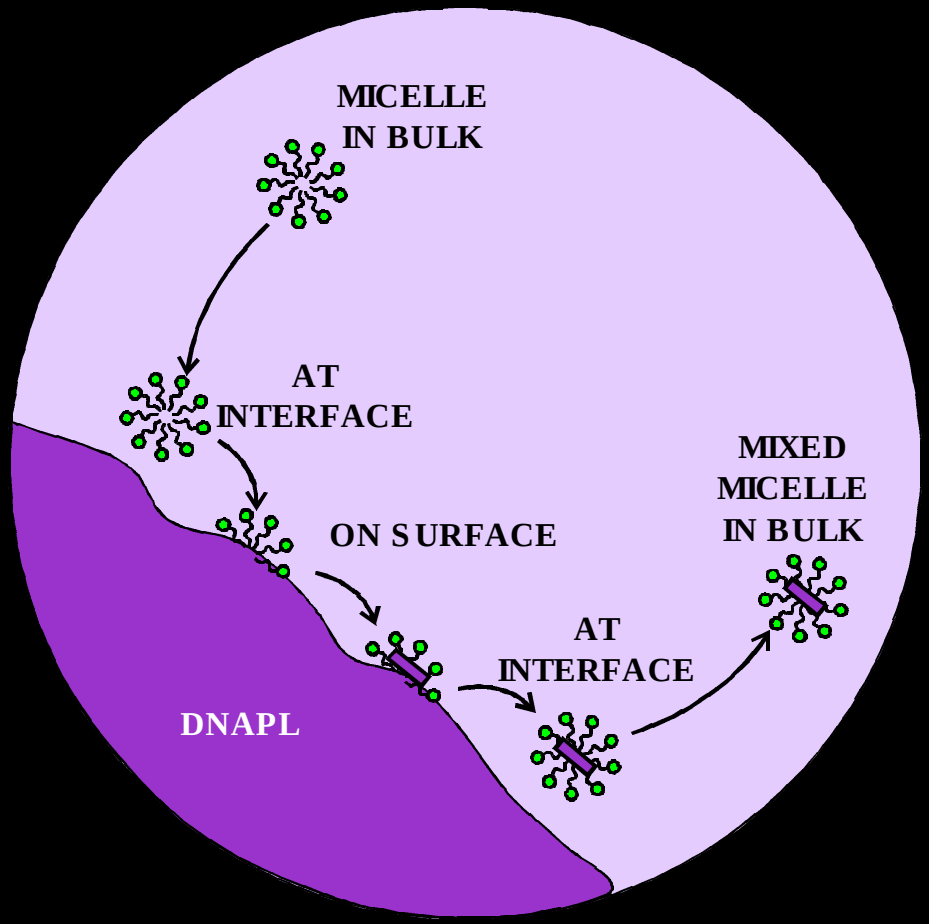
How do surfactants work?

- Surfactants increase the effective aqueous solubilities of DNAPL contaminants.
- Additionally, surfactants can accomplish a significant reduction in the interfacial tension between the DNAPL and water phases to mobilize the DNAPL.

Conceptual picture of SEAR



Surfactants in the subsurface



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Applicability

- For saturated zone contamination, not vadose zone
- Can be applied to mixed NAPLs
- In order to be economical, subsurface geology should be permeable (not applicable to clays or fractured clays)
- Sites with heterogeneity can be remediated by the addition of polymer.
- Regulators prefer sites with confining layers to prevent downward mobilization of DNAPL.

Comparisons to other technologies

Category	In Situ Surfactant Flushing	In Situ Oxidation	In Situ Thermal
Unsaturated zone			
Permeable	NA	Best-Medium	Best
Impermeable	NA	Best-Medium	Medium
Fractured Bedrock	NA	Best-Medium	NA
Saturated zone			
Permeable	Best	Medium-Worse	Medium
Impermeable	Medium	Medium-Worse	Medium

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Site characterization

- In addition to performing the DNAPL characterization steps previously discussed, it is necessary to:
  - collect additional data on the source area boundaries so that the DNAPL zone will be properly targeted for surfactant flushing
  - measure the GW temperature and pH within the test zone
  - perform vertical capillary pressure testing to confirm the integrity of the aquitard as a barrier to downwards DNAPL migration

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Design objectives

- Demonstrate good hydraulic capture of surfactants and DNAPL within test zone
- Minimize the potential for vertical migration of solubilized DNAPL (especially for an unconfined aquifer)
- Choose the most effective surfactant system for the site DNAPL and hydrogeology
- Examine optimum well spacing/geometry and injection/extraction rates

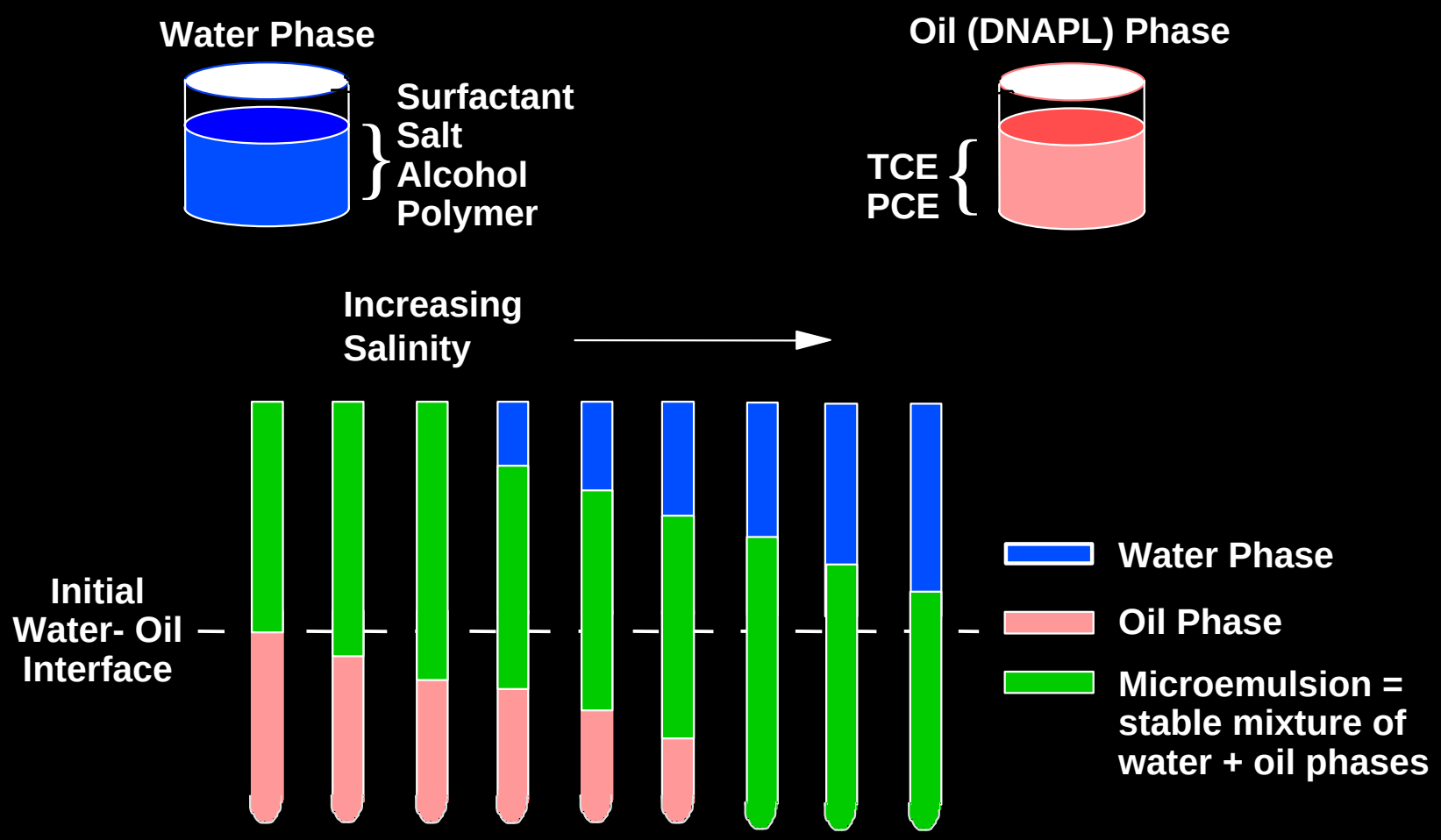
Design approach

- **Select surfactant**
- Develop geosystems model for the aquifer and make preliminary simulations
- Install complete well array
- Conduct PITT (optional but highly recommended)
- Further refine geosystems model and conduct final simulations to complete the test design

Surfactant selection

- Phase behavior experiments
  - identify nontoxic and biodegradable surfactants that are effective and rapid in solubilizing the DNAPL at the GW temperature and pH
  - adjust and optimize surfactant properties as needed using additives such as salt, alcohol, and polymer
    - check for phase stability
    - viscosity of the surfactant formulation with varying concentrations of DNAPL should be < 2 cP
- Soil column experiments
  - identify surfactants that are compatible with aquifer solids
  - quantify any surfactant losses on aquifer solids

Surfactant phase behavior



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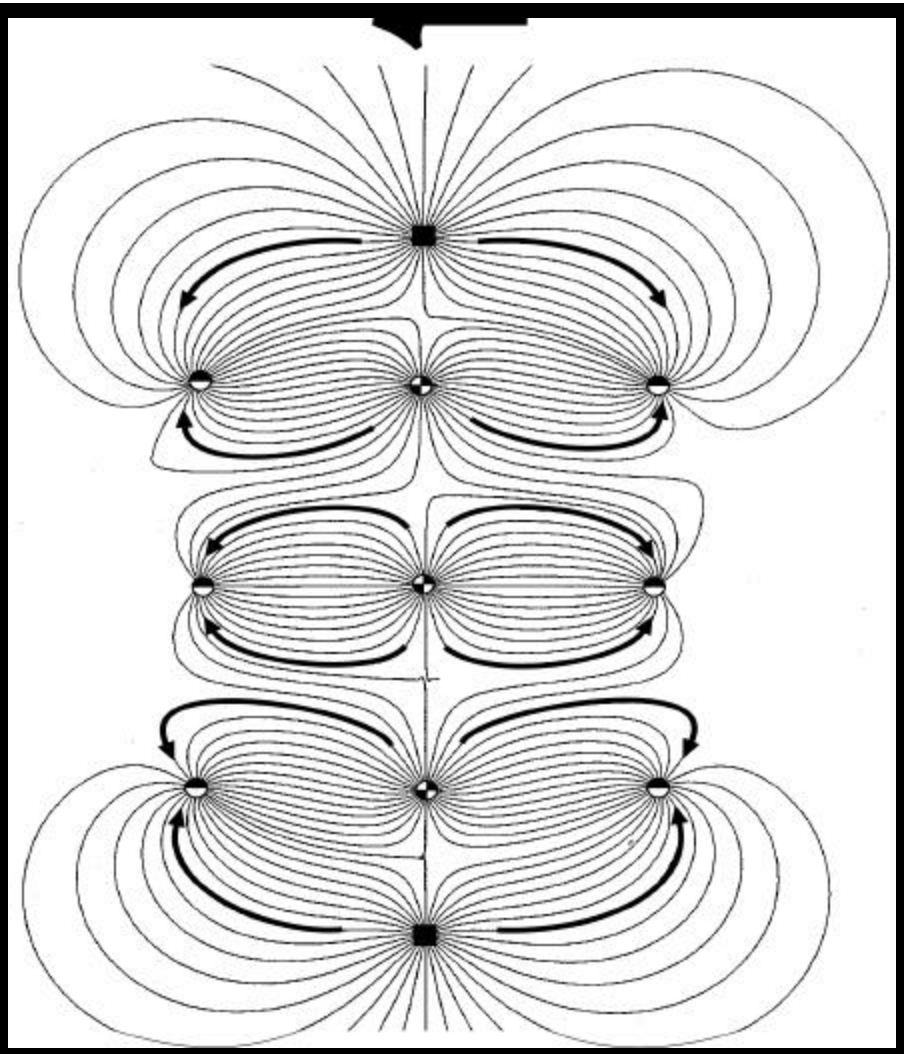
Objectives of geosystem modeling

- Determine:
  - well geometry and spacing
  - injection and extraction rates
  - mass and concentration of surfactant required
  - time for post-surfactant injection waterflooding to recover the surfactant
- Predict:
  - effluent contaminant concentrations for sample collection and surface treatment design
  - recoveries of surfactants and DNAPL to meet permitting requirements

One model used is UTCHEM (the University of Texas chemical flooding simulator).

Modeling results showing hydraulic containment



- Hydraulic control well
- Injection well
- Extraction well
- Resulting groundwater flow

Design approach

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Field operations

1. Establish steady-state flow field before injecting surfactants.

2. Mix surfactants with water and additives that are used (e.g. salt, alcohol, polymer).

3. Inject 0.5 to 5 pore volumes (PV) of surfactant solution.

4. Follow surfactant injection with 4 to 5 PV of water to remove remaining surfactant and DNAPL.

Field operations (cont.)

5. Once surfactant injection begins, field operations continue uninterrupted, 24 hr/day, until the test is completed.

6. Typical daily field measurements: water levels; flow rates; surfactant and DNAPL concentrations; conductivity (for salt)

7. Subsequent to the surfactant test, perform post-PITT (if pre-PITT was conducted) and post-soil core sampling

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Full-scale SEAR costs*

TASK	COST
Additional site characterization	$50,200
Design	$205,000
Field demonstration	$505,100
Facility design	$273,910
Construction	$3,144,891
Full-scale operation (297 days)	$3,020,014
Demolition and Site Restoration	($184,645)
TOTAL COST	**$7,014,470**
UNIT COST	**$118/gal DNAPL removed**

*** 1-acre site, TCE DNAPL contamination 30 to 33 ft BLS; permeability 0.01 cm/sec; Source: Ref. 1**

Compare to full-scale pump-and-treat costs

TASK	UNIT COST*
Pump & treat at Tinker AFB	$8K/gal
Pump & treat at Hill AFB OU2	$32K/gal
Pump & treat costs at DOE Portsmouth	$40K/gal

***TCE DNAPL**

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Case Study: SEAR demonstration at Hill AFB, Operable Unit (OU) 2, Utah

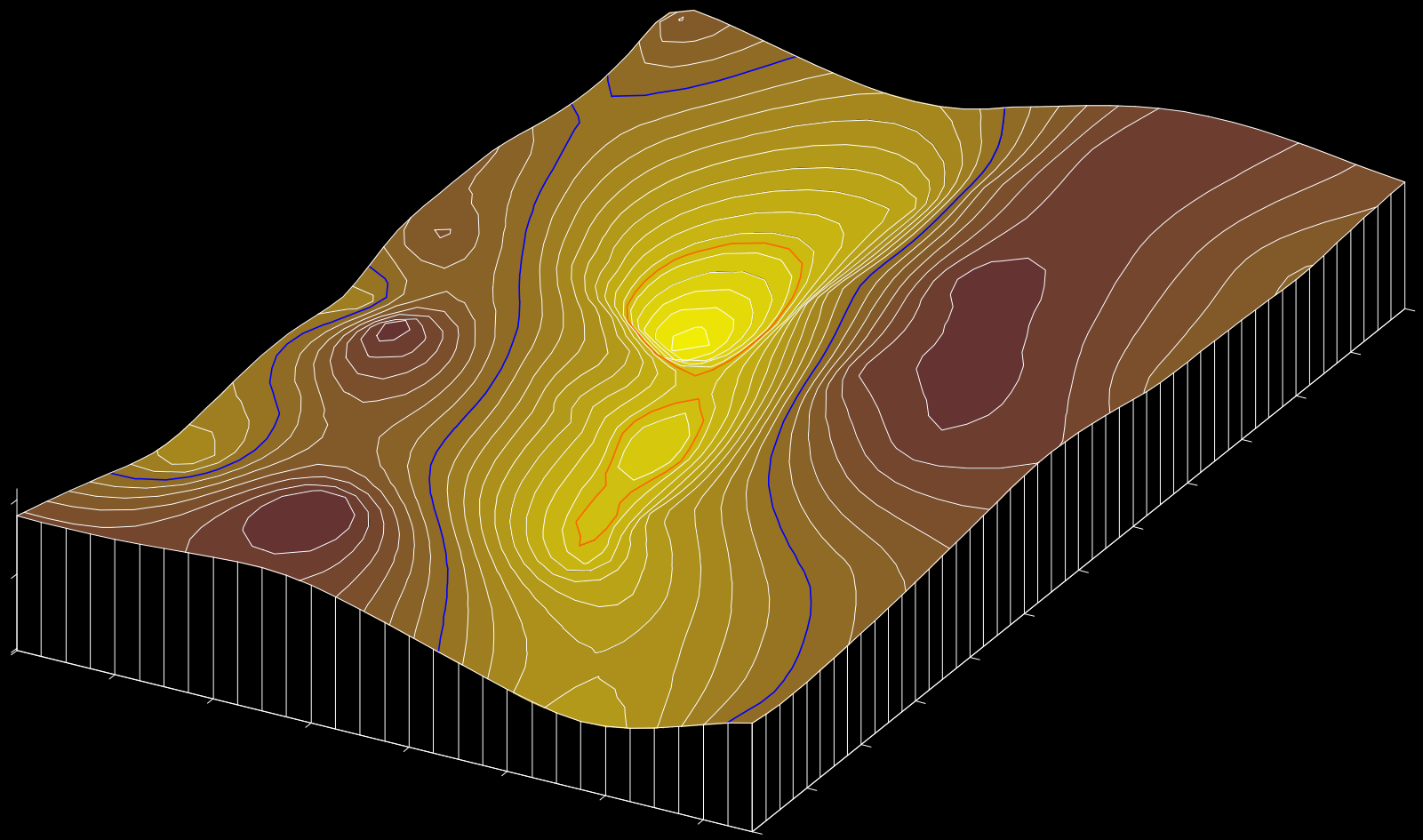
The Hill AFB OU2 geosystem

- Heterogeneous alluvium, with K = 10-2 to 10-3 cm/s;
- Capillary barrier, clay beneath alluvium can support > 10 ft of DNAPL (therefore called an aquiclude)
- >30,000 gallons free-phase DNAPL pumped out of the subsurface during prior site operations
- DNAPL = 60% TCE, 5% PCE, 10% 1,1,1-TCA, 25% oil & grease

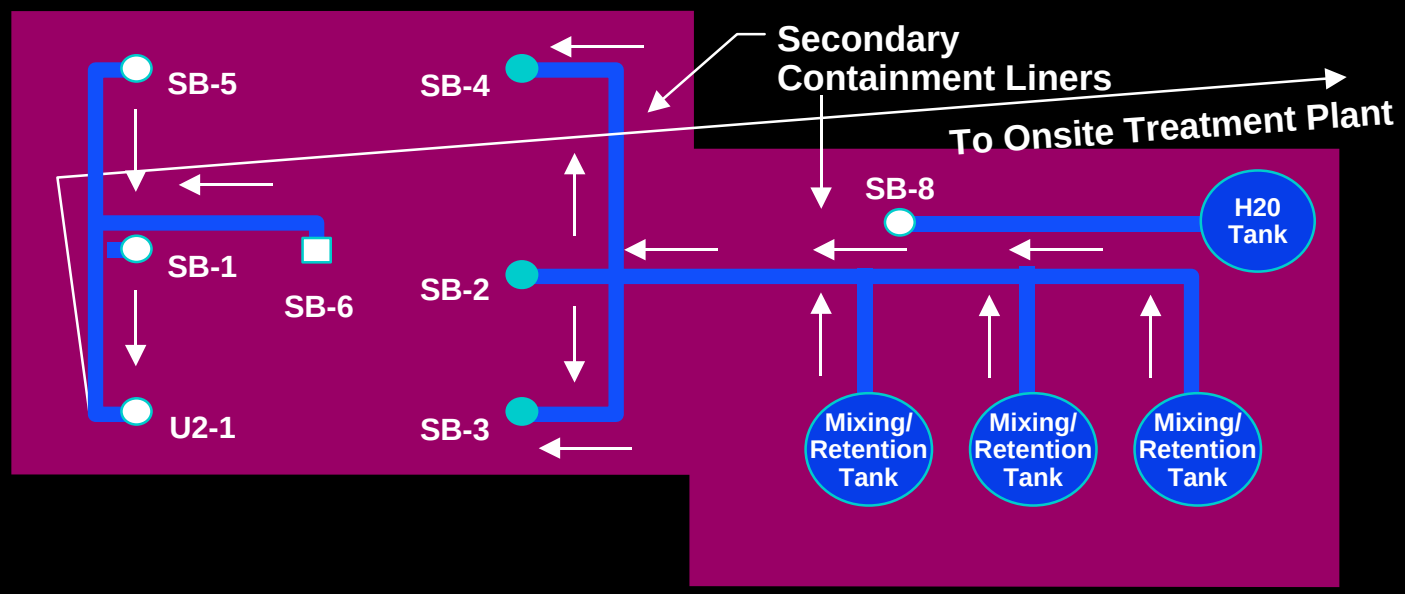
PITTs and surfactant floods at Hill AFB OU 2, during 1996-7:

- Five PITTs to measure interwell DNAPL volume for the design of surfactant floods.
- Three surfactant floods conducted.
  - Two-phase surfactant flood by DE&S and UT Austin
  - Surfactant-*foam* flood by DE&S and Rice University to improve DNAPL removal from lower permeability zones.

Hill AFB OU2 clay aquiclude topography



Schematic of Hill AFB OU2 Wellfield



LEGEND

- Injection Well
- Groundwater Monitoring Well
- Extraction Well

Description of Phase I and II surfactant floods at Hill AFB OU2

- Phase I
  - 0.6 PV of 8% surfactant, maximum contaminant solubilization = 70,000 mg VOCs/L
- Phase II
  - 2.4 PV of 7.5% surfactant, 3.8% isopropanol, 7,000 mg NaCl/L, maximum contaminant solubilization = 625,000 mg VOCs/L

Summary of Phase I SEAR demonstration at Hill AFB OU2

Segment	Purpose	Injection wells (3)	Injection time (days)	Cumulative time (days)
Water injection	Establish steady-state flow field	Water	2.5	2.5
Tracer injection	Start initial PITT	Water + Tracers	0.5	3.0
Water injection	Flush out tracers	Water	5.5	8.5
Surfactant injection	Start Phase I surfactant test	Water + surfactant	0.6	9.1
Water injection	Flush out surfactants + DNAPL	Water	8.5	17.6

Monitoring well samples, Hill OU2, Phase I

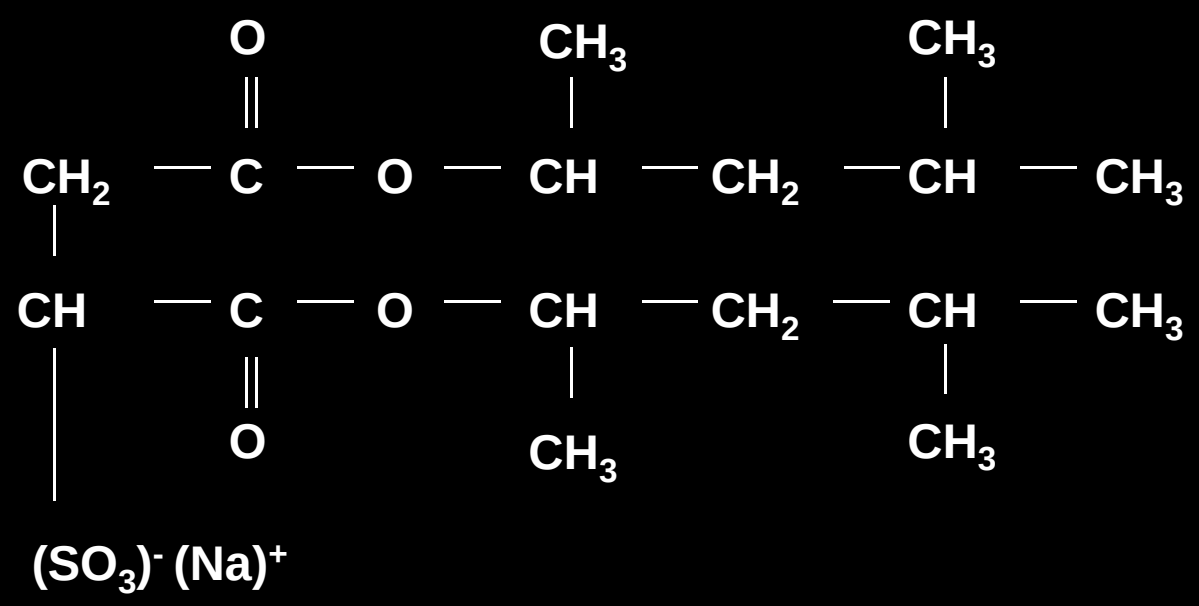
May 13								May 14					
5	6	7	8	9	10	11	12	1	2	3	4	5	6
pm							am						

Before surfactant remediation: 900 mg/L
After surfactant remediation: 8 mg/L

Summary of Phase II SEAR demonstration at Hill AFB OU2

Segment	Purpose	Injection wells (3)	Injection time (days)	Cumulative time (days)
Electrolyte injection	Establish steady conc. of NaCl in the aquifer	Water + NaCl	1.0	1.0
Surfactant injection	Start Phase II surfactant test	Water + Alcohol + surfactant	3.4	4.4
Water injection	Flush out surfactants + alcohol + DNAPL	Water	11.0	15.4
Tracer injection	Start final PITT	Water + tracers	1.0	16.4
Water injection	Flush out tracers	Water	5.1	21.5
Water extraction	Recover any residual injected chemicals	--	2.4	23.9

Surfactant Used at Hill OU2

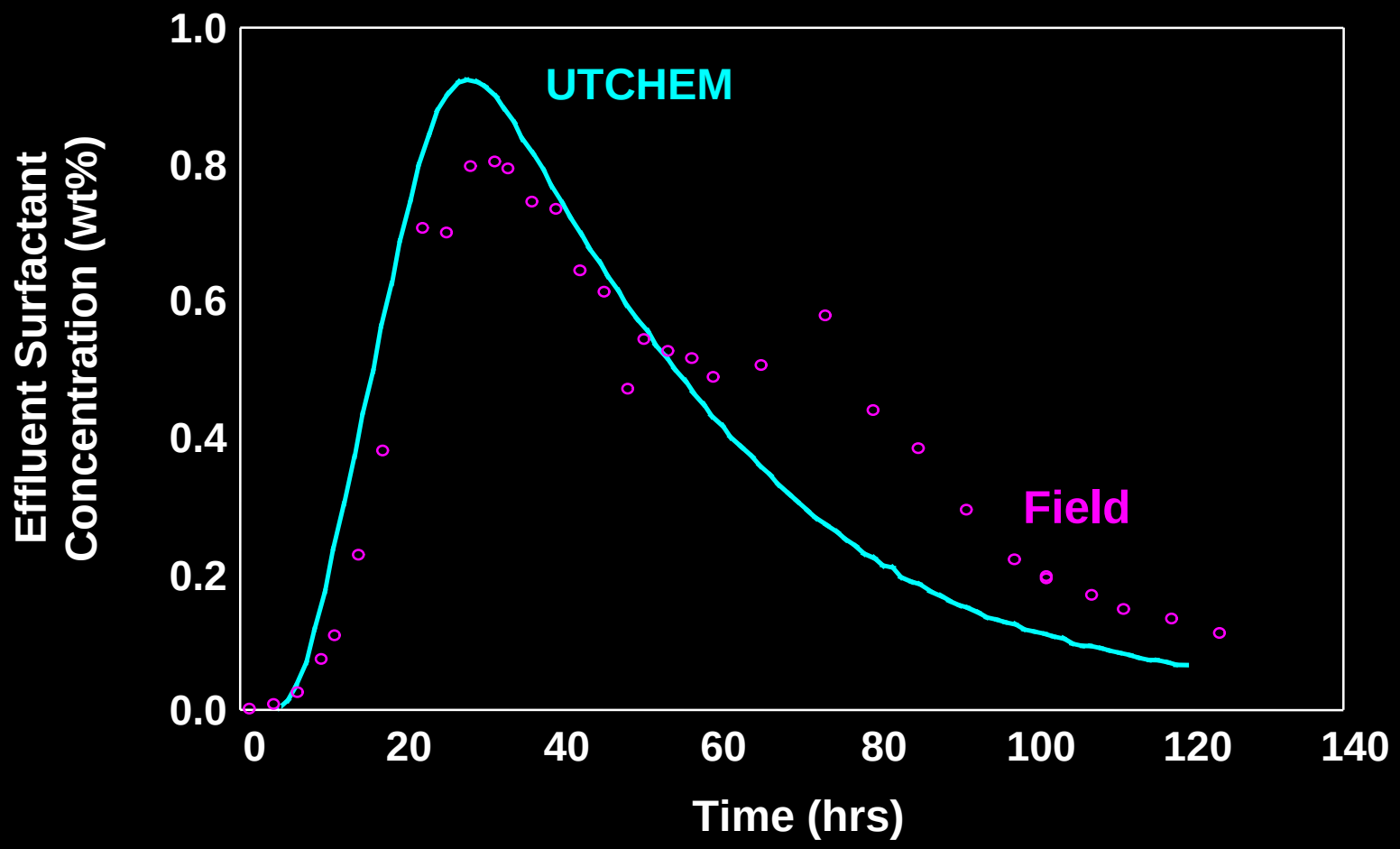


Aerosol MA-80I, sodium dihexyl sulfosuccinate,
a food-grade surfactant,
CMC 4-10 g/l (depends on salinity)

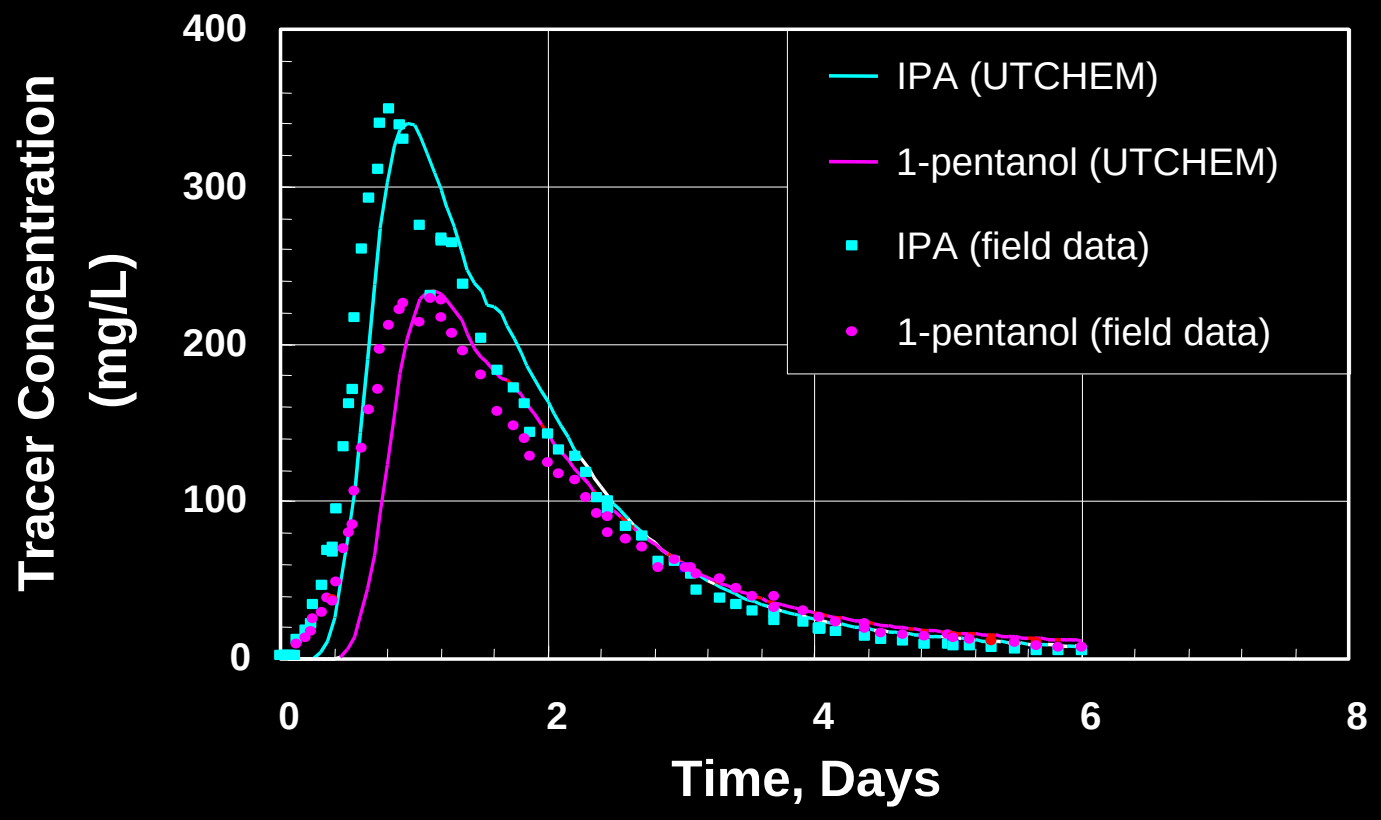
Regulatory Approval

- Surfactants accepted by EPA Region VIII and Utah Dept. of Environmental Quality as harmless
- Hydraulic capture predicted in Work Plan and demonstrated during Phases I and II
- Vertical mobilization of DNAPL prevented by underlying clay.

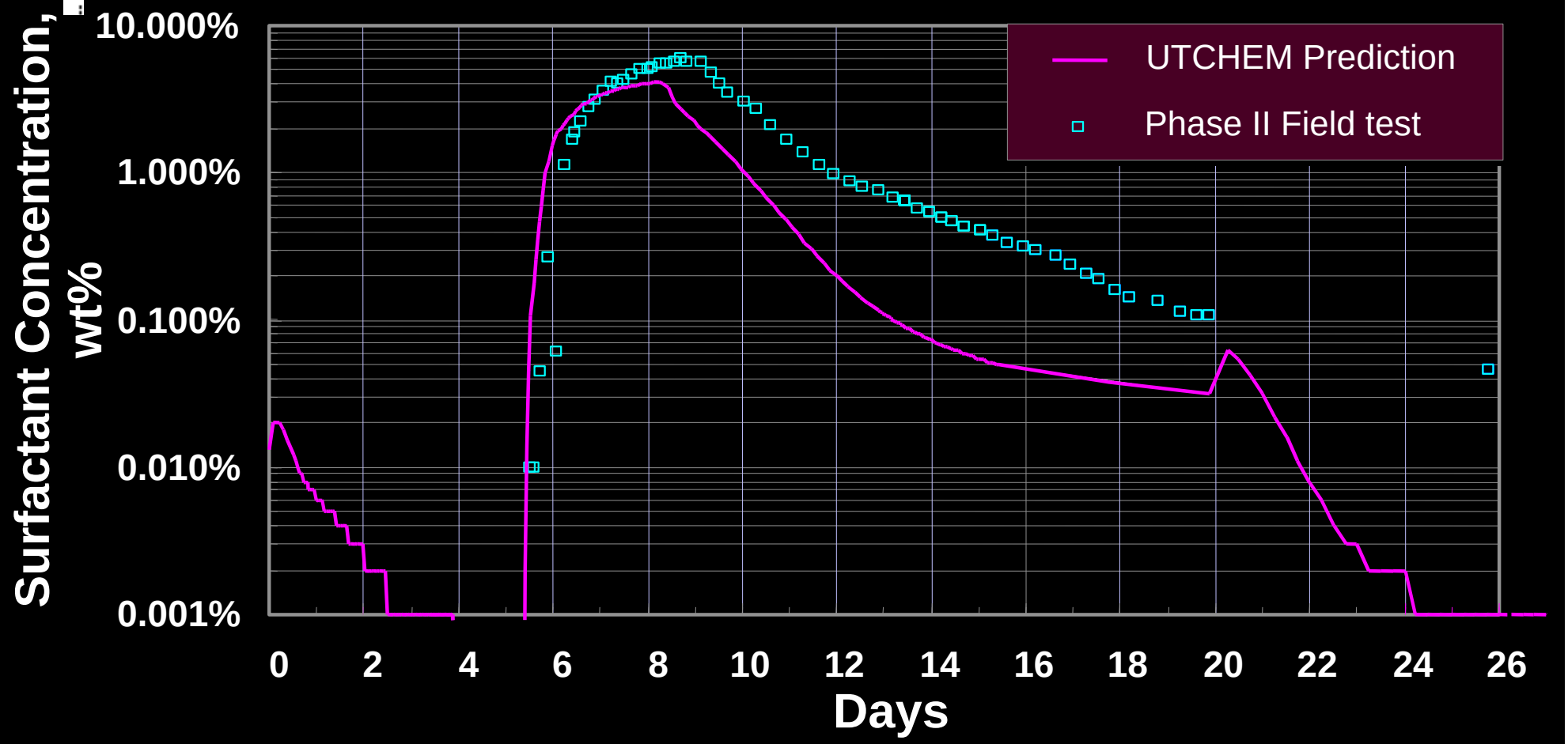
Comparison of predicted and measured surfactant concentration at Hill OU2



Comparison of predicted and measured tracer concentrations at Hill OU2

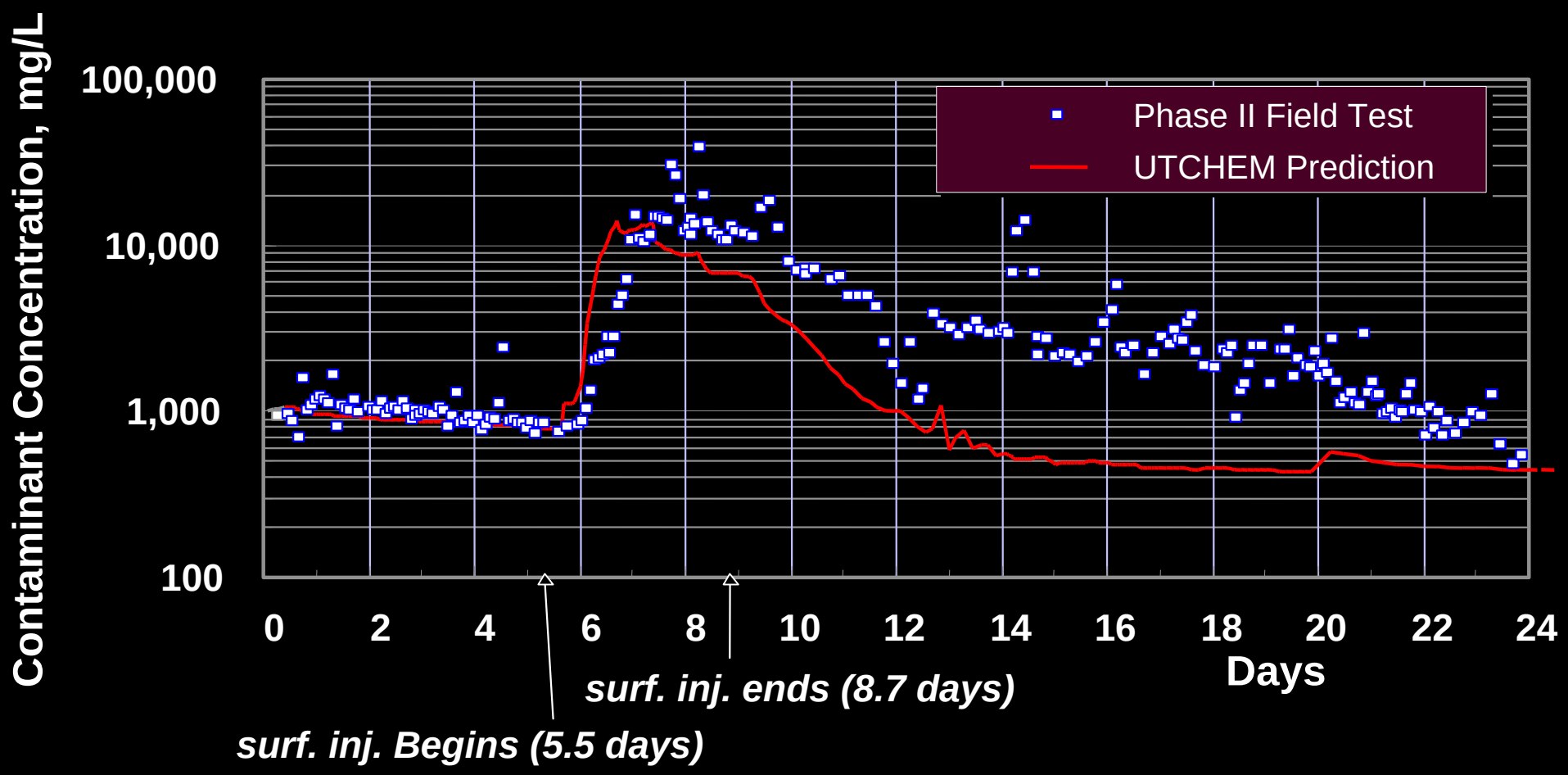


Estimating effluent surfactant concentrations, Hill AFB OU2, Phase II



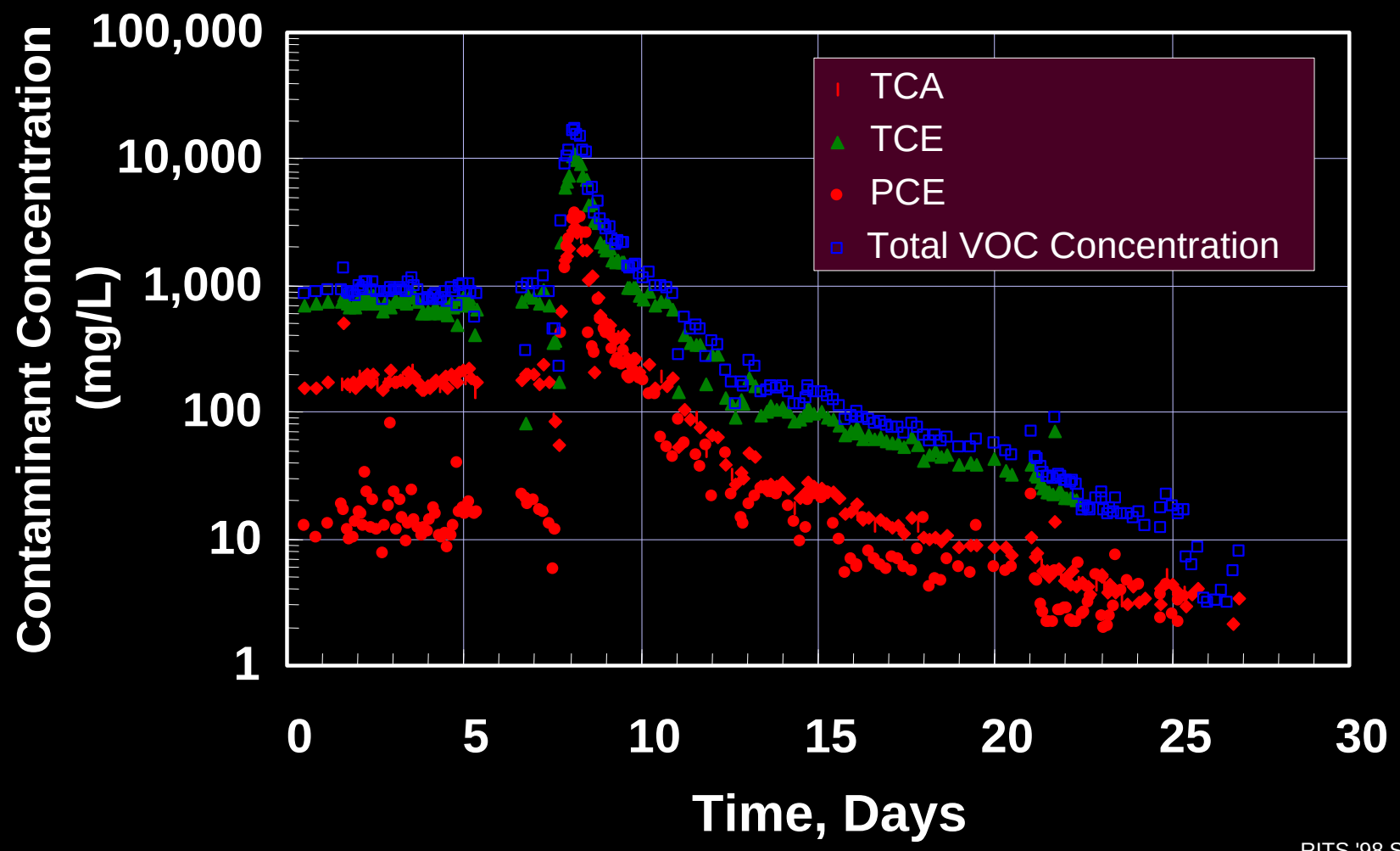
Actual concentrations are higher because of higher flowrates used in simulations

Estimating effluent contaminant concentrations, Hill AFB OU2, Phase II

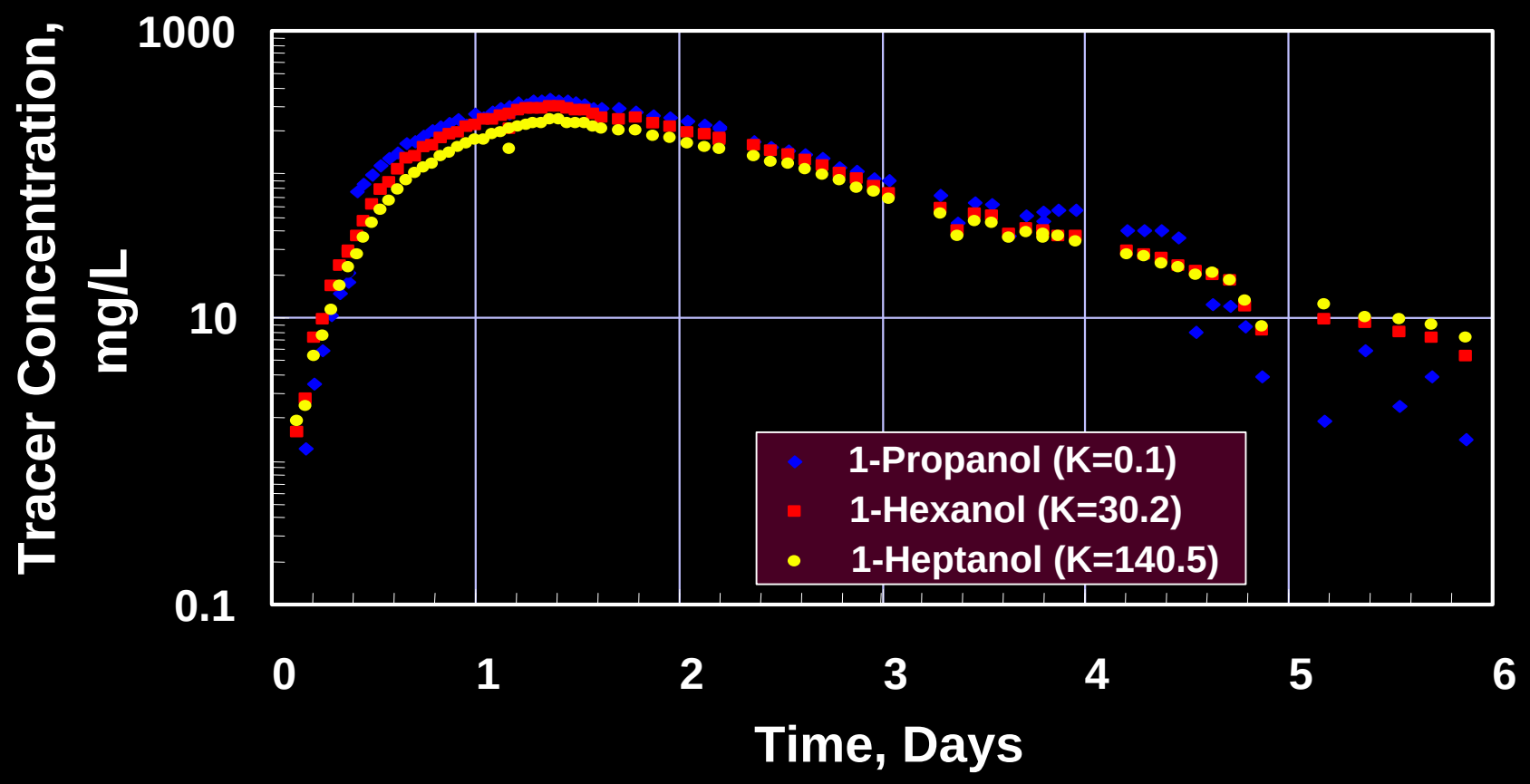


Actual concentrations are higher because of higher flowrates used in simulations.

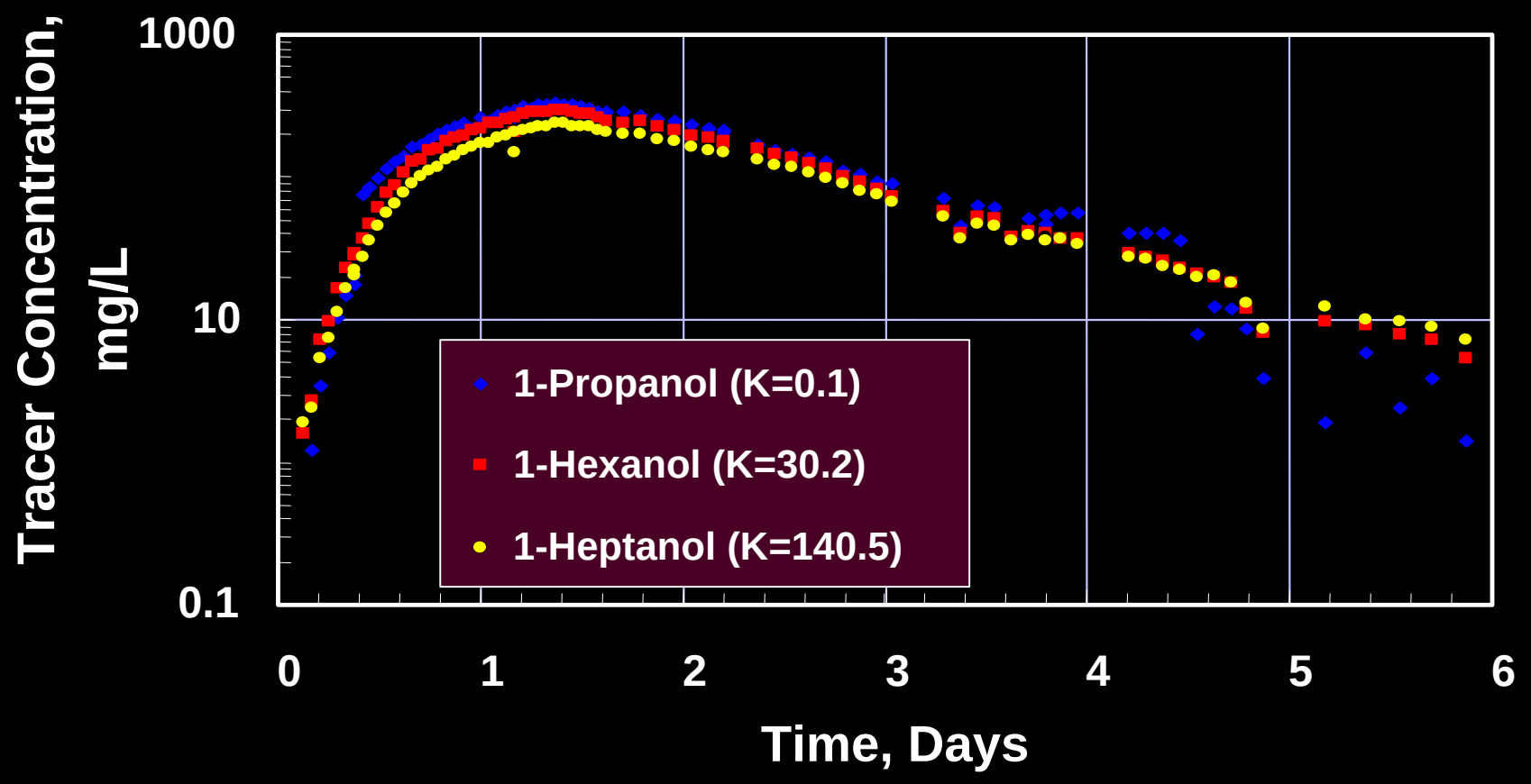
Contaminant concentrations in effluent from monitoring well, Hill OU2, Phase II



Pre-Surfactant (Phase I) Partitioning Tracers at Hill OU2



Post-Surfactant (Phase II) Partitioning Tracers at Hill OU2



Hill AFB OU2
PITT results

- Pre-surfactant (Phase I) PITT
  ~ 346 gallons residual DNAPL present initially

- Post-surfactant (Phase II) PITT
  ~ 5 gallons residual DNAPL remaining

Hill AFB OU2 Phase II, Recovery of liquids

- Tracer recovery = 98%
- Surfactant recovery = 94%
- DNAPL recovery = 98.5%

Hill AFB OU2
Phase II, Recovery of liquids

Sample collection

Nighttime operations

Nighttime site layout

Comparison of completed surfactant floods

Organization	Date	Swept Pore Volume	% Removed	Average Final Contaminant Concentration (mg/kg)	NAPL
SURTEK, CH2MHill	1989	140,000	84	4,000	Creosote
SUNY, Buffalo	1990-91	2,400	77	1,200	PCE
Univ. of Florida	1996	1,200	86	2,150	mixed NAPL
DE&S/UT	**1996**	**15,000**	**98**	**75**	**TCE***
DE&S/Rice	**1997**	**8,200**	**90**	**75**	**TCE***

*60% TCE + other contaminants

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New developments

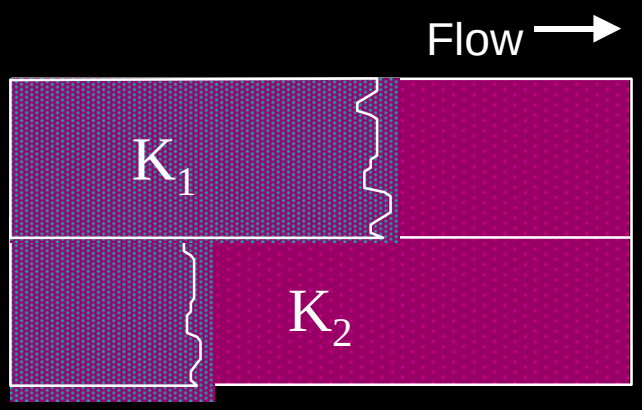
- Overcoming heterogeneities introduced by clay lenses etc. at the site. (use polymer, surfactant foam)
- Development of surfactant systems that are neutrally buoyant, i.e. the overall density of the surfactant/DNAPL mixture is the same or less than water.
- Heating surfactants for the removal of NAPLs with high viscosities.
- Processes for surfactant recovery and reuse.

Overcoming heterogeneities with polymer

Flow within an aquifer with $K_1 > K_2$

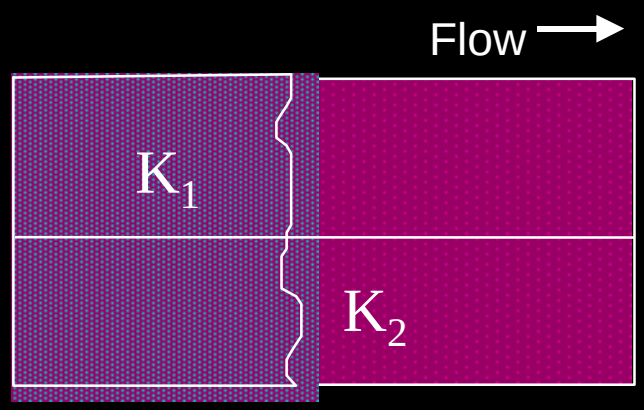
K = permeability

Without Polymer



Non-Uniform Front

With Polymer



Uniform Front

Points of Contact

- NFESC contact:

  Laura Yeh
  (805) 982-1660
  lyeh@nfesc.navy.mil

- U.S. EPA contact:

  Dr. A. Lynn Wood
  (580) 436-8552
  wood.lynn@epamail.epa.gov

SEAR references

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DNAPL references

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