Sampling and Analytical Methods for SEAR

Duke Engineering & Services

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SEAR Workshop

Outline

- Why sample and analyze during SEAR?
- From where are samples collected during SEAR?
- What is analyzed during SEAR?
  - Analysis of surfactant
  - Analysis of contaminants/co-solvents
  - Analysis of electrolytes
- Challenges

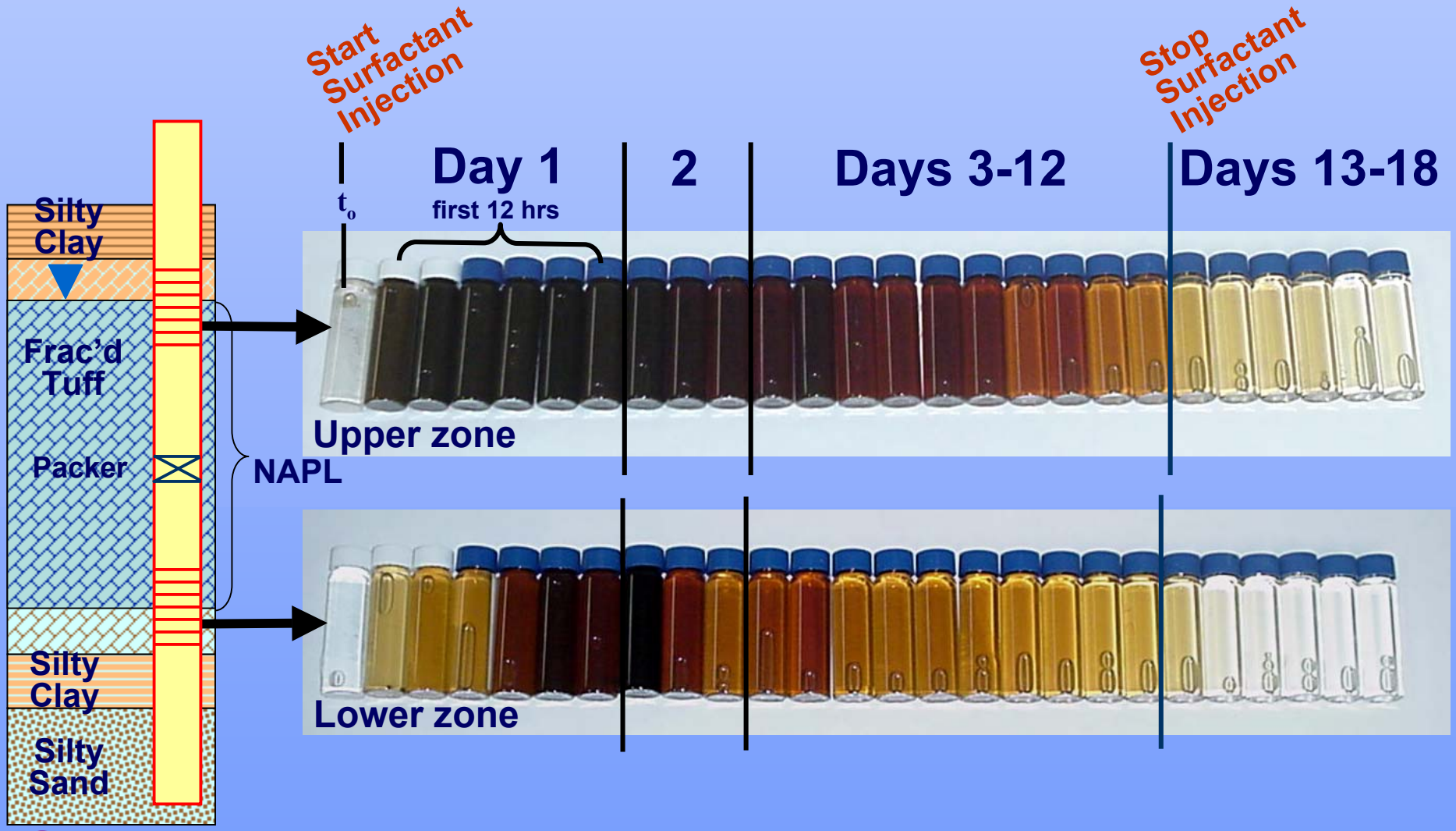
Why Sample and Analyze During SEAR?

- To assess and monitor the performance of SEAR
  - Estimate the mass of contaminants recovered
  - Estimate the mass of surfactant recovered
  - Determine whether there is effective hydraulic control of the injected chemicals
  - Determine whether the remediation is proceeding according to design predictions

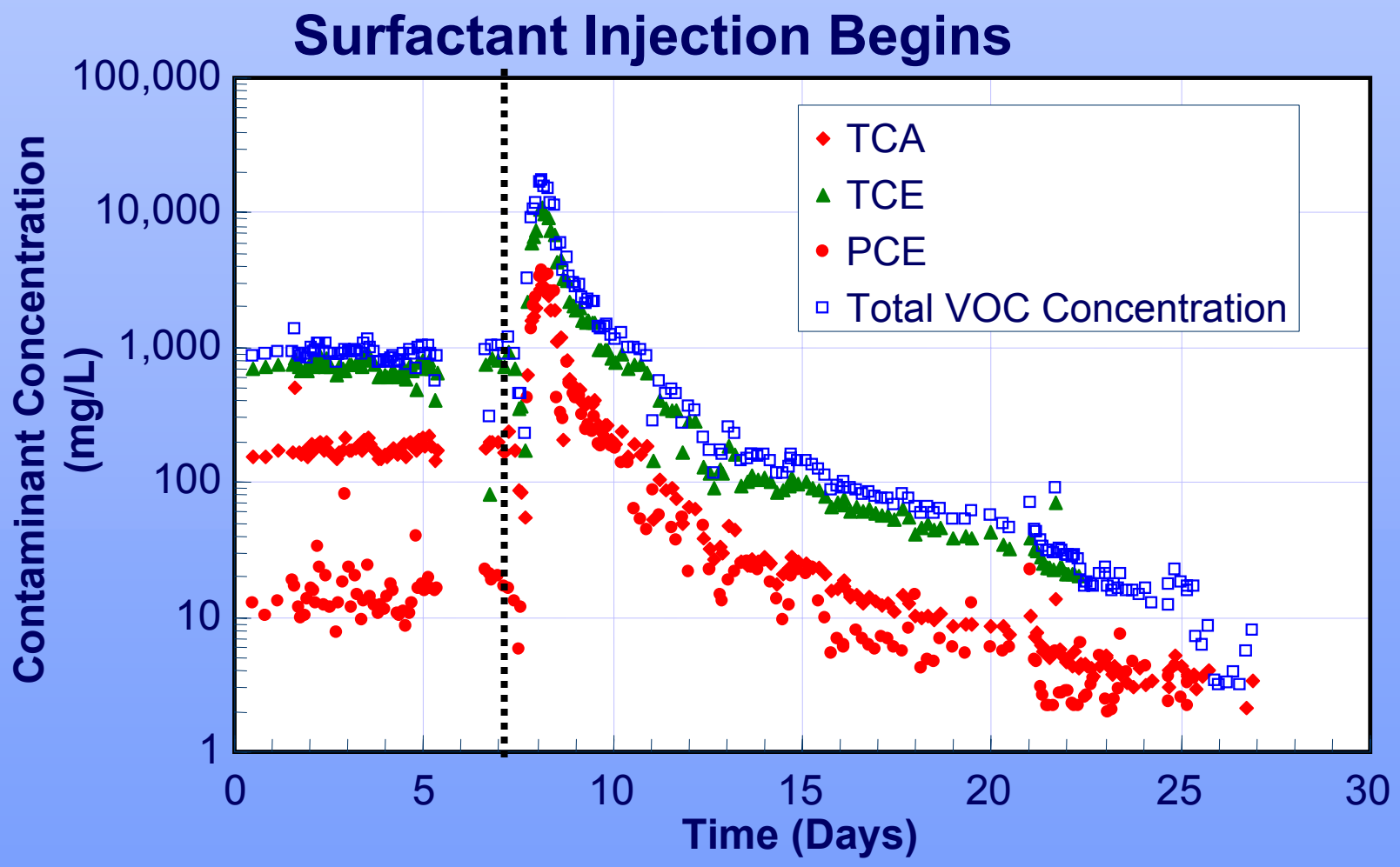
Why Sample and Analyze During SEAR? (cont.)

- Interpret and obtain insights into the behavior of injected chemicals and contaminants in the subsurface
  - Is contaminant removal occurring?
  - Are surfactants sweeping the contaminated zones?
  - Are injected chemicals being recovered or lost in the subsurface, i.e., adequate hydraulic control?

Visual Evidence of Contaminant Removal

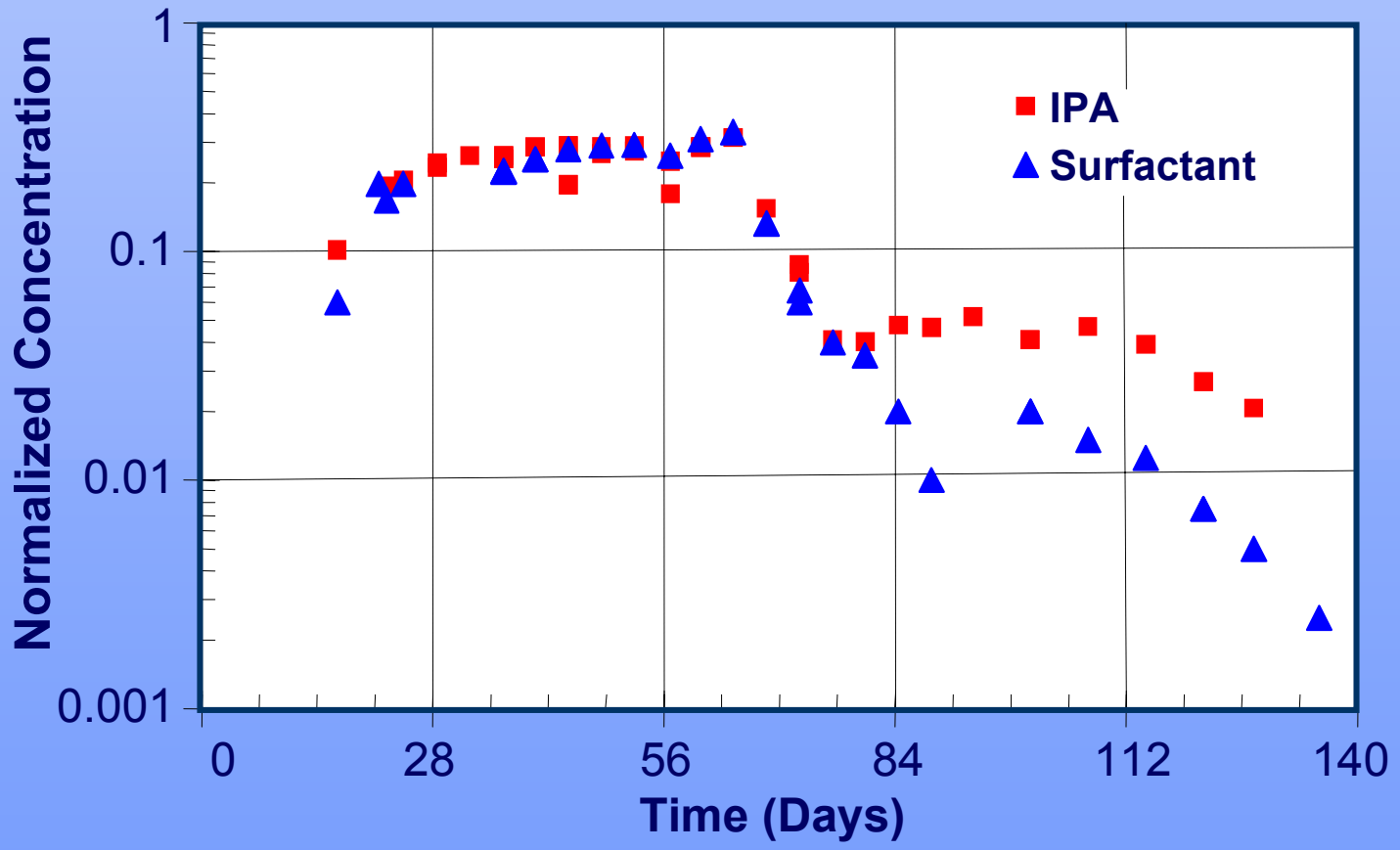


Concentration History of Contaminants During SEAR at Hill AFB, UT

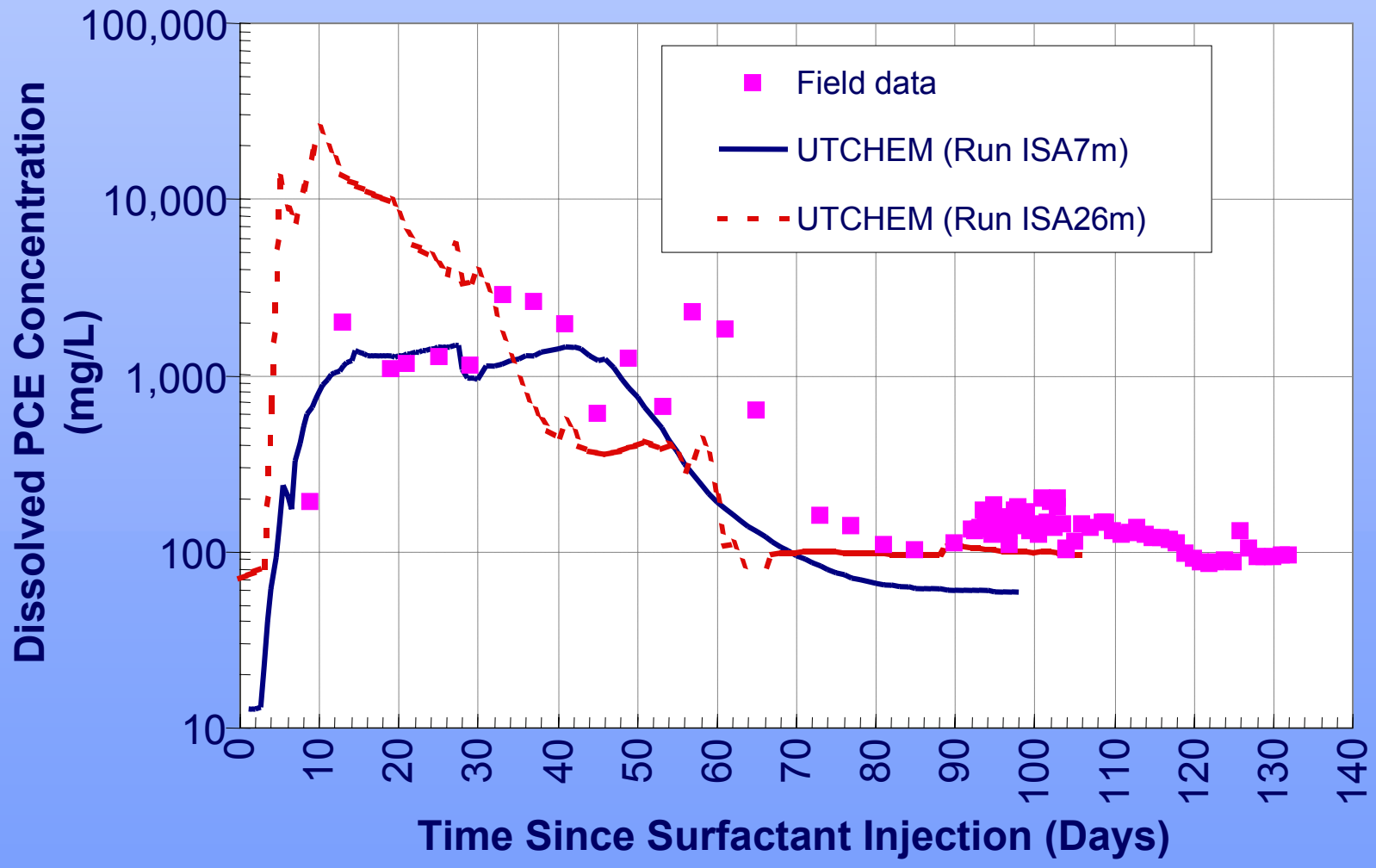


Surfactant and IPA Concentration Histories During SEAR at MCB Camp Lejeune, NC

The separation of surfactant and IPA curves indicates that late-term biodegradation of surfactant occurred.



Compare Field Data to Design Simulations



From Where Are Samples Collected During SEAR?

- Extraction wells
- Monitoring wells/points
  - Intermediate points between injection and extraction wells
    - Use of multi-level samplers provides depth-discrete data to evaluate performance at specific depths in the treatment zone
  - Beneath the test zone (underlying aquitard/deeper aquifer)
  - Adjacent to the test zone

What is Analyzed During SEAR?

- Contaminant concentrations in water
  - e.g., PCE, TCE, TCA, benzene, etc.
- Surfactant concentration
  - Both injected and extracted fluids
- Electrolyte concentration in water
  - Both in the injected and extracted fluids
- Co-solvent concentration
  - Both in the injected and extracted fluids

Surfactants Used in SEAR

- Anionic surfactants are preferred to minimize sorption in the subsurface:
  - Sodium ether sulfates (e.g., Alfoterra's used by DE&S/UT at MCB Camp Lejeune and Naval Station Pearl Harbor)
  - Sulfonates and disulfonates (e.g. Dowfax series of surfactants used by OU at OU 1, Hill AFB)
  - Sulfosuccinates (e.g. sodium dihexyl sulfosuccinate used at OU 2, Hill AFB by DE&S/UT)

Analysis of Surfactants

- Titration: Advantages
  - Inexpensive
  - Can be used when surfactants have many isomers, such as the Alfoterra's
  - Detection limits as low as 0.01 wt% (MCB Camp Lejeune)

Analysis of Surfactants (cont.)

- Titration: Disadvantages
  - Interference from sulfates, nitrates in groundwater
  - Ion-selective electrode can be damaged by chlorinated contaminants such as PCE, TCE
  - Will not detect chromatographic separation of different surfactant isomers

Analysis of Surfactants (cont.)

- HPLC techniques: Advantages
  - Can detect chromatographic separation of surfactant components
  - Can be used for nonionic surfactants

Analysis of Surfactants (cont.)

- HPLC techniques: Disadvantages
  - More expensive
  - Higher detection limits ~ 0.03 wt%
  - Requires more method development to quantify mixed isomer surfactants such as the Alfoterra's

Summary

- Both titration and HPLC are useful for analysis of surfactant
- Titration techniques can quantify anionic surfactant concentrations inexpensively

Summary (cont.)

- A few HPLC measurements will be useful in determining whether the surfactant composition is altered in the subsurface due to sorption, or preferential filtration
- Baseline analyses should be conducted to quantify potential interferences

Analysis of Contaminants and Co-Solvents

- GC analyses for both contaminants and co-solvents
  - Contaminant concentrations typically vary between <1 mg/L to ~10,000 mg/L
  - Co-solvent concentrations vary between 0 to 16 wt% (Note: SEAR-NB will use 16%)
- Surfactant interference can potentially affect the analysis of contaminants and co-solvents

GC Analysis of Contaminants

- For direct injection, packed columns are preferred because they can take much higher sample loading and are less affected by surfactants
  - A 6-ft-long, 1/8-in.-diameter Carbopak (60-80) with 1% SP-1000 is an excellent candidate for analyzing TCE and PCE with IPA as a co-solvent
- For purge & trap, capillary columns can be used but sample dilution is required and may lead to inaccuracies

GC Analysis of Contaminants (cont.)

- A FID can be used to quantify between 25-5,000 mg/L, while a TCD may be used above 5,000 mg/L of contaminant (used successfully for the MCB Camp Lejeune analysis of PCE)
- The use of a GC/MS to quantify complex multi-component NAPLs such as the MCB Camp Lejeune DNAPL, which has Varsol components (used by U.S. EPA at MCB Camp Lejeune)

Analysis of Co-Solvent

- Packed columns are preferred for co-solvent
- A TCD is preferred for analyzing high co-solvent concentrations
- For the MCB Camp Lejeune analysis we were able to quantify up to 18 wt%IPA using a TCD and a 6-ft-long, 1/8-in.-diameter Carbopak (60-80) with 1% SP-1000

Analysis of Electrolyte

- It is essential to determine the cation concentration in the injectate when anionic surfactants are used
- Can use atomic adsorption (AA) or inductively coupled plasma (ICP) for quantifying cation concentrations
- ICP techniques are generally more robust and less prone to error and are preferred

Sampling Challenges

- Properly purging sampling points
- Obtaining sufficient sample volume from multi-level sampling points

Analytical Challenges

- Interference from anions in the groundwater can affect titrations (sulfates, nitrates)
  - Should run enough background samples to determine matrix effects
- PCE, TCE can damage ion-specific electrode membranes
  - The electrodes should be replaced regularly

Analytical Challenges (cont.)

- Surfactant can plug chromatography columns and interfere with contaminant and co-solvent analysis
  - Sufficient method development must be carried out to quantify potential interferences with candidate surfactants

Any Questions?

Remediation Performance Assessment

Fred J. Holzmer

Duke Engineering & Services

SEAR Workshop

Performance Assessment

Remediation PA defined:

1) Evaluation of the effectiveness of a remedial action to remove NAPL contaminants

2) Monitoring for effective hydraulic control of injected fluids (e.g., recovery of surfactant, co-solvent, and electrolyte)

3) Monitoring for unintended mobilization of contaminants beyond the treatment zone

Performance Assessment

Motivation for PA:

- Regulatory requirements
- User assurance
- Economics

The need for PA is **independent** of the remedial technology employed.

Performance Assessment

Primary Objectives:

- Determine the volume of NAPL removed
- Determine the volume and spatial distribution of NAPL remaining in the treatment zone
- Evaluate the potential effects of any remaining NAPL with respect to long-term risk (e.g., continuing effect on the dissolved-phase plume)

Performance Assessment

Secondary Objectives:

- Determine the mass recovery of injected chemicals (injectate) at the extraction wells
- Monitor for NAPL mobilization both inside and outside the treatment zone
- Monitor water levels in the treatment area to evaluate hydraulic containment of injectate
- Monitor groundwater for escape of injectate at wells located outside the treatment zone

Current PA Status

- No standard practice
- No existing guidelines
- This condition has generally led to poor quality PA at most sites that have undertaken remedial actions

[Committee on Innovative Remediation Technologies of the National Research Council (1997), U.S. EPA]

PA Methods for Evaluating the Volume of NAPL Removed

- Groundwater monitoring
- Soil sampling
- Partitioning interwell tracer test (PITT)

PA by Groundwater Samples

- Most popular PA method to date, likely because it is the least expensive and easiest data to collect

PA by Groundwater Samples

Method is based on the following assumption:

- That there is a unique relationship between the aqueous concentrations (at a monitoring well) and the mass or volume of NAPL in adjacent portions of the aquifer

PA by Groundwater Samples

Assumption (cont.):

- This assumption is invalid, otherwise we would have successfully characterized NAPL zones 10 years ago by groundwater sampling

PA by Groundwater Samples (?)

Groundwater sampling is useful for plume monitoring, **but this technique does not quantify the volume or saturation of NAPL.**

Therefore, groundwater sampling is **not** an acceptable method for PA of a NAPL remedial action.

PA by Soil Sampling

Collect Soil Samples With Field Preservation

Issues for PA by Soil Sampling

- There are 3 significant issues with respect to PA of NAPL remediation by soil sampling:

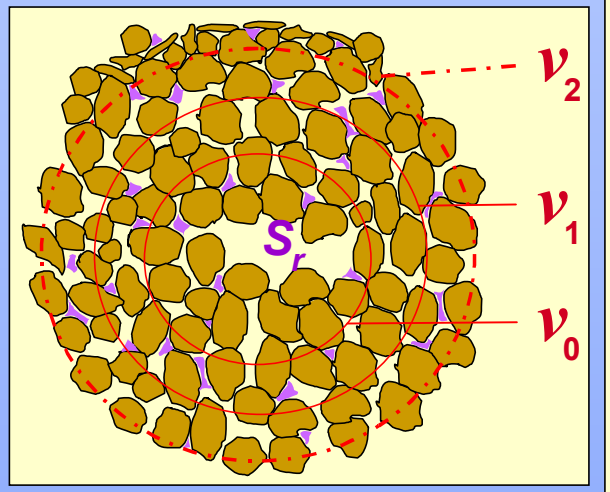
Issues for PA by Soil Sampling

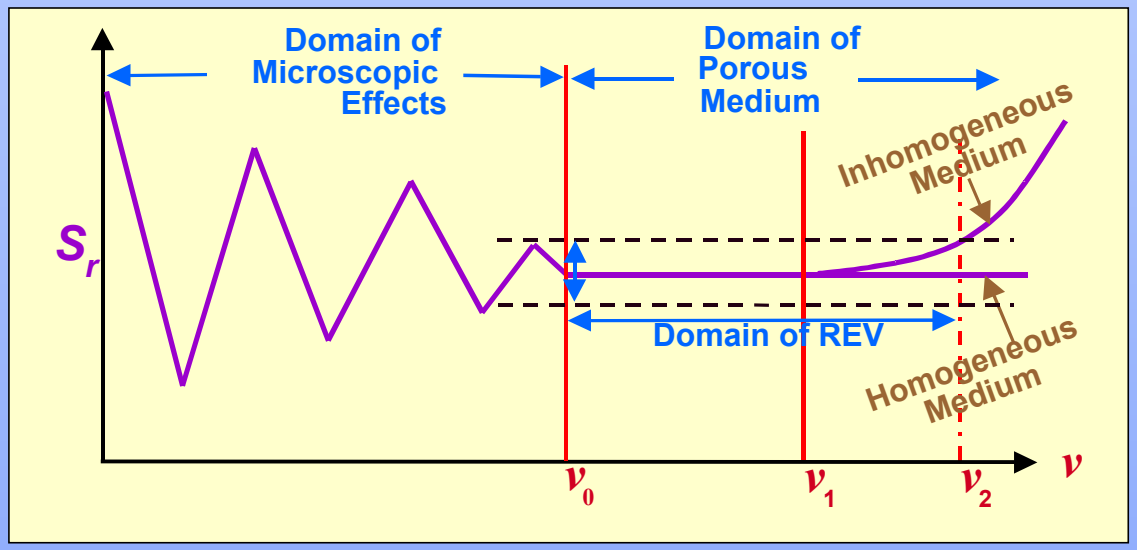
1) Is the sample representative of the area it is selected to represent (REV)?

2) Has all of the NAPL present been recovered? (problematic especially for volatile contaminants)

3) Have soil samples been recovered from all parts of the targeted NAPL zone (i.e., from both high and low permeability zones)?

Soil Sampling Issue #1: Representative Elemental Volume





Est . range of REV for NAPL in soil = 10-10^4 cm^3
= 0.0003 to 0.3 ft^3

Volume of typical soil sample = 30-10^2 cm^3
= 0.001 to 0.01 ft^3

Soil Sampling Issue # 1: Representative Elemental Volume

- REV is specific to the grain-size distribution of individual strata
- Vertical: Experience at Borden (Feenstra) and various DoD/DOE sites (DE&S) suggests that a sampling interval of 5-15 cm (2-6 in.) is required to obtain a representative estimate of saturation and volume in the vertical direction
- Horizontal ?

Soil Sampling Issue # 2: NAPL Losses During Sampling

Sources of NAPL loss during recovery and sampling:

- Drainage of interstitial fluids upon retrieval from the subsurface (function of grain size and type of sampler)
- Volatilization during collection, shipment, lab preparation, and analysis (function of grain size, type of sampler, and method of preservation)

Soil Sampling Issue # 3: Samples Collected From All Pertinent Zones?

- Bias: Fine-grained sediments are more likely to be recovered than coarse sediments
- Drilling locations: Areal coverage (e.g., were all of the lows in the capillary barrier sampled?)
- Sampling is destructive (can't sample twice in the same location)
- Sampling errors are not quantifiable (no error bars around DNAPL volume estimate)
- Historical lack of soil sampling successes (where are all the source zones?)

PA by PITTs

- PITTs provide measurements on a meaningful scale (address REV issue)
- PITTs can sample the sample volume pre- and post-remediation
- PITT results and error can be quantified (error bars)

PA by PITTs

- PITTs typically are used both before and after remediation:
- **Before**
  - Remedial design basis
  - Baseline volume and extent of NAPL
- **After**
  - Volume and spatial distribution of NAPL remaining

PITT PA Assumptions

- Tracer Ks measured accurately
- Reversible sorption to sedimentary organic matter quantified
- Tracers penetrate all parts of the NAPL zone:
  - Free-phase NAPL zones
  - Low intrinsic permeability or relative permeability
- Multiple tracers with a wide range of Ks
- Sufficient time to allow tracer signals from all parts of NAPL zone to be measured at the monitoring or extraction wells

Conclusions on PA Methods for Quantifying NAPL Volume

- Groundwater sampling is not valid for even semi-quantitative assessment of remedial performance
- Soil sampling is semi-quantitative because of: REV limitations; potential loss of contaminants from the samples; and the level of uncertainty is not quantifiable
- PITTs are more complex, but when properly designed and implemented, provide a means of accurately and quantitatively measuring NAPL volumes with quantifiable uncertainty.

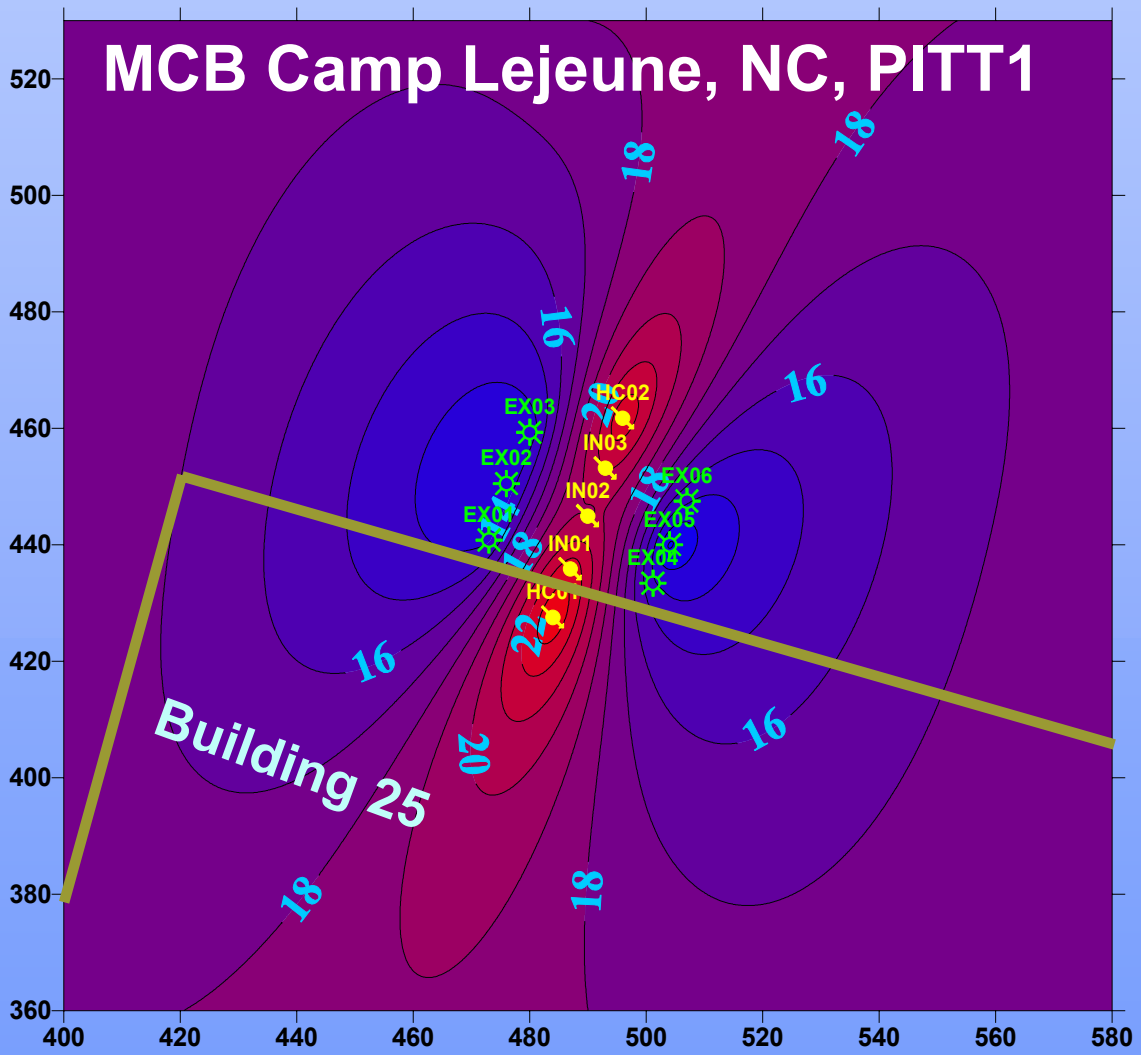
Site Conditions and Costs Implications

- For small-scale homogeneous sites (e.g. <400 yd^3), PA by soil sampling may provide a significant cost savings (note: cost vs. defensible PA are separate issues)
- For sites with a high degree of vertical heterogeneity (e.g. permeability variations > an order of magnitude), soil sampling may provide confirmation of DNAPL conditions in the lowest permeability zones
- For large-scale sites with a moderate degree of heterogeneity, PITTs will be more cost effective and provide much more defensible performance assessment

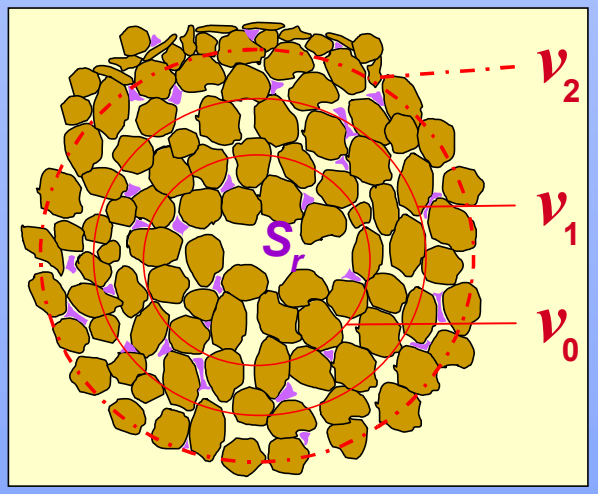
Hydraulic Control Monitoring

- Water-level data is used to generate water-level contour maps (i.e. potentiometric surface maps)
- Groundwater samples collected from monitoring points from both inside and outside the treatment zone are examined for unusual trends

A Potentiometric Surface Demonstrating Hydraulic Control



Monitoring Beyond Treatment Zone "Boundaries"

- **Collect groundwater samples for comparison to baseline conditions (to monitor for any changes during NAPL remediation):**
  - Monitoring points beneath the test zone for vertical migration of DNAPL (e.g., aquitard and/or underlying aquifer)
  - Monitoring points outside the treatment area for lateral migration of contaminants

Any Questions?